

Uptake and retardation of Cl during cement carbonation

A.E. Milodowski*, C.A. Rochelle, G. Purser

*British Geological Survey,
Environmental Science Centre,
Keyworth, Nottingham,
NG12 5GG, UK*

Abstract

The presence of ^{36}Cl in low- and intermediate-level radioactive waste (L/ILW) is of concern in repository performance assessment. Its mobility and its relatively long half-life (302,000 years) could potentially lead to early release from the waste and its return to the biosphere within the 10^6 timescale. Experiments have been undertaken to examine the impact of carbonation on the mineralogical and physical properties of NRVB cement in relation to the degradation of organic material in the L/ILW, and with oilwell Type-G cement in relation to borehole sealing for carbon capture and storage. These show that the cements can uptake a significant amount of Cl through the formation of transient secondary calcium chloroaluminate and Cl-rich calcium silicate hydrate phases. The formation of the Cl-rich phases is enhanced by carbonation reactions and also low temperatures (20 °C). The process may be important in retarding the migration of ^{36}Cl from a repository for L/ILW.

*Corresponding author. Tel.: 00 44 115 9363548; E-mail address: aem@bgs.ac.uk

1. Introduction

Radionuclide mobility is a key issue in performance assessment (PA) of a geological disposal facility (GDF) for radioactive waste. The anionic radionuclides ^{36}Cl , ^{129}I , and ^{79}Se present as fission and activation products in spent fuel and low- and intermediate-level radioactive waste (L/ILW) [1], are of potential concern because of their relatively long half-lives (e.g. 302,000 years for ^{36}Cl) and their high mobility [2]. Consequently, PA calculations take a conservative approach and suggest that these radionuclides will be leached from the repository, migrate through the far-field, and enter the biosphere within 10^6 years [2]. Therefore, the recognition of any processes that retard these mobile radionuclides will enhance and build confidence in a safety case for a GDF.

The current UK repository concept for low and intermediate wastes involves using large quantities of cementitious materials for both construction and buffer/backfill. The potential alteration of cement by reaction with carbon dioxide (CO_2), from the degradation of organic material in the wastes, and its impact on the physical properties, has been investigated within the EC Framework 7 Fate of Repository Gases (FORGE) project. Experimental studies of CO_2 -cement interaction have also been undertaken to evaluate the long-term stability of cement seals of injection wells in reservoirs and aquifers for geological storage of CO_2 . Both of these experimental studies utilized saline pore fluids and show that significant interaction between chloride from the fluid and the cement matrix takes place during carbonation of the cement.

2. Methodology

Samples of Nirex Reference Vault Backfill (NRVB) cement were prepared as described by Francis et al. [3], cured at 40 °C for 28 days, and then stored in $\text{Ca}(\text{OH})_2$ -saturated water at room temperature. They were sub-cored to produce samples of 25 mm diameter x 50 mm long. The samples were reacted in batch reactors with a Na-Ca-OH- SO_4 -Cl rich synthetic ‘evolved’ cement porewater (16,391 mg l⁻¹ Cl⁻, initial pH 12.05 at 20 °C) under gaseous CO_2 , 40 bar, 40 °C; liquid CO_2 , 80 bar, 20 °C; supercritical CO_2 80 bar, 40 °C; and under gaseous N_2 with the same range of conditions. The experimental system is described in detail in Rochelle and Sivers [4] and illustrated in Fig. 1.

A very similar experimental set up was used for the CO_2 storage cement interaction experiments (above), but experiments ran at 30 °C and 80 bar for 110 days [5]. The cement sample used was a low-permeability oilwell Type G cement, and the starting fluid used was a Na-K-Ca-Cl porewater of approximately seawater composition (20,100 mg l⁻¹ Cl⁻, initial pH 8.35 at 25 °C).

The reacted cement cores were vacuum-dried at 20 °C. Polished thin sections were prepared (under ethanol) after impregnation with epoxy-resin. These were examined by optical petrographic microscope with detailed petrographic observations made by backscattered scanning electron microscopy (BSEM) supported by microchemical analysis by energy-dispersive X-ray microanalysis (EDXA). Digital element distribution maps were also recorded from selected areas of the sections using EDXA. Bulk mineralogical composition of the altered cement was determined by X-ray diffraction analysis (XRD).

3. Results

The experiments with NRVB and oilwell Type G cement all showed a significant removal of Cl⁻ from the porewater phase (e.g. Table 1). Reduction in Cl⁻ was observed regardless of whether the porewater was in contact with gaseous N_2 , or with gaseous, liquid or supercritical CO_2 . Cl⁻ removal was greater with CO_2 than with N_2 , and increased with time. However, the reduction in Cl⁻ concentration was considerably greater in the experiments at 20 °C with both gaseous N_2 (77% reduction in Cl⁻) and liquid CO_2 (81% reduction in Cl⁻), showing that temperature, rather than either the presence of CO_2 or N_2 , or the phase of CO_2 had the greater controlling effect on Cl⁻ uptake by the cement. This suggests that any secondary phases responsible for Cl⁻ uptake in the cement are more stable at lower temperature.

The reacted cements in contact with gaseous N_2 exhibited little evidence of alteration. EDXA maps for Cl showed uniformly-distributed low concentration of Cl throughout the cement. However, cement from experiments with CO_2 all showed significant carbonation alteration, with extensive replacement of the hydrated calcium silicates and aluminates by calcium carbonate (Fig. 2). Cement carbonation mainly occurred along a sharp front (Fig. 2), which progressively migrated from the edge to the centre of the cement cores. Carbonation was accompanied by volume reduction, with the development of shrinkage fractures parallel to, ahead and behind the carbonation front. EDXA mapping revealed that Cl was concentrated at, or just ahead of, the carbonation front in the cement. Detailed BSEM observations showed that fine-grained radial fibrous crystal aggregates of a calcium chloroaluminate phase and gel-like Cl-rich CSH had formed within or ahead of the carbonation front. XRD analysis of the altered cement indicates that the crystalline product is probably hydrocalumite ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$). The Cl-rich phases are progressively dissolved and removed as the carbonation front moves forward, but reform on the cement side of the main reaction front. They are absent in the fully-carbonated cement zones.

4. Summary and conclusions

NRVB and oilwell Type-G cement can both remove significant amounts of Cl^- from porewater in contact with a non-reactive gas phase (N_2) or with gaseous, liquid or supercritical CO_2 . However, Cl^- removal is greatest during cement carbonation and at lower temperatures, implying that the formation of the secondary hydrocaluminate and Cl-rich CSH, responsible for incorporating Cl^- , is encouraged by reaction with CO_2 and stabilized by lower temperatures. However, the Cl^- phase is metastable, and is progressively removed as the carbonation front moves through the cement. Cl^- uptake by cement and formation of a Cl-rich secondary phase has been observed previously in experimental studies on cement carbonation and in oilwell cement exposed to CO_2 for over 30 years [6][7]. The uptake of Cl^- by the formation of transient secondary calcium chloroaluminate phases may provide an important mechanism for retarding the migration of ^{36}Cl from a GDF for radioactive waste.

Acknowledgements

This work supported through the European Commission Sixth Framework CO_2 GeoNet (EC Project SES6-CT-2004-502816), the European Atomic Energy Community's Seventh Framework Programme (FORGE project Grant Agreement no230357), and the Nuclear Decommissioning Authority Radioactive Waste Management Directorate (NDA/RWMD). This paper is published with permission of the Executive Director of the British Geological Survey (NERC).

References

- [1] Nirex. Generic Repository Studies. Nirex Report N/80, United Kingdom Nirex Limited, 2003, 225p.
- [2] Grambow B. Mobile fission and activation products in nuclear waste disposal. *J Cont Hydrol* 2008;**102**:180-186.
- [3] Francis AJ, Cather R., Crossland IG. Development of the Nirex reference vault backfill; report on current status in 1994. Nirex Science Report S/97/014, United Kingdom Nirex Limited, 1997, 57p.
- [4] Rochelle CA, Sivers, G. (2010). Towards D3.6: Results of the tests on concrete (part 1). Laboratory experiments at the BGS. FORGE Report D3.6.
- [5] Rochelle CA, Milodowski AE. Carbonation of borehole seals:comparing evidence from short-term laboratory experiments and long-term natural analogues. *Appl Geochem* 2012 ; *in press*.
- [6] Carey JW, Wigand M, Chipera SJ, Woldegabriel G, Pawar R, Lichtner PC, Wehner SC, Raines MA, Guthrie J.. Analysis and performance of oil well cement with 30 years of CO_2 exposure from the SACROC Unit, West Texas, USA. *Int J Greenhouse Gas Control* 2007;**1**:75-85.
- [7] Wigand M, Kaszuba JP, Carey JW, Hollis WK. Geochemical effects of CO_2 sequestration on fractured wellbore cement at the cement/caprock interface. *Chem Geol* 2009;**265**:1122-1133.

Table 1. Chloride concentrations in the reacted fluid from batch experiments with NRVB cement under gaseous, liquid and supercritical CO₂ and gaseous N₂ environments.

Experiment	Temp (°C)	Pressure (bar)	Time	Porewater Cl (mg l⁻¹)
Liquid CO ₂	20	80	40 days	3182
Gaseous CO ₂	40	40	40 days	11325
Supercritical CO ₂	40	80	40 days	12636
SupercriticalCO ₂	40	80	1 year	11205
Gaseous N ₂	20	80	40 days	3773
Gaseous N ₂	40	40	40 days	13074
Gaseous N ₂	40	80	40 days	13408
Gaseous N ₂	40	80	1 year	13007
Starting porewater				16391

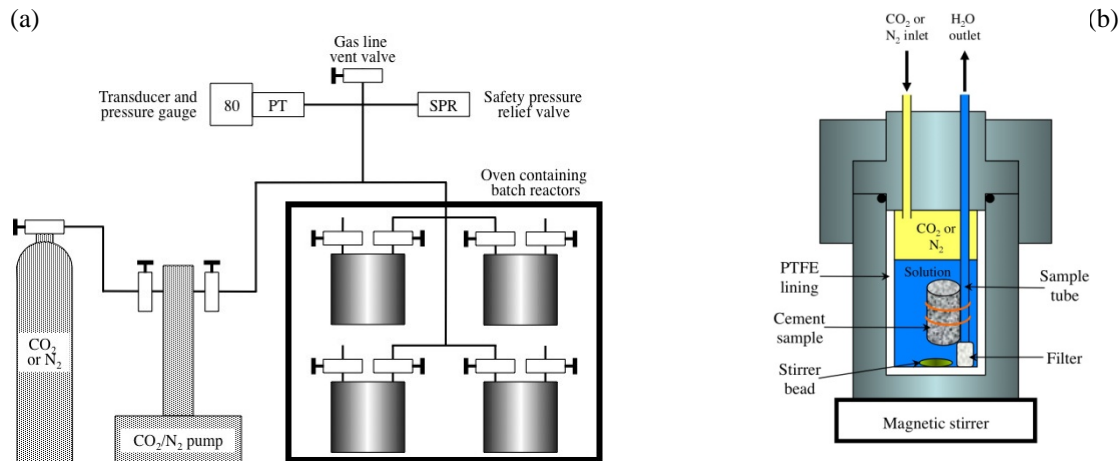


Fig. 1(a). Schematic diagram of an assembled batch reactor. (b) Diagram of the typical arrangement of batch reactors inside an oven.

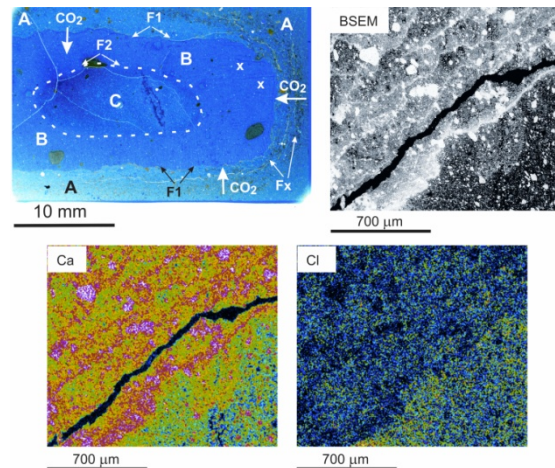


Fig. 2. Top left: Transmitted light photomicrograph of thin section through NRVB cement reacted for 40 days with FORGE evolved cement porewater and exposed to supercritical CO₂. A = fully-carbonated cement; B = partially carbonated cement; C = residual weakly carbonated cement core; F1 = main carbonation reaction front; F2 = diffuse inner reaction front; Fx = position of old reaction fronts; x = shrinkage cracks developed perpendicular to main carbonation front Top right: BSEM image detail of reaction front between fully carbonated cement zone (top) and partially carbonated cement. Bottom: EDXA distribution maps for Ca and Cl corresponding to same area as in BSEM image (colour scale: red = high concentration; black = low concentration).