



Retention of chlorine-36 by a cementitious backfill

E. VAN ES^{1,†}, J. HINCHLIFF¹, M. FELIPE-SOTELO^{1,*}, A.E. MILODOWSKI², L.P. FIELD², N.D.M. EVANS¹ AND D. READ¹

¹ Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

² British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

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ABSTRACT

Radial diffusion experiments have been carried out to assess the migration of ³⁶Cl, as chloride, through a cementitious backfill material. Further experiments in the presence of cellulose degradation products were performed to assess the effect of organic ligands on the extent and rate of chloride diffusion. Results show that breakthrough of ³⁶Cl is dependent on chloride concentration: as the carrier concentration increases, both breakthrough time and the quantity retained by the cement matrix decreases. Experiments in the presence of cellulose degradation products also show a decrease in time to initial breakthrough. However, uptake at various carrier concentrations in the presence of organic ligands converges at 45% of the initial concentration as equilibrium is reached. The results are consistent with organic ligands blocking sites on the cement that would otherwise be available for chloride binding, though further work is required to confirm that this is the case. Post-experimental digital autoradiographs of the cement cylinders, and elemental mapping showed evidence of increased ³⁶Cl activity associated with black ash-like particles in the matrix, believed to correspond to partially hydrated glassy calcium-silicate-sulfate-rich clinker.

KEYWORDS: ³⁶Cl, diffusion, radioactive waste, cellulose degradation products, Nirex Reference Vault Backfill.

Introduction

THE UK concept for geological disposal of intermediate level (ILW) and some long-lived low-level (LLW) radioactive waste is based on a multi-barrier system. According to the generic design (Hicks *et al.*, 2008), the waste will be grouted in steel drums, transported to a vault 300–1000 m underground and backfilled with a porous cement matrix. One potential candidate material is Nirex Reference Vault Backfill or NRVB (Francis *et al.*, 1997), comprising a mixture of Ordinary Portland Cement,

limestone flour and calcium hydroxide. It is expected that the backfill will generate high-pH conditions, with the eventual corrosion of the metal canisters used for disposal promoting a low-Eh environment. The intended safety functions of the cement within the near field include a reduction in the solubility of many radionuclides and retardation of their migration by adsorption and incorporation (Nuclear Decommissioning Authority, 2010). Reactive transport modelling suggests that the NRVB is likely to remain highly alkaline (pH ≥ 11) for many thousands of years post-closure.

Reduced solubility arises from the formation of radionuclide-containing solid phases, commonly the corresponding oxides and hydroxides for metallic species at high pH. There is much less evidence in support of the precipitation or co-precipitation of anionic species and conventionally

* E-mail: m.felipe-sotelo@lboro.ac.uk

[†]Present address: National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, UK

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these are regarded as conservative tracers in post-closure safety calculations. Consequently, long-lived species, such as ^{129}I and ^{36}Cl , are recognized as key radionuclides in the safety assessment of nuclear waste disposal, being described as non-solubility-limited and largely non-sorbing components of the inventory (Nuclear Decommissioning Authority, 2010). The migration of radioiodide through NRVB has been described in a recent paper by Felipe-Sotelo *et al.* (2014). The current paper focuses on ^{36}Cl .

Chlorine-36 is a beta emitter ($E_{\text{max}} = 709 \text{ KeV}$) with a half-life of $3.01 \times 10^5 \pm 4.00 \times 10^3$ years (Parrington *et al.*, 1996). The United Kingdom's inventory currently stands at 11.6 TBq. It is produced by neutron activation of non-radioactive ^{35}Cl and the most common source is as an impurity in graphite. Halogens or halogenated compounds containing chlorine are used in purification and this residual chlorine is then irradiated when the graphite is used in component materials in nuclear reactors.

Chloride is a highly mobile monovalent ion and is often used as a groundwater tracer (IAEA, 1997). The level of interaction of chloride ions with a cement matrix depends on several parameters including the associated cation (Na^+ , Ca^{2+} or occasionally Mg^{2+}), the cement and mineral admixtures, the ratio of water to cement, the curing period and the amount of sulfate in the system (Ogard *et al.*, 1988). Although it is often assumed to be non-retarded in safety calculations, chloride can react with unhydrated aluminate phases to form new compounds, most commonly Friedel's Salt (Birnin-Yauri and Glasser, 1998). Friedel's Salt comprises part of the AFm (alumina-ferric oxide mono-) phase in cement when chloride ions are present within the pore solution. The AFm phase has a complex chemical and structural composition: $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6 \cdot m\text{H}_2\text{O}]^+ X^-$ (Suryavanshi *et al.*, 1996) where the excess positive charge is balanced by anions (denoted X^-), in the interlayer spaces. The hydroxide ions can be replaced with various anions, e.g. SO_4^{2-} , CO_3^{2-} or Cl^- .

The most important parameter affecting the chloride binding capacity of cement is bulk composition. The tricalcium aluminate (C_3A) content will determine the amount of the AFm phase produced, whereas silicate phases, such as C_3S and C_2S , determine the amount of calcium silicate hydrogel (C–S–H) formed upon hydration. The amount of sulfate in the anhydrous cement will determine the composition of the AFm phase, as well as the quantity of AFt (alumina–ferric oxide tri-) phase (Birnin-Yauri and Glasser, 1998).

Several studies have investigated the binding of chloride ions to the C–S–H phase (Beaudoin *et al.*, 1990; Yu and Kirkpatrick, 2001); they identify four states of chloride: 'free', surface adsorbed ('chemisorbed'), interlayer and lattice-bound. The amount of chloride chemisorbed appears to be dependent on the H/S and C/S ratios as well as on the surface area. It has been proposed that most of the chloride ions are chemisorbed on the hydrated C_3S phase. It is also suggested that chemisorbed and interlayer species may be removed by leaching, whereas lattice-substituted chlorides cannot (Beaudoin *et al.*, 1990). Research by Yu and Kirkpatrick (2001) using ^{35}Cl NMR relaxation methods on cement hydrate suspensions indicated that the majority of the chloride adsorbed on the surface of matrix phases, such as calcium hydroxide and jennite ($\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$), are in a solid-solution environment in rapid exchange with free chloride ions in the pore solution. It was shown that jennite has a limited number of binding sites; however, the number of bound chloride ions exceeds this. This excess is thought to be due primarily to the formation of alkaline metal chloride complexes or ion pairs such as calcium chloride (Yu and Kirkpatrick, 2001).

In an ionic solution, such as cement pore water, the transport of ions is restricted by electrostatic fields due to other ions present in solution. Cement is neither inert nor a medium fully open to water; it also evolves with time as gel phases develop crystallinity. As noted previously, chloride may be taken up by cement to form Friedel's Salt. The formation of Friedel's Salt and the adsorption of alkali ions by the C–S–H phase to maintain charge neutrality reduces effective concentration gradients within the pore solution, hindering diffusion. The influence of the electrical double layer and anion exclusion may counteract this effect and lead to chloride moving faster on average than tritiated water (Ogard *et al.*, 1988). Models of simple Fickian diffusion therefore need to be applied with caution.

Some waste packages will include a significant amount of cellulose-containing material, including paper and fabrics, which will degrade at high pH. Cellulose degradation products (CDP) are a complex mixture of water-soluble polyhydroxylic ligands and may affect both the solubility and the sorption behaviour of radionuclides by forming stable complexes with transition metals, the lanthanides and the actinide series (Glaus *et al.*, 1999). Even where significant complexation does not occur, CDP have been shown to modify radionuclide migration by impacting cement matrices (Felipe-Sotelo *et al.*, 2014).

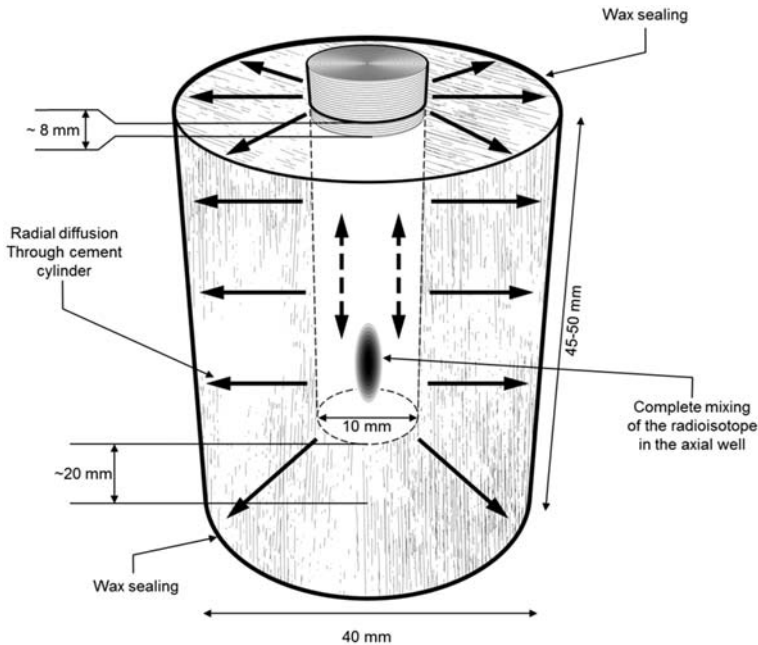


FIG. 1. Schematic of the radial diffusion experiments.

The aim of the present work is to assess the retention of chloride in a cementitious admixture, namely NRVB, which is a candidate backfill for a geological disposal facility (GDF). The effect of different salinity conditions are tested in addition to the effect of CDP mixtures present in ILW and LLW packages. The results obtained for chloride are compared to the diffusion of iodide under similar conditions.

Experimental

The experimental approach adopted is based on through-diffusion in a radial configuration (Markovaara-Koivisto *et al.*, 2008; Felipe-Sotelo *et al.*, 2014). NRVB is a high-porosity cement containing a specific ratio of OPC (450 kg m^{-3}), calcium hydroxide (495 kg m^{-3}), calcium carbonate (170 kg m^{-3}) and water (615 kg m^{-3}). The three solid phases were mixed at 6 r.p.m. for at least four hours on a bench top mixer in a polypropylene hexagonal barrel (Pascall Lab-mixer II, Pascall Engineering, Crawley, UK). Deionized water was then added to the cement powder and mixed by hand. The cement paste was added to polypropylene containers (50 cm^3) and tapped to remove any air

bubbles formed during mixing. The paste was allowed to set for a 24 hour period before being removed from the moulds and transferred into a water-filled, sealed container for 6–12 weeks to cure. Once cured, the cylinders of NRVB (diameter, 40 mm; height, 40–45 mm) were removed from the water and carefully drilled to create a well ($\sim 1 \text{ cm}^3$ volume). The cylinders were left to dry for 1 hour before adding the solutions and the top and bottom sealed with wax to ensure that only radial diffusion occurs (Fig. 1). The experiments were carried out with non-radioactive chloride (NaCl, Aldrich) carrier concentrations between 10^{-4} and $10^{-1} \text{ mol dm}^{-3}$ (after equilibration), containing $13 \text{ kBq } ^{36}\text{Cl}$ tracer (Amersham International). Known concentrations of chloride were added to the central well, which was then sealed and submerged in either NRVB-equilibrated water or a CDP solution. For experiments in the absence of organic ligands, the solution used for the tests was the water in which the cylinders had been cured; this minimizes changes in the NRVB matrix owing to leaching or precipitation (see Felipe-Sotelo *et al.* (2014) for a detailed description of the composition of the NRVB-equilibrated water and CDP solution used in the present work). The preparation of CDP followed a modification of the procedure reported by

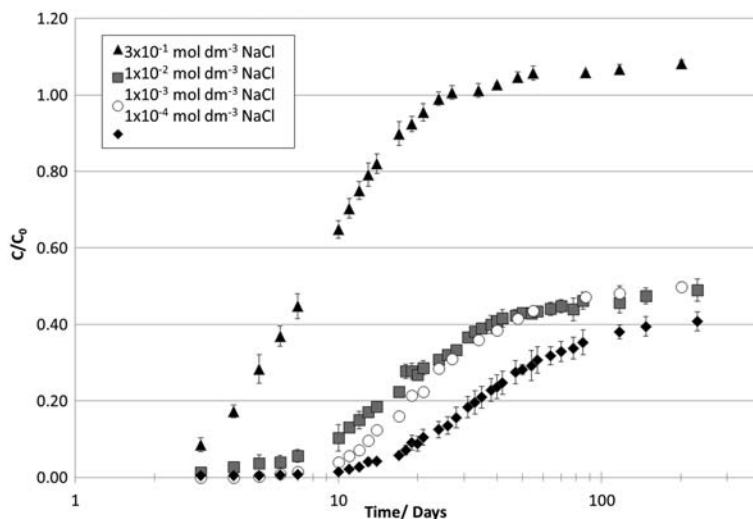


FIG. 2. Breakthrough curves for ^{36}Cl at various carrier levels ($\text{NaCl } 10^{-4} - 3 \times 10^{-1} \text{ mol dm}^{-3}$) in NRVB equilibrated water.

Chambers *et al.* (2004). The CDP solution was prepared by adding 750 cm^3 of deionized water to stainless steel cans and sparging with nitrogen gas for one hour. Then 15 g of Kimwipe® tissues were cut into 2 cm^2 pieces and added to the steel containers, followed by 285 g of powdered NRVB (5% dry w/w cellulosic load). Note that the expected cellulosic load for ILW and LLW in the UK has been estimated at around 0.7% and 2–2.5%, respectively (Defra and NDA, 2008; DECC and NDA, 2011). After mixing and sparging for a further 30 mins, the containers were sealed, weighed and placed in an oven at 80°C for 30 days. The CDP mixture was allowed to cool to room temperature and then filtered under gravity in a N_2 -atmosphere glove box before commencing the experiments with the cured NRVB cylinders. As previous work by Rizoulis *et al.* (2012) has shown no significant microbial activity at $\text{pH} \geq 12$, sterilization of the solutions and materials for the experiment was not deemed necessary. For the CDP diffusion experiments, the blocks were pre-equilibrated with CDP solution in individual containers for 4–6 weeks prior to injection of the chloride tracer and carrier. This ensured equilibration of the CDP throughout the NRVB. The equilibration time was determined in a separate experiment using total organic carbon (TOC) analysis (Felipe-Sotelo *et al.*, 2014).

For all experiments, the total volume of the system was 250 cm^3 , of which 200 cm^3 corresponded to the external solution and 50 cm^3 to the cylinder; the

latter equates to 25 cm^3 pore volume, based on a volumetric porosity of 0.5. To avoid carbonation of the solutions and cement specimens, all the experiments were carried out in a glove box under N_2 -atmosphere. The solution surrounding the NRVB cylinders was sampled periodically and ^{36}Cl activity measured by liquid scintillation counting using a Packard TR 2100 analyser. Upon completion of the experiments, one of the duplicate cylinders was sectioned longitudinally using a circular masonry saw and a series of digital autoradiographs produced. A Packard Cyclone Scanner and storage phosphor imaging plates ($\text{SR } 12.5 \times 25.2 \text{ cm}$) were used to produce the images. Six-hour exposure times were found to be adequate. The central cores were plugged with modelling clay to ensure that they were clearly demarcated on the images.

A thin section of post-experimental NRVB core was examined using a FEI QUANTA 600 environmental scanning electron microscope (ESEM), and phases identified from microchemical information obtained, using an Oxford Instruments INCA Energy 450 energy-dispersive X-ray microanalysis (EDXA) system to record X-ray spectra from specific phases and for mapping element distribution.

Results and discussion

The mean results and standard deviations of the duplicate experiments are shown in Figs 2–4, as

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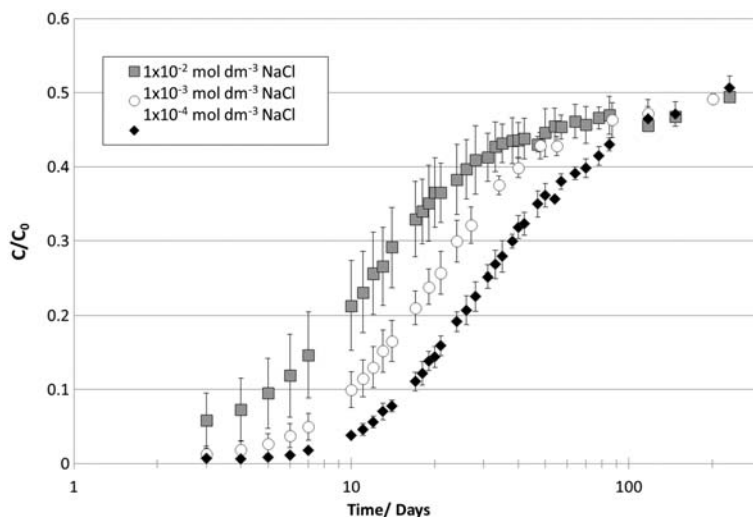


FIG. 3. Breakthrough curves for ^{36}Cl at various carrier levels ($\text{NaCl } 10^{-4}\text{--}10^{-2} \text{ mol dm}^{-3}$) in the presence of CDP.

the ratio of counts found in solution (C) over the maximum counts for input (C_0) against time. Given its half-life of 3×10^5 years, decay of ^{36}Cl was negligible over the duration of the experiments. The breakthrough curve for the diffusion of ^{36}Cl through NRVB cylinders shows a clear dependence on NaCl carrier concentrations (Fig. 2). Far from being a conservative tracer, the appearance of ^{36}Cl in the solution surrounding the cylinder is delayed significantly at low chloride levels and recovery (C/C_0) is only 40%. Faster breakthrough and

slightly higher recovery ($\sim 50\%$) is found at more typical fresh water concentrations in the range $10^{-3}\text{--}10^{-2} \text{ mol dm}^{-3}$ but, nevertheless, a substantial fraction of the isotope is retained by the cement (see Shand *et al.*, 2007, for comparison of the NaCl concentrations used in the diffusion experiments with the typical values of Cl and Na in groundwater in England and Wales). The curves appear to reach a steady state with a plateau at around 100 days, indicating that equilibrium between the NRVB cylinder and the surrounding solution had been

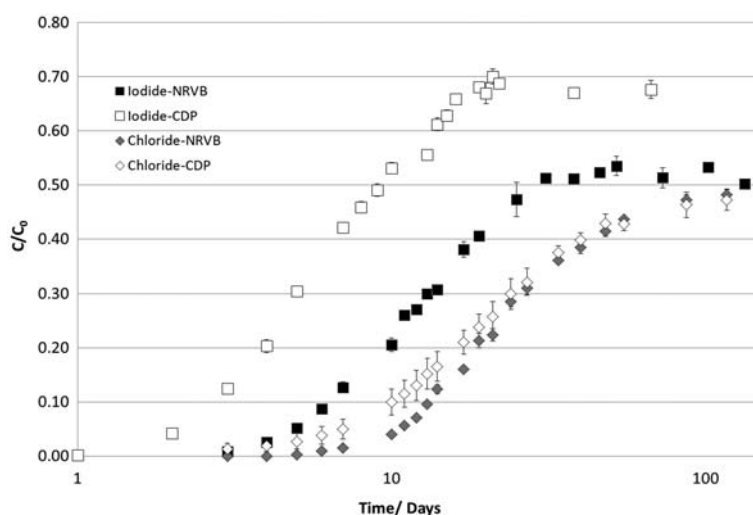


FIG. 4. Comparison of breakthrough curves for carrier-free ^{36}Cl and ^{125}I in NRVB equilibrated water.

reached. Similar elution profiles were observed by Abdel Rahman *et al.* (2007) when studying the leaching of ^{137}Cs , ^{60}Co and $^{152/154}\text{Eu}$ from cements.

Marked differences are observed at higher ionic strength (Fig. 2). At a carrier concentration corresponding to seawater ($3 \times 10^{-1} \text{ mol dm}^{-3}$), breakthrough is almost instantaneous with full recovery. The experiments show that the capacity for chloride retention within NRVB is finite and that salinity will have a large bearing on the potential effect of anion exchange (OH^- , etc.) or isotope exchange (stable $^{35/37}\text{Cl}$) in retarding the migration of ^{36}Cl through cementitious backfill. The effect of the carrier concentration on the diffusion profiles of ^{36}Cl could be explained by the work by Tang (1999*a,b*) who studied the theoretical and experimental concentration dependence of chloride diffusion in concrete; the author concluded that an increase in the effective diffusion coefficient for high- Cl^- concentrations can be described by a complex relationship between the activity coefficient, the counter-electrical potential, the ratio of cation velocity to anion velocity and a friction coefficient, which reflects the ionic interaction. In particular, in the case of NaCl , it is the effect of the counter-electric fields that has the greatest influence on the chloride diffusion (Tang, 1999*b*).

Breakthrough occurs more rapidly with CDP-containing solutions, particularly at lower chloride concentrations, and reaches a higher plateau (Fig. 3). This effect of CDP on the migration of anionic species through NRVB has also been reported previously (Felipe-Sotelo *et al.*, 2014). The proportion of chloride retained on the NRVB cylinders converges at around 50% (C/C_0); this may reflect organic ligands occupying sites on the cement which were previously available for chloride binding. However, Pointeau *et al.* (2008) observed a reduction of Cl^- sorption to cement pastes as a result of the decalcification of the C–S–H phases. The same authors also suggested that isosaccharinic acid (ISA, the main component of the CDP mixture) may form complexes with Ca^{2+} . There is some evidence that ^{36}Cl concentrations in the receiving solution are still increasing, albeit slowly, after 250 days. The presence of CDP also appears to suppress differences in carrier concentration, at least within the range 10^{-4} – $10^{-2} \text{ mol dm}^{-3}$. The effect of the CDP on the migration of Cl^- clearly requires further investigation. Many researchers are opting for a “multi-species” approach (Nielsen *et al.*, 2005; Song *et al.*, 2014) in order to understand electrical interactions

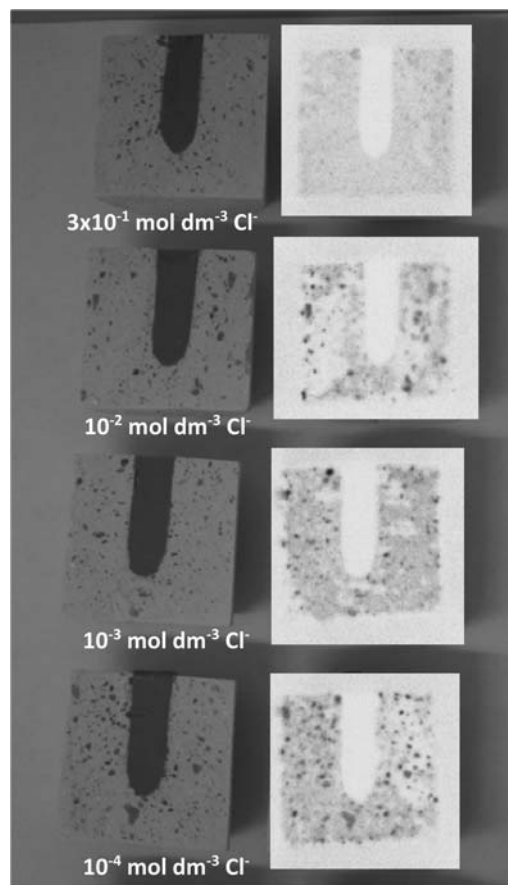


FIG. 5. Photographs and autoradiographs of longitudinally sectioned NRVB cylinders without CDP.

between diffusing ions and to predict the retardation of Cl^- by cementitious materials. Not only the concentration of Cl^- but also the nature of the counter ions (i.e. Na^+ or Ca^{2+}) and decalcification of the cement hydrate, together with alkali binding and leaching (Song *et al.*, 2014), appear to play a role in Cl^- interaction with cement. Consequently the changes to any of these factors caused by the presence of CDP may explain the increased chloride diffusion.

For comparison purposes, the results of an equivalent diffusion experiment are presented in Fig. 4, in which ^{125}I tracer at similar activity (12 kBq) and carrier concentration ($10^{-3} \text{ mol dm}^{-3}$ KI) was used in place of ^{36}Cl . The decay-corrected data show significantly faster breakthrough of ^{125}I and lower retention by the cement, implying less

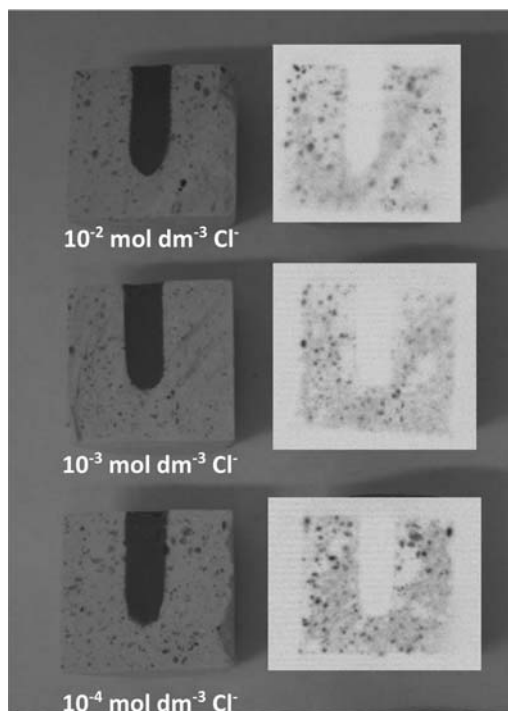


FIG. 6. Photographs and autoradiographs of longitudinally sectioned NRVB cylinders from the experiments with CDP.

efficient exchange of iodide with cement mineral phases. Nevertheless, iodide is retarded and does not behave as a conservative tracer. It should also be

noted that the effect of CDP at the same carrier concentration ($10^{-3} \text{ mol dm}^{-3} \text{ KI}$ vs. $10^{-3} \text{ mol dm}^{-3} \text{ NaCl}$) had a more noticeable effect on the diffusion of I^- than Cl^- ; size exclusion effects might explain the difference between the two anionic species as well as the variation observed in the presence of CDP, since the interaction of CDP with the cement matrix may hinder access of the larger anions to the binding sites. Further studies would be required to confirm this hypothesis. The results obtained here for the diffusion of I^- and Cl^- through NRVB do not tally with the findings of Pointeau *et al.* (2008), who observed a higher partition coefficient (R_d) for I^- than Cl^- , when studying the sorption of these anions to hydrated cement pastes under batch conditions at different stages of degradation from pH 13.2 to 12 ($R_d(\text{I}^-) = (3-4) \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ vs. $R_d(\text{Cl}^-) = (4-5) \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ at pH 12.8 in the absence of organic compounds). The differences between the two studies could be due to the fact that Pointeau *et al.* (2008) used ground material for their work, whereas intact NRVB cores were used here.

Digital autoradiographs are shown in Figs 5 and 6 along with photographs of the sectioned cylinders for the experiments in the absence and presence of CDP, respectively. It is clear that retention of the ^{36}Cl is limited at seawater concentration and similar at all of the lower concentrations used. It is not possible to differentiate between the CDP (Fig. 5) and non-CDP (Fig. 6) autoradiographs; however, the most striking feature is the increased activity associated with black particles in the NRVB matrix.

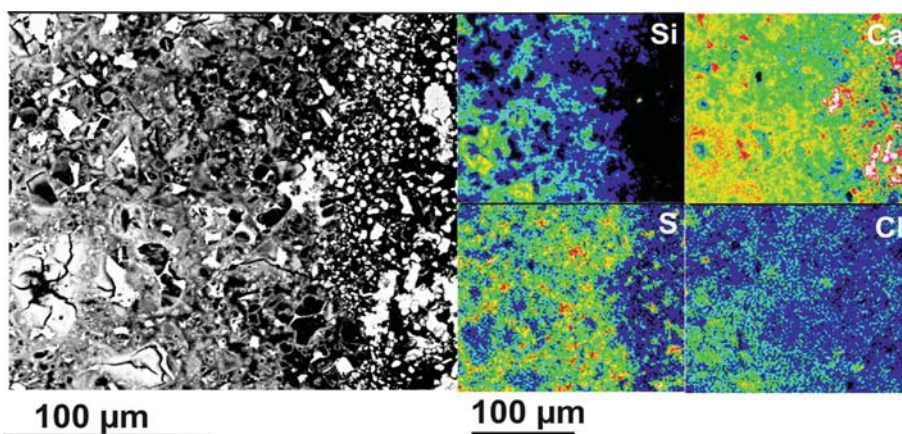


FIG. 7. Backscattered scanning electron microscope image of a partially hydrated calcium-silicate-sulfate cement clinker particle (left) with corresponding EDXA element distribution maps for Si, Ca, S and Cl. Higher concentrations of Cl are associated with the margins of this particle.

SEM-EDXA observations show that the black particles associated with uptake of ^{36}Cl comprise partially-hydrated glassy-clinker material, dominated by Ca, Si and S, although the particles are not homogeneous. Elemental mapping indicates that chlorine is broadly concentrated around the edges of these particles (Fig. 7). However, more detailed petrographic analysis shows that this is concentrated in the Si-rich areas of the particles, which are correspondingly low in sulfur.

Conclusions

Radial diffusion experiments using cylinders of a cementitious backfill material (NRVB) have been used successfully to assess the effect of chloride concentration and cellulose degradation products on the migration of ^{36}Cl . Breakthrough is rapid and increases with chloride carrier concentration. Cellulose degradation products promote migration, decreasing the time to breakthrough and retention on the cement. The CDP reduced retention of Cl^- by the cement matrix, though differences in diffusion rates owing to CDP are suppressed in more saline solutions. The decrease in uptake may be attributed to the CDP containing polyhydroxylic ligands occupying potential sites for chloride binding.

Notwithstanding the above, NRVB does have some capacity to retard ^{36}Cl , except in brines approaching seawater salinity. The mechanism is still not fully understood; anion exchange, isotope exchange and new phase formation may all play a part; one candidate phase, Friedel's Salt, has been synthesized in pure form for further investigations. However, the autoradiographs and elemental mapping also suggest that binding to partially-hydrated glassy, sulfate-bearing calcium silicate-clinker particles in the matrix is an important retardation mechanism where these particles are present. The greater mobility of iodide in comparison to chloride through the same matrix is probably a reflection of the lower compatibility of the larger ion for these sites.

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