CEMENT / ROCK INTERACTION IN GEOTHERMAL WELLS

ΒY

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ABSTRACT

One of the main issues associated with the exploitation of geothermal energy is the durability of the cement that is used downhole to cement the steel casing to the formation. Cement durability can have a major impact on the lifetime of geothermal wells, which do not usually last as long as desirable. The cement formulations used in the construction of geothermal wells are designed to provide mechanical support to the metallic well casings and protect them against the downhole harsh environment, which often leads to corrosion.

This research is focused on the way that these formulations interact with the surrounding rock formation in geothermal environments, and aims to understand whether these are likely to affect the cement durability and, consequently, the geothermal well lifetime.

The experimental work in this thesis consists of examining the changes in the interfacial transition zone (ITZ) that forms between geothermal cements and the volcanic rocks, after hydrothermal treatment. Holes were drilled in blocks of volcanic rocks and cement slurries with distinct formulations were poured into the cavities. The assemblages were autoclaved under typical geothermal conditions. The main variables under study were the cement formulation, the temperature of curing (150° C and 290° C), the presence of drilling mud, CO₂ exposure and the type of rock.

The results show that with all the Portland cement based systems a series of chemical reactions occur at the interface between the cement and the rock, the ITZ, where migration of Ca^{2+} and OH⁻ ions occurs from the cement into the rock pores. These reactions are ongoing, which occur faster during the first days/few weeks of curing, mostly driven by physical process of cement movement into the rock, followed by a slower second stage, controlled mostly by chemical driving forces.

This work highlights the interdependence between the chemical and physical interactions between geothermal cements and volcanic rocks which are complex. Variables such as temperature and time of curing and silica addition affect the cement phases that form, while the amount of amorphous silica and rock permeability dictate the extent of rock interaction. The presence of carbon dioxide influences the extent of rock/cement interaction and this can be controlled by the rock permeability and cement formulation. Consequently, most of the above mentioned variables were found to have an impact on the geothermal cement durability, which depends on the way these factors are combined.

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I. GLOSSARY, ACRONYMS AND ABBREVIATIONS

I.1 Cement Notation (Oxide Nomenclature)

- $\mathbf{A} Al_2O_3$.
- **C** CaO.
- Ĉ CO₂.
- **F** Fe₂O₃.
- **H** H₂O.
- **K** K₂O.
- **M** MgO.
- \mathbf{N} Na₂O.
- \mathbf{S} SiO₂.
- **Ŝ** SO₃.
- \mathbf{T} TiO₂.

I.2 Others

A (cement) - API class A cement.

AAR - alkali aggregate reaction.

ACR - alkali carbonate reaction.

Alkali metasomatism - geological process occuring widely in nature accompanied with multimetallic mineralization that is studied extensively by many geologists.

Amphibole - dark coloured inosilicate mineral, with either igneous or metamorphic origin.

Andesitic - mostly composed of andesite.

Andesite - extrusive igneous rock of intermediate composition, typically with 55-65% of silica (SiO₂).

Apatite - phosphate mineral.

API - American Petroleum Institute.

Argillite - fine-grained sedimentary rock composed predominantly of indurated clay particles.

Argillic alteration - hydrothermal alteration of wall rock which produces clay minerals including kaolinite, smectite and illite. The process generally occurs at low temperatures and may occur in atmospheric conditions. Argillic alteration is of supergene environments representative where low temperature groundwater becomes acidic.

ASR - alkali silica reaction.

B (cement) - API class B cement.

Biotite - sheet silicate (phyllosilicate) mineral (mica group) found in a wide variety of igneous and metamorphic rocks.

C (cement) - API class C cement.

D (cement) - API class D cement.

Dacite - extrusive igneous rock, typically intermediate in composition between andesite and rhyolite.

DTG - Differential thermogravimetry.

E (cement) - API class E cement.

EDS - Energy Dispersive Spectrometry.

Embayed - an embayed crystal in an igneous rock is a crystal with an irregular cavity penetrating a crystal face. The embayment is often filled with groundmass or another mineral.

EMPA - electron microprobe analysis.

F (cement) - API class F cement.

Felsic - term used in geology to refer to silicate minerals, magma, and rocks which are enriched in the lighter elements such as silicon and oxygen (over 69% of SiO₂), aluminium, sodium, and potassium; the term "felsic" combines the words "feldspar" and "silica".

G (cement) - API class G cement.

G10MS - class G cement plus 10% (in weight) of Microsilica 600.

G20MS - class G cement plus 20% (in weight) of Microsilica 600.

G30MS - class G cement plus 30% (in weight) of Microsilica 600.

G40MS - class G cement plus 40% (in weight) of Microsilica 600.

G30MS20SF - class G cement plus 30% (in weight) of Microsilica 600 and 20% (in weight) of silica flour.

G20SF - class G cement plus 20% (in weight) of silica flour.

G40SF - class G cement plus 40% (in weight) of silica flour.

Geobrine - fluid found in hydrothermal environments, especially in geothermal well zones.

GNS - (Institute of) Geological and Nuclear Sciences.

Graben - depressed block of land bordered by parallel faults.

Greisenisation - postmagmatic process associated with the origin of leucocratic high silica granites; in its course feldspars and Fe-micas are decomposed.

Greywacke - sedimentary rock (variety of sandstone), which contains abundant quartz and feldspar in a very fine matrix of clay.

H (cement) - API class H cement.

HAC (cement) - High Alumina cement.

Hornblende - dark amphibole.

Hydrothermally cured - cured in hydrothermally simulated conditions in the lab.

Hydrothermally altered (or just altered) - altered in situ, over the years, through a hydrothermal process.

Hypersthene - inosilicate mineral which belongs to the group of pyroxenes.

Ignimbrite - extrusive igneous rock of felsic composition, typically with over 65% of silica (SiO₂).

Ilmenite - weakly magnetic titanium-iron oxide mineral.

Inosilicates - chain silicates, have interlocking chains of silicate tetrahedra with either SiO_3 , 1:3 ratio, for single chains or Si_4O_{11} , 4:11 ratio, for double chains.

IRL - Industrial Research Limited.

ITZ - Interfacial Transition Zone.

ITZ-C - Cement zone adjacent to the ITZ.

ITZ-R - Rock zone adjacent to the ITZ.

Lapilli - material that falls out of the air during a volcanic eruption.

Mafic - term used in geology to refer to a silicate mineral or rock that is rich in magnesium and iron and has between 45-52% of SiO₂; the term is a combination of the words "magnesium" and "ferric".

Magnetite - mineral composed of iron oxide which has magnetic properties.

Mass Spec - Mass Spectrometry.

Metasomatism alteration - is the chemical alteration of a rock by hydrothermal and other fluids; metasomatism can occur via the action of hydrothermal fluids from an igneous or metamorphic source.

Microsilica 600 - highly reactive pozzolan. It is processed from a natural, white, silica deposit found in New Zealand. Like silica fume, it is a very fine amorphous silica and falls in the microsilica family of products.

MS or MS600 - Microsilica 600.

OPC - Ordinary Portland Cement.

Orthosilicates - minerals that have isolated (insular) $[SiO_4]^{4-}$ tetrahedral that are connected only by interstitial cations.

Phenocrysts - relatively large and usually conspicuous crystals distinctly larger than the grains of the rock groundmass of (aporphyritic) igneous rock.

Phonolite - rare extrusive volcanic rock of intermediate chemical composition between felsic and mafic.

Phyllic alteration - hydrothermal alteration typically resulting from removal of sodium, calcium, and magnesium from calc-alkalic rocks, with pervasive replacement of silicates, muting the original rock texture. It is a common style of alteration in porphyry base-metal systems around a central zone of potassic alteration.

Potassium silicate alteration - hydrothermal alteration type, which forms water-soluble and glass-forming silicate salt of general formula K_2SiO_3 .

Propylitic alteration - is the chemical alteration of a rock, caused by iron and magnesium hydrothermal fluids, altering e.g. biotite or amphibole groundmass material; it typically results in epidote-chlorite-albite alteration.

Pumice - extrusive igneous light porous rock, typically with over 69% of silica in its composition.

Pyroxene - Group of important inosilicate minerals found in many igneous and metamorphic rocks.

Rhyolite - extrusive volcanic rock, typically with over 69% of SiO₂.

SEM - Scanning Electron Microscopy.

Sericitic alteration - process which causes the rock to be converted to the mineral sericite, which is a fine white mica; it forms through the decomposition of feldspar.

SF - Silica Flour (pure ground fine quartz).

SCM - Supplementary Cimentitious Materials.

TG/TGA - Thermogravimetry or Thermogravimetric Analysis.

TVZ - Taupo Volcanic Zone or Taupo Geothermal Region.

VUW - Victoria University of Wellington.

W (cement) - White cement.

XRF - X-ray Fluorescence.

XRD - X-ray diffraction.

Zircon - belongs to the group of orthosilicate minerals.

II. INTRODUCTION

II.1 Rationale

New Zealand is a country rich in geothermal resources, with some of the largest and most spectacular examples of geothermal activity in the world. Many are untapped and provide a tourist attraction (**Figure II.1**). Most of the New Zealand geothermal energy exploitation has been developed in the Taupo Volcanic Zone (TVZ), due to its highest geothermal potential (**Figure II.2**). There is a plan to expand this country's geothermal production of electricity over the next 15-20 years to double the present level. This demands an improvement in capacity of both existing and new geothermal power plants along with advances in technology from drilling the well to electricity production.



Figure II.1 - Champagne pool, Rotorua, New Zealand Figure II.2 - Taupo Volcanic Zone (TVZ)

One of the main issues associated with exploitation of these resources has been the durability of the cement that is used downhole and its impact on the lifetime of wells, which do not usually last as long as desirable. For this reason, the Ministry of Science and Innovation (MSI, formerly Foundation for Research, Science and Technology (FRST)) let a contract to Industrial Research Limited (IRL) for a research programme to improve the understanding of how the current cement formulations perform in the high temperature, high CO₂ concentration/pressure and low pH ground waters found within New Zealand's geothermal systems and to develop alternative cement formulations which might have more durability.

The cementing job is part of the well's drilling process and is intercalated with the actual drilling of the well (Figure II.3). The well is drilled in stages with each stage cased and

cemented in place separately. In a typical production geothermal well, the first casing to be placed is the surface casing, with a diameter of under 22in (~56cm) which is placed from the surface down to ca. 40m depth. The intermediate casing, also known as anchor casing is $13^{3}/(1 - 34 \text{ cm})$ in diameter and goes from the surface down to ca. 100m depth. The final casing, the production casing through which the production fluid (2 phase mixture) is collected, has a diameter of ~8⁵/₈in (22cm) and can extend up to several km in depth (Figure II.4).



Figure II.3 - Rig utilized in the construction of a geothermal well



Cement

geothermal well

Well cement grouts are pumpable formulations designed to be pumped downhole and when hardened, provide several roles in geothermal wells. These are:

- to provide a seal between the steel casing and rock formation (Figure II.5);
- to protect the steel against corrosion;
- to support the casing against vibration.

Acidic hydrothermal fluids can cause corrosion of the cement, leaving the steel casing subject to its own attack and corrosion, which can lead to failure of the integrity of the well and ultimate abandonment. This is expensive, as each well costs around \$NZ 12M to complete. As the cements have to stand aggressive environments downhole, several studies on specialised cementing formulations have been conducted (Sugama, 2006). New systems have been developed with different chemistries to those of the conventional Portland cement based grouts (Sugama, 2006). Notwithstanding the cement itself, the way in which cement interacts with the surrounding rock formation as well as with the steel casing are also important factors that contribute to the durability of the well.



Figure II.5 - Schematic cross section of the system rockcement-casing

Figure II.6 - Well head with valve and control equipment on the top of a geothermal well

II.2 Research Project

The research in this thesis considers the cement-rock interaction, which has rarely been studied but usually assumed to be low. Most of the thermal waters tapped for power generation lie in pervious acid silicate rocks such as rhyolite, andesite or ignimbrite. These rocks have all been used as aggregates in concrete, where they have been shown to interact with alkalis from the cement to give rise to the phenomenon of alkali silica reaction or ASR, which causes expansion and cracking, particularly when present in the sand fraction (Chaterji, 2005). Preliminary experiments conducted by the IRL Cement Team with the conventional grouts cured in ignimbrite at elevated temperatures, showed that the acidic volcanic formation through which the wells were drilled, reacted with the cement to form layers of altered rock and cement.

To date, very few investigations related to this specific field of expertise have been conducted. The IRL Cement Team has a long history of research on cement formulations used in geothermal wells using conventional oilwell cements. Additionally, a large number of investigations have been undertaken on cement-rock interactions in concrete or mortar (cement-aggregate reactions) for civil construction purposes. Many of these were presented and published in the Alkali-Aggregate Reaction in Concrete conferences proceedings. Although these are at completely different conditions to those found in geothermal environments, the results are relevant for the current research. It cannot be assumed that

under hydrothermal conditions, the volcanic formation will be inert. Hence this research project aims to study interactions of cement with the rock.

II.3 Objectives

The overall goal of this investigation is to enhance the understanding of the chemical and physical interactions between cements and the most common rock formations within the New Zealand geothermal environments by:

- □ Identifying and characterizing the main factors and variables affecting the cement/rock interaction in geothermal wells;
- □ Understanding which conditions can directly affect the performance of the cement;
- □ Determining whether these interactions contribute to the failure of the cement annulus and, consequently, to the shortening of well life;
- □ Providing recommendations on the requirements for geothermal cements.

This study involves the combination of several fields of expertise, namely chemistry, physics and geology, together with an understanding of drilling engineering procedures.

II.4 Thesis Structure

This thesis is composed of ten chapters. The first chapter is the Glossary, where most technical terms utilized in the current work are mentioned. The second chapter, Introduction, aims to introduce the topic, with some general background, objectives and explaination of the thesis structure. The third chapter, Literature Review, reviews the most relevant state-of-the-art knowledge on the topic and is divided into three main sections: Geothermal environments, Cement and Cement-rock Interactions. The first of these considers all the geothermal variables which are expected to participate in this research, including the rock itself. The second one focuses mostly on Portland based cements, the ones most commonly used in geothermal wells, and their behaviour when exposed to extreme environments (high temperatures, high pressures and high CO_2 concentrations) while the third compiles the most significant studies on the interactions between cement and rock.

The fourth chapter, Methodology, describes, explains and justifies the methods, procedures and materials utilized in the experimental work. The Results are divided between chapters five and six. The fifth chapter represents the first stage of the experimental work, in which the samples were cured for only one month. The sixth chapter presents the second and last stage, with three months curing time.

In the seventh chapter, Discussion of the Results, the results are interpreted, evaluated and compared along with those from other studies. This chapter is organized in two main sections: Portland based systems and alternative cementing systems. Each section is divided in distinct sub-sections, as a function of the specific cement formulation.

The eighth chapter, Conclusion and Future Work, presents the main deductions achieved during the discussion of the results, by pointing out patterns featuring several samples from which relevant conclusions were obtained.

The nineth chapter, Presented and Published Work, contains the papers that have been orally presented in international conferences and published in peer reviewed proceedings.

Finally, the tenth chapter, Appendices, provides further detailed information regarding the results presented in the Methodology and Results chapters.

III. LITERATURE REVIEW

This literature review is divided in three sub-chapters. The first focuses on geo/hydrothermal environments, and introduces the main factors within these environments that affect the current research, as these conditions will affect the cement performance and, consequently, the cement-rock interaction. It refers the most common types of rock found within these environments, some of which were chosen for the experimental work. The second presents the current cement types and their respective behaviour when used in geothermal wells, so-called "oilwell" or, simply, well cements. The features of each type of the most common cement formulations (including additions) within geothermal well exploitation are discussed, as well as a few alternative cements. Finally, the third sub-chapter introduces what is known regarding cement-rock interactions, mostly based on previous concrete studies of the alkaliaggregate interaction. This last sub-chaper also refers to studies related to cement/rock interaction at conditions closer to the geothermal ones, e.g. Carbon Capture and Storage (CCS), as the papers in this specific field are scarce.

III.1 Geothermal Environments

Geothermal resources have been used for the last 2000 years, either for mineral extraction or for cultural purposes. However, it was only in 1856 that the first deep bore (over 100 meters) was drilled (Grant and Bixley, 2011). From then on, the utilisation of geothermal resources has been slow, when compared with petroleum or ground water resources' exploitation (Zinszne and Pellerin, 2007).

The characteristics of geothermal systems vary widely, but three components are essential for their exploitation (New Zealand Geothermal Association, 2012):

- a subsurface heat source that may be igneous magma or heat stored in other rocks;
- a fluid to transport the heat;
- faults, fractures or permeability within sub-surface rocks that allow the heated fluid to flow from the heat source to the surface or near-surface.

Geopressured geothermal reservoirs are generally deep, so that to tap the geothermal reservoir temperatures over 100°C, wells may need to be drilled to ~ 2km. The origin of these reservoirs is explained by a fluid caught in a permeable stratigraphic trap, followed by a raising of the lithostatic pressure by crustal movement over the years (Zinszne and Pellerin,

2007). At Wairakei, the wells were relatively shallow, ~600 to ~800m. In the Kawerau geothermal field, the typical production well depth is between 950m and 2100m with injection wells varying from 300m to 3000m. The production at Rotokawa is made from wells around 2.0km to 2.5km depths (New Zealand Geothermal Association, 2012).

In geothermal systems, several variables need to be considered for assessment:

- A high temperature (up to 320°C) hydrothermal fluid; in New Zealand these are often CO₂-enriched brines with >40,000ppm CO₂ and sometimes very acidic environments;
- The rock formation itself; some of the main factors to consider are stratigraphic distribution, mineral composition, permeability, porosity and hydrothermal alteration;
- Finally, the fluids used during the drilling of the well, must be considered as a relevant/important factor, as they may affect the rock properties and, therefore, further cement-rock interactions.

By the 1980's, all of the easily accessible New Zealand's high temperature geothermal resources had been identified (**Figure III.1**). Most of the high temperatures New Zealand geothermal fields are located in the Taupo Volcanic Zone (TVZ) (**Figure III.2**) which extends from White Island (in the Bay of Plenty) southwest to Mt Ruapehu (New Zealand Geothermal Association, 2012).

III.1.1 Temperature

In non-geothermal areas, there is an average downward temperature gradient of 30°C/km, which, in certain areas, can reach 60°C/km. However, in geothermal wells, temperatures up to 320°C are often found at around 1 km depth (Zinszne and Pellerin, 2007; Sugama, 2006). Depending on the temperature, geothermal resources can be classified into three categories (New Zealand Geothermal Association, 2012):

- High temperature, usually magmatic-related resources, with temperatures of 200-350°C at an economically-drillable depth;
- Moderate to low temperature resources, of non-magmatic origin, usually associated with deep faults, with maximum temperatures at drillable depth that do not exceed 140°C;

• Very low temperature resources, which are widespread but close to ambient temperature.



Figure III.1 - Map of New Zealand Geothermal Fields (New Zealand Geothermal Association, 2012)

Figure III.2 - Map of Geothermal Fields in the TVZ (New Zealand Geothermal Association, 2012)

Of New Zealand's identified geothermal areas, 14 lie in the 70-140°C range (low temperature geothermal energy), 7 in the 140-220°C range and 15 in the >220°C range. In the Taupo Volcanic Zone (TVZ), magma intruded into the stretched and fractured crust of the zone has resulted in temperatures of at least 350°C at depths of less than 5 km (New Zealand Geothermal Association, 2012). In Table III.1 the localisation and temperatures of several New Zealand geothermal systems/fields are presented.

Table III.1 – Location and temperatures of some NZ geothermal wells (mostly in TVZ)

Geothermal field	Localization	Temperature features
Wairakai		From 1960 to 1970, decreased from ca. 255°C to ca. 235°C
Wairakai Tauhara	E of Taupo township	(2°C/year)
(wallakel-laulara		From 1970 to 1985, slow decline at about 0.5°C/year
geothermal system)		After 1985, increase in the feed water temperatures
Tauhara		Reservoir base temperature approx. 260-265°C
(Wairakei-Tauhara	E of Taupo township	Maximum temperature recorded is 279°C
geothermal system)		Production temperature is about 250 °C
Potokawa	14 km NE of Taupo	
KOlokawa	9 km E of Wairakei	High-temperature resource of up to 320°C
Atiamuri	40 km north of Taupo	Maximum temperature of 165°C (between 350 m and 600
	1	m)
	15 km SW of Rotorua	Geothermometry suggests temperatures 150-160°C in the
Horohoro	City	aquifer
	5	
Kawerau	E of Kawerau township	Maximum temperatures 250-310°C
Mangakino	E of Mangakino township	Deepest wells reaching a temperature of 254°C
		Conductive temperature gradient of about 75°C/km
Mokai	20 km N of Taupo	Has some of the hottest geothermal wells in New Zealand
		Recorded downhole temperatures of up to 326°C
Ngatamariki	17km NE of Taupo	Resource temperature ranges from 255°C up to 290°C
Ngawha	Northland, 6 km E of	
(not in the TVZ)	Kaikohe	Gas ratios suggest that a deeper reservoir at 300-320°C
	23 km N of Taupo	
Orakeikorako	37 km S-SW of Rotorua	Temperatures of up to 265°C in the wells
	City	
Rotoma	30 km E of Rotorua	Reservoirs temperatures 220-250 °C
Rotorua	Rotorua City	90 wells are less than 200 m deep with geothermal fluid at
Rotorua		temperatures of 120 to 200°C
Tikitere	18 km NE of Rotorua City	Estimated at 140-190°C
Tokaanu Waihi	S of Lake Taupo	2 shallow wells with 154°C at 76 m and 169°C at 107 m
	10 km NW of Turangi	Geothermometer indicate a deep hot fluid of at least 250°C
Wajotanu	23 km S-SE of Rotorua	Wells drilled in the 1950s and 1980s recorded high
w atotapu	City	temperatures up to 295°C

(Contact Energy, 2007; New Zealand Geothermal Association, 2012)

III.1.2 Hydrothermal Fluids

Pirajno (2010) defines hydrothermal fluids as a hot (ca. 50° C to > 500° C) aqueous solution, containing solutes that are frequently precipitated as the solution changes its physical properties. These fluids are subject to variations in temperature, pressure and density, three very important variables in hydrothermal systems. Hydrothermal solutions usually are a mix of waters from several origins and can contain volatiles, like H₂O, CO₂, H₂S, HCl, SO₂ and CH₄.

The reservoir fluids in the Rotokawa, Ohaaki and Kawerau geothermal fields are gas-rich. In the Kawerau field the shallow reservoir fluids consist of mixtures of a near neutral chloride fluid, an acid sulfate condensate and a sodium bicarbonate fluid (Christenson, 1997). The deep fluids within the Broadlands-Ohaaki geothermal system, prior to the initiation of boiling at depths of 1500m, have temperatures above 300°C. As the West Bank production well fluids begin to ascend, they boil and cool and quickly shift from the Na-K feldspar equilibrium. In contrast, the ascent of fluids in the East Bank involves relatively deep (> 1000 m) mixing with steam-heated waters prior to their discharge to production wells. This dilution shifts the deep fluid from the Na-K feldspar equilibrium, where the diluent has a relatively low Na⁺/K⁺ ratio, when compared to the feldspar equilibrium. It is likely that equilibria other than that involving the feldspars, control the lower temperature Na⁺/K⁺ ratios of the steam-heated waters (Hedenquist, 1990).

The shift of the Broadlands mineral-fluid composition equilibria from a "full equilibrium" assemblage of Na-feldspar/K-feldspar into the K-mica equilibrium field is mainly due to the dilution of the deep fluid by marginal steam-heated waters, as boiling by the ascending fluid generally favors K-feldspar stability. The shift to illite (and even kaolinite) stability at Broadlands is hastened by the fact that the diluent is steam-heated and CO₂-rich (Giggenbach, 1984, 1988).

According to Wolley and Carroll (2010), the high levels of CO_2 found in Broadlands-Ohaaki are from CO_2 -rich waters flowing up from fractures in the low permeability basement greywacke into the overlying reservoir, which is dominated by rhyolites, dacite, pyroclastics, and some lake sediments. Hedenquist (1990) stated the best approximation to the "parent fluid" contained 2.7 wt% CO_2 (or 0.6 mol/kg), based on a sample from a specific well in the TVZ. Furthermore, this author estimated a corresponding H₂S content of 0.015 wt% (or 0.0044 mol/kg). These were combined in a model where the temperature was 300°C. Ambient total pressure at the top of the basement is in the range 100-250 bars (normal hydrostatic), depending on location, which, in geothermal wells is commonly within the range 10-100 bars, with a CO_2 overpressure of 6 bars (Wolley and Carroll, 2010; Henneberger, 1983)

III.1.3 Downhole CO₂

Depending on the downhole conditions, CO_2 may be present as a gaseous compound (CO_2 (g)) in dry steam, as an aqueous solute ($HCO_3^--CO_2$ (aq)) in ground waters or as supercritical CO_2 (Figure III.3) (Milodowski *et al.*, 2011). The gaseous and aqueous states are commonly found in geothermal fields, whereas supercritical CO_2 is mostly associated with Carbon Capture and Storage (CCS) operations. Any one of these phases is a potential source of carbonation, although low CO_2 solubility may substantially limit the kinetics of cement alteration, as less CO_2 is then available in the system to react with cement (Rimmele *et al.*, 2008).



Figure III.3 - CO₂ pressure-temperature phase diagram

The effects of supercritical CO_2 have been considered despite its conditions of lower temperature and higher pressures when compared to geothermal environments. There is significant information available in this field on its effect on cement carbonation where the products are similar.

III.1.3.1 CO₂ in geothermal environments

Most geothermal plants utilise hydrothermal systems with temperatures within the 100°C to 300° C range. Over this range, neutral pH decreases with temperature, from 6.14 at 100°C, to 5.83 at 150°C reaching a minimum of 5.6 around 250°C. As the temperature increases, CO₂ becomes less soluble and a weaker acid. While dissolved CO₂ levels in production fluids are typically around 0.064 moles/kg with a pH_T of 6.00 (neutral pH_T is 5.83), beneath caprocks and impermeable zones where gases boiled off in the production zone dissolve in the cooler fluid, the dissolved CO₂ concentration can be greater than 0.34 moles/kg giving a pH_T of ~4.59 which is mildly acidic. Total ambient pressure at the top of the basement is probably in the range 100-250 bars (normal hydrostatic), depending on location, translating into pressures in geothermal wells within the range 10-100 bars, with a CO₂ overpressure of 6 bars (Wolley and Carroll, 2010; Henneberger, 1983; Ellis, 1959).

 CO_2 normally dissolves in the hydrothermal fluid as a separate phase, becoming 'carbonic acid', H_2CO_3 , which dissociates (Equation III.1) (Duguid, 2009; Brandvoll, 2009).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$
 Equation III.1

This dissolution process depends on several factors including the solubility of CO_2 in water which increases with pressure, decreases with salinity and decreases with temperature up to 100-200°C, increasing hereupon (Milodowski *et al.*, 2011; Hangx, 2005). The specific composition of the fluid (e.g. hydrothermal brine) also affects the way the carbon dioxide reacts with it, as there is a general trend of decreasing CO_2 solubility with increasing ionic strength (**Figure III.4**) and with decreasing pH (Rochelle *et al.*, 2004). The hydrothermal brine (geobrine) chemistry, in turn, depends on several factors, including the chemical interaction with the rock formation. Therefore, the rates of mineral reaction also have an impact on CO_2 solubility. Other factors that influence CO_2 solubility are the degree of CO_2 -water mixing or contact surface with CO_2 and water (Rochelle *et al.*, 2004).



Figure III.4 - CO₂ solubility as a function of the total dissolved solids (TDS) (based upon data at 20-250°C, 3-85MPa, Enick and Klara, 1990 in Rochelle *et al.*, 2004)

Ellis *et al.* (1963) studied the solubility of CO_2 as a function of the sodium chloride (NaCl) content, commonly present in appreciable amounts in the hydrothermal fluid at temperatures up to 350°C and salt (NaCl) concentrations up to 3 molal. Values of p_c (partial pressure of CO_2) ranging from 15 to 90 atm were used in the solubility determinations.

In order to correlate all these variables, they used the Henry's Law coefficient, *K* (Equation III.2 and Figure III.5), as well as the Ostwald coefficient, λ (Equation III.3 and Figure III.6) (Ellis *et al.*, 1963).

$$K = \frac{f_c}{x} = \frac{\propto p_c}{x}$$
 Equation III.2

with,

 f_c the fugacity of CO₂;

- \propto , the fugacity coefficient;
- p_c , the partial pressure of CO₂;

x, the ratio of the moles of carbon dioxide to the sum of moles of carbon dioxide and water in the solution.


Figure III.5 - Values of the Henry's Law constant K for the solution of CO₂ in water and sodium chloride solutions, as a function of temperature (Ellis *et al.*, 1963)



Figure III.6 - Values of the Ostwald distribution coefficient λ for the solubility of CO₂ in water and sodium chloride solutions, as a function of temperature (Ellis *et al.*, 1963)

III.1.3.2 CO₂ in CCS

In a CCS context, the injected supercritical CO_2 is usually relatively dry, as this reduces corrosion of infrastructure. Initial reactions are likely to involve dissolution into water and vice-versa, according to the **Equation III.4**, where significant CO_3^{2-} will probably be only found in highly alkaline environments (e.g. cement pore water) (Rochelle *et al.*, 2004; Hangx, 2005).

$$CO_2(g) + H_2O \leftrightarrow CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$
 Equation III.4

This series of reversible reactions is influenced by temperature and pressure (which control the solubility of CO_2) and by the ability of the host aquifer to buffer pH, as the dissociation reaction involves generation of H⁺ (Rochelle *et al.*, 2004).

For supercritical CO₂ at temperatures between 37°C and 100°C and pressures below 300 bars (\approx 304 atm), its solubility in water decreases with increasing temperature and increases with increasing pressure. At higher temperatures and pressures, however, CO₂ solubility increases with increasing temperature (**Figure III.7**) (Rochelle *et al.*, 2004).



Figure III.7 - Solubility of CO₂ in pure water (based upon data Wiebe & Gaddy (1940) and Wiebe (1941) in Rochelle *et al.*, 2004)

The density of supercritical CO_2 varies depending on pressure and temperature, but it is less dense than water so will rise until it reaches an overlying aquiclude where it will be physically trapped.

III.1.4 Stratigraphy

The crust of the Earth is composed by several different rock formations, the compositions of which also depend on the depth. This distribution of rock type as function of the depth is termed stratigraphy. Each rock type has its own distinct mineralogic characteristics, and even the same rock type can have slightly different properties, depending on its origin, age and surrounding environment. This section presents typical stratigraphies of a geothermal zone.

The Ohaaki-Broadlands geothermal system near the eastern fault margin of the Taupo Volcanic Zone (TVZ) (**Figure III.8** and **Figure III.9**) comprises a principal andesitic arc and, further west, a marginal basin, with welded pyroclastic flows, plus airfall tufts and pumice breccias, overlying a block-faulted Mesozoic greywacke and argillite basement. There are also several interbedded (laterally discontinuous) rhyolite and dacite flows. These rocks originally contained an assemblage of quartz and andesine phenocrysts set in a glassy to fine grained groundmass. Minor amounts of hornblende, biotite, hypersthene, magnetite, ilmenite, apatite and zircon are also present (Hedenquist, 1990; Browne and Ellis, 1970; Browne, 1973a). According to the New Zealand Geothermal Association (2012), the Ohaaki-Broadlands geothermal field stratigraphy can be generally explained with the following layers:

- Huka Falls Formation: a mudstone cap which overlies much of the field;
- Ohaaki Rhyolite: a lava with high horizontal permeability and hydraulically connected to groundwater aquifers;
- Waiora Formation: the main producing aquifer, with heterogeneous uncompacted pumice and lapilli tuffs;
- Rautawiri Breccia: the second important aquifer composed of coarse breccias;
- Rangitaiki Ignimbrite, Ohakuri Group volcanics and Waiora Formation conglomerates: rocks of poorly known material;
- Greywacke: permeability will exist in fractures.

For the Rotokawa geothermal system it was concluded that the subsurface is composed of basement greywacke, which is overlain by the Rotokawa Andesite (a sequence of andesitic

lava flows and breccias up to 2000m thick). Overlying the Rotokawa Andesite, and infilling the graben, are the volcaniclastic and sedimentary deposits (Tahorakuri and Waikora formations - members of the Reporoa Group), which are in turn overlain by the Wairakei Ignimbrite. Overlying the Wairakei Ignimbrite are the rhyolitic tuffs, ashes and breccias of the Waiora Formation. Haparangi Rhyolite lavas and breccias occur within the Waiora Formation, which is then overlain by mudstones, siltstones and sandstones of the Huka Formation intercalated with the Parariki hydrothermal eruption breccias (New Zealand Geothermal Association, 2012). According to Rae (2007), the most commonly found rock formations in Rotokawa are rhyolites, ignimbrites, andesites and sediments. A typical stratigraphy of a Rotokawa well is shown in Table III.2.



Figure III.8 - Northwest-southeast cross section through the Broadlands system showing stratigraphy and isotherms and interfered (schematic) distribution of CO₂-rich steam-heated waters, as well as general patterns boiling and dilution (Hedenquist, 1990)



Figure III.9 - North northeast-south southwest cross-section through West Bank wells (in Ohakii- Broadlands system), showing stratigraphy and isotherms and interfered (schematic) distribution of CO₂-rich steam-heated waters, as well as general patterns boiling and dilution (Hedenquist, 1990)

The reservoir of the Kawerau geothermal field (located at the northern end of the Taupo Volcanic Zone) is composed of volcanic lavas, pyroclastics and sediments, lying on basement greywackes. The existing volcanic rocks range from andesite to rhyolite in composition, with silicic ignimbrite (Christenson, 1997). In accordance with Bignall *et al.* (1996), the stratigraphy of the Orakeikorako geothermal field comprises a complex sequence of interbedded ignimbrites, airfall tuffs, lavas and hydrothermal eruption breccias, which are all silica-rich (> 72 wt.% SiO₂) when fresh and usually more so when altered.

From the literature review, together with recommendations by Browne (2011) and the IRL cement research team, ignimbrite, rhyolite, andesite, greywacke and pumice were considered as the most relevant rocks in order of decreasing importance.

Thickness range (m)	Lithology
10 to 30	Unaltered/termally oxidized pumice tuff, rhyolite lava
	Unaltered quartz and feldspar crystals
15 to 150	Fine sandstone and siltstone with pumice rich subunits
20 to 220	Strongly altered quartz-feldspar rich tuffaceous breccia with a silty-clay matrix
90 to 550	Crystal-rich, hornblende bearing vitric tuff
110 to 660	Crystal-poor, rhyolite lava and breccia
200 to 390	White, crystal-rich, not too densely welded ignimbrite
	Large quartz crystals are often heavily embayed
10 to 250	Rounded to sub-rounded greywacke and argillite gravels
20 to 250	White, crystal-vitric-lithic tuff
865 to 2190	Mottled, pale green and reddish purple, pyroxene-bearing andesite lava
-	Dark to pale grey, weakly metamorphosed argillite and fine silty sandstone

Table III.2 - Typical stratigraphy of a Rotokawa geothermal well (Rae, 2007)

III.1.4.1 Mineralogy

Ignimbrite, rhyolite, andesite and pumice are fine grained igneous rocks, whereas greywacke is a sedimentary rock of marine origin with fine to medium sized grains.

Ignimbrite is a volcanic rock that consists of crystal and rock fragments held in a matrix of glass shards which are usually welded together in a matrix of volcanic ash (tephra) made up of shards and fragments of volcanic glass, pumice fragments, and anhedral crystals. The phenocrysts are biotite (K(Mg,Fe)₃AlSi₃O₁₀(F,OH)₂), quartz, SiO₂, feldspars (XAl₍₁₋₂₎Si₍₃₋₂₎O₈, where X represents a combination of Na and/or K and/or Ca), and occasionally hornblende ((Ca,Na)₂₋₃(Mg,Fe,Al)₅(Al,Si)₈O₂₂(OH,F)₂), but rarely pyroxene (XY(Si,Al)₂O₆, where X represents Ca and/or Na and/or Fe²⁺ and/or Mg and Y represents ions of smaller size, such as Cr and/or Al and/or Fe³⁺). In the case of phonolite tuffs, the feldspathoid

minerals are nepheline (Na₃KAl₄Si₄O₁₆) and leucite (K[AlSi₂O₆]). Chemically, the ignimbrite composition is generally over 65 wt% SiO₂, with varying contents of sodium, potassium, and calcium, and lesser amounts of iron and magnesium (Pellant, 2000; Henneberger, 1983). Most of the current research will be mostly focused on this rock, which is the most common one found in geothermal fields in New Zealand.

Rhyolite is an extrusive volcanic rock, typically over 69% SiO₂, with varying textures. The mineral assemblage is typically composed of quartz, alkali feldspar and plagioclase, with biotite and hornblende as the most common accessory minerals (Pellant, 2000).

Andesite is an intermediate (between basalt and dacite) volcanic rock, within a range of 55 to 65% SiO₂. Its mineral assemblage is typically dominated by plagioclase feldspars (andesine or oliogoclase) and hornblende (dark amphibole) with alkali feldspars present in minor amounts. Magnetite, zircon, apatite, ilmenite, biotite and garnet are common accessory minerals (Pellant, 2000).

Pumice is a light, porous rock with a silica-rich composition (typically over 69% SiO₂). It may contain a variety of minute crystals of silicate minerals, such as feldspar and ferromagnesians, but contains a considerable amount of glass (Pellant, 2000). Due to its similarity to ignimbrite (in chemical composition), the pumice is not a priority for further studies in the current research programme.

Finally, greywacke, which contains abundant quartz, feldspar and rock fragments in a very fine matrix of clay (aluminosilicate), chlorite $((Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6)$, quartz and pyrite (FeS₂), where the minerals are too small to be seen with the unaided eye (Pellant, 2000).

Bignall *et al.* (1996) studied three different types of ignimbrites in the Orakeikorako geothermal field (in the TVZ) the *Paeroa*, *Te Kopia* and *Akatarewa* ignimbrites. These ignimbrites were distinguished from each other by their stratigraphy, origin and degree/type of alteration but were mineralogically, physically and chemically similar to one another. The *Paeroa* ignimbrite occurred at the surface, east of Orakeikorako and in drillholes at Waiotapu (22 km to the northeast) and was found to be over 300m thick in some areas. The *Te Kopia* ignimbrite, was hard, crystal-rich and welded (where fresh) and up to 360m thick in some wells. Finally, the *Akatarewa* ignimbrite was the oldest and deepest unit encountered by drilling at Orakeikoro with a thickness exceeding 440m. It comprised at least two subunits

separated by up to 80m of rhyolitic lava and is one of the important older units in the central segment of the TVZ. From their studies Bignall *et at.* (1996) drew the following conclusions:

- the three ignimbrites contain similar assemblages of primary minerals;
- there is a wide range in the proportions of the primary minerals present in all three ignimbrites;
- the variation in primary mineral proportions is clearly an inherited feature that depends on several factors including the homogeneity of the magma and its eruption characteristics;
- the degree of welding will affect the proportions of phenocrysts and clasts to groundmass within a cooling unit because shards fuse and rock porosity reduces as welding occurs;
- the sizes and shapes of the phenocryst phases are not diagnostic of each ignimbrite.
- petrographic characteristics of these ignimbrites made it difficult for them to be distinguished from one another, with confidence, even where they were little altered.

Although the whole-rock ignimbrite compositions are influenced by the initial magma chemistry and contamination by lithic fragments (the pumice represents a better primary magma composition than does the host rocks), using that correlation to understand the origin of the ignimbrite through the pumice composition is an almost impossible task in geothermal fields, since the pumice alters very quickly in those environments.

III.1.4.2 Porosity and Permeability

Porosity is an important variable used in the formulation and calculation of the mathematical models of the rocks. In Rotokawa, it ranges from 5 to 33%, with an average of 10% for rhyolites, ignimbrites, andesites and sediments (Rae, 2007). However, pumice has an average porosity of 90%, and has density <1 (Pellant, 2000).

Permeability is intimately connected with porosity as it is given by the amount of fluid flowing through the rock pores per unit of time. Permeability is a very important factor to consider in the cementing of geothermal wells and is controlled by three factors (Rae, 2007):

• distribution of primary permeable zones, related to the texture and mode of formation of the geological unit;

- distribution of secondary permeable zones, related to brittle faulting and fractures generated by earthquakes, thermal stresses and/or regional strain;
- distribution of secondary permeable zones, related to effects of prolonged hydrothermal alteration causing either dissolution of fluid pathways and/or mineral deposition.

In the context of the current research programme, two of the above mentioned permeability types are considered: the primary one, related to the texture and mode of formation of the geological unit, and the one related to the hydrothermal alteration of the rocks. The above mentioned secondary permeable zone related to brittle faulting is not an important variable in the context of this research programme, so it will be neglected when simulating the downhole conditions.

It will be assumed that the rocks used in the experimental work have standard porosity and permeability properties, similar to that found in geothermal environments, which also depend on the hydrothermal alteration of the rock (the alteration may increase or decrease the permeability, depending on the respective chemical reactions) (Hodgkinson and Hughes, 1999).

III.1.5 Hydrothermal Alteration

Hydrothermal alteration is a complex process involving mineralogical, chemical and textural changes in the rocks as a consequence of the interaction of the rock with hydrothermal fluids. The alteration can be classified according to the nature, chemistry, temperature and pressure of the circulating fluids and the nature and composition of the resulting rocks. In simple terms, the hydrothermal fluids chemically attack the mineral constituents of the wall rocks, re-equilibrating to form new mineral assemblages that are in equilibrium with the new conditions. It is a form of metasomatism, i.e., an exchange of chemical components between the fluids and the wall-rocks. The main variables in the rock alteration process are the nature of the wall-rock, composition and concentration of the fluid components, in particular H⁺, CO_2 , O_2 , K^+ , H_2S and SO_2 (Pirajno, 2010).

Hydrothermal alteration can be classified either as a function of recognised mineral assemblages and/or chemical changes. The first is carried out through extensive thin section studies (Pirajno, 2010). Grifkins *et al.* (2005) suggested the alteration could be classified

using a combination of four variables: the extent of mineral modification, distribution, texture and mineral assemblage. The modification can be subtle, weak, moderate, strong or intense, while the distribution variable can be local or regional, on the footwall, hanging wall, pipe, stratabound, etc.; the texture (hand specimen or thin section) includes shape, grainsize, fabric and can be selective, pervasive or vein halo; while the mineral assemblage lists the minerals in order of decreasing abundances. The main types of alteration can be called "pervasive" (replacement of most original rock forming minerals), "selectively pervasive" (replacement of specific original minerals) and "non-pervasive" (only certain portions of the rock have been affected) (Pirajno, 2010).

In general terms, the interactions of hydrothermal solutions with wall rock are dependent on the variations in the a_{K+}/a_{H+} ratio; i.e., the activities of the K⁺ and H⁺ ions in the system. This ratio decreases as the system tends towards lower temperatures and pressures, i.e., with increasing [H⁺], alteration processes move from alkali to argilic in a theoretically continuous evolving system. From the highest to the lowest rate a_{K+}/a_{H+} (lowest to highest metasomatism), the types of alteration suggested by Pirajno (2010) are: 1) alkali metasomatism and potassium silicate alteration, 2) propylitic 3) phyllic or sericitic alteration and greisenisation, 4) intermediate argillic, and 5) advanced argillic.

Prince *et al.* (2000) considered there were two different processes often involved in the rock alteration: direct conversion of the initial minerals into another mineral and the hydrolysis of the initial mineral constituents in the surrounding water, which gradually becomes saturated with silica, alumina and various cations.

According to Henneberger (1983), there are seven alteration types of ignimbrite in the Ohakuri field, each the product of a particular hydrothermal environment. Each one of these alteration types is reflected in the mineralogy which corresponds to a particular range of alteration rank and intensity. The rank of alteration is determined by the assemblage of hydrothermal minerals formed: higher rank assemblages generally reflect higher temperatures, but may in part reflect higher water-to-rock ratios.

In the Broadlands-Ohaaki hydrothermal system, quartz and apatite have been little affected by the hydrothermal alteration, whereas the other primary minerals have reacted to varying degrees, with the highly porous and permeable Breccia Formations generally being completely altered (Browne, 1978). Within this field, the principal hydrothermal mineral assemblage at 260°C (600-800m depth) is quartz-albite-illite-adularia-calcite-chlorite-pyrite. Calcite is common and abundant and present in the core from all wells. It forms as a replacement mineral and also occurs as a groundmass and fracture filling. Quartz is one of the most abundant minerals, both as a coarsely crystalline fracture filling (to 2cm), as well as a fine grained product (including cristobalite at lower temperatures) (Browne and Ellis, 1970).

It is not clear whether a rock alteration will result in net dissolution or net precipitation of material. The former leads to higher porosity and higher permeability, whereas the consequence of precipitation depends on several factors. In their experiments/models on the study of the evolution of rock porosity when exposed to a cementitious alkaline environment, Bradney *et al.* (1993) and Eikenberg and Lichtner (1992) observed a porosity decrease and, eventually, a permeability decrease. The fractures are repaired within decades (Rochelle *et al.*, 1992) due to precipitation of high density phases, whereas low density phases might cause expansion and consequent micro-cracking which increases permeability (Hughes *et al.*, 1995). Expansion mechanisms can be either due to the reaction of alkali feldspars with calcium hydroxide, resulting in the formation of tetra-calcium aluminate hydrate (or AFm phases, which cause expansion in concrete by altering to sulfate/carbonate-bearing phases such as ettringite, although this mineral decomposes at 60°C) and alkali silicate gels (which are commonly known as very prejudicial to the concrete, since they take in water, expand and thereby fracture) (Hodgkinson and Hughes, 1999).

III.1.6 CO₂/Formation Interaction

There have been several studies on the geology and geochemistry within the New Zealand TVZ, where the existent CO_2 -rich fluid interacts with felsic rocks (namely greywackes, rhyolites and ignimbrites) at temperatures up to 300-400°C (Wolley and Carroll, 2010).

The interaction of the geothermal fluid with the rocks in which it occurs depends on the temperature, pressure, amount of CO_2 (and other acid gases, like H_2S and SO_2), amount of H_2O , fluid phase compositions, host rock type and physical properties of the rock (namely permeability and porosity) (Wolley and Carroll, 2010). Generally, CO_2 (as well as other brine components) is expected to react (by dissolution/precipitation) in a lower degree with rocks of a more felsic nature (such as granite and many sandstones), when compared with rocks of a more mafic nature (*e.g.* andesite, basalt, peridotite), due to the less reactive nature of the felsic rocks' dominant minerals (Wolley and Carroll, 2010; Duguid, 2009; Brandvoll, 2009).

The potential host rocks for CCS storage will be either carbonate or sandstone formations (Rochelle *et al.*, 2004), whereas in geothermal environments igneous rocks are predominant, e.g. ignimbrite, rhyolite and andesite. The most common/predominant minerals in any of these rocks are feldspars and quartz, with exception of carbonate formations where calcite is the predominant compound.

Some of the chemical equations representing reactions between CO_2 and carbonate and some feldspars minerals in an aqueous CCS environment are given below. The reaction between carbon dioxide and the carbonate rock (CaCO₃) is similar to that between CO_2 and the carbonate from cement (Gunter *et al.*, 1993). This reaction involves some calcium leaching within a carbonate host formation and is expressed in the **Equation III.5**:

$$CO_{2(aq)} + H_2O + CaCO_3(calcite) \leftrightarrow Ca^{2+} + 2HCO_3^-$$
 Equation III.5

With feldspathic rocks, the precipitation of calcite is mainly limited by Ca-rich plagioclase content and water content (Hangx, 2005). Between CO_2 and anorthite, Gunter *et al.* (1997) predicted the reaction represented in the Equation III.6:

 $CaAl_2Si_2O_8(anorthite) + CO_{2(aq)} + 2H_2O \rightarrow$ $CaCO_3(calcite) + Al_2Si_2O_5(OH)_4(kaolinite)$ Equation III.6

Whereas for a Na-rich plagioclase feldspar, Gunter *et al.* (1997) considered the Equation III.7 applied.

$$7NaAlSi_{3}O_{8}(albite) + 6CO_{2(aq)} + 6H_{2}O \rightarrow$$

$$Na-smectite + 6HCO_{3}^{-} + 6Na^{+} + 10SiO_{2}(quartz)$$

Equation III.7

For K-rich feldspar in saline solutions Johnson *et al.* (2001) have postulated the precipitation of a different carbonate mineral, dawsonite, according to the **Equation III.8**.

 $KAlSi_3O_8(K\text{-}feldspar) + Na^+ + CO_{2(aq)} + H_2O \rightarrow NaAlCO_3(OH)_2(dawsonite) + 3SiO_2(quartz, chalcedony or cristobalite)$

Equation III.8

From their model simulating a CCS environment, Rochelle *et al.* (2004) concluded that albite, biotite and K-feldspar would dissolve, whereas calcite, dolomite, kaolinite, muscovite, quartz and siderite would be precipitated. Also, the major CO₂-trapping reactions were the precipitation of calcite and siderite, and the formation of aqueous bicarbonate ions.

There are, however, other factors that have to be considered, as several variables are interlinked. For instance, as CO_2 solubility decreases with decreasing pH, more dissolved CO_2 can be 'trapped' in an aquifer that can maintain (buffer) the pH of the formation water compared to one where formation water pH decreases (Rochelle *et al.*, 2004).

The temperature, pressure and salinity may also affect the rate of reaction, by affecting the feldspars dissolution rate. For instance, the dissolution rate of anorthite is enhanced by ≈ 1.5 orders of magnitude when the temperature is raised from room temperature to 100° C, ≈ 2.75 orders of magnitude when raised to 200° C and ≈ 3.5 of magnitude when raised to 300° C. The pressure appears to significantly affect the reaction rate by increasing the CO₂ dissolution (rather than affecting the feldspar dissolution) as pressure increases. Salinity decreases the dissolution rate of plagioclase feldspars at both near neutral and acid pH (Hangx, 2005).

The porosity-permeability evolution of the formation during the reaction with CO_2 may be dependent on the dissolution mechanism, as well as the location of precipitation (Hangx, 2005).

Although there is some uncertainty in the rates of reaction, it appears that CO_2 -trapping reactions under CCS conditions (54°C and 260 bars) would take hundreds of years to complete (Rochelle *et al.*, 2004).

III.1.7 Drilling Fluids

Another factor that has to be considered before cementing the well (although not belonging to the natural geothermal environment) are the changes caused by drilling. The most relevant one is due to fluids used during the drilling of the well, which have several functions (Culver, 1998; IPIECA and OGP, 2009):

- provides a barrier for well control;
- removes cuttings from the well bore as they are produced;
- maintains drill cuttings in suspension when drilling circulation is stopped;
- transmits hydraulic power to the drilling bit;
- maintains formation stability;
- maintains pressure on the formation;
- minimizes fluid losses to the formation;
- minimizes formation fluid migration into the hole;
- cools and lubricates the mud pump, bit and the annulus between the drill string and the hole;
- reduces drill string corrosion;
- assists in collection and interpretation of samples and borehole geophysical logs and release cuttings in the mud tank or pit.

There are 3 classes of drilling fluids: water-based, air-based and oil-based. The latter two classes can be used in petroleum drilling, but are not appropriate for low to moderate temperature geothermal drilling because of the danger of contamination of aquifers. Therefore, mud is the most common drilling fluid and, while useful for the purposes listed above, presents many of the problems encountered in geothermal drilling (Culver, 1998). There are numerous cases where just pure water is used, as the drilling mud can be expensive.

One of the most important issues encountered during drilling is the phenomenon called lost circulation, which is characterised by the loss of drilling fluid from the borehole through cracks, crevices, or porous formations. It can be partial or complete, depending on the conditions, with consequential loss of expensive fluid components and loss of drilling time. Use of potentially expensive lost circulation materials to keep the losses from plugging

possible production zones can lead to cementing problems (Culver, 1998). The only drilling fluid that concerns the current investigation is the use of mud to maintain minimum weight, viscosity, and filtration and whether it has an effect on the cement-rock interaction.

drilling muds are primarily mixtures of western bentonite (sodium Currently, montmorillonite) and water. Additionally, organic polymers, dispersants, wetting agents, weighting materials, thinners and lubricants are used to modify properties of drilling mud to meet changing hole conditions or counteract changes previously made by the driller. When bentonite is added to the water, the density and viscosity of the slurry increase, improving the carrying capacity of cuttings up the hole. Gelation, lubricity, and filtration properties can also be added. Moreover, as the mud is used, it gains density, which has both positive and negative consequences. The positive properties are an increase of its buoyancy effect (carrying capacity for cuttings) and increased borehole pressure (consequently, the ability to prevent caving and flow into the hole). The negative consequence is a decreased settling rate in the mud pit. Other relevant bentonite properties are sand content (which affect the mud density and apparent viscosity) and thixotropy (its ability to gel) (Culver, 1998). While it is common practice to wash the annulus between the casing and formation before cementing, much of the mud adheres to the formation and, consequently, interacts with the cement, playing a relevant role on the way that the cement interacts with the rock, by modifying the reaction products when compared to the ones obtained from a pure cement-rock interaction.

III.2 Cement

III.2.1 Introduction

Oil, gas and geothermal well cements are intimately interrelated. There has been limited research on geothermal wells, particularly in the materials' properties whereas use and conditions in oil and gas wells have been studied for a longer time, mainly because of the fast cash return (in contrast to geothermal projects). Consequently, most available data is based on low temperature exposure. The result of this is that geothermal well cementing still does not have its own distinct character, as much of it is based on the oil and gas industry. One can clearly understand this affirmation, as oilwell cements are classified by the American Petroleum Institute (API) regulations. Geothermal well cementing engineers have adopted the same nomenclature and standards as those used for oil and gas wells.

Initially, conventional well cement formulations focussed on the use of Portland based cements where the binder consists of calcium silicate hydrates (CaO-SiO₂-H₂O system) and calcium aluminium silicate hydrates (CaO-Al₂O₃-SiO₂-H₂O system). However, serious concerns, associated with the vulnerability of these hydrates to attack at elevated temperatures in geothermal conditions by corrosive CO_2 and H_2SO_4 have been raised. The damaged wells needed to be repaired as soon as possible to avoid catastrophic collapse of the wells. Hence, the susceptibility of cements to these harsh environments has been a major impediment to the development of geothermal energy resources (Sugama, 2006).

For over a hundred years, deep drilling has only been associated with the oil and gas industry. With the advent of Hot Dry Rock (HDR) geothermal exploitation, deep drilling also became a requirement for geothermal activities (Teodoriu and Falcone, 2008) and the concern over materials properties at high temperatures and pressures has come to prominence.

III.2.2 Portland Cement

Portland cement clinker is made by heating a homogeneous mixture of raw materials to a sintering temperature of about 1450° C in a rotary kiln. The raw feed consists mainly of limestone (mostly composed of CaCO₃) and clay (aluminosilicate, Al₂O₃.2SiO₂). The aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) present work as a flux, so the material partially melts or clinkers.

The cement chemists often utilize their own chemical notation, which is based on the oxide nomenclature¹, also given in the beginning of the *glossary*. The understanding of this notation is essential to fully comprehend the chemical composition of the Portland based cements given hereafter. The main clinker compounds are alite (tricalcium silicate, C_3S - approx. 55%), belite (β -dicalcium silicate, C_2S - approx. 20%), aluminate (tricalcium aluminate, C_3A - approx. 12%) and ferrite (tetra-calcium aluminoferrite, C_4AF - approx. 8%) (Bensted and Hewlett, 2008; Milestone, 2008). The clinker is mixed up with gypsum to make up the powdered Ordinary Portland Cement (OPC).

Compressive strength is mainly derived from a binder formed from the reaction of the silicate phases with water to form calcium silicate hydrate (C-S-H). C₃S is the principal cementing phase, while β -C₂S reacts at a much slower rate to form similar hydration products. Whereas C₃S is largely responsible for the early strength, the C₂S contributes to strength at later ages (28 days and beyond) (Bensted and Hewlett, 2008).

The chemical formulae representing the silicate reactions with water to form an amorphous calcium silicate hydrate, at ambient temperatures (or just above) can be expressed according to the **Equation III.9** and **Equation III.10**.

$$2Ca_3SiO_5 + 6H_2O \rightarrow 'Ca_3Si_2O_7.3H_2O' + 3Ca(OH)_2$$
 Equation III.9

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7.3H_2O + Ca(OH)_2$$
 Equation III.10

The poorly crystalline C-S-H is non-stoichiometric so these reactions are only approximate. The Ca/Si ratio of a typical C-S-H gel varies with temperature from ~ 2.00 at -40° C, ~1.72 at 20°C to about 1.52 at 85°C (Milestone, 2008). However, according to Bensted and Hewlett (2008), the hydration of alite and belie phases at up to approximately 100°C, does not differ greatly from that at ambient temperature. In their experimental work, Cowan and Hale (1992) did not find any changes in the mechanism of hydration from ambient temperature to 90°C, although more polysilicates hydrates in relation to the dimer were found in the calcium

¹ Cement chemical nomenclature:

 $[\]mathbf{A} - Al_2O_3; \mathbf{C} - CaO; \mathbf{\hat{C}} - CO_2; \mathbf{F} - Fe_2O_3; \mathbf{H} - H_2O; \mathbf{K} - K_2O; \mathbf{M} - MgO; \mathbf{N} - Na_2O; \mathbf{S} - SiO_2; \mathbf{\hat{S}} - SO_3; \mathbf{T} - TiO_2.$

silicate hydrate pastes at 65°C than at 25°C. Nonetheless, at elevated temperatures, the hydration of the belite is accelerated in relation to the alite, which may be related to the higher solubility of the silica and lower solubility of calcium hydroxide under these conditions (Skalny and Young, 1980).

The gypsum added to control setting will react with the aluminate and the ferrite phases, forming ettringite, according to the Equation III.11 and Equation III.12.

$$Ca_{3}Al_{2}O_{6} + 3\{CaSO_{4}.2H_{2}O\} + 26H_{2}O \rightarrow Ca_{6}[Al(OH)_{6}]_{2}(SO_{4})_{3}.26H_{2}O$$
 Equation III.11

 $Ca_{2}AlFeO_{5} + Ca(OH)_{2} + 3\{CaSO_{4}.2H_{2}O\} + 25H_{2}O \rightarrow Ca_{6}[Al_{0.5}Fe_{0.5}(OH)_{6}]_{2}(SO_{4})_{3}.26H_{2}O$ Equation III.12

In fact, only one form of ettringite is formed, since the ettringite derives from the aluminate and ferrite mixed together with some impurities to produce one continuous mass (Bensted and Hewlett, 2008).

III.2.3 Hydration at Elevated Temperatures

At elevated temperatures and pressures, a series of different hydration reactions occur in Portland cement. The hydrates no longer lose water but change their characteristics and form new compounds depending on temperature. Continuous exposure to hydrothermal conditions induces a gradual compressive strength loss in hardened Portland cement. This phenomenon of strength retrogression was investigated by Kalousek and his co-workers (1951, 1954, 1955), and has been shown to be caused by the formation and slow growth of new crystalline phases, associated with increased porosity and permeability, as the crystals enlarge and densify leaving a rather porous matrix that has little strength (Milestone, 2001).

At temperatures above 120°C in wells, crystalline α -di-calcium silicate hydrate (α C₂SH) may form, causing a high permeability and low (compression) strengths, when compared with any other hydration product. This compound readily forms at about 150°C. At the same time, Ca(OH)₂ is also generated, ensuring the Ca/Si ratio in the crystalline calcium silicate hydrates that forms remains high (Milestone, 2011). Pure quartz flour is often used as strength retrogression inhibitor. Kalousek (1954) found that by adding >30wt% silica flour (pure quartz which decreases the overall Ca/Si ratio in the binder), strength retrogression could be avoided through the formation of yet further crystalline phases tobermorite and xonotlite, depending on the temperature. Below 100° C quartz will not react readily. Even higher amounts of silica are now being considered to counter the loss in strength at high temperatures (Iverson *et al.*, 2010).

If no addition is made to the cement, above about 200°C, the pure OPC pastes transform still further to new, high Ca/Si ratio crystalline compounds, namely reinhardbraunsite (C_5S_2H), jaffeite ($C_6S_2H_3$) or kilchoanite (C_3S_2), which, again exist alongside with Ca(OH)₂. These products do not act as binders, giving very low strength and high porosity to the grout (Milestone, 2011).

On the other hand, with the addition of quartz, tobermorite (C_5S_6H) is formed at about 150°C (Ca/Si ratio between 0.8 and 1.0). This is a desirable crystalline binder, with low permeability and good compressive strength. Additionally, above about 180°C, tobermorite transforms into two further crystalline phases, namely xonotlite (C_6S_6H) and gyrolite ($C_6S_7H_2$) (this latter one is rare in geothermal wells) with Ca/Si ratios close to 1.00. Both have higher permeability (though still acceptable for the well cementing needs) and acceptable compressive strength. Finally, at about 250°C , gyrolite can transform to a weaker and more permeable material, truscottite ($C_{14}S_{24}H_2$) (Bensted and Hewlett, 2008; Ramachandran and Beaudoin, 1999). This transformation is characterized by a change of Ca/Si ratio from approximately 1.2 to 0.6 (Milestone, 2011).

The equilibrium reaction between the C-S-H gel and the $Ca(OH)_2$ is a characteristic of Portland cement hydration with the Ca/Si ratio of the gel dependent on temperature. However, in hydrothermal conditions $Ca(OH)_2$ is not usually found due to the reaction between it and the added silica, to form more C-S-H gel (Bensted and Hewlett, 2008) so it is difficult to define the Ca/Si ratios at elevated temperatures.

Two further substituted crystalline calcium silicate hydrates are often found, where the calcium is substituted. Pectolite (sodium substituted calcium silicate hydrate – NaCa₂HSi₃O₉) and scawtite (calcium silicate carbonate hydrate - Ca₇(Si₆O₁₈)CO₃.2H₂O) (Bensted and Hewlett, 2008) can occur. Pectolite is formed above 150°C, through exposure of tobermorite to sodium salt solutions, and is characterised by its higher permeability and similar compressive strength when compared with xonotlite, although combinations of pectolite and truscottite usually have permeabilities slightly lower than that of xonotlite (Eilers *et al.*,

1983). Scawtite is found mainly in high temperature wells, and in small amounts improves the performance of the cement, though its formation seems to be restricted by the presence of aluminium and alkali metal salts. Scawtite seems to have its origin when carbon dioxide solutions enter the pores of hydrating cement and react on cement surface, releasing silica which may seal some small fractures and pores. On the other hand, when present in large quantities, scawtite shows poor performance and brittleness. Scawtite forms from cements with ~35% silica and less than 10% sodium carbonate, sodium hydrogen carbonate or finely ground calcium carbonate, from 215 to 315° C (Bensted and Hewlett, 2008). According to Eilers *et al.* (1983) and Taylor and Roy (1980), scawtite is a xonotlite structure in which about 5% of CO₂ replaces part of the silica.

The reactions with silica depend critically on the form of silica present. For instance, the use of a coarse silica sand gives rise to the formation of poor cementitious products, whereas the use of silica flour enhances the formation of tobermorite which, as we have already seen, is a favourable mineral for cement performance. With silica fume (specific surface of about $20,000 \text{ m}^2/\text{kg}$), the silica reacts faster than the lime, forming an amorphous hydrate, which then reacts with spare lime to form gyrolite and truscottite, without the intermediate formation of tobermorite (Bensted and Hewlett, 2008).

However, the conditions in wells are not ideal (Langton *et al.*, 1980), and standard equilibrium conditions are rarely found (Babushkin *et al.*, 1985). Therefore, the actual hydration products that form depend on the particular conditions in each well.

III.2.4 Alternative Cements: Calcium Aluminate Cements

High-Alumina Cement (HAC) or Calcium Aluminate Cement (CAC), was produced as a cement resistant to sulfate attack and it also has better performance than OPC in characteristics such as rapid hardening, chemical and fire resistance, with good refractory performance. The hydration of CAC is greatly influenced by the temperature. Below 23°C, the hydration products are mostly CAH₁₀ with C₂AH₈ forming above 25°C. These hexagonal phases are metastable. Hydrogarnet (C₃AH₆) tends to form above 35°C. The hexagonal hydrates (CAH₁₀ or C₂AH₈) slowly convert to cubic hydrogarnet (C₃AH₆) and AH₃ with a consequent strength loss and increased porosity (reversion) which has restricted in its use in construction. It is believed that high temperature and high relative humidity are critical for the conversion reaction (Ding, 1995; Scrivener *et al.*, 2008).

To overcome this problem of reversion, a number of studies have been undertaken to prevent it occurring, one of them being the use of siliceous additives, which leads to formation of gehlenite hydrate, also as known as Strätlingite (C_2ASH_8), a stable mineral at ambient temperatures when compared to the metastable hexagonal hydrates (Scrivener *et al.*, 2008).

These cements offer an alternative to the Portland based well cements as they do not rely on formation of calcium silicates and the concerns about the durability associated with calcium/silicon ratios.

III.2.5 Oilwell Cement

From the beginning of oil exploitation, it was clear that construction cements designed for satisfactory early compression strength were not always suitable for use in well cementing. Well cements need to be prepared as low-viscosity slurries, which remain pumpable to considerable depths but which rapidly can change from a fluid to a hardened state, once they are pumped into place (Bensted and Hewlett, 2008). All this must occur under different conditions, particularly increased temperature and pressure as well as chemical attacks (Milestone, 2011).

Bensted and Hewlett (2008) believe that the primary function of a well cement was one of sealing to prevent the flow of fluids other than where this is specifically required in the well. The major application is in primary cementing, the process whereby at several stages during drilling of the well, the borehole is lined with a steel casing down which the cement slurry is pumped and then displaced up into the annular space between the casing and the borehole wall to provide a seal (Arens and Akstinat, 1982).

Initially, the main differences between oil well and construction cements were lower amounts of the fast setting components, such as C_3A and C_3S , as well as lower alkali content (Milestone, 2011).

The American Petroleum Institute (API) has developed a standard for operating procedures for well cements, known as API Specification 10A or BS EN ISO 10426-1:2009, now adapted by most countries. Eight classes of oilwell cements are specified for use at different depths, Classes A-H. These cements are based on Portland cement, consisting essentially of hydraulic calcium silicates, to which no additions other than set-modifying agents have been interground or blended during manufacture. The API specifications are accepted as an international standard (ISO) (Bensted and Hewlett, 2008). Definitions related to oil well

cementing are specified in the API Bulletin on Well Cement Nomenclature (API BULL 10C). Several countries have developed their own oil well cement standards and their requirements are highlighted elsewhere (Bensted, 1987).

The API Class A cement classification was originally given to OPC, and this was the cement used in the initial wells at Wairakei (Milestone, 2011). However, not all current Portland cements may be classified as Class A cements, as compositions have changed, which may or may not be in accordance with the API classification for Class A cements (Bensted and Hewlett, 2008). Many contain up to 10% minor constituents as allowed by various standards, such as the European Standards EN197-1 (typically flyash or limestone).

Cement classes B to F were introduced as alternatives to Class A, in response to the difficulties found in deeper wells but they are not commonly used today since the conditions found in geothermal wells are more demanding.

Class B cement is similar to G cement (the most common one used nowadays in well cements), with cementing requirements less strict as those for Class G. Class C cement, is a rapid-hardening (or ASTM type III) Portland cement and essentially a more finely ground A.

Classes D, E and F cements are pre-retarded cements, with D the least retarded and F the most retarded, with the additive (retarder, which is typically sodium or calcium salts of lignosulfonic acid, aka lignosulfates) added to the clinker and gypsum.

The most common cements, Classes G and H are manufactured as basic cements with their chemical and cementing properties more strictly controlled with the aim of providing consistent properties. Both cements are available as moderately or highly sulfate-resistant types. Class H cement is more coarsely-ground, giving a specific surface of approx. 220-250 m²/kg. Iron oxide is added to the raw feed to reduce C₃A content to below 3% so C₄AF content is typically 10-14%. For the sulfate resisting API Classes B-H, ettringite is mainly formed from the aluminoferrite phase, which means that the main reaction to form ettringite is the one represented by **Equation III.12**, which is slow compared to that represented in **Equation III.11**. After gypsum is completely used up (after several hours), ettringite changes to the monosulfoaluminate hydrate (Ca₄[(Al,Fe)(OH)₆)]2SO₄.6H₂O), which readily enters into solid solution with the calcium aluminate hydrate Ca₂(Al,Fe)(OH)₇.3H₂O formed at this stage from aluminate and aluminoferrite reacting with water (Bensted, 1983). Most oilwell cements used today are sulfate resisting for two different reasons: sulfates are commonly

found in ground waters and with the substitution of C_4AF for C_3A , the cement becomes more workable and, consequently, more appropriate for use in wells.

There are only small quantities of alkali in oilwell cements, present either as alkali sulfates or incorporated in the main clinker phases. In the API Specification 10A for the G and H cements, there is a limit of 0.75% equivalent Na₂O (see Equation III.27 in the page 67), ensuring thickening times are sufficient for the cement to flow downhole (Bensted and Hewlett, 2008).

Class H cement hydrates at a slower rate than class G because of its increased coarseness. According to the API Specification 10A, to achieve acceptable thickening and compressive strength, in a Class H cement, the water/cement ratio (0.38) is much lower when compared with class G cement (0.44) (Bensted and Hewlett, 2008). However, *in situ*, these API indicators are not strictly applied. Also, oilwell cements generally hydrate at high temperatures and pressures, which results in different products from those obtained in ordinary hydration, where the C-S-H products are usually amorphous (Bensted and Hewlett, 2008).

The API test methods have 3 main features: physical, chemical and cementing properties tests. The the latter ones were created specifically for the purpose, as the conditions found downhole are quite different from those found in civil construction, even though some standard tests, like thickening time and compressive strength standards, could already be found (Bensted, 1987).

To create the API standards (API Specification 10, and later on, modifications for Recommended Practice 10B), the wells used as references to determine the well conditions were those situated in the Gulf of Mexico and south-western USA. The chemical limits for the API oilwell cements were mainly taken from ASTM C150 for construction Portland cements with some modifications, while the physical limits used ASTM C115 or ASTM C204 (this last one only for Class A, B and C cements). Regarding the cement properties themselves, they involve compressive strength, thickening (or setting) time and free water determinations. However, we should always bear in mind that while API testing standards may be adapted for use in actual downhole conditions we must take into account that the conditions downhole also vary within the same well (Bensted and Hewlett, 2008).

III.2.5.1 Geothermal Cements

As mentioned previously, the well cements used for geothermal applications nowadays are essentially those devised for oil and gas wells. This section compiles information exclusively directed for well cements used in a geothermal environment.

Sugama's opinion (Sugama, 2006) is that the principal application of geothermal well cementing materials is to mechanically support the metallic well casings as well as to protect them against hot brine-initiated corrosion at brine temperatures up to 320°C.

In geothermal wells, the hardened cement performs four main roles (Milestone, 2011):

- Providing a seal between the casing and the formation, which contains the high pressure steam;
- By forming a bond to the steel, it anchors the casing to the formation, allowing a valve fixed to the top of the casing to control the steam outlet;
- Supporting the casing, to prevent buckling and vibration which could cause metal fatigue;
- Protection against corrosion, due to its alkaline nature.

Besides high-hydrothermal temperature stability, geothermal well cements must be inert and resistant to very harsh geothermal environments involving CO₂-enriched brine (> 40,000 ppm CO₂) encountered at a bottomhole depth of ~1700 m and temperature of ~ 320°C, often with high concentrations of H₂SO₄ (pH <1.5). The cement is also exposed in brine containing at least 5000 ppm CO₂ in the upper well region between the surface and ~ 1000 m depth at temperatures of up to 200°C (Sugama, 2006).

III.2.6 Carbonation of Cement

Generally, the commonly used Portland cement based systems carbonate when exposed to CO_2 , either through reaction with HCO_3^-/CO_2 dissolved in ground waters, direct reaction with supercritical CO_2 or reaction with gaseous CO_2 (Milodowski *et al.*, 2011) to form calcium carbonate (CaCO₃) from both portlandite (Ca(OH)₂) and calcium silicate hydrates (C-S-H).

In civil construction, carbonation of Portland cement systems is an expansive reaction that occurs rapidly, where a cement often forms a protective, low porosity sheath of calcite (CaCO₃), due to the reaction between the atmospheric CO₂ and the Ca(OH)₂. However, when

siliceous additives are added to the cement, carbonation might be a concern, as these additions reduce the amount of $Ca(OH)_2$ and, consequently, CO_2 will attack the hydration products, C-S-H, rather than the $Ca(OH)_2$ (Milestone *et al.*, 2012).

Cement carbonation might occur through different chemical reactions, depending on the reactants (Ca(OH)₂ vs C-S-H and CO₃⁻ vs HCO₃⁻) (Equation III.13-Equation III.16) (Duguid, 2009).

$$Ca(OH)_{2}(s) + 2H^{+} + CO_{3}^{-} \rightarrow CaCO_{3}(s) + 2H_{2}O$$
Equation III.13
$$C_{3,4} - S_{2} - H_{8}(s) + 2H^{+} + CO_{3}^{-} \rightarrow CaCO_{3}(s) + SiO_{x}OH_{x}$$
Equation III.14

$$Ca(OH)_2(s) + H^+ + HCO_3^- \rightarrow CaCO_3(s) + 2H_2O$$
 Equation III.15

$$C_{3,4} - S_2 - H_8(s) + H^+ + HCO_3^- \rightarrow CaCO_3(s) + SiO_xOH_x$$
 Equation III.16

These carbonation reactions, however, do not occur simultaneously for each of the cement phases, with calcium hydroxide (CH) reacting earlier than C-S-H (Duguid, 2009). Despite the initial rapid CH carbonation (rather than C-S-H), this situation reverses because of the formation of a layer of CaCO₃ microcrystals at the surface of CH (Groves *et al.*, 1991). However, the CO₂ only reacts with cement hydrates when there is sufficient water to dissolve it in pore water. The optimal relative humidity for carbonation to take place is an intermediate level, around 50-70%. So cement pastes dried at low relative humidity have little reaction with carbon dioxide, while in a fully saturated paste or concrete the carbonation reaction, which is governed by rate of diffusion of CO₂, is slow (Borges *et al.*, 2012).

Portlandite carbonation

At lower temperatures, the direct carbonation mechanism of $Ca(OH)_2$ is greatly accelerated by the presence of adsorbed water on the surface of $Ca(OH)_2$ and it is very slow in its absence. For a given value of relative humidity, carbonation proceeds to a given extent. An increase in the relative humidity around the $Ca(OH)_2$ can restart a stalled carbonation (Beruto and Botter, 2000).

When $Ca(OH)_2$ is heated in CO_2 , slow direct carbonation of $Ca(OH)_2$ is expected to occur (Equation III.19) until the temperature reaches about 350-400°C when rapid dehydration of $Ca(OH)_2$ occurs (Equation III.17) and the CaO formed continues reacting with CO_2 (Equation III.18) until maximum carbonation is reached (Materic and Smedley, 2011).

$Ca(OH)_2 \rightarrow CaO + H_2O$	Equation III.17
$CaO + CO_2 \rightarrow CaCO_3$	Equation III.18
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3(s) + H_2O$	Equation III.19

However, experiments conducted with hydroxides heated in CO₂ (Materic *et al.*, 2010; Materic and Smedley, 2011) did not report the expected sequence of reactions (**Equation III.19** up to 400° C then **Equation III.17** and **Equation III.18**). Carbonation of Ca(OH)₂ usually means a volume increase, as the molar volume of calcium carbonate (normally calcite) formed is 11-12% greater than that of Ca(OH)₂. This results in heavier, less porous and stronger carbonated samples (Borges *et al.*, 2010). In the Borges *et al.* (2010) experiments, the calcium carbonate (CC) phase formed appeared to be determined by the amount of available CH.

Calcium silicate hydrate carbonation

When paste porosity permits constant CO_2 diffusion, the CH is further depleted and the interlayer calcium from C-S-H also reacts with carbon dioxide. The removal of interlayer Ca^{2+} ions creates an excess of negative charges, which are balanced through subsequent formation of Si-OH groups with neighbouring Si-OH groups condensing to Si-O-Si linkages and formation of silica gels. This condensation increases the mean silicate chain length and forms bridges between neighbouring regions, pulling them closer together and leading to shrinkage. As a result, CO_2 attack causes polymerisation of the silicate chains in C-S-H which may cause a volumetric decrease (decalcification of C-S-H increases the mean pore diameter) and cracking (Borges *et al.*, 2010; Borges *et al.*, 2012).

The extent of carbonation of C-S-H is a function of the CaO:SiO₂ (C/S) ratio, i.e., pastes with different C/S ratio have distinct C-S-H anion polymerisation (Black *et al.* 2008), with an accelerated carbonation rate when the C/S molar ratio is reduced below 1.2 (Borges *et al.*, 2010). In their experiments on cement with added blast-furnace slag (BFS), Borges *et al.* (2010) realized that the extent of C-S-H carbonation increased as the initial amounts of CH present before carbonation decreased, due to pozzolanic reaction. On the other hand, carbonation of the low C/S ratio C-S-H might not be an issue when the blended pastes have

low permeability to hinder the CO₂ ingress. In the same experimental work, Borges *et al.* (2010) found lower carbonation rates and decreased levels of both total carbonation and C-S-H carbonation in samples cured at a higher temperature (60°C), rather than ambient conditions (20°C). According to these authors, the increased curing temperature promoted the hydration of blast-furnace slag (BFS) forming a denser microstructure, which reduced diffusion of CO₂ into the matrices, improving the durability of these pastes to carbonation (Borges *et al.*, 2010).

III.2.6.1 Carbonation in Geothermal Environments

In a geothermal environment where the fluids are enriched with dissolved CO_2 , carbonation is a common issue due to the dissolved CO_2 interacting with the calcium silicate or calcium aluminium silicate hydrates present in conventional cements. This carbonation results in the formation of CaCO₃, the exact form depending on the exposure conditions.

Generally, at 150° C, Ca(OH)₂ carbonates to calcite, while carbonation of C-S-H is slower and forms metastable aragonite, which slowly converts to calcite (Milestone *et al.*, 1986). Carbonation of Ca(OH)₂ is expansive so the carbonated layer occupies more volume than that from where it has come and it can separate (Milestone *et al.*, 2012). On the other hand, carbonation of C-S-H causes volumetric decrease. For instance, tobermorite carbonation may result in a contraction of 33% and with a consequent increase in porosity (Milodowski *et al.*, 2011).

Milestone *et al.* (1986) concluded that the rate of carbonation of a cementitious binder varied considerably, depending on the addition of silica flour (SF), normally added to counter the strength retrogression at high temperatures (over 100° C). In their experiments, they showed that the crystalline low Ca/Si ratio phases tobermorite and xonotlite that form with addition of ca. 40% SF and give low permeability and high strength to the cement, carbonated rapidly and became porous when exposed to CO₂. This contrasted with the samples with neat Portland cement, with high Ca/Si ratio phases, α C₂SH at 150°C and reinhardbraunsite or kilchoanite at 260°C, that behave better when exposed to CO₂. Despite being poor binders, these high Ca/Si ratio phases carbonated slowly, and formed a dense protective carbonation sheath with low permeability and high strength. Carbonation rate is very dependent on the volume of available Ca in any unit volume, particularly if any Ca(OH)₂ was present. Thus the

impact of the CO_2 on the cement is extremely dependent on the overall Ca/Si ratio (Milestone and Aldridge, 1990).

Carbonation and subsequent corrosion of cement are the direct consequences on the cement exposed to high levels of CO₂. During the corrosion process, the cement becomes more permeable and allows ions such as Cl⁻ and H₂S, which may also be present in geothermal fluid, to penetrate the cement sheath and attack the casing. This has apparently happened in the CO₂-rich Broadlands field in New Zealand, where rapid corrosion of cement occurred within a few months (Milestone *et al.*, 1986). In this hydrothermal system, the problem was noted not in the production zone, but in a CO₂-rich zone above the production zone that is penetrated and cemented off. Temperatures are approximately 150°C, with CO₂ levels of approximately 10,000 ppm, so the fluid is acidic and moves through the zone. Downhole testing with samples containing 30% silica were completely carbonated in a few months with considerable corrosion. While these conditions are not likely to be encountered in a direct use well, there are scattered springs and wells with several hundred ppm of CO₂ that are slightly acidic. Because carbonation of cement is time and concentration dependent, and a direct use well should last at least several decades, well drillers and designers should be aware of the potential problem (Zinszne and Pellerin, 2007).

III.2.7 Calcium Carbonate Forms

Borges *et al.* (2010) found different forms of $CaCO_3$ depending on the phases being carbonated.

III.2.7.1 Crystalline Calcium Carbonate

According to Sawada (1997), and Plummer and Busenberg (1982) there are three crystalline CaCO₃ polymorphs: calcite, aragonite and vaterite. Calcite (solubility product: log K_{sp}=-8.48 at 25°C) is the thermodynamically most stable form and the most common in nature. Aragonite (solubility product: log K_{sp}=-8.34 at 25°C), is mainly found in biosynthetic CaCO₃ such as shells and corals whereas vaterite (solubility product: log K_{sp}=-7.91 at 25°C) is the most unstable crystalline polymorph, and rarely occurs in nature, but plays an important role in the calcium carbonate formation from solution.

The formation of vaterite and aragonite might represent different stages of carbonation in different pH conditions (high pH seemed to favour the formation of vaterite over aragonite) (Cole and Kroone, 1960) or distinct C/S ratio of the C-S-H phases (with vaterite forming

when C-S-H C/S \geq 0.67 and aragonite when C-S-H C/S \leq 0.50) (Breen *et al.*, 2007). While aragonite formation appears to be a good indicator for C-S-H carbonation (Borges *et al.*, 2010), vaterite forms preferentially on CH because of similarities in their symmetries and their positive surface charge (Black *et al.* 2008).

Well-crystalized calcite decomposition happens within the 780° C-990°C temperature range, whereas vaterite and aragonite decompose at slightly lower temperatures (680° C<T< 780° C). Although often metastable, aragonite has been shown to undergo an endothermic transformation into calcite at approx. 400° C- 420° C (Thiery *et al.*, 2007; Galan *et al.*, 2003).

III.2.7.2 Calcium Carbonate Hydroxide/Hydrate Phases

There are a number of calcium carbonate hydroxide/hydrate phases reported in the literature. Stepkowska *et al.* (2007) stated that portlandite carbonation may proceed through intermediate steps of calcium carbonate hydroxide/hydrate (CCH), accommodating besides carbon dioxide, water molecules, which in turn are gradually lost resulting in pure (or almost pure) calcium carbonate. CCH-1 (calcium carbonate hydroxide, $Ca_3(CO_3)_2(OH)_2$) and CCH-3 (calcium carbonate hydroxide hydrate, $Ca_3(CO_3)_2(OH)_2$.1.5H₂O) are probably poorly crystalline/amorphous compounds and have origins in lime hydration and its carbonation; CCH-2 (defernite, $Ca_6(CO_{2.65})_2(OH_{0.657})_7(H_2O)_2$) has a fractional stoichiometry, indicating a continuous reaction; CCH-4 (ikaite, $CaCO_3(H_2O)_6$) is a low temperature species, containing high amount of water; CCH-5 (monohydrocalcite, $CaCO_3(H_2O)$) forms in solution or suspension (Stepkowska *et al.*, 2007).

III.2.7.3 Amorphous Calcium Carbonate

There is also the possibility that relatively stable amorphous calcium carbonates (ACC) form, rather than crystalline ones. Amorphous calcium carbonate (ACC) is the thermodynamically least stable form among calcium carbonates, which forms in vitro only from a supersaturated solution. ACC is usually metastable, tends to dissolve easily and transforms rapidly into a crystalline stable phase (Kellermeier *et al.*, 2010; Raz *et al.*, 2002).

ACC formation is kinetically favoured and thus it is frequently observed first in the course of precipitation from solution, to subsequently transform more or less rapidly toward phases of higher stability (Kellermeier *et al.*, 2010). Mineral frameworks in which calcite and ACC

coexist in separate domains have also been reported (Aizenberg *et al.*, 2002; Aizenberg *et al.*, 1996). Similar to other amorphous minerals, ACC is isotropic in polarized light; and is particularly difficult to identify and characterise when a crystalline mineral is also present (Raz *et al.*, 2002). The decomposition of ACC is within the 550°C-680°C range (Thiery *et al.*, 2007).

Although not fully understood to date, there are some ACC stabilisation mechanisms, which seem to inhibit ACC transformation by hindering dissolution, delimiting exchange with the surrounding solution, or selectively impeding crystal growth. The degree of hydration and the particular short range order of the amorphous phase are important factors for ACC stabilization (Levi-Kalisman *et al.*, 2002; Radha *et al.* 2010). Stable forms of biogenic ACC were found to incorporate appreciable amounts of water, typically 1 mol per mol of CaCO₃ (Taylor *et al.*, 1993; Levi-Kalisman, 2000). This structural water probably hampers transformation into any of the anhydrous crystalline polymorphs (Addadi, 2003). Conversely, when serving as a transient intermediate, ACC contains little/no water or transforms to a dehydrated state prior to crystallization (Beniash, 1997; Politi, 2004; Raz, 2003). Additionally, previous work has already shown that the lifetime of ACC in solution can be prolonged by addition of magnesium ions (Loste, 2003), triphosphate (Clarkson, 1992), polyphosphonate species (Sawada, 1997) or silica (Kellermeier *et al.*, 2010).

The presence of sodium silicate during precipitation of $CaCO_3$ from supersaturated solutions at elevated pH produced temporary or permanent storage of metastable ACC and seemed to delay gradual transformation to crystalline polymorphs and promote the coexistence of amorphous and crystalline phases, all based on the spontaneous deposition of siliceous skins around growing ACC particles (Kellermeier *et al.*, 2010).

This seems to be in accordance with Black *et al.* (2008), who observed that the decalcification of C-S-H led to ACC until free silica was formed, whereupon the carbonate was converted into aragonite, meaning the ACC was kept stabilized while associated with silica. Also Martinez *et al.* (1998) seems to be in agreement, as they concluded that the particles formed incipiently upon precipitation of CaCO₃ in silica-containing solutions are composites consisting of ACC and hydrated amorphous silica.

Besides wrapping single ACC nanoparticles, the presumed silica skins seem to favour aggregation and interconnect grains by spanning a continuous envelope over multiple individuals (Kellermeier *et al.*, 2010). Depending on the amount of silica added, Kellermeier

et al. (2010) observed both total inhibition of calcite formation (ACC material is effectively cemented in a siliceous matrix, for values well above 1000ppm SiO₂) and the coexistence of both ACC and calcite, even 1 year after the initial CaCO₃ precipitation. They ended up concluding that these compounds may coexist over time scales of years. Moreover, Kellermeier *et al.* (2010) suspect that the ACC formed in their experiments is hydrated to a certain, yet unknown degree, meaning the role of stabilising the amorphous particles may not be confined to just acting as a barrier which limits the release of ions into the solution and hence restrains dissolution of ACC. They reckon it may also prohibit the expulsion of water molecules from the core, preventing possible transformations of hydrated ACC to anhydrous crystalline polymorphs inside the particles.

III.2.8 Durability

The main concern with the cement for geothermal purposes is its durability. Even if the strengths are considerably lower than those found in a civil construction context, it will not be an issue, as long as the cement is able to keep its properties for several decades. The cement response to CO_2 exposure is one of the main concerns for the durability of these cements, which will depend on the different exposure conditions (pressure, temperature, pH, CO_2 phase, etc.).

III.2.8.1 Corrosion of Cement

In high CO₂ content solutions the carbonate is converted into water-soluble calcium bicarbonate, Ca(HCO₃)₂, and leached from the cement hydrate phases (Equation III.20). This leaching process continues in the presence of excess CO₂ which forms 'carbonic acid' (H₂CO₃) thereby producing a large amount of an amorphous silica and aluminum silicate gels which dissociate from the Ca-depleted hydrate phases, e.g. Ca(OH)₂ and calcium silicate hydrate (C-S-H). As the calcium hydroxide and alkali phases are depleted, the pH of the pore solution will fall, and carbonate will no longer be the dominant species, and be replaced by bicarbonate (HCO₃⁻) (Equation III.21-Equation III.23) (Duguid, 2009; Kutchko *et al.*, 2008; Sugama and Carciello, 1992).

$$\begin{aligned} \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 &\rightarrow \text{Ca}(\text{HCO}_3)_2 & \text{Equation III.20} \\ \\ CO_2 + H_2O + CaCO_3(s) &\leftrightarrow Ca^{2+} + 2HCO_3^- & \text{Equation III.21} \\ \\ 2H^+ + CaCO_3(s) &\leftrightarrow Ca^{2+} + H_2O + CO_2 & \text{Equation III.22} \\ \\ 2H^+ + C - S - H(s) &\rightarrow Ca^{2+}(aq) + H_2O(aq) + am - SiO_2(s) & \text{Equation III.23} \end{aligned}$$

As consequence of the Ca leaching process, several carbonated well cements have failed in less than a year, and in the worst case, well casings have collapsed within three months (Sugama, 2006). On the other hand, when the hydrates from conventional cement come in contact with H_2SO_4 , the Ca²⁺ cations are rapidly leached from the cement hydrates, and react with the SO_4^{2-} ions from H_2SO_4 to deposit a gypsum (CaSO₄.2H₂O) scale as the acid-corrosion product on the surface of the cements. Firstly, the gypsum scale clings to the cements and serves as a primary barrier layer against a further acid attack from the exterior. However, further gypsum crystal growth from the cement can promote acid erosion of the cement. Additionally, an excessive growth of this corrosion product may cause undesirable expansion and swelling phenomena of the cements, following the development of weakening cracks or complete failure (Sugama, 2006).

At present, published guidelines regarding the CO_2 concentrations that cause various degrees of attack or estimated corrosion rates at given CO_2 concentrations are only general. Considerable work has been performed investigating cement corrosion, both in geothermal wells and CO_2 -enhanced recovery in oil wells. Unfortunately, most of the work was performed at lower temperatures and/or higher CO_2 partial pressures than are usually found in direct use geothermal wells.

Bruckdorfer (1985), using micro cylindrical cement samples 0.275 in. diameter by 0.5 in. long, found there was only a 5 to 10% decrease in strength loss of samples at 125°F (ca. 50°C) compared to samples at 175°F (ca. 80°C). This indicates that, at least below 230°F (ca. 100°C), the corrosion is not temperature sensitive. There is good agreement in the industry literature that nonporous, high-density cements made with low water-to-cement ratios are more resistant to attack, with the addition of diluents such as lost circulation materials and silica decreasing resistance. Silica additions above 10 to 20%, even at temperatures above 230°F, and the addition of bentonite at only 3%, decrease resistance (Milestone *et al.*, 1985).

Downhole conditions obviously have an important part in the corrosion rate. If there is no water flux around the cement, the carbonic acid would soon be neutralised and the corrosion rate would diminish; however, if there is a continuing supply of CO_2 rich fluid, corrosion will continue. Cements high in calcium hydroxide are more resistant to corrosion by CO_2 because an impervious layer of calcite forms on the outside, slowing attack by CO_2 and other species (Milestone *et al.*, 1986).

III.2.8.2 Diffusion Process and Reaction Rims

The cement degradation usually starts from the outermost layer moving progressively into the interior layers, and is controlled by diffusion, which is proportional to the square root of time. Ficks second law of diffusion with constant concentration boundary condition is often used to estimate the depth of ordinary carbonation in cement (Kutchko *et al.*, 2008), and is given by the **Equation III.24**.

$$L=\alpha t^{1/2}$$

where,

L - depth of carbonation;

t - time of exposure;

 α - constant related to the rate of diffusion of ionic species through the cement matrix and depends on the cement permeability, porosity, tortuosity and chemical composition.

There are several studies in which either experimental or theoretical models were built in order to predict the durability of the cement downhole.

Using a simple diffusion model at 90°C, Barlet-Gouedard *et al.* (2006) created their own penetration prediction for Portland cement (w/c=0.44) as a function of the CO₂ phase, based on Fick's second law of diffusion: for CO₂ dissolved in water (exposed to HCO₃⁻), L=0.22t^{1/2} (8mm penetration after 3 months); for water saturated supercritical CO₂, L=0.26t^{1/2} (12 mm radius sample was totally penetrated after 3 months). After 20 years the depth of penetration

Equation III.24

depth was estimated as 90 mm for the samples exposed to HCO_3^- and 110 mm for samples exposed to water-saturated supercritical CO_2 . Within the same project, for the CO_2 resistant cement these authors did not report any carbonation reactions.

By extrapolating his results, Duguid (2009) estimated the time for a 25mm thick layer of class H well cement to react as function of the temperature and pH. He predicted that for a well with good zonal isolation submitted to temperatures up to 50°C, the rate of degradation would be between 30,000 (pH 3) and 700,000 years (pH 5) for 25 mm of neat paste in a sandstone reservoir, and possibly longer to destroy the cement which passed through the cap rock.

Duguid (2009) and Kutchko *et al.* (2008) reckoned their cement degradation extrapolations based on previous lab works were conservative, with real diffusion being slower, as some previous studies based in cements exposed to a CO_2 in situ exposure did not show as much degradation as the one usually seen in laboratory. By comparing their work with observations of Carey *et al.* (2007), Kutchko *et al.* (2008) found that the reaction layer (penetration depth) of the cement exposed to real conditions was similar to their lowest penetration estimation for 30 years, which ranged from 1 to 10mm.

In several cases, the diffusion process gave rise differentiated layers/rims, which correspond to different carbonation/corrosion stages. After six months cured in CO₂ sequestration conditions (supercritical CO₂, at 90°C and 290 bar), Rimmele *et al.* (2008) observed that class G cement samples exhibited 3 distinct altered zones: a carbonated zone (outermost altered rim, with calcium carbonate, silica gel and calcium depleted calcium silicate phases); a carbonation front (thin layer with 50-200 μ m wide of very low porosity); and a dissolution front (innermost altered rim of high porosity where cement phases progressively dissolve to form calcium carbonates backwards). This is similar to that reported by Milestone *et al.* (1986a) and Grant-Taylor *et al.* (1996).

Rimmele *et al.* (2008) observed that the concentric reaction fronts translate towards the central part of the samples, and relicts of these fronts are commonly observed backwards through the carbonated zone. According to them, these "paleofronts" are made of zones with low amounts of silica gel and well crystalised calcium carbonate, intercalated by silica gel-rich zones that contain only micrometre-scale calcium carbonate nodules. From their experiments on Class H neat cement (w/c=0.38) cured for 28 days at 50°C and 30.3 MPa and only then exposed to either CO₂-saturated brine or supercritical CO₂ under similar conditions

for 9 and 61 days respectively, Kutchko *et al.* (2008) noticed that the differentiated rims depended on the CO₂ phase. For the cement exposed to the CO₂ saturated brine, they observed an orange smooth textured altered cement. In a similar way to that observed by Rimmele *et al.* (2008), the altered cement had 3 distinct zones: carbonated zone (degraded zone), carbonation front (CaCO₃ barrier) and Ca(OH)₂ depleted zone (Figure III.10). The initial carbonation rate was rapid followed by a decrease in rate. The rate of cement carbonation is diffusion limited because the rate of acid-base carbonation reactions is much faster than the diffusion of ionic species through the cement matrix. This is a non-linear process, meaning that the cement alteration process is complex, as the rate of diffusion, α , is not constant, probably due to the precipitation of a dense CaCO₃ (s) rich layer, which has a protective effect. As this phase (CaCO₃) grows faster than it is dissolved, slower diffusion rates are observed over time, i.e. α decreases with time (Kutchko *et al.*, 2008; Duguid *et al.*, 2005). Kutchko *et al.* (2008) described the scenario observed for cement degradation from exposure to CO₂-saturated brine as identical to an acid attack by carbonic acid (Figure III.11). The maximum alteration depths after one year for any sample were 1 mm.



Figure III.10 - SEM/BSE image of class H cement cured for 28 days at 50°C and 30.3 MPa and exposed for 9 days to CO₂-saturated brine under the same conditions (Kutchko *et al.*, 2008)



Figure III.11 - Original cement (top) and cement exposed to CO₂ after 9 days (bottom) (Kutchko *et al.*, 2008)

There are studies in which only one altered rim was reported in the cement. In other studies, several altered rings were reported in the cement. For instance, in their work on cement samples exposed for 61 days to supercritical CO_2 , Kutchko *et al.* (2008) observed a light grey rough textured, with one single altered ring/reaction front. This ring was composed of CaCO₃ (s) distributed throughout the reacted portion (**Figure III.11** and **Figure III.12**).



Figure III.12 – SEM/BSE image of Class H neat cement cured for 28 days at 50°C and 30.3 MPa and exposed for 61 days to supercritical CO2 under the same conditions shows the formation of a single carbonated zone in the cement. Dashed line approximates boundary of degradation (Kutchko *et al.*, 2008)

In their work Kutchko *et al.* (2007), described a degradation front 440 μ m wide after 90 days, which included two differentiated rings: an outermost ring, with depletion of calcium from cement grains, followed by the hardest zone, a ring with increased Ca.

Andac and Glasser (1999) reported five individual degraded layers, with a total leached depth of 600 to 800 μ m after 3 months. These authors have described the different layers mostly based on their calcium content (from exterior to the center): 1) 200-300 μ m wide, low in
calcium ($\approx 20\%$); 2) cracked zone; 3) 100-200 µm wide, low in calcium ($\approx 20\%$); 4) 80 µm wide, lower in calcium than unleached cement, but richer in Ca than the outer leached layers ($\approx 30\%$); 5) transition between layer four and the unleached portion of the sample ($\approx 35\%$).

Unexpectedly, the results obtained by Rimmele *et al.* (2008) with supercritical CO₂ are similar to those obtained by Kutchko *et al.* (2008) in CO₂-saturated brine, rather than supercritical CO₂. This emphasises the complexity of these reactions, which seem to be dependent on several variables. The main differences between these two studies which considered together, could justify the similar results for the different CO₂ phases, are the curing time (6 months v's 28 days), exposure time (6 months v's 9 days), exposure timing (exposed to CO₂ from the beginning v's exposed to CO₂ only after 28 days) and the type of cement (class G v's class H).

Based on observations of a 30-year-old production well from a natural CO_2 reservoir, and after comparing them with earlier studies, Crow *et al.* (2010) justified the distinct results by highlighting variables such as timing (the moment in which the cement started being exposed to CO_2), CO_2 concentration and the type of rock in the reservoir (which provides less buffering of the potential corrosive effects of CO_2 on the barrier system than a carbonate reservoir). Nonetheless, the actual rate of cement degradation in the field will also depend on the quality of the cement and the quality of the cementing job within the well.

III.2.9 Natural analogues

Natural analogue systems can provide an insight into the long term behaviour of cement. There are a few studies based on natural minerals where an understanding of the cement behaviour when exposed to CO_2 on a long timescale can be obtained.

Examination of natural CSH minerals and gels similar to those found in hydrated OPC-based cements shows that they carbonate readily on reaction with bicarbonate containing groundwaters or atmospheric CO_2 to form a range of minerals, including: calcite, aragonite, vaterite, scawtite and hydrotalcite (Alexander, 1992; Linklater 1998; McConnell, 1960; Milowdowski *et al.* 1989; Smellie, 1998). Rochelle (2004) and Milodowski *et al.* (2011) showed that moderately sized nodules of CSH phases present in rock formations had not undergone total carbonation, even after several thousand years. They suggested that similar minerals in well cements may possibly have significant longevity. Rochelle (2004) justified that by the dense carbonate reaction rim which had formed in the outermost layer, which

appears to have restricted further reaction, allowing the CSH mineral to be preserved beneath the carbonate rim. In similar work, Milodowski *et al.* (2011) concluded that natural CSH minerals do not react with the high concentration of CO_2 in supercritical CO_2 .

III.3 Cement-Rock Interactions

There is little published literature on cement/rock interaction under hydrothermal conditions. However, references and investigations on cement-rock aggregate interactions which occur in concrete for civil construction are extensive and form the bulk of this review. These show that reaction can be extensive.

III.3.1 Interfacial Transition Zone in Concrete

The processes responsible for the formation of the microstructure of the cement-aggregate ITZ2 in concrete are still not well understood. The forces of adhesion of coarse aggregate grains to cement paste are commonly believed to have a twofold nature. On the one hand, there are physical forces whose magnitude depends on the topography of aggregate grain surface and on the grain shape and are believed to have a considerably strong influence on the cement-aggregate bonding. On the other hand, there are chemical driving forces created at the aggregate-cement paste interface, which are dependent on the chemical potential of the rock (Prokopski and Halbiniak, 2000; Scrivener, 1999; Xing *et al.*, 2011).

III.3.1.1 Physical Features

In concrete, the microstructure of the ITZ^2 is determined by the packing of the anhydrous cement grains against much larger particles. The so-called "wall effect" leads to a depletion of anhydrous cement in the ITZ, approaching zero at the aggregate surface. As a result there is an increase in the amount of porosity in the ITZ. The thickness of the zone affected by the packing of the cement grains extends to at least the size of the largest cement particles, which may be up to 100μ m. However, as large areas filled with water are available in the vicinity of the aggregate particles, the hydration mostly follows Le Chatelier's principle. After the dissolution of anhydrous compounds, the more mobile ions move under the influence of concentration gradients, i.e. from bulk to the interface. In OPC, the more mobile ions, Na⁺, K⁺, SO₂⁻⁴, Al(OH)₄⁻ and Ca²⁺, diffuse faster, whereas the mobility of silicate ions is lower and they diffuse more slowly from the silicate grains to the aggregate surface (Maso, 1980). This results in a preferential deposition of hydration products in the more open ITZ, which ameliorates the effects of cement packing. Consequently, the distance over which there is a

² ITZ: Interfacial Transition Zone

significant porosity increase has been reported to be only around 35-50µm (Scrivener and Nemati, 1996; Ollivier *et al.*, 1995; Prokopski and Halbiniak, 2000; Stroeven and Stroeven, 2001).

The concentration of C_3S in the ITZ has been studied by Ollivier (1981) using the composite model and X-ray diffraction analysis, where he observed an exponential decrease in C_3S within 45µm around the aggregate as the OPC paste approaches it. Srivener and Pratt (1994) calculated the amounts of CH and C-S-H were in excess of the amounts expected if all the hydration products were precipitated in the immediate vicinity of the anhydrous cement from which they have formed. From this work, they concluded the portlandite/anhydrous cement ratio is much higher in the ITZ than in the bulk paste. Furthermore, they observed a still higher C-S-H/anhydrous cement ratio in the ITZ, although not as clear as with portlandite, due to the lower mobility of the silicate ions. These authors also studied the CaO/SiO₂ ratio (C/S) in the ITZ between C₃S paste and marble, from which they have observed that the C/S is much higher in the vicinity of the aggregate than in the bulk paste. According to these authors, this was due to a Ca²⁺ and OH⁻ ions migration process.

III.3.1.2 Chemical Features

In concrete, the reactions which occur between the pore fluid (cement paste) and aggregate may affect the mechanical performance and the durability if the reaction causes a volume change after the setting of the cement, which causes mechanical fracture (Giuovambattista *et al.*, 1986). Conversely, in some aggregates, these reactions, which take place at the interfaces, are helpful as they increase cement paste-aggregate bond strength. This results in making high strength concrete with improved chemical resistance (Tasong *et al.*, 1998-a). The concentration of the pore fluid in mortar or concrete can be affected by the aggregate type and it is believed that the use of reactive aggregates significantly affects the amount and the degree of orientation of Ca(OH)₂ crystals in the ITZ. Reaction of Ca(OH)₂ with the aggregate was suggested to be responsible for a considerable portion of the ITZ strength (Tasong *et al.*, 1998-a). Studies undertaken by Monteiro *et al.* (1985), Maso (1980), Bernes (1978), Brenton and Carles-Gibergues (1993) and Struble (1988) explained this by differential ion diffusion caused by the zone's high porosity, which resulted from the arrangement of the cement grains in contact with the aggregate (rock). According to these authors, calcium hydroxide (Ca(OH)₂) precipitates on the aggregate surface by heterogeneous nucleation and subsequently grows and crystallises.

Cement composition

The cement blend grain size distribution is an important factor controlling the ITZ characteristics (Scrivener, 1999). The properties of the ITZ seem also to depend on the amount and nature of the hydration products formed in the ITZ (Tasong *et al.*, 1998-a; Yuan and Guo, 1987; Bentur *et al.*, 1987), whereas the water/cement ratio (w/c) has been considered to have only small effect on the ITZ microstructure (Scrivener, 1999).

Mineral admixtures and other additives may influence the development of the microstructure in the ITZ because of two main factors: modification of the hydration process and densification of the particle packing if the size of the additions is much finer than the size of the cement grains. These two factors may act simultaneously making it difficult to analyse their individual effect (Ollivier *et al.*, 1995). Silica fume, for instance, reduces the porosity of the cement paste by filling its micropores, thereby improving the mechanical properties of the paste within the inter transition zone and enhancing the quality of aggregate-cement paste interface. When the ITZ is densified by means of silica fume additions, for example, the w/c ratio gradient is lowered and the diffusion is reduced as well. The hydration products however, are also dependent on the amount of silica fume added, which may affect the porosity of the cement paste, which decreases with age due to filling by hydrates (Ollivier *et al.*, 1995; Prokopski and Halbiniak, 2000). Aquino *et al.* (1995) observed that the bond properties between the cement paste and aggregate were substantially improved by additions of latex and silica fume, with both leading to a decreased porosity in the ITZ.

Aggregate type

It is usually assumed that the cement-aggregate bonding mechanism depends on the mechanical interlocking aided by the aggregate surface texture, as it has been indirectly shown to increase for the rougher surfaces (Tasong *et al.*, 1998-b). These assumptions are based on comparisons between the bond strength of fractured rock surfaces with that of polished rock surfaces. However, the true surface area of the aggregate is either not considered or poorly estimated (Tasong *et al.*, 1998-b). They concluded that the interfacial bond strength for a given cement paste depends not only on the aggregate roughness, but also on the parent rock structure and strength, both of which determine the topography and fracture properties of aggregates at the ITZ.

Elsharied *et al.* (2003) found that reducing the aggregate size from 2.36-4.75mm range to 150-300 μ m range tends to reduce the porosity and increase the content of unhydrated cement particles in the cement surrounding the aggregate. Furthermore, although not noticeable with the larger aggregates, the w/c reduction from 0.55 to 0.40 appeared to reduce the porosity in the vicinity of the 150-300 μ m range aggregates.

According to Xing *et al.* (2011), calcareous aggregate concretes show better performance at high temperatures than the siliceous aggregate concretes. This fact is generally attributed to the higher thermal expansion of siliceous aggregates and to the volume increase due to the phase transition (at 573°C) from α -quartz to β -quartz.

III.3.2 Alkali Aggregate Reaction

III.3.2.1 Types of Reaction

Hobbs (1988) initially differentiated two different kinds of cement aggregate reactions and later work by Okada *et al.* (1989), sub-divided them further into three groups - alkali-silicate, alkali-carbonate and alkali-silica reactions (Park *et al.*, 1996; Freitag *et al.*, 2003):

- <u>The alkali-silicate reaction</u> is believed to be a reaction between the alkali ions in the pore water of a concrete and an interlayered precipitate in phyllosilicates (which are often present in greywackes, phyllites or argillites); this precipitate is a mineral related to vermiculite and, after being removed, the phyllosilicate is then able to expand by taking up water and, consequently, causing expansive stresses, which may cause expansion and cracking of the concrete (Hobbs, 1988);
- <u>The alkali-carbonate reaction</u> is the reaction between certain dolomitic limestones (containing clay impurities) and the metal hydroxides in the pore solution of a concrete (dedolomitisation reaction) and is uncommon (Hobbs, 1988);
- <u>The alkali-silica reaction</u> is the reaction between the alkaline pore solution (hydroxyl ions) in the pore water of a concrete and certain forms of silica minerals (such as opal, chalcedony, micro and cryptocrystalline quartz, cristobalite and tridymite and volcanic glasses), rather than a primary reaction between sodium and potassium ions and reactive silica. Alkali-silica reaction (ASR) is the most common cause of deterioration of concrete and a better understood process when compared with the other two processes (Hobbs, 1988; Park *et al.*, 1996; Freitag *et al.*, 2003). For this reason, this is

the most important to be considered also in a cement-rock interaction within a geothermal context (despite the low OH⁻ solubility at high temperatures). The New Zealand Construction Industry often refers to AAR instead of ASR.

III.3.2.2 Factors Influencing ASR

ASR is a very complex reaction between silica and alkalis from the pore solution, which, in some conditions may be similar to the pozzolanic reaction³, giving hydrates close to that of cement paste, C-S-H or tobermorite (cation exchanges between calcium and sodium or potassium) (Okada *et al.*, 1989). However, this reaction is dependent of several factors/conditions, including the reactants themselves.

ASR variables

The requirements for the development of an ASR are: reactive siliceous component (a component of the aggregate which can react with hydroxyl ions to produce a new reaction product which can absorb water); alkalis (sodium and potassium hydroxides derived principally from the cement); a source of moisture; sufficient time; and is facilitated by conductive temperature and humidity of the environment. Despite the increase of the alkali-silica-reaction with the increasing temperature, long-term expansion due to alkali-silica reaction is lower at high temperatures. Variables like reactant quantities, environmental conditions, cement quality and action of pozzolans should also be taken into account for better understanding of the ASR. Nevertheless, the main controlling factor is the cement-aggregate-pore system (Vivian, 1992; Shrimer, 1996; Lombardi *et al.*, 1996; Chatterji, 2005).

ASR mechanism

The alkali metal ions in Portland cement are usually present as soluble sulfates (Na_2SO_4 and K_2SO_4). When water is added to Portland cement, these alkali sulfates readily dissolve and the sulfate ions react with the hydrating tricalcium aluminate and calcium hydroxide to precipitate ettringite, releasing the alkalis as sodium and potassium ions into the pore solution, which are taken up by the cement hydrates as they form. The resulting pore solution contains considerable amounts of sodium and potassium ions and very low concentrations of calcium, sulfate and chloride. This results in a significant hydroxyl concentration (pH between 13 and 14) which originates the ASR (Freitag *et al.*, 2003).

³ Pozzolan reaction: chemical reaction that occurs in hydraulic cement, calcium hydroxide with amorphous silicious materials (namely, pozzolans), forming calcium silicate hydrates, according to the following formula: $Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2 H_2O \rightarrow CaH_2SiO_4 \cdot 2 H_2O$

Diamond *et al.* (1981) considered that silica distress in concrete arose from two processes, chemical and physical, which could be distinguished: the chemical reaction produced the reaction product gel which eventually expanded and cracked the concrete. They and Poole (1992-a) divided ASR in the two stages: initially, a chemical reaction between reactive silica and the alkalis in the cement paste, which produces a gel reaction product (normally taking place within the boundary of the reacting aggregate); subsequently, a physical or physicochemical sorption of fluid by this gel, which may produce local swelling.

Glasser and Katoaka (1981) also explained ASR as a two-step process: first, an acid base reaction in which OH⁻ groups from the alkali solution react with the acid silanol groups (**Equation III.25**), where the charge on the terminal oxygen is balanced by Na⁺; afterwards, further OH⁻ attacks the siloxane (Si-O-Si) bridge within the structure (**Equation III.26**). This process loosens and breaks up the structure, leading to the formation of an alkali-silica gel polymer.

$$\equiv Si - OH + OH^{-} \rightarrow \equiv Si - O + H_2O$$
Equation III.25
$$\equiv Si - O - Si \equiv +2OH^{-} \rightarrow \equiv Si - O^{-} + O^{-} - Si \equiv +H_2O$$
Equation III.26

This acid/alkali reaction occurs at the accessible surfaces of the silica, where a hydrous silicate is formed. Hydroxyl ions (OH⁻) are absorbed into the silica particle and some of the silicon oxygen linkages are attacked, weakening the local bonding. Consequently, the free K⁺ and Na⁺ ions (from the NaOH and KOH) diffuse and attract water to form a gelatinous metal alkali ion hydrous silicate (Hobbs, 1988; Park *et al.*, 1996; Freitag *et al.*, 2003). It has been also shown that the rate of ASR is increased by raising the ionic strength of the ambient solution (Chatterji and Thaulow, 2000; Chatterji, 2005).

French (1989) suggested that the migration of water and alkalis to reacting aggregate particles depends on the 'hygroscopic' nature of the silicon ions produced by the reaction, as the silicon ions remain within or close to the reacting material to form a gel which will not migrate away until it has become fluid enough through absorption of water into the gel network. The more open the structure and the greater its hydration state, the more rapidly it is attacked. Calcium ions, because of their double charge and large envelope of water

molecules, tend to remain near the surface of the developing gel as a C-S-H phase, which is less soluble in alkali solution than sodium or potassium gels (Poole, 1992-a).

The formation of the alkali silicate gel consumes alkali and reduces pH. Significant reaction occurs only when there is sufficient alkali in the pore solution, giving an initial pH of 13.65 (Freitag *et al.*, 2003).

ASR products

The reaction products observed in concrete structures altered by ASR appear as gels and rarely crystals and they can be characterized taking into account different factors such as their location around the aggregates, their microstructure (massive/textured gel and rose/lamella crystals), their elemental composition (alkalis, silicon, calcium and other minor elements such as aluminium or iron) and their coexistence with secondary products (eg. ettringite and carbonates) (Okada et al., 1989). According to several studies by Lombardi et al. (1996), the product of alkali reactions was a hydrated gel containing silica, calcium and alkali gels which were present in variable proportions: SiO_2 (S) from 28 to 86%, CaO (C) from 0.1% to 60%, K₂O (K) from 0.4 to 19% and Na₂O from 0% to 20%. The most important constituents were SiO_2 and CaO, which defines CaO/SiO₂ (C/S) ratio and the composition. These usually dictate the chemical properties of this gel as well as the physical ones of adsorption and swelling (Lombardi et al., 1996). They found the variation of values of CaO and SiO₂ with natural and synthetic alkali-silica gels were similar for both natural and synthetic alkali-silica gels. Moreover, whatever the original C/S value was, the representative points of the synthetic gels were grouped around C/S of 0.48, which was close to the characteristic average (0.43) of the natural gels. Their observations made them believe that there was an instantaneous mechanism of formation by precipitation of calcium and silica ions from solution. Generally, they concluded that the Si-Ca structures of gels did not incorporate alkali cations. They reckoned that the sodium and potassium present were simply the result of the trapping of the solution of precipitation into the texture of gels (Lombardi et al., 1996). Nevertheless, Dron and Brivot (1996) believe that the alkali-silica products should not be characterised by its C/S (and/or K/C) ratio, as it was a complex system, with four independent constituents (CaO, K₂O, SiO₂, H₂O). Rather than a solid comparable to a mineral grain or crystal, the alkali silica products were the result of drying of a two phase product initially saturated with water like a sponge. It was not possible to assume a unique composition of ASR products, as compositions varied depending on the composition of the final liquid phase. Generally, if the ratio [K]/[SiO₂] was greater than 4, the solid appeared in

the form of precipitate; otherwise, when lower than 4, the solid consisted of a gel. They believed that the final value of the ratio $[K]/[SiO_2]$ was related to the initial chemical conditions, i.e., relative quantity of the reagents. In a system where the silica is consumed as it goes into the solution, this ratio tends to increase; otherwise, in a system where silica can accumulate locally because of diffusion barriers, gels will form.

Diamond (2000) defended the proposition that there are at least two distinct ASR products or phases, one relatively rich in Ca and trending toward an alkali-bearing C-S-H of limited (or non-existent) swelling capacity, the other the traditional "swelling gel" composed primarily of potassium (or sodium) silicate hydrate with only a little calcium. Other authors consider that the influence of calcium content on swelling of the alkali silica gel component is not due to a separate phase. Monteiro et al. (1997) considered that these two different behaviours were due to the fact that the divalent calcium ions reduce swelling by not forming a diffuse double layer responsible for swelling, while Lombardi et al. (1996) explained this phenomenon by proposing that ASR gels formed a series defined structurally only by CaO/SiO₂ ratios where the alkalis present were the result of the trapping of the solution of precipitation into the texture of gels (Diamond, 2000). The main point is that the variation of Ca content in ASR products is associated with the physical location of the ASR gel. Close to a reacting grain the calcium content is low whereas in one that migrates along the cracks (away from the reacting grain) the CaO content tends to be progressively higher. It has been suggested that this is a mechanism of regeneration of alkalis within the cement paste, allowing continued alkali-aggregate reaction and modifying the viscosity of the gel initially formed. In addition, the ASR gel tends to change composition over time, usually accumulating calcium from the surrounding cement paste (Diamond, 2000; French, 1989; Poole, 1992-a; Scrivener, 1994).

ASR potential

Even though ASR potential is given by the concentration of hydroxyl ions of the pore solution, the alkali content of concrete is expressed as the concentrations of oxides of the alkali metal ions sodium and potassium which are easily measured. Calcium hydroxide in the cement hydrate dissolves to balance these ions in solution, so their concentration reflects the amount of hydroxide ions that will be produced. Therefore, the "alkali content" is actually the content of sodium and potassium ions (rather than pH or hydroxyl ion content) (Freitag *et al.*, 2003).

Durand (2000) noted that several papers have identified the contribution of alkalis in concrete from other than the cement; for instance, there are alkalis in the supplementary cementitious materials (SCM), in the chemical admixtures and also in the aggregates themselves (albeit in very low quantities). In this sub-section, the main alkali sources are introduced: cement, admixtures and aggregates.

Alkali sources

In Portland cement, the sodium and potassium alkalis originate from the raw materials used in its manufacture, and are usually present in clinker as alkali metals sulfates (Jawed, 1977). As soon as the cement is mixed with water, the water soluble alkali metals sulfates are converted into alkali hydroxides, increasing the hydroxyl concentration in the liquid phase (Hobbs, 1980). When high amounts of clinker SO₃ are present in the cement, a higher fraction of the total alkali gets dissolved into the solution within a few minutes, followed by an increase in the alkali concentration for the next 28 days, when almost the whole alkali is already in the solution (Hobbs, 1980; Hobbs, 1988). According to Hobbs (1988) and Freitag *et al.* (2003), there is a conventional methodology to calculate the equivalent sodium oxide (reference) content of a Portland cement, which is expressed by the **Equation III.27**.

$$[Na_2O]_{equivalent} = [Na_2O] + 0.658 \times [K_2O]$$
 Equation III.27

Besides their main goal of improving various aspects of concrete performance, SCM⁴ can be also utilised to reduce ASR expansion. This improvement can be explained by several factors (which depend on the SCM): reduction of total alkali content if SCM has a lower available alkali content than the cement it replaces; reaction of the SCM with calcium hydroxide reducing the available $Ca(OH)_2$ that keeps the high pH necessary for ASR and forming a product that binds alkalis so that they are unavailable to participate in the ASR. The lower permeability of the concrete also reduces ingress of moisture slowing diffusion of alkalis to reactive minerals, and ultimately the expansive forces the cement can withstand without cracking (Freitag *et al.*, 2003).

⁴ Supplementary Cementitious Materials

Although the main source of alkali in concrete comes from cementitious materials, chemical admixtures such as water reducing, air entraining, superplasticising, high early strength early plasticising, set accelerating, set retarding, pump aid and shrinkage reduction may also make a relevant contribution. Moreover, the alkalis added to the cement to disperse any pigments also need to be considered (Freitag *et al.*, 2003).

In well cements, the formation water is often used for mixing the cement which will incorporate the alkali from the brine. The alkaline pore solutions of the cement may dissolve these minerals along accessible intergranular surfaces, causing a release of alkaline material into the pore solution (Freitag et al., 2003). Grinding aggregate particles containing reactive silica below 20µm in size can also have the similar effect of microsilica, i.e., promoting the alkali-silica reaction while the slurry is in the fresh state (Diamond and Thaulow, 1974; Asgeirsson and Gudmandsson, 1979). Goguel and Milestone (2000) observed that high concentrations of alkali can be released by sand derived from nepheline basanite, a type of basalt, particularly when the mortars were cured under conditions of high humidity. As a consequence, the pore solution pH was high, even if a low alkali cement was used. At Industrial Research Limited (IRL), an investigation concluded that alkalis released by acidic rocks (rhyolites, granites and dacites) imbedded in concrete did not add to the alkalinity of the pore solutions, but were taken up by solid silicate phases. For ASR to occur through alkali release from aggregates, three conditions are necessary: presence of alkali releasing mineral phases; readily accessible surfaces of the alkali releasing phases in the sand fraction; and high humidity (Freitag et al., 2003).

Silica sources (reactivity of the aggregate/rock)

The only source of silica in ASR is the aggregate/rock where the reactivity depends on several factors. Aggregates of the same general type from different regions can have quite different alkali reactivity. Reactive aggregates receive different classifications (deleterious, potentially deleterious and potentially reactive) depending on the test method used to determine reactivity (Freitag *et al.*, 2003).

According to French (1992), the amount of the component in each type of rock which reacts is quite small as only about 1% of the silica in the rocks is converted into gel. Additionally, the gel outside the aggregate has usually much less alkali than that in the aggregate, but there is usually remnant alkali in the surrounding cement paste. Thus, the silica consumption during the reaction between the rock and the cement paste is a very small fraction of the total mass of the aggregate. It is particularly difficult to identify the reactive components. French

(1992) also believed that reactions normally took place inside the aggregate so the reactive silica had to be accessible to both the alkalis and to the moisture. He suggested that the reactivity of each rock depends on a range of characteristics. These include microporosity, fracturation (or protofracturation), particle size and silica content, accessible dislocations in quartz, evidence of specifically reactive phases, identification (by X-ray) of amorphous or exceptionally fine material and traces of gel produced when particles over 0.5mm in diameter were treated with molar NaOH/KOH solution. He also asserted that the potential for reaction may be infered simply from the first observation, when the particle size is too fine for the particles to be resolved with a high quality petrological microscope.

According to Tasong *et al.* (1998-a), insufficient studies have been made on the influence of the aggregate on the interfacial transition zone (ITZ), since it had been widely believed that the rock aggregates are chemically inert. From their studies of reactivity of basalt, limestone, quartzite and silica sand aggregates, they concluded that basalt is, by far, the most reactive when exposed to a OPC solution. Basalt absorbed very significant amounts of OH⁻, SO²⁻, Ca²⁺ and K⁺ and released significant amounts of Si⁴⁺, Na⁺, Mg²⁺ and Al³⁺ to a cement solution. According to these authors, the absorption of Ca²⁺, OH⁻ and SO₄²⁻ is due to the formation of hydrated calcium silicates as well as sulfates on the hydrating surface layer of the aggregate particles.

Amongst the New Zealand rocks, Freitag *et al.* (2003) suggested that the following aggregates are generally non-reactive: greywacke, argillite, basalt (if under 50% SiO₂), phonolite, granite, schist, quartz, quartz-feldspar, limestone and lightweight aggregates such as rhyolitic pumice, perlite and vermiculite; whereas aggregates made of basalt (if over 50% SiO₂), andesite, dacite, rhyolite, quartzite, volcanic glass, cristobalite, tridymite, alluvial gravels and sands and amorphous and cryptocrystalline silicas including opal and chalcedony were generally reactive. ASR reactivity is also characterised by combinations between different aggregates. From the studies to date, it was found that there is a certain proportion (under 100%) of a reactive aggregate that results in the greatest expansion due to ASR. This is called pessimum proportion, which can only be defined with empirical methodologies, based on reaction of the aggregate with mortar and/or concrete (Freitag *et al.*, 2003).

III.3.3 Cement-Rock Interaction in Extreme Environments

The quality of a cement job and, therefore, the cement-rock bond, is heavily dependent on how good the cement job design was. Information about the wellbore configuration and environment are crucial to a cement job design as they affect the cement slurry design and determine the cement placement technique to be utilized (Agbasimalo, 2012).

The geothermal environment will modify the way that the cement-rock interaction takes place. The most important environmental variables include the temperature, the CO_2 exposure/pressure and the composition of the hydrothermal fluids (geobrine). Relevant studies on cement-rock interactions under hydrothermal conditions are scarce. A few works on cement-rock interaction at high temperatures have been found that are relevant to the current research, and these are presented in this section. Although at lower temperatures (under 60°C) and much higher pressures than the ones encountered in geothermal wells, a few studies on the effect of CO_2 and brine in the context of CCS are also presented in the current section.

III.3.3.1 Effect of Temperature

Generally, and in accordance with several references (Poole, 1992-a; Criaud *et al.*, 1994; Andrei *et al.*, 1994; Criaud and Defausse, 1995), it is possible to assume that there is some similarity of reaction products in ASR between a normal and high temperature cure, regardless of the cement hydrates and the microstructure of the cement-rock system. On the other hand, silica gel is more viscous at high temperature, with a decrease of its migration rate. According to Jones and Poole (1989), the cut-off humidity below which ASR does not occur is proportional to temperature. Diamond *et al.* (1981) and Herr and Wieker (1992) showed that the temperature has an opposite and significant effect in the expansion attributed to the ASR. Initially, the expansion proceeds faster at elevated temperatures, but the rate declines more rapidly at higher temperatures and the final values of the expansions are inversely proportional to the temperature.

Hodgkinson and Hughes (1999) tested the reaction at 85°C between a selection of rockforming minerals and calcium hydroxide, used as a simple representative of the cement pore fluid. After about 1 month (800 hours), they observed as expected, calcite and/or portlandite had precipitated. Because of the presence of calcite in most of the samples, they concluded that most of the calcium hydroxide had easily carbonated. The samples of quartz, albite and anorthite underwent dissolution (often along preferred crystallographic directions, to form etch pits visible by SEM). New calcium aluminosilicate phases precipitated in high yield in the anorthite, chlorite and muscovite samples. The product of muscovite contained high levels of Al³⁺ and was located almost within the zeolite compositional field. In the anorthite tests, katoite was formed at about 4 days old, at about 8 days, kaotite and poorly ordered fibrous C-A-S-H phase had formed; and at about 1 month, katoite and well-ordered fibrous C-A-S-H phase were present. For quartz and albite, only a very minor precipitation of new phases was observed. The fluid products were, in general, in agreement with the solid products of the anorthite. The chlorite and muscovite tests indicated dissolution of Al and Si bearing material with indication of a decrease in pH and with the Al buffered to a roughly constant level, possibly caused by precipitation of aluminous material.

Up to 110°C with calcium hydroxide present in the reactant fluid, the precipitating phases were CSH amorphous/poorly crystalline gels (though stoichiometrically related to the fully crystalline CSH ones, such as tobermorite and jennite) and other cement minerals (hydrogarnet, hydrocalumite, zeolites, feldspars,...) (Bateman *at al.*, 1998; Rochelle *et al.*, 1992; Savage and Rochelle, 1993; van Aardt and Visser 1977a,b; Hodgkinson and Hughes, 1999).

From the extensive literature review they conducted, Hodgkinson and Hughes (1999) concluded that the main reactions up to 110°C were the formation of calcium silicate hydrate (CSH) gels, while the main products at higher temperatures over 110°C were zeolites and feldspars (especially, in the presence of NaOH or KOH).

Andrei and Criaud (1996) concluded that the products of reaction obtained at 150°C had a similar texture (amorphous and polyamorphous gels) to the ones at ambient conditions, which have a broad range of chemical composition. At temperatures above 150°C, experiments conducted with alkali hydroxides (NaOH and KOH), rapidly formed zeolites and feldspars with the high pH, causing the alteration of smectite to illite or illite/smectite interlayers (Chermak, 1992, 1993; Inoue, 1983; Komarneni and White, 1981, 1983; Johnston and Miller, 1984; Hodgkinson and Hughes, 1999).

Langton *et al.* (1980), aiming to understand the relationship between the chemical and physical properties of the interfacial region formed between cement paste and rock, undertook some hydrothermal cement-rock interaction experiments at temperatures of 200°C and 250°C, at 51.7MPa pressure. They used an API class J cement, with tuscarora quartzite

(95% quartz) and Valentine limestone (99.9% calcium carbonate), which they considered unreactive.

From the shear strength measurements, they observed that:

- the cement-quartzite bond seemed dependent on temperature for the first 7 days of curing, as the 200°C sample achieved much higher shear strength compared with that at 250°C. However, after seven days, the shear strengths were closer, with the 250°C higher than the 200°C sample;
- the cement-limestone sample was more stable and the shear strength was not dependent on the temperature (200/250°C) or on the curing time, although it did not achieve as high shear strengths as the quartzite sample.

From chemical analysis across the cement-rock interface, after only one day of curing, they observed that:

- cement-quartzite sample: there was a relatively sharp decrease in silicon up to 50μm into the cement, and a sharp decrease in calcium over about the same range in the rock, which they attributed to the volume of sample excited by electrons during the X-ray emission. Additional silica was also detected further inside the cement, which could be due to quartz grains that made up part of the composition of the class J cement. There was also some calcium rich areas, explained by the authors as a high concentration of calcium hydroxide crystals;
- cement-calcite sample: as with the cement-quartzite sample, there was a sharp gradational change for calcium and silicon, across the interfacial region.

They concluded that the both shear strength and hydration changes for both samples depended on the temperature and on curing time. Moreover, they believed that the degree of paste hydration (in normal cement pastes) or of belite (C_2S)-quartz reaction (in hydrothermal cements) increased with the degree of crystallinity of calcium silicate hydrates in the interfacial region and the paste, which increased with time and temperature.

It was suggested that the shear bond strength that developed between 'unreactive' wall rock and cement reasonably approximated, within experimental error, the tensile strength of the hydrothermally cured cement itself. They concluded that mechanical bonding was primarily responsible for the shear strength of the unreactive wall rock-cement contact, rather than any chemical bonding.

III.3.3.2 Effect of Drilling Fluid (Mud)

The bond between the cement and the rock is defined by the mechanical interlocking of cement hydration products with the rock grains and the chemical reaction between the cement paste and rock grains. The contamination of cement by drilling fluid alters the mechanical and chemical properties of the cement and this in turn affects the character of the bond between the cement and the rock (Agbasimalo, 2012).

When a well is being drilled, partially dehydrated-gelled drilling fluid and mud cake are deposited on the wall of the wellbore (Ravi *et al.*, 1992). The presence of mud channels has been shown to reduce cement-formation bond strength and create pathways for fluid migration. Scratchers in conjunction with casing movement are usually used to remove the mud before cement placement but they do not remove all the mud (Agbasimalo, 2012).

Peterson (1963) evaluated the effect of mud cake and mud contamination of cement on the cement-formation bond. Shear bond experiments were performed using cement-sandstone composites with either the presence of mud cake at the interface or the contamination of the cement by mud. The interface was tested in four different modes: with the presence of the mud cake; with mud cake scraped off; with the mud cake scraped off plus the surface washed with water; and mud cake scraped off plus the surface washed with surfactant⁵. The mud thinkness was one mm. The bond strength of the cement mudstone composite without mud cake was 1.27 MPa with no significant bond strength measured in the presence of the mud cake. For the mud cake treatments, the highest bond strength was recorded with mud cake scraped off plus the surface washed with surfactant (1.02 MPa), while the lowest bond strength was obtained with mud cake scraped off only (0.5 MPa).

Ladva *et al.* (2005) investigated the effect of the mud cake on porous formations as well as the effect of mud treatment on shale. These authors concluded that the presence of mud cake reduced the cement-sandstone bond strength drastically, from over 0.8 MPa to 10^{-3} MPa. Additionally, they observed that the bond strength was 3 times greater when the mud cake was washed out compared to the unwashed mud cake.

Oyibo and Radonjic (2014) have also investigated the effect that both physical and chemical drilling mud contamination have on the cement-rock interface. They considered the mud

⁵ Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid.

cake forming between the cement and the rock, provides physical contamination which acts as physical barrier. The chemical contamination consists of 5-10% of the drilling mud (bentonite) mixing with the cement outermost layer, i.e. bentonite is incorporated in the cement outermost layer during the hydration stage. From this study, these authors concluded that physical contamination (mud cake) has the most negative impact on cement-formation shear bond strength and the mud cake was considered detrimental to bonding.

III.3.3.3 Effect of CO₂ and Brine

Besides affecting the natural rock formation and the engineered materials (cement and steel casing), the brine along with the presence of CO_2 also plays a key role on how the rock and materials interact with one another. Hodgkinson and Hughes (1999) recognised the significance of the effect that the CO_2 had in the cement-rock system: CSH gels and portlandite have a tendency to become carbonated and calcite readily precipitates whenever the calcium hydroxide comes into contact with a carbonate source.

Duguid and his co-workers (2009, 2011) used an experimental set up consisting of sandstone cylinders filled with class H neat paste (W/C=0.38) (Figure III.13), cured for 7 months in a SiO₂ saturated 0.5 *M* NaCl brine, at different temperature/pH combinations, e.g. 20°C/pH 3, 20°C/pH 4, 20°C/pH 5 and 50°C/pH 3. Following curing in a CO₂ free environment, the filled cylinders were sliced into discs with the faces sealed (so that diffusion only occurred in the radial direction), and cured in the CO₂ saturated brine and checked every month for 1 year. The design of the experiment and the samples forced the degradation to be controlled by diffusion through the pores of the sandstone, a relatively permeable rock when compared with most of the rocks found downhole.



Figure III.13 - sectioned schematic of stone-cement sample prior to slicing (A) and measurement locations (B) (Duguid *et al.*, 2011)

They observed a general degradation pattern with a single visible reaction zone formed, which progressed over time. After 1 month the colour was cream. After 2 months, light orange with bright orange at the interface, becoming lighter towards the centre of the cement. Visible degradation of the front showed a change in rate after 2 to 3 months. This was attributed to the precipitation of calcium carbonate in the larger cement pores and a switch from the degradation of Ca(OH)₂ (and C-S-H) to the degradation of CaCO₃ (Figure III.14).



Figure III.14 - Photos of the sandstone samples reacted over a year at pH 3 and 20°C (Duguid, 2009)

The depth of reaction was measured from the outer edge of the invaded zone (and not from the cement-sandstone interface) and at different locations, with variable rock section thicknesses. In the 50°C experiments, the cement invaded the stone to a depth of 0.8-1mm. The maximum depths of the visible reaction zone for 20°C was 0.310mm (pH 3), 0.307mm (pH 4) and 0.270mm (pH 5), whereas at 50°C it was 0.577mm (pH 3) (Figure III.15).



Figure III.15 - Reaction depth data versus the square root of time divided by the shortest distance, r, to the outside of the sample for all measurements points (Duguid, 2009).

[A] = 20°C-pH 3; [B] = 20°C-pH 4; [C] = 20°C-pH 5; [D] = 50°C-pH 3

The EDX maps of calcium, iron and silicon for one of these samples are presented in **Figure III.16**. The map for the cement region shows iron and silicon are homogeneously distributed. The map for calcium shows two regions: the bottom of the map, extending up between 600 μ m and 800 μ m, shows a higher intensity (more white) than the 1000-micron-wide region starting between 600 μ m and 800 μ m extending to the interface with the sandstone.

Some calcium deposits could be seen by X-ray mapping at the leading edge of the visible (orange) reaction front. These calcium deposits have no corresponding features for iron and silica in the X-ray maps so these authors postulated they were not unhydrated cement phases. Furthermore, due to the long (6 months) exposure to carbonic acid, the calcium grains were not likely to be calcium hydroxide, which should be the first calcium phase in the cement to be destroyed.



Figure III.16 - X-ray maps of the 20°C - pH 3 sample at 6 months showing white grains outlined by the rectangular boxes in the calcium map (left) and showing no corresponding grains in the iron map (center) and the silicon map (right) (Duguid, 2009).

Whilst some interactions are expected (e.g. contact of CO_2 with the cement outermost layer), others are consequences of relatively unpredictable leakages. Leakages can occur along micro-annuli present at the cement-formation or cement-casing interfaces due to poor bonding between these materials (Crow *et al.*, 2009). The cement-rock and the cement-steel interfaces represent particularly important features, and may represent zones of preferential fluid movement should chemical changes in the cement alter its physical properties (**Figure III.17**). Additionally, Rochelle (2004) reckons that a good cement-to-formation or cement-to-casing seal relies strongly on a physical rather than a chemical bond.



Figure III.17 - Small section of an abandoned well used for CCS purposes: (A) CO₂ migration through the pores or pathways of the well cement; (B) CO₂ migration through annuli or defects that exist between the casing and the cement; (C) CO₂ travelling through an annulus or pathway at the interface between the cement and the formation; (D) CO₂ entering the wellbore through a damaged casing and travelling up the inside of the well (Duguid *et al.*, 2006)

Most of these leakages are due to: 1) deficient well construction (e.g. most of the wells are only partially cemented and there is often no cement behind the borehole casing between the top of the production interval and the uppermost few hundred metres of well); 2) improperly abandoned wells; or 3) geochemically or geomechanically compromised barrier system (Crow *et al.*, 2009; Rochelle, 2004). While the steel casing is not a concern within the current work, the way the CO_2 interacts with the well cement assumes an extremely important role on the cement performance, durability and, consequently, on the way it interacts with the surrounding rock formation.

Carey *et al.* (2007) studied a core of metal casing, well cement and shale caprock, which had been in CO₂-rich brine at 54°C and 18MPa for 30 years. Besides the alteration depths of the cement, one of the main conclusions was that CO₂ migrated along a pre-existing gap along the cement-shale interface. This seems to highlight the importance of the cementing job to avoid leakage pathways; something that is not usually considered in laboratory work. These authors have also reported a potential "self-healing" by deposition of carbonate in the cement fractures as well as in the interface defects. These defects may exist because of inadequate removal of drill cuttings, formation of a drilling mud filter cake, formation damage during drilling or geomechanical stresses. Aiming to better understand the importance of these defects, Newell and Carey (2013) have commenced a laboratory experiment in order to evaluate the evolution of the Portland cement-caprock deficient interface (mix of 20% crushed hydrated cement with 80% siltstone) during CO₂ leakage. The simulated downhole environment was 60°C at a confining pressure of 18MPa, with posterior co-injection of a mixture of scCO₂ and brine into the sample. While the rock seemed not to be affected, the

cement has carbonated up to 5mm away from the gap, with a 100 μ m dense carbonation front, which is in accordance with the previously mentioned carbonation sheath that protects the cement from further CO₂ intrusion through the deposition of dense carbonate. Additionally, there was a significant decrease in the permeability in the interface (defect), despite the calcite-undersaturated conditions. According to these authors, this might have been a consequence of migration of fines and redistribution of dissolved cement phases in the defect (e.g. alumina hydroxides and amorphous silica), rather than the carbonate deposition reported by Carey *et al.* (2007).

IV. METHODOLOGY

IV.1 Justification for the paradigm and methodology

This work examines the changes in composition and properties of the Interfacial Transition Zone (ITZ) that develops between formation and cement in a simulated geothermal environment. To simulate a real geothermal well cement/formation interface, cavities were drilled/cored within rock blocks and cement grouts were set into the holes, after which the whole assembly was exposed to simulated downhole conditions in an autoclave.

New Zealand geothermal wells are commonly drilled through acid silicate rocks such as ignimbrite, andesite, rhyolite, pumice and greywacke. Following discussions with the IRL/Callaghan Innovation cement research team, as well as recommendations from Browne (2011) the most relevant rocks for the current study were considered. These include, from the most to the least relevant, ignimbrite, rhyolite, andesite, greywacke and pumice. Due to time restrictions, this work has focused only on ignimbrite and rhyolite, with four ignimbrites (including two hydrothermally altered ones) and one rhyolite being tested.

The cements currently used in geothermal applications are predominantly API oilwell cements. This research has used an API Class A, an API Class G, white cement and high alumina cement (HAC). The API class G cement has been modified with additions/replacements used to improve the cement performance, namely Silica Flour (pure quartz) and Microsilica 600 (amorphous silica). These additions are common within the geothermal industry, as they have already been tested and proved satisfactory. The selected combinations of cements and admixtures were:

- API class G cement (G): the most commonly used cement in geothermal wells, which is currently a reference for any kind of well cementing.
- API class G + 20% MS600 (G20MS): addition of 20% (in weight) of Microsilica 600 to the reference well cement. This mixture has already been proved successful in geothermal well cementing due to added properties imparted by the amorphous silica.
- ✤ API class G cement + 20% Silica Flour (G20SF): addition of 20% (in weight) of silica flour to the reference well cement, aiming to compare it with G20MS and G40SF.
- API class G cement + 40% silica flour (G40SF): addition of 40% (in weight) of Silica Flour (quartz) to the reference well cement in order to form tobermorite, a desired hydration product which forms with over 30% quartz addition.

- API class A cement (A): despite belonging to the API range, it is basically an Ordinary Portland Cement (OPC) and was chosen as a reference because most of the studies within the cement research field are based on OPC.
- White cement (W): this Portland based cement lacks tetra-calcium alumina ferrite (C₄AF), which provides lower workability and lower resistance to sulphates when compared with A and G. Consequently, W may also show interesting changes in the way it interacts with the rock formation when compared with A and G.
- High Alumina cement (HAC): contains, which, during the hydration, may release some Al³⁺ ions from the alumina content and, possibly, have a different interaction with the rock.

Simulation of the geothermal environment has been made in large autoclaves, with hydrothermal fluids exposure and varying temperature and CO₂ concentration.

The hydrothermal solution (geobrine) utilised is that used in the experimental work undertaken by the IRL/Callaghan Innovation cement research team. The recipe is based on a geothermal fluid assay based on NZ typical geothermal fluid, supplied by Mighty River Power in 2009, and confirmed by GNS Science in February 2010. It consists of 0.19 g sodium sulfate (NaSO₄), 0.05 g calcium chloride dihydrate (CaCl₂.2H₂O), 15.6 g colloidal silica (SiO₂), 4.1 g potassium chloride (KCl), 15.8 g sodium chloride (NaCl). These are well mixed and made up to 20 litres with distilled water.

Two different temperatures have been found to be the most relevant to simulate the conditions downhole:

- 150°C: this temperature was chosen to mimic conditions in the lowest temperature wells, and the middle of the highest temperature wells. Two new crystalline phases (not expected at lower temperatures) form when silica flour is added, both with lower permeability and improved compressive strength, when compared to the equivalent product at temperatures lower than 150°C. This temperature also represents the temperature where the levels of dissolved CO₂ and corrosion are highest.
- 290°C: at over 220°C, a transformation to a weaker and more permeable material occurs at both high and low Ca/Si ratio formulations. Additionally, this is close to the maximum temperature measured in geothermal wells in New Zealand, which is above 300°C. Nevertheless, as a safety procedure, the maximum temperature currently utilized now in the IRL autoclaves is 290°C.

Regarding the CO_2 concentration, the literature (Henneberger, 1983; Wolley and Carroll, 2010) states that the total ambient pressure in geothermal environments is situated within the range 10-100bars, with a CO_2 overpressure of 6bars. At 150°C, the autoclave pressures were approximately 11bars, whereas at 290°C the pressure went up to about 74bars, both with a CO_2 overpressure of approximately 6 bars.

IV.2 Raw Materials

The different materials utilised in the current experimental work: the rocks; the powdered cement; the admixtures; and powdered bentonite used to simulate the drilling fluid are characterised in this section. The tests undertaken on these materials include X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD), optical microscopy (OM) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), particle size, density/porosity and mercury porosometry. The procedures for these tests were:

- XRF: this test identifies the major elements present in the sample and was carried out on all the raw materials. The material to be examined was ground with a mortar and pestle to obtain a powder as fine as possible. It was then sent to CRL Energy Ltd (Spectrachem), for analysis using a Siemens (Bruker) SRS3000 sequential wavelength-dispersive X-ray fluoresence spectrometer, equipped with a 3kW Rhodium x-ray tube. The data were presented in major oxide format, a standard geological analysis protocol. Samples were analysed on an oven-dried basis (110°C), with Ignition loss (LOI) determined for one hour at 1000°C, and all data are corrected back to the "oven-dried" basis. The resulting 'ignited material' is combined with a proprietary fluxing agent (mixture of lithium tetraborate and metaborate x-ray flux) in known ratios. The sample is then mixed and heated to 1100°C, producing a glass melt, that is annealed to form a flat glass disc for analysis. Data for all oxides are considered 'total' present, rather than 'extractable' or 'recoverable'.
- XRD: this test identifies all the crystalline components present in the rocks and in the admixtures. The rock samples were submitted for Rietveld XRD quantitative analysis, which required a distinct and more accurate sample preparation. Firstly, in order to obtain a representative sample of the rock, over one dm³ of rock was crushed (Figure IV.1), ground with a milling machine and riffled (Figure IV.2). A small amount of sample (approx. one gram) was further ground with the bouncing ball equipment (Figure IV.3) and 33,(3)% (by weight) of corundum was added as reference. This

mixture was then scanned for ca. five hours within the diffraction range from 4° to 80° 20, with cobalt (Co) as X-ray diffraction source. This result was analysed using the powder diffraction data software TOPAS, which calculates the amount (in percentage) of each crystalline material present in the rock by comparison with the reference sample for which the amount is previously known (addition of 33,3% is equivalent of 25% of the total weight). A complementary analysis was made by considering the XRF results, the stoichiometric compositions and the element weights. From these results an approximate estimation of the amount of silica present in the volcanic glass was obtained.



Figure IV.1 - Scheme of the crushers utilized to crush the rock samples for XRD quantitative analysis

Figure IV.2 - Type of riffler used to get a representative sample of the rock for XRD quantitative analysis

Figure IV.3 - Bouncing ball used for milling the rock for XRD quantitative analysis

Particle size: The particle size distribution of all the cements and admixtures was measured by using a Shimadzu Sald 2001 laser diffraction particle size analyser, with a 0.1µm to 700 µm measurement range. This method relies on the variations between the emission and reception of a scattered laser trough a small transparent chamber where the particles of the sample stand. The variations between the light waves that are emitted by the laser and the ones that are detected in the sensor provide the size of the particles present in the chamber. The procedure consists in dispersing a small amount (approximately 100 mg) of powdered sample into the small glass cup with 100 mL of dry isopropyl alcohol (which does not react with the cements) or distilled water (for the admixtures). The particles in the colloidal solution are dispersed by stirring and ultrasonic treatment. The suspension is pumped through the instrument

starts which does not stabilise until all the sample particles are dispersed. The final data is collected once the measurements stabilise.

Density and porosity: the density and porosity were obtained for all the rock samples. This method calculates the bulk density as well as the apparent porosity, through the measurement of the dry, submersed and saturated surface dry (SSD) weights of the sample, at a carefully controlled temperature (18°C), as the density of water slightly changes depending on its temperature (Figure IV.4 and Figure IV.5). After measuring the mass of the samples using a high precision scale, the bulk density, apparent density and apparent porosity are calculated for each of the rock types according to, respectively, Equation IV.1, Equation IV.2 and Equation IV.3:

$$BulkDensity = \frac{DryWeight}{WetWeight - SubmersedWeight}$$
Equation IV.1
$$ApparentDensity = \frac{DryWeight}{DryWeight - SubmersedWeight}$$
Equation IV.2
$$ApparentPoosity = \left(1 - \frac{BulkDensit}{ApparentDesity}\right) \times 100\%$$
Equation IV.3

where,

Dry Weight - the mass of the object at the ambient conditions (room humidity and temperature) (g);

Submersed Weight - the mass of the object immersed in water at 18°C (g);

Wet Weight - the weight of the object measured while fully saturated with water at 18°C (SSD) (g);

Bulk.Density - the mass of the material divided by the total volume it occupies (this volume includes particle volume, inter-particle void volume and internal pore volume) (kg/dm³);

Apparent.Density - the mass of the material divided by the volume it occupies, (this volume excludes the amount of volume occupied by open voids/pores) (kg/dm³);

Apparent.Porosity - the amount of void (or pores) within a volume of sediment or porous solid (the real porosity includes the volume of the sealed pores also, but it is much more difficult to obtain) (%).



Figure IV.4 - Precision scale used to
measure the dry, wet and
submersed weights of the sampleFigure IV.5 - Vacuum system used to replace the water with air
in order to fully saturate the sample with water

Mercury porosometry was performed for all the rock samples and measures the pore size distribution through mercury intrusion. The samples were sent to the external Australian company Particle and Surface Sciences Pty. Limited, for analysis. The pressure required to intrude mercury into the sample's pores is inversely proportional to the size of the pores. The instrument used was a Micromeritics Autopore 9520 – Pore Size Range 350um – 0.003um (60,000psi). The procedure comprises the following steps: 1) 0.8 to two grams of sample were loaded into the penetrometer, which consists of a sample cup connected to a metal clad, precision-bore, glass capillary stem; 2) the penetrometer is sealed and placed in low pressure port, where the sample is evacuated to remove air and moisture; 3) the penetrometer's cup and capillary stem are then automatically backfilled with mercury, with the excess mercury being automatically drained back into the internal reservoir; 4) as pressure on the filled penetrometer increases, mercury intrudes into the sample's pores, beginning with those pores of larger diameter; 5) the penetrometer is moved to the high pressure chamber, where high pressure measurements are taken; 6) the data are automatically

reduced using the low and high pressure data points, along with values entered by the operator, such as the weight of the sample and the weight of the penetrometer loaded with mercury.

• OM: a transmitted light microscope was used for petrographic analysis. More details about this test and procedure are given in the section III.3 (research procedures) section of the current chapter.

IV.2.1 Rocks

The rocks chosen for the experimental work were ignimbrite and rhyolite. Ignimbrite is the predominant rock in geothermal environments in New Zealand, whereas rhyolite, although not as common as ignimbrite, was chosen as it has significantly different properties to ignimbrite. Different hydrothermal alteration types of ignimbrite were tested. The rocks were all analysed by XRF, XRD, density and porosity assessment, OM and SEM/EDS analysis. The rocks tested were Ongatiti Ignimbrite (IGN), Unaltered Ignimbrite (UNI), Ignimbrite with Kaolinite alteration (KAO), Ignimbrite with Mordenite Alteration (MOR) and Whakaroa Rhyolite (RHY). Their origin and composition is given in the following sub-sections.

IV.2.1.1 Ongatiti ignimbrite (IGN)

This rock is also known as Hinuera Stone, as it is quarried at Hinuera in the Waikato region (**Figure IV.6**). After quarrying, this rock is sawn and cleaned (washed with water) by the company, Hinuera Natural Stone, for comercialisation. This rock was used as a reference as it was available from the start of the experimental work and in sufficient amounts to cover all the combinations under evaluation.



Figure IV.6 - Block of IGN

XRF analysis:

The major oxides composition of IGN are presented in the Table IV.1.

ROCK	Major oxides composition (weight % on oven dried [110°C] basis)											
	SiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	LOI*	SUM
IGN	70.56	13.80	2.81	0.04	0.36	1.90	3.75	3.30	0.31	0.07	2.62	99.53
UNI	71.16	13.57	2.27	0.08	0.34	1.59	3.21	3.45	0.27	0.02	3.74	99.69
KAO	69.74	16.42	2.13	0.06	0.17	0.87	0.77	1.62	0.36	0.02	7.61	99.78
MOR	70.87	13.72	2.23	0.03	0.21	2.53	2.41	3.47	0.30	0.05	4.11	99.93
RHY	74.09	13.46	2.34	0.06	0.50	2.02	4.54	2.27	0.30	0.07	0.08	99.72

Table IV.1 - XRF analysis of the rocks

*LOI = loss on ignition at 1000° C

Rietveld XRD/quantitative analysis:

The XRD diffractogram shows distinctive peaks as well as some large humps attributed to the amorphous material in this rock (composed of amorphous volcanic glass). The minerals identified by XRD analysis were ca. 15 wt% feldspars (mostly plagioclases ranging from albite to anorthite - typically and ca. 1.5 wt% quartz (SiO₂). No other crystalline minerals were identified so it can be inferred that the rock is \approx 83.5 wt% amorphous (further XRD quantitative information on spiked samples is presented in the **appendix X.1** (XRD quantitative information).

Considering only 15wt% of feldspars are present (from the quantitative XRD analysis) and assuming that calcium, sodium and potassium oxides (CaO, Na₂O and K₂O) are evenly used to form the end member feldspars (anorthite, albite and orthoclase, respectively), the silica necessary to form these feldspars is approximately 10wt%. This implies, however, that only ca. 40wt% of the calcium, sodium and potassium oxides are being used to form feldspars, i.e. the rest of these oxides, ca. 60wt%, are present in the rock as constituents of the glass.

Furthermore, by subtracting the silica present in the crystalline materials (10wt% present in the feldspars and 1.5wt% from the quartz) from the total amount of silica present, ca. 70.5wt% (obtained in the XRF), it can be concluded that ca. 59wt% of silica is present in the volcanic glass of the rock (see **appendix X.1**).

Density and porosity:

The results obtained for the density and porosity of IGN are presented in the Table IV.2.

ROCK	Dry weight (g)	Submersed weight (g)	Wet weight (g)	Bulk density (kg/dm ³)	Apparent density (kg/dm ³)	Apparent porosity (%)
IGN	9.202	5.327	11.088	1.595	2.372	32.737
UNI	16.973	9.922	22.740	1.322	2.404	44.991
KAO	26.097	14.772	36.535	1.198	2.301	47.962
MOR	32.183	18.288	40.454	1.450	2.313	37.314
RHY	43.431	26.220	46.001	2.193	2.520	12.992

Table IV.2 - Density and porosity results of the rocks

Mercury porosometry:

The most relevant results regarding the mercury porosimetry are presented in the **Table IV.3** and **Table IV.4**. Detailed analysis is presented in the **appendix X.2**. IGN is the second least porous rock, with only 32.94% porosity. This result is in very good agreement with the apparent porosity calculated above (32.74%). The total mercury intrusion was 0.2869 mL/g, which is the third highest amongst all the rocks. The mercury intrusion in pores with a diameter above 0.5 μ m is 0.2066 mL/g. Considering the bulk density given above for this rock (1.595 kg/dm³ = 1.595 g/mL), it corresponds to 0.3295 mL of mercury intrusion per mL of rock, which is the highest for pores with a diameter above 0.5 μ m.

ROCK	TOTAL Intrusion (mL/g)	Intrusion in Ø* > 0.1µm pores (mL/g)	Intrusion in Ø > 0.5μm pores (mL/g)	Intrusion in Ø > 1µm pores (mL/g)	Intrusion in Ø > 5µm pores (mL/g)	Intrusion in Ø > 10µm pores (mL/g)	Intrusion in Ø > 50µm pores (mL/g)	Intrusion in Ø > 100µm pores (mL/g)
IGN	0.2869	0.2410	0.2066	0.1578	0.0109	8.6070E-03	5.7380E-03	4.8773E-03
UNI	0.2294	0.2019	0.1636	0.1145	0.0156	1.1241E-02	6.8820E-03	5.5056E-03
KAO	0.3938	0.2008	0.0985	0.0764	0.0197	1.5752E-02	9.4512E-03	7.0884E-03
MOR	0.2983	0.2178	0.0835	0.0567	0.0200	1.6407E-02	8.3524E-03	6.2643E-03
RHY	0.0615	0.0517	0.0461	0.0421	0.0286	2.3985E-02	1.0148E-02	6.7650E-03

Table IV.3 - Mercury Intrusion as a function of the Pore Size (volume of pores per weight of sample)

* Ø =diameter

ROCK	Bulk density (g/mL)	TOTAL Intrusion (mL/mL)	Intrusion in Ø > 0.1µm pores (mL/mL)	Intrusion in Ø > 0.5µm pores (mL/mL)	Intrusion in Ø > 1µm pores (mL/mL)	Intrusion in Ø > 5µm pores (mL/mL)	Intrusion in Ø > 10µm pores (mL/mL)	Intrusion in Ø > 50µm pores (mL/mL)	Intrusion in Ø > 100µm pores (mL/mL)
IGN	1.595	0.4576	0.3844	0.3295	0.0520	0.0006	4.8785E-06	2.7993E-08	1.3653E-10
UNI	1.322	0.3033	0.2669	0.2162	0.0248	0.0004	4.3401E-06	2.9869E-08	1.6444E-10
KAO	1.198	0.4718	0.2406	0.1179	0.0090	0.0002	2.7947E-06	2.6413E-08	1.8723E-10
MOR	1.450	0.4325	0.3158	0.1211	0.0069	0.0001	2.2508E-06	1.8799E-08	1.1776E-10
RHY	2.193	0.1349	0.1133	0.1012	0.0043	0.0001	2.9229E-06	2.9660E-08	2.0065E-10

 Table IV.4 - Mercury Intrusion as a function of the Pore Size (volume of pores per volume of sample)

OM (thin section):

This rock is mostly glassy, with a eutaxitic texture, i.e. a matrix of glass shards welded together with fine ash (glass), and containing lithic (rock) fragments and pieces of pumice. The predominant minerals are plagioclase (strongly zoned and with Na/Ca composition ratio in between albite and anorthite - typically andesine) and quartz. Very small amounts of amphibole noted (hornblende: high relief and strong pleochroism). This rock is not altered (**Figure IV.7**).





i. Plane Polarised Light (PPL) Figure IV.7 - Optical microscope images: IGN

IV.2.1.2 Unaltered Ignimbrite (UNI)

A second ignimbrite was collected from Ohakuri, in the TVZ, based on the data provided by Henneberger (1983) (Figure IV.8). This rock was selected for the current work because it represents the unaltered ignimbrite from the TVZ.



Figure IV.8 - Block of UNI

XRF analysis:

The major oxides composition of UNI is presented in the Table IV.1. It has a very similar composition to IGN.

Rietveld XRD/quantitative analysis:

The XRD diffractogram contains a few distinctive peaks superimposed on several large humps distributed over a wide range due to the amorphous nature of this rock. The minerals identified by XRD analysis were ca. 16 wt% feldspar (plagioclases range from albite to anorthite) and ca. three wt% quartz (SiO₂). No other crystalline minerals were identified by XRD, from which can be inferred that the rock is ≈ 81 wt% amorphous (further XRD quantitative information on spiked samples in the **appendix X.1**).

Considering the same procedure adopted to IGN, it was found that, from the total amount of silica present in the rocks, ca. 11 wt% is present in the feldspars and ca. 57 wt% is present as a component of the volcanic glass (see **appendix X.1**).

Density and porosity:

The results obtained for the density and porosity of UNI are presented in the **Table IV.2**. This material has a higher apparent porosity and slightly higher apparent density than IGN.

Mercury porosometry:

The most relevant results from mercury porosimetry are presented in **Table IV.3** and **Table IV.4**. The detailed analysis is presented in **appendix X.2**. UNI is the second most porous rock, with 43.62% porosity. This result is in excellent agreement with the apparent porosity calculated above (44.99%). Total mercury intrusion was 0.2294 mL/g, which is the second lowest of all the rocks studied with intrusion into pores above a diameter of 0.5 μ m is 0.1636 mL/g. Considering the bulk density given above for this rock (1.322 kg/dm³ = 1.322 g/mL), this corresponds to 0.2162 mL of mercury intrusion per mL of rock, which is the second highest for pores with a diameter above 0.5 μ m.

<u>OM (thin section)</u>: This ignimbrite shows a matrix of glass shards welded together with fine ash (glass). The predominant minerals are plagioclase and quartz. A few pumice fragments are also present, as well as spherulites (radiating cristobalite/tridymite) that are indicative of devitrification. Orthopyroxene and Fe-Ti oxides (magnetite) are also identified. This rock shows almost no alteration, except for minor glass devitrification (**Figure IV.9**).




i. PPL ii. XPL Figure IV.9 - Optical microscope images: UNI

IV.2.1.3 Ignimbrite with kaolinite alteration (KAO)

This rock was also collected from Ohakuri, in the TVZ, based on the data provided by Henneberger (1983) (Figure IV.10). It was selected for the current work because it represents an altered ignimbrite from the TVZ. It is important to understand the role that hydrothermal alteration may play as many of the rocks present in hydrothermal systems have suffered some degree of alteration.



Figure IV.10 - Block of KAO

XRF analysis:

The major oxide composition of KAO is presented in the Table IV.1.

Rietveld XRD/quantitative analysis:

The XRD diffractogram shows distinctive peaks as well as superimposed on some large humps distributed over a wide range, due to the amorphous nature of the glass. The minerals identified by XRD analysis are ca. 15wt% feldspar (mostly plagioclases range from albite to anorthite - typically and esine), ca. 2.2wt% quartz (SiO₂) and kaolinite. No other crystalline minerals were identified by XRD, from which it can be inferred that the rock is \approx 75.8wt% amorphous (further XRD quantitative information on spiked samples in the **appendix X.1**.

Considering the same procedure adopted for IGN, it was found that from the total amount of silica present in the rocks, ca. 9wt% is present in feldspars. Moreover, assuming all the weight left in the feldspars is composed of alumina, then ca. 2.8wt% alumina is present in the form of feldspars. Thus, considering that all the alumina left is used to form kaolinite, there is approximately 7wt% kaolinite, of which ca. 3wt% is silica.

By subtracting the silica present in the crystalline materials (9wt% present in the feldspars, 2.2wt% from the quartz and 3wt% present in the kaolinite) from the total amount of silica present, ca. 70wt% (obtained in the XRF), it can be concluded that ca. 56wt% of silica is amorphous and is the volcanic glass (see **appendix X.1**).

Density and porosity:

The results obtained for the density and porosity of KAO are presented in the **Table IV.2**. This material has a higher apparent porosity and slightly lower apparent density compared to IGN.

Mercury porosometry:

The most relevant results from mercury porosimetry are presented in the **Table IV.3** and **Table IV.4** with the detailed analysis presented in **appendix X.2**. KAO is the most porous rock studied, with 47.68% porosity. This result is in very good agreement with the apparent porosity calculated above (47.96%). The total mercury intrusion was 0.3938 mL/g, which is the highest amongst all the rocks. Intrusion into pores above 0.5 μ m diameter is 0.0985 mL/g.

Considering its bulk density of $1.198 \text{ kg/dm}^3 = 1.198 \text{ g/mL}$, this corresponds to approximately 0.1179 mL of mercury intrusion per mL of rock, making it the second lowest for pores with a diameter above 0.5 µm.

OM (thin section):

This rock has a eutaxitic texture with glass shards welded together within a fine ash matrix of glass. The predominant minerals are compositionally zoned plagioclase (albite - anorthite – typically andesine) and quartz. Kaolinite was not identified by optical microscope analysis. The degree of alteration is higher than IGN or UN as a new mineral is forming, kaolinite (confirmed by XRD) (Figure IV.11).





Figure IV.11 - Optical microscope images: KAO

IV.2.1.4 Ignimbrite with mordenite alteration type (MOR)

Similarly to UNI and KAO, this rock was collected from Ohakuri, in the TVZ, based on the data provided by Henneberger (1983) (Figure IV.12). This rock was selected as it has the highest type of alteration among all the ignimbrites studied in the current work.



Figure IV.12 - Block of MOR

XRF analysis:

The major oxide composition of MOR is presented in the Table IV.1.

Rietveld XRD/quantitative analysis:

The XRD diffractogram has some distinctive peaks as well as some large humps distributed over a wide range. The minerals identified by XRD analysis are ca. 25wt% feldspars, ca. 3.2wt% quartz (SiO₂) and 25wt% mordenite. No other crystalline minerals were identified by XRD, from which it can be inferred that the rock is composed of ~46.8wt% amorphous (further XRD quantitative information on spiked samples in the **appendix X.1**.

Considering the same procedure adopted to IGN, it was found that, from the total amount of silica present in the rocks, ca. 15wt% is present in the feldspars. Moreover, from the 25wt% of mordenite present, ca. 17wt% is silica.

By subtracting the silica present in the crystalline materials from the total amount of silica present, ca. 71wt%, it can be concluded that ca. 36wt% of silica is present in the glass (see **appendix X.1**).

Density and porosity:

The results obtained for the density and porosity of MOR are presented in the **Table IV.2**. It has a slightly lower apparent density and slightly higher apparent porosity than IGN.

Mercury porosometry:

Results are presented in **Table IV.3** and **Table IV.4** with the detailed analysis presented in **appendix X.2**. MOR is the third most porous rock, with 41.11% porosity, reasonably close to the apparent porosity of 37.31%. The total mercury intrusion was 0.2983 mL/g, which is the second highest amongst all the rocks. Intrusion into pores with a diameter above 0.5 μ m is 0.0835 mL/g. The bulk density 1.450 kg/dm³ = 1.450 g/mL, corresponds to approximatelly 0.1211 mL of mercury intrusion per mL of rock, which is the third lowest for rocks with pores above 0.5 μ m in diameter.

OM (thin section):

Although the phenocryst minerals show almost no alteration, the matrix is strongly altered. The minerals present are plagioclase (strongly zoned), quartz and mordenite. Much of the primary glass has been replaced by finely crystalline mordenite (**Figure IV.13**).



i. PPL



ii. XPL

Figure IV.13 - Optical microscope images: MOR

IV.2.1.5 Whakaroa rhyolite (RHY)

This rock was selected due to its considerably different composition and porosity when compared to all the other rocks under study, to explore the effect that these features have on the way the formation interacts with the cement. This rock was obtained from the northwest end of Whakaipo Bay, Lake Taupo (**Figure IV.14**).



Figure IV.14 - Block of RHY

XRF analysis:

The major oxide composition of RHY is presented in the Table IV.1. It contains a slightly higher amount of silica than IGN.

Rietveld XRD/quantitative analysis:

The XRD diffractogram shows distinctive peaks as well as some large humps distributed over a wide range, due to the amorphous nature of this rock. The minerals identified by XRD analysis are ca. 50wt% feldspars, ca. 14.5wt.% cristobalite (SiO₂) and ca. 4.5wt.% tridymite (SiO₂) (further XRD quantitative information on spiked samples in the **appendix X.1**).

No other crystalline minerals were identified by XRD, from which it can be inferred that the rock is composed of ca. 100-50-14.5-4.5=31wt% amorphous material.

If 50wt% of feldspar is present and that calcium, sodium and potassium oxides (CaO, Na₂O and K₂O) are evenly used to form the end member feldspars (anorthite, albite and orthoclase, respectively), the silica used to form these feldspars is approximately 30wt%. However, the calcium, sodium and potassium oxides present in the rock are only enough to form a total of ca. 40wt% feldspars, which would mean that only ca. 24wt% silica is present in the form of feldspars.

Furthermore, by subtracting the silica present in the crystalline materials (24-30wt% present in the feldspars, 14.5wt% from the cristobalite and 4.5wt% from tridymite) from the total amount of silica present, ca. 74wt% (obtained in the XRF), it can be concluded that ca. 25-29wt% of silica is present in the amorphous volcanic glass (see **appendix X.1**).

Density and porosity:

The results obtained for the density and porosity of IGN are presented in the **Table IV.2**. It has a significantly higher apparent density and a considerably lower porosity than IGN.

Mercury porosometry:

The most relevant results regarding the mercury porosimetry are presented in the **Table IV.3** and **Table IV.4** with the detailed analysis presented in the **appendix X.2**. RHY is the least porous rock, with only 13.09% porosity. This result is in very good agreement with the apparent porosity calculated above (12.99%). The total mercury intrusion was 0.0615 mL/g, which is the lowest of all the rocks. The mercury intrusion into pores with a diameter above 0.5 μ m is 0.0461 mL/g. Considering the bulk density of 2.193 kg/dm³ = 2.193 g/mL), this corresponds to 0.1012 mL of mercury intrusion per mL of rock, which is the lowest for pores with a diameter above 0.5 μ m.

<u>OM (thin section)</u>: This rock is not as glassy as the ignimbrites. It shows a cryptocrystalline matrix due to the advanced devitrification of matrix glass. The devitrification is present as cristobalite, albite and tridymite (**Figure IV.15**).





i. PPL ii. XPL Figure IV.15 - Optical microscope images: RHY

IV.2.2 Cements

All the cement powders were submitted to XRF analysis, respectively, to identify their major oxides composition and all the crystalline materials.

IV.2.2.1 API Class G

The API class G cement was chosen as it is the most commonly used well cement. As referred at the start of the current chapter, it was utilised as both neat and with admixtures. The brand used for this cement was Holcim.

XRF analysis:

The major oxides composition of G is presented in the Table IV.5.

CEM		Major oxides compositon (weight % on oven dried [110°C] basis)											
CEM	SiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	SO ₃	LOI*	SUM
G	21.19	3.80	5.34	0.05	1.82	63.20	0.07	0.47	0.95	< 0.01	2.08	0.89	99.86
Α	20.30	4.32	2.52	0.16	0.87	64.20	0.19	0.61	0.52	0.09	3.00	2.82	99.60
HAC	3.88	39.46	13.92	0.04	0.59	38.94	0.03	0.05	1.90	0.05	< 0.01	0.21	99.06
W	21.87	3.54	0.49	0.01	0.97	65.59	0.11	0.46	0.18	0.04	3.45	2.96	99.68

Table IV.5 - XRF analysis of the cements

*LOI = loss on ignition at 1000°C

Particle size distribution:

The incremental and cumulative particle size distributions for the API class G cement are given in **Figure IV.16**. From this diagram, it can be observed that almost all the API Class G cement particles have a diameter within the 0.5 to 90 μ m diameter range. The average particle diameter is 16.569 μ m.



Figure IV.16 - Incremental (bars) and Cumulative (line) Particle Size Distribution for the Class G cement

IV.2.2.2 API Class A

The API class A cement is an OPC and was chosen because of the extremely high impact that the OPC assumed in the cement industry and, subsequently, in cement research. The brand used for this cement was Holcim and the XRF results are presented below.

XRF analysis:

The major oxides composition of A is presented in the Table IV.5. As expected, it contains significantly lower amounts of iron compared to G.

Particle size distribution:

The incremental and cumulative particle size distributions for the API class A cement are given in **Figure IV.17**. From this diagram, it can be observed that almost all the API Class A cement particles lie in the 0.5 to 90 μ m diameter range, with a particle size distribution very similar to the one observed for API Class G cement. The average particle diameter is 15.927 μ m, which is very close to the one observed for class G cement.



Figure IV.17 - Incremental (bars) and Cumulative (line) Particle Size Distribution for the Class A cement

IV.2.2.3 HAC

High Alumina cement (HAC) is known as an alternative to the Portland based cements. It does not depend on the calcium silicate hydrates as the binder.

XRF analysis:

The major oxide composition of HAC is presented in the **Table IV.5**. It contains much lower amounts of silica and higher amounts of alumina than G or A.

Particle size distribution:

The incremental and cumulative particle size distributions for the HAC are given in Figure IV.18. From this diagram, it can be observed that the HAC cement is coarser than Portland cement with almost all particles having a diameter within the 0.3 to 250 μ m range. The average particle diameter is 28.573 μ m, which is significantly higher than observed for any other cement or admixture.



Figure IV.18 - Incremental (bars) and Cumulative (line) Particle Size Distribution for the HAC

IV.2.2.4 White

As mentioned at the beginning of the current chapter, the White cement (W) was chosen to study the effect reduced C_4AF and, consequently, increased C_3A , has on the cement/rock interaction, i.e. to understand how the reduced setting time affects the cement/rock interaction.

XRF analysis:

The major oxides composition of W is presented in the Table IV.5. It contains much lower amounts of iron than G or A.

Particle size distribution:

The incremental and cumulative particle size distributions for the White cement are given in **Figure IV.19**. From this diagram, it can be observed that almost all the White cement particles lie within the 0.5 to 90 μ m diameter range. This cement shows a very similar particle size distribution to the API class G cement. The average particle diameter is 14.308 μ m, which is very close to the class A and class G cements.



Figure IV.19 - Incremental (bars) and Cumulative (line) Particle Size Distribution for the White cement

IV.2.2.3 Admixtures

The admixtures, Silica Flour (SF) and Microsilica 600 (MS), were both submitted to XRF and XRD analysis.

IV.2.2.3.1 Silica Flour

Silica Flour (SF) is almost pure quartz and is obtained by grinding pure silica sand to a very fine powder. When used in geothermal cements at 40wt% it forms tobermorite and avoids strength retrogression.

XRF analysis:

The major oxides composition of SF are presented in the Table IV.6.

	Table 17.0 - ART analysis: Tunnatures												
A dunin		Major oxides compositon (weight % on oven dried [110°C] basis)											
Admix	SiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	SO ₃	LOI*	SUM
SF	99.73	0.13	0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.10	>99.9
MS	86.22	4.93	0.46	0.02	0.08	0.30	0.19	0.66	0.69	0.04	0.03	5.31	98.93

 Table IV.6 - XRF analysis: Admixtures

*LOI = loss on ignition at 1000°C

Particle size distribution:

The incremental and cumulative particle size distributions for the Silica Flour are given in **Figure IV.20**. From this diagram, it can be observed that almost all the Silica Flour particles have a diameter within the 0.5 to 100 μ m diameter range. The average particle diameter is 20.673 μ m., slightly higher than the average particle size for API class G cement.



Figure IV.20 - Incremental (bars) and Cumulative (line) Particle Size Distribution for the Silica Flour

XRD analysis:

The XRD analysis of SF (diagram in the **appendix X.3**) shows the presence of very well defined peaks of quartz (SiO₂).

IV.2.2.3.2 Microsilica 600

Microsilica 600 (MS) is a highly reactive pozzollan processed from a natural, white, silica deposit found in Rotorua, New Zealand. It is a very fine amorphous silica and falls in the microsilica family of products.

XRF analysis:

The major oxides composition of MS are presented in the **Table IV.6**. It shows considerably less silica and significantly more aluminium than SF.

Particle size distribution:

The incremental and cumulative particle size distributions for the Microsilica 600 are given in **Figure IV.20**. From this diagram, it can be observed that most of the Microsilica 600 particles have a diameter within the 0.5 to 80 μ m range. The average particle diameter is 5.717 μ m. This admixture has a significantly lower average particle size when compared with any of the other cements or admixtures under study.



Figure IV.21 - Incremental (bars) and Cumulative (line) Particle Size Distribution for the Microsilica 600

XRD analysis:

The XRD analysis of the MS (diagram in the **appendix X.3**) shows a relatively high background hump which indicates the presence of a significant amount of amorphous material, together with small amounts of quartz (SiO₂), cristobalite (SiO₂), tridymite (SiO₂) and alunite (KAl₃(OH)₆(SO₄)₂).

IV.2.2.4 Bentonite

Western bentonite was obtained from Opta Minerals Inc.. This is a sodium based bentonite and it swells approximately 15 times their un-wetted volume. It was mixed with water to simulate drilling mud, as it is the most common drilling fluid utilised in the construction of geothermal wells. This raw material was also submitted to XRF and XRD analysis.

<u>XRF analysis</u>: the major oxides composition of Bentonite are presented in the Table IV.7.

Table IV.7 - ART analysis. Dentointe													
Drilling	Major oxides compositon (weight % on oven dried [110°C] basis)												
mud	SiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	SO ₃	LOI*	SUM
Bentonite	51.50	14.99	12.98	0.09	3.32	2.39	2.42	0.29	2.57	0.14	0.05	8.76	99.50

 Table IV.7 - XRF analysis: Bentonite

*LOI = loss on ignition at 1000°C

XRD analysis:

The large humps observed in the XRD curve indicate the presence of a lot of amorphous material. Minerals identified by XRD analysis were quartz and a mixture of different clay minerals (hydrous aluminium phylosilicates), mostly from smectite group

 $((Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2 \bullet nH_2O, i.e. montmorillonite, nontronite, sauconite, stevensite and saponite. Titanium oxide (Ti_8O_{15}), anatase (TiO_2) and hydrobiotite ([K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2] \bullet [(Mg,Fe^{2+},Al)_3(Si,Al)_4O_{10}(OH)_2 \bullet 4(H_2O)]: a clay mineral from the illite group) are present as well.$

IV.3 Research procedures

This section describes the methodology for the preparation and analysis of each one of the studied combinations (cement mixture, rock type, temperature, CO₂-exposure), aiming to simulate a real cement/rock interactions in a geothermal well. Most of the experimental work was undertaken at IRL/Callaghan Innovation at Gracefield, using their facilities. The optical microscopy was done using the petrographic microscope with a camera from the School of Geography, Environment and Earth Sciences, at Victoria University of Wellington.

The procedure undertaken for the preparation of each one of the hydrothermally cured cement/rock assemblages was as follows:

- 1. The rock block was cut and shaped so that it could fit in the autoclave.
- ≈25mm diameter cylindrical cavities were cored into the top of the rock block (Figure IV.22).
- The block was washed with tap water and placed in the oven at 90°C in the syntetic geobrine⁶ solution for a couple of days to allow the rock to absorb the brine (Figure IV.23).



Figure IV.22 - Cavities being drilled into rock



Figure IV.23 - Rock blocks in the container with geobrine solution, just before being exposed to 90°C in the oven

 $^{^{6}}$ Recipe for geobrine: 0.19 g sodium sulfate (NaSO₄), 0.05 g calcium chloride dehydrate (CaCl₂.2H₂O), 15.6 g liquid precipitated silica (SiO₂), 4.1 g potassium chloride (KCl), 15.8 g sodium chloride (NaCl) are well mixed and filled with water to make up 20 litres.

- 4. Where the effects of drilling fluid were simulated, a bentonite slurry⁷ was injected into each cavity several days before the addition of the cement by using the following method:
 - a. Each rock cavity was capped with a cork/rubber cap with a small hole on it.
 - b. The bentonite was injected through the cap hole with a syringe, so that the bentonite could penetrate into the walls of the cavity.
 - c. After soaking the bentonite was topped out and the rock allowed to drain.
- 5. About 444,(4) g of solids (powdered cement plus admixtures when applicable) was mixed with 200 ml of water in a juice blender (used for small amounts of cement pastes) for about one minute to obtain a paste with the water/solids ratio (in weight) of 0.45 (Figure IV.24).
- 6. The paste was poured in each one of the cavities immediately after being mixed (Figure IV.25).



Figure IV.24 - Mixing the cement paste in the blender



Figure IV.25 - The cement/rock system, just after pouring the cement paste into the cavities

- The whole system was cured in brine for two days in the oven at 90°C (Figure IV.26). This stage simulates the first few days after the cementing job, when the well is still at cementing temperature before it heats up.
- The whole system was transferred from the oven to the autoclave, for 26 days (total: 28 days cure) or 82 days (total: 84 days cure), at either 150°C or 290°C, with or

 $^{^{7}}$ Recipe for Bentonite: 100 g of sodium bentonite powder, per 1L of water and mix it in the blender for 1 minute.

without carbon dioxide injection. The total pressure was approximately 17 bars at 150° C and 80bars at 290°C, including 6 bars of CO₂ partial pressure, monitored by a computorized system. (Figure IV.27). This stage simulates the normal operating temperature of the well.



Figure IV.26 - Assemblages in the containers, precured in brine for two days in the oven at 90°C



Figure IV.27 - Assemblages transferred to the autoclave, at either 150°C or 290°C, without or with CO₂ injection

9. After being removed from the autoclave (Figure IV.28), the samples were dried out in a 40°C room and 60°C oven, cut in halves (in order to obtain cross sections of cement rock) with a saw (Figure IV.29). The photos of samples just after being cut in half are presented in the *Results* chapters and prepared for each one of the desired analyses.



Figure IV.28 - Samples after being removed from the autoclave



Figure IV.29 - Big (left) and small diamond (right) saws used to cut the samples

The samples under study involve distinct combinations of the previously mentioned variables: cement mixture, curing temperature, drilling fluid, CO_2 -exposure and rock type. Two curing times were used. The first corresponds to one month cured samples, whereas the second, the samples were cured for three months. All the combinations tested are referred in the section III.4 (*Sample labelling*).

Each of the samples/combinations under study were analysed by X-ray diffraction analysis (XRD), optical microscopy (OM), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). Some complimentary tests were undertaken on samples, in order to clarify some of the results obtained. These were the hydrochloric acid test (Acid test), the Thermogravimetry (TG) and the Mass Spectrometry (Mass Spec).

IV.3.1 XRD

This identified the minerals present in the tested material (powder). It cannot identify the minerals present in very minor amounts (under 5%) or the amorphous material.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons which are accelerated toward a target by applying a voltage, bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra with specific wavelengths characteristic of the target material are produced. The instrument used is a Philips PW1700 series diffractometer running Co K alpha radiation Long Fine Focus tube with tube power settings of 40kV and 35mA. The instrument is equipped with an automatic divergence slit maintaining 12mm square irradiated region on the sample, 0.2mm receiving slit, no antiscatter slit. incident and diffracted beam soller slits. graphite diffracted beam monochromator and Xe-filled gas proportional counter.

Cobalt (Co) radiation is used to avoid fluorescence with iron containing samples. As the sample and detector are rotated, the intensity of the reflected X-rays is processed and recorded by the detector. Each one of the crystalline materials has a unique and well-marked XRD pattern, making it easy to distinguish between them all.

Four different XRD samples were collected from each one of the combinations mentioned above. The four distinct zones (illustrated in the Figure IV.38) are:

- 1) ROCK: the rock itself (IGN, UNI, KAO, MOR or RHY).
- 2) ITZ-R: the interfacial transition zone adjacent to the rock.
- 3) ITZ-C: the interfacial transition zone adjacent to the cement.
- 4) CEM: the cement itself (A, G, G20SF, G40SF, G20MS, HAC, W or GEOI/II).

It was essential to very accurately collect the powder from the ITZ-R and ITZ-C, as these two zones consist of a very fine line. A small driller was used as an aid for the sample collection (**Figure IV.30**). This step was extremely challenging due to its demanding accuracy.

In a similar way to the preparation method for the XRF analysis, samples are reduced to a fine powder (through the use of mortar and pestle) with 250mg of sample compacted in a 17mm diameter well in an aluminium holder (**Figure IV.31**), to be then scanned in the XRD instrument. The typical XRD scan was a 0.04 degree step interval between $10^{\circ} 2\theta$ and $100^{\circ} 2\theta$. The sample was not spun.

The aim was to identify and interpret the differences in phases between each one of the four zones, namely by comparing the ITZ-C with the cement and the ITZ-R with the rock.



Figure IV.30 - Collection of a XRD sample (ITZ-C) with the aid of a small driller



Figure IV.31 - Preparation of the XRD sample: placing the powder in the sample holder

IV.3.2 OM

The OM thin section preparation of the cement/rock hydrothermally cured systems was made at GNS (Institute of Geological and Nuclear Sciences). The procedure utilised by the GNS technician was to impregnate the sample in epoxy resin and cut a 30 μ m (0.03 mm) thin section, which was placed on a microscope slide and covered with a cover slip.

After being prepared, the thin sections were analysed by a petrographic (transmitted light) optical microscope and images of the interfacial transition zones were taken with the camera incorporated in the microscope.

IV.3.3 SEM/EDS

Sample preparation for SEM consisted of cutting a small cement/rock section using a small diamond precision saw, to fit inside a resin cup mould (which is 25 mm diameter X 20 mm height). It was then submitted to the following procedure:

Impregnation in resin

- 1. Epoxy resin (EpoFix from Struers) was mixed with hardener at 25:3 ratio in a disposable jar.
- 2. The mix was evacuated for 20 minutes using the house vacuum (Figure IV.32), after which the air was slowly released into the dessicator.
- 3. Step 2 was repeated and the jar was removed from the desiccator.
- 4. The sample was placed at the bottom of a resin mould with the face to be scanned (and, thus, polished) facing down.
- 5. The degassed resin was poured into the cup mould, over the sample.
- 6. The cup mould went into the desiccator and Step 2 was repeated three times.
- 7. The samples were left to set overnight.
- 8. The samples were taken from the mould and the sharp edges and surface were ground and smoothened with the cup wheel to give an impregnated sample with a disc shape (Figure IV.33).



Figure IV.32 - Desiccator attached to the house vacuum, used for degassing the epoxy resin used to impregnate the samples

Figure IV.33 - Grinding and shaping an impregnated sample in the cup wheel

Water polishing

- The impregnated samples (three per run) were fitted in the polishing instrument sample holder and the polishing pressure was adjusted for the all the three samples (Figure IV.34).
- 10. The water tap was turned on and the water flow was directed to the center of the disc.
- 11. The samples were polished with the Struers Gekko system at 150 r.p.m. for 10 minutes with a #1200 SiC polishing pad.
- 12. The previous step was repeated for the #1000, #800, #500, #220, #180, #120 and #80SiC polishing pads to give samples suitable for SEM (Figure IV.35).



Figure IV.34 - Water polishing of the impregnated samples

Figure IV.35 - Samples after being impregnated in resin and polished, ready for SEM/EDS work

A Scanning Electron Microscope (SEM) is an instrument that produces images of a sample by scanning it with focused electron beams. These electrons interact with the atoms in the sample, producing signals that give information about the samples' surface topography and composition. The SEM is commonly associated with a EDS (Energy Dispersive Spectroscopy) which is a system that provides information about the elemental composition of a specimen, obtained from the interaction of X-rays and the sample. The unique atomic structure of each element, gives a unique set of peaks in its X-ray spectrum.

SEM images were taken on a Quanta 450 SEM equipped with a tungsten filament. The backscatter electron images were acquired operating the Quanta SEM, typically at 20 keV using a spot size of 7. Under these conditions an EDAX Energy Dispersive X-ray Spectroscopy (EDS) detector attached to the SEM was used for elemental analysis using Texture & Elemental Analytical Microscopy (TEAM) software (version V3.1).

A series of line scans were undertaken in order to determine the element combination and migration trends in the ITZ. These are presented in **appendix X.4**. According to the information presented, the line scans within the same region of the sample are very variable, and do not provide an overall picture of the sample, particularly across the ITZ. This is a consequence of the very heterogeneous nature of the materials being studied: the cement and, especially, the rock.

Therefore the SEM/EDS work in the current study have been mostly based on the element and generated Ca/Si ratio maps, which provide much clearer information about the overall trends in the interfacial transition zone, which is the aim of the current work. The EDS element maps of the interfacial transition zone (ITZ) were obtained at magnifications of 100X and 250X. Several EDS spot analyses were made in order to complement the information give in the EDS maps.

In the aluminium (Al) and sodium (Na) maps presented in **appendix X.4**, little relevant information regarding the trends of these elements across the ITZ of the samples. Unlike Al and Na, the maps for calcium (Ca) and silicon (Si) provide very relevant information regarding changes in the ITZ. The Ca ion is an extremely mobile cation in which the Portland based cements are rich. The Si map is an extremely helpful image which allows the cement to be distinguished from the siliceous rocks. Comparison between the Ca and Si element maps provides a very good evidence for the extent of Ca mobility across the ITZ. Moreover, the carbon (C) map is helpful to characterize the carbonate present in the sample, whereas that for iron (Fe) could be useful to understand the Fe dissolution, migration and precipitation processes within the sample.

After obtaining the individual calcium (Ca) and silicon (Si) maps, a map of Ca/Si ratio zones or phases was built up by using the EDS software available. To identify the way that calcium and silicon combine across the ITZ, having a knowledge of the calcium-silicon (Ca/Si) ratios in the phases present is essential. There is software supplied with the SEM that is available to use the results to produce relative scans. During the EDS scan, the software automatically generates spectra and consequently phases, by combining the chemical elements in different proportions, based on the number of the EDS counts. These automatically generated phases are created based on an unknown algorithm that was completely unsatisfactory for the current work. The built in software created random phases which were not consistent across a set of samples and did not permit the creation of spectrum/phases based on theoretical data. So it was necessary to prepare reference samples with different Ca/Si ratios, in order to create their equivalent phases and apply these to the cement/rock combined samples. Some considerations and assumptions had to be made, and this has a strong influence on the phase maps obtained. The actual Ca/Si ratio (theoretical) is actually not equivalent to the Ca/Si ratio measured from the raw counts generated from the EDS (empirical). This can be attributed to several reasons.

* Firstly, the theoretical Ca/Si ratio is the Ca/Si chemical element ratio, whereas the empirical one uses the number of counts from each element obtained by EDS. The lighter, larger atoms such as Si tend to have lower counts when compared to heavier, more compact atoms such as Ca.

* Secondly, the EDS software data processing is dependent on an unknown algorithm which does not seem to be consistent for every phase map. This empirical methodology is obviously not as accurate as if the theoretical data had been used as an input. The phases obtained in the reference samples are the result of experimental work, prepared under non-perfect conditions and based on non-perfectly homogeneous cement mixtures.

Rather than representing a specific Ca/Si ratio, each of the generated phases represents a range of Ca/Si ratios, which is also dependent on the software which generates a transition point between two Ca/Si ratios. For example where Ca/Si \approx 2.45 and Ca/Si \approx 1.70 it was assumed that this range was the midpoint between the ratios represented by these two consecutive phases, i.e. \approx 2.08.

To overcome some of these issues, a correlation between the theoretical (calculated) and empirical (measured by EDS counts) data (**Table IV.8**) was created, in which the empirical Ca/Si ratios are correlated with the theoretical Ca/Si ratios. This correlation was based on the reference samples (G10MS, G20MS, G30MS, G40MS and G30MS20SF), for which the theoretical Ca/Si ratio was known and the empirical Ca/Si ratio was assumed to be the arithmetic mean of the software automatically generated phases, for each sample.

OPC	SiO_2	Theoretical Ca/Si ratio	Empirical Ca/Si ratio
	(by weight of cement)	(obtained by calculation)	(obtained by EDS counts)
100%	10%	2.25	approx. >3.5
100%	20%	1.70	approx. 1.9-3.5
100%	30%	1.37	approx. 1.3-1.9
100%	40%	1.14	approx. 1.0-1.3
100%	50%	0.98	< 1.0

Table IV.8 - Correlation of the actual Ca/Si of the samples with the Ca/Si obtained in the software

Nonetheless, the phase maps presented in the results chapter do not match with the ratios presented in the **Table IV.8** as these were not fixed values and seemed to be flexible, changing with each sample to which it was applied. Thus the Ca/Si ratios eventually still had to be properly interpreted as they failed to accurately represent the actual calcium-silicon ratio in each sample, although still providing a good indication of how the Ca/Si ratio around the sample changed, particularly along the ITZ. Considering this, a new phase diagram was created and is presented in the results chapter ("key" for each phase map).

Even when using this approach, the software development and interpretation was not fully stable and some of the maps that were rebuilt could not be saved and had to rely on a "print screen" in order to record the desired map.

IV.3.4 Acid test

The procedure was simple and consisted of placing a drop of dilute HCl (10% solution) on the sample and checking whether there was any effervescence (fizz). Any effervescence indicates the presence of carbonate minerals caused by the reaction between the calcium carbonate minerals (CaCO₃) and HCl, according to **Equation IV.4**.

$$CaCO_3 + 2HCI \rightarrow CO_2 \uparrow +H_2O + Ca^{2+} + 2Cl^{2-}$$
 Equation IV.4

IV.3.5 TGA/DTG

Thermogravimetric analysis (TG) provides a continuous recording of mass changes as a function of temperature with time, by using a thermobalance (**Figure IV.36**). Each compound decomposes at a specific temperature allowing differentiation of distinct chemical compounds. A TGA plot provides a mass loss versus temperature. This information can be complemented with differential thermogravimetry (DTG), which outputs the differential TG curve, i.e. the rate of mass loss versus temperature curve. This data provides clearer information than that from TG on when the weight loss occurs. The TG was used to identify the presence of calcium carbonate minerals (CaCO₃), which decompose into CaO (solid) and CO_2 (gas) within a known decomposition range.

The instrument used in the current work was a TA Instruments SDT Q600 V8.2 Build 100. Over 10 mg powdered sample (after being finely ground with mortar and pestle, similarly to XRF and XRD) was placed in aluminium crucibles. These were heated from ambient temperature up to 1000°C, at a heating rate of 20°C/minute in argon (Ar), with a flow of 20ml/min. Ar was chosen as it is not expected to interfere in the decomposition reaction.

IV.3.6 Mass Spec

The mass spectrometer is an instrument which collects and identifies the composition of the gases lost during the thermogravimetry (**Figure IV.37**). The relative quantities of gas species in the carrier gas stream were analysed using a Dycor quadrupole mass spectrometer system (Ametek). This test was made in order to complement the information given by the TGA, by measuring the amount of CO_2 released during the CaCO₃ decomposition.



Figure IV.36 - Thermogravimeter used in the current work

Figure IV.37 - Wire attached to the thermogravimeter to collect the gases lost during the TG run for the Mass Spec

IV.4 Sample labelling

Due to the large number of combinations involved in this study, it was necessary to create a non-exaustive but still efficient sample labelling which distinguishes the samples from one another. The reference to the abbreviations used for each material and condition are firstly introduced. This information is followed by the way they are combined along the current work.

Five types of rock were used with abbreviations summarized in Table IV.9.

Table IV.9 - Abbreviations used for the rocks under study				
Type of rock	Abbreviation			
Ongatiti ignimbrite (Hinuera stone)	IGN			
Ohakuri unaltered ignimbrite	UNI			
Ohakuri ignimbrite with kaolinite alteration	KAO			
Ohakuri ignimbrite with mordenite alteration	MOR			
Whakaroa rhyolite	RHY			

Eight cement mixtures were studied and their abbreviations are summarized in Table IV.10. The water/cement ratio (in weight) utilised was always 0.45.

Table 1 v.10 - Abbi eviations used for the rocks under study				
Type of cement mixture	Abbreviation			
API class A cement	А			
API class G cement	G			
API class G cement + 20% wt. Silica Flour	G20SF			
API class G cement + 40% wt. Silica Flour	G40SF			
API class G cement + 20% wt. Microsilica 600	G20MS			
High Alumina cement	HAC			
White cement	W			

 Table IV.10 - Abbreviations used for the rocks under study

The curing variables are: curing temperature (150° C and 290° C); curing time (either 28 days or 84 days cure); drilling mud (through the use of bentonite); and CO₂ exposure (creation of CO₂ enriched environment through injection of CO₂ during the curing). These are summarized, respectively, in Table IV.11-Table IV.14.

Table IV.11 - Abbre	viations used			
for the variable curing temperature				
Curing temperature	Abbreviation			

Curing temperature	Abbreviation
150°C	150
290°C	290

Table IV.12 - Abbreviations used for the variable curing time

Curing time	Abbreviation
28 days	28d
84 days	84d

 Table IV.13 - Abbreviations used

for the variable drilling mud				
Drilling mud				
simulation	Abbreviation			
no bentonite	N/A			
bentonite	b			

Table IV.14 - Abbreviations used	for
the variable CO ₂ exposure	

CO ₂ injection	Abbreviation
no CO ₂ inject.	N/A
with CO ₂ inject.	CO_2

The combination of the above nomenclature is made in the following way: firstly, rock type (ROCK); then cement type (CEM) separated by a dash; then, between brackets, the curing conditions, with a full stop separating each condition, starting with temperature (temp), followed by the drilling mud (b, when present), CO_2 -exposure (CO₂, when exposed to carbon dioxide) and the curing time (time).

In summary,

- samples without bentonite layer or CO₂-exposure: ROCK/CEM(temp.time).
- samples with bentonite layer: ROCK/CEM(temp.b.time).
- samples exposed to CO₂: ROCK/CEM(temp.CO₂.time).

In the first stage (1 month cure), the variables under study were type of cement (CEM), curing temperature (temp) and drilling mud (b, when present). At this stage, only one type of rock was tested (ROCK=IGN), CO₂-exposure was not tested and the samples were cured for only 28 days (time=28d). For example, IGN/HAC(150.28d) represents the sample with Ongatiti ignimbrite and high alumina cement cured at 150°C for 28 days, whereas IGN/HAC(150.b.28d) refers to the equivalent sample, with drilling mud simulation (b=bentonite layer). A total of 24 combinations/samples were tested in this stage (Table IV.15).

Rock type	Cement mixture	Curing temperature (°C)	Drilling mud (bentonite layer)	Curing time (days)
	G	150	N/A* (no drilling mud simulation)	28d
	G20SF			
	G40SF			
	G20MS			
	А			
IGN	HAC			
	W			
	G	150	b (use of bentonite to simulate drilling mud)	
	G20SF			
	G40SF			
	G20MS			
	А			
	HAC			
	W			
	G	290	N/A* (no drilling mud simulation)	
	G20SF			
	G40SF			
	G20MS			
	А			
	HAC			
	W			

 Table IV.15 - Combinations tested in the first stage (1 month cure)

In the second stage (3 months cure), there were two more variables considered: CO₂-exposure and type of rock. Hence it became necessary to exclude some variables previously considered from further experimental work in order to focus on the new variables. Due to their lower relevancy, the variable drilling fluid along with three cement mixture types (A, HAC and W) were excluded from this stage, as they have poorer performance than the API class G based mixtures, in geothermal applications. Therefore, the cements selected for the 3 months curing experiments were G, G20SF, G40SF and G20MS. These are the most common cement mixtures within the geothermal industry, and previous studies have shown that their performance in geothermal applications is relatively successful.

The variables under study were type of cement (CEM), curing temperature (temp), CO_2 exposure (" CO_2 " when curing conditions included CO_2 -exposure), type of rock (ROCK) was not tested and the samples were cured for 84 days (time=84d). For example, KAO/G20SF(290.CO₂.84d) refers to the sample with Ohakuri ignimbrite with kaolinite

^{*}No abbreviation was used, as there was no simulation of drilling mud

alteration, class G plus 20% (in weight) silica flour, cured at 290° C for 84 days with CO₂ exposure. A total of 28 combinations/samples were tested during this stage (**Table IV.16**).

The reference variables/conditions used in the control samples are: API class G cement (G), one month curing time (28d), no drilling mud simulation (no bentonite layer), 150° C curing temperature (150), no CO₂ exposure simulation and Ongatiti ignimbrite (IGN). In addition to the control samples, other references were used in order to better assess the effect of a certain variable. For example, for the G40SF formulation, the G20SF is also considered reference, as the 20% quartz addition is half way between the control formulation (G) and the one under study (G40SF).

Rock type	Cement mixture	Curing temperature	CO ₂ exposure	Curing time
IGN	G G20SF G40SF G20MS	150	N/A* (no CO ₂ exposure)	84d
IGN	G G20SF G40SF G20MS	150	CO ₂ (carbon dioxide injected during the cure)	84d
UNI	G G20SF G40SF G20MS			
KAO	G G20SF G40SF G20MS			
MOR	G G20SF G40SF G20MS			
RHY	G G20SF G40SF G20MS			
IGN	G G20SF G40SF G20MS	290	CO ₂ (when carbon dioxide is injected during the cure)	84d

Table IV.16 - Combinations tested in the second stage (3 months cure)

*No abbreviation was used, as there was no CO₂ exposure

Finally, it is often necessary to mention the specific area within the interfacial transition zone (ITZ). Besides the rock (ROCK) and the cement (CEM) themselves, the areas under study

are: the rock side of the interfacial transition zone (ITZ-R) and the cement side of the interfacial transition zone (ITZ-C) (Figure IV.38).



Key ROCK - the rock under analysis CEM - cement under analysis Blue line: rock zone adjacent to the interfacial transition zone (ITZ-R) Orange line: cement zone adjacent to the interfacial transition zone (ITZ-C)

Figure IV.38 - Illustration of the nomenclature utilised to distinguish the four different zones under analysis

V. RESULTS: 1 MONTH CURE

The results presented below for each of the curing conditions are arranged as follows:

- a) Cut surface photographs
- b) X-Ray diffraction
- c) Optical Microscopy
- d) Electron microscopy/Energy Dispersive Spectroscopy

V.1 150°C cure

V.1.1 No drilling mud

a) Mesoscopic Images

Samples of cut surfaces are shown at approximately 50% of actual size in Figure V.1.



i. IGN/G(150.28d)



ii IGN/G20SF(150.28d)



iii IGN/G40SF(150.28d)



iv IGN/G20MS(150.28d)



v. IGN/A(150.28d)



vi. IGN/HAC(150.28d)



Figure V.1 - Photos of the cross section of the IGN/CEM assemblages exposed at 150°C for 28 days in brine

b) XRD

Table V.1 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features			
IGN/G	CEM	Largely amorphous, portlandite , unhydrated cement . Traces of calcite .			
(150.28d)	ITZ-C	Reduced portlandite from CEM.			
	ITZ-R	Reduced quartz and feldspars from IGN.			
	CEM	Largely amorphous, quartz. Traces of calcite, tobermorite, αC_2SH and			
IGN/G20SF		unhydrated cement.			
(150.28d)	ITZ-C	Increased quartz from CEM.			
	ITZ-R	Reduced quartz and feldspars from IGN.			
	CEM	Amorphous, quartz, tobermorite. Traces of unhydrated cement.			
IGN/G40SF (150-28d)	ITZ-C	Increased quartz from CEM.			
(130.200)	ITZ-R	Reduced feldspars (no reduced quartz).			
	CEM	Mostly amorphous. Traces of calcite , αC_2SH and unhydrated cement .			
IGN/G20MS	ITZ-C	Slightly reduced calcite from CEM.			
(150.28d)	ITZ-R	Reduced quartz and feldspars from IGN. Traces of calcite and			
		hibschite.			
	CEM	Largely amorphous, portlandite, calcite. Traces of unhydrated			
IGN/A		cement.			
(150.28d)	ITZ-C	Reduced portlandite from CEM.			
	ITZ-R	Reduced quartz and feldspars from IGN.			
	CEM	Amorphous, katoite, bohmite and kaotite silicatian.			
IGN/HAC (150-28d)	ITZ-C	Slight reduced katoite, bohmite and kaotite silicatian from CEM.			
(150.200)	ITZ-R	Reduced feldspars from IGN.			
	CEM	Largely amorphous, portlandite. Traces of calcite and unhydrated			
IGN/W	CEM	cement.			
150 (28d)	ITZ-C	Reduced portlandite from CEM.			
	ITZ-R	Reduced feldspars and quartz from IGN. Traces of calcite.			
	CEM	Totally amorphous. No minerals identified by XRD.			
IGN/GEOI (150/284)	ITZ-C	Similar to CEM.			
(130.20u)	ITZ-R	Reduced feldspars and quartz from IGN.			

Table V.1 - compounds identified by XRD analysis for samples exposed at 150°C for 28 days in brine

c) OM

Thin section micrographs for each sample are shown in Figure V.2-Figure V.8. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

IGN/G(150.28d)





i. ITZ in PPL

ii. ITZ in XPL

<u>CEM</u>: Under the optical microscope, the cement (CEM) is brownish with dark spots in plane polarized light (PPL) which show as very bright **pleochroic grains** / **crystals** in crossed-polarized light (XPL).

Figure V.2 - IGN/G(150.28d) OM images

<u>ITZ</u>: In PPL, a \approx 300µm darker plus a \approx 200µm lighter (total=500µm) wide brown ITZ-R rims are seen, whereas a \approx 300µm wide beige ITZ-C rim is distinguishable. Both ITZ-R and ITZ-C show, respectively, increasing amount of milky material (from IGN) closer to the CEM and sharply reduced grains/crystals (from CEM). Additionally, the area of the ITZ-R close to the IGN has more bright spots (crystals, grains) than IGN.

IGN/G20SF(150.28d)



i. ITZ in PPL



ii. ITZ in XPL

Figure V.3 - IGN/G20SF(150.28d) OM images

<u>CEM</u>: Compared to IGN G 150 (28d), the most noticeable differences by OM are the lighter colour in PPL and the presence of **quartz** crystals: colourless in PPL and a 90° extinction angle in XPL.

<u>ITZ</u>: In PPL, a $\approx 250 \mu m$ wide darker brown plus $\approx 250 \mu m$ wide lighter brown ITZ-R rims are observed, whereas the cement side seems to have been quite affected, with a light $\approx 500 \mu m$ wide ITZ-C rim. Although in much smaller amounts than in the IGN/G(150.28d), the XPL shows some **milky material**. There is also an increase in small and medium sized **bright grains** in the ITZ-R from IGN. The XPL image also shows a **bright fine line** splitting the ITZ-R/ITZ-C and a sharp increase in the number of crystals the ITZ-C from CEM.

IGN/G40SF(150.28d)



Figure V.4 - IGN/G40SF(150.28d) OM images

CEM: The most noticeable difference to IGN/G20SF(150.28d) is the larger amount of bright spots, which are quartz crystals.

ITZ: A relatively thin ≈100µm wide dark brown ITZ-R rim is easily seen in PPL. No differences were found between the ITZ-C and the CEM, by optical microscope.



ii. ITZ in XPL

Figure V.5 - IGN/G20MS(150.28d) OM images

CEM: Under the optical microscope, the cement (CEM) looks light brown with amorphous in PPL and shows a very bright colour in XPL, which seems to be composed mostly of **pleochroic grains**.

<u>ITZ</u>: In PPL, a \approx 150µm wide dark brown ITZ-R rim can be observed, with a high concentration of bright spots in the line between the ITZ-R and the rest of the rock. Regarding the ITZ-C, it can barely be distinguished from CEM, except for slightly higher concentration of dark spots.
IGN/A(150.28d)



Figure V.6 - IGN/A(150.28d) OM images

<u>CEM</u>: Under the optical microscope, the cement (CEM) looks beige (very light brown) with dark spots in plane polarized light (PPL) and shows very bright **pleochroic grains** and **small sized crystals** in crossed-polarized light (XPL).

<u>ITZ</u>: In plane polarized light (PPL), a $\approx 200 \mu m$ wide brown ITZ-R rim is seen, which seems to be extended in some regions. A $\approx 400 \mu m$ wide ITZ-C rim is distinguishable by XPL, with slight increase of bright spots in the ITZ-C from CEM. Similarly to IGN/G(150.28d), the ITZ-R shows more bright spots (crystals, grains) than IGN as well as some milky material.

IGN/HAC(150.28d)



i. ITZ in PPL



ii. ITZ in XPL

<u>CEM</u>: Under the optical microscope, the cement (CEM) looks very dark with even darker spots in PPL. This cement has different colour tones than the Portland based cements and shows areas with brown milky material mixed with bright **grains / crystals** in crossed-polarized light (XPL).

Figure V.7 - IGN/HAC(150.28d) OM images

ITZ: The ITZ is difficult to distinguish by OM.

IGN/W(150.28d)



Figure V.8 - IGN/W(150.28d) OM images

<u>CEM</u>: Under the OM the cement (CEM) looks beige (very light brown) in PPL. This grout exhibits the lowest number of dark spots within all the Portland based cement mixtures. Also, very bright **pleochroic grains** and **small sized crystals** can be seen in XPL.

<u>ITZ</u>: In PPL, a $\approx 200 \mu m$ wide dark brown plus $\approx 200 \mu m$ wide light brown ITZ-R rims are observed. The $\approx 400 \mu m$ wide ITZ-C rim is characterized by significant increase in the amount of bright grains/crystals from CEM. Similarly to the other samples where Portland cement grouts were used, the ITZ-R shows some **milky material** (from IGN) closer to ITZ-C and more **bright spots** (from IGN) closer to the IGN.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure V.9-Figure V.15. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

In the phase maps, the cement shows the highest Ca/Si ratio (blue/green colours) and the rock shows the lowest Ca/Si ratio (red), with the ITZ showing intermediate Ca/Si compositions.

In the element maps, the cement is typically Ca rich (green side) and the rock is typically Si rich (lilac side). The cement with silica addition also shows high amounts of Si present, although in lower amounts than the rock.

IGN/G(150.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map





iii. ITZ Si map

Figure V.9 - IGN/G(150.28d) SEM/EDS images

<u>Phase map</u>: Gradual Ca/Si ratio change across the ITZ can be seen. There are variations within the cement and the rock as these materials are not homogeneous.

<u>Element maps</u>: Ca penetrated in up to 100 μ m plus a lower but still clear migration up to about 200 μ m into the rock (total=300 μ m). Highest concentration of Si in the ITZ-R. When comparing the Ca and Si map, it is obvious that the migration happens mostly through the rock pores, as the Ca areas within the rock mostly match with the lowest concentration of Si.

IGN/G20SF(150.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.10 - IGN/G20SF(150.28d) SEM/EDS images

<u>Phase map</u>: gradual phase change across the ITZ, although not as obvious as for the IGN/G(150.28d) sample. The cement phase is closer (in Ca/Si ratio) to the rock phase due to the silica addition (silica flour).

<u>Element map</u>: Similar Ca migration when compared with the IGN/G(150.28d). Again, the concentration of Si in the ITZ-R is higher than in the rock or in the cement.

IGN/G40SF(150.28d)





 $= 100 \, \mu m$

ITZ Ca/Si phase map

i.



ii. ITZ Ca map

iii. ITZ Si map

Figure V.11 - IGN/G40SF(150.28d) SEM/EDS images

<u>Phase map</u>: The phase change is abrupt, without obvious intermediate Ca/Si ratio phases between the rock and the cement.

Element map: when compared with the samples IGN/G(150.28d) and IGN/G20SF(150.28d), there is a much shallower **Ca** migration (\approx **50µm**) from ITZ-C into ITZ-R. There are high levels of both **Ca** and **Si** in the cement from the silica flour, less homogeneous in the cement due to the unreacted **quartz** crystals. The ITZ has the highest concentration and more uniform distribution of **Ca**, **Si** and **O** in the ITZ, rather than in the rock or in the cement.

IGN/G20MS(150.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.12 - IGN/G20MS(150.28d) SEM/EDS images

<u>Phase map</u>: gradual phase change across the ITZ, although not as obvious as the IGN/G(150.28d) sample. The cement phase is closer to the rock phase due to the silica addition (MS).

<u>Element map</u>: lower **Ca** migration compared with the IGN/G(150.28d). Again, the concentration of **Si** in the ITZ-R is higher than in the rock or in the cement. As opposed to the samples where silica flour was added, there is little or no unreacted silica in the cement.

IGN/A(150.28d)









ii. ITZ Ca map

iii. ITZ Si map

Figure V.13 - IGN/A(150.28d) SEM/EDS images

<u>Phase map</u>: From the Ca/Si phase map, similarly to the IGN/G(150.28d), a gradual Ca/Si ratio change across the ITZ can be seen, with the cement and the rock varying between two main phases.

<u>Element maps</u>: In the ITZ, similarly to the IGN/G(150.28d), **Ca** seems to penetrate in high amounts up to **100 \mum** plus a lower but still clear migration up to about **150 \mum** into the rock (total=**250 \mum**). When comparing the **Ca** and **Si** map, the migration happens mostly through the rock pores, as the **Ca** areas do not coincide with the highest concentration of **Si**.

IGN/HAC(150.28d)



i. ITZ phase map



ii. ITZ Ca map



iii. ITZ Si map



iv. ITZ Al map



v. ITZ Na map



Phase map: Abrupt phase change from CEM to ROCK.

Element maps: Little Ca migration detected across the ITZ.

IGN/W(150.28d)





 $= 100 \, \mu m$

i. ITZ Ca/Si phase map



iii. ITZ Si map

Figure V.15 - IGN/W(150.28d) SEM/EDS images

Phase map: From the Ca/Si phase map, similar to the IGN/G(150.28d), a gradual Ca/Si ratio change across the ITZ can be seen with the cement and rock varying between two main phases. This may mean that these materials are not as homogeneous as it could be expected.

Element maps: In the ITZ, similar to the IGN/G(150.28d), Ca seems to penetrate in high amounts up to 100 μ m plus a lower but still clear migration up to about 100 μ m into the rock (total=200 μ m).

V.1.2 With drilling mud (bentonite)

a) Mesoscopic Images

Samples of cut surfaces are shown at approximately 60% of actual size in Figure V.16.





G405FB



i. IGN/G(150.b.28d)

ii. IGN/G20SF(150.b.28d)

iii. IGN/G40SF(150.b.28d)

iv. IGN/G20MS(150.b.28d)



v. IGN/A(150.b.28d)



vi. IGN/HAC(150.b.28d)



vii. IGN/W(150.b.28d)

Figure V.16 - Photos of the cross section of the IGN/CEM assemblages with drilling mud simulation, exposed at 150°C for 28 days in brine

b) XRD

Table V.2 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features
IGN/G (150.b.28d)	CEM	Largely amorphous, portlandite and calcite . Traces of unhydrated cement .
	ITZ-C	<u>Reduced</u> portlandite from CEM. Traces of aragonite and gehlenite.
	ITZ-R	<u>Reduced</u> feldspars and quartz from IGN. Traces of gehlenite.
IGN/G20SF	CEM	Largely amorphous, quartz and calcite . Traces of tobermorite , unhydrated cement , kilchoanite and aragonite .
(150.b.28d)	ITZ-C	Slightly increased quartz from CEM. Traces of gehlenite.
	ITZ-R	<u>Reduced</u> feldspars and quartz from IGN. Traces of gehlenite.
IGN/G40SF (150.b.28d)	CEM	Amorphous, quartz . Traces of calcite , tobermorite , kilchoanite , aragonite and unhydrated cement .
	ITZ-C	<u>Increased</u> calcite and slightly increased quartz from IGN. Traces of gehlenite.
	ITZ-R	<u>Reduced</u> feldspars and quartz from IGN. Traces of gehlenite.
LONGOOME	CEM	Largely amorphous, calcite. Traces of unhydrated cement, kilchoanite and aragonite.
(150 h 28d)	ITZ-C	Increased calcite from CEM.
(130.0.200)	ITZ-R	Reduced feldspars and quartz from IGN. Traces of gehlenite .
IGN/A (150.b.28d)	CEM	Largely amorphous, portlandite and calcite . Traces of unhydrated cement .
	ITZ-C	Reduced portlandite, increased calcite and gehlenite.
	ITZ-R	Similar to IGN. Traces of gehlenite.
IGN/HAC (150.b.28d)	CEM	Largely amorphous, katoite, boehmite and kaotite silicatian.
	ITZ-C	<u>Reduced</u> katoite and boehmite. <u>Traces</u> of calcite and aragonite.
	ITZ-R	Similar to IGN.
IGN/W (150.b.28d)	CEM	Largely amorphous, portlandite and calcite . Traces of unhydrated cement .
	ITZ-C	Decreased portlandite from CEM. Traces of aragonite.
	ITZ-R	Similar to IGN. Traces of gehlenite.

Table V.2 - compounds identified by XRD analysis for samples with drilling mud simulation exposed at 150° C for 28 days in brine

c) OM

Thin section micrographs for each sample are shown in **Figure V.17-Figure V.23**. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

IGN/G(150.b.28d)



i. ITZ in PPL



ii. ITZ in XPL Figure V.17 - IGN/G(150.b.28d) OM images

<u>CEM</u>: The cement looks similar to the equivalent sample without **bentonite**, IGN/G(150.28d).

<u>ITZ</u>: The ITZ looks also similar to the one observed in the sample IGN/G(150.28d), except for the homogeneous light brown \approx 150µm wide rim (bentonite) in between the ITZ-R and ITZ-C and slightly wider ITZ-R and ITZ-C with, respectively \approx 400-500µm and \approx 400µm.

IGN/G20SF(150.b.28d)





ii. ITZ in XPL Figure V.18 - IGN/G20SF(150.b.28d) OM images

<u>CEM</u>: The cement looks similar to the equivalent sample without **bentonite**, IGN/G20SF(150.28d).

<u>ITZ</u>: The ITZ has several differences from the one observed in IGN/G20SF(150.28d). The main differences are the homogeneous light brown rim $\approx 100 \mu m$ in between the ITZ-R and ITZ-C and a generally much wider ITZ-R, with $\approx 400-500 \mu m$.

IGN/G40SF(150.b.28d)



i. ITZ in PPL



Figure V.19 - IGN/G40SF(150.b.28d) OM images

<u>CEM</u>: The cement looks similar (although slightly darker) to the equivalent sample without **bentonite**, IGN/G40SF(150.28d).

<u>ITZ</u>: The ITZ shows several differences from the one observed in IGN/G40SF(150.28d). The main differences are the homogeneous light brown \approx 50µm wide rim in between the ITZ-R and ITZ-C and a generally significantly wider ITZ-R, with \approx 200 µm darker brown rim, plus a \approx 300µm lighter brown rim (total \approx 500µm). Some slight changes in the ITZ-C (\approx 400µm rim) from CEM are observed as well, namely a darker colour and an increase in **bright grains**, most of them **quartz crystals**.

IGN/G20MS(150.b.28d)



i. ITZ in PPL



ii. ITZ in XPL

Figure V.20 - IGN/G20MS(150.b.28d) OM images

<u>CEM</u>: The cement looks darker than the equivalent sample without **bentonite**, IGN/G20MS(150.28d). <u>ITZ</u>: The ITZ shows several differences from the one observed in IGN/G20MS(150.28d). The main differences are the homogeneous light brown \approx 200µm wide rim in between the ITZ-R and ITZ-C and a significantly wider (\approx 400µm) ITZ-R. Although not easily distinguishable from CEM, the ITZ-C seems to be slightly darker with a slight increase in bright small and medium sized grains (in XPL). A narrow fissure in between the cement and the rock can also be observed, as these materials started detaching from each other.

IGN/A(150.b.28d)



i. ITZ in PPL

Figure V.21 - IGN/A(150.b.28d) OM images

<u>CEM</u>: The cement looks similar to the equivalent sample without **bentonite**, IGN/A(150.28d).

ITZ: The ITZ looks similar to the one observed in the sample IGN/A(150.28d), except for the homogeneous light brown $\approx 200 \mu m$ wide rim in between the ITZ-R and ITZ-C and slightly wider ITZ-R, with $\approx 400-500 \mu m$. Additionally, a fissure in between the cement and the rock can also be observed.

IGN/HAC(150.b.28d)



i. ITZ in PPL



ii. ITZ in XPL Figure V.22 - IGN/HAC(150.b.28d) OM images

<u>CEM</u>: The cement looks similar to the equivalent sample without **bentonite**, IGN/HAC(150.28d).

ITZ: The ITZ looks similar to the one observed in the sample IGN/HAC(150.28d), except for the homogeneous light brown $\approx 200 \mu m$ wide rim in between the ITZ-R and the fissures around it, as the cement and the rock detached from each other.

IGN/W(150.b.28d)



Figure V.23 - IGN/W(150.b.28d) OM images

<u>CEM</u>: The cement looks similar to the equivalent sample without **bentonite**, IGN/W(150.28d).

<u>ITZ</u>: The ITZ looks similar to the one observed in the sample IGN/W(150.28d), except for the homogeneous light brown $\approx 100 \mu m$ wide rim in between the ITZ-R and ITZ-C and slightly wider ITZ-R, with $\approx 250-400 \mu m$. Additionally, a narrow fissure in between the cement and the rock can also be observed, as these materials started detaching from each other.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure V.24-Figure V.30. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part.

These maps are presented in accordance with the description given in the section V.1.1 d).

IGN/G(150.b.28d)



ii. ITZ Ca map



Figure V.24 - IGN/G(150.b.28d) SEM/EDS images

<u>Phase map</u>: Similar to the IGN/G(150.28d), a gradual Ca/Si ratio change across the ITZ is observed. <u>Element maps</u>: In the ITZ, similarly to IGN/G(150.28d), **Ca** penetrates in high amounts up to **100 \mum** into the rock. There is, however, further **Ca** migration in slightly lower amounts, which goes up to **500 \mum** into the rock (total=**600 \mum**).

IGN/G20SF(150.b.28d)







*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map

iii. ITZ Si map

Figure V.25 - IGN/G20SF(150.b.28d) SEM/EDS images

<u>Phase map</u>: relatively gradual phase change across the ITZ, similarly to IGN/G20SF(150.28d).

Element map: further Ca migration when compared with the IGN/G20SF(150.28d).

IGN/G40SF(150.b.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.26 - IGN/G40SF(150.b.28d) SEM/EDS images

<u>Phase map</u>: Similar to the equivalent sample without **bentonite**, IGN/G40SF(150.28d), the phase change is sudden, without obvious intermediate Ca/Si ratio phases between the rock and the cement.

<u>Element map</u>: the **Ca** migration (over **300µm**) from ITZ-C into ITZ-R in this sample seems to be significantly deeper than the one observed in the equivalent sample without **bentonite**, IGN/G40SF(150.28d).

IGN/G20MS(150.b.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

 $= 100 \, \mu m$

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.27 - IGN/G20MS(150.b.28d) SEM/EDS images

Phase map: Gradual phase change across the ITZ, similarly to IGN/G20MS(150.28d).

<u>Element map</u>: deeper **Ca** migration compared with the equivalent sample without **bentonite** addition, IGN/G20MS(150.28d).

IGN/A(150.b.28d)





i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.28 - IGN/A(150.b.28d) SEM/EDS images

Phase map: Similar to the IGN/A(150.28d), a gradual Ca/Si ratio change across the ITZ is observed.

<u>Element maps</u>: In the ITZ, similarly to the IGN/A(150.28d), **Ca** seems to penetrate in high amounts up to **100 \mum** plus a lower but still clear migration up to about **200 \mum** into the rock (total=**300 \mum**). There is a micro fissure across the ITZ-C.

IGN/HAC(150.b.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map





Figure V.29 - IGN/HAC(150.b.28d) SEM/EDS images

<u>Phase map</u>: From the Ca/Si phase map we can see only 2 main phases: one for the rock and another for the cement, with the sudden phase change.

Element maps: Little Ca migration detected across the ITZ.

IGN/W(150.b.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.30 - IGN/W(150.b.28d) SEM/EDS images

<u>Phase map</u>: From the Ca/Si phase map, similarly to the IGN/W(150.28d), a gradual Ca/Si ratio change across the ITZ can be seen.

<u>Element maps</u>: In the ITZ Ca seems to penetrate in high amounts up to 200 μ m plus a lower but still clear migration up to about 100 μ m into the rock (total=300 μ m). This is bit further than the equivalent sample without bentonite addition (IGN/W(150.28d).

V.2 290°C cure

a) Mesoscopic Images

Samples of cut surfaces are shown at approximately 70% of actual size in Figure V.31.









i.. IGN/G(290.28d)

- ii IGN/G20SF(290.28d)
- iii IGN/G40SF(290.28d)

iv IGN/G20MS(290.28d)



v. IGN/A(290.28d)



vi. IGN/HAC(290.28d)

vii. IGN/W(290.28d)

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Figure V.31 - Photos of the cross section of the IGN/CEM assemblages exposed at 290°C for 28 days in brine
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The most noticeable features from this 290°C samples is the colour changes in the rock and in most of the cements.

b) XRD

Table V.3 details the phases detected by XRD within each of the zones of the ITZ.

Zone	Identified peaks and other relevant features
	Amorphous, portlandite, reinhardbraunsite. Traces of
CEM	jaffeite, killalaite, unhydrated cement and calcite.
ITZ-C	Reduced Portlandite from CEM.
ITZ-R	Similar to IGN. Traces of reinhardbraunsite and calcite.
	Amorphous, kilchoanite, xonotlite, reinhardbraunsite and
CEM	unhydrated calcium silicates. Traces of calcite, killalaite,
	portlandite, quartz and unhydrated cement.
	Increased quartz and xonotlite. Reduced kilchoanite and
112-0	unhydrated calcium silicates.
ITZ-R	Reduced feldspars from IGN.
CEM	Amorphous, quartz, xonotlite, killalite, unhydrated cem.
ITZ-C	Increased quartz and reduced xonotlite from CEM.
ITZ-R	Reduced feldspars from IGN.
CEM	Amorphous, kilchoanite, killalaite, calcite and xonotlite.
	Traces of reinhardbraunsite and unhydrated cement .
ITZ-C	Increased killalaite and reduced kilchoanite from CEM.
IIZ-C	Traces of jaffeite and aragonite .
ITZ-R	Similar to IGN. Traces of jaffeite, reinhardbraunsite and
	calcite.
CEM	Amorphous, portlandite, reinhardbraunsite, calcite, katoite
	silicatian. Traces of unhydrated cement and killalaite.
ITZ-C	<u>Reduced</u> portlandite and <u>increased</u> calcite and killalaite from
	CEM. Traces of kilchoanite.
IIZ-R	Similar to IGN. Traces of katoite silicatian and kilchoanite .
CEM	Amorphous, boenmite, katolte, calcium aluminium oxide
	nydrate, kaoute silicatian.
TTZ-C	<u>Reduced</u> kaotite and kaotite sincatian from CEM.
ITZ-R CEM	<u>Similar</u> to IGN. Traces of calcium aluminium oxide hydrate
	and katolie sincatian.
	of jeffoite kilchoopite and unhydrated compat
ITZ-C	Increased calcite reduced reinharbraunsite and sharply
	reduced portlandite from CEM Xonotlite present as well
ITZ-R	Similar to IGN Traces of reinhardbraunsite
	Zone CEM ITZ-C ITZ-R CEM ITZ-R ITZ-R <tr td=""> ITZ-R</tr>

Table V.3 - compounds identified by XRD analysis for samples exposed at 290°C for 28 days in brine

c) OM

Thin section micrographs for each sample are shown in Figure V.32-Figure V.38. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

IGN/G(290.28d)



Figure V.32 - IGN/G(290.28d) OM images

<u>CEM</u>: Under optical microscope, this cement exhibits a darker and more homogeneous brown tone (in PPL) than the class G exposed at 150° C. In XPL shows some bright white and reddish spots (although different red tones by XPL and naked eye).

<u>ITZ</u>: As expected, there is a fissure splitting the ITZ-C and the CEM. A \approx 50 µm wide ITZ-R dark brown ITZ-R rim is seen in PPL, with an extension into the rock of a much lighter up to \approx 200µm wide rim, barely distinguishable from the rock. In XPL, the ITZ-R seems to be mostly composed of **milky material** and a \approx 300µm ITZ-C rim is distinguishable due to its reduction in bright white/increased red spots.

IGN/G20SF(290.28d)



i. ITZ in PPL



ii. ITZ in XPL

Figure V.33 - IGN/G20SF(290.28d) OM images

<u>CEM</u>: As seen for the class G cement under same conditions, also this exhibits a darker and more homogeneous brown tone than its equivalent exposed at 150° C. In XPL this cement shows few bright white and reddish spots (although different red tones by XPL and naked eye).

<u>ITZ</u>: There is a fissure splitting the ITZ-C and the ITZ-R and a $\approx 100 \,\mu\text{m}$ wide ITZ-R dark brown ITZ-R rim (in PPL), which also extendes further into the rock in a lighter colour that is almost undistinguishable from the rock. In XPL, the ITZ-R seems to be mostly composed of **milky material** and a $\approx 200-400 \,\mu\text{m}$ ITZ-C rim is distinguishable due to its **lighter reddish colour**, reduction in **small bright white spots** and presence of medium sized **bright grains**.

IGN/G40SF(290.28d)



Figure V.34 - IGN/G40SF(290.28d) OM images

<u>CEM</u>: Although red coloured to the naked eye, the colour of this cement doesn't change much when compared with the same cement exposed to 150° C in PPL. In XPL, however, similarly to the G20SF exposed to 290° C, this cement shows bright white and reddish spots, not seen in the 150° C one.

<u>ITZ</u>: There is a fissure splitting the ITZ-C and ITZ-R. In PPL, a $\approx 100 \ \mu m$ wide dark ITZ-R rim, with another similar rim delimiting ITZ-C from CEM. In XPL, the $\approx 500 \mu m$ ITZ-C rim is distinguishable due to a significant increase in medium sized **bright grains** (quartz).

IGN/G20MS(290.28d)



i. ITZ in PPL



ii. ITZ in XPL

Figure V.35 - IGN/G20MS(290.28d) OM images

<u>CEM</u>: Under optical microscope, the colour and texture of this cement do not change much when compared with the same cement exposed to 150° C in PPL (although slightly darker). In XPL, however, similarly to the G20SF exposed to 290° C, this cement shows several red spots, not seen in the 150° C one.

<u>ITZ</u>: Again, a fissure splitting the ITZ-C from the ITZ-R is observed. In PPL, a \approx **50 µm** wide ITZ-R, with another similar rim delimiting ITZ-C from CEM. In XPL, the \approx **500µm** ITZ-C rim is distinguishable due to a significant decrease in small sized **bright grains**.

IGN/A(290.28d)



i. ITZ in PPL

Figure V.36 - IGN/A(290.28d) OM images

CEM: Under optical microscope, this cement exhibits a darker and more homogeneous brown tone (in PPL) than the class A exposed at 150°C. Some white spots can be distinguished. In XPL this cement shows some bright spots with a brownish colour.

<u>ITZ</u>: The fissure splits the ITZ-R and the rock. A $\approx 200 \,\mu m$ wide ITZ-R dark brown ITZ-R rim is seen in PPL. In XPL, the ITZ-R seems to be mostly composed of milky material.

IGN/HAC(290.28d)



i. ITZ in PPL

ii. ITZ in XPL

Figure V.37 - IGN/HAC(290.28d) OM images

CEM: Under optical microscope, this cement exhibits a darker colour (in PPL) than the HAC exposed at 150°C. In XPL this cement shows some bright spots/zones with a reddish colour.

ITZ: The fissure splits the ITZ-R and the rock. The very dark colour of the cement makes it very difficult to distinguish the cement from the ITZ, which is also extremely dark. It seems the ITZ-R is about ≈ 100 **µm** wide which, in PPL is slightly darker than the surrounding area and in XPL seems to be mostly composed of **milky material**. The CEM and the ITZ-C are extremely difficult to distinguish.

IGN/W(290.28d)



i. ITZ in PPL

ii. ITZ in XPL

Figure V.38 - IGN/W(290.28d) OM images

<u>CEM</u>: Similarly to the class G one, this cement exhibits a darker and more homogeneous brown tone (in PPL) than the white cement exposed at 150°C. In XPL this cement shows some bright white spots.

<u>ITZ</u>: The fissure splits the ITZ-R and the rock. A $\approx 200 \,\mu m$ wide ITZ-R dark brown ITZ-R rim is seen in PPL. This ITZ-R is connected with the ITZ-C through a zone where little cement is present. Still in PPL, a $\approx 50 \mu m$ ITZ-C rim is distinguishable due to its dark colour. In XPL, the ITZ-R seems to be mostly composed of milky material.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure V.39-Figure V.45. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

IGN/G(290.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.39 - IGN/G(290.28d) SEM/EDS images

Phase map: There is a gradual Ca/Si ratio change across the ITZ.

<u>Element maps</u>: In the ITZ, **Ca** penetrates up to $\approx 100 \ \mu m$, which is significantly less than the migration observed in the equivalent sample exposed to a 150°C, IGN/G(150.28d).

IGN/G20SF(290.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure V.40 - IGN/G20SF(290.28d) SEM/EDS images

Phase map: Gradual phase change across the ITZ, although not as obvious as for the IGN/G(290.28d).

<u>Element maps</u>: Similarly to IGN/G(290.28d), the **Ca** penetrates only about **50\mum** into the rock, which is considerably less than the **Ca** penetration observed in the equivalent sample exposed at 150°C, IGN/G20SF(150.28d).

IGN/G40SF(290.28d)



i. ITZ-C Ca/Si phase map (CEMENT SIDE)

Key*

Ca/Si > 2.5
2.5 > Ca/Si > 1.5
1.5 > Ca/Si > 1
1 > Ca/Si > 0.1
0.1 > Ca/Si

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



ii. ITZ-R Ca/Si phase map (ROCK side)



iii. ITZ-C Ca map (CEMENT side)



iv. ITZ-R Ca map (ROCK side)





v. ITZ-C Si map (CEMENT side) Figure V.41 - IGN/G40SF(290.28d) SEM/EDS images

<u>Phase maps</u>: The phase change is relatively abrupt, with little intermediate Ca/Si ratio phases between the rock and the cement.

Element maps: little Ca migration (<50µm) from cement into the rock.

IGN/G20MS(290.28d)



i. ITZ-C Ca/Si phase map (CEMENT SIDE)

Key*

Ca/Si > 2.5
2.5 > Ca/Si > 1.5
1.5 > Ca/Si > 1
1 > Ca/Si > 0.1
0.1 > Ca/Si

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



ii. ITZ-R Ca/Si phase map (ROCK side)



iii. ITZ-C Ca map (CEMENT side)



iv. ITZ-R Ca map (ROCK side)



v. ITZ-C Si map (CEMENT side)



vi. ITZ-R Si map (ROCK side)

Figure V.42 - IGN/G20MS(290.28d) SEM/EDS images

<u>Phase map</u>: the ITZ phases are not obvious as the cement has detached from the cement across the line between ITZ-R and ITZ-C.

<u>Element map</u>: difficult to access from these maps whether the depth of **Ca** migration, as the detachment zone is very rough.

IGN/A(290.28d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map

iii. Si map

Figure V.43 - IGN/A(290.28d) SEM/EDS images

<u>Phase map</u>: From the Ca/Si phase map, similar to the IGN/A(150.28d), a gradual Ca/Si ratio can be seen change across the ITZ.

<u>Element maps</u>: In the ITZ the **Ca** seems to penetrate in low amounts up to $100\mu m$, which significantly lower than IGN/A(150.28d).

IGN/HAC(290.28d)



-
Ca/Si > 2.5
2.5 > Ca/Si > 1.5
1.5 > Ca/Si > 1
1 > Ca/Si > 0.1
0.1 < Ca/Si

Key*

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map





iii. Si map



Figure V.44 - IGN/HAC(290.28d) SEM/EDS images

<u>Phase map</u>: From the Ca/Si phase map a relatively abrupt phase change is observable.

<u>Element maps</u>: Similar to the equivalent sample exposed at 150°C, IGN/HAC(150.28d), no significant **Ca** migration is evident across the ITZ.

IGN/W(290.28d)



i. ITZ-C Ca/Si phase map (CEMENT SIDE)

Key*

Ca/Si > 2.5
2.5 > Ca/Si > 1.5
1.5 > Ca/Si > 1
1 > Ca/Si > 0.1
0.1 > Ca/Si

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



ii. ITZ-R Ca/Si phase map (ROCK side)



iii. ITZ-C Ca map (CEMENT side)



iv. ITZ-R Ca map (ROCK side)





v. ITZ-C Si map (CEMENT side) vi. ITZ-Figure V.45 - IGN/W(290.28d) SEM/EDS images

Phase map: Similar to the IGN/W(150.28d), a gradual Ca/Si ratio change across the ITZ can be observed.

<u>Element maps</u>: In the ITZ the cement **Ca** penetrates in low amounts up to 100 μ m into the rock, which considerably lower than IGN/W(150.28d).
VI. RESULTS: 3 MONTHS CURE

The results presented below for each of the curing conditions/rock type combinations are arranged as follows:

- a) Cut surface photographs
- b) X-Ray diffraction
- c) Optical Microscopy
- d) Electron microscopy/Energy Dispersive Spectroscopy
- e) HCl test
- f) Thermogravimetry and Mass Spectrometry

VI.1 150°C cure

VI.1.1 No CO₂ exposure

VI.1.1.1 IGN

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.1.



i. IGN/G(150.84d)







ii. IGN/G20SF(150.84d)



iv. IGN/G20MS(150.84d)



b) XRD

Table VI.1 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features					
	CEM	Largely amorphous. Portlandite and unhydrated cement. Traces of αC_2SH , kilchoanite and calcite.					
IGN/G (150.84d)	ITZ-C	Similar to CEM, with reduced portlandite and increased calcite .					
	ITZ-R	Similar to IGN, with reduced feldspars and quartz and presence calcite , aragonite and unhydrated cement . Traces of portland kilchoanite , hillebrandite and killalaite .					
IGN/G20SF (150.84d)	CEM	Largely amorphous. Quartz, unhydrated cement and αC_2SH . Traces of hillebrandite, killalaite, kilchoanite, aragonite, calcite and tobermorite.					
	ITZ-C	Similar to CEM, with increased amorphous material and sharply reduced quartz . Calcite and aragonite increase.					
	ITZ-R	Similar to IGN, with reduced feldspars and quartz . Traces of aragonite , unhydrated cement , hillebrandite and killalaite .					
IGN/G40SF (150.84d)	CEM	Largely amorphous. Quartz and tobermorite. Traces of calcite, aragonite, calcite, unhydrated cement, hillebrandite and killalaite.					
	ITZ-C	Similar to CEM, with slight calcite and aragonite increase.					
	ITZ-R	Similar to IGN, with reduced feldspars and quartz . Traces hillebrandite and unhydrated cement .					
IGN/G20MS (150.84d)	CEM	Largely amorphous. Calcite. Traces of aragonite, αC_2SH , unhydrated cement, killalaite and kilchoanite.					
	ITZ-C	Similar to CEM, with reduced calcite.					
	ITZ-R	Similar to IGN, with reduced feldspars and quartz . Traces of calcite , aragonite and unhydrated cement .					

Table VI.1 - compounds identified by XRD analysis: 150°C, no CO₂-exposure, 84 days cure

c) OM

Thin section micrographs for each sample are shown in Figure VI.2-Figure VI.5. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

IGN/G(150.84d)



i. ITZ in PPL ii. I Figure VI.2 - IGN/G(150.84d) OM images

<u>CEM</u>: Large numbers of small sized grains/crystals which are portlandite.

<u>ITZ</u>: In PPL, a \approx 450µm wide ITZ-R brown rim is observed. In XPL, a \approx 300µm wide ITZ-C rim can be seen, with fewer small sized bright grains/crystals than the rest of the cement (CEM). Most of these crystals seem to be concentrated in the line between ITZ-C and ITZ-R.

IGN/G20SF(150.84d)



Figure VI.3 - IGN/G20SF(150.84d) OM images

<u>CEM</u>: small and large sized grains/crystals.

<u>ITZ</u>: In PPL, a \approx 500µm wide dark ITZ-R rim can be seen which is likely to be amorphous as it is isotropic, whereas the ITZ-C is a \approx 300µm wide rim, barely distinguishable.

IGN/G40SF(150.84d)



i. ITZ in PPL



Figure VI.4 - IGN/G40SF(150.84d) OM images

<u>CEM</u>: In PPL, it is similar to IGN/G20SF(150.84d), with small and large sized grains/crystals. In XPL it is noticeable that it has considerably fewer bright spots than in IGN/G20SF(150.84d).

<u>ITZ</u>: In PPL, there is a $\approx 400 \mu m$ wide dark ITZ-R rim, which is narrower than those in IGN/G(150.84d) or IGN/G20SF(150.84d). The ITZ-C cannot be distinguished from the rest of the cement (CEM).

IGN/G20MS(150.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.5 - IGN/G20MS(150.84d) OM images

<u>CEM</u>: It is similar to that observed for IGN/G20SF(150.84d), with a large number of bright spots (in XPL).

<u>ITZ</u>: The ITZ-R is a $\approx 600 \mu m$ wide dark ITZ-R rim, wider than any other IGN/CEM(150.84d) combination. The ITZ-C cannot be distinguished from CEM.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure VI.6-Figure VI.9. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

IGN/G(150.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map





nap iii. ITZ Si map Figure VI.6 - IGN/G(150.84d) SEM/EDS images

Phase map: Relatively gradual/broad phase change.

<u>Element maps</u>: Ca migration (\approx 300µm) relatively uniform from the cement into the rock with pockets of concentration in rock pores.

IGN/G20SF(150.84d)







*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map





Figure VI.7 - IGN/G20SF(150.84d) SEM/EDS images

Phase map: Relatively broad but not as gradual phase change as for IGN/G(150.84d).

<u>Element maps</u>: Ca has migrated over $300\mu m$, from the cement into the rock, and is mostly concentrated in the rock voids.

IGN/G40SF(150.84d)







*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map





Figure VI.8 - IGN/G40SF(150.84d) SEM/EDS images

<u>Phase map</u>: Almost no high Ca/Si ratio phases due to the high amount of silica added to the cement. No obvious intermediate Ca/Si ratio phase.

<u>Element maps</u>: Ca has migrated $\approx 200 \mu m$ and in significantly lower amounts than any other IGN/CEM(150.84d) combination.

IGN/G20MS(150.84d)



Ca/Si > 2.5 2.5 > Ca/Si > 1.5 1.5 > Ca/Si > 1 1 > Ca/Si > 0.1 0.1 > Ca/Si

Key*

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

= 100 μm

i. ITZ Ca/Si phase map



ii. ITZ Ca map

100 um

iii. ITZ Si map

Figure VI.9 - IGN/G20MS(150.84d) SEM/EDS images

<u>Phase map</u>: Almost no high Ca/Si ratio phases, probably due to the fast reaction rate of the silica added to the cement. Relatively broad but not as gradual phase change as in IGN/G(150.84d).

Element maps: Ca has penetrated over 350µm into the rock.

e) HCl test

This test was undertaken on the ITZ-C of IGN/G(150.84d) and significant effervescence was observed, indicating presence of carbonates.

f) TGA and Mass Spec

The TGA was undertaken on the ITZ-C of IGN/G(150.84d) and shows material decomposing within the range 450° C to 650° C (**Figure VI.10**). From the Mass Spec, it can be seen that some CO₂ was released over this temperature range (although it appears at a higher temperature, as the detection of released CO₂ during the TG is delayed due to the time the gases take to get to the mass spectrometer) (**Figure VI.11**). These results indicate carbonate decomposition over this temperature range. There is other carbonate decomposing at higher temperatures, which is probably calcite and, perhaps, small amounts of aragonite (which decomposes at slightly lower temperatures than calcite). In the **appendix X.5**, the comparison of the CO₂ released in this sample with the other ones and with calcite (the reference calcium carbonate) can be found.



Figure VI.10 - TGA result of IGN/G(150.84d) ITZ-C



Figure VI.11 - Mass Spec result of IGN/G(150.84d) ITZ-C

VI.1.2 With CO₂ exposure

VI.1.2.1 IGN

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.12.



i. IGN/G(150.CO₂.84d)



iii. IGN/G40SF(150.CO₂.84d)



ii. IGN/G20SF(150.CO₂.84d)



iv. IGN/G20MS(150.CO2.84d)

Figure VI.12 - Photos of the cross section of the IGN/CEM assemblages exposed at 150°C for 84 days in brine, with CO₂ injection

Although more or less uniform all around the G40SF interior outermost layer, the carbonation rim observed seems to be dependent on the surrounding rock thickness. The top of the cement, for instance, has a thicker carbonation layer which is probably associated with the absence of surrounding rock.

b) XRD

Table VI.2 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features						
	CEM	Largely amorphous with portlandite , unhydrated cement , hillebrandite and calcite . Traces of calcite , kilchoanite and αC_2SH . The traces of calcite in CEM indicate a slight carbonation rate in the cement core.						
IGN/G (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with sharply reduced portlandite and slight increase in hillebrandite and calcite . Traces of aragonite . The reduced portlandite along with the increased calcium carbonates indicates a higher carbonation rate in the cement outermost layer.						
	ITZ-R	Similar to IGN.						
	CEM	Largely amorphous with quartz, unhydrated cement , hillebrandite , kilchoanite , killalaite . Traces of aragonite , calcite and tobermorite . The traces of aragonite and calcite in CEM indicate a slight carbonation rate in the cement core.						
IGN/G20SF (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with a slight increase in amorphous material and aragonite . The aragonite increase in ITZ-C seems to confirm a higher carbonation rate in the cement outermost layer, whereas the increase in amorphous material might, again, mean that some ACC is forming in addition to crystalline calcium carbonate.						
	ITZ-R	Similar to IGN, with traces of calcite . The traces of calcite in the ITZ-R seem to indicate Ca^{2+} and OH^{-} migration into the rock and subsequent carbonation.						
	CEM	Largely amorphous with quartz and unhydrated cement . Traces of aragonite, calcite, hillebrandite, kilchoanite, αC_2SH , tobermorite and killalaite . As expected, the addition of over 30% quartz to Portland based cement caused the formation of tobermorite, although in low amounts. The traces of aragonite and calcite in CEM indicate a slight carbonation rate in the cement core.						
(150.CO ₂ .84d)	ITZ-C	Considerably different from CEM, due to a sharp increase in aragonite and quartz . The amount of amorphous material seems to have increased as well. The sharp aragonite and amorphous material increase in the ITZ-C indicate higher carbonation rate in the outermost layer, when compared to the cement core. The increase in amorphous material may indicate the formation of ACC.						
	ITZ-R	Similar to IGN.						
	CEM	Largely amorphous with calcite and unhydrated cement . Traces of kilchoanite , $\alpha C_2 SH$ and hillebrandite . The presence of calcite in CEM indicate a slight carbonation rate in the cement core.						
IGN/G20MS (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with increased calcite , aragonite and amorphou material . The calcite and amorphous material increase in the ITZ-C indicat higher carbonation rate in the outermost layer, when compared to the cemer core. The increase in amorphous material may indicate the formation of ACC.						
	ITZ-R	Similar to IGN, with traces of calcite . The traces of calcite in the ITZ-R seem to indicate Ca^{2+} and OH^{-} migration into the rock and subsequent carbonation.						

							1 = 0.0 ~		~ ~		~	
Table	VI.2 ·	- comr	ounds ide	entified by	v XRD	analysis:	150°C.	with	CO ₂ -ex	posure.	84 da	vs cure
					,				00200	p 0.0 cm 0 9	· · · · · ·	<i>,</i>

c) OM

Thin section micrographs for each sample are shown in Figure VI.13-Figure VI.16. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

IGN/G(150.CO₂.84d)



Figure VI.13 - IGN/G(150.CO₂.84d) OM images

<u>CEM</u>: Many small crystals.

<u>ITZ</u>: While a \approx 300µm wide ITZ-R rim can barely be distinguished in PPL, in XPL it is evident. A \approx 200µm wide bright ITZ-C rim can be distinguished, with a slightly brighter colour in comparison with the rest of the cement (CEM). A thin dark line splits the ITZ-R and ITZ-C.

IGN/G20SF(150.CO₂.84d)





Figure VI.14 - IGN/G20SF(150.CO₂.84d) OM images

<u>CEM</u>: There is a number of small grains/crystals with a few bigger crystals. Under XPL a few orange/reddish/brownish (Fe) spots can be seen.

<u>ITZ</u>: A \approx 450µm wide ITZ-R is barely distinguishable in PPL, whereas in XPL it appears extremely bright (brighter than either CEM or IGN). The ITZ-C is not distinguishable from the rest of the cement (CEM) by OM.

IGN/G40SF(150.CO₂.84d)



i. ITZ in PPL



ii. ITZ in XPL





iii. Carbonation rim in PPL

iv. Carbonation rim in XPL

Figure VI.15 - IGN/G40SF(150.CO₂.84d) OM images

<u>CEM</u>: Similar to IGN/G20SF(150.CO₂.84d), with small sized grains/crystals and a few larger sized crystals with plenty of orange/reddish spots seen in XPL.

<u>ITZ</u>: A \approx 200µm wide ITZ-R is barely distinguishable in PPL. In XPL it appears as bright colours (white and orange) (as bright as in CEM), but not as bright as the same zone in the IGN/G(150.CO₂.84d) and G20SF(150.CO₂.84d). From the carbonation rim image, it can be seen over 2mm carbonation rim in the ITZ-C.

IGN/G20MS(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.16 - IGN/G20MS(150.CO₂.84d) OM images

<u>CEM</u>: Similar to IGN/G20MS(150.84d), with a few orange/reddish spots.

<u>ITZ</u>: The ITZ-R is barely distinguishable in PPL, whereas in XPL it has distinctive bright colours (brighter than either CEM or IGN). The ITZ-C is distinguishable by its darker colour in comparison to CEM.

d) SEM/EDS

Detailed below are the SEM images, elementa dna phase maps ands spot analysis in Figure VI.17-Figure VI.37. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

IGN/G(150.CO₂.84d) - SEM/EDS - Region 1



^{*}these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample







ii. ITZ Ca map



iii. ITZ Si map



Phase map: Relatively gradual/smooth phase change.

Element maps: Ca migration has penetrated more or less uniformly about 300µm into the rock.

ROCK ROCK CEMENT CEMENT NU them I i. ITZ SEM image ii. ITZ SEM backscattered image iv. ITZ Si map iii. ITZ Ca map v. ITZ C map vi. ITZ Fe map

IGN/G(150.CO₂.84d) - SEM/EDS - Region 2

Figure VI.18 - IGN/G(150.CO₂.84d) SEM/EDS images - Region 2

<u>Element maps</u>: Ca has penetrated over 300µm into the rock. A carbon rim is observed in the ITZ. This C rim is more concentrated in the fissure that has formed in the outermost layer of the cement.







ii. ITZ EDS SPOT 2



iii. ITZ EDS SPOT 3

Figure VI.19 - IGN/G(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part I)



Figure VI.20 – IGN/G(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part II)

ii. ITZ EDS SPOT 5









i. ITZ EDS SPOT 7

Figure VI.21 - IGN/G(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part III)

The EDS SPOT analysis for the Region 2 of the IGN/G(150.CO₂.84d) is mapped in the Figure VI.18 and the results are presented in the Figure VI.19-Figure VI.21.

SPOT 1 is located in the ITZ-R. Si and O are the prevalent elements, with some Al, Ca, K and Na present. This composition indicates that this region is mostly composed of volcanic glass. The presence of Ca is probably due to calcium migrating from the cement into the rock. On the other hand, the considerable amounts of Al along with the small amounts of Ca, K and Na may indicate the presence of a small feldspar crystal. The presence of C is not obvious, as the C K peak is coincident with the Si L peak. Nevertheless, the presence of C indicates some degree of carbonation.

SPOTs 2 and 3 are located in the ITZ-C and have similar compositions. Ca and O are the prevalent elements with considerable amounts of C, Si and Al also detected. This composition indicates that this region is mostly composed of cement. The relatively high amounts of of Si and O suggest that small amounts of volcanic glass from the rock are present as well, as Si is not typically present in this cement formulation in such high amounts. The prescence of C indicates the presence of a carbonate. The relatively large amounts of C (compared to Ca) suggest that this is calcium carbonate, CaCO₃. Nevertheless, considering that Si and O are present as well, scawtite, Ca₇Si₆(CO₃)O₁₈•2(H₂O), could be present, although this mineral needs much less C than the CaCO₃ (only \approx 1.5% in weight). Dawsonite, NaAlCO₃(OH)₂, is not present as no Na was detected.

SPOT 4 is also located in the ITZ-C. Ca and O are the prevalent elements, with considerable amounts of C. Small amounts of Al and Si and minor amounts of Fe were also detected. This composition indicates that this region is mostly composed of cement hydrates, along with considerable amounts of carbonate. The relatively large amounts of C (compared to Ca) suggest that this is calcium carbonate, CaCO₃. This carbonate needs just over 3 times more Ca than C (in weight), whereas scawtite, Ca₇Si₆(CO₃)O₁₈•2(H₂O), would need over 23 times more Ca than C to form. This means that even if all the Ca present was present as scawtite, it would not be enough to use up most of the C present.

SPOT 5 is also located in the ITZ-C, next to a micro-crack. Ca, C and O are the prevalent elements, with considerable amounts of Si present as well. Small amounts of Al and small amounts of K were also detected. This composition indicates that this region is likely to be composed of a mix of cement, carbonated cement and volcanic glass from the rock. On the other hand, the sharp increase in Si, C and O compared to SPOT 4 seems to be a consequence of the micro-crack, which may have enhanced the presence of silica and carbon dioxide in this zone.

SPOT 6 is located in the ITZ-C and has a similar chemical composition to SPOT 4 with Ca and O as the prevalent elements. C is also present in considerable amounts. This composition indicates that this region is mostly composed of cement. Again, the relatively high amounts of C indicate the presence of large amounts of calcium carbonate. Similar to SPOT 4, while large amounts of Ca combined with the relatively high amounts of C compared to Ca suggest this is calcium carbonate, CaCO₃.

SPOT 7 is also located in the inner region of the ITZ-C. Again Ca is the prevalent element with O present in considerable amounts but Si and C are present in small amounts. The relative amounts given in the quantitative analysis (Ca / C / O = 40.91 / 11.45 / 43.10) are very similar to those observed for CaCO₃ (40.04 / 12.00 / 47.96). This also indicates that this region is mostly composed of CaCO₃.

IGN/G20SF(150.CO₂.84d) - SEM/EDS - Region 1





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map



<u>Phase map</u>: Phase change similar to the one observed in IGN/G(150.CO₂.84d).

<u>Element maps</u>: \approx 350µm Ca migration is detected, unevenly distributed in the ITZ-R, it is mostly concentrated in the bigger rock voids.

IGN/G20SF(150.CO₂.84d) - SEM/EDS - Region 2



i. ITZ SEM image







iii. ITZ C map



iv. ITZ Fe map

Figure VI.23 - IGN/G20SF(150.CO₂.84d) SEM/EDS images - Region 2

Element maps: Ca has penetrated over 300µm into the rock. Some C was detected in both the cement outermost layer (ITZ-C) and the rock side of the ITZ (ITZ-R). This carbon is unevenly distributed within these zones. This is a consequence of the heterogeneous nature of the materials involved, particularly the rock.



18-27-1-2





ii. ITZ EDS SPOT 2



i. ITZ EDS SPOT 1







i. ITZ EDS SPOT 4



ii. ITZ EDS SPOT 5



Figure VI.25 - IGN/G20SF(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part II)













The EDS SPOT analysis for the Region 2 of the IGN/G20SF(150.CO₂.84d) is mapped in the **Figure VI.23** and the results are presented in the **Figure VI.24-Figure VI.26**.

SPOT 1 is located in the ROCK. Si and O are the prevalent elements, with considerable amounts of Al. This composition indicates that this region is mostly composed of volcanic glass.

SPOT 2 is located in the ITZ-R. O, Si, Ca and C are all present in relatively high amounts. This composition indicates that this region is composed of a mix of volcanic glass and carbonated cement. The high amounts of Ca have originated from cement that has penetrated the rock. The levels of Si and O suggest the presence of cement (with 20% quartz) or the formation of silica gel. The considerable amounts of C indicate the presence of a carbonate likely to be CaCO₃, which needs only \approx 3.3 times more Ca than C (in weight). Scawtite, Ca₇Si₆(CO₃)O₁₈•2(H₂O), is not likely to be present as it needs \approx 23.4 times more Ca than C (in weight) in its composition.

SPOT 3 is located in the ITZ-R, next to the bright white area, which is amorphous. C, O, Si and Ca are all present in considerably high amounts. This composition indicates that this region is composed of volcanic glass (or/and, perhaps, silica gel) mixed with some cement. The fact that the C K peak coincides with the Si L peak makes it hard to assess the exact amount of C present. Nevertheless, the high amounts of C indicate the presence of high amounts of carbonate. The relatively low amounts of Ca compared to C suggest that the Ca is present only as carbonate.

SPOT 4 is located in the ITZ-R, next to the bright white area, which is amorphous. O, Ca, Si and C are present in relatively high amounts. This composition indicates that this region is mostly composed of cement hydrates and carbonated cement. The high amount of Ca along with large amounts of Si and O suggest that this silica rich cement formulation has penetrated into the rock and formed calcium silicates, likely to be a consequence of the migration by capillarity of the unhydrated cement. Some of the Si, O and Al is probably from the volcanic glass, whereas some of the Ca has been used up to form CaCO₃.

SPOT 5 is located in the ITZ-R, just besides the bright area located between the ITZ-R and ITZ-C. It has a similar composition to the one observed in SPOT 4, i.e. presence of cement hydrates and carbonated cement. This confirms the penetration of cement into the rock.

The reduced Ca from SPOT 4 to SPOT 5 may be a consequence of Ca being leached from this region (dissolution front/depleted zone) and moving outwards during the carbonation

process, which end up being part of the calcium carbonate composition in the carbonation front. A similar phenomenon was observed in other studies (Rimmele *et al.*, 2008; Milestone *et al.*, 1986; Grant-Taylor *et al.*, 1996).

SPOT 6 is located in the bright white area, between the ITZ-R and ITZ-C. This has a similar composition to the one observed for SPOTs 4 and 5, but with even more reduced Ca. The gradual Ca reduction (from SPOT 4 to SPOT 5 and from SPOT 5 to SPOT 6) confirms the existence of a dissolution front, from which the Ca is being depleted to form $CaCO_3$ in the outer layers. The distinct amorphous texture of this region indicates that silica gel is present. This compound could have formed as a product of corrosion of the cement (loss of Ca in the dissolution front) or/and as a product of the alkali-silica reaction (between the cement and the rock).

SPOT 7 is located in the fine line between the ITZ-C and the bright area that splits the ITZ-R and ITZ-C. This composition indicates that this region is mostly composed of hydrated cement, with some carbonated cement.

SPOT 8 is located in the fine line between the ITZ-C and the bright area that splits the ITZ-R and ITZ-C. O, Ca, C and Si are all present in relatively high amounts. This composition is similar to that observed for SPOT 7 and indicates that this region is mostly composed of cement hydrates, with even higher amounts of carbonated cement than in SPOT 7.

SPOT 9 is located in the ITZ-C, close the cement core. This seems to have a similar composition to SPOT 7, but with even lower amounts of C, which suggests a lower amount of carbonated cement.

IGN/G40SF(150.CO₂.84d) - SEM/EDS - Region 1





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

 $= 100 \, \mu m$

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.27 - IGN/G40SF(150.CO₂.84d) SEM/EDS images - Region 1

<u>Phase map</u>: Phase change more abrupt than in IGN/G(150.CO₂.84d).

<u>Element maps</u>: Ca has migrated $\approx 250 \mu$ m, but is unevenly distributed through the ITZ, mostly being concentrated in the bigger rock voids.



v. ITZ C map vi. ITZ Fe n Figure VI.28 - IGN/G40SF(150.CO₂.84d) SEM/EDS images - Region 2

<u>Element maps</u>: Ca has penetrated over 250μ m into the rock. Significant amounts of carbon were detected in ITZ-R and, mainly, ITZ-C. This indicates that carbonate has formed and that it is heterogeneously distributed within these zones. This is a consequence of the heterogeneous nature of the materials involved, especially the rock.





ii. ITZ EDS SPOT 2

Element Weight % Si K 14.4K СК 12.56 12.8K οк 47 11.2K NaK 1.33 9.6K MgK 0.6 8.0K 0 AIK 3.68 6.4K SiK 20.31 4.8K MoL 0.42 Ca Ko 3.2K КΚ 1.83 SiL 1.6K Mo LB 10.95 CaK Mo L Fe Ko Fe Kß 0.0K 5.00 7.00 8.00 9.00 3.00 6.00 1.00 2.00 4.00 FeK 1.31 Lsec: 30.0 0 Cnts 0.000 keV Det: ApolloXPSDD Det Status: Collecting CPS DT Reso

iii. ITZ EDS SPOT 3

Figure VI.29 - IGN/G40SF(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part I)



i. ITZ EDS SPOT 4 Figure VI.30 - IGN/G40SF(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part II)

The EDS SPOT analysis for the Region 2 of IGN/G40SF(150.CO₂.84d) is mapped in the Figure VI.28 and the results are presented in Figure VI.29 and Figure VI.30.

SPOTs 1 and 2 are located in the ITZ-R, close to the ROCK. Si and O are the prevalent elements. This composition indicates that this region is mostly composed of volcanic glass. The minor peak observed for C K may mean that there is a small amount of C present as carbonate, combined with O and perhaps the small amount of Ca present.

SPOT 3 is located on the line between the ITZ-R and ITZ-C. Si and O are the prevalent elements with Ca and C present in considerable amounts. This composition indicates that this region is mostly composed of volcanic glass. The relatively low amounts of Ca compared to C suggests that the Ca is present as carbonate, likely to be CaCO₃, which needs only \approx 3.3 times more Ca than C (in weight). Scawtite, Ca₇Si₆(CO₃)O₁₈•2(H₂O), is not likely to be present as it needs \approx 23.4 times more Ca than C (in weight).

SPOT 4 is located in the ITZ-C. Si and O are present in large amounts. The composition in this region indicates that this is mostly silica from the cement so is probably a small quartz crystal. Again, the small amounts of Ca and C suggest that these are also present in the form of calcium carbonate, CaCO₃. This is supported by the XRD analysis which detected considerable amounts or aragonite (CaCO₃) in this zone.

IGN/G40SF(150.CO₂.84d) - SEM/EDS - Region 3



iii. Carbonation rim C map Figure VI.31 - IGN/G40SF(150.CO₂.84d) SEM/EDS images - Region 3

Element maps: The carbon observed in this C map is from the aragonite detected by XRD analysis.



iii. ITZ EDS SPOT 7

Figure VI.32 - IGN/G40SF(150.CO₂.84d) SEM/EDS SPOT analysis in Region 3 (Part I)



i. ITZ EDS SPOT 8 Figure VI.33 - IGN/G40SF(150.CO₂.84d) SEM/EDS SPOT analysis in Region 3 (Part II)

The EDS SPOT analysis for the Region 3 of IGN/G40SF(150.CO₂.84d) is mapped in the Figure VI.31 and the results are presented in the Figure VI.32 and Figure VI.33.

SPOT 5 is located in the ITZ-R, close to the ROCK. The relatively high amounts of Si, O, Al along with the considerable amounts of Na and Ca mean that this SPOT is composed of a plagioclase. According to the XRD analysis, this is probably andesine, as this mineral is part of the rock composition.

SPOTs 6 and 7 are located in the core of the carbonation rim. Ca and O are present in high amounts with slightly less C and Si present. This composition indicates that this region is mostly composed of calcium silicate hydrates from the cement.

SPOT 8 is located at the in the region between the carbonation rim and the cement core, i.e. in the inner layer of the carbonation rim. Si, Ca and O are all present in relatively high amounts. This composition is similar to that observed for SPOTs 6 and 7, but with a significant decrease in the amount of Ca.

IGN/G20MS(150.CO₂.84d) - SEM/EDS - Region 1





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.34 - IGN/G20MS(150.CO₂.84d) SEM/EDS images - Region 1

Phase map: Phase change a bit more abrupt than in IGN/G(150.CO₂.84d).

<u>Element maps</u>: \approx 300µm Ca migration, unevenly distributed across the ITZ, mostly concentrated in the rock voids.


III. 11Z C map Figure VI.35 - IGN/G20MS(150.CO₂.84d) SEM/EDS images - Region 2

<u>Element maps</u>: Ca migration has penetrated over 300µm into the rock. Relatively high amounts of carbon were detected in the ITZ, especially in the ITZ-R. Most of the C detected in the ITZ-R is located in the rock pores, as the C rich zones coincide with the Si free zones, i.e. the rock pores.





Element Weight %



ii. ITZ EDS SPOT 2



iii. ITZ EDS SPOT 3

Figure VI.36 - IGN/G20MS(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part I)

44.0K



iv. ITZ EDS SPOT 4 Figure VI.37 - IGN/G20MS(150.CO₂.84d) SEM/EDS SPOT analysis in Region 2 (Part II)

The EDS SPOT analysis for the Region 2 of the IGN/G20MS(150.CO₂.84d) is mapped in the **Figure VI.35** and the results are presented in the **Figure VI.36** and **Figure VI.37**.

SPOT 1 is located in the ITZ-R. Si and O are present in high amounts. This composition indicates that this region is mostly composed of volcanic glass. The presence of C and Ca suggests that there is some carbonate present.

SPOT 2 is located in the amorphous bright area in the ITZ. Si and O are the prevalent elements, with Ca present in considerable amounts as well. This composition along with the texture observed in the SEM image indicates that this region is mostly composed of silica gel, which may have formed either from the alkali-silica reaction or from the loss of calcium in the calcium silicate hydrates. The significant amounts of Ca and C indicate the presence of calcium carbonate, CaCO₃.

SPOTs 3 and 4 are located in the ITZ-C. O and Ca are the prevalent elements, which indicates these spots are mostly composed of cement hydrates with the presence of C indicating the presence of considerable amounts of carbonate. Nevertheless, this cement outermost layer shows the lowest carbonation degree compared to the other class G based cements.

e) HCl test

This test was undertaken on the ITZ-C of IGN/G(150.CO₂.84d), IGN/G20SF(150.CO₂.84d), IGN/G40SF(150.CO₂.84d) and IGN/G20MS(150.CO₂.84d). Significant effervescence was observed in all of them, indicating presence of carbonates in these samples.

f) TGA and Mass Spec



Figure VI.38 - TGA result of IGN/G(150.CO₂.84d) ITZ-C



Figure VI.39 - Mass Spec result of IGN/G(150.84d) ITZ-C



Figure VI.40 - TGA result of IGN/G20SF(150.CO₂.84d) ITZ-C



Figure VI.41 - Mass Spec result of IGN/G20SF(150.84d) ITZ-C



Figure VI.42 - TGA result of IGN/G40SF(150.84d) ITZ-C



Figure VI.43 - Mass Spec result of IGN/G40SF(150.84d) ITZ-C



Figure VI.44 - TGA result of IGN/G20MS(150.84d) ITZ-C



Figure VI.45 - Mass Spec result of IGN/G20MS(150.84d) ITZ-C

Generally, these four TGs show material decomposing within the range 450° C to 650° C. From the Mass Specs, it can be seen that CO₂ was released over this temperature range (**Figure VI.38-Figure VI.45**). These results indicate carbonate decomposition occurs over this temperature range. Other carbonate also decomposes at higher temperatures, which is calcite and perhaps small amounts of aragonite. From G to G20SF and from G20SF to G40SF the amount of crystalline material decomposing at lower temperatures seems to increase, probably associated with the increasing amounts of aragonite in the sample, which forms mostly from C-S-H and tobermorite, as opposed to calcite which forms mostly from portlandite. There is some water released just before the CO₂ decomposition which indicates dehydration, meaning these 2 compounds could be associated in the same phase, e.g. an amorphous calcium carbonate hydroxide. In the **appendix X.5** the comparison of the CO₂ released in these samples with the other ones and with calcite (the reference calcium carbonate) is shown.

VI.1.2.2 UNI

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.46.



i. UNI/G(150.CO₂.84d)



ii. UNI/G20SF(150.CO2.84d)



iii. UNI/G40SF(150.CO₂.84d)



iv. UNI/G20MS(150.CO₂.84d)

Figure VI.46 - Photos of the cross section of the UNI/CEM assemblages exposed at 150°C for 84 days in brine, with CO₂ injection

The less uniform carbonation rim width (when compared with the other ignimbrites under study) observed in the outermost layer of the G40SF is probably due to the heterogeneous nature of this rock in both composition and texture.

b) XRD

Table VI.3 details the phases detected by XRD within each of the zones of the ITZ.Table VI.3 - compounds identified by XRD analysis: 150°C, with CO2-exposure, 84 days cure

Sample	Zone	Identified peaks and other relevant features							
	CEM	Largely amorphous, with portlandite, unhydrated cement and calcite. Traces of kilchoanite, killalaite and hillebrandite. Calcite is forming in higher amounts, whereas portlandite seems to be present in lower amounts, when compared with IGN/G(150.CO ₂ .84d). The high amounts of calcite present in the CEM may mean that the carbonation rate is a bit higher in the current sample, due to its higher porosity and, consequently, higher permeability of the rock when compared with IGN, allowing a higher CO ₂ flow rate into the cement.							
UNI/G (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with sharply reduced portlandite and increased calcite. Perhaps with a small increase in amorphous material. The sharply reduced portlandite and increased calcite in ITZ-C confirm the hypothesis previously put forward about a higher carbonation rate in the grout outermost layer, where the portlandite replacement rate by calcite is higher than in the cement core. The increased amorphous material in the ITZ-C might be due to the amorphous material forming in the ITZ, perhaps amorphous calcium carbonate.							
	ITZ-R	Similar to UNI, with traces of calcite and hillebrandite. The presence of calcite and hillebrandite seem to confirm the idea of cement compounds moving into the rock, where most of them seem to be replaced by calcium carbonates (have to check if there is not amorphous material forming in the samples without CO_2 exposure, otherwise this may be silica gel, rather than ACC).							
UNI/G20SF (150.CO ₂ .84d)	CEM	Largely amorphous, with quartz, αC_2SH , unhydrated cement and calcite. Traces of kilchoanite, hillebrandite, killalaite and tobermorite. The presence of traces of tobermorite in CEM confirms the previously put forward about zones where the Ca/Si ratio dropped low enough for this mineral to form.							
	ITZ-C	Similar to CEM, with slightly increased calcite and slightly reduced kilchoanite, killalaite and tobermorite. Traces of aragonite. The decreased amounts of C-S-H and aragonite presence (although in traces) confirms the idea previously put forward about a higher carbonation rate in the grout outermost layer, where the C-S-H replacement rate by calcium carbonates is higher than in the cement core. Considering the theoretical high carbonation rate of tobermorite, this mineral could be initially forming in higher amounts (as some Ca migration and carbonate formation lowers the Ca/Si ratio) and being then							
	ITZ-R	replaced by calcium carbonates. Similar to UNI, with traces of hillebrandite and aragonite. The presence of calcite and hillebrandite seem to confirm the idea of cement compounds moving into the rock, where some of them seem to be then replaced by calcium carbonates.							
	CEM	Largely amorphous, with quartz. Traces of aragonite, unhydrated cement, tobermorite, killalaite and hillebrandite. As expected, the addition of over 30% quartz to Portland based cement caused the formation of tobermorite, although in low amounts.							
UNI/G40SF (150.CO ₂ .84d)	ITZ-C	Considerably different to CEM, due to the aragonite sharp increase. Quartz and amorphous material seem to increase as well, whereas unhydrated cement, tobermorite, killalaite and hillebrandite seem to be reduced. The aragonite sharp increase along with the C-S-H increase seems to confirm an extremely high replacement rate of cement crystals by aragonite in the outermost layer, i.e. extremely high carbonation rate in the outermost layer of the cement. As previously seen for other samples, the sharp increase in quartz may be a consequence of Ca^{2+} and OH migration into the rock, leaving bigger amounts of unreacted quartz than in the cement core							
	ITZ-R	Similar to UNI. No traces of cement compounds, perhaps due to the lower migration rate of this cement, which is not to be enough to be detected by the XRD analysis.							
	CEM	Largely amorphous, with calcite, unhydrated cement and kilchoanite. Traces of hillebrandite and killalaite.							
UNI/G20MS (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with increase in calcite and slight decrease in killalaite and hillebraunsite. The calcite increase along with the C-S-H decrease seems to confirm a higher replacement rate of cement crystals by calcium carbonates.							
	ITZ-R	Similar to UNI, with slight increase in hillebrandite. The presence of hillebrandite seems to confirm the idea of cement compounds moving into the rock.							

c) OM

Thin section micrographs for each sample are shown in Figure VI.47-Figure VI.50. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

UNI/G(150.CO₂.84d)



ITZ in PPL

ITZ in XPL

Figure VI.47 - UNI/G(150.CO₂.84d) OM images

<u>CEM</u>: The cement does not look as bright as the one observed in $IGN/G(150.CO_2.84d)$.

ITZ: The bright ITZ doe not look as wide as in IGN/G(150.CO₂.84d).



UNI/G20SF(150.CO₂.84d)

ITZ in PPL

ITZ in XPL

Figure VI.48 - UNI/G20SF(150.CO₂.84d) OM images

<u>CEM</u>: The cement looks similar to that observed in IGN/G20SF(150.CO₂.84d).

ITZ: The bright ITZ-R (in XPL) has some orange tones and does not look as wide as in IGN/G20SF(150.CO₂.84d).

UNI/G40SF(150.CO₂.84d)



i. ITZ in PPL



ii. ITZ in XPL



iii. Carbonation rim in PPL



iv. Carbonation rim in XPL

Figure VI.49 - UNI/G40SF(150.CO₂.84d) OM images

<u>CEM</u>: Looks similar to the one observed in IGN/G40SF(150.CO₂.84d).

<u>ITZ</u>: Similar to the one observed in IGN/G40SF(150.CO2.84d), with a slightly wider carbonation rim.

UNI/G20MS(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.50 - UNI/G20MS(150.CO₂.84d) OM images

<u>CEM</u>: Looks similar to the one observed in IGN/G20MS(150.CO₂.84d).

<u>ITZ</u>: The ITZ-R has some orange tones and is not as bright (in XPL) and as wide as in $IGN/G20MS(150.CO_2.84d)$.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure VI.51-Figure VI.54. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

UNI/G(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.51 - UNI/G(150.CO₂.84d) SEM/EDS images

<u>Phase map</u>: The cement/rock phase transition is more abrupt than the one observed in $IGN/G(150.CO_2.84d)$.

Element maps: The calcium does not seem to migrate as much as in IGN/G(150.CO₂.84d).

UNI/G20SF(150.CO₂.84d)



Key*



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.52 - UNI/G20SF(150.CO₂.84d) SEM/EDS images

Phase map: The phase transition is more abrupt than the one observed in IGN/G20SF(150.CO₂.84d).

<u>Element maps</u>: The calcium doesn't seem to migrate from ITZ-C to ITZ-R as much as in IGN/G20SF(150.CO₂.84d).

UNI/G40SF(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample





ii. ITZ Ca map





Figure VI.53 - UNI/G40SF(150.CO₂.84d) SEM/EDS images

Phase map: Similar phase change to the one observed in IGN/G40SF(150.CO₂.84d).

Element maps: Lower calcium migration than the one observed in IGN/G40SF(150.84d).

UNI/G20MS(150.CO₂.84d)



Key*



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.54 - UNI/G20MS(150.CO₂.84d) SEM/EDS images

Phase map: Phase change similar to the one observed for IGN/G20MS(150.CO₂.84d).

Element maps: Ca migration shallower than IGN/G20MS(150.CO₂.84d).

VI.1.2.3 KAO

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.55.



i. KAO/G(150.CO₂.84d)



iii. KAO/G40SF(150.CO₂.84d)



ii. KAO/G20SF(150.CO₂.84d)



iv. KAO/G20MS(150.CO₂.84d)

Figure VI.55 - Photos of the cross section of the KAO/CEM assemblages exposed at 150°C for 84 days in brine, with CO₂ injection

The G40SF carbonation pink layer looks slightly wider than the one observed for IGN/G40SF(150.CO₂.84d).

b) XRD

Table VI.4 details the phases detected by XRD within each of the zones of the ITZ.

Table VI.4 - compounds identified by XRD analysis: 150°C, with CO ₂ -exposure, 84 days cure	
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Sample Zone Identified peaks and other relevant features							
	CEM	Largely amorphous, with portlandite, unhydrated cement and hillebrandite. Traces of calcite and killalaite. The traces of calcite in CEM indicate a slight carbonation rate in the cement core.					
KAO/G (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with decreased portlandite. Slight increase in hillebrandite and calcite. The reduced portlandite in the ITZ-C, as previously put forward, is probably a consequence of Ca^{2+} and OH^{-} into the rock, leaving lowers amounts of these elements to form portlandite.					
	ITZ-R	Similar to KAO.					
	CEM	Largely amorphous with quartz. Traces of αC_2SH , calcite, unhydrate cement, kilchoanite, killalaite and hillebrandite. The traces of calcite i CEM indicate a slight carbonation rate in the cement core.					
KAO/G20SF (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with increased quartz. The increased quartz in the ITZ- C, as previously seen, is probably a consequence of Ca^{2+} and OH ⁻ into the rock, leaving here larger amounts of unreacted quartz than observed in the core.					
	ITZ-R	Similar to KAO, with traces of calcite. The traces of calcite in the ITZ confirm the idea of Ca^{2+} and OH ⁻ migration into the rock and subseque carbonation.					
	CEM	Largely amorphous with quartz. Traces of kilchoanite, hillebrandite killalaite and tobermorite.					
KAO/G40SF (150.CO ₂ .84d)	ITZ-C	Substantially different to CEM, due to the presence of aragonite considerably high amounts). The amount of amorphous material seems increase as well. The high amounts of aragonite present in the ITZ-C opposed to the absence of aragonite in CEM) confirm the idea previou put forward about the highest carbonation rate in the outermost lay when compared to the cement core. The increase in amorphous mater may confirm the formation of amorphous calcium carbonate.					
	ITZ-R	Similar to KAO.					
	CEM	Largely amorphous, with calcite and kilchoanite. Traces of killalaite at hillebrandite. The calcite in CEM indicates a considerable carbonation rate in the cement core.					
KAO/G20MS (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with increase in calcite and amorphous material. Again, the increased calcite in the ITZ-C confirms the higher carbonation rate in the cement outermost layer, when compared with the core. Again, the increase in amorphous material may indicate that there is some ACC forming as well.					
	ITZ-R	Similar to KAO, with traces of calcite. Again, the traces of calcite in the ITZ-R confirm the idea of Ca ²⁺ and OH ⁻ migration into the rock and subsequent carbonation.					

c) OM

Thin section micrographs for each sample are shown in Figure VI.56-Figure VI.59. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

KAO/G(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.56 - KAO/G(150.CO₂.84d) OM images

<u>CEM</u>: Similar to the one observed in IGN/G(150.CO₂.84d).

ITZ: The ITZ-R is similar to the one observed in IGN/G(150.CO2.84d), although this one looks slightly narrower and more uniform.

KAO/G20SF(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.57 - KAO/G20SF(150.CO₂.84d) OM images

<u>CEM</u>: Similar to the one observed in IGN/G20SF(150.CO₂.84d).

ITZ: More uniform and narrower ITZ-R in comparison to the one observed in IGN/G20SF(150.CO₂.84d).

KAO/G40SF(150.CO₂.84d)



i. ITZ in PPL



ii. ITZ in XPL



iii. Carbonation rim in PPL



iv. Carbonation rim in XPL



CEM: Similar to IGN/G40SF(150.CO₂.84d).

<u>ITZ</u>: Slightly wider carbonation rim when compared to the one observed in IGN/G40SF(150.CO₂.84d).

KAO/G20MS(150.CO₂.84d)



i. ITZ in PPL



Figure VI.59 - KAO/G20MS(150.CO₂.84d) OM images

<u>CEM</u>: Similar to the one observed in IGN/G20MS(150.CO₂.84d).

<u>ITZ</u>: More uniform and narrower bright ITZ-R in comparison with the one observed in IGN/G20MS(150.CO₂.84d). It assumes an orange tone, not so obvious in IGN/G20MS(150.CO₂.84d).

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure VI.60-Figure VI.63. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

KAO/G(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

 $= 100 \, \mu m$

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.60 - KAO/G(150.CO₂.84d) SEM/EDS images

<u>Phase map</u>: Slightly narrower phase transition zone in comparison to the one seen in $IGN/G(150.CO_2.84d)$. <u>Element maps</u>: Slightly shallower and more uniform Ca migration when compared to

IGN/G(150.CO₂.84d).

KAO/G20SF(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map





Figure VI.61 - KAO/G20SF(150.CO₂.84d) SEM/EDS images

Phase map: More abrupt phase transition compared to the one seen in IGN/G20SF(150.CO₂.84d).

Element maps: Lower and more uniform Ca migration than in IGN/G20SF(150.CO₂.84d).

KAO/G40SF(150.CO2.84d)



Key*



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map



Phase map: Similar phase change to the one seen in IGN/G40SF(150.CO₂.84d).

Element maps: Similar Ca migration to the one observed in IGN/G40SF(150.CO₂.84d).

KAO/G20MS(150.CO2.84d)





<u>Key</u>*

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.63 - KAO/G20MS(150.CO₂.84d) SEM/EDS images

Phase map: Phase change similar to the one seen in IGN/G20MS(150.CO₂.84d).

Element maps: The Ca migration is lower than in IGN/G20MS(150.CO₂.84d).

VI.1.2.4 MOR

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.64.



iii. MOR/G40SF(150.CO₂.84d)

iv. MOR/G20MS(150.CO₂.84d)

Figure VI.64 - Photos of the cross section of the MOR/CEM assemblages exposed at 150 $^{o}\rm{C}$ for 84 days in brine, with CO₂ injection

The carbonation rim observed for the G40SF seems to be the narrowest compared to the other equivalent ignimbrite assemblages.

b) XRD

Table VI.5 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features						
	CEM	Largely amorphous, with portlandite, unhydrated cement and hillebrandite.						
MOR/G (150.CO ₂ .84d)	ITZ-C	Traces of calcite and aragonite . Similar to CEM, with reduced portlandite and unhydrated cement , and slight increase in calcite , aragonite and hillebrandite . The reduced portlandite in the ITZ-C, again, may be justified with the Ca ²⁺ and OH ⁻ migration into the rock, leaving less of these to form portlandite . The calcite and aragonite increase in the ITZ-C seem to support the idea of a higher carbonation rate in this zone.						
	ITZ-R	Similar to MOR, with traces of calcite . The traces of calcite in the ITZ-R confirm the idea of Ca^{2+} and OH^{-} migration into the rock and subsequent carbonation.						
	CEM	Largely amorphous, with quartz, αC_2SH and unhydrated cement. Traces of kilchoanite, hillebrandite, calcite and aragonite.						
MOR/G20SF (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with reduced quartz and slightly increase in aragonite and amorphous material . Despite the quartz reduction (which goes against the idea previously put forward about higher amounts of unreacted quartz in the outermost layer of the cement as a consequence of Ca^{2+} and OH ⁻ migration into the rock – this may be justified by a quartz crystal from the rock falling into the the ITZ-C XRD sample), the increase in aragonite seems to confirm a higher carbonation rate in the cement outermost layer, whereas the increase in amorphous material might, again, mean that some ACC is forming in addition to crystalline calcium carbonate.						
	ITZ-R	Similar to MOR, with traces of calcite. The traces of calcite in the ITZ-R confirm the idea of Ca^{2+} and OH^{-} migration into the rock and subsequent carbonation.						
	CEM	Largely amorphous with quartz . Traces of killalaite and hillebrandite .						
MOR/G40SF (150.CO ₂ .84d)	ITZ-C	Considerably different to CEM, mainly due to the presence of high amounts of aragonite as well as some calcite. There is a reduction in killalaite and hillebrandite and increase in quartz and amorphous material . The high amounts of aragonite present in the ITZ-C (as opposed to the absence of aragonite in CEM) confirm the idea previously put forward about the highest carbonation rate in the outermost layer, when compared to the cement core. The quartz increase support the idea of higher amounts of unreacted quartz in the outermost layer of the cement as a consequence of Ca^{2+} and OH ⁻ migration into the rock, reducing the amount of these elements to react with the quartz. The increase in amorphous material may confirm the formation of amorphous calcium carbonate.						
	ITZ-R	Similar to MOR, with traces of calcite. The traces of calcite in the ITZ-R confirm the idea of Ca^{2+} and OH^{-} migration into the rock and subsequent carbonation.						
	CEM	Largely amorphous, with calcite and unhydrated cement . Traces of aragonite .						
MOR/G20MS	ITZ-C	Similar to CEM, with calcite and aragonite increase. The calcite and aragonite increase in the ITZ-C seem to support the idea of a higher carbonation rate in this zone.						
(13 0.CO2.04u)	ITZ-R	Similar to MOR, with traces of calcite and hillebrandite. The traces of calcite in the ITZ-R confirm the idea of Ca^{2+} and OH^{-} migration into the rock and subsequent carbonation.						

Table	VI.5	- com	ounds	identified	l hv	XRD	analysis	: 150°C	with	СОл-ех	nosure.	84 da	vs cure
Lanc	11.0	- com	Jounus	iucintiticu	L D J	m	anarysis	. 150 0	, WIUII	CO_2 - CA	posure,	UT ua	ys curc

c) OM

Thin section micrographs for each sample are shown in Figure VI.65-Figure VI.68. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

MOR/G(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.65 - MOR/G(150.CO₂.84d) OM images

<u>CEM</u>: Similar to that observed in IGN/G(150.CO₂.84d).

ITZ: Narrower bright ITZ-R than that observed in IGN/G(150.CO₂.84d).

MOR/G20SF(150.CO₂.84d)



i. ITZ in PPL



ii. ITZ in XPL

Figure VI.66 - MOR/G20SF(150.CO₂.84d) OM images

<u>CEM</u>: Similar cement to the IGN/G20SF(150.CO₂.84d).

<u>ITZ</u>: Similar width but less homogeneous bright ITZ-R than that observed in IGN/G20SF(150.CO₂.84d).

MOR/G40SF(150.CO₂.84d)



i. ITZ in PPL



iii. Carbonation rim in PPL



ii. ITZ in XPL



iv. Carbonation rim in XPL

Figure VI.67 - MOR/G40SF(150.CO₂.84d) OM images

<u>CEM</u>: Similar to that observed in IGN/G40SF(150.CO₂.84d).

ITZ: Narrower carbonation rim compared to that observed in IGN/G40SF(150.CO₂.84d).

MOR/G20MS(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.68 - MOR/G20MS(150.CO₂.84d) OM images

<u>CEM</u>: Similar to that observed in IGN/G20MS(150.CO₂.84d).

<u>ITZ</u>: More uniform and slightly narrower bright ITZ-R. Unlike in the IGN/G20MS(150.CO₂.84d), some brownish tones seem to appear in the ITZ-R.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure VI.69-Figure VI.72. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

MOR/G(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.69 - MOR/G(150.CO₂.84d) SEM/EDS images

<u>Phase map</u>: More abrupt phase change than the ones observed in IGN/G(150.CO₂.84d).

Element maps: Lower Ca migration than the one observed in IGN/G(150.CO₂.84d).

MOR/G20SF(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.70 - MOR/G20SF(150.CO₂.84d) SEM/EDS images

Phase map: More abrupt phase changes than those observed in IGN/G20SF(150.CO₂.84d).

Element maps: Lower Ca migration than that observed in IGN/G20SF(150.CO₂.84d).

MOR/G40SF(150.CO₂.84d)



Key*



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



100 tam

iii. ITZ Si map

Figure VI.71 - MOR/G40SF(150.CO₂.84d) SEM/EDS images

<u>Phase map</u>: Similar phase change to that observed in IGN/G40SF(150.CO₂.84d).

Element maps: Similar Ca migration to that observed in IGN/G40SF(150.CO₂.84d).

MOR/G20MS(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

 $= 100 \, \mu m$

i. ITZ Ca/Si phase map





ii. ITZ Ca map Figure VI.72 - MOR/G20MS(150.CO₂.84d) SEM/EDS images

Phase map: Similar phase change to that seen in IGN/G20MS(150.CO₂.84d).

<u>Element maps</u>: Similar Ca migration extent, but in lower amounts, when compared to that observed in IGN/G20MS(150.CO₂.84d). The Ca is clearly concentrated in the rock voids.

VI.1.2.5 RHY

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.73.



ii. RHY/G20SF(150.CO₂.84d)

4

6

iii. RHY/G40SF(150.CO₂.84d) iv. RHY/G20MS(150.CO₂.84d) Figure VI.73 - Photos of the cross section of the RHY/CEM assemblages exposed at 150°C for 84 days in brine, with CO₂ injection

Little pink carbonation was found in the outermost layer of G40SF.
b) XRD

Table VI.6 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features		
	CEM	Largely amorphous with portlandite and unhydrated cement . Traces of hillebrandite , kilchoanite and killalaite . Perhaps small traces of calcite		
RHY/G (150.CO ₂ .84d)	ITZ-C	Similar to CEM, with reduced portlandite and increased amorphous material . Perhaps, small traces of calcite . The reduced portlandite confirms the migration of Ca^{2+} and OH ⁻ and, consequently, restricting portlandite formation in the cement outermost layer. There are no obvious traces of calcite. This seems to be due to the low permeability of this rock, as a consequence of its low porosity (lower than any of the other rocks under study). This low permeability reduces the CO_2 flow into the cement. The significant increase in amorphous material, however, may mean some amorphous calcium carbonate forming, rather than crystalline calcium carbonate. This could mean that this lower CO_2 flow may be forming less calcium carbonates and/or enhancing the formation of ACC rather than CC.		
	ITZ-R	Similar to RHY, perhaps with small traces of calcite . The presence of calcite (although in very low amounts) seems to indicate migration of the cement compounds into the rock (mostly Ca^{2+}), and subsequent carbonation.		
	CEM	Largely amorphous with quartz. Traces of kilchoanite, αC_2SH , unhydrated cement, kilchoanite, killalaite, hillebrandite and, perhaps, calcite and aragonite.		
RHY/G20SF (150.CO ₂ .84d)	ITZ-C	Similar to CEM. Perhaps some very small increase in amorphous material . The XRD results couldn't identify obvious presence of calcium carbonates, although the slight increase in amorphous material might be due to the presence of small amounts of ACC. Anyway, the lower amounts of calcium carbonates are, again, probably due to the low permeability of this rock, as a consequence of its low porosity.		
	ITZ-R	Similar to RHY.		
RHY/G40SF (150.CO ₂ .84d)	CEM	Largely amorphous with quartz and tobermorite . Traces of kilchoanite , killalaite and unhydrated cement . The presence of significant amounts of tobermorite along with absence of calcium carbonate in the CEM (more than in the G40SF in the same conditions and combined with the other rocks) may mean that the tobermorite is not carbonating as faster as observed for the others. This seems to support the idea of a reduced carbonation rate, when compared with the cement combined with the ignimbrites due to the lower permeability of this rock		
	ITZ-C	Similar to CEM, with reduced tobermorite and slight increase amorphous material . Traces of a ragonite . The reduced tobermorite along with the traces of aragonite (not detected in the CEM) seem to indicate some small carbonation in the ITZ-C, whereas the slight increase in amorphous material may mean that some ACC is forming as well.		
	ITZ-R	Similar to RHY. Perhaps some small traces of aragonite and increase in amorphous material . The traces of aragonite and the increase in amorphous material in the ITZ- R seem to confirm some Ca ²⁺ and OH ⁻ migration and subsequent carbonation, where some ACC may be forming as well (besides aragonite).		
RHY/G20MS (150.CO ₂ .84d)	CEM	Largely amorphous with killalaite , kilchoanite , hillebrandite and unhydrated cement . Perhaps some traces of calcite .		
	ITZ-C	Similar to CEM. Perhaps some decrease in unhydrated cement and slight increase in amorphous material . There are no obvious traces of calcite. Again, this is probably due to the low permeability of this rock, as a consequence of its low porosity (lower than any of the other rocks under study). This low permeability reduces the CO_2 flow into the cement. The significant increase in amorphous material, however, may mean some amorphous calcium carbonate forming, rather than crystalline calcium carbonate.		
	ITZ-R	Similar to RHY. Perhaps some increase amorphous material and traces of aragonite and hillebrandite. The traces of hillebrandite and aragonite seem to confirm some Ca^{2+} and OH ⁻ migration and subsequent carbonation, whereas the increase in amorphous material in the ITZ-R may indicate the formation of ACC.		

T 11 T T T			1 = 00 0 101 00	0.4.1
Table VI.6 - com	pounds identified by	XRD analysis:	150°C, with CC	$_2$ -exposure, 84 days cure

c) OM

Thin section micrographs for each sample are shown in Figure VI.74-Figure VI.77. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

RHY/G(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.74 - RHY/G(150.CO₂.84d) OM images

CEM: Similar to IGN/G20SF(150.CO₂.84d).

ITZ: This is much narrower bright ITZ-R than the one observed in IGN/G(150.CO₂.84d).

RHY/G20SF(150.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.75 - RHY/G20SF(150.CO₂.84d) OM images

CEM: Similar to IGN/G20SF(150.CO₂.84d).

ITZ: This is a much narrower (almost unnoticeable) bright ITZ-R than the one observed in IGN/G20SF(150.CO₂.84d).

RHY/G40SF(150.CO₂.84d)



i. ITZ in PPL



iii. Carbonation spot in PPL



ii. ITZ in XPL



iv. Carbonation spot in XPL

Figure VI.76 - RHY/G40SF(150.CO₂.84d) OM images

<u>CEM</u>: Similar to the one observed in IGN/G40SF(150.CO₂.84d).

<u>ITZ</u>: There are just a few random spots in the ITZ-C that are fully carbonated, in which the cement shows a different pattern to the rest.

RHY/G20MS(150.CO₂.84d)



i. ITZ in PPL



Figure VI.77 - RHY/G20MS(150.CO₂.84d) OM images

<u>CEM</u>: Lighter colour than the one observed in IGN/G20MS(150.CO₂.84d)

ITZ: Much narrower bright ITZ-R than the one observed in IGN/G20MS(150.CO₂.84d).

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure VI.78-Figure VI.81. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

RHY/G(150.CO₂.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

 $= 100 \, \mu m$

100 um





ii. ITZ Ca map



iii. ITZ Si map

Figure VI.78 - RHY/G(150.CO₂.84d) SEM/EDS images

<u>Phase map</u>: More abrupt cement/rock phase change than that observed in IGN/G(150.CO₂.84d). <u>Element maps</u>: Much lower Ca migration in comparison with that observed in IGN/G(150.CO₂.84d). **RHY/G20SF(150.CO₂.84d)**





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

Ξ= 100 μm

i. ITZ Ca/Si phase map



ii. ITZ Ca map







Phase map: More abrupt phase change than the one observed in IGN/G20SF(150.CO₂.84d).

<u>Element maps</u>: Very reduced and shallower Ca migration in comparison with the one observed in IGN/G20SF(150.CO₂.84d).

RHY/G40SF(150.CO₂.84d)





Key*

*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map

100 um



Figure VI.80 - RHY/G40SF(150.CO₂.84d) SEM/EDS images

Phase map: More abrupt phase change than IGN/G40SF(150.CO₂.84d).

<u>Element maps</u>: Much shallower Ca migration in comparison with the one observed in IGN/G40SF(150.CO₂.84d).

RHY/G20MS(150.CO₂.84d)



Key*



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



i. ITZ Ca/Si phase map



ii. ITZ Ca map





Figure VI.81 - RHY/G20MS(150.CO₂.84d) SEM/EDS images

Phase map: More abrupt phase change than the one observed in IGN/G20MS(150.CO₂.84d).

Element maps: Much shallower Ca migration than the one observed in IGN/G20MS(150.CO₂.84d).

VI.2 290°C cure

VI.2.1 With CO₂ exposure

VI.2.1.1 IGN

a) Mesoscopic Images

Samples of cut surfaces are shown in Figure VI.82.



iii. IGN/G40SF(290.CO₂.84d)

iv. IGN/G20MS(290.CO2.84d)

Figure VI.82 - Photos of the cross section of the IGN/CEM assemblages exposed at 290°C for 84 days in brine, with CO_2 injection

The most noticeable features are the reddish colour in both the rock and the cements, except for the G20MS.

b) XRD

Table VI.7 details the phases detected by XRD within each of the zones of the ITZ.

Sample	Zone	Identified peaks and other relevant features				
	CEM	Largely amorphous, with portlandite, calcite and reinhardbraunsite. Traces of unhydrated cement.				
IGN/G (290.CO ₂ .84d)	ITZ-C	Similar to CEM.				
	ITZ-R	Similar to IGN.				
IGN/G20SF (290.CO ₂ .84d)	CEM	Large amounts of calcite. Traces of xonotlite.				
	ITZ-C	Similar to CEM.				
	ITZ-R	Similar to IGN.				
IGN/G40SF (290.CO ₂ .84d)	CEM	Large amounts of calcite and quartz. Traces of xonotlite.				
	ITZ-C	Similar to CEM with quartz increase.				
	ITZ-R	Similar to IGN.				
IGN/G20MS (290.CO ₂ .84d)	CEM	Large amounts of calcite and xonotlite.				
	ITZ-C	Similar to CEM, perhaps with a slight increase in amorphous material.				
	ITZ-R	Similar to IGN.				

Table VI.7 -	 compounds identified by X 	(RD analysis: 290°C, with	CO ₂ -exposure, 84 days cure

c) OM

Thin section micrographs for each sample are shown in Figure VI.83-Figure VI.86. The cement is on the left and the rock on the right. Micrographs under plane polarised light are the left figure and crossed polars on the right.

IGN/G(290.CO₂.84d)



i. ITZ in PPL

ii. ITZ in XPL

Figure VI.83 - IGN/G(290.CO₂.84d) OM images <u>CEM</u>: In PPL this cement looks similar to the IGN/G(290.28d) one, whereas by XPL is brighter. <u>ITZ</u>: Like in IGN/G(290.28d), a fissure has formed along the ITZ-C. The ITZ-C looks extremely bright in XPL, whereas the ITZ-R is not easily noticeable.



$IGN/G20SF(290.CO_2.84d)$

ITZ in PPL

ITZ in XPL

Figure VI.84 - IGN/G20SF(290.CO₂.84d) OM images

<u>CEM</u>: In PPL this cement looks darker than the IGN/G20SF(290.28d), whereas in XPL looks brighter.

<u>ITZ</u>: Like in IGN/G20SF(290.28d), a fissure has formed, splitting the ITZ-C and ITZ-R. The ITZ-C looks extremely bright in XPL, whereas the ITZ-R is not easily noticeable.

$IGN/G40SF(290.CO_2.84d)$



Figure VI.85 - IGN/G40SF(290.CO₂.84d) OM images

<u>CEM</u>: This cement is substantially darker when compared with the IGNG40SF(290.28d).

<u>ITZ</u>: No obvious differences between ITZ-C and CEM. Like in IGN/G40SF(290.28d), a fissure has formed between ITZ-C and ITZ-R.

IGN/G20MS(290.CO₂.84d)



Figure VI.86 - IGN/G20MS(290.CO₂.84d) OM images

CEM: This cement is substantially darker when compared with the IGN20MS(290.28d).

<u>ITZ</u>: No obvious differences between ITZ-C and CEM. Like in IGN/G20MS(290.28d), a fissure has formed between ITZ-C and ITZ-R.

d) SEM/EDS

Detailed below are the phase and elemental maps in Figure VI.87-Figure VI.90. The phase map showing approximate Ca/Si ratios has been created from a short software package developed as part of this work as the supplied analytical package was unsuitable.

These maps are presented in accordance with the description given in the section V.1.1 d).

IGN/G(290.CO₂.84d)





^{*}these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



iii. ITZ Si map

Figure VI.87 - IGN/G(290.CO₂.84d) SEM/EDS images

<u>Phase map</u>: Relatively sudden phase change from cement (blue) to the rock (red).

<u>Element maps</u>: There is not much Ca migration, which goes only up to $100\mu m$.

IGN/G20SF(290.CO2.84d)





*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample

i. ITZ Ca/Si phase map



ii. ITZ Ca map



Figure VI.88 - IGN/G20SF(290.CO₂.84d) SEM/EDS images

<u>Phase map</u>: This phase map shows an odd ITZ, which may be consequence of the stressed induced in the sample during the cure and/or during the sample preparation.

Element maps: The Ca migration is not visible in this image.

IGN/G40SF(290.CO2.84d)



i. ITZ-C Ca/Si phase map (CEMENT side)



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



ii. ITZ-R Ca/Si phase map (ROCK side)



iii. ITZ-C Ca map (CEMENT side)



v. ITZ-C Si map (CEMENT side) Figure VI 89 - IGN/(



iv. ITZ-R Ca map (ROCK side)



vi. ITZ-R Si map (ROCK side)

Figure VI.89 - IGN/G40SF(290.CO₂.84d) SEM/EDS images

<u>Phase maps</u>: Relatively abrupt phase change.

Element maps: Ca migration lower than in IGN/G40SF(150.CO₂.84d).

IGN/G20MS(290.CO2.84d)



i. ITZ-C Ca/Si phase map (CEMENT side)

Key*



*these are just approximate value ranges for the Ca/Si ratios and they may vary for each sample



ii. ITZ-R Ca/Si phase map (ROCK side)



iii. ITZ-C Ca map (CEMENT side)



iv. ITZ-R Ca map (ROCK side)





v. ITZ-C Si map (CEMENT side) Figure VI.90 - IGN/G20MS(290.CO₂.84d) SEM/EDS images

<u>Phase maps</u>: There is a relatively abrupt phase change between the rock and the cement.

Element maps: Shallower Ca migration than IGN/G20MS(150.CO₂.84d).

e) HCl test

This test was undertaken on the ITZ-C of IGN/G(290.CO₂.84d) and significant effervescence was observed, indicating presence of carbonates in this sample.

f) TGA and Mass Spec



Figure VI.91 - TGA result of IGN/G(290.CO₂.84d) ITZ-C



Figure VI.92 - Mass Spec result of IGN/G(290.CO₂.84d) ITZ-C

This sample also shows material decomposing within the range 450° C to 650° C, where CO₂ is being released (**Figure VI.91** and **Figure VI.92**). This may mean that also here there is formation of significant amounts of other carbonates, rather than crystalline calcium carbonates (namely calcite and aragonite). In the **appendix X.5** it can be found the comparison of the CO₂ released in this sample with the other ones and with calcite (the reference calcium carbonate).

VII. DISCUSSION OF THE RESULTS

The requirements for a suitable geothermal cementing system were first enunciated over 30 years ago by the API task force when geothermal development first started to become popular. (API Task Force, 1985). These are:

- Compressive strength, > 1000 psi 24 hours after placement;
- Permeability to water, < 0.1 m Darcy;
- Bond strength to steel casing, > 10 psi;
- Stability, no significant reduction in strength or increase in permeability after prolonged exposure at 400°C to 25% brine solutions, flashing brine, or dry steam;
- Placement ability, capable of 3 to 4 hr retardation at expected placement temperatures;
- Compatibility of the cement with drilling mud;
- Noncorrosive to steel well casing.

These are still cited as desirable properties, despite a better understanding of the reactions that occur downhole (Herianto and Fathaddin, 2005). Surprisingly, a corresponding set of requirements regarding the mechanical and chemical interaction between the cement formulation and the rock formation in geothermal wells have not been developed, despite considerable work being conducted on well integrity. Work on shear stress analysis is now appearing (Oyibo and Radinjic, 2014; Agbasimalo and Radonjic, 2011), Herianto and Fathaddin (2005) and a revival of the cement bond logging which was largely discontinued in New Zealand wells. The literature review presented in this thesis has raised several issues which are associated with distinct variables, some of which have been examined. Above all, it can be inferred that a good mechanical bond between the cement and the formation is crucial to the performance of the whole well system and could extend the life time of the well. Any gaps that occur between the cement and the formation are undesirable, as these are potential pathways for the geothermal fluids, which are usually prove detrimental for the cement.

The API Task Force (1985) recommended a "Placement ability" of a cement, which should be capable of 3 to 4 hour retardation at the expected placement temperatures for wells. This suggests a relatively slow rather than a rapid setting is required for geothermal cements, in order to allow sufficient time for the cement to be able to flow down the well, before it reaches its ultimate destination. It would also allow time for fine cement particles to penetrate the porous formation enabling a good bond to form. From the literature review, it could be anticipated that the physical migration of cement into the rock improves the bonding between the cement and the rock. The experimental results have reported migration of Ca^{2+} ions towards the rock, driven by chemical gradient, which will reduce the Ca/Si ratio of the cement. This may affect the phases formed in the outermost layer of the cement and, consequently, decrease the bonding properties of the cement in this zone. Anything which detracts from that bond formation will lead to an inferior performance. The results obtained in this work show that both CO_2 and the presence of a drilling mud layer will affect this migration.

This chapter focuses on the analysis and interpretation of the interactions occurring in the Interfacial Transition Zones (ITZ's), tying in the experimental results and addressing these two important issues. The cement (CEM) and the rock are also analysed when necessary along with their respective ITZ's, as these materials are used as reference for ITZ-C and ITZ-R respectively. Results are discussed as a function of the cement formulation, and divided in three main sections: 1) Portland based cements; 2) Alternative Cementing System: Calcium aluminium cement; and 3) Overall discussion. The latter one summarizes the main findings and, based on these along with the literature review, proposes some recommendations for geothermal well cements.

In the first two sections, several comparisons are made, in order to understand the effect of each one of the variables on the way that the cement interacts with the rock formation. Control reference samples have been exposed at the same conditions as the studied specimens and are further explained in the section III.4 (*sample labelling*).

In order to discuss the effect of each variable, the formulations are presented in the following sequence:

- <u>Standard</u>: IGN/CEM(150.28d) Evaluation and interpretation of the main features in the ITZ between the cement formulation under study and IGN, exposed at 150°C for 28 days in brine. When necessary, it is compared with other cement formulations.
- Curing time: IGN/CEM(150.84d) Assessment and analysis of the main features in the ITZ between the cement formulation under study and IGN, exposed at 150°C for 84 days in brine. The most relevant differences between the current sample and the control one (IGN/CEM(150.28d): same conditions, but cured for only 28 days) are

discussed as well. This analysis is only available for the API class G based cements, as the other cements have only been cured for 28 days.

- Drilling mud (bentonite): IGN/CEM(150.b.28d) Discussion of the main features in the ITZ between the cement formulation under study and IGN with a **bentonite** layer, exposed at **150°C** for **28 days** in brine. The results are compared to the control (IGN/CEM(150.28d): same conditions, but without drilling mud simulation).
- Curing temperature: IGN/CEM(290.28d) Evaluation and interpretation of the main features in the ITZ between the cement formulation under study and IGN, exposed at 290°C for 28 days in brine. The most relevant differences between the current sample and the control one (IGN/CEM(150.28d): same conditions, but exposed to 150°C) are discussed as well.
- 4 <u>CO₂ exposure</u>: Only the API class G based formulations were exposed to CO₂. This section is divided in two sub-sections: a) 150° C and b) 290° C.
 - a) <u>150°C</u>: IGN/CEM(150.CO₂.84d) Assessment and analysis of the main features in the ITZ between the cement formulation under study and IGN, exposed at **150°C** for **84 days** in **CO**₂ enriched brine. The most relevant differences between the current sample and the control one (IGN/CEM(150.84d): same conditions, but without CO₂ injection) are also discussed.
 - b) <u>290°C</u>: IGN/CEM(290.CO₂.84d) Discussion of the main features in the ITZ between the cement formulation under study and IGN, exposed at **290°C** for **84 days** in **CO₂** enriched brine. As opposed to all the other samples, these do not have ideal control samples, as the ones cured at 290°C without CO₂ exposure have another variable changing, i.e. curing time (28 days rather than 84 days). Therefore, both variables (CO₂ exposure and curing time) will be taken into consideration in the discussion of the most relevant differences between the current sample and the control one (IGN/CEM(290.28d): same conditions, but without CO₂ exposure and exposed for only 28 days).
- Rock type: This analysis is only available for the API class G based cements, as the other ones were only tested with IGN. This section is divided in four sub-sections: a) UNI; b) KAO; c) MOR and d) RHY.
 - a) <u>UNI</u>: UNI/CEM(150.CO₂.84d) Evaluation and interpretation of the main features in the ITZ between the cement formulation under study and UNI, exposed at 150°C for 84 days in CO₂ enriched brine. The results are compared to the control (IGN/CEM(150.CO₂.84d): same conditions with different rock type).

- b) <u>KAO</u>: KAO/CEM(150.CO₂.84d) Similar to a). The similarities in apparent porosity and amorphous silica content make it also relevant to compare it with UNI/CEM(150.CO₂.84d).
- c) MOR: MOR/CEM(150.CO₂.84d) Similar to a).
- <u>RHY</u>: RHY/CEM(150.CO₂.84d) Similar to a). As this is the only non-ignimbrite under study, general comparisons between this rock type and all the other studied ignimbrite rocks are made.

VII.1 Portland cement based systems

VII.1.1 API Class G

VII.1.1.1 <u>Standard</u>: IGN/G(150.28d)

XRD shows the crystals seen in CEM by OM are mostly portlandite $(Ca(OH)_2)$, with small amounts of unhydrated cement, along with isotropic material that is mostly amorphous. Small quantities of calcite were also detected in the cement. The lower amount of crystals in the ITZ-C seen by XPL compared to CEM is due to the reduced amount of portlandite. This is a consequence of migration of Ca²⁺ and OH⁻ ions from the cement into the ITZ-R and perhaps into the bulk of the ignimbrite. Although not confirmed by XRD, the increase of bright spots from IGN to ITZ-R is most probably due to portlandite that has formed from migrating Ca²⁺ and OH⁻.

The very distinctive dark ITZ zone seen by OM indicates a reaction rim at the interface where new compounds may form. No new compounds were detected in the ITZ by XRD, despite the marked decrease in the amount of portlandite in the ITZ-C compared to the CEM. The milky material seen under XPL suggests that amorphous silica gel has formed in the ITZ-R, confirmed by the homogeneous Si concentration across the whole ITZ-R.

The SEM/EDS phase and element maps show that the migration of Ca^{2+} ions occurs mainly through the rock pores. Additionally, the Si concentration seems to be the highest in the ITZ-R, particularly where it is closest to the cement, meaning that a Si containing material is also filling the rock pores, complementing the high Si content in the rock. This observation, combined with the two distinct ITZ-R rims in OM (darker and lighter brown in PPL),

suggests that cement migration occurs in two distinct stages/processes: an initial/physical one and a final/chemical one, already been reported by Duguid *et al.* (2011).

The physical migration happens initially before the cement has set, so all the cement constituents flow together in an aqueous suspension (by capillarity), into the rock pores. The fact that the rock has pores which are larger than the unhydrated class G cement particles is in agreement with this idea. Consequently, there is a significant presence of additional Si (from the cement) in the rock pores and a distinguishable darker ITZ-R rim. Duguid (2011) stated that the penetration of the cement particles into the formation is a good thing, as the cement that invades the stone blocks some of the rock pores and reduces the the amount of CO_2 enriched brine able to contact the cement. He suggests this will prevent the damage of the cement in the outermost layer and therefore delay the development of a gap at the interface.

The chemical migration occurs after the cement has set, but the chemical elements (mostly Ca^{2+} and OH^{-}) continue to migrate into the rock through a chemical driving gradient. The final stage is characterized by a slower migration of mostly Ca (no significant amounts of Si available in the rock pores), forming the second ITZ-R rim (lighter brown in PPL).

The amorphous silica gel formation mentioned above could be a consequence of an alkalisilica reaction which occurs due to the presence of SiO_2 coming from either the cement by physical migration and lodging in the rock pores of the ITZ-R zone closest to the cement, or from the rock itself solubilised by OH⁻ ions migrating from the cement into the rock. The zeolites and feldspars reported by Hodgkinson and Hughes (1999) were not detected here. Their formation may have been inhibited or transformed by the prescence of calcium, through a pozzolanic reaction to form other calcium aluminosilicates, rather than zeolites. The feldspars were impossible to track as they are also present in the heterogeneous rock.

VII.1.1.2 Curing time: IGN/G(150.84d)

In a similar way to the one month cured sample, there is a decrease in portlandite and an increase in calcite going from CEM to ITZ-C due to migration of Ca^{2+} and OH^- ions into the ITZ-R with carbonation of the outermost exposed layer fixing Ca^{2+} ions as insoluble carbonate. Portlandite, hillebrandite and killalaite, along with calcite seem to be present in the ITZ-R, indicating that the migrating Ca^{2+} and OH^- ions may be reacting with the siliceous glass in the rock to form these compounds, although in much lower amounts than in the cement.

OM shows a very distinctive ITZ rim, which is wider than in the equivalent one month cured sample. In the ITZ, these crystals are mostly concentrated along the line between ITZ-C and ITZ-R, which could be explained by formation of small amounts of calcite (detected by XRD) from the reaction between the migrating Ca^{2+} with CO_2 from the air during the setting of the cement. It is possible that the interaction with the geobrine at the cement surface enhances this reaction.

The lighter and darker ITZ-R rims distinguished in the IGN/G(150.28d) sample by OM, have coalesced into one single uniform and slightly wider, dark rim. This may indicate that during the second and third months of cure, the Ca^{2+} and OH^{-} migration is still happening, although slower than during the first month and only through chemical driving forces (rather than physical forces). This is in agreement with the SEM/EDS results, which show that Ca has penetrated further and in higher amounts into the rock than after 28 days curing.

VII.1.1.3 <u>Drilling mud</u>: IGN/G(150.b.28d)

The presence of the bentonite layer, which can be easily seen by OM, changes the reaction sequence, which occurs over a wider ITZ. From XRD, a new mineral forms, mostly in ITZ-R. This is gehlenite, Ca₂Al₂SiO₇, which is due to an interaction of cement with bentonite. Milestone *et al.* (1987b) showed bentonite reacted readily and affected the phases formed. This suggests that the calcium and silica from the cement, and, perhaps the silica from the rock as well, may react with aluminium from the bentonite (likely to be more reactive than the ignimbrite) to form gehlenite or that compound may crystallise directly from the mixture of ions in an alkaline environment. It is unusual to see this compound which is normally associated with slag cements.

The addition of a bentonite layer decreases the bonding between the cement and the rock, in other words a weak zone seems to form in the ITZ. This may be due to the formation of more crystalline phases, probably due to the ready availability of aluminium as the bentonite reacts. Bensted and Hewlett (2008) examined hydrogarnet-type cements, where the predominant strätlingite or gehlenite hydrate, $Ca_2Al_2(SiO_2)(OH)_{10}\bullet 2.5(H_2O)$, binder had high compressive strengths (ca. 110-136 MPa) and low porosities (1-10 %). However, these cements are unstable above 100°C forming gehlenite, which may be the reason for the poor cement-rock bonding performance of samples with bentonite, as the specimens were cured at 150°C.

The decreased bond between the cement and the rock as a consequence of the use of drilling mud has been reported in several studies (Agbasimalo, 2012; Ravi *et al.*, 1992; Peterson, 1963; Ladva *et al.*; 2005; Oyibo and Radonjic, 2014). These studies have concluded that both physical (formation of mud cake in the ITZ) and chemical (formation of different hydrates in the cement outermost layer) are detrimental to the bond between the cement and the rock. Oyibo and Radonjic (2014) compared these two types of drilling mud contamination and have concluded that the formation of the mud cake was the most detrimental one. The current work has focused on the physical contamination and is consistent with the above mentioned references. The formation of a thin physical barrier (comparable to the mud cake) between the cement and the rock.

When compared with the equivalent sample without bentonite, IGN/G(150.28d), Ca penetrates significantly deeper into the rock. This further migration might be driven by cation exchange as when Al from bentonite is substituted into a silicate network, it requires a counter cation.

VII.1.1.4 <u>Curing temperature</u>: IGN/G(290.28d)

The most noticeable feature of this cement sample is the reddish colour seen by the unaided eye which is likely due to the iron oxidation, i.e. dissolution of the iron present and subsequent precipitation as a red coloured iron oxide, perhaps hematite, with iron as Fe(III). A similar process seems to have happened in the rock, where the interior zones have also turned red, probably indicating a high concentration of iron oxide, whereas the external zones became light green, losing their light brown colour, which has been ascribed to the homogeneous presence of oxidised Fe (Henneberger, 1983). This suggests the iron is dissolving under the hydrothermal conditions, which are harsher in the external areas of the rock, and moving and precipitating in the interior areas of the rock, where the conditions are not as harsh as in the exterior. The traces of hematite detected in the IGN red zone by XRD support this idea.

The increased temperature of curing leads to the formation of other minerals in the cement, namely reinhardbraunsite and jaffeite. These are the high temperature, high Ca/Si ratio phases not present in the 150°C specimens, forming along with portlandite and considerably less amorphous material.

Although both Ca^{2+} and SiO_2 penetrate into the rock, there is a fissure in the ITZ which splits the cement from the rock, and indicates a loss of bonding. The calcium silicate phases formed at 290°C are weak and loss of Ca^{2+} and OH⁻ due to migration could have weakened the binder still further. This fissure seen by OM, may have been caused by stresses induced in the ITZ during cooling due to the differential thermal expansion/contraction between the cement and the rock. This break has happened in the ITZ-C, splitting the outermost layer of the cement from the rest of the cement, and may be a consequence of Ca^{2+} and OH^- migration into the rock, which would have weakened the binder in the ITZ-C.

The Ca migration is shallower compared to the 150°C specimens. This could be due to faster setting/cure of the cement at 290°C, restricting further migration. Additionally, the above mentioned fissure might have worked as a physical constraint, preventing Ca^{2+} migration.

VII.1.1.5 CO₂ exposure:

a) <u>150°C</u>: IGN/G(150.CO₂.84d)

The feature that stands out in this sample is the increased amount of calcium carbonates in ITZ-C, the zone most exposed to CO_2 and, especially, HCO_3^- (dissolved CO_2). According to Duguid (2009), this result is predictable due to the high porosity and permeability of the rock which allows CO_2 (aq) to be in permanent contact with the exterior layer of the cement. Furthermore, any possible gaps in the ITZ (between the rock and cement) may increase the amount of dissolved CO_2 in the ITZ, as seen by Carey *et al.* (2007). They realized that CO_2 could migrate along a pre-existing gap in the interface between a well cement and shale caprock that was exposed to CO_2 -rich brine at 54°C.

The outermost layer of the cement itself seems to restrict the CO_2 from penetrating further into the cement, due to its very low permeability after carbonation. This is in accordance with several studies undertaken at lower temperatures, where differentiated layers formed. The exterior ones being more carbonated than the interior ones, due to a diffusion mechanism (Andac and Glasser, 1999; Milestone *et al.*, 1986 a, b; Kutchko *et al.*, 2007, 2008; Carey *et al.*, 2007; Barlet-Gouedard *et al.*, 2006; Duguid *et al.*, 2005; Duguid, 2009). The differentiated layers found in some of these studies are not obvious in the current research. Rimmelé *et al.* (2008) suggested this distinct banding was probably due to different exposure conditions. Most of the studies were made in EGS-CO₂ or CO₂ sequestration conditions, where the CO_2 overpressure is significantly higher than in the current study, where the carbonation rate is slower.

The extremely bright ITZ seen by OM indicates the presence of new compound(s), likely to be a product of carbonation. The considerably high amounts of C detected by EDS and shown in the map and spot analyses, confirm the presence of a carbonate. The relatively large amounts of C (compared to Ca) suggest that this is calcium carbonate, CaCO₃, which has formed according to the **Equation III.13**, **Equation III.14**, **Equation III.15** and/or **Equation III.16**. This carbonate needs just over 3 times more Ca than C (in weight), whereas scawtite, $Ca_7Si_6(CO_3)O_{18}\bullet 2(H_2O)$, would need over 23 times more Ca than C to form. Moreover, the composition of SPOT 7 (Ca=40.91wt.%; C=11.45wt.%; O=43.10wt.%) shows a very similar composition to the characteristic composition of CaCO₃ (Ca=40.04wt%; C=12.00wt.%; O=47.96wt.%). This confirms that significant amounts of CaCO₃ are present in the ITZ.

Thermogravimetry (TGA) showed a relatively broad temperature range (450-800°C) for CaCO₃ decomposition. Large amounts of material decomposed at temperatures under 650°C, which is well below that for calcite (or any other crystalline CaCO₃ polymorph), while the Mass Specrometry (Mass Spec) detected significant amounts of CO₂ released over this decomposition range. Several studies (Cole and Kroone, 1960; Sauman, 1971; Villain and Platret, 2006; Thiery et al., 2007; Galan et al., 2003) also reported the existence of a relatively broad thermal decomposition of CaCO₃, some of which agreed with the distinction of three modes of decomposition of CaCO₃, as a function of the temperature, T: mode I (780°C<T<990°C), mode II (680°C<T<780°C) and mode III (550°C<T<680°C). These modes correspond to different carbonation products and can coexist in the ultimate state of carbonation (Thiery et al., 2007). Suman (1971) stated that these modes of decomposition progressively rise as the level of carbonation increases. According to this author, mode I is due to the decomposition of well crystallised calcite, whereas mode II is the consequence of the decomposition of a poorly crystalline calcite. He felt this thermally less stable "calcite" associated with the mode II was a product of the transformation of the metastable polymorphs vaterite and aragonite, when heated to 440-470°C. Mode III has been more difficult to characterise.

Cole and Kroone (1960) demonstrated that the amount of CO_2 measured by TGA over the temperature range 650-950°C (modes I and II) largely underestimated all the chemically fixed CO_2 in carbonated Portland cement. Furthermore, Kondo et al. (1969) demonstrated that the total amount of crystallized CaCO₃ determined by XRD underestimated the carbon dioxide

quantified by chemical analysis. These authors justified this discrepancy by the presence of amorphous calcium carbonate (ACC). In addition, ACC had been previously characterized (Brecevic and Nielsen, 1959) and, according to Thiery et al. (2007), could be associated with thermal mode III. In their work, Thiery et al. (2007) found the mode III to be a consequence of high CO_2 concentration which accelerated the carbonation rate. These authors felt this rapid carbonation process did not allow enough time for the Ca²⁺ ions to migrate to form a well ordered crystalline CaCO₃, namely calcite. Instead, they suggested that metastable (vaterite and aragonite) and amorphous CaCO₃ were present.

The references above along with the fact that little material decomposes at temperatures above $780^{\circ}C$ (corresponding to the decomposition mode I) indicates that there is little well crystallised (the most thermally stable) calcite present in the ITZ-C of this sample. This is consistent with the XRD results, which have detected only traces of (well crystallised) calcite. Moreover, the previously cited decomposition modes II and III are also in good agreement with the two main TGA/Mass Spec decomposition stages observed in the current work. This suggests that the material that decomposed at temperatures over $650^{\circ}C$ (corresponding to mode II) is likely to be poorly crystalline CaCO₃ (perhaps calcite) whereas the one that decomposed at temperatures under $650^{\circ}C$ (corresponding to mode III) may well be amorphous calcium carbonate (ACC). Furthermore, carbonation of calcium-rich phases (such as those present in class G cement) has been shown previously to result in formation of ACC, vaterite and hydrated silica (Black *et al.*, 2007).

There is extensive literature on amorphous calcium carbonate (ACC), most in the biomineralisation field. Many of these studies have presented stabilisation mechanisms for the ACC. For instance, the presence of silica helps to stabilise the material which may coexist with crystalline polymorphs in the presence of sodium silicate and elevated pH (Kellermeier *et al.*, 2010; Black *et al.*, 2007; Black *et al.*, 2008; Martinez *et al.*, 1998). In the current work, the silica liberated from the rock may have analogously enhanced the stabilisation of the ACC formed in the ITZ. Several authors (Stepkowska *et al.*, 2007; Kellermeier *et al.*, 2003) suggested that some of these forms of ACC also have structural water in their composition, which may restrict the transformation of amorphous into crystalline calcium carbonate, i.e., stabilise the ACC (Thiery *et al.*, 2007). The relatively high amounts of water released just before the first CaCO₃ decomposition observed in this sample suggests that this may also be the case.

Considering that Ca, Si, O and C coexist in considerable amounts in several spots, poorly crystalline scawtite, $Ca_7Si_6(CO_3)O_{18}\bullet 2(H_2O)$, could be present as well, although this mineral needs much less C than the CaCO₃ (only $\approx 1.5\%$ C in weight). Scawtite is a calcium silicate carbonate hydrate that forms sporadically in calcium silicate or cement systems when exposed to carbonate temperature. It is similar to tobermorite with $\approx 5\%$ of CO₂ replacing silica and has been reported in several well cement studies (Eilers *et al.*, 1983; Taylor and Roy, 1980; Gallus *et al.*, 1979).

Dawsonite, NaAl(CO₃)(OH)₂, which has been identified in traces in carbonated well cement (Carey *et al.*, 2007), could also be present in the ITZ. Johnston (2001) predicted formation of dawsonite from the reaction of K-rich feldspar (from the rock) with CO₂, in the presence of an aqueous solution with sodium ions. According to Huggins and Green (1973) the dawsonite decomposes in two steps. The first, between 300°C and 375°C, where all the hydroxyl water and two-thirds of the carbon dioxide are given off, leaves a residue which shows no crystalline structure by X-ray diffraction. The second is a slower step, in which the balance of the carbon dioxide is released over the range of 360°C to 650°C, producing crystalline sodium aluminate. This second decomposition step seems to match with the decomposition process observed in the current work. The first step coincides with the mass loss and water release observed in the TG and Mass Spec respectively. However, the spots analysed by EDS have little or no Na in their composition, which does not support this hypothesis.

The current work indicates carbonation is a very complex system where several products may form, including poorly crystalline and amorphous calcium carbonates as well as scawtite. These findings are in accordance with Rimmelé *et al.* (2008), who described carbonation as a complex series of reactions giving multiple zones of carbonation and dissolution which could possibly explain the extremely bright colour of ITZ.

b) <u>290°C</u>: IGN/G(290.CO₂.84d)

Like IGN/G(290.28d), this cement shows a reddish colour which could be due to the iron leaching from the ignimbrite, but might also be associated with the carbonation of the cement, which, unlike the equivalent 150° C sample, is almost totally carbonated. The higher carbonation rate at 290°C was surprising, as the lower solubility of Ca(OH)₂ at these temperatures was expected to slow its dissolution and therefore, the carbonation of portlandite. Another factor that might have accelerated the carbonation is the higher

permeability of the calcium silicate hydrate phases formed at these temperatures, although the ones at 150°C are quite permeable as well. Finally, it could be due to a faster reaction at 290°C compared to 150°C, as the increase in temperature is known to accelerate the chemical reactions.

The fissure seen by OM may be the consequence of stresses induced in the ITZ due to the differential thermal expansion/contraction between the cement and the rock. As in IGN/G(290.28d), this breakdown along the ITZ-C may be due to the Ca^{2+} and OH^{-} migration from ITZ-C to ITZ-R, which has weakened the binder in the ITZ-C.

VII.1.1.6 Rock type:

Generally, reactions in the assemblages in this section seem to be consistent with what has already been found for the equivalent assemblage with IGN, namely the presence of high amounts of calcium carbonates in the outermost layer of the cement and possible formation of perhaps, amorphous calcium carbonate.

It was anticipated that the most relevant variables which could affect the interaction of the cement with the rock would be its porosity, composition and volcanic glass content. The porosity and, consequently, the permeability, seem to play a key role in some of the samples previously analysed. Volcanic glass is known to react quickly with the Portland based cements because it is mostly composed of reactive silica. The cement/rock alkali silica reaction has been extensively investigated in several papers presented and published in several international conferences on alkali aggregate reaction (AAR) in concrete.

a) <u>UNI: UNI/G(150.CO₂.84d)</u>

This rock's volcanic glass content is comparable to IGN. Thus the lower porosometry of UNI compared to IGN, was expected to reduce the penetration of cement into the pores of this rock. The OM showed a narrower ITZ-R bright rim than the comparable sample with IGN, which indicates that the cement has not migrated as far as in IGN. This is confirmed by the phase and element maps.

This is a consequence of a lower penetration of the cement particles into the rock pores, i.e. reduced physical migration of the unhydrated cement into the rock. This was predictable as the total volume of pores into which the cement particles can readily penetrate (i.e. pores with

diameter above 0.5 μ m), this rock with only 0.2162 mL of pores/mL of rock is significantly lower than for IGN (0.3295 mL/mL). This is also true for pores with diameter above one and 5 μ m. The volume of mercury intrusion for pores above 10 μ m is not significant because it is extremely low.

b) <u>KAO</u>: KAO/G(150.CO₂.84d)

This rock has a similar volcanic glass content to that observed for IGN and UNI. KAO is the most porous amongst the rocks under study. However, this porosity is mostly very fine pores, i.e. it has a relatively low volume and amount of pores in which the unhydrated cement can penetrate. The pores with diameter above 0.5 μ m occupy only a volume of 0.1179 mL per mL of rock (0.3295 mL/mL for IGN and 0.2162 for UNI). For larger pores, it shows a volume of 0.0090 mL/mL for pores with diameter above one μ m and 0.0002 mL/mL for pores with diameter above five μ m. Similar to the other rocks, the volume of mercury intrusion for pores above 10 μ m is not significant because it is extremely low.

Therefore, the narrower bright ITZ-R and lower Ca migration compared to $IGN/G(150.CO_2.84d)$ is in agreement with the idea that the pore size distribution of the rock plays a key role in the interaction between the cement and the rock. Accordingly with what was previously said, the reduced amount of pores in which the cement can penetrate was the cause for this shallower penetration of cement particles into the rock compared to IGN.

Nevertheless, when compared to UNI/G(150.CO₂.84d), this sample shows a slightly wider ITZ-R by OM, and the EDS maps suggest that Ca has penetrated further into the rock. This is surprising, as the amount and volume of pores into which the unhydrated cement particles can penetrate (diameter above $0.5 \ \mu\text{m}$) is considerably lower than for UNI. On the other hand, the values of mercury intrusion for smaller pores are much higher than for pores above 0.5 μ m. For example, for pore diameters above 0.1 μ m, the values of mercury intrusion of KAO (0.2406 mL/mL) are very similar to UNI (0.2669 mL/mL). Moreover, the mercury intrusion in even smaller pores is higher for KAO than for UNI. This indicates that although the pores in which the unhydrated cement particles cannot penetrate (under 0.5 μ m) are reduced, the increased number of fine pores may significantly enhance the migration of cement elements into the rock. In this case, the migration is likely to be driven by the chemical gradient, as only the dissolved chemical elements are able to penetrate in these smaller pores.

c) <u>MOR</u>: MOR/G(150.CO₂.84d)

This rock has significantly lower amounts of volcanic glass in comparison to the other ignimbrites (IGN, UNI and KAO). This was expected to enhance the understanding of the role of the volcanic glass content on the cement rock interaction. However, the porosometry of this rock is considerably different to the other ones, particularly IGN and UNI.

Similar to KAO, the amount and volume of pores in which the unhydrated cement particles can penetrate (with diameter above 0.5 μ m) is considerably less than IGN or UNI. This is because its relatively high porosity is mostly composed of very fine pores, i.e. it has a relatively low volume and amount of pores in which the unhydrated cement can penetrate. Pores with a diameter above 0.5 μ m occupy only 0.1211 mL/mL of rock as opposed to 0.3295 mL/mL for IGN, 0.2162 mL/mL for UNI and 0.1179 mL/mL for KAO. It only shows a volume of 0.0069 mL for pores with diameter above one μ m and 0.0001 mL/mL for pores with diameter above 5 μ m with nothing significant above 10 μ m.

In summary, the lower amounts of volcanic glass along with the lower porosity for pores where cement can penetrate were expected to reduce the interaction between the cement and MOR. This is true compared to IGN as the OM and EDS maps show respectively a narrower ITZ-R and lower Ca migration. But when compared to UNI as reference, the MOR/G(150.CO₂.84d) OM images show a slightly wider the ITZ-R, whereas the EDS element maps show a deeper Ca penetration into the rock.

The relatively wide ITZ-R observed in KAO is attributed to the impact of the pores where the unhydrated cement particles cannot penetrate (with a diameter under 0.5 μ m) and the reaction is driven by the chemical gradient through the fine pores.

While the volume of pores with diameter above 0.5 μ m are similar for MOR and KAO (0.1211 mL/mL and 0.1179 mL/mL, respectively), the volume of pores with diameter above 0.1 μ m is significantly higher in MOR (0.3158 mL/mL for MOR and 0.2406 mL/mL for KAO). While this fact is likely to have facilitated the chemical migration into the smaller rock pores, the lower volcanic glass content of the MOR was expected to reduce the chemical reaction between the cement and the rock. In this case, the glass content seems to be the prevailing variable, as the MOR shows a slightly narrower ITZ-R along with a slightly lower Ca penetration compared to the KAO/G(150.CO₂.84d).

d) <u>RHY</u>: RHY/G(150.CO₂.84d)

This rock has the lowest overall volume of pores (0.1349 mL of pores per mL of rock), the lowest volume of pores in which the cement can penetrate (pores with a diameter above 0.5 μ m: 0.1012 mL/mL), the lowest volume of pores with a diameter above 0.1 μ m: 0.1133 mL/mL) and the lowest amount of volcanic glass. The combination of all of the above mentioned variables has drastically reduced the reaction extent between the cement and the rock. Hence, these results seem to support the theory that features such as porosimetry and volcanic glass content play a key role in the way the cement interacts with the rock formation.

VII.1.2 G20SF

VII.1.2.1 <u>Standard</u>: IGN/G20SF(150.28d)

The low intensity peaks in XRD indicate that the cement matrix remained largely amorphous, but the added silica flour has restricted the formation of portlandite. Its presence is confirmed by XRD analysis and OM/XPL images.

Small amounts of tobermorite have formed in the cement zone, indicating the Ca/Si ratio has dropped low enough through Ca migration, and the availability of additional Si. There is more quartz in the ITZ-C than CEM, suggesting that Ca leaching into and through the ITZ is rapid, leaving less available Ca to react with the quartz in the interior of the binder matrix. In addition to this, the quartz might also dissolve in the alkaline environment of the cement core, with the resulting silica moving from CEM to ITZ-C and finally precipitating in the outermost layer, where the pH is lower than in the cement core.

The increase in bright grains from IGN to ITZ-R, is probably again due to migration of cement compounds from the cement into the rock, some of which are trapped between the ITZ-R and the ITZ-C, which explains the fine bright line. Although not confirmed by XRD analysis, these compounds are probably cement matrix minerals, namely calcite, tobermorite, αC_2SH , unhydrated cement and quartz.

The ITZ-R width (by OM) and Ca penetration depth (by SEM) are similar to that found in the IGN/G(150.28d). This indicates that the addition of Silica Flour has little effect on the physical or chemical migration stages of this formulation compared to pure class G cement. The physical migration was predictable, as the particle size distribution of this admixture and therefore of this formulation is very similar to the that of class G cement. It also suggests that the added quartz has not reduced the migration of Ca²⁺ ions across the ITZ into the rock by an expected Ca/SiO₂ reaction. Hence 20wt% of silica flour addition is not been enough to significantly change the migration process of the cement mixture. The OM and SEM/EDS work indicate that the milky material found in the ITZ is silica gel, a typical product of the alkali-silica reaction, i.e. it is likely to be a consequence of the resulting reaction of the volcanic glass with migrating OH⁻.

Like IGN/G(150.28d), the ITZ-R is composed of two distinct rims, one beside the ITZ-C with a darker colour and other with a lighter brown colour. These may have originated from physical and chemical migration respectively.

VII.1.2.2 Curing time: IGN/G20SF(150.84d)

The feature which stands out compared to the class G cement is the complete absence of portlandite which has reacted with the added quartz (20wt% SF), a feature also observed for the equivalent 1 month cured sample.

The calcite and aragonite content increases going from CEM to ITZ-C, supporting the idea that the carbonation rate (although still low) is faster in the outermost layer of the cement. As in IGN/G20SF(150.28d), there are some unexpected trace amounts of tobermorite that might be explained by random sites where the Ca/Si ratio was low enough for this mineral to form. According to Kalousek (1954), over 30% fine quartz addition to cement is needed to give a Ca/Si ratio of around one for this mineral to form.

The XRD analysis detected small amounts of calcium carbonates and calcium silicates in the ITZ-R, confirming that cement constituents have migrated into the rock, in accordance with that observed in the equivalent one month cured sample.

By OM, the cement matrix (CEM) contains both small and large sized crystals, the bigger ones might be quartz or/and non-hydrated cement grains.

The ITZ-R is considerably wider than the equivalent one month cured sample, indicating the current system has kept reacting during the second and/or third months. The ITZ-C, however, seems to be narrower than in IGN/G(150.84d), meaning the migration processes within this cement mixture may be less affected than for pure class G cement.

The SEM/EDS results support the OM results where the Ca migration observed at 84 days is considerably greater than at 28 days. Furthermore, unlike the 1 month cured samples, there is a minor difference between the ITZ-R and Ca migration between G and G20SF. The ITZ-R looks slightly wider and the Ca migrated in higher amounts, which may mean the G20SF has penetrated a little further into the rock than the G within the second and/or third months of cure.

VII.1.2.3 Drilling mud: IGN/G20SF(150.b.28d)

As in IGN/G(150.b.28d), the bentonite layer can be observed as a homogeneous light brown rim by OM (PPL). Gehlenite has formed here as a product of a reaction of Ca migrating from the cement with the Al oxide present in the bentonite, as well as with the SiO₂ present in the

bentonite and, perhaps, in the cement (silica flour). Again, there is a wider ITZ-R and a weaker cement/rock bond.

The aluminium may have enhanced the formation of tobermorite. As explained by Klimesch and Ray (1998), the ready availability of Al makes the formation of tobermorite easier. In the current sample, Al can be supplied into solution from both bentonite and the glass in the ignimbrite as migrating OH^{-} ions react along with soluble SiO₂. Tobermorite will then precipitate in the ITZ.

The seemingly narrower bentonite layer, when compared with IGN/G(150.b.28d), suggests an increased reaction of the bentonite with silica flour present in the cement. On the other hand, the thickness of the bentonite layer seen by the optical microscope may be relatively random. It depends on the way it has adhered to the rock after being injected in and washed out from the rock cavity.

The OM images and SEM/EDS maps support further the greater migration of some cement components into the rock compared to the equivalent sample without bentonite, IGN/G20SF(28d), confirming the suggestion put forward for IGN/G(150.b.28d) that Ca migration is being driven by cation exchange with Al from bentonite.

VII.1.2.4 Curing temperature: IGN/G20SF(290.28d)

Unlike IGN/G20SF(150.28d), there is little quartz present, indicating that most has reacted at this temperature, i.e., the reaction of quartz with the cement is faster at 290° C than at 150° C. There are some red coloured spots in the ITZ-C which, in a similar way to IGN/G(290.28d), are the consequence of iron dissolution/precipitation process within the cement.

The fissure seen by OM, again, may be the consequence of stresses induced in the ITZ due to the differential thermal expansion/contraction between the cement and the rock. This break happened at the contact between ITZ-C and ITZ-R. This could mean that, unlike in the IGN/G(290.CO₂.28d) sample, this line splits the outermost layer of the cement from the outermost layer of the rock where it is the weakest. This could be also caused by the slower Ca^{2+} migration from the cement into the rock caused by the added SF. This results in poorer bonding properties between these materials in comparison to the equivalent sample where Class G cement was used. This could mean that unlike at 150°C, the 20% quartz addition restricts the Ca²⁺ migration in a significant way.
The other most noticeable changes from IGN/G(290.28d) is the formation of kilchoanite along with xonotlite and the disappearance of portlandite. This will be due to the reaction with SF.

Xonotlite was detected by XRD in significant amounts. This is unexpected at this Ca/Si ratio and probably results from extensive leaching of Ca^{2+} ions, effectively lowering the Ca/Si ratio in the matrix. Accordingly, the bright grains in the ITZ-C are unreacted quartz crystals from SF, which might be due to lack of Ca^{2+} ions to react with them.

The narrower ITZ compared to the 150°C sample (seen by either OM and SEM/EDS) may, again, be attributed to the faster setting/cure of the cement at 290°C and/or the fissure between the ITZ-C and the rest of the cement. While the faster cement setting decreases the amount of available Ca, the fissure/discontinuity might have stopped the Ca supply to the ITZ-C from the inner cement, as there was no physical interface for further Ca to move to the outermost layer. In both cases, the amount of free Ca in the ITZ-C is reduced.

VII.1.2.5 CO₂ exposure:

a) <u>150°C</u>: IGN/G20SF(150.CO₂.84d)

Similar to IGN/G20SF(150.84d), no portlandite was observed in this sample. The amount of aragonite increased from CEM to ITZ-C, meaning there is more carbonation in the outmost layer of the cement. The traces of tobermorite formed could be expected. Milestone *et al.* (2012) showed that the low Ca/Si ratio tobermorite formed as Ca^{2+} was removed by formation of CaCO₃ during the early curing process before the final silicate phases can form.

The extremely bright wide ITZ-R may mean that significant calcium carbonate (CaCO₃) is present, although again that is not consistent with the XRD analysis where little calcite or aragonite is identified. This may, again, be justified by the presence of amorphous calcium carbonate. Both the TGA and Mass Spec results show significant amounts of material decomposing at temperatures well under 650°C (significantly below that of calcite or aragonite) with significant amounts of CO₂ released over this decomposition range. When compared with the IGN/G20SF(150.CO₂.84d), the TGA and Mass Spec results show a considerable higher amount of carbonate decomposing at lower temperatures (under 700°C). This is consistent with the work undertaken by Thiery et al. (2007), who concluded that poorly crystallised and thermodynamically metastable forms of CaCO₃ correspond to the carbonation of C-S-H, which is expected to be present in greater amounts in G20SF than in G.

The relatively high amounts of C detected by EDS map and spot analyses, and similarly observed for the comparable sample with class G cement, indicate relatively high amounts of carbonate present which are likely to be CaCO₃, rather than scawtite, Ca₇Si₆(CO₃)O₁₈•2(H₂O) as CaCO₃ needs only \approx 3.3 times more Ca than C (in weight), whereas scawtite needs \approx 23.4 times more Ca than C (in weight) in its composition.

Ca is gradually reduced, going from the outermost to the innermost ITZ-C (SPOTs 4, 5 and 6), and is a consequence of Ca being leached from this region (dissolution front/depleted zone) and moving outwards during the carbonation process. Eventually, this Ca reacts with the CO_2 or HCO_3^- to form calcium carbonate at the carbonation front. A similar phenomenon was observed in other studies (Rimmele *et al.*, 2008; Milestone *et al.*, 1986; Grant-Taylor *et al.*, 1996). The composition along with the distinct amorphous texture of some areas in the ITZ region indicate that silica gel is present. This compound could have formed as a product of corrosion of the cement, i.e. loss of Ca in the dissolution front (**Equation III.23**) or/and as a product of the alkali-silica reaction between the cement and the rock (**Equation III.25** and **Equation III.26**).

The ITZ-C is not as easily distinguishable as that observed in IGN/G(150.CO₂.84d), which may be explained by the distinct carbonation processes and products of C-S-H and portlandite, that occur at these conditions. While calcite (the most common portlandite carbonation product) is usually white to the unaided eye, aragonite, the most common product of carbonation of C-S-H according to Milestone *et al.* (1986), shows a reddish colour, similar to observed in the work by Milestone *et al.* (2012). This suggests distinct carbonation processes, where the reddish ITZ-C indicates the presence of aragonite/pseudo-aragonite/non-crystalised aragonite (ACC) combination, whereas the ITZ-R seems to show brighter carbonation products, i.e. calcite/pseudo-calcite/non-crystalized calcite (ACC). This could be explained by the absence of portlandite in the ITZ-C with a possible portlandite formation in the ITZ-R due to the migration of Ca²⁺ and OH⁻ (where insufficient free silica is present to restrict the formation of portlandite).

The SEM/EDS results are in agreement over the wider ITZ-R carbonation rim seen by OM, as the element mapping shows calcium has migrated further into the rock, compared to $IGN/G(150.CO_2.84d)$. This fact might be explained by the faster carbonation of portlandite

present in IGN/G(150.CO₂.84d) ITZ-C but not in IGN/G20SF(150.CO₂.84d) ITZ-C. Carbonation seals the surface to further migration when exposed to CO₂, whereas the calcium silicate hydrates take longer to react with CO₂ and, consequently, do not, or take longer to, form a CaCO₃ barrier. The Ca²⁺ seems to migrate unevenly into the rock and is mostly localized in rock pores, whereas in the IGN/G(150.CO₂.84d) ITZ-R it is more uniformly distributed. This might be due to the formation of CaCO₃ in pockets in the rock pores as no Si is present from the EDS mapping.

b) <u>290°C</u>: IGN/G20SF(290.CO₂.84d)

Unlike the equivalent 150°C sample, the quartz has fully reacted with the cement, supporting an increase in the cement/quartz reaction rate going from 150°C to 290°C.

Like IGN/G20SF(290.28d), the cement in this sample is reddish in colour and due to the iron dissolution/precipitation/oxidation processes within the cement. Similar to IGN/G(290.CO₂.84d), it might also be partially associated with the carbonation of the cement, which, unlike in the equivalent 150° C sample is fully carbonated all the way through from the outermost layer to the cement core.

As described above, the fissure seen by OM may be the consequence of stresses induced in the ITZ due to the cement shrinkage and/or differential thermal expansion between the cement and the rock. As in IGN/G20SF(290.28d), this breakdown has happened in the line between ITZ-C and ITZ-R. This could mean that, unlike in IGN/G(290.CO₂.84d), this line splits the outermost layer of the cement from the outermost layer of the rock. This weakness could be a consequence of a slower Ca²⁺ migration from the cement into the rock due to the added silica, which would have reduced the cement/rock bonding.

VII.1.2.6 Rocktype:

These assemblages seem to be consistent with what has already been found for the equivalent IGN samples, namely the absence of portlandite and increased aragonite in ITZ-C from CEM and, perhaps, the presence of amorphous calcium carbonate.

a) <u>UNI</u>: UNI/G20SF(150.CO₂.84d)

As observed for the equivalent assemblage with class G formulation, the ITZ-R is narrow along with a shallower Ca penetration into the rock in comparison to IGN/G20SF(150.CO₂.84d). Analogous to UNI/G(150.CO₂.84d), this is likely to be due to the lower amount and volume of pores into which the cement can penetrate, which implies a penetration of lower amounts of cement particles into the rock pores, i.e. reduced physical migration of the unhydrated cement formulation constituents into the rock.

b) <u>KAO</u>: KAO/G20SF(150.CO2.84d)

In a similar way to the equivalent assemblage with G formulation, the bright ITZ-R seems to be narrower and the Ca penetration is shallower in comparison to IGN/G20SF(150.CO₂.84d), due to the lower amount and volume of pores in which the unhydrated cement mixture particles can penetrate (with diameter above $0.5 \mu m$).

Nonetheless, when compared to UNI/G20SF(150.CO₂.84d), this sample shows a slightly wider ITZ-R by OM, whereas the EDS maps suggest that Ca has penetrated further into the rock. This is in agreement with that observed for the KAO/G(150.CO₂.84d), and supports the idea that the high amount and volume of fine pores into which the unhydrated cement particles cannot penetrate (under 0.5 μ m) facilitate the migration driven by chemical gradient.

c) <u>MOR</u>: MOR/G20SF(150.CO₂.84d)

Again, the lower amounts of volcanic glass, along with the lower porosity of pores into which cement can penetrate compared to IGN, have reduced the interaction between the cement and the rock. Also, when compared to UNI/G20SF(150.CO₂.84d), the smaller pores seem to have facilitated the migration of the dissolved cement mixture particles into the rock, driven by chemical gradient.

However, this sample shows a relatively wide, although heterogeneous ITZ-R. When compared to KAO/G20SF(150.CO₂.84d), the amount of ITZ-R reaction observed by OM appears lower, which is in agreement with the idea that the lower volcanic glass content reduces the chemical reaction between the cement and the rock.

On the other hand, the extension of penetration seems to be greater than for $KAO/G20SF(150.CO_2.84d)$. This is likely to be a consequence of the higher volume of pores

with diameter above 0.1 μ m significantly higher in the MOR (0.3158 mL/mL for MOR and 0.2406 mL/mL for KAO), which may be allowing further penetration of dissolved cement.

d) <u>RHY</u>: RHY/G20SF(150.CO₂.84d)

The results obtained for this sample also agree with what has previously been stated about the role of porosity and amorphous silica content, i.e. when both of these variables are significantly reduced, the extent of reaction of this cement with this rock is also considerably reduced.

VII.1.3 G40SF

VII.1.3.1 <u>Standard</u>: IGN/G40SF(150.28d)

The greater number of medium and large sized bright spots seen by XPL in the cement compared to both IGN/G(150.28d) and IGN/G20SF(150.28d) appears due to the larger amount of unreacted quartz crystals together with tobermorite formation, which has been enhanced by 40wt% silica flour addition resulting in complete removal of portlandite. However, the bulk of the binder still remains amorphous indicating tobermorite crystallization is slow.

By OM, the ITZ-C is barely distinguishable from CEM and the ITZ-R is significantly narrower than for any other Portland type cement mix tested, at the same conditions. This is not likely to be a consequence of a distinct physical migration compared to G or G20SF as the particle size distribution for these three formulations is very similar. Instead, this seems to be a consequence of the relatively rapid reaction of the large amount of added quartz with the available Ca which partially restricts the migration of Ca into the rock compared to the samples with lower Silica Flour additions. Although present in smaller amounts than in IGN/G(150.28d), the milky material found in the ITZ-R of the current sample is also probably silica gel.

The abrupt change in the cement/rock interface phase map, rather than the gradual change seen for both IGN/G(150.28d) and IGN/G20SF(150.28d), may be due to a combination of two factors: the slower migration of Ca resulting in less Ca present in the ITZ-R, and the reduced difference in the Ca/Si ratio between the cement and the rock.

VII.1.3.2 <u>Curing time</u>: IGN/G40SF(150.84d)

The addition of 40wt% silica flour restricts the formation of portlandite and enhances the formation of tobermorite in the cement matrix, consistent with the idea put forward for the equivalent sample cured for 1 month. Both calcite and aragonite increase going from CEM to ITZ-C, meaning this cement mixture also shows a higher carbonation rate in the outermost layer. Only slight traces of calcium silicates and calcium carbonates are found in the ITZ-R (even lower than in the IGN/G20SF(150.84d)), which confirms that 40wt% SF addition slows the migration of cement constituents into the rock. This is supported by the OM results,

which show a considerably narrower ITZ-R than that observed in both IGN/G(150.84d) and IGN/G20SF(150.84d).

The SEM/EDS data is in accordance with the details mentioned above, as the Ca^{2+} has not migrated as far into the rock as for IGN/G(150.84d) or IGN/G20SF(150.84d), again consistent with the idea that large additions of silica flour slow the migration of Ca^{2+} ions across the ITZ.

The ITZ-R is considerably wider compared to IGN/G40SF(150.28d), which means that ongoing cement/rock interaction occurs during the second and/or third months of cure.

VII.1.3.3 Drilling mud: IGN/G40SF(150.b.28d)

Like IGN/G(150.b.28d) and IGN/G20SF(150.b.28d), gehlenite forms in the ITZ, where a bentonite layer is observed, widening the ITZ-R and weakening the cement/rock bond.

The increased number of bright spots in the ITZ-C are mostly quartz, which suggests that with the larger amounts of added silica flour, the outermost areas of the cement remain unreacted, as significant amounts of Ca²⁺ and OH⁻ move into the rock, reducing the amount of these constituents left to react with the quartz from the cement formulation. On the other hand, the small bright grains are probably calcite, which XRD showed was greater in ITZ-C than CEM.

The bentonite layer is narrower than for either IGN/G(150.b.28d) or IGN/G20SF(150.b.28d), which again, may be the consequence of the bentonite being consumed in the reaction between the silica flour present in the cement and rocks. Following this line of thought, the more quartz added to the cement, the more will react with the bentonite. However, the width of the bentonite layer also depends on other factors such as its initial width, which was probably not the same for all the samples or even for different zones within the same sample.

The optical microscope images and the element map analyses support the idea that the Ca migration is driven by cation exchange with Al from the bentonite, as the cement seems to migrate further and in higher amounts into the rock, when compared with the equivalent sample without the bentonite layer, IGN/G40SF(150.28d).

VII.1.3.4 <u>Curing temperature</u>: IGN/G40SF(290.28d)

The large addition of silica flour ensures complete reaction of portlandite and the Ca/Si ratio is low enough that xonotlite readily forms at the expense of other calcium silicate hydrates.

The ITZ is mostly composed of ITZ-C, as the ITZ-R is narrow. The wide ITZ-C is easily distinguished due the increased amount of quartz crystals and its different colour and texture and increased iron content (similar to that seen for the other Portland cement types), which might be migrating from the rock into the cement and precipitating. Like the 150°C samples, the narrower ITZ-R compared to IGN/G(290.28d) or IGN/G20SF(290.28d) is probably due to the overall reduced amounts of free Ca in the cement matrix, most of which is consumed in the reaction with the large amount of added silica flour. When compared to the equivalent sample at 150°C, the shallower Ca migration might due to the faster setting and the fissure observed at 290°C.

The fissure seen by OM may be the consequence of stresses induced in the ITZ due to the differential thermal expansion/contraction between the cement and the rock. This break down has happened at the contact between ITZ-C and ITZ-R. This could mean that, like for the G20SF, the added quartz weakens the bonding between the cement and the rock by restricting Ca^{2+} migration from the cement into the rock.

VII.1.3.5 <u>CO₂ exposure</u>:

a) <u>150°C</u>: IGN/G40SF(150.CO₂.84d)

The carbonation layer is easily noticeable with the unaided eye, as a pink, thick outer-layer formed in the cement. Duguid (2009) has reported a similar colour in his experiments, which he attributed to the precipitation of CaCO₃. This layer is well distinguishable by OM, and ranges from ca. 2 to 4 mm thick and depends on the thickness of the surrounding rock. This is in accordance with the work by Duguid *et al.* (2011), who observed a decrease in the cement degradation rate with the increase of the surrounding rock thinckness.

The EDS map and spot analyses suggest that calcium carbonate, $CaCO_3$, is present in considerable amounts. The XRD analysis confirms this and indicates that the most prevalent crystalline calcium carbonate is aragonite, which increases sharply going from CEM to ITZ-

C. This is probably due to the faster rate of carbonation of tobermorite (rather than portlandite or other calcium silicate hydrates), making the carbonated sample more porous.

Calcium silicate hydrates and calcium carbonates are not identified by XRD in ITZ-R, probably because of the slower migration of calcium from cement to the rock. This may be due to the formation of tobermorite, as this mineral seems to carbonate faster than the other calcium silicates so the chemical driving forces are reduced. A number of orange/reddish/brownish spots seen by XPL in CEM are the consequence of carbonation as this effect has been previously reported (Milestone *et al.*, 1987a).

Similar to that observed in the comparable sample with G20SF as well as in other studies (Rimmele *et al.*, 2008; Milestone *et al.*, 1986; Grant-Taylor *et al.*, 1996), the Ca reduction across the ITZ-C (going inwards) may be a consequence of Ca being depleted and moving to outwards to the carbonation front.

The bright (white and orange) colour of ITZ-R indicates carbonation of the migrating cement constituents, including formation of ACC. The narrower ITZ-R compared to IGN/G(150.CO₂.84d) or IGN/G20SF(150. CO₂.84d) is due to the rapid carbonation of tobermorite (Milestone et al., 1986), which might be creating an early carbonation barrier in ITZ-C, restricting further migration of cement constituents into the rock. This idea seems to be supported by the SEM/EDS, which shows a slower migration of Ca²⁺ than the comparable samples G and G20SF. Like in IGN/G20SF(150.CO₂.84d), the Ca²⁺ is concentrated in 'pockets' in the rock voids, emphasising the importance of the rock permeability in the migration process.

b) <u>290°C</u>: IGN/G40SF(290.CO₂.84d)

Like IGN/G40SF(290.28d), this cement also shows a reddish colour which is due to the iron dissolution/precipitation processes, which might also be partially associated with the carbonation of the cement. Unlike the equivalent 150°C sample, the cement seems to be fully carbonated all the way through from the outermost layer to the cement core.

The amount of xonotlite in the cement phase was low compared to that found for the G20SF, which suggests that most of the xonotlite that had formed, has carbonated.

Again there is a fissure seen by OM, which is in accordance with the hypothesis previously put forward, i.e. a consequence of stresses induced in the ITZ due to the differential thermal

expansion/contraction between the cement and the rock. Like IGN/G40SF(290.28d), this break has occurred at the contact between ITZ-C and ITZ-R, meaning that the added quartz has weakened the bonding between the cement and the rock by restricting Ca^{2+} migration from the cement into the rock.

VII.1.3.6 Rocktype:

The assemblages of the different rocks are consistent with what has already been found for the equivalent samples with IGN, namely the pink aragonite carbonation layer is noticeable with the unaided eye (except for the RHY) and lower migration of Ca (when compared to the other API class G based cements).

a) <u>UNI: UNI/G40SF(150.CO₂.84d)</u>

Although less homogeneous than the comparable IGN assemblage, the pink carbonation layer observed in this sample with the unaided eye is wider and confirmed by OM. The higher variability in its width is due to the more heterogeneous nature of the rock. This feature, although not obvious in the XRD, OM and SEM/EDS results, might also be affected by the region of the rock over which these tests have been undertaken as the rock is very heterogeneous. This might reduce the reliability of these tests, in particular migration and carbonation depths.

b) <u>KAO</u>: KAO/G40SF(150.CO₂.84d)

The slightly wider pink carbonation layer compared to $IGN/G40SF(150.CO_2.84d)$ indicates that the overall higher porosity of the rock enhances the CO₂ enriched brine availability around the cement and causes a higher carbonation rate in the outermost layer of the cement. Nevertheless, another variable that might also enhance the amount of CO₂ around the sample is the width of the rock around the cement. Unfortunately, the impact of this variable cannot be precisely analysed because this variable was not accurately monitored, although the samples varied little in size.

c) <u>MOR</u>: MOR/G40SF(150.CO₂.84d)

The similarity between this and the IGN/G40SF($150.CO_2.84d$) pink carbonation layer width are also in agreement with the major role of the rock porosity in the carbonation rate of the cement sample. Again, it was not possible to accurately measure the impact of the width of surrounding rock layer has on the carbonation rate of the outermost layer.

d) <u>RHY</u>: RHY/G40SF(150.CO₂.84d)

The results obtained for this sample is also in agreement with what has previously been said about the role of porosity. The pink carbonation layer is only evident in a few small spots in the ITZ-C. Thus, the reduction of the rock porosity and, consequently, permeability, has reduced the carbonation in the cement in comparison with all the other rocks. This is due to the reduced availability of CO_2 enriched brine in the outermost layer of the cement, due to the lower permeability of the rock compared to the other rocks. The few pink spots, however, indicate some areas to which the CO_2 has been able to access the cement, although still in lower amounts than in any of the other rocks.

VII.1.4 G20MS

VII.1.4.1 <u>Standard</u>: IGN/G20MS(150.28d)

Like the samples with silica flour additions, portlandite reacts with the added silica but more rapidly. However, unlike the other class G cement based mixtures, G20MS has a higher carbonation resistance, especially when compared with the samples with silica flour addition. The larger number of bright spots observed by OM are amorphous silica. According to the OM and SEM/EDS work, the milky material found in the ITZ of the current sample is silica gel, formed as a product of the alkali-silica reaction between the cement and the rock.

The ITZ is relatively narrow, indicating less cement/rock reaction compared to IGN/G(150.28d) or IGN/G20SF(150.28d), but it is still wider than IGN/G40SF(150.28d). This reduced overall migration compared to G and G20SF is likely to be a consequence of the fast reaction of MS with the cement restricts the Ca^{2+} chemical migration.

This formulation has a slightly lower average particle size due to the lower particle size of the admixture. This variable seems not to have significantly affected the physical migration process. This cement mixture is thickest when fresh, which might have partially restricted physical movement of this into the rock.

VII.1.4.2 Curing time: IGN/G20MS(150.84d)

This sample confirms the higher carbonation resistance found for the 1 month cured sample, as the XRD does not detect any calcium carbonate increase going from CEM to ITZ-C.

The ITZ-R is much wider and Ca penetration into the rock is much deeper than for the equivalent 1 month cured sample, which means this cement has reacted much further with the rock during the second and/or third months of cure.

VII.1.4.3 Drilling mud: IGN/G20MS(150.b.28d)

Similar to the other samples with bentonite addition, the bentonite barrier is easily distinguishable by OM, in which formation of gehlenite occurs, widening the ITZ-R and weakening the cement/rock bond. The darker colour of the ITZ-C might have to do with the bentonite reacting with the cement and therefore extending the ITZ-C reaction zone. This is

in accordance with the idea previously put forward that Ca migration is driven by cation exchange as Al from bentonite is substituted into the silicate structure, as the cement migrates further and in higher amounts into the rock, compared to the equivalent sample without the bentonite layer (IGN G20MS 150 (28d)).

The increased light grains in the ITZ-C from CEM (observed by OM and XRD) are silica, suggesting that larger amounts of silica from the outermost areas of the cement remain unreacted, as significant amounts of Ca and OH⁻ move towards the rock, leaving lower amounts of these constituents to react with the quartz from the cement grout.

The bentonite layer in this sample is the widest from all the other class G cement based grouts, which seems to refute the previously discussed hypothesis that the silica from the cement reacts with the bentonite. The amorphous silica added to this cement mix is much more reactive than the silica flour, which means this silica should react further with the bentonite than the silica flour from the other cement mixtures. The width of the bentonite layer is random, as it depends on factors which cannot be thoroughly monitored, e.g. the width of the bentonite layer before pouring the cement.

VII.1.4.4 Curing temperature: IGN/G20MS(290.28d)

This was the only Portland based cement system which remained grey at this temperature. This might be due to the presence of sulphur in the MS600, which restricts the transformation of Fe(II) to Fe(III).

Once again the fissure seen by OM may have been the consequence of stresses induced in the ITZ due to the differential thermal expansion/contraction between the cement and the rock. Similar to the equivalent samples with silica flour addition, this break happened at the contact between ITZ-C and ITZ-R. This is in agreement with the idea previously put forward that silica addition slows Ca^{2+} migration into the rock and, thus, good bonding with the rock does not occur.

VII.1.4.5 CO2 exposure:

a) <u>150°C</u>: IGN/G20MS(150.CO₂.84d)

The EDS map and spot analyses indicate that a significant amout of carbonate is present. This is seemingly not consistent with the XRD analysis where little calcite or aragonite is

identified. This suggests that amorphous calcium carbonate is present. This is confirmed by TGA/Mass Spec and, perhaps, XRD, where the increase in amorphous material (in ITZ-C from CEM) may indicate presence of an amorphous material, which could be silica gel and/or amorphous calcium carbonate.

The ITZ-R and the Ca migration into the rock looks similar to that observed in IGN/G20SF(150.CO₂.84d). This, again, seems to be due to the predominant carbonation reaction (C-S-H), process and final products (aragonite/pseudo-aragonite/non-crystalized aragonite). The sharply reduced amount of small bright spots in the ITZ-C from CEM may indicate either absence of C-S-H or its carbonation.

b) <u>290°C</u>: IGN/G20MS(290.CO₂.84d)

Surprisingly, xonotlite is present in this cement. This compound is expected to form only when higher amounts of quartz are added to the mixture. Like the other class G cement mixtures, this cement shows similar carbonation which penetrates all the way through from the outermost layer to the core.

The fissure seen by OM may have been the consequence of stresses induced in the ITZ due to the differential thermal expansion/contraction between the cement and the rock. Like in IGN/G20MS(290.28d), this break down has happened at the contact between ITZ-C and ITZ-R, meaning that the added silica weakens the bonding between the cement and the rock by restricting Ca^{2+} migration from the cement into the rock.

VII.1.4.6 Rocktype:

These assemblages are consistent with what has already been found for the equivalent with IGN, namely there is higher carbonation in the outermost layer and perhaps, formation of amorphous calcium carbonate.

a) <u>UNI: UNI/G20MS(150.CO₂.84d)</u>

Like that observed for the equivalent assemblages with G and G20SF formulations, this sample has a narrower and bright orange ITZ-R along with shallower Ca penetration into the rock in comparison to $IGN/G20SF(150.CO_2.84d)$. This is in agreement with the idea that the

physical migration is very dependent on the volume and amount of pores in which the unhydrated formulation particles can penetrate.

b) <u>KAO: KAO/G20MS(150.CO₂.84d)</u>

The wider ITZ-R compared to UNI/G20MS(150.CO₂.84d) is in accordance with the idea previously put forward for the G and G20SF formulations, which highlights the importance of the smaller pores (where the unhydrated particles cannot penetrate) in the chemical migration of the dissolved cement into the rock.

c) <u>MOR</u>: MOR/G20MS(150.CO₂.84d)

Again, the extension of penetration of Ca into the rock seems to longer than for the comparable sample with KAO. This is in agreement with what was previously said for MOR/G20SF(150.CO₂.84d) where the pores with diameter above 0.1 μ m are facilitating further penetration of dissolved cement, i.e. enhancing the chemical migration.

d) <u>RHY</u>: RHY/G20MS(150.CO₂.84d)

The results obtained for the current sample also indicate that the decreased porosity and reduction in volcanic glass are the main causes for the reduced reaction extent of the cement with this rock.

VII.1.5 API class A

VII.1.5.1 <u>Standard</u>: IGN/A(150.28d)

The light colour of the cement observed under PPL compared to IGN/G(150.28d) is due to the lower amounts of iron than in the class G cement. The narrower ITZ-R observed is a consequence of the faster setting time associated with class A cement, due to the presence of higher amounts of C₃A. As the cement hardens, Ca²⁺ and OH⁻ become fixed in new products, an idea that is confirmed by the element maps, as the second/chemical stage of migration of Ca²⁺ ions is slightly lower than that observed in IGN/G(150.28d) (150µm and 200µm respectively). The physical migration looks similar to that observed for class G cement. The very similar particle size distribution between class A and class G unhydrated cements explains the similar degree of penetration of their respective particles into the pores of the rock.

Although present in smaller amounts than in IGN/G(150.28d), the amorphous material found in the ITZ-R is also silica gel.

As opposed to IGN/G(150.28d), there is a slight increase of bright spots in the ITZ-C from CEM. If these spots are mostly portlandite formed from the higher C_3S content, the XRD results disagrees with the OM analysis, which shows there is portlandite reduction in going from CEM to ITZ-C.

VII.1.5.2 Drilling mud: IGN/A(150.b.28d)

Similar to the other samples with bentonite addition, the bentonite barrier is easily distinguishable by optical microscopy, gehlenite forms and widens the ITZ-R but weakens the cement/rock bond. The fissure in the ITZ-C is obvious in this specimen, where most of the bentonite remained attached to the rock. This could be due to the lower amounts of Ca in the inner ITZ-C when compared with the rest of the cement, reducing the cementing properties and thus weakening this zone of the cement. It should be noted, however, that the bonding seemed to have decreased equally in all the samples in which bentonite was added, as it does not seem to depend much on the type of cement. Otherwise, there are few significant differences in comparison with the equivalent sample without bentonite.

Regarding the ITZ width (optical microscope) and the Ca migration (element maps), the analysis of this sample also supports the idea that bentonite enhances the cement migration into the rock due Ca/Al cation exchange.

VII.1.5.3 Curing temperature: IGN/A(290.28d)

In a similar way to the class G based formulations, there is a homogenous reddish tone along with white spots seen in PPL, which is the consequence of the iron dissolution and further precipitation all around the specimen.

The contrast between the ITZ and the rest of the sample is much higher here than in the equivalent sample with class G cement.

As for the other Portland cement type samples, the narrowed ITZ and shallower Ca migration at 290°C compared to that at 150°C (seen by both optical microscopy and element mapping) may be attributed to the faster setting/cure of the cement at 290°C and/or the fissure between the ITZ-C and the rest of the cement.

VII.1.6 White cement

VII.1.6.1 <u>Standard</u>: IGN/W(150.28d)

The lighter colour of this cement and the lowest number of dark spots observed under PPL (in comparison with any other Portland based mixture) is due to the low amounts of iron, where little C_4AF is present.

Similar to IGN/A(150.28d), the ITZ-R is narrower than IGN/G(150.28d). Although not obvious by optical microscopy, the element map results show a lower Ca chemical migration (second stage migration) than that observed in IGN/A(150.28d), with 100 μ m and 150 μ m thickness respectively. This is probably due to the faster setting associated with the white cement, due to the presence of higher amounts of C₃A, rather than C₄AF (low iron content). As the cement hardens, its components become unavailable to migrate as they form new products within the cement matrix. The physical migration stage is likely not to have been significantly affected compared to all the other Portland based cements, as they all have a similar particle size distribution.

Although present in smaller amounts than in IGN/G(150.28d), the milky material found in the ITZ-R of the current sample is also probably silica gel.

Like IGN/A(150.28d) and as opposed to IGN/G(150.28d), the XPL image shows an increase in bright spots in the ITZ-C over CEM, but with a portlandite reduction by XRD analysis.

VII.1.6.2 Drilling mud: IGN/W(150.b.28d)

Similar to the other samples with bentonite addition, the bentonite barrier is easily distinguishable (by optical microscope image) and causes formation of gehlenite, widening the ITZ-R and weakening of the cement/rock bond.

From the SEM/EDS results, it seems that the Ca has migrated in higher amounts, further evidence that bentonite enhances cement migration into the rock due Ca/Al cation exchange.

VII.1.6.3 <u>Curing temperature</u>: IGN/W(290.28d)

As for the other Portland cement type samples, the narrower ITZ and shallower Ca penetration compared to the 150°C sample (seen by both optical microscopy and element

mapping) are attributed to the faster setting/cure of the cement at 290°C and/or the fissure between the ITZ-C and the rest of the cement.

VII.2 Alternative cementing system

VII.2.1 Calcium Aluminate Cement

VII.2.1.1 Standard: IGN/HAC(150.28d)

This cement forms different compounds compared to Portland cement, which are not based on the calcium-silica combination, but, instead, the cementitious properties rely mostly on calcium aluminate hydrates. At these temperatures, this is due to katoite, C_3AH_6 , and the aluminium oxide hydroxide, boehmite, AlO(OH). The absence of calcium silicate minerals (the calcium aluminate silicate, katoite silicatian, C_3ASH_4 , is present in small amounts) drastically reduces the cement/rock reaction, as the ITZ is barely distinguished by OM and is confirmed by the element maps, which show little Ca migration.

Compared to Portland cement blends, this cement hardens quicker, which also justifies the lower amount of reaction of the cement with the rock. The rapid reaction of the cement compounds has probably restricted Ca migration into the rock. This HAC rapid hardening is not desirable, as a longer workability/slow setting is one of the most desirable properties of any well cement. Another factor that might have contributed to a lower migration is the distinct particle size distribution compared to any other cement or admixture. The significantly higher average particle size is likely to have reduced the physical migration of cement into the rock, as the larger cement particles are less likely to penetrate in the rock pores.

VII.2.1.2 Drilling mud: IGN/HAC(150.b.28d)

Similarly to the other samples with bentonite addition, the bentonite barrier is easily distinguishable (by optical microscope image) and weakens the cement/rock bond. The gehlenite did not form due to the absence of significant amounts of silica in the cement. Otherwise, there is little change in ITZ-R and ITZ-C zones when compared with that found in the equivalent sample without bentonite, IGN/HAC(150.28d).

The Ca/Al cation exchange reported for the Portland based cements is not happening in this calcium aluminate cement, perhaps due to the high amounts of Al, which is fixed as aluminate hydrate in the cement.

VII.2.1.3 <u>Curing temperature</u>: IGN/HAC(290.28d)

This sample has a very thin ITZ. As stated for the 150°C sample this may be due to the sharp reduction of calcium silicate minerals but katoite silicatian is present in small amounts. This seems to drastically reduce the cement/rock reaction extent.

The milky material that is forming suggests the presence of amorphous silica gel, a consequence of the reaction of the calcium aluminiate silicates with the silica in the rock.

VII.3 Overall discussion

The overall discussion aims to summarize the discussion as a function of the main variables studied in the current work.

• <u>Cement formulation</u>:

Physical and chemical interaction with the formation was observed in all the cement formulations under study. The milky material seen under XPL suggests that silica gel forms in ITZ as a consequence of an alkali-silica reaction between the cement and the rock. The SEM/EDS phase and element maps show that the cement/rock reaction is an ongoing reaction where there is migration of Ca^{2+} ions occurs, mainly through the rock pores.

Two main stages can be distinguished in the migration of cement into the rock: an initial/physical and a final/chemical one, a phenomenon also reported by Duguid *et al.* (2011).

The physical migration happens initially before the cement has set, so all the cement constituents flow together in an aqueous suspension (by capillarity), into the rock pores. This physical penetration of cement into the rock tends to improve the bond by increasing the mechanical interlocking between the two materials (Agbasimalo, 2012). Duguid *et al.* (2011) postulated that the penetration of the cement particles into the formation is a good thing, as the cement that invades the stone blocks some of the rock pores and reduces the the amount of harmful brine in contact with the cement. This will prevent the damage of the cement in the outermost layer and delaying the development of a gap in the ITZ. These gaps are not desirable as they represent zones of preferential fluid movement by enhancing the amount of brine in contact with the cement and, subsequently, causing a more rapid damage to the outermost layer of the cement (Crow *et al.*, 2009; Duguid *et al.*, 2006; Carey *et al.*, 2007).

The chemical process occurs after the cement has set, with the chemical ions (mostly Ca^{2+} and OH^- , which are the most mobile) migrating into the rock through a chemical driving gradient. This stage is characterized by a slower migration of mostly Ca^{2+} (no significant amounts of Si available in the rock pores), forming the second ITZ-R rim (lighter brown in PPL). It is not clear whether the migration of Ca^{2+} and OH^- from the cement into the rock is beneficial to the quality and/or durability of the ITZ. It is, however, anticipated that the loss

of high amounts of Ca^{2+} may have a negative impact on the ITZ, as it may ultimately alter the hydration products that form in the outermost layer of the cement.

With addition of 20wt.% quartz (SF), the physical migration stage was not expected to be significantly affected as the particle size distribution of the admixture is very similar to the cement. On the other hand, the chemical migration was expected to slow down, as the added silica is expected to fix higher amounts of Ca^{2+} and OH^{-} in the cement, limiting the avaiability of migrating ions. Nonetheless, the addition of 20wt.% SF proved to have little effect on both the physical and chemical interactions of the cement with the rock, as it shows a similar reaction extent as the comparable sample with pure class G cement.

However, the addition of 40wt.% SF to the class G cement was sufficient to significantly reduce the reaction extent. This indicates that, unlike in the G20SF, the addition of 40wt.% of quartz to the cement is high enough to partially restrict the chemical migration of Ca^{2+} and OH⁻ into the rock. This formulation is very well regarded in the geothermal industry due to the good mechanical performance provided by its hydration products.

Like the sample with 40wt.% SF addition, the addition of 20wt.% microsilica 600 (MS) to the class G also caused a reduction in the reaction extent between the cement and the rock. This suggests that, unlike the G20SF, the relatively low amount of silica addition (20wt.% MS) is enough to fix the Ca²⁺ and OH⁻, and limit their migration into the rock. This is justified by the considerably faster reaction of the Portland based cements with MS (mostly amorphous SiO₂) compared to SF (mostly quartz, i.e. crystalline SiO₂).

The class A and white cements showed a relatively narrower reaction extent with the rock, which is likely to be a consequence of their faster setting, associated with the higher amounts of C_3A , compared to G. The higher the C_3A , the faster the setting is. The faster setting will also fix the ions faster than in the class G cement, restricting the migration of these into the rock. The faster setting of these two formulations is not desirable in geothermal wells as they do not allow enough workability for the cement to be placed downhole.

HAC has the narrowest reaction rim with the rock, compared to all the Portland cement blends. This is due to the different chemical and physical composition of this cement. Firstly, it hardens quicker, limiting the time in which the ions are available to migrate. Secondly, the lower amount of mobile ions (such as Ca^{2+}) has certainly constricted the amount of reaction compared to the Portland based cements. Lastly, the significantly higher average particle size of HAC compared to the Portland based formulations is likely to have reduced the physical

migration of cement into the rock, as the larger cement particles are less likely to penetrate in the rock pores. In any case, the HAC rapid hardening is not desirable, as a longer workability/slow setting is one of the most desirable properties of any well cement.

• <u>Temperature:</u>

There are obvious differences between the cements cured at 150°C and 290°C. Most of the Portland based formulations showed a red colour after the cure at 290°C, whereas at 150°C they kept their greyish colour. The rocks also acquired a partially reddish colour after exposed to 290°C in brine. In both cases, this was due to the oxidation of the iron present in these materials.

The increased temperature of curing from 150° C to 290° C has also affected the minerals formed in the cement. The phases formed at 290° C are generally known for their higher permeability and lower strength than those formed at 150° C. All the 290° C cured speciments showed a fissure in the ITZ, which indicates that the cement/rock bond was drastically reduced compared with the 150° C samples. This suggests that the weaker phases formed at this temperature, along with the loss of migrating Ca²⁺ and OH⁻ in the outermost layer of the cement, are the mainly responsible for the extremely low bond.

These clearly indicate that the performance and durability of the cement and, consequently, the ITZ is drastically reduced at 290°C compared to 150°C.

• <u>Drilling mud</u>:

Bentonite used as drilling mud alters the mechanical and chemical properties of the ITZ and, consequently, reduces the bond between the cement and the rock. This finding is supported by several studies (Agbasimalo, 2012; Ravi *et al.*, 1992 Peterson, 1963; Ladva *et al.*, 2005; Oyibo and Radonjic, 2014), who concluded that the formation of a mud cake as a consequence of the use of drilling mud, has a detrimental effect on the bond between the cement and the rock. Some of these authors have compared different types of drilling fluid contamination, namely the physical (mud cake) and chemical contamination, from which they have agreed that the physical barrier imposed by the mud cake has the most negative effect on the bond between the cement and the rock.

• <u>CO₂ exposure</u>:

This work confirms that the presence of high concentrations of CO_2 cause relatively rapid carbonation of geothermal cements, which will eventually corrode. Thus it has a negative impact on the outermost layer of the cement and, consequently, on the ITZ between the cement and the rock formation. However, the rate of carbonation is also a function of the formulation.

The API class G cement tends to have a better carbonation resistance than the ones where silica is added. This is due to the due to its lower permeability after carbonation caused by the expansive carbonation of portlandite (that is not present in the cements with silica addition) in the outermost layer of the G cement, which restrict the CO_2 from penetrating further into the cement. The sample with highest amount of silica (G40SF) showed a higher carbonation rate. Thus, despite the good mechanical performance provided by its hydration products, the G40SF has an extremely reduced durability in CO_2 enriched fields.

The XRD, SEM/EDS and TGA/Mass Spec results along with several studies (Cole and Kroone, 1960; Sauman, 1971; Villain and Platret, 2006; Thiery et al., 2007; Galan et al., 2003) indicate the presence of a poorly-crystallised and/or amorphous calcium carbonate (ACC) in the cement in which CO_2 was injected. According to some of these authors, these different CaCO₃ phases can co-exist in a complex carbonation system.

• <u>Rock type</u>:

The study of the different rock types has enhanced the knowledge of the physical and chemical interactions occurring between the cement and the rock. Besides improving the understanding of the physical and chemical migration processes, comparing the results for each distinct rock has permitted confirmation of the physico-chemical migration.

As stated above, the physical penetration consists of the migration of the cement particles (particularly the unhydrated ones) into the rock pores by capillarity. This was shown to be very dependent on the number of bigger rock pores into which the cement particles can penetrate. IGN is the rock with the greatest amount of these pores, which justifies the fact that this is the rock with the widest ITZ-R. It indicates that this is the dominant migration process.

The chemical interaction is based on the reactivity of the rock, which strongly depends on its volcanic glass content. Rhyolite (RHY) showed a much narrower reaction band than any of

the ignimbrites. This is likely to be a consequence of the combination of two different factors: the significantly reduced porosity (physical) and the considerably reduced amount of volcanic glass (chemical).

The physico-chemical migration relies mostly on the smaller pores, through which the dissolved cement species (namely Ca^{2+} and OH) penetrate. This type of migration is more significant in the rocks (KAO and MOR) with a porosity mostly composed of smaller pores, i.e. pores where the unhydrated cement is not able to penetrate.

The porosity of the rock also dictates the amount of CO_2 / HCO_3^- that can come in contact with the outermost layer of the cement. The higher the porosity, the higher amount of carbon dioxide in contact with the cement and, therefore, the higher the carbonation rate. However, the rock porosity might not be directly proportional to its permeability, which can depend on other factors such as the mechanism of dissolution of the rock minerals and pore size (Hangx, 2005; Soler and Mader, 2010).

VIII. CONCLUSIONS AND FUTURE WORK

This chapter aims to compile the most relevant findings during the current work, as well as suggest future work within this field. Some final observations and general recommendations are provided, for the drilling engineers to take into account before and during the cementing job. It also presents the difficulties encountered during the experimental work, which should be considered in future analogous experiments.

VIII.1 Conclusions

This work highlights the importance of understanding both the chemical and the physical processes associated with the way that the cement and the formation interact in geothermal environments, where both processes are interdependent. Regardless of the environmental conditions, a good chemical bond must be preceded by a good physical interaction/contact between these materials, which strongly depends on the quality of the cementing job.

Several variables were found to have an impact on the way that cement interacts with the rock formation in a geothermal environment and, consequently, on the geothermal cement durability. These variables are:

• <u>Cement formulation</u>

All the cement formulations tested have undergone significant chemical reactions as well as forming a good bond with the rocks at 150° C. All the Portland cement based systems show migration of Ca²⁺ and OH⁻ ions from the cement into the rock, a process which happens mostly through the rock pores. These are ongoing reactions, occurring faster during the first days/few weeks of cure. Initially they are driven mostly by a physical process (mainly capillarity) of cement movement into the porous rock, and a slower second migration stage, mostly driven by chemical gradient. New compounds (including silica gel) are formed in the rock side of the interfacial transition zone. For the neat API class G and A cements, there was a decrease in portlandite content in the outermost layer of the cement. This compound was not formed at all in the formulations with silica addition.

The addition of silica to API class G cement tends to reduce the amount of reaction between the cement and the rock due to its relatively rapid reaction with Ca^{2+} and OH^{-} which end up being retained in the cement. However, this reduction of migration

seems to be strongly dependent on the type and amount of silica added, with the amorphous silica reducing the reaction further due to its faster reaction with the cement compounds.

For the other cement formulations, the reduced reaction extent of API class A (OPC) and White cement compared to class G cement seems to be consequence of the decreased setting time. The higher amounts of aluminate (C_3A) in the class A and white cements induces a faster setting reaction, reducing permeability of the cement matrix and leaving lower amounts of available cement compounds to migrate. The almost complete absence of calcium silicate minerals in the HAC cement, drastically reduces the cement/rock reaction, which it is also likely to be a consequence of the significantly larger particle size as well as the reduced setting time.

• Drilling mud

The presence of a bentonite barrier (mud cake) such as that formed from drilling mud has a number of consequences on the cement/rock interactions. The most relevant are the formation of a new compound, gehlenite, and enhancement of the cement/rock reaction. The presence of gehlenite was identified in small amounts in the ITZ of each one of the samples with Portland based cement where bentonite had been injected. The presence of the bentonite layer, despite seemingly to enhance the chemical reaction between the Portland based cements and the rock, resulted in a significantly reduced bond between the cement and rock at 150°C. This is due to the chemical reaction (formation of gehlenite) and, mostly, the physical barrier formed between cement and rock, i.e. the so-called mud cake.

• <u>Temperature</u>

The reddish colour found in both the cement and some areas of the ignimbrites in samples cured at 290°C was due to the dissolution/precipitation process plus oxidation of the iron present in both materials. The increased temperature of curing results in weakened hydration products which end up opening a fissure in the outermost layer of the cement, due to a general loss of bonding. The losses of migrating Ca^{2+} and OH^{-} (from cement to the rock) have weakened the cement phases further and consequently, the cement/rock bonding.

• <u>CO₂ exposure</u>

In the presence of dissolved CO_2 , there is a significant increase in carbonation in the outermost layer of the cement for all the API class G based (Portland cement based)

formulations. This carbonation process is complex, with both crystalline and poorly crystalline/amorphous calcium carbonates appearing to form as well as perhaps, scawtite. The extent of the carbonation reaction is regulated by the carbonation of the various cement minerals present, as they have possibly blocked the cement and/or rock pores and therefore restricted further migration. The neat API class G cement reaction with the rock seems to be slowed by the portlandite carbonation, known to be a relatively fast carbonation reaction compared to that of the calcium silicate hydrate minerals. This early carbonation causes an early carbonation barrier. In the sample with 20% silica flour addition, the reaction rim is wider, due to the absence of portlandite. The extreme carbonation of tobermorite in the sample with 40% silica flour addition reduces the amount of free calcium and consequently shows the lowest reaction extent. Despite the formation of calcium carbonates, CO_2 exposure at 150°C makes little change to the cement/rock bonding.

The carbonation of the samples exposed at 290°C was much faster than at 150°C, due to the higher permeability of the cementing phases formed at these conditions combined with the faster chemical reactions at 290°C. This is compromising the durability of the cement and, consequently, affecting the bonding with the rock.

• <u>Rock type</u>

The volcanic glass content and, especially, the pore size distribution of the rock play a key role in the cement/rock interaction. While the pore size distribution of the rock affects the physical and physico-chemical migration processes, the volcanic glass content enhances the chemical reactions between the cement and the rock formation. Nonetheless, the bond between the cement and the rock depends mostly on the physical characteristics of the rock itself (such as porosity) rather than on the chemical composition of the rock or the cement. The cement paste penetrates into the rock pores by capillarity, creating a bond which relies mostly on the mechanical interlocking between these two materials.

While the optimum conditions for formation of a "good" cement rock bond remain unknown, some final observations and recommendations can be drawn from the current research work, as function of each variable. In any case, the durability of the ITZ and subsequently the cement, is strongly dependent on the quality of the bond between the cement paste and the

rock formation. Any gaps formed between the cement and the rock will be detrimental for the durability of the whole system.

- <u>Cement formulation</u>: generally, in a CO₂ free environment, the cement that shows better mechanical performance is the one where 40% quartz is added, as it avoids "strength retrogression", which is a gradual loss of strength.
- <u>Drilling mud</u>: The use of bentonite as drilling fluid should be avoided if possible, as it creates a barrier which drastically reduces the bond between the cement and the rock. Despite its inferior properties, the use of water as drilling fluid should be considered as an alternative to replace bentonite drilling mud.
- <u>Temperature</u>: The bond between the cement and the rock is drastically reduced when the curing temperature increased from 150°C to 290°C. This is a consequence of the reduced performance and durability of the cement itself, as the hydration products formed at temperature above 200°C have low strength along with the faster chemical (deleterious) reactions that occur as the temperature rises.
- <u>CO₂</u>: CO₂ enriched fields are not desirable, regardless of the conditions and materials involved. However, when CO₂ is not avoidable, the addition of SF must be avoided, as it will form low Ca/Si phases, which carbonate more rapidly, due to the porosity of their carbonation products.
- <u>Rock type</u>: Amongst the rock features, the pores in which the unhydrated cement can penetrate were shown to have a dominant role in the bond between the cement and the rock. The rock with the greater number of relatively big pores (bigger than the smallest unhydrated particles, i.e. typically above 5 µm) tends to perform a better bond with the cement. This is due to a better mechanical interlocking between these materials, as a consequence of the penetration of cement into the rock pores.

All this information should be assessed by the drilling engineers during the well design and construction stages. They should take into account the pros and cons associated with each variable. However, variables like temperature, CO_2 concentration and rock type are usually not controlable. In any case, a study of the life cycle cost of a geothermal well is recommended.

VIII.2 Future Work

This work provides a new insight on this specific topic. It highlights that further understanding of how each variable studied affects the cement performance and the way it interacts with the surrounding environment is needed. Other geothermal cementing formulations should be tested as well.

In order to better understand the relation between the actual bond between the cement and the rock, it is recommended to complement the chemical and physical analysis with a mechanical one. This will be useful to assess how the bonding (measured through the mechanical strengths, e.g. pull out test) is related with the physical (capillarity) and chemical (phases formed in ITZ) migrations.

Further study of the compounds formed in the ITZ should be made. The amorphous material forming in this zone should be further investigated, namely amorphous calcium carbonate and silica gel, in order to better understand those chemical reactions which occur in a similar way to the alkali-silica reaction in concrete. The reactions which do occur are shown to be extremely complex.

However, some precautions should be taken. For instance, the collection of samples for XRD analysis is a challenge when collecting samples from both sides of the ITZ (ITZ-C and ITZ-R), as these zones are very narrow. Moreover, the amorphous nature of both the rock formation and cement formulation make it extremely hard to accurately analyse the XRD results, as for many of them the trace obtained contains many small peaks which are very difficult to distinguish from the background of the amorphous material typified by a large hump. In order to increase the reliability of the XRD results and subsequent analysis, considerable effort should be put in the collection and analysis of samples from the ITZ.

Some other alternative formulations such as geopolymer cements should be investigated in the context of geothermal applications. Additional work carried out by IRL/Callaghan Innovation suggests that typical geopolymer formulations may experience some problems (e.g. unable to set, shrinkage) when exposed to geothermal environments. Geopolymer cements are generally formed by reaction of an aluminosilicate powder with an alkaline silicate solution at ambient conditions. Metakaolin, generated by thermal activation of kaolinite clay, is a commonly used starting material for laboratory synthesis of geopolymers but much work has been conducted using flyash which is more readily available. The published literature on geopolymers is extensive with many review papers, e.g. Majidi (2009) and Lloyd and Rangan (2010). Some authors defend that Geopolymer cement is more chemically resistant and/or more temperature stable, which would make it an attractive option for geothermal wells, in a corrosive environment. However, it has not been used for these purposes yet. The binder is essentially a cross-linked aluminosilicate with an amorphous structure similar to that found in zeolites. Extensive leaching of sodium hydroxide can occur if all the flyash precursor does not react.

The present work has been conducted under static conditions where solution saturation can readily occur. Corrosion of the carbonated species cannot occur under such conditions where a barrier may be formed and testing in a flowing situation is required to fully understand what can happen in the field. The protective carbonation barriers may not be stable where there is the potential to be dissolved. This fact combined with the limitations of laboratory simulated geothermal environment suggests that in situ (downhole) testing should be undertaken.

IX. PRESENTED AND PUBLISHED WORK

Some of the work presented in the current thesis was presented and published in peer reviewed International Conference Proceedings.

IX.1 Conference Presentations

• Geothermal Research Council meeting 2013 - Las Vegas, Nevada, USA. Presentation entitled "The Effect of CO₂-exposure and curing time on the Cement-Rock Interaction in Geothermal Wells".

 Geothermal Research Council meeting 2012 - Reno, Nevada, USA. Presentation entitled "The Effect of Drilling Fluid and Temperature on the Cement-Rock Interaction in Geothermal Wells".

IX.2 Publications

Silva, João R. M. C.; Milestone, Neil B.; Johnston, James H. (2013): "The Effect of CO₂exposure and curing time on the Cement-Rock Interaction in Geothermal Wells", Geothermal
Resources Council Transactions 37, pp. 75-82.

 Silva, João R. M. C.; Milestone, Neil B.; Johnston, James H. (2012): "The Effect of Drilling Fluid and Temperature on the Cement-Rock Interaction in Geothermal Wells", Geothermal Resources Council Transactions 36, pp. 277-285.

A copy of the above mentioned publications is provided below.

The Effect of Drilling Fluid and Temperature on the Cement-Rock Interaction in Geothermal Wells

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Cement-rock interaction, geothermal well cements, ignimbrite, bonding, drilling-fluid, bentonite

ABSTRACT

The current study has investigated the interactions between well cements and one of the most common types of rocks found in geothermal environments, under hydrothermal conditions.

Holes were drilled in blocks of ignimbrite rock and API class G cement with 0, 20 and 40% added silica flour, was poured into the cavities. The whole assemblage was autoclaved, under typical geothermal conditions at 150° and 300°C for 28 days.

The results show that chemical reactions occur in the intertransition zone, which are dependent on both drilling fluid and temperature. The use of bentonite as a drilling fluid and the exposure to higher temperatures (300°C) when compared to 150°C, seem to exacerbate the reactions occurring in the ITZ. Consequently, there is formation of new crystalline products, which have worse performance when the physical bonding between the cement and the rock is considered.

The effect of other variables such as CO₂ exposure, the hydrothermal alteration of the rock and the curing time are currently being investigated within this research project.

1.0 Introduction

Numerous investigations into geothermal well cements have been conducted in an attempt to develop a cement formulation that will handle the aggressive environments in geothermal wells and give increased durability. One of the issues to be considered is the interaction that can occur between the cement and the rock formation which can change the direction of reactions which occur within the cementing matrix. The work conducted in this field has been limited. Four factors need to be considered, the type of rock, the temperature, and the hydrothermal fluid along with the characteristics of the cement grout itself.

1.1 Geothermal Environments

Although there are considerable variations in conditions, even within the same geothermal field, several factors emerge which can influence the cement rock interactions. These are:

 The hydrothermal fluid, which Pirajno (2010) defines as a hot (ca. 50 to >500°C) aqueous solution, containing solutes that are commonly precipitated as the solution changes its proprieties. These fluids are subject to variations in temperature, pressure and density. Hydrothermal solutions are a mix of waters from several origins and can contain volatile gases, such as H₂O, CO₂, H₂S, HCI, SO₂ and CH₂.

In NZ, the brines are often enriched with CO₂ (up to >40,000 ppm CO₂) arising from boiling at depth where gases are concentrated beneath a cap rock or sediment. Sometimes high concentrations of H₂SO₄ in the supergene zone near the surface render the waters acidic (pH <1.5). Ambient total pressure at the top of the basement is presumably in the range 100-250 bars (normal hydrostatic), depending on location, giving well head pressures commonly within the range 10-100 bars, with a CO₂ overpressure of 6 bars (Wolery *et al.*, 2010; Henneberger, 1983).

- The rock formation, with its own factors of stratigraphic distribution, mineral composition, permeability, porosity and hydrothermal alteration of the rock influence the reaction. The Ohaaki-Broadlands geothermal system near the eastern fault margin of the TVZ, is a good example of a common geothermal field in NZ, (Hedenquist, 1990; Browne and Ellis, 1970; Browne, 1973) which can be generally explained with the following layers:
 - Near the surface, a mudstone cap overlies much of the field (Huka Falls Formation, a lava with high horizontal permeability and hydraulically connected to groundwater aquifers (Ohaaki Rhyolite), the main producing aquifer with heterogeneous uncompacted pumice and lapilli tuffs (Waiora Formation), the second important aquifer composed of coarse breccias (Rautawiri Breccia), rocks of poorly known material (Rangitaiki Ignimbrite, Ohakuri

Group volcanics and Waiora Formation conglomerates), and very low permeability material (Greywacke, where permeability will only exist in fractures).

This study has focussed on interactions with a fresh ignimbrite but a weathered sample will be considered later along with andesite, greywacke and pumice.

Ignimbrite is a fine grained igneous rock found in large exposed sheets in New Zealand and consists of crystalline rock fragments in a matrix of glass shards which are usually welded together in a matrix of volcanic ash (tephra) made up of shards and fragments of volcanic glass, pumice fragments, and anhedral crystals. The phenocrysts contain biotite, quartz, sanidine (or other alkali feldspar), and occasionally homblende, but rarely rarely pyroxene. Chemically, the ignimbrite composition is generally over 65 wt% SiO₂, with varying contents of sodium, potassium, and calcium, and lesser amounts of iron and magnesium (Pellant, 2000; Henneberger, 1983). These rocks can, however, be altered due to the long-time exposure to the hydrothermal fluid.

Drilling muds provide a barrier for well control, removing cuttings during drilling, transmitting hydraulic power to the drilling bit, maintaining formation pressure and stability and minimizing fluid losses to the formation (Culver, 1998; IPIECA and OGP, 2009). Currently, drilling muds are primarily mixtures of western bentonite (sodium montmorillonite) and water. While it is common practice to wash the annulus between the casing and formation before cementing, much of the mud still adheres to the formation, particularly if it is porous and so can interact with the cement, modifying its reaction with the formation.

1.2 Geothermal Well Cements

Well cementing grouts are formulations designed to be pumped downhole and when hardened, provide a seal between the steel casing and rock formation, protecting the steel against corrosion and supporting the casing against vibration (Nelson and Guillot, 2006).

Geothermal well cementing engineers have adopted the same nomenclature and standards as those used by the American Petroleum Institute (API). The most common API cement is Class G, a calcium silicate cement similar to Ordinary Portland Cement (OPC).

At elevated temperatures and pressures, the hydration reactions are different to those that occur at ambient temperature. The hydrates no longer lose water but form new compounds depending on temperature and overall Ca/Si ratio. Continuous exposure of high Ca/Si ratio cement to hydrothermal conditions induces a gradual and slow compressive strength loss in the hardened cement investigated by Kalousek and his co-workers (1951, 1954, 1955). They showed this to be caused by the formation and slow growth of new high Ca/Si ratio crystalline phases which are associated with an increased porosity and permeability (e.g.: aC_SH over 120°C), as the crystals enlarge and densify leaving a rather porous matrix that has little strength. Above 200°C, further high Ca/Si ratio phases form, namely reihardbraunsite (C.S.H), jaffeite (C.S.H.) or kilchoanite (C₃S₂), alongside Ca(OH)₂. These products do not act as binders, giving very low strength and high porosity to the grout (Milestone, 2011).

However, Kalousek (1954) found that by adding >30 wt% silica flour (pure quartz) the overall Ca/Si ratio in the binder was decreased, which avoided strength retrogression through the formation of yet further crystalline phases, tobermorite (Ca/Si ratio 0.8 - 1.0) between 150°C and 180°C and xonotlite (Ca/Si ratio 1.00), above about 200°C. Below 100°C quartz will not react readily with Portland cement (Iverson *et al.*, 2010).

1.3 Cement-Rock Interaction

At ambient temperatures a chemical reaction can occur between certain concrete aggregates and alkalis from cement, the alkali-silicate reaction (ASR) which has been widely studied. The reaction between silica and alkalis from the pore solution is complex, and in some conditions, may be similar to the pozzolanic reaction (Hobbs, 1988). From several references it is likely similar reactions will occur at high temperatures, even though the reaction products will be modified (Poole, 1992; Criaud *et al.*, 1994; Andrei *et al.*, 1996).

Hodgkinson and Hughes (1999) examined the reaction at \$5°C between a selection of rock-forming minerals and calcium hydroxide. After about 1 month they observed, as expected, carbonation but in samples containing quartz, albite, muscovite and anorthite, dissolution occurred, often along preferred crystallographic directions, to form etch pits visible by SEM. New calcium aluminosilicate phases were precipitated. The product from muscovite contained so much Al¹⁵ that it lay close to the zeolite compositional field. From anorthite katoite was formed at 4 days with a poorly ordered fibrous C-A-S-H phase also forming after 8 days which became well-ordered after a month. For quartz and albite, only a very minor precipitation of new phases was observed.

Where Ca(OH)₂ was present in the reactant fluid, the precipitating phases were an amorphous or poorly crystalline CSH gels (though stoichiometrically related to the fully crystalline CSH forms of tobermorite and jennite) and other cement minerals (hydrogarnet, hydrocalumite, zeolites, feldspars,...) (Bateman at al., 1998; Rochelle et al., 1992; Savage and Rochelle, 1993; van Aardt and Visser 1977a, b; Hodgkinson and Hughes, 1999).

Hodgkinson and Hughes (1999) concluded that at low temperatures (<110°C) the main reactions were formation of calcium silicate hydrate (CSH) gels, while at higher temperatures (>110°C) the main products were zeolites and feldspars (especially, in the presence of NaOH or KOH). Andrei and Criaud (1996) showed that the products of reaction obtained at 150°C were similar in texture (amorphous and polymorphous gels) to those at normal conditions, with a broad range of chemical composition. Over 150°C, experimental work conducted with alkali hydroxides (NaOH and KOH) and clays, formed zeolites and sometimes feldspars rapidly, with a high pH causing the alteration of smectite to illite or illite/smectite interlayers (Chermak, 1992, 1993; Inoue, 1983; Komarneni and White, 1981, 1983; Johnston and Miller, 1984; Hodgkinson and Hughes, 1999).

Langton et al. (1980), aiming to understand the relationship between the chemical and physical proprieties of the interfacial region formed between cement paste and rock, undertook hydrothermal cement-rock interaction experiments at temperatures of 200°C and 250°C, at 51.7MPa pressure. They used an API class J cement (C₂S + quartz), with tuscarora quartzite (95% quartz with a silica cement) and Valentine limestone (99.9% calcium carbonate), which they considered as unreactive.

From the shear strength measurements, they observed that the cement-quartzite bond seemed dependent on temperature for the first 7 days of curing, as the 200°C sample achieved much higher shear strength compared with that at 250°C, whereas the cement-limestone sample was more stable and not dependent on the temperature (200/250°C) or on the curing time, although it did not achieve as high shear strengths as the quartzite sample.

From chemical analysis across the cement-rock interface, after only one day of curing, they observed that the cement-quartzite sample had relatively sharp decrease in silicon up to 50µm into the cement and a sharp decrease in calcium over about the same range into the rock, whereas the cement-quartzite sample had a sharp gradational change for calcium and silicon, across the interfacial region.

They concluded that the both shear strength and hydration changes for both samples depended on the temperature and on curing time. Moreover, they reckoned that the degree of paste hydration (in normal cement pastes) or of belite (BC₂S)-quartz reaction (in hydrothermal cements) increased with time along the degree of crystallinity of calcium silicate hydrates in the interfacial region and the paste, which increased with time and temperature. It was suggested that the shear bond strength that developed be-

tween 'unreactive' wall rock and cement reasonably approximated, within experimental error, the tensile strength of the hydrothermally cured cement itself and they felt that mechanical bonding was primarily responsible for the shear strength of the unreactive wall rock-cement contact, rather than any chemical bonding.

2.0 Methodology

2.1 Raw Materials

The raw materials ignimbrite (supplied from the Hinuera Stone quarry), silica flour (SSA-1) unhydrated bentonite (Western bentonite) and class G cement (Holcim) were analysed by X-ray fluorescence (XRF) and X-ray diffraction (XRD). A thin section of ignimbrite was prepared and analysed in optical microscope.

2.2 Hydrothermally cured cement-rock system

Three different cementing formulations were used to examine rock/cement interactions, with and without the presence of a layer of bentonite. These were API class G cement (G), API Class G + 20 %wt silica flour (G20SF) and Class G cement + 40%wt silica flour (pure quartz) (G40SF).

25 mm cavities were drilled in small ignimbrite blocks, which were immersed in geobrine solution¹ at 90°C for 7 days. One set were filled with a 3% bentonite suspension and exposed at 90°C before being emptied, quickly washed and filled with cement. Cement shuries were prepared according to API RP10 at a w/s ratio of 0.45 and poured into different holes. The assemblages were then cured for 2 days in geobrine at 90°C and cured in autoclaves for 26 days (making a total of 28 days cure). Two curing temperatures were used, 150°C and 300°C.

After curing, each cement-rock system was cut in half, photographed and prepared for x-ray diffraction (XRD), optical microscopy, SEM/EDS and TG analysis.

2.3 Sample Identification

Four distinct zones were identified in each sample, namely: interior zone of the cement (int); cement side of the ITZ (cem); rock side of the ITZ (rock) and exterior side of the rock (IGN). This nomenclature (int, cem, rock and IGN) was combined with the type of cement mixture (G, G20SF and G40SF) and the previously explained bentonite/temperature combinations (150,



IND

Figure 1. Cross section, with class G cement cured at 150°C (no bentonite).

Figure 2. Cross section, class G cement plus 20wt% stilica flour, cured at 150°C (no bentonite).



Figure 3. Cross section, class G cement plus 40wt% silica flour, cured r at 150°C (no bentonite).

Figure 4. Cross section, class G cement cured at 150°C, with bentonite laver.





Figure 5. Cross section, class G cement plus 20wt% silica flour, cured at 150°C, with bentonite layer.

Figure 6. Cross section, class G cement plus 40wi% silica flour, cured at 150°C, with bentonite layer.







Figure 9. Cross section, class G cement plus 40wt% stilca flour, cured at 300°C (no bentonite).

at 300°C (no bentonite).
b150 and 300). This nomenclature is used so that each zone can be simply and clearly distinguished from the others, according to Figures 1, 2, 3, 4, 5, 6, 7, 8 and 9.

3.0 Results

3.1 XRD Analysis

XRD results are presented in Table 1.

Table 1. Compounds identified by XRD analysis

Specimen	Sample	Identified Peaks and Other Relevant Features						
	G150int	Amorphous with portlandite and traces of calcite and unhydrated cement.						
G150 (Figure 2)	GI 50cem	Reduced amount of portlandite with traces of calcite and unhydrated cement						
	G150rock	Similar minerals to the centre of rock with reduced amounts of quartz from IGN 150.						
C1001120	G20SF150int	Amorphous with traces of calcite, quartz, tobermorite and $\alpha C_2 SH$.						
(Figure 3)	G20SF150cem	Similar to above but with slight increase in quartz.						
(rightes)	G20SF150rock	Similar to G150rock.						
G405F150	G40SF150int	Large amorphous component with significant quartz and tober morite.						
(Figure 4)	G40SF150cem	Similar to G20SF150cem.						
	G40SF150rock	Similar to G150rock but without reduced quartz from IGN150.						
	Gb150int	Amorphous with portlandite and traces of calcite, kilchoanite and $\alpha C_2 SH$.						
Gb 150 (Figure 5)	Gb150cem	Amorphous with decreased portlandite from Gb150int. @C2SH and kilchoanite not present. Aragonite and geblenite present.						
	Gb150rock	Similar to G150 but without the reduction in quartz from IGN150. Gehlenite present.						
	G20SFb 150int	Amorphous with quartz and trace amounts of $\alpha C_2 SH$, katoite an calcite.						
G20S- Fb150 (Eigurg 6)	G20SFb150cem	Amorphous with decreased amounts of quartz, aC ₅ SH and calcite from G20SFb150int. No katoite. Gehlenite also present.						
	G20SFb150rock	Albite, anorthite are present with no reduction in quartz from IGN150. Gehlenite also present.						
	G40SFb 150int	Large quartz present with QC2SH, tobermorite, calcite and gismondine.						
G40S- Fb150 (Figure 7)	G40SFb150cem	Quartz and tobermorite present with traces of aC2SH, gismondi and calcite which are unchanged from G40SFb150int. Slightfrace of gehtenite.						
	G40SFb150rock	Albite, anorthite and no reduction in quartz from IGN150. Traces of gehlenite.						
	G300int	Portlandite, calcite and reinhardbraunsite with small amounts of killalite and aC2SH. Perhaps some katoite present.						
G300 (Figure 8)	G300cem	Portlandite decreased substantially from G300int but a mount of katoite, killalite and QC_SH appear to remain the same while the amount of reinarbraunsite and calcite increase.						
	G300rock	Albite, anorthite and quartz are present with small amounts of reinhardbraunsite and $\alpha C_2 SH$ seem to be present as well, although the noisy results make it difficult to fully identify phases.						
G205E300	G20SF300int	Killalite, kilchoanite and quartz are present with traces of xonolite.						
(Figure 9)	G20SF300cem	Killalite, kilchoanite, xonotolite with increased quartz.						
	G20SF300rock	Albite, anorthite, no reduction in quartz from IGN 300.						
22	G40SF300int	Quartz, xonolite and killalite are present.						
G40SF300	G40SF300cem	Increased quartz and xonolite from G40SFb300int.						
(rigure 10)	G40SF300rock	Albite, anorthite and no reduction in quartz from IGN300.						

3.2 Microscopy (Optical Microscopy and SEM/EDS)

G150

Figure 10. G150 ITZ In PPL (100X).



Figure 11. G150 ITZ In XPL (100X).



Figure 12. G150 ITZ In SEM (100X).

Under the optical microscope in plane polarized light (PPL), the unhydrated cement is seen as pleochroic grains and small sized crystals but in crossed-polarized light (XPL), most seems amorphous.

The interaction zone (ITZ) in PPL is a dark brown rim of about 100 μ m, (150cem+A150rock), whereas both the rock and cement are mostly colourless. In XPL, this zone appears totally dark (except for a few quartz or feldspar crystals present). <u>SEM/EDS</u> analysis shows very high amounts of Ca in the cement, with significant amounts of Fe and Si. In the ITZ, Ca seems to penetrate up to about 300 µm into the rock, and the Si concentration in the ITZ seems to be more uniform than in the rock or in the cement.

G20SF150



Figure 13. G205F150 ITZ In PPL (100X).

Compared to G150, the most noticeable difference by optical microscopy is the presence of quartz crystals, which are colourless in PPL, with a 90°C extinction angle in XPL.

The ITZ is dark brown with more small and medium sized grains (assumed to be **non-hydrated cement** particles and/or silica) than



Figure 14. G205F150 ITZ In XPL (100X).



Figure 15. G20SF150 ITZ In SEM BSK (100X).

G20SF150cem than in the G20SF150int. There are less quartz crystals in G20SF150cem than in G20SF150int.

From SEM/EDS Ca migration from G20SF150ccm to G20S-F150rock has occurred. Within the ITZ the concentration of Ca and Si is higher and more uniform distribution than in the rock or in the cement.

G40SF150

In optical microscopy, the most noticeable difference to G20SF150 is the large amount of unreacted quartz crystals in the cement matrix.

The ITZ is again a dark brown rim. There are less quartz crystals in G40SF-150cem than in G40SF150int.



Figure 16. G40SE150 ITZ In PPL (100X).



Figure 17. G405F150 ITZ In XPL (100X).



Ca has moved from G40SF150cem into G40SF150rock. There are high levels of both Ca and Si in the cement from the silica flour.

The ITZ has the highest concentration and more uniform distribution of Ca, Si and O in the ITZ, rather than in the rock or in the coment.

Gb150



Figure 19. Gb150 ITZ In PPL (100X).

As this is a similar sample to G150 we would expect similar results. However, under the optical microscope, there is clearly a higher concentration of **non-hydrated cement grains in the ITZ, and** the bentonite barrier is easily distinguished.

Nevertheless, the ITZ seems to be about the same,



Figure 20, Gb150 ITZ In XPL (100X).



Figure 21. Gb150 ITZ In SEM (100X).

 $300 \ \mu m$, although calcium has migrated to about $600 \ \mu m$. The Si is more uniformly distributed in the interaction zone than anywhere else.

G20SFb150



Figure 22. G20SFb150 ITZ In PPL (100X).

Similar results to G20SF150 were seen.

While the EDS data was not of acceptable quality, but from the optical microscope and SEM analysis, the bentonite barrier was very easily distinguished from the rest of the specimen.



Figure 23. G20SFb150 ITZ In XPL (100X).



Figure 24. G20SFb150 ITZ In SEM (100X).

G40SFb150



Figure 25, G405Fb150 ITZ In PPL (100X)



Figure 26. G40SFb150 ITZ In XPL (100X).

Figure 27. G40SFb150 ITZ In SEM

(100X)



Little difference from G40SF150 is noted but with a noticeable bentonite barrier. The EDS data was not of acceptable

G300



Figure 28. G300 ITZ In PPL (100X).





Figure 29. G300 ITZ In XPL (100X).

Figure 30. G300 ITZ (cement) In SEM (100X).

Figure 31. G300 ITZ (ignimbrite) in SEM (100X

The first noticeable feature of this cement is its reddish colour although this is not obvious under the optical microscope. The cement seems to have penetrated into the rock but afterwards, it detached, as there is a distinct loss of bonding. The ITZ is about 700 µm (0.7 mm) across.

Considerable calcium migration has occurred in this sample, from the cement to the rock.

G20SF300

Similar to G300, this cement also appears reddish which is not noticeable under the optical microscope. Unlike G20SF150, the



Figure 32. G205F300 ITZ In PPL (100X).

quartz crystals in the cement are not present. In the ITZ, the cement has detached from the rock. There are some red coloured spots on the cement side of the boarder which may be the consequence of movement of iron from the rock to the cement.

The EDS data was not of acceptable quality.

G40SF300



Figure 33, G205F300 ITZ In XPL (100X).



Figure 34. G205F300 ITZ In SEM (100X).



Figure 35. G405F300 ITZ In PPL (100X).



Figure 36. G405F300 ITZ In XPL

(100X).



Figure 37. G40SF300 ITZ (Ignimbrite) In SEM (100X).

Figure 38, C40SF300 ITZ (cement) In SEM (100X).

This sample is also reddish. Abundant quartz crystals are present (confirmed by XRD).

The ITZ is wide and brown with a dark rim. As noticed in the other 300°C samples, the Ca2+ cations seemed to have penetrated in the rock, which was probably followed by a detachment in the rock side.

From the SEM/EDS analysis, high amounts of Ca and Si were observed to be present in this cement. There are also considerable amounts of Fe, K, Mg and O. The iron is more homogeneous in the cement than in the rock.

4.0 Discussion 4.1 G150 and Gb150

Along with the amorphous component, portlandite was found in large amounts in the centre of the cement matrix in these samples, along with small quantities of calcite (possibly derived from handling) and unhydrated cement. The substantial decrease of portlandite from G150int to G150cem is due to migration of Ca²⁶ (and OH) ions from the cement into G150rock and ultimately the ignimbrite mould, confirmed by SEM/EDS results.

The very distinctive dark ITZ rim seen by optical microscopy supports the hypothesis of a reaction rim at the interface where new compounds may form. New compounds are not seen with G150int, although there is a marked decrease in the amount of portlandite in this zone. The highly uniform Si concentration across the whole ITZ, suggests this element also moves through this zone from the rock, solubilised by OH ions migrating from the cement into the rock, a reaction which is not readily detected.

The presence of the bentonite layer in Gb150 changes the reaction sequence which occurs in a wider ITZ with small amounts of several crystalline phases forming e.g. $\alpha C_2 SH$ and kilchoanite (C_1S_2). Their formation seems due to interaction with bentonite as gehlenite also forms in Gb150rock. This suggests that the first two compounds may react with aluminium from the bentonite (likely to be more reactive than the ignimbrite as it is not seen by XRD) to form gehlenite or that compound may crystallise directly from the mixture of ions in an alkaline environment. Ca penetrates deeper into the rock (up to about 600 μ m) which may be driven by cation exchange as more aluminium is substituted into a silicate network which requires a counter cation.

The addition of a bentonite layer also decreases the bonding between the cement and the rock, in other words the ITZ that forms, is a weak zone. This may be due to the formation of more phases that are more crystal line, probably due to the ready availability of aluminium as the bentonite reacts. Bensted and Hewlett (2008) examined hydrogarnet-type cements, where the predominantly gehlenite hydrate binder had high compressive strengths (ca. 110-136 MPa) and low porosities (1-10 %). However, it was instable at above 100°C, which may be the reason for the poor performance in the cement-rock bonding, as the specimens were submitted cured to 150°C.

4.2 G20SF150 and G20SFb150

The quartz present in this matrix would be expected to slow the migration of Ca³⁶ ions across the ITZ into the rock but the SEM/ EDS results show it still occurs. The low intensity peaks in XRD indicate that the cement matrix still remains largely amorphous even though the added silica flour has restricted the formation of portlandite. In both G20SF150int and G20SF150eem, small amounts of tobermorite have formed, indicating the Ca/Si ratio in these zones has dropped low enough through Ca migration, and the availability of additional Si to allow tobermorite to form.

There appears more quartz in G20SF150int than G20SF-150cem, suggesting Ca leaching into and through the ITZ is rapid, leaving less available Ca to react with the quartz in the interior of the binder matrix. As explained by Klimesch and Ray (1998), the ready availability of aluminium makes the formation of tobermorite easier. Aluminium can be supplied into solution as both bentonite and the glass in ignimbrite react with the migrating OH ions along with soluble SiO₂. Tobermorite will then precipitate in the ITZ. There are also slightly lower amounts of quartz in the G20SF150rock than IGN150 indicating even in the ignimbrite, the quartz is able to reacts with the migrating OH and available Al. The complete lack of portlandite in the cement side of the interface is due to reaction with quartz and Ca²⁰ ion migration.

The addition of the bentonite layer in G20SFb150 again causes gehlenite to form, mostly on the rock side of the ITZ as a product of a reaction of Ca migrating from the cement with the AI and Si oxides present in the bentonite. Again there is a weakening of the cement/rock bond.

4.3 G40SF150 and G40SFb150

As expected, 40% silica flour addition has enhanced the formation of tobermorite with complete removal of portlandite, although the bulk of the binder still remains amorphous. The SEM/EDS analysis shows Ca migration from G40SF150ccm into G40S-F150rock still occurs indicating the reaction with quartz is slow and attack on the glass phases in the rock is preferential. There is also tobermorite formed on the rock side of the ITZ confirming the movement of Ca.

In a similar way to the Gb150 and G20SFb150 specimens, gehlenite seems to be present mostly in the rock side of the boarder (G40SF150rock).

4.4 G300

The most noticeable feature of this cement sample is the reddish colour noticed by the unaided eye in all 300°C samples which is likely due to the presence of iron. The ignimbrite when sold as a building stone is often heat treated around 600°C to obtain a brown colour which has been ascribed to the presence of oxidised Fe. Iron is know to leach in hydrothermal conditions so the red colur could be iron leaching from the ignibrite.

Chemically the increased temperature of curing leads to the formation of killalite and reinhardbraunsite, the high temperature high Ca/Si ratio phases not present in the 150°C specimens, portlandite and considerably less amorphous material. Deeper calcium migration occurs compared to the 150°C specimens and leads to more complex reaction increasing the width of the ITZ. No obvious alumina containing phases have crystallised but that may be because the reaction with ignimbrite has not released much compared to the samples with bentonite.

The fact that the cement has easily detached from the rock suggests that in crystallising, the cement has lost a lot of its cementing/bonding proprieties at 300°C although this may be due to differential expansion of the cement and ignimbrite.

4.5 G20SF300

For this matrix, the most noticeable change is the formation of kilchoanite and xonolite along with killalite (present also in the G300 specimen), whereas reinhardbraunsite has diappeared (un-

like in the G300). This will be due to the addition of silica flour which has completely reacted removing any portlandite. Nevertheless, xonotlite is unexpected at this Ca/Si ratio and probably results from extensive leaching of Ca²⁺ ions effectively lowering the Ca/Si ratio in the matrix.

The ITZ is wider and the cement and the rock have become completely detached from each other. On the cement side of the border are some red coloured spots, which may be the consequence of Fe moving from the rock into the cement and precipitating in the alkaline environment. The wider ITZ may, again, be attributed to a possible enhancement of Ca migration and further reaction due to the higher temperature or perhaps differential expansion during cooling to retrieve the samples has widened the discontinuity into a clear crack..

4.6 G40SF300

Similarly to the G20SF300 specimen, the large addition of silica flour will ensure complete reaction of portlandite and the Ca/ Si ratio is low enough that xonotlite readily forms at the expense of other calcium silicates.

There is still a wide reaction zone when compared to the 150°C specimens (due to the higher temperature) where the cement separates from the rock, but it is smaller than G300, probably because there is less Ca overall in the cement matrix to migrate, it being consumed in the reaction with the large amount of added silica flour.

5.0 Conclusion

From the current work, it is obvious that reactions occur between the rock and the cement as Ca²⁺ and OH ions migrate. The extent of the reaction is dependent on temperature (increasing from 150°C to 300°C) and on the presence of a drilling mud such as bentonite.

These migration reactions driven by Ca²⁰ ion migration would appear to occur faster than the expected reaction of Ca(OH)₂ with quartz. The presence of bentonite from the drilling fluid exacerbates the reaction in the ITZ, generally giving a wider reaction rim. The formation of the aluminosilicate gehlenite in the ITZ of the three specimens with a bentonite layer (unlike the other specimens) seems to be a consequence of the reaction between the cement and the bentonite and perhaps the rock, releasing Al and allowing this phase to form.

Despite a deeper penetration of Ca²² ions into the rock, the specimens at 300°C seem to have lower cement-rock bonding (as they have detached easier than the other 150°C specimens), after being autoclaved. This discontinuity is enhanced with bentonite at 150°C and appears associated with the presence of geblinite. The crystalline phases formed appear to have little strength and lead to a distinct break between the cement and formation which may be due to differences in molar volumes or shrinkage or differences in thermal expansion of the phases.

Further work on cement-rock interaction in a geothermal context is being conducted, where other important variables like such CO₂ exposure, hydrothermal alteration of the rock, rock type and curing time will be considered.

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¹ Geobrine recipe: 0.19 g sodium sulphate (NaSO₄), 0.05 g calcium chloride dehydrate (CaCl₂ 2H,O), 15.6 g liquid precipitated silica (SiO₅), 4.1 g potassium chloride (KCl), 15.8 g sodium chloride (NaCl) are well mixed and filled with water to make up 20 litres.

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The Effect of CO₂ Exposure and Curing Time on the Cement-Rock Interaction in Geothermal Wells

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Bonding, cement-rock interaction, CO₂, curing time, geothermal well cements, ignimbrite

ABSTRACT

The current study is focused on the interactions between well cements and one of the most common types of rocks found in geothermal environments, under hydrothermal conditions.

Holes were drilled in blocks of ignimbrite rock and slurries of API class G cement with 0, 20 and 40% added silica flour (SF), were poured into the cavities. The whole assemblage was autoclaved under typical geothermal conditions at 150°C for 84 days.

The results show that chemical reactions occur in the intertransition zone (ITZ) which are dependent on both carbon dioxide (CO.) exposure and the curing time. By comparing results with those of only 28 days curing it is clear that ongoing reactions continue to occur but at a slower rate than in the first 28 days.

When exposed to CO₂, the cement-rock interaction is very dependent on the amount of added quartz. When 20% of SF is added to the cement mix, the CO₂ presence seems to exacerbate the reaction between the cement and the rock, when compared with neat cement. On the other hand, 40% addition of SF seems to slow the migration of Ca²⁶ and OH ions and formation of cementing compounds in the rock, compared to 0% and 20% SF addition.

Work is ongoing in order to investigate the effect of these and other variables such as drilling fluid, temperature, rock type and cement mixture.

1.0 Introduction

The high CO₂ concentration in New Zealand geothermal fields has been a concern over its effect on well performance and durability. Besides affecting the natural rock formation and engineered materials (cement and steel casing), the presence of CO₂ in geothermal fields also plays a key role on how the rock and materials interact with one another. Knowledge of how rock and cement interact in geothermal environments is very limited. Significant research has been undertaken on the interaction between cement and/or rock and/or CO₂ in the context of carbon capture and storage (CCS), CO₂ enhanced geothermal systems (EGS-CO₂) or even for civil engineering purposes. However, these studies are at considerably different conditions (e.g. lower temperatures and/or lower pressures) than those found in geothermal wells.

Most geothermal plants utilise hydrothermal systems with temperatures within the 100°C to 300°C range. Over this range neutral pH decreases with temperature, from 6.14 at 100°C, to 5.83 at 150°C teaching a minimum of 5.6 around 250°C. As the temperature increases, CO2 also becomes less soluble and a weaker acid. While dissolved CO, levels in production fluids are typically around 0.064 moles/kg with a pH of 6.00 (neutral pH is 5.83), beneath caprocks and impermeable zones where gases boiled off in the production zone dissolve in the cooler fluid, the dissolved CO, concentration can be greater than 0.34 moles/kg giving a pH of -4.59 which is mildly acidic. Total ambient pressure at the top of the basement is probably in the range 100-250 bars (normal hydrostatic), depending on location, translating into pressures in geothermal wells within the range 10-100 bars, with a CO. overpressure of 6 bars (Wolley and Carroll, 2010; Henneberger, 1983; Ellis, 1959).

The commonly used Portland cement based systems carbonate when exposed to CO₂, either through reaction with HCO₂//CO₂ dissolved in ground waters, direct reaction with supercritical CO₂ or reaction with gaseous CO₂ (Milodowski et al., 2011) to form calcium carbonate (CaCO₂) from both portlandite (Ca(OH)₂) and calcium silicate hydrates (C-S-H). CO₂ dissolves in the hydrothermal brine becoming 'carbonic acid', H₂CO₃, which dissociates (Eq. 1). Bicarbonate ions are the predominant species and carbonate the cement (Eq. 2-3). If dissolved CO₂ levels are high enough this carbonate will dissolve, transforming the cement into a porous silica gel as the Ca(OH)₂ and calcium silicate hydrate (C-S-H) disappear (Eq. 4-5) (Duguid, 2009).

CO, dissociation: $CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{--}$ (1) Competer carbonation: $Ca(OH)_{-}(s) + H^+ + HCO_3^- \rightarrow CaCO_{-}(s) + 2H_{-}O_{-}$ (2) $C_{3,4} - S_2 - H_8(s) + H^* + HCO_5^- \rightarrow CaCO_5(s) + SiO_2OH_s$ (3)

Calcium carbonate dissolution: $CO_2 + H_2O + CaCO_3(s) \leftrightarrow Ca^{2*} + 2HCO_3^-$ (4)

 $2H^* + CaCO_1(s) \leftrightarrow Ca^{3*} + H_2O + CO_2$ (5)

There is disagreement in literature of the impact CO₂ has on cement, namely whether it seals or increases the cement porosity. Bruckdorfer (1986) proposed that the formation of CaCO₃(s) decreased cement permeability and increased its compressive strength. However, as R ochelle *et al.* (2004) noted there is a major change in molar volume between cement phases and carbonate alteration products but pointed out that it was dependent on the values used for tobermorite. Certainly, the impact depends on the overall Ca/Si ratio (Milestone and Aldridge, 1990). Milestone et al. (1986, 1987a) showed that carbonation of tobermorite increased permeability.

At 150°C, Ca(OH)₂ carbonates to calcite, while carbonation of C-S-H is slower and forms metastable aragonite, which slowly converts to calcite (Milestone *et al.*, 1986). Carbonation of Ca(OH)₂ is expansive so the carbonated layer occupies more volume than that from where it has come and can separate (Milestone *et al.*, 2012). The carbonation of tobermorite however, results in a contraction of 33% and increase in porosity. (Milodowski *et al.*, 2011).

Milestone et al. (1986) concluded that the rate of carbonation of the cementitious binder varied considerably, depending on the addition of silica flour (SF), normally added to counter the strength retrogression at high temperatures (over 100°C). In their experiments, they showed that

the crystalline low Ca/Si ratio phases tobermorite and xonotlite that form with addition of ca. 40% SF and give low permeability and high strength to the cement, carbonated rapidly and became porous when exposed to CO₂. This contrasted with the samples with neat Portland cement, where the high Ca/Si ratio phases, α C₂SH at 150 °C and reinhardbraunsite or kilchoanite

at 260°C, which form in association with Ca(OH)₂, that behaved better when exposed to CO₂. Despite being poor binders, these high Ca/Si ratio phases carbonated slowly, and formed a dense protective carbonation sheath with low permeability and high strength. Therefore, carbonation rate was very dependent on the volume of available Ca in any unit volume, particularly if any Ca(OH)₂ was present.

In rock interactions with CO₂, the felsic or acidic rocks (such as ignimbrite, granite and many sandstones) are expected to have a lower reaction degree than the basic rocks of a more mafic nature (e,g) and esite, basalt, periodite), as the dominant minerals are less reactive (Wolley and Carroll, 2010). In studies undertaken in order to understand the long term cement behaviour Milodowski et al. (2011) used natural analogues, and showed that moderately sized nodules of CSH phases had not undergone total carbonation, even after several thousand years. They suggested that similar minerals in well cements may possibly have significant longevity. By extrapolating the results of his experiments with sandstone cylinders filled with class H cement exposed to CO₂-containing

fluids, Duguid (2009) predicted that for a well with good zonal isolation, the rate of degradation was such that it would take between 30,000 and 700,000 years to degrade 25mm of neat cement paste in a sandstone reservoir. However, these experiments were conducted at low temperatures without the presence of mildly acidic geothermal fluids.

This paper will examine changes that occur in the inter-transition zone (ITZ) between geothermal cement and ignimbrite after exposure to CO₂ saturated water at hydrothermal temperatures.

2.0 Methodology

2.1 Raw Materials

The rock used was Ongatiti ignimbrite (from Hinuera Stone quary). XRF analysis showed the ignimbrite was mainly silica (approx. 70.5% SiO₃) with alumina (13.8% Al₂O₃) (Table 1). XRD analysis showed the major crystalline phases to be the feldspars anorthite and albite with smaller amounts of andesine, an intermediate feldspar, along with quartz. Optical microscopy showed the ignimbrite to be mostly a glassy (isotropic) groundmass, with irregular glass shards with distinct quartz phenocrysts and zoned feldspars (anorthite and albite) crystals. A few fine grained xeenoliths (rock fragments) were also found, which have probably mctamorphic origin.

Class G cement (Holcim) and quartz silica flour (SSA-1) were used to prepare the cement binders. Their XRF analyses are shown in Table 1.

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MnO	MgO	SO3	K ₂ O	Na ₂ O	TiO:	LOI*
Ignimbrite	70.56	13.80	2.81	1.90	0.04	0.36		3.30	3.75	0.31	2.62
API class G Holeim cement	20.1 21.19	4.1 3.8	2 5.34	66.1 63.2	0.05	0.9 1.82	2.5 2.08	0.5	0.2	0.2 0.95	0.89
Quartz silica flour (SSA-1)	99.73	0.13	0.02	<0.01	0,06	< 0.01	<0.01	<0.01	<0.01	<0.01	0.10

Table 1. Major oxides analysis of the raw materials utilized

"Lost On Againion at 1000°C

2.2 Hydrothermally Cured Cement-Rock System

Three different cementing formulations were used to examine rock/cement interactions, both with and without CO, injection. These were API class G cement (G), API Class G + 20 %wt silica flour (G20SF) and Class G cement + 40%wt silica flour (G40SF).

25 mm cavities were cored in small ignimbrite blocks, which were immersed in geobrine solution¹ at 90°C for a couple of days. Cement slurries were prepared according to API RP10 at a w/s tatio of 0.45 and poured into different holes. The assemblages were then set/cured for 2 days in geobrine at 90°C and cured in autoclaves for 82 days at 150°C (making a total of 84 days of curing). One set was submitted to carbon dioxide exposure, by maintaining a CO₂ overpressure of 6 bar.

After curing, each cement-rock system was cut in half, photographed and samples prepared for x-ray diffraction (XRD), Transmitted Light Optical Microscopy (OM), Scanning Electron Microscopy with Electron Dispersive Spectroscopy (SEM/EDS), Thermogravimetry (TGA) and Mass Spectrometry.

2.3 Sample Identification

Four distinct zones were distinguished across the interstitial zone (ITZ) in each specimen, namely: pure cement (CEM); cement side of the ITZ (ITZ-C); rock side of the ITZ (ITZ-R) and rock (IGN). This nomenclature (CEM, ITZ-C, ITZ-R and IGN) was combined with the type of cement mixture (G, G20SF and G40SF) and CO, exposure (+CO₂) is added to the nomenclature. This nomenclature is used so that each zone can be simply and clearly distinguished from the others, as in Figures 1-6.



neat class G cement (no CO2).



Figure 1. G(84d): cross section, with Figure 2. G205F(84d): cross section, with class G cement plus 20wt% silica flour (no CO2).



Figure 3. G40SF(84d): cross section, with class G cement plus 40wt% silica flour (no CO2).



Figure 4. G(84d+CO2): cross section, with neat class G cement, with CO2 exposure).



Figure 5. G205F(84d+CO2): cross section, with class G cement plus 20wt% silica flour, with CO2 exposure.



Figure 6. G405F(84d+CO2): cross section, with class G cement plus 40wt% silica flour, with CO2 exposure.

3.0 Results

3.1 XRD Analysis

Table 2. Compounds identified by XRD analysis.

Specimen	Sample	Identified Peaks and Other Relevant Features
G(84d)	G(84d)-CEM	Largely anorphous, with portlandite, unhydrated cement. Traces of aCSUL kilchoanite, calcite and aragonite.
(84 days	G(84d)-ITZ-C	Reduced portlandite; unhydrated cement stable. Traces of aC ₂ SU, kilchoanite and calcite, aragonite, hillebrandite and killalaite.
	G(84d)-ITZ-R	Similar to the rest of the rock, but with reduced feldspars and quartz; presence of calcite, uragonite, unhydrated cement; traces of portlandite, kilchoanite, hillebrandite and killalaite.
G20SF(84d)	G20SF(84d)-CEM	Largely amorphous, with quartz, aC,SH, and unhydrated cement. Traces of hillebrandite, kilkalaite, kilchoanite, aragonite, catoite and tobermorite
(84 days NO CO.)	G20SF(84d)-ITZ-C	Calcite and aragonite increase; oC,SH and unhydrated cement stable; reduced quartz. Traces of hillebrandite killalaite killebrandite and tobermorite
	G20SF(84d)-ITZ-R	Similar to the rest of the rock, with traces of anagonite, calcite, unhydrated cement, hillebrandite and killalaite.
G40SF(84d)	G40SF(84d)-CEM	Largely amorphous, with quartz tobermorite and catcite. Traces of a ragonite. unhydrated cement hillebrandite and_ killalaite
(84 days	G40SF(84d)-ITZ-C	Similar to CEM, but with slight aragonite increase.
	G40SF(84d)-ITZ-R	Similar to the rest of the rock with traces of hillebrandite and unhydrated cement.
G (84d+CO ₂)	G(84d+CO_)-CEM	Largely amorphous with portlandite unhydrated cement, Traces of a ragonite, kilchoanite, aC, SH, hillebrandite and calcite.
(84 days	G(\$44+CO_)-ITZ-C	Reduced portlandite; unhydrated cement stable; increased hillebrandite in d catche. Traces of anagonite, kilchoanite and $\alpha C_{\rm S}$ S1.
meery.	G(84d+CO_)-ITZ-R	Similar to the rest of the rock, with traces of coleite, aragonite, hillebrandite and unhydrated cement
G20SF (84d+CO ₂)	G20SF(84d+CO_)-CEM	Largely amorphous with quartz, unhydrated cement hillebrandite kilchoanite killalaite Traces of aragonite, calcite and tobermorite
(84 days	G205F(84d+CO_)-ITZ-C	Similar curve to CEM, except for slight increase in calcite and aragonite.
wCO.)	G205F(84d+CO_)-ITZ-R	Similar to the rest of the rock, plus calcite, anagonite and traces of unhydrated cement and hillebrandite
G40SF	G40SF(84d+CO_)-CEM	Largely amorphous with quartz, tobermorite, calcite and unhydrated cement. Traces of aragonite and hillebrandite
(84d+CO.) (84 days	G40SF(84d+CO_)-ITZ-C	Sharp increase in aragonite and quartz reduced tobermorite and unhydrated cement. Calcite stable.
wCO ₂)	G40SF(84d+CO.)-ITZ-R	Similar to the rest of the rock, with traces of hillebrandite, unhydrated cement calcite and a ragonite.

3.2 Microscopy (Optical Microscopy (OM) and SEM/EDS)

G(84d)

Figure 7. Optical Microscope Images of the G(84d) ITZ.





Figure 7a. Optical Microscope, Plane Polarised Light.

Figure 7b. Optical Microscope, Cross Polarised Light.

Figure 8. SERVEDS Images of the G(84d) ITZ.



Figure 8a. Ca mapping.

Figure 8b. SI mapping.

Under the OM large numbers of small sized grains/crystals can be seen in the G(84d) cement matrix (CEM). These are probably portlandite. In plane polarised light (PPL), a distinguishable brown rim (\approx 500µm wide) is observed in ITZ-R while in Cross Polarised Light (XPL), a \approx 500µm wide ITZ-C rim can be seen, with fewer small sized bright grains/ crystals than the rest of the cement (CEM). These crystals seem to be concentrated in the line between ITZ-C and ITZ-R.

The SEM/EDS images show Ca migration (≈300µm) to be more or less uniform from the cement into the rock with pockets of concentration in rock pores.

G20SF(84d)

Figure 9. Optical Microscope Images of the G20SF(84d) ITZ.



Figure 9a. OM, PPL.

Figure 9b. OM, XPL.

Under OM, the G20SF(84d) cement matrix (CEM) consists of small and large sized grains/crystals. In PPL, a ${\approx}500\mu m$ wide

Figure 10. SEM/EDS Images of the G20SF(84d) ITZ.

Figure 10a. Ca mapping.

Figure 10b. SI mapping.

dark ITZ-R rim can be seen which is likely to be amorphous as it is isotropic, whereas the ITZ-C is a \approx 300µm wide rim, barely distinguishable in either PPL or XPL. From SEM/EDS, we can see Ca²⁺ has migrated 300µm, from the cement into the rock, and is mostly concentrated in the rock voids.

G405F(84d)

Figure 11. Optical Microscope Images of the G405F(84d) ITZ.



Figure 11a. OM, PPL.

Figure 11b. OM, XPL

Figure 12. SEM/EDS Images of the G40SF(84d) ITZ.





Figure 12a. Ca mapping.

Figure 12b. St mapping,

Similar to G20SF(84d), the OM examination of G40SF(84d) cement matrix (CEM) shows small and large sized grains/crystals. In PPL, there is a \approx 400µm wide, dark ITZ-R, which is narrower than those in G(84D) or G20SF(84D) while in XPL, there are fewer bright spots in the cement matrix than in G20SF(84D) and the ITZ-C cannot be distinguished from the rest of the cement (CEM).

By SEM/EDS, Ca[≥] has migrated ≈250µm and in significantly lower amounts than for G(84d) and G20SF(84d).

G(84+CO2)

Under OM, the G(84+CO.) cement matrix (CEM) contains many small crystals. While a \approx 300 μ m wide ITZ-R rim can barely

Figure 13. Optical Microscope Images of the G(84d+CO2.



Figure 13b, OM, XPL.

Figure 14. SEM/EDS Images of the G(84d+CO2) ITZ.





Figure 14b. SI mapping.

be distinguished in PPL, in XPL it looks very bright. Also in XPL, a ≈300µm wide bright ITZ-C rim can be distinguished, with slightly more smaller sized grains/crystals than the rest of the cement (CEM). A thin dark line splits the ITZ-R and ITZ-C.

From the SEM/EDS images, Ca² migration has penetrated more or less uniformly about 300µm into the rock.

G205F(84+CO2)

Under OM, the G20SF(84d+CO.) cement matrix (CEM) has a number of small grains/crystals with a few bigger crystals. Under

Figure 15. Optical Microscope Imag es of the G205F(84d+CO2) ITZ



Figure 15a. OM, PPL.

Figure 15b. OM, XPL

Figure 16. SEM/EDS Images of the G20SF(84d+CO2) ITZ.





Figure 16a. Ca mapping.

Figure 16b. SI mapping.

XPL a few orange/reddish/brownish spots can be seen. A ≈450µm wide ITZ-R is barely distinguishable in PPL, whereas in XPL it appears extremely bright (brighter than either CEM or IGN). The ITZ-C is not distinguishable from the rest of the cement (CEM) by optical microscopy

By SEM/EDS, a ≈350µm Ca migration is detected, unevenly distributed in the ITZ-R, it is mostly concentrated in the bigger tock voids

G405F(84d+CO2)

Figure 17. Optical Microscope Images of the G40SF(84d+CO2) ITZ.



Figure 17b. OM, XPL.

Figure 18. SEM/EDS Images of the G40SF(84d+CO2) ITZ.



Figure 18a, Ca mapping,

Figure 18b. SI mapping.

Under OM, the G40SF(84d+CO₂) cement matrix (CEM) is similar to G20SF(84d+CO.), with small sized grains/crystals and a few larger sized crystals with plenty of orange/reddish/ brownish spots seen in XPL. A ≈200µm wide ITZ-R is barely distinguishable in PPL. In XPL it appears as bright colours (white and orange) (as bright as in CEM), but not as bright as the same zone in the G(84d+CO₂) and G20SF(84d+CO₂) samples. The ITZ-C is indistinguishable from the rest of the cement (CEM) by optical microscopy

By SEM/EDS, it can be seen that Ca has migrated ≈250µm, but is unevenly distributed through the ITZ, mostly being concentrated in the bigger rock voids.

4.0 Discussion

4.1 Samples Without CO2 Exposure

Comparing these results with samples subjected to the same preparation methodology and exposed under the same conditions but cured for just 28 days (Da Silva et al., 2012) gives an understanding of the effect of longer curing has on the cement-rock interaction

G(84d)

Portlandite has decreased in ITZ-C from CEM due to migration of Ca2 and OH ions into ITZ-R as seen by Da Silva et al. (2012). There is more calcite in the ITZ than CEM where carbonation in the outermost exposed layer of the cement fixes Ca2+ ions as insoluble carbonate, possibly caused by handling. Portlandite, hillebrandite and killalaite, along with ealcite are present in the ITZ-R, indicating that migration of Ca2 and OH and reaction with the siliceous glass in the rock allows these compounds to form in the rock although in much lower amounts than in the cement. As in the previous results (Da Silva et al., 2012), optical microscopy shows a very distinctive ITZ rim. There are much lower amounts of small sized grains/crystals, which from XRD are mostly portlandite, in ITZ-C than CEM. In the ITZ, these crystals are mostly concentrated in a line between ITZ-C and ITZ-R, which may be explained by formation of small amounts of calcite (confirmed by XRD), as soon as the Ca2+ ions get close to the outermost layer of the cement reacting with CO, possibly from handling or held in the rock. It is possible interaction of geobrine at the cement surface enhances the reaction.

The SEM/EDS results show Ca^{2+} has penetrated further into the rock (\approx 300 µm) than after 28 days curing, and the ITZ is substantially wider than that described by Da Silva *et al.* (2012).

G205F(84d)

The feature which stands out compared to G(84d) is the absence of portlandite, which has reacted with the added quartz (20%wt SF). As in G(84d), the calcite content, as well as a small amount of aragonite, increases from CEM to ITZ-C, supporting the previous idea that the carbonation rate (although still small) is faster in the outermost layer of the cement. Furthermore, the unexpected traces of tobermorite might be explained by random sites where the Ca/Si ratio was low enough for this mineral to form. According to Kalousek (1954), over 30% fine quartz addition to cement is needed to give a Ca/Si ratio of around 1 for this mineral to form. Quartz decreases from CEM to ITZ-C, which Da Silva et al. (2012) suggested meant Ca leaching into and through the ITZ was rapid, leaving less available Ca to react with the quartz in the interior of the binder matrix. Calcium carbonate (mainly calcite) and small amounts of calcium silicates are still present in the ITZ-R, but in lower amounts than that in G(84d) indicating there is less migration of cement constituents to the rock

Under OM, the cement matrix (CEM) contains both small and large sized grains/crystals, the bigger ones are probably quartz, although Da Silva *et al.* (2012) felt they might well be non-hydrated cement grains. The G20SF(84d) ITZ-C appears brighter under OM than the G(84d) ITZ-C, which may be due to the quartz crystals (SF) in G20SF(84d) ITZ-C, along with the lack of portlandite in the G(84d) ITZ-C.

The ITZ-R in G20SF(84d) is as wide as that in G(84d) ITZ-R (500µm), suggesting both systems have reacted to a similar extent with the rock. However, the ITZ-C is not as wide as in G(84d), and the cement has markedly reduced portlandite. The darker zone in PPL could be due to amorphous silica gel forming from reaction of the glass from the rock with migrating OH⁺. The SEM/EDS results show little difference in the depth of calcium migration in G20SF(84d) and G(84d). Compared to the SEM/EDS results at 28 days obtained by Da Silva *et al.* (2012) where the ITZ at was 250µm, at 84 days it is broader with 300µm wide. The Ca has also penetrated further into the tock after 84 days curing.

G405F(84d)

The addition of 40% SF has restricted the formation of portlandite with formation of tobermorite in the cementing matrix. Both calcite and aragonite increase from CEM to ITZ-C. Only slight traces of calcium silicates and calcium carbonates are found in the G40SF(84d) ITZ-R (even lower than in the G20SF(84d) ITZ-R), which confirms that 40%SF addition has slowed the migration of Ca2+ and OH from the cement to the rock. This is also consistent with OM results, which show that the G40SF(84d) ITZ is narrower than for either G(84d) or G20SF(84d). As in G20SF(84d), OM shows a mixture of small and large sized grains in the cement matrix (CEM) with the large ones assumed to be quartz. With XPL, there is a significant decrease in the amount of bright spots in the cement matrix of G40SF(84d), compared to that G20SF(84d). From XRD analysis, this might be explained by the presence of tobermorite in the cement matrix, along with the absence of aC SH and unhydrated cement. The dark colour in PPL may be amorphous silica gel.

The SEM/EDS data for G40SF(84d) also shows the Ca²⁺ has not migrated as far into the rock as for G(84d) or G20SF(84d), consistent with the idea put forward by Da Silva *et al.* (2012) that large additions of SF slows the migration of Ca²⁺ ions across the ITZ.

The ITZ is \approx 300 µm wide compared to 250-300 µm at 28 days (Da Silva *et al.* (2012)) so the Ca has penetrated further into the rock and the ITZ is wider.

4.2 Samples Exposed to CO₂

The following samples were exposed to CO₂ compared to those presented above where no CO₂ was injected.

$G(84d+CO_2)$

As seen in the equivalent specimen without CO₂ exposure (G(84d)), less **PORTLANDITE** IS FORMED IN ITZ-C THAN INCEM. HOWEVER, ONE FEATURE THAT STANDS OUTIS THE INCREASE IN THE AMOUNT OF **CALCIUM CARBON-ATES** (MAINLY CALCITE) in ITZ-C, the zone most exposed to the CO₂ (or HCO₂). According to Duguid (2009), this result is predictable due to the high porosity and permeability of the rock allowing CO₂ (or HCO₃) to be in permanent contact with the cement exterior layer. Furthermore, any possible gaps in the ITZ (between the rock and cement) may enhance the presence of CO₂ (or HCO₃) in the ITZ, as seen by Carey *et al.* (2007), where they realized that CO₂ could migrate along a pre-existing gap in the interface between a well cement and shale caprock, exposed to CO₂-rich brine at 54°C.

The outermost layer of the cement itself seems to restrict the CO₂ (or HCO₄) from penetrating further into the cement, due to its very low permeability after carbonation. This is in accordance with several studies undertaken at lower temperatures, where differentiated layers formed, the exterior ones being more carbonated than the interior ones, justified by the authors as a diffusion mechanism (Andac and Glasser, 1999; Milestone et al., 1986 a, b; Carey et al., 2007; Kutchko et al., 2007, 2008; Carey et al., 2007; Barlet-Gouedard et al., 2006; Duguid et al., 2005; Duguid, 2009). The differentiated layers found in some of these studies are not obvious in the current research, which, according to Rimmelé et al. (2008), is probably due to the different exposure conditions and, consequently, to a slower carbonation rate, since most of those studies used EGS-CO₂ or CO₂ sequestration conditions, where the CO₂ overpressure is significantly higher than in the current study.

The extremely bright ITZ-R seen in the optical microscope may indicate the presence of new compound(s) which could be calcite (CaCO₁), although little of this compound was found by XRD.

However, TGA shows a significant amount of carbonate material which decomposes at temperatures well below that of calcite. Mass spectrometry detects significant amounts of CO₂ released over this decomposition range, supporting the presence of amorphous rather than crystalline calcium carbonate as little crystalline material was detected by XRD. Rimmelé *et al.* (2008) indicated that carbonation was a complex series of reactions giving multiple zones of carbonation and dissolution which could possibly explain the brighter colour of ITZ-C, compared to the rest of the cement (CEM). The literature on amorphous calcium carbonate is extensive in the biomimeralisation field and Kellermeier *et al.* (2010) showed that the presence of silica helped stabilise the material. From the SEM/EDS images, it seems that the depth and amount of penetration of Ca²⁺ into the rock is similar to the equivalent sample without CO₂ exposure (G(84d)).

G205F(84d+CO2)

Similarly to G20SF(84d), no portlandite was observed in this sample. As in G(84d+CO.), the amount of calcite and aragonite increased from CEM to ITZ-C, meaning there is more carbonation in the outmost layer of the cement. The traces of tobermorite could be expected. Milestone *et al.*, 2012 showed that the low Ca/Si ratio tobermorite formed as Ca²⁺ was removed by formation of CaCO₃ during the early curing process, before the final silicate phases form.

The ≈400µm wide ITZ-R is difficult to distinguish in PPL, whereas in XPL it appears extremely bright (brighter than in either CEM or IGN), which may mean that significant calcium carbonate (CaCO.) is present, although again that is not consistent with the XRD analysis where little crystalline calcite or aragonite are identified. This may be due to the presence of amorphous calcium carbonate, confirmed by TGA and mass spectrometry analysis. The typical amorphous hump in the XRD curve of the ITZ-C compared to that of the CEM seems to support the presence of an amorphous calcium carbonate. Also, the few orange/reddish/ brownish spots seen in XPL may be a pseudo-aragonite.

The calcium seems to migrate further into the tock, compared to G(84d+CO₂) (350 against 300µm). This fact might be explained by the faster carbonation of portlandite present in G(84d+CO₂) but not in G20SF(84d+CO₂), sealing the surface to further migration when exposed to CO₂, whereas the calcium silicates will take longer to react with CO₂ and not form the barrier. The Ca²⁺ seems to migrate uneventy into the rock and is mostly localized in rock pores, whereas in the G(84d+CO₂) it is more uniformly distributed. This might be due to the formation of CaCO₃ in pockets in the rock pores as no Si is present from the EDS mapping.

G405F(84d+CO2)

The G40SF(84d+CO₂) is the only specimen where the carbonation layer is easily noticeable with unaided eye, as a pink, ≈ 3 mm thick outer-layer formed in the cement (Figure 6). This layer ranges from ca. 2 to 4 mm thick, and seems to depend on the thickness of the surrounding rock. The most prevalent calcium carbonate is aragonite which increases sharply in going from CEM to ITZ-C. This is probably due to the faster rate of carbonation of tobermorite (rather than portlandite or other calcium silicate hydrates). The amount of tobermorite is reduced going from CEM to ITZ-C, as the exterior tobermorite is almost totally carbonated to angonite.

In a similar way to the samples without CO₂ exposure, the calcium silicates and calcium carbonates are only formed in traces in the ITZ-R in even lower amounts than in G(84+CO₂) or G20SF(84d+CO₃), probably caused by the slower migration of calcium from cement to the rock. This may be due to the formation of tobermorite, as this mineral seems to carbonate faster than the other calcium silicates. A number of orange/reddish brownish spots seen by XPL in CEM may be the consequence of carbonation as this effect has been reported previously (Milestone et al., 1987b).

A \approx 250µm wide ITZ-R is barely distinguishable in PPL, but in XPL it appears brighter (white and orange) than in either CEM or IGN, although not as bright or as wide as the ITZ-R in G(84d+CO₂) or G20SF(84d+CO₂).

SEM/EDS shows that Ca²⁺ has migrated ≈250-300µm but is unevenly distributed in the ITZ, mostly being concentrated as 'pockets' in the rock voids.

5.0 Conclusion

The current research supports the idea initially put forward by Da Silva et al. (2012) that quartz (SF) addition restricts calcium migration from the cement to the rock

Comparing the current experimental work with that undertaken by Da Silva et al. (2012) where the conditions are the same but with a shorter curing time, the ITZ seems to be wider and calcium has migrated further. This indicates that the reactions which create the ITZ reactions are still occurring during the second and third months, although to a much lower degree when compared to those seen after a month.

When CO₂ is present most calcium carbonate is formed in the outermost layer of the cement, although some seems to form in the rock side of the ITZ, as well as in the rest of the cement.

The rock-cement interaction is influenced by CO₂-exposure and seems to be very dependent on the way that the various cementing minerals carbonate. When portlandite is present, Ca seems to be restricted from migrating to the rock by the carbonation of Ca(OH)₂ to calcite, a relatively fast carbonation step which blocks the pores. When 20% quartz is added to the binder, no portlandite is present so Ca migrates further, as the CSH present take longer to carbonate. However, when 40% quartz is added to the mix, tobermorite forms and rapidly carbonates to aragonite (faster than the carbonation of portlandite to calcite), which restricts migration further.

The effect of CO₂-exposure on the behaviour of cement and, consequently, on the way it interacts with the rock formation, is very dependent on the CO₂ concentration. The 'armoured sheath' described by other researchers is hindered here as the CO₂ levels are much lower in our experiments. The rock, despite being quite porous, reduces the CO₂ flow to the cement and the carbonation reaction is complex with an amorphous calcium carbonate being formed.

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Geobrine recipe: 0.19 g sodium subhate (NaSO.), 0.05 g calcium chloride de hydrate (CaCl.,2)(.0), 15.6 g liquid precipitated silica (SiO.), 4.1 g potassium chloride (KCI), 15.8 g sodium chloride (NaCl) are well mixed and filled with water to make up 20 litres.

X. APPENDICES

X.1 XRD quantitative information <u>IGN</u>

		60	102				56	62	94.2								
		00	102				50	02	5112					· · · · · · · · · · · · · · · · · · ·			-
	SAMPLE	SiO ₂		Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K₂O	TiO ₂	P ₂ O ₅	LOI	SUM				
						Ũ											
	IGN - Ongatiti ignimbrite	70.56	13.80	2.81	0.04	0.36	1.90	3.75	3.30	0.31	0.07	2.62	99.53				
														Feldspars (40% CaO, Na2O and K2O used		Silica (estimation)	
														in order to match the XRD quantitative)	MWt	,	
Al	NaAlSi3O8							3.75						6.347010978	262	4.360541894	
Or	KAISi3O8								3.30					5.928493278	278.1	3.837212477	
An	CaAl2Si2O8						1.90							3.770809464	278	1.627687539	
														16.04631372		9.82544191	
													Total Feldspars	15	>	Silica in the feldspar	10
													Total Quartz	1.5			
Na	23												Total Amorphous material	83.5	>	Amorphous silica	59
Ca	40												TOTAL	100			
К	39.1																
Si	28																
0	16																

IGN: sample 1 Structure 1

Structure I	
Phase name	Corundum
R-Bragg	2.075
Spacegroup	R-3c
Scale	0.00523234409
Cell Mass	611.768
Cell Volume (Å^3)	255.16351
Wt% - Rietveld	66.366
Wt% in Spiked sample	22.580
Wt% in Original sample	0.000
Crystallite Size	
Cry size Lorentzian (nm)	51.5
Crystal Linear Absorption Coeff. (1/cm)	217.155
Crystal Density (g/cm^3)	3.981
Preferred Orientation (Dir 1 : 1 1 3)	1.099063
Lattice parameters	
a (Å)	4.7609828
c (Å)	12.9985443
Structure 2	
Structure 2 Phase name	Quartz
Structure 2 Phase name R-Bragg	<mark>Quartz</mark> 7.371
Structure 2 Phase name R-Bragg Spacegroup	Quartz 7.371 P3221
Structure 2 Phase name R-Bragg Spacegroup Scale	Quartz 7.371 P3221 0.00202402896
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass	Quartz 7.371 P3221 0.00202402896 180.252
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1 163.063
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1 163.063 2.648
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1 163.063 2.648 0.841214
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1 163.063 2.648 0.841214
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters a (Å)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1 163.063 2.648 0.841214 4.9141461
Structure 2 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters a (Å) c (Å)	Quartz 7.371 P3221 0.00202402896 180.252 113.03581 3.351 1.140 1.473 303.1 163.063 2.648 0.841214 4.9141461 5.4049202

Nt% in Original sample 13.308 Crystallite Size 203.1 Crystal Linear Absorption Coeff. (1/cm) 122.551 Crystal Density (g/cm^3) 20.663 Preferred Orientation (Dir 1 : 0 0 1) 0.7153091 Lattice parameters 8.1735950 b (Å) 12.8733866 c (Å) 7.1164730 alpha (°) 93.46693 beta (°) 116.3556 gamma (°) 90.02335 Gorundum R-Bragg 1.783 Spacegroup R-3c Scale 0.00533539673 Cell Mass 611.768 Cell Volume (Å^3) 255.06201 wt% in Spiked sample 22.580 wt% in Spiked sample 22.580 wt% in Original sample 0.000 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Prefered Orientation (Dir 1 : 1 1 3) 1.155282 Lattice parameters 4 a (Å) 4.7605966 c (Å) 12.9954814	Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample	Andesine 11.277 C-1 0.000518599182 1073.520 669.43565 30.283 10.303
Crystallite Size 203.1 Crystal Linear Absorption Coeff. (1/cm) 182.551 Crystal Density (g/cm^3) 2.663 Preferred Orientation (Dir 1 : 0 0 1) 1.153091 Lattice parameters a (Å) 8.1735950 b (Å) 12.8733866 c (Å) c (Å) 7.1164730 alpha (°) 93.46693 beta (°) 90.02335 IGN: sample 2 Structure 1 Phase name Corundum R-Bragg 1.783 Spacegroup R-3c Scale 0.00533539673 Cell Mass 611.768 Cell Mass 611.768 Cell Mass 611.768 Cell Mass 0.000 Crystallite Size 0.000 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Prefered Orientation (Dir 1 : 1 1 3) 1.155282 a (Å) 4.7605966 c (Å) 12.9954814 Structure 2 Phase name Quertz Phase name	Wt% in Original sample	13.308
a (Å) 8.1735950 b (Å) 12.8733866 c (Å) 7.1164730 alpha (°) 93.46693 beta (°) 116.3556 gamma (°) 90.02335 IGN: sample 2 Structure 1 Phase name Corundum R-Bragg 1.783 Spacegroup R-3c Scale 0.00533539673 Cell Volume (Å^3) 255.06201 Wt% - Rietveld 65.204 Wt% in Spiked sample 22.580 Wt% in Original sample 0.000 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Preferred Orientation (Dir 1 : 1 1 3) 1.155282 Lattice parameters a (Å) c (Å) 12.9954814 Structure 2 Phase name Phase name Quartz R-Bragg 8.430 Spacegroup 522 Cell Mass 180.252 Cell Mass 180.252 Cell Mass	Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 1)	203.1 182.551 2.663 0.7153091
IGN: sample 2 Structure 1 Phase name Corundum R-Bragg 1.783 Spacegroup R-3c Scale 0.00533539673 Cell Mass 611.768 Cell Volume (Å^3) 255.06201 Wt% - Rietveld 65.204 Wt% in Spiked sample 22.580 Wt% in Original sample 0.000 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Preferred Orientation (Dir 1 : 1 1 3) 1.155282 Lattice parameters a (Å) 4.7605966 c (Å) 4.7605966 c (Å) Structure 2 Phase name Quartz R-Bragg 8.430 Spacegroup Spacegroup P3221 Scale Scale 0.00221176629 Cell Mass Cry size Lorentzian (nm) 12.98919 Wt% in Spiked sample W% in Original sample 1.578 Crystallite Size Cry size Lorentzian (nm) 206.2 Crystal Linear Absorption Coeff. (1/cm) 163.130 <t< th=""><th>a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°)</th><th>8.1735950 12.8733866 7.1164730 93.46693 116.3556 90.02335</th></t<>	a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°)	8.1735950 12.8733866 7.1164730 93.46693 116.3556 90.02335
Structure 1 Phase name Corundum R-Bragg 1.783 Spacegroup R-3c Scale 0.00533539673 Cell Mass 611.768 Cell Volume (Å'3) 255.06201 Wt% - Rietveld 65.204 Wt% in Spiked sample 0.000 CrystalLite Size Crysize Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Preferred Orientation (Dir 1 : 1 1 3) 1.155282 Lattice parameters a (Å) a (Å) 4.7605966 c (Å) 12.9954814 Structure 2 Phase name Phase name Quartz R-Bragg 8.430 Spacegroup P3221 Scale 0.00221176629 Cell Mass 180.252 Cell Mass 180.252 Cell Mass 180.252 Cell Mass 15.78 Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Linear Absorption Coeff. (1/cm)	IGN: sample 2	
Phase name Corundum R-Bragg 1.783 Spacegroup R-3c Scale 0.00533539673 Cell Mass 611.768 Cell Volume (Å^3) 255.06201 Wt% - Rietveld 65.204 Wt% in Spiked sample 0.000 CrystalLite Size 0.000 CrystalLinear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Preferred Orientation (Dir 1 : 1 1 3) 1.155282 Lattice parameters a (Å) a (Å) 4.7605966 c (Å) 12.9954814 Structure 2 Phase name Phase name Quartz R-Bragg 8.430 Spacegroup P3221 Scale 0.00221176629 Cell Mass 180.252 Cell Mass 180.252 Cell Nolume (Å^3) 112.98919 Wt% - Rietveld 3.528 Wt% in Original sample 1.222 Wt% in Original sample 1.222 Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Linear Absorption Coeff. (1/cm	Structure 1	
Cell Volume (Å^3)255.06201Wt% - Rietveld65.204Wt% in Spiked sample22.580Wt% in Original sample0.000Crystallite SizeCry size Lorentzian (nm)Crystal Linear Absorption Coeff. (1/cm)217.241Crystal Density (g/cm^3)3.983Preferred Orientation (Dir 1 : 1 1 3)1.155282Lattice parameters4.7605966c (Å)12.9954814Structure 2Phase nameQuartzR-Bragg8.430SpacegroupF3221Scale0.00221176629Cell Mass180.252Cell Volume (Å^3)112.98919Wt% in Spiked sample1.578Crystallite SizeCry size Lorentzian (nm)Crystal Linear Absorption Coeff. (1/cm)163.130Crystal Density (g/cm^3)2.649Preferred Orientation (Dir 1 : 0 1 0)0.8850511Lattice parametersa (Å)a (Å)4.9144135c (Å)5.4021030	Phase name R-Bragg Spacegroup Scale Cell Mass	Corundum 1.783 R-3c 0.00533539673 611.768
Cry size Lorentzian (nm) 53.0 Crystal Linear Absorption Coeff. (1/cm) 217.241 Crystal Density (g/cm^3) 3.983 Preferred Orientation (Dir 1 : 1 1 3) 1.155282 Lattice parameters 4.7605966 c (Å) 4.7605966 c (Å) 12.9954814 Structure 2 Phase name Quartz R-Bragg 8.430 Spacegroup P3221 Scale 0.00221176629 Cell Mass 180.252 Cell Volume (Å^3) 112.98919 Wt% - Rietveld 3.528 Wt% in Spiked sample 1.578 Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Density (g/cm^3) 2.649 Preferred Orientation (Dir 1 : 0 1 0) 0.8850511 Lattice parameters 4.9144135 a (Å) 4.9144135 c (Å) 4.9144135 c (Å) 5.4021030 Structure 3 Phase name </th <th>Cell Volume (Å^3) Wt% – Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size</th> <th>255.06201 65.204 22.580 0.000</th>	Cell Volume (Å^3) Wt% – Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	255.06201 65.204 22.580 0.000
a (Å) 4.7605966 c (Å) 12.9954814 Structure 2 Phase name Quartz R-Bragg 8.430 Spacegroup P3221 Scale 0.00221176629 Cell Mass 180.252 Cell Volume (Å^3) 112.98919 Wt% - Rietveld 3.528 Wt% in Spiked sample 1.222 Wt% in Original sample 1.578 Crystallite Size Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) 2.649 Preferred Orientation (Dir 1 : 0 1 0) 0.8850511 Lattice parameters a (Å) 4.9144135 c (Å) 5.4021030	Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm ³) Preferred Orientation (Dir 1 : 1 1 3) Lattice parameters	53.0 217.241 3.983 1.155282
c (Å) 12.9954814 Structure 2 Phase name Quartz R-Bragg 8.430 Spacegroup P3221 Scale 0.00221176629 Cell Mass 180.252 Cell Volume (Å^3) 112.98919 Wt% - Rietveld 3.528 Wt% in Spiked sample 1.222 Wt% in Original sample 1.578 Crystallite Size Crystal Linear Absorption Coeff. (1/cm) Crystal Linear Absorption Coeff. (1/cm) 163.130 Crystal Density (g/cm^3) 2.649 Preferred Orientation (Dir 1 : 0 1 0) 0.8850511 Lattice parameters a (Å) 4.9144135 c (Å) 5.4021030	a (Å)	4.7605966
Structure 2Phase nameQuartzR-Bragg8.430SpacegroupP3221Scale0.00221176629Cell Mass180.252Cell Volume (Å^3)112.98919Wt% - Rietveld3.528Wt% in Spiked sample1.222Wt% in Original sample1.578Crystallite SizeCry size Lorentzian (nm)Crystal Linear Absorption Coeff. (1/cm)163.130Crystal Density (g/cm^3)2.649Preferred Orientation (Dir 1 : 0 1 0)0.8850511Lattice parametersa (Å)4.9144135c (Å)5.4021030Structure 3Phase name	c (Å)	12.9954814
Phase nameQuartzR-Bragg8.430SpacegroupP3221Scale0.00221176629Cell Mass180.252Cell Volume (Å^3)112.98919Wt% - Rietveld3.528Wt% in Spiked sample1.222Wt% in Original sample1.578Crystallite SizeCrystal Linear Absorption Coeff. (1/cm)Crystal Density (g/cm^3)2.649Preferred Orientation (Dir 1 : 0 1 0)0.8850511Lattice parameters4.9144135c (Å)5.4021030Structure 3Andesine	Structure 2	
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters a (Å) c (Å) Structure 3 Phase name Andesine	Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	Quartz 8.430 P3221 0.00221176629 180.252 112.98919 3.528 1.222 1.578
Cry size Lorentzian (nm)206.2Crystal Linear Absorption Coeff. (1/cm)163.130Crystal Density (g/cm^3)2.649Preferred Orientation (Dir 1 : 0 1 0)0.8850511Lattice parameters4.9144135c (Å)5.4021030Structure 3Phase name	Crystallite Size	
a (Å) 4.9144135 c (Å) 5.4021030 Structure 3 Andesine	Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm ³) Preferred Orientation (Dir 1 : 0 1 0)	206.2 163.130 2.649 0.8850511
Structure 3 Phase name Andesine	a (Å) c (Å)	4.9144135 5.4021030
	Structure 3 Phase name	Andesine

R-Bragg	5.949
Scale	0 000555624873
Cell Mass	1073.520
Cell Volume (Å^3)	669.30217
Wt% - Rietveld	31.267
Wt% in Spiked sample	10.828
Wt% in Original sample	13.986
Crystallite Size	
Cry size Lorentzian (nm)	127.8
Crystal Linear Absorption Coeff. (1/cm)	182.587
Crystal Density (g/cm^3)	2.663
Preferred Orientation (Dir 1 : 0 0 1)	0.856891
Lattice parameters	
a (Å)	8.1711290
b (Å)	12.8727158
C (Å)	7.1158123
alpha (°)	93.47007
beta (°)	116.3261
gamma (°)	90.0306
IGN: sample 3	
Structure 1	
Phase name	Corundum
R-Bragg	2.519
Spacegroup	R-3c
Scale	0.00532527437
Cell Mass	611.768
Cell Volume (Å^3)	255.17204
Wt% - Rietveld	62.775
Wt% in Spiked sample	22.580
Wt% in Original sample	0.000
Crystallite Size	
Cry size Lorentzian (nm)	51.6
Crystal Linear Absorption Coeff. (1/cm)	21/.14/
Droferred Orientation (Dir 1 · 1 1 2)	J. J66042
Lattice parameters	1.100043
$\Delta (\hbar)$	1 7610002
	12 9983924
Structure 2	12.))00024
Phase name	Ouartz
R-Bragg	6.592
Spacegroup	P3221
Scale	0.00211712541
Cell Mass	180.252
Cell Volume (Å^3)	113.04323
Wt% - Rietveld	3.258
Wt% in Spiked sample	1.172
Wt% in Original sample	1.513
Crystallite Size	
Cry size Lorentzian (nm)	255.7
Crystal Linear Absorption Coeff. (1/cm)	163.052
Crystal Density (g/cm^3)	2.648
Preferred Orientation (Dir 1 : 0 1 0)	0.8400647
Lattice parameters	
a (Ă)	4.9160660
C (A)	5.4010539
Structure 3	
Phase name	Andesine
K-Bragg	8.046

Spacegroup	C-1
Scale	0.00062597703
Cell Mass	1073.520
Cell Volume (Å^3)	669.38213
Wt% - Rietveld	33.968
Wt% in Spiked sample	12.218
Wt% in Original sample	15.782
Crystallite Size	
Cry size Lorentzian (nm)	132.1
Crystal Linear Absorption Coeff. (1/cm)	182.566
Crystal Density (q/cm^3)	2.663
Preferred Orientation (Dir 1 : 0 0 1)	0.8350383
Lattice parameters	
a (Å)	8.1727251
b (Å)	12.8729241
с (Å)	7.1148347
alpha (°)	93.44998
beta (°)	116 3231
gamma (°)	90 04194
ganana ()	50.01151
ICN: sample 4	
IGIN: Sample 4	
Structure I	C a second al second
Phase name	Corunaum
R-Bragg	3.508
Spacegroup	R-3C
Scale	0.00559699933
Cell Mass	611./68
Cell Volume (A^3)	255.20054
Wt% - Rietveld	62.039
Wt% in Spiked sample	22.580
Wt% in Original sample	0.000
Crystallite Size	
Cry size Lorentzian (nm)	50.7
Crystal Linear Absorption Coeff. (1/cm)	217.123
Crystal Density (g/cm^3)	3.981
Preferred Orientation (Dir 1 : 1 1 3)	1.251994
Lattice parameters	
a (A)	4.7615478
c (A)	12.9973457
Structure 2	
Phase name	Quartz
R-Bragg	13.963 D2001
Spacegroup	P3ZZI 0.00070010710
Scale Call Mars	0.002/3318/12
Cell Mass	112 10104
Cell Volume (A°3)	2 050
Wto - Rielveid	3.956
Wto in Spiked Sample	1.440
Crystallita Siza	1.000
Crystallite Size	20E C
Crysize Lorentzian (nm)	200.0
Crystal Linear Absorption Coeff. (1/Cm)	162.969
Crystal Density (g/cm ⁻³)	2.040
Preferred Unientation (Dir I : U I U)	0.85299/4
Lattice parameters	4 0104041
a (A)	4.9134041
C (A)	5.4096729
Structure 3	a 1 ·
Phase name	Andesine
K-Bragg	14.3/2
spacegroup	C-I

Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample <mark>Wt% in Original sample</mark>	0.000665876352 1073.520 670.02654 34.005 12.376 15.986
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 1) Lattice parameters	164.6 182.390 2.661 0.805678
a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°)	8.1722743 12.8808949 7.1204809 93.54504 116.3609 89.94117
IGN: sample 5	
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	Corundum 1.809 R-3c 0.005371743 611.768 255.04160 63.148 22.580 0.000
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 1 1 3) Lattice parameters	53.7 217.258 3.983 1.162165
a (Å) c (Å)	4.7605506 12.9946930
Structure 2	
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Quartz 5.237 P3221 0.00167124002 180.252 113.09125 2.567 0.918 1.186
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters	315.9 162.983 2.647 0.8507591
a (Å) c (Å)	4.9151230 5.4054220
Structure 3	And octors
Phase name R-Bragg Spacegroup Scale	Andesine 9.430 C-1 0.000633284282

Cell Mass Cell Volume (Å^3) Wt% – Rietveld Wt% in Spiked sample	1073.520 669.35756 34.286 12.260
Wt% in Original sample	15.835
Crystallite Size	
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 1) Lattice parameters	128.0 182.572 2.663 0.8714045
<pre>a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°)</pre>	8.1719843 12.8741694 7.1163325 93.43985 116.354 90.04011

UN

SAMPLE SiO2 A_{2O} Fe_{2O} M_{OO} A_{0} K_{2O} TiO_2 P_{2O} LOI SUM SUM GU			60	102				56	62	94.2								
SAMPLE SiO2 Alg.O3 Fe2O3 MO MgO CaO Na2O Fi2O Fi2O Fi2O Fi2O Fi2O Fi2O Fi2O SUM SUM SUM Image: Constraint of the state of the stat						·		·							·			
All Na/ISI3O8 C <thc< th=""> C <thc< th=""> C C <thc<< th=""><th></th><th>SAMPLE</th><th>SiO₂</th><th>Al₂O₃</th><th>Fe₂O₃</th><th>MnO</th><th>MgO</th><th>CaO</th><th>Na₂O</th><th>K₂O</th><th>TiO₂</th><th>P₂O₅</th><th>LOI</th><th>SUM</th><th></th><th></th><th></th><th></th></thc<<></thc<></thc<>		SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K₂O	TiO₂	P ₂ O ₅	LOI	SUM				
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$																		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$																		
Image: constraint of the state of the st		UN - unaltered	71.16	13.57	2.27	0.08	0.34	1.59	3.21	3.45	0.27	0.02	3.74	99.69				
Al NaAISJ3O8 A A B I I I I Feldspars (45% CaO, Na2O and K2O used In order to match the XBO quantitative In order to match the																		
Al Nalsi308 Imode in order to match the XD quantitative) NWt Onde Calmer Al Nalsi308 Imode in order to match the XD quantitative) NWt Onde Calmer Al Kalsi308 Imode in order to match the XD quantitative) NWt Onde Calmer Al Kalsi308 Imode in order to match the XD quantitative) NWt Onde Calmer Al Kalsi308 Imode in order to match the XD quantitative) NWt Onde Calmer Al Kalsi308 Imode in order to match the XD quantitative) NWt Alsequence Al Kalsi308 Imode in order to match the XD quantitative) NWt Alsequence Al Kalsi308 Imode in order to match the XD quantitative) NWt Alsequence An Call 25108 Imode in order to match the XD quantitative) NWt Alsequence Al Call 25108 Imode in order to match the XD quantitative) NWt Alsequence Imode in order to match the XD quantitative) Imode in order to match the XD quantitative) NWt Alsequence Imode in order to match the XD quantitative) Imode in order to match the XD quantit at the XD quantit at the XD quantit at the XD quantitat the XD															Feldspars (45% CaO, Na2O and K2O used		Silica (estimation)	
Al NaAlSi3O8 Image: Single Singl															in order to match the XRD quantitative)	MWt	Since (estimation)	
Or KAISI308 O O O 3.45 O 6.595440016 278.1 4.504919 An CaA12Si208 O O A A A A A.594919 3.551627032 278.1 4.5944919 An CaA12Si208 O O A A A A A.594919 3.551627032 278.1 4.5944919 An CaA12Si208 O O O O A A A.594919	Al	NaAlSi3O8							3.21						6.101223083	262	4.191679981	
An CaAl2Si208 An 1.59 An An 3.551627032 278 2.2996146 An An An An An An 3.551627032 278 2.2996146 An An An An An An An An 3.551627032 278 2.2996146 An	Or	KAISi3O8								3.45					6.959440016	278.1	4.504491919	
A A <td>An</td> <td>CaAl2Si2O8</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>1.59</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>3.551627032</td> <td>278</td> <td>2.299614625</td> <td></td>	An	CaAl2Si2O8						1.59							3.551627032	278	2.299614625	
A A <td></td>																		
Image: Constraint of the constr															16.61229013		10.99578652	2
Na 23 Ca O O Total Feldspars 16 > Silica in the fe Ca 40 O O Total Amorphous material 81 > Amorphous silica																		
Na 23 Ca 40 Ca Ca<														Total Feldspars	16	>	Silica in the feldspar	11
Na 23 Total Amorphous material 81 > Amorphous sill Ca 40 0 0 TOTAL 100														Total Quartz	3			
Ca 40 TOTAL 100	Na	23												Total Amorphous material	81	>	Amorphous silica	57
	Ca	40												TOTAL	100			
K 39.1	К	39.1																
Si 28	Si	28																
0 16	0	16																

UN: sample 1 Structure 1

Corundum
2.529
R-3c
0.00545565919
611.768
255.13389
59.871
22.580
0.000
52.6
217.180
3.982
1.227997
4.7612882
12.9953682
Quartz
13.544
P3221
0.00491770268

Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	180.252 113.01725 7.044 2.657 3.431
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters	278.4 163.090 2.648 0.8576583
a (Å) c (Å)	4.9140395 5.4042671
Structure 3	7 1
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)	Andesine 6.446 C-1 0.00065456169 1073.520 669.66800
Wt% - Rietveld	33.085
Wt% in Spiked sample	12.478
Wt% in Original sample	16.117
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3)	104.4 182.488 2.662
Preferred Orientation (Dir 1 : 0 0 1)	0.893867
Lattice parameters a (Å) b (Å)	8.1746531 12.8731517
c (Å) alpha (°) beta (°) gamma (°)	7.1175540 93.46563 116.3471 90.00865
UN: sample 2 Structure 1	
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Corundum 2.039 R-3c 0.00544124715 611.768 255.15373 60.698 22.580 0.000
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm ³) Preferred Orientation (Dir 1 : 1 1 3) Lattice parameters	53.0 217.163 3.981 1.21041
a (\AA) c (\AA)	4.7611632 12.9970608
Phase name	Quartz
R-Bragg Spacegroup Scale Cell Mass	6.780 P3221 0.00403250199 180.252

Cell Volume (Å^3)	113.05355
Wt% - Rietveld	5.873
Wt% in Spiked sample	2.185
Wt% in Original sample	2.822
Crystallite Size	
Cry size Lorentzian (nm)	268.9
Crystal Linear Absorption Coeff. (1/cm)	163.037
Crystal Density (g/cm^3)	2.648
Preferred Orientation (Dir 1 : 0 1 0)	0.7614518
Lattice parameters	
a (Å)	4.9141010
c (Å)	5.4058678
Structure 3	
Phase name	Andesine
R-Bragg	8.416
Spacegroup	C-1
Scale	0.000650738625
Cell Mass	1073.520
Cell Volume (Å^3)	669.61631
Wt% - Rietveld	33.429
Wt% in Spiked sample	12.436
Wt% in Original sample	<mark>16.063</mark>
Crystallite Size	
Cry size Lorentzian (nm)	122.4
Crystal Linear Absorption Coeff. (1/cm)	182.502
Crystal Density (g/cm^3)	2.662
Preferred Orientation (Dir 1 : 0 0 1)	0.8449235
Lattice parameters	
a (Å)	8.1732486
b (Å)	12.8745107
C (Å)	7.1174882
alpha (°)	93.46186
beta (°)	116.3469
gamma (°)	90.02335

<u>KAO</u>

		60	102				56	62	94.2								
	SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	К₂О	TiO ₂	P ₂ O ₅	LOI	SUM				
		-		2 0		Ŭ		-	-	-							
	KAO - Kaolinite alteration	69.74	16.42	2.13	0.06	0.17	0.87	0.77	1.62	0.36	0.02	7.61	99.78				
														Feldspars (100% CaO, Na2O and K2O			
														usedCaO, Na2O and K2O used in order to		Silica (estimation)	
														match the XRD quantitative)	MWt		Alumina (left overs estimation)
AI	NaAlSi3O8							0.77						3.263100275	262	2.241824617	0.25
Or	KAISi3O8								1.62	2				7.257106545	278.1	4.69715634	0.94
An	CaAl2Si2O8						0.87							4.335327456	278	1.87136437	1.59
TOTAL														14.85553428	Matches w/ Quant. XRD	8.810345326	2.78
														Kaolinite (estimation using all the alumina			
														left over from feldspars)			
Као	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O		2.78											7.03629776	258	3.272696632	
													Total Feldspars	15	>	Silica in the feldspar	9
													Total Quartz	2.2			
													Total Kaolinite	7	>	Silica in the kaolinite	3
Na	23												Total Amorphous material	75.8	>	Amorphous silica	55.5
Ca	40												TOTAL	100			
К	39.1																
Si	28																
0	16																

KAO: sample 1 Structure 1

Phase name R-Bragg Spacegroup

Corundum 2.708 R-3c

Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	0.00565745029 611.768 255.09053 62.214 22.580 0.000
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 1 1 3)	57.8 217.217 3.982 1.197094
a (Å) c (Å)	4.7606842 12.9964560
Structure 2	
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Quartz 12.072 P3221 0.00327883797 180.252 113.03717 4.708 1.709 2.207
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters	402.0 163.061 2.648 0.5933327
a (Å) c (Å)	4.9145574 5.4040808
Dhago namo	Andocino
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	Andesine 0.743 C-1 0.00065246789 1073.520 670.17100 33.078 12.005 15.507
Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 1) Lattice parameters	2.0 182.351 2.660 3.372094
a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°)	8.1808912 12.8716989 7.1184261 93.33744 116.3556 90.19659
KAO: sample 2 Structure 1	
Phase name R-Bragg Spacegroup	Corundum 2.414 R-3c

Scale

0010000
2.414
R-3c
0.00564228132

Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm)	611.768 255.15309 64.143 22.580 0.000 56.7 217.163
Crystal Density (g/cm ³)	3.981
Preferred Orientation (Dir 1 : 1 1 3)	1.170255
Lattice parameters a (Å)	4.7611052
Structure 2	12.9973447
Phase name	Quartz
R-Bragg	9.360
Spacegroup	P3221
Scale	0.00322148156
Cell Mass	180.252
Cell Volume (Å^3)	113.05145
Wt% - Rietveld Wt% in Spiked sample	4.781 1.683
Crystallite Size	2.1/4
Cry size Lorentzian (nm)	362.4
Crystal Linear Absorption Coeff. (1/cm)	163.040
Crystal Density (g/cm^3)	2.648
Preferred Orientation (Dir 1 : 0 1 0)	0.9021693
a (Å)	4.9150389
c (Å)	5.4037042
Structure 3	Andonino
Phase name	Andesine
R-Bragg	0.714
Spacegroup	C-1
Scale	0.00059310192
Cell Mass	1073.520
Cell Volume (Å^3)	670.17100
Wt% - Rietveld	31.076
Wt% in Spiked sample	10.940
Wt% in Original sample	14.130
Cry size Lorentzian (nm)	2.0
Crystal Linear Absorption Coeff. (1/cm)	182.351
Crystal Density (g/cm^3)	2.660
Preferred Orientation (Dir 1 : 0 0 1)	4.37529
a (Å)	8.1808912
b (Å)	12.8716989
c (Å)	7.1184261
alpha (°)	93.33744
beta (°)	116.3556
gamma (°)	90.19659

<u>MOR</u>

		60	102	2			56	62	94.2								
	SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI	SUM	·			
	MOR - mordenite alteration	70.87	13.72	2.23	0.03	0.21	2.53	2.41	3.47	0.30	0.05	4.11	99.93				
														Feldspars (65% CaO, Na2O and K2O used in order to match the XRD quantitative)	MWt	Silica (estimation)	
AI	NaAlSi3O8							2.41						6.61104588	262	4.541939918	
Or	KAISi3O8								3.47					10.12056405	278.1	6.550526893	
An	CaAl2Si2O8						2.53							8.168598375	278	3.526013687	
														24.90020831		14.6184805	
														Kaolinite (from XRD quantitative)			
Mor	Na _{1.1} Ca _{0.5} K _{0.1} Al _{2.2} Si _{9.8} O ₂₄ •5.9(H ₂ O)													25	873.21	17.17799842	
													Total Feldspars	25	>	Silica in the feldspar	15
													Total Quartz	3.2			
													Total Mordenite	25	>	Silica in the mordenite	17
Na	23												Total Amorphous material	46.8	>	Amorphous silica	36
Ca	40												TOTAL	100			
К	39.1																
Si	28																
0	16																
Al	27																

MOR: sample 1 Structure 1

Structure 1	
Structure 1 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm)	Corundum 2.384 R-3c 0.00525226538 611.768 255.28283 34.761 22.580 0.000
Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm ³) Preferred Orientation (Dir 1 : 1 1 3) Lattice parameters a (Å)	217.053 3.979 1.213393 4.7617303
c (Å)	13.0005398
Structure 2	
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Quartz 9.073 P3221 0.00461356552 180.252 113.13622 3.987 2.590 3.345
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 0) Lattice parameters a (Å) c (Å) Structure 3	205.9 162.918 2.646 0.8286498 4.9149604 5.4079291
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)	Andesine 11.238 C-1 0.000562579396 1073.520 670.05967

Wt% - Rietveld	17.149
Wt% in Spiked sample	11.140
Wt% in Original sample	14.389
Crystallite Size	
Cry size Lorentzian (nm)	238 5
Crystal Linear Absorption Coeff (1/cm)	182 381
Crystal Density (a/cm^3)	2 660
Preferred Orientation (Dir $1 \cdot 0 \cdot 0 \cdot 1$)	0 7054276
Lattico parameters	0.7034270
Lattice parameters	0 1757200
d (A)	0.1/3/309
D (A)	12.8/8/360
C(A)	/.1191635
alpha (°)	93.50006
beta (°)	116.3683
gamma (°)	89.97149
Structure 4	
Phase name	Mordenite
R-Bragg	4.825
Spacegroup	Cmcm
Scale	7.57773612e-005
Cell Mass	3459.110
Cell Volume (Å^3)	2788.71745
Wt% - Rietveld	30.978
Wt% in Spiked sample	20.122
Wt% in Original sample	25.991
Crystallite Size	
Cry size Lorentzian (nm)	50.0
Crystal Linear Absorption Coeff (1/cm)	112 614
Crystal Density (a/cm^3)	2 060
$\frac{\text{Crystar Density (g/em 3)}}{\text{Preferred Orientation (Dir 1 · 0 1 0)}}$	1 0/1371
Lattico parameters	1.0413/1
ration = r	10 1170755
a (A)	10.11/0/55
	20.4706620
C (A)	1.5194233
Structure 5	
Phase name	Sanidine
R-Bragg	5.251
Spacegroup	C12/m1
Scale	0.00038570065
Cell Mass	1113.325
Cell Volume (Å^3)	721.23740
Wt% - Rietveld	13.125
Wt% in Spiked sample	8.525
Wt% in Original sample	11.012
Crystallite Size	
Cry size Lorentzian (nm)	65.0
Crystal Linear Absorption Coeff. (1/cm)	215.644
Crystal Density (g/cm^3)	2.563
Lattice parameters	
a (Å)	8.6100985
b (Å)	13.0219356
C (Å)	7 1667694
beta (°)	116.1588
	110.1000
MOR: sample 2	
Structure 1	
Phase name	Corundum
R-Bragg	2.875
Spacegroup	R-3c
Scale	0.00518463042

611.768

Cell Mass

<pre>Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 1 1 Lattice parameters</pre>	255.18398 34.572 22.580 0.000 54.8 217.137 3.981 3) 1.117729 4.7613578
c (Å)	12.9975394
Phase name	Quartz
R-Bragg	10.080
Spacegroup	P3221
Scale	0.00440665674
Cell Mass	180.252
Cell Volume (Å^3)	113.02401
Wt% - Rietveld	3.835
Wt% in Spiked sample	2.505
Wt% in Original sample	3.235
Crystallite Size	200 0
Crysize Lorentzian (nm)	300.9
Crystal Density (g/cm^3)	2 648
Preferred Orientation (Dir 1 · 0 1	0) 0.7938567
Lattice parameters	
a (Å)	4.9139725
c (Å)	5.4047377
Structure 3	
Phase name	Andesine
<mark>Phase name</mark> R-Bragg	Andesine 9.339
<mark>Phase name</mark> R-Bragg Spacegroup	Andesine 9.339 C-1
Phase name R-Bragg Spacegroup Scale	Andesine 9.339 C-1 0.000571951305
Phase name R-Bragg Spacegroup Scale Cell Mass	Andesine 9.339 C-1 0.000571951305 1073.520
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 175.9
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 175.9 ./cm) 182.505
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 175.9 175.9 182.505 2.662
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 2.0000
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4 Phase name B-Bragg	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426 Mordenite 4.853
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4 Phase name R-Bragg Spacegroup	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426 Mordenite 4.853 Cmcm
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4 Phase name R-Bragg Spacegroup Scale	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426 Mordenite 4.853 Cmcm 7.47743637e-005
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4 Phase name R-Bragg Spacegroup Scale Cell Mass	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426 Mordenite 4.853 Cmcm 7.47743637e-005 3459.110
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426 Mordenite 4.853 Cmcm 7.47743637e-005 3459.110 2785.65862
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1 Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 Lattice parameters a (Å) b (Å) c (Å) alpha (°) beta (°) gamma (°) Structure 4 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld	Andesine 9.339 C-1 0.000571951305 1073.520 669.60457 17.561 11.470 14.815 ./cm) 182.505 2.662 1) 0.7321235 8.1727461 12.8752354 7.1171110 93.48456 116.3414 89.98426 Mordenite 4.853 Cmcm 7.47743637e-005 3459.110 2785.65862 30.776

Wt% in Original sample	25.963
Crystallite Size	
Cry size Lorentzian (nm)	50.0
Crystal Linear Absorption Coeff. (1/cm)	112.738
Crystal Density (g/cm^3)	2.062
Preferred Orientation (Dir 1 : 0 1 0)	1.028293
Lattice parameters	
a (Å)	18.1099604
b (Å)	20.4662550
c (Å)	7.5157445
Structure 5	
Phase name	<mark>Sanidine</mark>
R-Bragg	4.988
Spacegroup	C12/m1
Scale	0.000386770878
Cell Mass	1113.325
Cell Volume (Å^3)	720.68337
Wt% - Rietveld	13.255
Wt% in Spiked sample	8.657
Wt% in Original sample	11.182
Crystallite Size	
Cry size Lorentzian (nm)	65.0
Crystal Linear Absorption Coeff. (1/cm)	215.810
Crystal Density (g/cm^3)	2.565
Lattice parameters	0 0004100
	8.60/410/
(A) (A)	13.0202727
C(A)	/.1653/00
Dela (~)	110.1/43

<u>RHY</u>

		60	102				56	62	94.2								
	SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na₂O	K₂O	TiO₂	P ₂ O ₅	LOI	SUM				
	RHY - rhyolite	74.09	13.46	2.34	0.06	0.50	2.02	4.54	2.27	0.30	0.07	0.08	99.72				
														Feldspars (considering a Quantitative XRD overestimation)	MWt	Silica (estimation)	
Al	NaAlSi3O8							4.54						24.00000438	262	16.48855263	
Or	KAISi3O8								2.27					12.70953512	278.1	8.226236323	
An	CaAl2Si2O8						2.02							12.52386351	278	5.40598425	
														49.23340301		30.1207732	
													Total Feldspars	50	>	Silica in the feldspar	30
													Total Cristobalite	14.5			
													Total tridymite	4.5			
Na	23												Total amorphous	31	>	Amorphous silica	25
Ca	40												TOTAL	100			
К	39.1																
Si	28																
0	16																

RHY: sample 1

Structure 1 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample

Corundum 3.059 R-3c 0.00471163713 611.768 254.93012 29.180 22.580

Wt% in Original sample	0.000
Crystallite Size Cry size Lorentzian (nm)	58 0
Crystal Linear Absorption Coeff. (1/cm)	217.353
Crystal Density (g/cm^3)	3.985
Preferred Orientation (Dir 1 : 1 1 3)	1.214243
Lattice parameters	
a (Å)	4.7599599
c (Å)	12.9922372
Structure 2	Duchaniuna
Phase name	Andesine 9 649
R-DL ayy Spacegroup	9.049 C-1
Scale	0.00129718669
Cell Mass	1073.520
Cell Volume (Å^3)	669.37799
Wt% - Rietveld	37.016
Wt% in Spiked sample	28.644
Wt% in Original sample	<mark>36.998</mark>
Crystallite Size	
Cry size Lorentzian (nm)	53.9
Crystal Linear Absorption Coeff. (1/cm)	182.567
Crystal Density (g/cm ³)	2.663
Preferred Orientation (Dir 1 : 0 0 1)	0.954/244
Lattice parameters a (لمُ)	8 1728483
a (A) b (Å)	12.8653307
c (Å)	7.1175748
alpha (°)	93.45473
beta (°)	116.2964
gamma (°)	90.11107
Structure 3	
Structure 3 Phase name	Cristobalite low
Structure 3 Phase name R-Bragg	Cristobalite low 6.531
Structure 3 Phase name R-Bragg Spacegroup Scale	Cristobalite low 6.531 P41212
Structure 3 Phase name R-Bragg Spacegroup Scale Coll Mass	Cristobalite low 6.531 P41212 0.00880849685 240 336
Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)	Cristobalite low 6.531 P41212 0.00880849685 240.336 173 45300
Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm)</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm)</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3)</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) </pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters </pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.0885643
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters a (Å) c (Å)</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters a (Å) c (Å) Structure 4 Phase name R-Bragg Spacegroup Scale</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005 2884.037
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Original sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters a (Å) c (Å) Structure 4 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3)</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005 2884.037 2077.95293
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Original sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters a (Å) c (Å) Structure 4 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% - Rietveld </pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005 2884.037 2077.95293 4.252 2.001
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005 2884.037 2077.95293 4.252 3.291
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Original sample Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters</pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005 2884.037 2077.95293 4.252 3.291 4.250
<pre>Structure 3 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Original sample Crystallite Size Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 1 1) Lattice parameters a (Å) c (Å) Structure 4 Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size Crystallite Size Crystallite Sample Wt% in Original sample </pre>	Cristobalite low 6.531 P41212 0.00880849685 240.336 173.45300 14.582 11.284 14.575 50.0 141.686 2.301 0.5864178 4.9885643 6.9699661 Tridymite 8.835 Clc1 1.78687776e-005 2884.037 2077.95293 4.252 3.291 4.250 50.0

Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3)	141.924 2.305
Lattice parameters a (Å) b (Å) c (Å) beta (°) Structure 5	18.4972359 4.9804566 23.5453857 106.6697
Phase name	Sanidine
R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	7.528 C12/m1 0.000477629081 1113.325 708.92545 14.970 11.584 14.963
Crystallite Size	
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Lattice parameters	65.0 219.389 2.608
a (Å) b (Å) c (Å) beta (°)	8.4864787 12.9652468 7.1542479 115.764
DIIV. comple 2	
KHI: sample 2	
Structure 1	C
Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample Crystallite Size	Corundum 3.506 R-3c 0.00463460555 611.768 255.12036 30.570 22.580 0.000
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 1 1 3)	57.7 217.191 3.982 1.182027
a (Å) c (Å)	4.7610844 12.9957911
Structure 2	Indecine
Pliase lialle	Andesine 8 655
R-Bragg Spacegroup	8.600 C-1
Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Wt% in Spiked sample Wt% in Original sample	0.00115184872 1073.520 669.50624 34.988 25.843 33.380
Cry size Lorentzian (nm) Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 0 0 1)	56.6 182.532 2.663 0.914026

Lattice parameters	
a (Å)	8.1745125
b (Å)	12.8692410
c (Å)	7.1162159
alpha (°)	93.41232
beta (°)	116.3148
gamma (°)	90.14501
Structure 3	
Phase name	Cristobalite low
R-Bragg	6 556
Spacegroup	D/1212
Spacegroup	
Scale	0.00839243843
Cell Mass	240.336
Cell Volume (A^3)	1/3.58634
Wt% - Rietveld	14.797
Wt% in Spiked sample	10.930
Wt% in Original sample	14.117
Crystallite Size	
Cry size Lorentzian (nm)	50.0
Crystal Linear Absorption Coeff. (1/cm)	141.578
Crystal Density (g/cm^3)	2.299
Preferred Orientation (Dir 1 : 0 1 1)	0.5864473
Lattice parameters	
a (Å)	4.9901851
$C_{\rm c}$ (Å)	6.9707937
Structure 4	
Phase name	Tridymite
R-Bragg	7 743
Spacegroup	C1c1
Spacegroup	1 951016790 005
Scale Call Mass	1.031910/08-003
Cell Mass	2004.037
Cell Volume (A°3)	2080.73382
Wt% - Rietveld	4.697
Wt% in Spiked sample	3.469
Wt% in Original sample	4.481
Crystallite Size	
Cry size Lorentzian (nm)	50.0
Crystal Linear Absorption Coeff. (1/cm)	141.734
Crystal Density (g/cm^3)	2.302
Lattice parameters	
a (Å)	18.4863711
b (Å)	4.9866539
с (Å)	23.5640495
beta (°)	106.6909
Structure 5	
Phase name	Sanidine
R-Bragg	7.645
Spacegroup	C12/m1
Scale	0.000447110492
Cell Mass	1113 325
Cell Volume (\hbar^{3})	710 5/37/
Wts _ Rictuald	1/ 9/2
WES in Spiked sample	11 0/1
Wto III Spikeu Sample	14 261
Wto in Original Sample	14.201
Crystallite Size	
Cry size Lorentzian (nm)	65.U
Crystal Linear Absorption Coeff. (1/cm)	218.889
Crystal Density (g/cm^3)	2.602
Lattice parameters	
a (Ă)	8.4955133

c (Å) beta (°) 7.1561698 115.7846

X.2 Mercury Porosometry

The calculations for the most relevant results regarding the mercury porosimetry are presented below. These are obtained by the multiplication of the fraction of pores over the diameter under consideration ($\mathbf{0}$: 0.5, 1, 5, 10, 50 or 100 µm) with the total porosity of the rock under analysis.

ROCK	Total Mercury Intrusion (mL/g)	Intrusion in Ø*>0.1µm pores (mL/g)	Intrusion in Ø>0.5µm pores (mL/g)	Intrusion in Ø >1µm pores (mL/g)	Intrusion in Ø >5µm pores (mL/g)	Intrusion in Ø>10µm pores (mL/g)	Intrusion in Ø>50µm pores (mL/g)	Intrusion in Ø>100μm pores (mL/g)
IGN	0.2869	≈0.84*0.2869	≈0.72*0.2869	≈0.55*0.2869	≈0.038*0.2869	≈0.03*0.2869	≈0.02*0.2869	≈0.017*0.2869
UNI	0.2294	≈0.88*0.2294	≈0.713*0.2294	≈0.499*0.2294	≈0.068*0.2294	≈0.049*0.2294	≈0.03*0.2294	≈0.024*0.2294
KAO	0.3938	≈0.51*0.3938	≈0.25*0.3938	≈0.194*0.3938	≈0.05*0.3938	≈0.04*0.3938	≈0.024*0.3938	≈0.018*0.3938
MOR	0.2983	≈0.73*0.2983	≈0.28*0.2983	≈0.19*0.2983	≈0.067*0.2983	≈0.055*0.2983	≈0.028*0.2983	≈0.021*0.2983
RHY	0.0615	≈0.84*0.0615	≈0.75*0.0615	≈0.685*0.0615	≈0.465*0.0615	≈0.39*0.0615	≈0.165*0.0615	≈0.11*0.0615

Calculation of the Mercury Intrusion as a function of the Pore Size (volume of pores per weight of sample

Ø =diameter

Results of the Mercury Intrusion as a function of the Pore Size (volume of pores per weight of sample):

ROCK	TOTAL Intrusion (mL/g)	Intrusion in Ø * > 0.1µm pores (mL/g)	Intrusion in Ø > 0.5µm pores (mL/g)	Intrusion in Ø > 1µm pores (mL/g)	Intrusion in Ø> 5µm pores (mL/g)	Intrusion in Ø > 10μm pores (mL/g)	Intrusion in Ø > 50µm pores (mL/g)	Intrusion in Ø > 100µm pores (mL/g)
IGN	0.2869	0.2410	0.2066	0.1578	0.0109	8.6070E-03	5.7380E-03	4.8773E-03
UNI	0.2294	0.2019	0.1636	0.1145	0.0156	1.1241E-02	6.8820E-03	5.5056E-03
KAO	0.3938	0.2008	0.0985	0.0764	0.0197	1.5752E-02	9.4512E-03	7.0884E-03
MOR	0.2983	0.2178	0.0835	0.0567	0.0200	1.6407E-02	8.3524E-03	6.2643E-03
RHY	0.0615	0.0517	0.0461	0.0421	0.0286	2.3985E-02	1.0148E-02	6.7650E-03

* =diameter

Below, the bulk density is multiplied with the values obtained above in order to obtain the values of mercury intrusion per volume (mL) rather than per weight (g) of rock.

Results of the Mercury Intrusion as a function of the Pore Size (volume of pores per volume of sample)

ROCK	Bulk density (g/mL)	TOTAL Intrusion (mL/mL)	Intrusion in Ø * > 0.1µm pores (mL/mL)	Intrusion in Ø * > 0.5µm pores (mL/mL)	Intrusion in Ø > 1µm pores (mL/mL)	Intrusion in Ø > 5µm pores (mL/mL)	Intrusion in Ø > 10μm pores (mL/mL)	Intrusion in Ø > 50µm pores (mL/mL)	Intrusion in Ø > 100µm pores (mL/mL)
IGN	1.595	0.4576	0.3844	0.3295	0.0520	0.0006	4.8785E-06	2.7993E-08	1.3653E-10
UNI	1.322	0.3033	0.2669	0.2162	0.0248	0.0004	4.3401E-06	2.9869E-08	1.6444E-10
KAO	1.198	0.4718	0.2406	0.1179	0.0090	0.0002	2.7947E-06	2.6413E-08	1.8723E-10
MOR	1.450	0.4325	0.3158	0.1211	0.0069	0.0001	2.2508E-06	1.8799E-08	1.1776E-10
RHY	2.193	0.1349	0.1133	0.1012	0.0043	0.0001	2.9229E-06	2.9660E-08	2.0065E-10

* Ø =diameter

The detailed data for the mercury porosimetry for each rock is given below.

X.2.1 IGN

Summary Report

Penetrometer parameters



The overall porosity of the IGN is 0.2869 mL/g. Approximately 72% of this porosity is made up of pores with over 0.5 µm diameter, ≈55% with over 1 µm, ≈3.8% with over 5µm, ≈3% with over 10µm, ≈2% with pores over 50µm and ≈1.7% of pores with over 100µm.

Mean Radius (μm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)	% of Total Intrusion Volume
194 1987	0.0000	0.0000	0.000	0.000	0.0000
194,0466	0.0000	0.0000	0.000	0.000	0.0000
128,1025	0.0039	0.0039	0.000	0.000	1.3755
54.3311	0.0046	0.0007	0.000	0.000	1.6072
40.8881	0.0052	0.0006	0.000	0.000	1.8171
32.5223	0.0055	0.0003	0.000	0.000	1.9257
27.5336	0.0058	0.0003	0.000	0.000	2.0271
23.8617	0.0060	0.0002	0.000	0.000	2.1067
20.0786	0.0064	0.0003	0.000	0.000	2.2153
15.3449	0.0069	0.0005	0.000	0.000	2.4035
11.6854	0.0072	0.0003	0.000	0.000	2.5121
9.7741	0.0074	0.0002	0.000	0.000	2.5917
8.2/25	0.0077	0.0002	0.000	0.000	2.0/80
6.0602	0.0080	0.0003	0.001	0.000	2.7800
5.0951	0.0082	0.0002	0.001	0.000	3.0116
4 1499	0.0090	0.0004	0.001	0.000	3 1492
3,5009	0.0093	0.0003	0.001	0.000	3.2578
2.9859	0.0098	0.0005	0.001	0.000	3.4170
2.5159	0.0110	0.0012	0.002	0.001	3.8268
2.1452	0.0122	0.0012	0.004	0.001	4.2511
1.8389	0.0152	0.0030	0.007	0.003	5.2849
1.5542	0.0316	0.0165	0.028	0.021	11.0289
1.3681	0.0463	0.0147	0.049	0.021	16.1554
1.1891	0.0769	0.0305	0.101	0.051	26.7900
0.9882	0.0980	0.0218	0.145	0.044	34.3/51
0.8335	0.1130	0.01/0	0.180	0.041	40.3120
0.5944	0.1465	0.0163	0.282	0.055	51 0611
0.4937	0 1593	0.0128	0.333	0.052	55 5300
0.4154	0.1726	0.0133	0.397	0.064	60.1542
0.3431	0.1869	0.0144	0.481	0.084	65,1595
0.2861	0.1968	0.0099	0.550	0.069	68.6031
0.2413	0.2065	0.0097	0.630	0.080	71.9829
0.2019	0.2139	0.0074	0.703	0.073	74.5506
0.1637	0.2245	0.0107	0.834	0.130	78.2646
0.1355	0.2282	0.0037	0.889	0.055	79.5637
0.1166	0.2368	0.0086	1.035	0.147	82.5447
0.0345	0.2448	0.000.0	1 257	0.152	97 4154
0.0673	0.2548	0.0040	1.476	0.119	88,8142
0.0575	0.2592	0.0044	1.630	0.154	90.3529
0.0479	0.2627	0.0035	1.777	0.147	91.5813
0.0400	0.2656	0.0029	1.921	0.144	92.5863
0.0336	0.2680	0.0024	2.062	0.141	93.4103
0.0282	0.2703	0.0024	2.229	0.167	94.2316
0.0234	0.2724	0.0021	2.410	0.181	94.9688
0.0196	0.2742	0.0018	2.592	0.182	95.5915
0.0100	0.2768	0.0012	2 931	0.167	96 4994
0.0118	0.2780	0.0012	3.133	0.202	96,9146
0.0098	0.2788	0.0008	3.295	0.162	97.1928
0.0083	0.2797	0.0009	3.502	0.207	97.4926
0.0069	0.2805	0.0008	3.730	0.228	97.7681
0.0057	0.2812	0.0007	3.976	0.246	98.0136
0.0048	0.2859	0.0047	5.934	1.958	99.6462
0.0040	0.2864	0.0005	6.199	0.265	99.8307
0.0033	0.2868	0.0004	6.422	0.223	99,9600
0.0028	0.2869	0.0001	6.504	0.082	100.0000
0.0024	0.2869	0.0000	6.504	0.000	100.0000
0.0019	0.2869	0.0000	6 504	0.000	100.0000
0.0017	0.2869	0.0000	6.504	0.000	100.0000
0.0016	0.2869	0.0000	6.504	0.000	100.0000

X.2.2 UNI

Summary Report Penetrometer parameters 07-0817- 5 Bulb, 0.392 Stem, Solid 10.790 µL/pF Pen. Penetrometer: 61.6245 g Pen. Constant: Pen. Weight: Stem Volume: 0.3920 mL Max. Head Pressure: 4.4500 psia Pen. Volume: 5.9119 mL Assembly Weight: 136.4822 g **Hg** Parameters 130.000 degrees 13.5335 g/mL Adv. Contact Angle: Hg Surface Tension: 130.000 degrees Rec. Contact Angle: Hg Density: 485.000 dynes/cm **User Parameters** Param 1: 0.000 0.000 Param 2: 0.000 Param 3: Low Pressure: Evacuation Pressure: 25 µmHg Evacuation Time: 10 mins Mercury Filling Pressure: 0.47 psia Equilibration Rate: 0.001 µL/g/s **High Pressure:** Equilibration Rate: 0.001 µL/g/s No Blank Correction Intrusion Data Summary Total Intrusion Volume = Total Pore Area = Median Pore Radius (Volume) = 0.2294 mL/g 8.581 m²/g 0.4507 µm Median Pore Radius (Area) = 0.0047 µm Average Pore Radius (2V/A) = 0.0535 µm Bulk Density at 0.47 psia = 1.9010 g/mL Apparent (skeletal) Density = Porosity = 3.3717 g/mL 43.6184 % Stem Volume Used = 49 % Cumulative Intrusion vs Pore size Intrusion for Cycle 1 0.20 0.1 Cumulative Intrusion (mL/g) 0.1 0.05

The overall porosity of UNI is 0.2294 mL/g. Approximately 71.3% of this porosity is made up of pores with over 0.5 μ m diameter, \approx 49.9% with over 1 μ m, \approx 6.8% with over 5 μ m, \approx 4.9% with over 10 μ m, \approx 3.0% with pores over 50 μ m and \approx 2.4% of pores with over 100 μ m.

Pore size Radius (µm)

0.1

0.001

10

0.00
Mean Radius (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)	% of Total Intrusion Volume
104 1007	0.0000	0.0000	0.000	0.000	0.0000
194.0466	0.0000	0.0000	0.000	0.000	0.0000
128 1025	0.0000	0.0044	0.000	0.000	1 9220
54 0011	0.0052	0.0007	0.000	0.000	2 2456
40 0001	0.0052	0.0007	0.000	0.000	2.2400
40.8881	0.0059	0.0007	0.000	0.000	2.0092
32.0223	0.0003	0.0004	0.000	0.000	2.7359
27.0330	0.0000	0.0004	0.000	0.000	2.8928
23.8017	0.0070	0.0003	0.000	0.000	3.0301
20.0786	0.0074	0.0005	0.000	0.000	3.2360
10.3449	0.0082	0.0008	0.000	0.000	3.0094
0.7744	0.0080	0.0004	0.000	0.000	3.7000
9.7741	0.0090	0.0004	0.001	0.000	3.9225
8.2725	0.0094	0.0004	0.001	0.000	4.1180
7.0169	0.0099	0.0004	0.001	0.000	4.314/
0.0092	0.0103	0.0004	0.001	0.000	4.4912
5.0951	0.0113	0.0010	0.001	0.000	4.9320
4.1489	0.0125	0.0012	0.002	0.001	5.0010
3.5009	0.0152	0.0013	0.003	0.001	0.9910
2.9859	0.0152	0.0014	0.004	0.001	0.0192
2.5109	0.0155	0.0004	0.004	0.000	6.0100
2.1408	0.0109	0.0003	0.004	0.000	7.0100
1.8394	0.0100	0.0007	0.005	0.001	7.2120
1.0024	0.01/4	0.0009	0.006	0.001	7.0880
1.3035	0.0182	0.0008	0.007	0.001	7.9289
1.1820	0.0200	0.0024	0.011	0.004	8.9/30
0.9810	0.0270	0.0064	0.024	0.013	11./403
0.8281	0.0485	0.0215	0.076	0.052	21.1218
0.7048	0.0706	0.0222	0.139	0.003	30.7897
0.5919	0.0905	0.0258	0.220	0.087	42.0398
0.4921	0.1145	0.0181	0.300	0.074	49.9237
0.4144	0.1304	0.0159	0.376	0.005	00.8480
0.3423	0.1449	0.0145	0.401	0.065	63.1005
0.2855	0.1539	0.0090	0.524	0.003	71 2022
0.2409	0.1030	0.0036	0.604	0.080	74,6220
0.2010	0.1016	0.0077	0.000	0.076	79.0225
0.1055	0.1846	0.0021	0.007	0.045	00 4500
0.1165	0.1040	0.0050	0.052	0.100	02 0004
0.0945	0.1904	0.0038	1.042	0.000	04.0500
0.0793	0 1975	0.0029	1 115	0.073	96.0962
0.0672	0 1994	0.0019	1 171	0.056	86 9227
0.0574	0 2018	0.0023	1 252	0.081	87 9313
0.0479	0.2038	0.0020	1.337	0.086	88,8232
0.0400	0.2055	0.0017	1 423	0.086	89 5723
0.0336	0.2070	0.0014	1.509	0.086	90.2017
0.0282	0.2084	0.0015	1.614	0.105	90,8455
0.0234	0.2099	0.0015	1,740	0.126	91,4878
0.0196	0.2113	0.0014	1,883	0.143	92,0980
0.0166	0.2126	0.0013	2.036	0.154	92,6559
0.0141	0.2137	0.0011	2.191	0.155	93.1303
0.0118	0.2152	0.0015	2.453	0.261	93.8018
0.0098	0.2163	0.0011	2.672	0.220	94.2724
0.0083	0.2175	0.0012	2.966	0.294	94.8054
0.0069	0.2189	0.0014	3.357	0.391	95.3946
0.0057	0.2202	0.0013	3.806	0.449	95.9553
0.0048	0.2261	0.0059	6.268	2.461	98.5210
0.0040	0.2267	0.0007	6.610	0.343	98.8195
0.0033	0.2279	0.0012	7.305	0.695	99.3233
0.0028	0.2286	0.0007	7.807	0.501	99.6293
0.0024	0.2290	0.0004	8.138	0.332	99.8045
0.0021	0.2292	0.0002	8.366	0.227	99.9104
0.0019	0.2294	0.0002	8.581	0.215	100.0000
0.0017	0.2294	0.0000	8.581	0.000	100.0000
0.0016	0.2294	0.0000	8.581	0.000	100.0000

X.2.3 KAO

Summary Report Penetrometer parameters 07-0272 5 Bulb, 0.392 Stem, Solid Penetrometer: Pen. Constant: 10.790 µL/pF Pen. Weight: 61.8659 g Stem Volume: 0.3920 mL Max. Head Pressure: 4.4500 psia Pen. Volume: 6.0308 mL Assembly Weight: 134.5905 g **Hg** Parameters 130.000 degrees Rec. Contact Angle: 130.000 degrees Adv. Contact Angle: Hg Surface Tension: 485.000 dynes/cm Hg Density: 13.5335 g/mL **User Parameters** Param 1: 0.000 Param 2: 0.000 Param 3: 0.000 Low Pressure: Evacuation Pressure: 25 µmHg Evacuation Time: 10 mins Mercury Filling Pressure: Equilibration Rate: 0.46 psia 0.001 µL/g/s High Pressure: Equilibration Rate: 0.001 µL/g/s No Blank Correction Intrusion Data Summary 0.3938 mL/g 31.355 m²/g Total Intrusion Volume = Total Pore Area = Median Pore Radius (Volume) = 0.0480 µm Median Pore Radius (Area) = 0.0127 µm Average Pore Radius (2V/A) = 0.0251 µm Bulk Density at 0.46 psia = Apparent (skeletal) Density = 1.2108 g/mL 2.3141 g/mL 47.6793 % Porosity = Stem Volume Used = 88 % Cumulative Intrusion vs Pore size Intrusion for Cv 0.40 _{ztalal-lal l} 0.35 0.30 Cumulative Intrusion (mL/g) 0.25 0.2 0.1 0.10 0.05 0.00 10 0.1 0.001 Pore size Radius (µm)

The overall porosity of KAO is approximately 0.3938 mL/g. Approximately 25% of this porosity is made up of pores with over 0.5 μ m diameter, \approx 19.4% with over 1 μ m, \approx 5.0% with over 5 μ m, \approx 4.0% with over 10 μ m, \approx 2.4% with pores over 50 μ m and \approx 1.8% of pores with over 100 μ m diameter.

Mean Radius (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)	% of Total Intrusion Volume
194 5936	0.0000	0.0000	0.000	0.000	0.0000
104.5506	0.0000	0.0000	0.000	0.000	0.00055
100 4006	0.0050	0.0050	0.000	0.000	1.4005
E4 0070	0.0038	0.0056	0.000	0.000	1.4035
54.3278	0.0070	0.0011	0.000	0.000	1.7702
40.8728	0.0081	0.0011	0.000	0.000	2.0460
32.5143	0.0088	0.0007	0.000	0.000	2.2280
27.5227	0.0093	0.0006	0.000	0.000	2.3/13
23.8703	0.0098	0.0005	0.000	0.000	2.48/1
20.0928	0.0106	0.0008	0.000	0.000	2.6802
15.3493	0.0116	0.0010	0.001	0.000	2.9394
11.6883	0.0123	0.0007	0.001	0.000	3.1269
9.7754	0.0129	0.0006	0.001	0.000	3.2/58
8.2/2/	0.0135	0.0006	0.001	0.000	3.4247
7.0162	0.0141	0.0006	0.001	0.000	3.5846
6.0688	0.0147	0.0006	0.001	0.000	3.7280
5.0949	0.0159	0.0012	0.002	0.000	4.0423
4.1489	0.0172	0.0013	0.002	0.001	4.3622
3.5008	0.0183	0.0012	0.003	0.001	4.6544
2.9858	0.0196	0.0013	0.004	0.001	4.9798
2.5484	0.0199	0.0003	0.004	0.000	5.0456
2.1824	0.0202	0.0003	0.004	0.000	5.1294
1.8346	0.0212	0.0010	0.005	0.001	5.3758
1.5472	0.0223	0.0012	0.007	0.001	5.6684
1.3722	0.0235	0.0011	0.009	0.002	5.9565
1.1958	0.0265	0.0030	0.014	0.005	6.7297
0.9936	0.0319	0.0054	0.025	0.011	8.1114
0.8335	0.0428	0.0109	0.051	0.026	10.8770
0.7044	0.0543	0.0115	0.083	0.033	13.7905
0.5922	0.0680	0.0136	0.129	0.046	17.2566
0.4943	0.0761	0.0081	0.162	0.033	19.3134
0.4156	0.0837	0.0076	0.199	0.037	21.2433
0.3434	0.0903	0.0067	0.238	0.039	22.9371
0.2857	0.0956	0.0053	0.275	0.037	24.2754
0.2411	0.1004	0.0048	0.314	0.040	25.4909
0.2017	0.1052	0.0048	0.362	0.048	26.7212
0.1635	0.1148	0.0095	0.479	0.117	29.1453
0.1356	0.1183	0.0035	0.531	0.052	30.0332
0.1166	0.1296	0.0113	0.725	0.194	32.9104
0.0945	0.1447	0.0151	1.044	0.319	36.7353
0.0784	0.1607	0.0161	1.454	0.411	40.8197
0.0673	0.1733	0.0126	1.828	0.374	44.0116
0.0574	0.1894	0.0161	2.387	0.559	48.0919
0.0479	0.2060	0.0166	3.080	0.692	52.2996
0.0400	0.2233	0.01/3	3.945	0.865	56.6963
0.0336	0.2401	0.0168	4.944	0.998	60.9594
0.0282	0.2585	0.0185	0.254	1.311	70.0570
0.0234	0.2790	0.0205	8.008	0.100	70.8570
0.0196	0.2999	0.0209	10.137	2.129	/0.1048
0.0100	0.3230	0.0230	12.900	2.709	82.0135
0.0140	0.0570	0.01/0	10.413	2.500	00.4024
0.0000	0.3573	0.0167	18.252	2.839	90.7254
0.0098	0.3072	0.0099	20.274	2.021	93.2433
0.0083	0.3700	0.0066	22.330	1.610	06 0001
0.0057	0.3810	0.0056	25.400	1.019	97 9244
0.0057	0.3850	0.0040	26.107	0.605	00 0405
0.0048	0.3873	0.0016	26.107	0.005	99,6979
0.0040	0.3000	0.0004	27 220	0.084	99,0100
0.0033	0.3635	0.0003	07.607	0.047	00.0140
0.0028	0.3899	0.0004	27.007	0.208	99.0506
0.0024	0.3901	0.0001	20.674	2 040	99.0500
0.0021	0.0000	0.0032	20.674	0.000	00.0507
0.0013	0.3932	0.0006	21 255	0.601	100.0000
0.0016	0.3538	0.0000	01.055	0.001	100.0000
0.0010	0.3336	0.0000	31.300	0.000	100.0000

X.2.4 MOR

Summary Report Penetrometer parameters 07-0817- 5 Bulb, 0.392 Stem, Solid Penetrometer: Pen. Constant: 10.790 µL/pF Pen. Weight: 61.6589 g Stem Volume: 0.3920 mL Max. Head Pressure: 4.4500 psia Pen. Volume: 5.9119 mL Assembly Weight: 133.7488 g **Hg Parameters** Adv. Contact Angle: 130.000 degrees Rec. Contact Angle: 130.000 degrees Hg Surface Tension: 485.000 dynes/cm Hg Density: 13.5335 g/mL **User Parameters** 0.000 0.000 Param 1: Param 2: 0.000 Param 3: Low Pressure: Evacuation Pressure: 25 µmHg Evacuation Time: 10 mins 0.46 psia 0.001 µL/g/s Mercury Filling Pressure: Equilibration Rate: **High Pressure:** Equilibration Rate: 0.001 µL/g/s No Blank Correction Intrusion Data Summary 0.2983 mL/g Total Intrusion Volume = 22.331 m²/g Total Pore Area = Median Pore Radius (Volume) = 0.0879 µm Median Pore Radius (Area) = 0.0050 µm Average Pore Radius (2V/A) = Bulk Density at 0.46 psia = Apparent (skeletal) Density = 0.0267 µm 1.3783 g/mL 2.3406 g/mL 41.1145 % Porosity = 41.1145 Stem Volume Used = 68 % Cumulative Intrusion vs Pore size Intrusion for Cvo 0.30 0.25 0.2 Cumulative Intrusion (mL/g) 0.1 0. 0.05 0.00 10 0.1 0.001 Pore size Radius (µm)

The overall porosity of MOR is approximately 0.2983 mL/g. Approximately 28% of this porosity is made up of pores with over 0.5 μ m diameter, \approx 19% with over 1 μ m, \approx 6.7% with over 5 μ m, \approx 5.5% with over 10 μ m, \approx 2.8% with pores over 50 μ m and \approx 2.1% of pores with over 100 μ m.

Mean Radius (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)	% of Total Intrusion Volume
194,5936	0.0000	0.0000	0.000	0.000	0.0000
194,5596	0.0000	0.0000	0.000	0.000	0.0000
128,4296	0.0047	0.0047	0.000	0.000	1.5657
54,3278	0.0058	0.0011	0.000	0.000	1,9482
40.8728	0.0068	0.0010	0.000	0.000	2.2812
32,5143	0.0074	0.0006	0.000	0.000	2,4866
27.5227	0.0082	0.0008	0.000	0.000	2,7629
23,8703	0.0088	0.0005	0.000	0.000	2,9400
20,0928	0.0099	0.0011	0.000	0.000	3.3155
15.3493	0.0113	0.0014	0.001	0.000	3.7973
11.6883	0.0123	0.0009	0.001	0.000	4,1090
9.7754	0.0130	0.0007	0.001	0.000	4.3428
8.2727	0.0137	0.0007	0.001	0.000	4.5836
7.0162	0.0145	0.0008	0.001	0.000	4.8670
6.0688	0.0152	0.0006	0.002	0.000	5.0795
5.0949	0.0163	0.0011	0.002	0.000	5.4479
4.1489	0.0173	0.0010	0.002	0.000	5.7951
3.5008	0.0183	0.0010	0.003	0.001	6.1422
2.9858	0.0195	0.0012	0.004	0.001	6.5389
2.5486	0.0199	0.0004	0.004	0.000	6.6752
2.1828	0.0204	0.0005	0.005	0.000	6.8496
1.8365	0.0218	0.0014	0.006	0.002	7.3187
1.5492	0.0243	0.0024	0.009	0.003	8.1335
1.3728	0.0260	0.0018	0.012	0.003	8.7311
1.1969	0.0306	0.0046	0.020	0.008	10.2727
0.9947	0.0359	0.0053	0.030	0.011	12.0513
0.8337	0.0414	0.0055	0.043	0.013	13.8857
0.7043	0.0467	0.0052	0.058	0.015	15.6440
0.5918	0.0528	0.0062	0.079	0.021	17.7075
0.4939	0.0583	0.0054	0.101	0.022	19.533/
0.4152	0.0039	0.0050	0.128	0.027	21.4055
0.0452	0.0702	0.0003	0.105	0.037	23.5105
0.2850	0.0812	0.0055	0.242	0.078	27.2352
0.2411	0.0807	0.0050	0.200	0.050	20.7510
0 1625	0.1062	0.0146	0.516	0.179	25 6274
0.1356	0.1116	0.0053	0.594	0.078	37 4212
0.1166	0 1206	0.0190	0.920	0.326	42 7999
0.0945	0.1533	0.0227	1.400	0.480	51,3956
0.0784	0.1729	0.0196	1,900	0.499	57,9531
0.0673	0.1929	0.0200	2 4 9 4	0.595	64,6598
0.0575	0.2127	0.0198	3,184	0.690	71,3051
0.0479	0.2257	0.0130	3.728	0.544	75.6686
0.0400	0.2354	0.0097	4.213	0.485	78.9186
0.0336	0.2430	0.0076	4.662	0.449	81,4500
0.0282	0.2499	0.0069	5.152	0.490	83.7640
0.0234	0.2564	0.0065	5.706	0.554	85.9356
0.0196	0.2612	0.0049	6.205	0.499	87.5772
0.0166	0.2657	0.0044	6.737	0.532	89.0602
0.0140	0.2690	0.0033	7.207	0.471	90.1686
0.0118	0.2724	0.0034	7.781	0.574	91.3006
0.0098	0.2749	0.0025	8.301	0.520	92.1549
0.0083	0.2783	0.0034	9.127	0.826	93,3041
0.0069	0.2813	0.0029	9.980	0.853	94.2919
0.0057	0.2843	0.0030	11.025	1.045	95.2949
0.0048	0.2859	0.0016	11./0/	0.681	95.8407
0.0040	0.28/6	0.0017	12.555	0.849	96.409/
0.0033	0.2890	0.0014	14.050	0.800	07 1000
0.0028	0.2855	0.0009	14.053	0.637	97.1882
0.0024	0.2500	0.00064	19.620	5.042	99.9075
0.0019	0.2062	0.0004	10.020	0.246	99 2962
0.0017	0 2982	0.0021	22 321	2 466	100 0000
0.0016	0.2983	0.0000	22.331	0.000	100,0000
0.0010	0,2000	0.0000	Robert CO	0.000	100.0000

X.2.5 RHY

Summary Report Penetrometer parameters 07-0817- 5 Bulb, 0.392 Stem, Solid Penetrometer: 61.8327 g 4.4500 psia Pen. Constant: 10.790 µL/pF Pen. Weight: Max. Head Pressure: Stem Volume: 0.3920 mL Pen. Volume: Assembly Weight: 131.7808 g 5.9119 mL **Hg Parameters** Adv. Contact Angle: 130.000 degrees Rec. Contact Angle: 130.000 degrees Hg Surface Tension: 485.000 dynes/cm Hg Density: 13.5335 g/mL **User Parameters** Param 1: 0.000 0.000 0.000 Param 2: Param 3: Low Pressure: Evacuation Pressure: 25 µmHg Evacuation Time: 10 mins 0.46 psia 0.001 µL/g/s Mercury Filling Pressure: Equilibration Rate: High Pressure: Equilibration Rate: 0.001 µL/g/s No Blank Correction Intrusion Data Summary Total Intrusion Volume = 0.0615 mL/g 4.456 m²/g Total Pore Area = Median Pore Radius (Volume) = 1.4814 µm Median Pore Radius (Area) 0.0023 µm Average Pore Radius (2V/A) = Bulk Density at 0.46 psia = Apparent (skeletal) Density = 0.0276 µm 2.1275 g/mL 2.4478 g/mL 13.0871 % Porosity 13.0871 Stem Volume Used = 29 % Cumulative Intrusion vs Pore size Intrusion for Cycle 0.06 0.05 0.04 Cumulative Intrusion (mL/g) 0.03 0.02 0.01 0.00 10 0.1 0.001 Pore size Radius (µm)

The overall porosity of RHY is approximately 0.0615 mL/g. Approximately 75% of porosity is made up of pores with over 0.5 μ m diameter, \approx 68.5% with over 1 μ m, \approx 46.5% with over 5 μ m, \approx 39% with over 10 μ m, \approx 16.5% with pores over 50 μ m and \approx 11% of pores with over 100 μ m.

Mean Radius (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)	% of Total Intrusion Volume
 195,0808	0.0000	0.0000	0.000	0.000	0.0000
195,1150	-0.0000	-0.0000	-0.000	-0.000	-0.0164
128.7408	0.0055	0.0055	0.000	0.000	8.9099
54.3361	0.0065	0.0010	0.000	0.000	10.4881
40.8572	0.0073	0.0009	0.000	0.000	11.8854
32.4919	0.0094	0.0021	0.000	0.000	15.2554
27.5221	0.0100	0.0006	0.000	0.000	16.2417
23.8634	0.0104	0.0004	0.000	0.000	16.8829
20.0858	0.0111	0.0007	0.000	0.000	18.0336
15.3442	0.0121	0.0010	0.001	0.000	19.5953
11.6851	0.0131	0.0011	0.001	0.000	21.3543
9.7738	0.0138	0.0006	0.001	0.000	22.35/1
8.2/24	0.0144	0.0006	0.001	0.000	23.3598
6.0600	0.0150	0.0006	0.001	0.000	24.3402
5.0949	0.0243	0.0021	0.002	0.003	29 5522
4 1499	0.0256	0.0012	0.005	0.001	41 6400
3 5009	0.0266	0.0010	0.006	0.001	43 3168
2,9858	0.0281	0.0014	0.007	0.001	45.6347
2,5229	0.0287	0.0006	0.007	0.000	46.5846
2.1676	0.0292	0.0005	0.008	0.000	47.3976
1.8488	0.0300	0.0008	0.009	0.001	48.7499
1.5472	0.0311	0.0011	0.010	0.001	50.5377
1.3704	0.0323	0.0012	0.012	0.002	52.4622
1.1935	0.0343	0.0021	0.015	0.003	55.7999
0.9867	0.0359	0.0015	0.018	0.003	58.2799
0.8316	0.0375	0.0016	0.022	0.004	60.8806
0.7069	0.0390	0.0016	0.027	0.004	63,4602
0.5945	0.0407	0.0017	0.032	0.006	66.1858
0.4960	0.0421	0.0014	0.038	0.006	68.5053
0.416/	0.0436	0.0014	0.045	0.007	70.8477
0.3440	0.0450	0.0014	0.053	0.008	73.0843
0.2808	0.0458	0.0009	0.059	0.000	74.0198
0 2024	0.0473	0.0006	0.072	0.006	76 9949
0 1639	0.0482	0.0009	0.083	0.011	78 2949
0,1358	0.0485	0.0004	0.088	0.005	78,8686
0.1168	0.0492	0.0007	0.100	0.012	80.0332
0.0947	0.0499	0.0006	0.114	0.013	81.0693
0.0785	0.0504	0.0006	0.129	0.015	82.0111
0.0674	0.0509	0.0004	0.141	0.012	82.6801
0.0575	0.0515	0.0006	0.162	0.022	83.6943
0.0479	0.0521	0.0006	0.187	0.024	84.6370
0.0401	0.0526	0.0006	0.216	0.029	85.5830
0.0337	0.0532	0.0006	0.250	0.035	86.5361
0.0282	0.0538	0.0006	0.254	0.043	87.5270
0.0234	0.0550	0.0005	0.345	0.047	00.0740
0.0167	0.0555	0.0005	0.460	0.064	90 1971
0.0141	0.0559	0.0004	0.514	0.054	90,8200
0.0118	0.0563	0.0005	0.593	0.078	91,5701
0.0098	0.0566	0.0003	0.646	0.053	91,9965
0.0083	0.0569	0.0003	0.717	0.071	92.4785
0.0069	0.0572	0.0003	0.794	0.076	92.9085
0.0057	0.0574	0.0002	0.871	0.077	93.2672
0.0048	0.0576	0.0002	0.954	0.083	93.5902
0.0040	0.0578	0.0002	1.053	0.100	93.9138
0.0033	0.0580	0.0002	1.176	0.123	94.2462
0.0028	0.0581	0.0001	1.239	0.062	94.3882
0.0024	0.0582	0.0001	1.343	0.104	94.5936
0.0021	0.0615	0.0033	4.452	3.109	100 0000
0.0019	0.0615	0.0000	4,450	0.004	100.0000
0.0016	0.0615	0.0000	4.456	0.000	100.0000
0.0010	0.0010	0.0000	4.400	0.000	100.0000

X.3 XRD patterns

The first few scans are the ones related to the raw materials: bentonite, microsilica, silica flour and the ignimbrite, after being exposed to either 150° C or 290° C.

Afterwards, the scans of each one of the samples under study are presented, with the ITZ-C and CEM presented in the same graph and ITZ-R and ROCK in another one, in order to make it easier to compare the changes CEM/ITZ-C and ROCK/ITZ-R. The key used for these latter ones is the following:

Key

Brown line: XRD peaks obtained from a sample collected from the rock.

Black line: XRD peaks obtained from a sample collected from the cement core.

Blue line: XRD peaks obtained from a sample collected from the rock zone adjacent to the interfacial transition zone (ITZ-R).

Orange line: XRD peaks obtained from a sample collected from the cement zone adjacent to the interfacial transition zone (ITZ-C).

Bentonite



Microsilica



<u>Silica Flour</u>



<u>IGN</u>



IGN/G(150.28d)





IGN/G20SF(150.28d)





IGN/G40SF(150.28d)





IGN/G20MS(150.28d)





IGN/A(150.28d)





IGN/W(150.28d)





IGN/HAC(150.28d)





IGN/GEOI(150.28d)





IGN/G(150.b.28d)





IGN/G20SF(150.b.28d)





IGN/G40SF(150.b.28d)





IGN/G20MS(150.b.28d)





IGN/A(150.b.28d)





IGN/W(150.b.28d)





IGN/HAC(150.b.28d)





IGN/GEOII(150.b.28d)





IGN/G(290.28d)





IGN/G20SF(290.28d)





IGN/G40SF(290.28d)





IGN/G20MS(290.28d)





IGN/A(290.28d)





IGN/W(290.28d)





IGN/HAC(290.28d)





IGN/GEOII(290.28d)





IGN/G(150.84d)





IGN/G20SF(150.84d)




IGN/G40SF(150.84d)





IGN/G20MS(150.84d)





IGN/G(150.CO₂.84d)





IGN/G20SF(150.CO₂.84d)





IGN/G40SF(150.CO₂.84d)





IGN/G20MS(150.CO₂.84d)





UNI/G(150.CO₂.84d)





UNI/G20SF(150.CO₂.84d)





UNI/G40SF(150.CO₂.84d)





UNI/G20MS(150.CO₂.84d)





KAO/G(150.CO₂.84d)





KAO/G20SF(150.CO₂.84d)





KAO/G40SF(150.CO2.84d)





KAO/G20MS(150.CO₂.84d)





MOR/G(150.CO₂.84d)





MOR/G20SF(150.CO₂.84d)





MOR/G40SF(150.CO₂.84d)





MOR/G20MS(150.CO₂.84d)





<u>RHY/G(150.CO₂.84d)</u>





<u>RHY/G20SF(150.CO₂.84d)</u>





<u>RHY/G40SF(150.CO₂.84d)</u>





<u>RHY/G20MS(150.CO₂.84d)</u>





IGN/G(290.CO₂.84d)





IGN/G20SF(290.CO2.84d)





IGN/G40SF(290.CO2.84d)





IGN/G20MS(290.CO₂.84d)





X.4 Further SEM/EDS work

X.4.1 IGN/G(150.CO₂.84d)



i. ITZ SEM image

ITZ SEM backscattered image

Location of the line scans

The red line scan (diagram with red border, in the next page) shows that significant amounts of Ca are present in the rock, up to \approx 550µm. The Ca has penetrated much further and in higher amounts than observed for the green and yellow ones (other ones).

The green and yellow scans (diagrams with, respectively, green and yellow border lines, in the next page) show that Ca is present in the rock up to $\approx 400 \mu m$ and in lower concentrations than in the red one, with only one relatively high peak.

The green and yellow line scans are very similar due to their proximity. On the other hand, despite being close to the yellow and green lines, the red line scan is considerably different to the other ones. This is due to the heterogeneity of the materials under study, namely the rock.



i. ITZ Al map

ii. ITZ Na map

Regarding the Al and Na maps (same region as the SEM images presented above), they do not provide any relevant information regarding the trends in the ITZ. These maps are mostly useful to differenciate the feldspars (rich in Al and Na) from the quartz crystals (no Al or Na).

EDS element maps

Red line scan:



Green line scan:





<u>Yellow line scan</u>:

X.4.2 IGN/G20SF(150.CO₂.84d)



Location of the three line scans

These two line scans (diagrams in the next page) are also a good example of the heterogeneity of the materials involved, especially the rock. Despite of their proximity, the red and the green line scans show significantly different trends.

The red line scan shows a Ca penetration into the rock up to $350\mu m$, whereas the green one shows a Ca penetration of up to $500\mu m$.



i. ITZ Al map

ii. ITZ Na map

EDS element maps

Regarding the Al and Na maps (same region as the SEM images presented above), these again do not provide any relevant information regarding the trends in the ITZ between the cement and the rock.

Red line scan:



Green line scan:



X.4.3 IGN/G40SF(150.CO₂.84d)



Location of the line scans

Despite of their proximity, the red and the green line scans (diagrams in the next page) show considerably different Ca penetration depth into the rock. The red line scan shows a Ca penetration into the rock up to 350µm, whereas the green one shows a Ca penetration of under 300µm.

Therefore these two line scans are also a good example of the heterogeneity of the materials involved, especially the rock.



EDS element maps

ii. ITZ Na map

Again, the Al and Na maps (same region as the SEM images presented above) do not provide any relevant information regarding the trends in the ITZ between the cement and the rock.

Red line scan:



Green line scan:



X.4.4 IGN/G20MS(150.CO₂.84d)



i. ITZ SEM image

ii. ITZ SEM backscattered image Location of the line scans

These three line scans (red, green and yellow diagrams represented in the next page) are also in agreement with the idea put forward for the previous samples, i.e. the line scans are not enough reliable to work with due to the heterogeneous nature of the sample.



i. ITZ Al map

EDS element maps

Again, the Al and Na maps (same region as the SEM images presented above) do not provide any relevant information regarding the trends in the ITZ between the cement and the rock.

Red line scan:



Green line scan:



Yellow line scan:





X.5 Mass Spec: comparison of Mass Spec results
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