The effect of the rock type on the degradation of well cements in CO_2 enriched geothermal environments

João Conde Silva[a,b,c,*], Neil B. Milestone[a]

[a] Callaghan Innovation, 69 Gracefield Rd, 5010, Lower Hutt, New Zealand
[b] Victoria University of Wellington, 19 Kelburn Parade, 6012, Wellington, New Zealand
[c] National Laboratory for Civil Engineering, Avenida do Brasil 101, 1700-066, Lisbon, Portugal

ABSTRACT

The rock type plays a key role in the way in which the outermost layer of the cement interacts with the formation, in wells under geothermal environments. The penetration of cement into the rock is controlled by the porosity of the rock which also regulates the amount of CO_2 enriched brine that can contact the cement.

Samples were prepared by drilling holes into rock blocks, pouring in a cement slurry and hydrothermally treating the whole assembly at 150 °C under typical geothermal environments. The changes in the interfacial transition zone (ITZ) that forms between geothermal cements and volcanic rocks were examined.

Both porosity and the volcanic glass content of the rock have a considerable impact on the way in which the cement and the formation interact and, ultimately, affect the bond between these materials. The porosity has a major influence on the durability of the cement in carbonated brine.

1. Introduction

The formation of an interfacial transition zone (ITZ) between cement and rock has been described by Silva and Milestone (2016), where cement formulations were cured in ignimbrite moulds under hydrothermal conditions. Silva et al. (2013) and Silva and Milestone (2018) demonstrated that contact with a CO_2 enriched brine can play an important role on the makeup of this ITZ and associated durability of the cement.

According to Kutchko et al. (2008), the scenario observed for cement degradation in wells from exposure to CO_2-saturated brine is best described as an acid attack by carbonic acid, rather than ordinary carbonation. The rate of cement carbonation attack is diffusion limited because the rate of the acid-base carbonation reactions is much faster than the diffusion of ionic species through the cement matrix. Fick's second law of diffusion with constant concentration boundary conditions given by Eq. (1) is often used to estimate the depth of ordinary carbonation in cement (Kutchko et al., 2008).

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

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.

Barlet-Gouedard et al. (2006) used Eq. (1) in a simple diffusion model to represent the rate of degradation of Portland cement (w/c = 0.44) in CO_2 saturated water (1.2 mol/kg CO_2) at 90 °C with: $L = 0.22t^{1/2}$, with L in mm and t in hours. However, the cement alteration process when cement is exposed to CO_2-saturated water or brine is much more complex than a simple diffusion. Kutchko et al. (2008) reported there was an initial rapid reaction followed by a decrease in carbonation rate when cement was exposed to CO_2-saturated brine over 1 year. Duguid et al. (2011) also observed that the rate of carbonation slowed down after 3–6 months curing. The parameter α in Eq. (1) is therefore not constant, implying that the physical properties of the hardened cement phase change, likely due to the precipitation of a dense $CaCO_3$ rich, protective layer. This carbonation sheath, which has been previously reported (Milestone et al., 1986; Duguid et al., 2005), consists of a new, denser (less porous) region which forms within the cement. As this new phase grows faster than it is dissolved, slower diffusion rates are observed over time, i.e. α decreases with time (Kutchko et al., 2008).

The rock formation, with its own factors of stratigraphic distribution, mineral composition, permeability, porosity and hydrothermal alteration of the rock, affect this mechanism. Permeability, given by the amount of fluid flowing through the rock pores per unit of time (Rae,

2007) is intimately connected with porosity. However, the rock permeability is unlikely to be directly proportional to its porosity as it can depend on other factors such as the mechanism of dissolution of the rock minerals and pore size distribution (Hangx, 2005; Soler and Mader, 2010; Langton et al., 1980).

When the cement is surrounded by rock, as in the interface between the well cement and the formation, α tends to be even lower as the rock limits the amount of CO_2 enriched brine that can come in contact with the cement. In these situations, where the cement tends to partially penetrate the rock pores and $CaCO_3$ precipitates. This might block some of the larger pores and, therefore, reduce the amount of CO_2 enriched brine available for contact with the bulk of the cement. Consequently, the rate of degradation of the cement drops even further (Duguid et al., 2011).

Langton et al., (1980) undertook some hydrothermal cement-rock interaction experiments at temperatures of 200 °C and 250 °C, at 51.7 MPa pressure. They used an API class *J* cement (a belite cement no longer available), with tuscarora quartzite (95% quartz), and Valentine limestone (99.9% calcium carbonate) which they considered unreactive. In their study, they realised that the both shear strength and the hydration changed for both samples, depending 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 that formed in the interfacial region and the paste, and which increased with time and temperature. They also 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. From their work, Langton et al. (1980) and Rochelle et al. (2004) conclusion was that a good cement-to-formation seal relied strongly on a physical/mechanical interaction rather than on a chemical bond. A good bond is essential to avoid leakages along the cement-formation interface (Crow et al., 2010; Carey et al., 2007), leakage being something which is likely to increase the rate of cement degradation. 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 during the construction of the well (Crow et al., 2010).

According to several references (Rae (2007); Hedenquist (1990); Browne and Ellis (1970); Browne (1973); New Zealand Geothermal Association (2014)), the most predominant rocks in NZ geothermal fields are ignimbrites and rhyolites. The goal of this paper is to enhance the understanding of the role that the most relevant rock features play on the cement /rock interaction within typical New Zealand geothermal environments.

2. Materials and methods

2.1. Raw materials

2.1.1. Rocks
The rock types used were 4 different forms of ignimbrite and 1 form of rhyolite, all obtained in New Zealand. Ongatiti ignimbrite (IGN) was obtained from the Hinuera quarry and a further 3 forms of ignimbrite with different weathering were collected in the Ohakuri geothermal field: an unaltered ignimbrite (UNI), an ignimbrite with kaolinite alteration (KAO), and a zeolitised ignimbrite with mordenite alteration (MOR) along with a sample of Whakaroa rhyolite (RHY), collected from the margins of Lake Taupo. The XRF analyses of these are shown in Table 1 and the XRD results and some further analyses based on both XRF and XRD results presented in Table 2. The data obtained from the mercury porosometry of each rock is presented in Table 3.

2.1.2. Cement and silica flour
Holcim Class G cement (G) and Halliburton SSA-1 Silica Flour (SF - almost pure quartz) were used to prepare the formulations under study.

These materials are abbreviated respectively by G and SF and their XRF analyses are shown in Table 4. Their particle size distribution (PSD) is presented in Fig. 1. These materials have a very similar particle size distribution with most particles lying within the 0.5–90 μm diameter range.

2.2. Methodology

Twenty-five mm diameter and five mm deep cavities were cored in small blocks of rocks, which were immersed in geobrine solution[1] at 90 °C for 2–4 days to saturate with brine. Two cementing formulations were used: neat API Class G cement (G) and a blend of G with 40 wt.% addition of silica flour (G40SF). These were prepared according to API RP10 at a w/s ratio of 0.45 and poured into different holes. Five different rock types were tested with both formulations: IGN, UNI, KAO, MOR and RHY. Once poured, the assemblages were set/cured for 2 days in geobrine at 90 °C before being cured in autoclaves for 82 days at 150 °C (making a total of 84 days of curing) with an over pressure of 6 bar CO_2 giving a total pressure of 17 bar (0.042 mol/kg dissolved CO_2), maintained throughout the autoclaving step.

After curing, each cement-rock system was cut in half (see Fig. 2), photographed and samples prepared for X-ray diffraction (XRD), Transmitted Light Optical Microscopy (OM) and Scanning Electron Microscopy with Electron Dispersive Spectroscopy (SEM/EDS).

The instrument used for XRD was a Philips PW1700 series diffractometer running Co K alpha radiation Long Fine Focus tube with tube power settings of 40 kV and 35 mA. SEM images were taken on a Quanta 450 SEM equipped with a tungsten filament. The elemental images were obtained with an EDAX Energy Dispersive X-ray Spectroscopy (EDS) associated to a Quanta 450 SEM, using Texture & Elemental Analytical Microscopy (TEAM) software (version V3.1).

This work has focused on examining the changes observed on the interfacial transition zone (ITZ) compared to their respective parent materials, the rock and the cement. For these purposes, two different zones were distinguished in the ITZ: the interfacial transition zone closest to the rock (ITZ-R) and the cement side of the interfacial transition zone (ITZ-C).

3. Results

3.1. Mesoscopic images

The Fig. 2 shows the photos of each the sample after being cured and cut in half. No singularities were observed in the class G cement carbonations (Fig. 2i–v). On the other hand, there is a very well distinguished, pink coloured rim all over the outermost layer in the G40SF formulations (Fig. 2vi–ix) tested with ignimbrites (IGN, UNI, KAO and MOR), as opposed to the greyish colour observed in the cement core. The IGN/G40SF shows a relatively uniform pink layer, whereas UNI shows a very variable and slightly wider average layer. The KAO shows the widest pink rim and the MOR shows the narrowest one within the ignimbrites (in average). Regarding the RHY/G40SF (Fig. 2x), it exhibits only a few pink spots in the ITZ-C, except for the top of the sample, which is not surrounded by rock.

3.2. X-ray diffraction

Generally, the XRD pattern indicates that the core of the G cement is

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[1] The hydrothermal solution (geobrine) utilised is that used in the experimental work undertaken by the Callaghan Innovation (previous IRL) cement research team. The recipe is based on a geothermal fluid assay supplied by Mighty River Power in 2009, and prescribed by GNS Science in February 2010: 0.19 g sodium sulfate ($NaSO_4$), 0.05 g calcium chloride dehydrate ($CaCl_2.2H_2O$), 15.6 g liquid precipitated silica (SiO_2), 4.1 g potassium chloride (KCl), 15.8 g sodium chloride (NaCl) are well mixed and filled with water to make up 20 litres.