

The effect of cement superplasticisers on the solubility and sorption of radionuclides

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ABSTRACT

The influence of various concentrations of the commercial cement superplasticiser ADVA Cast 551 (a polycarboxylated poly ether comb type superplasticiser) on the solubility of Ni(II) and Eu(III) are reported. Experiments were carried out under nitrogen in 95% saturated Ca(OH)₂, 0.1 mol dm⁻³ NaOH and cement equilibrated solutions containing Ordinary Portland Cement (OPC), Blast Furnace Slag (BFS) and Pulverised Fly Ash (PFA). These solutions represent the high pH conditions of the near field of an intermediate level radioactive waste repository. ADVA Cast 551 was present at between 0-10% (w.v) and solubility measurements were approached from oversaturation.

The extent of sorption of ADVA Cast 551 to the individual cement components of OPC, BFS and PFA plus mixtures of two different crushed grouts: BFS:OPC and PFA:OPC prepared without superplasticiser was investigated.

Results showed that Ni(II) and Eu(III) solubilities increased in the presence of ADVA Cast 551 however the extent of the increase was dependent on the aqueous solution the experiment was conducted in. In some cases the increase was 3 orders of magnitude however when using NaOH, within errors, no increase in solubilities were observed.

Sorption of ADVA Cast 551 was greatest to OPC powder followed by PFA:OPC grout and BFS:OPC grout respectively. No sorption was observed to the BFS or PFA powders alone.

INTRODUCTION

One of the disposal concepts considered by the Nuclear Decommissioning Authority – Radioactive Waste Management Directorate (NDA- RWMD) for the disposal of intermediate-level wastes and some low-level wastes is that of grouted waste packages surrounded by a cementitious backfill. Superplasticisers have the potential to impart benefits to fresh cement pastes such as enhanced flow properties and self- leveling. However their impact on the post closure performance assessment of a geological disposal facility (GDF) needs to be considered.

The addition of organic compounds into a radioactive waste matrix is, in general, discouraged since metal complexation with organics has shown to increase the solubility of the metal [1, 2]. Superplasticisers are potentially complexing agents and the impacts of their addition must be fundamentally understood before implementation to allow accurate predictions of their behavior

under the conditions of the near field of a radioactive waste disposal facility.

First generation superplasticisers such as naphthalene formaldehyde and sodium lignosulphonate showed the ability to increase the aqueous concentrations of radionuclides [3]. The observed effects were not consistent and the use of such additives was, in general, discouraged. The composition of modern superplasticisers ('comb' type polymers) however, is better controlled than the composition of compounds used in the past. This suggests that their effects may be better understood and they may behave in a more predictable manner.

The present study will focus on the solubility of Ni(II) and Eu(III) in high pH aqueous solution. This will represent the high pH conditions within and surrounding a geological disposal facility. The expected pH of this system is between 12 and 13.5 and this is due to the influx of groundwater through

the facility over time. With the groundwater flow, the cement dissolves producing a groundwater of high pH.

The superplasticising mechanism of ADVA Cast 551 is that the molecule binds to the cement particles and steric hindrance between the grafted side chains on the polymer causes the particles to disperse. There is evidence that superplasticiser may leach from cement paste over time by dissolution of cement and degradation of hardened paste [4]. This will make the superplasticiser available in solution and its movement will be controlled by ground water flow. If the superplasticiser in solution comes into contact with a metal also in solution a superplasticiser-metal complex may form. If this complex is then sorbed to a cement surface the metal is then 'removed' from solution and rendered immobile so long as the sorption is irreversible.

The sorption study will investigate the extent of ADVA Cast 551 sorption to each cement component of interest. This will enable predictions of the likelihood of the polymer sorbing to the cementitious backfill of the radioactive waste repository, should it become available in solution through leaching.

EXPERIMENTAL

Solubility of Ni(II) and Eu(III)

The solubility of Ni(II) and Eu(III) was investigated in high pH and anoxic conditions representative of the conditions of the GDF. The experiments were conducted in a N₂ atmosphere glove box and all solutions were prepared using boiled and N₂ sparged deionised water to avoid the presence of carbonate. Solubility experiments were approached from oversaturation and conducted in seven high pH aqueous solutions: 95% saturated Ca(OH)₂, 0.1 mol dm⁻³ NaOH and cement equilibrated solutions containing OPC, PFA and BFS. Two further solutions were produced containing PFA:OPC at a ratio of 3:1 and BFS:OPC at a ratio of 9:1, these being the cement ratios used widely in the construction industry to produce cement paste [5]. To prepare the cement equilibrated solution, the relevant cement powders were contacted with deionised water for 28 days and then filtered for use.

A range of ADVA Cast 551 concentrations were prepared in each solution at 0, 0.1, 1 and 10% (w/v). These concentrations represent the manufacturers recommendations for use (0.3 to 0.8%) and then a worst case scenario of a high concentration of ADVA becoming available in solution.

20cm³ of test solution were placed in a sample vial, quadruplicate samples were prepared for each concentration in each solution. An excess of the

metal on interest was added so that a precipitate formed. In the case of Eu(III), a radioactive spike of ¹⁵²Eu was added to the metal solution so that Eu(III) could be measured radiometrically. The samples were allowed to equilibrate with agitation for 28 days. At 7 day intervals, 2cm³ were removed, filtered through 0.45µm syringe filters and then analysed for the metal of interest. Ni(II) was measured by ICP-OES and Eu(III) was measured by gamma spectroscopy.

Sorption of ADVA Cast 551 to cement materials

The extent of sorption of ADVA Cast 551 superplasticiser to the cement components: OPC, BFS and PFA was investigated. The sorption of ADVA Cast 551 to two crushed grouts of PFA:OPC and BFS:OPC hardened paste (<180µm fraction) was also investigated. 0.5g of solid (either powder or crushed grout) were placed in a glass sample vial and 10cm³ of an ADVA Cast solution prepared in the relevant cement equilibrated water was added (0.2%, 0.5% and 1% (w/v)). The samples were prepared in triplicate and allowed to equilibrate with agitation for 28 days in total. The extent of sorption was calculated by measuring the TOC (Total Organic Carbon) for blank samples with no solid and TOC of samples containing solid. The difference between the two represents the amount of ADVA Cast 551 sorbed to the solid.

RESULTS AND DISCUSSION

Solubility of Ni(II) and Eu(III)

The SEFs for the Ni(II) samples are shown in Table 1.

Table 1 Solubility Enhancement Factors of Ni(II) in the presence of ADVA Cast 551

Solution	0% (mol dm ⁻³)	10% (mol dm ⁻³)	SEF
Ca(OH) ₂	8.7 x 10 ⁻⁵	1.5 x 10 ⁻⁴	2
NaOH	9.6 x 10 ⁻⁶	1.2 x 10 ⁻⁵	1
BFS:OPC	9.5 x 10 ⁻⁵	7.1 x 10 ⁻⁴	8
PFA:OPC	9.0 x 10 ⁻⁵	6.1 x 10 ⁻⁴	7
OPC	9.5 x 10 ⁻⁵	1.5 x 10 ⁻³	16
BFS	7.3 x 10 ⁻⁵	1.5 x 10 ⁻³	20
PFA	5.7 x 10 ⁻⁵	1.5 x 10 ⁻⁴	3

In the case of Ni(III) in the NaOH solution, within errors, there were no changes in the solubility of nickel after the addition of ADVA Cast 551. The solubility of Ni(II) in the presence of ADVA Cast 551 was most significantly increased in OPC water and BFS water. In both cases the increase was of the order of 2 orders of magnitude. The least significant increase in solubility was observed in NaOH. To make comparisons of the results observed in each solution, the Solubility Enhancement Factor (SEF) was calculated. The concentration of metal in solution in the presence

of 10% ADVA Cast 551 was divided by the concentration of metal in solution with no ADVA Cast 551 added (baseline solubility).

The SEFs for the Eu(III) samples are shown in Table 2.

Table 2 Solubility Enhancement Factors of Eu(III) in the presence of ADVA Cast 551

Solution	0% (mol dm ⁻³)	10% (mol dm ⁻³)	SEF
Ca(OH) ₂	2.7 x 10 ⁻¹¹	2.9 x 10 ⁻¹⁰	11
NaOH	2.3 x 10 ⁻¹⁰	2.8 x 10 ⁻¹⁰	1
BFS:OPC	1.9 x 10 ⁻¹²	2.5 x 10 ⁻¹⁰	131
PFA:OPC	1.2 x 10 ⁻¹¹	3.0 x 10 ⁻¹⁰	25
OPC	2.6 x 10 ⁻¹²	2.2 x 10 ⁻¹⁰	88
BFS	2.9 x 10 ⁻¹²	2.9 x 10 ⁻¹⁰	100
PFA	1.8 x 10 ⁻¹²	3.8 x 10 ⁻¹⁰	211

In the absence of ADVA Cast 551, Eu(III) has a much lower solubility than Ni(II). In the test solution of NaOH, there was little notable increase in the Eu(III) solubility and the metal concentration was constant (within errors) for the duration of the experiment and at each concentration of ADVA Cast 551. It may be said therefore that in NaOH, the ADVA Cast 551 has little or no effect on Eu(III) solubility.

The greatest solubility enhancement was observed in the PFA water samples. The BFS:OPC, OPC and BFS water samples have similar SEF values. In the case of Eu(III) it is clear that with a more complex matrix, there is an effect on the solubility of the metal of interest.

The solubility in each solution of Eu(III) does not appear to increase above approximately 3x10⁻¹⁰ mol dm⁻³, whereas for Ni(II) the solubility increases to 1.5x10⁻³ mol dm⁻³. This shows therefore that although the SEF values are higher for Eu(III), the real concentration of metal Eu(III) in solution is many orders of magnitude less than Ni(II).

Sorption of ADVA Cast 551 to Cement Materials

The results for the sorption study are shown in Figure 1. In the case of the PFA:OPC grout, BFS:OPC grout and the OPC powder significant sorption was observed. For the PFA and BFS powders, at each concentration of ADVA Cast 551 there was no measurable sorption within errors observed.

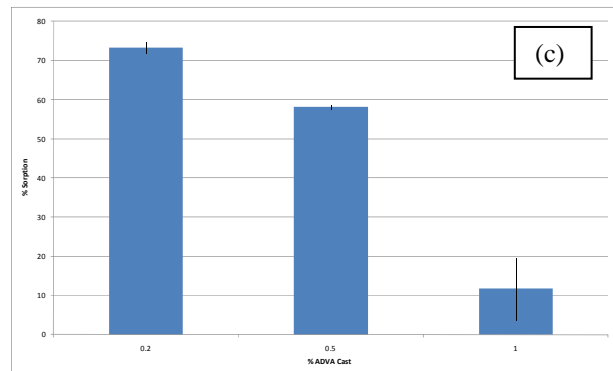
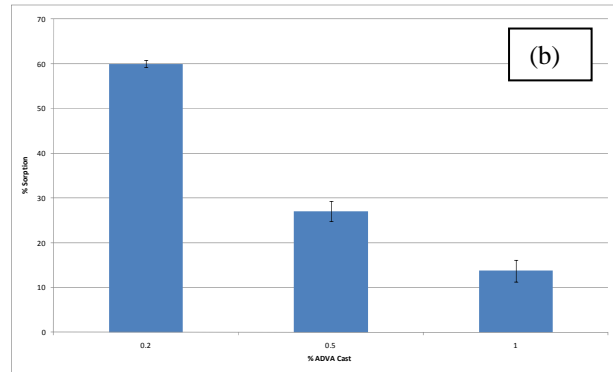
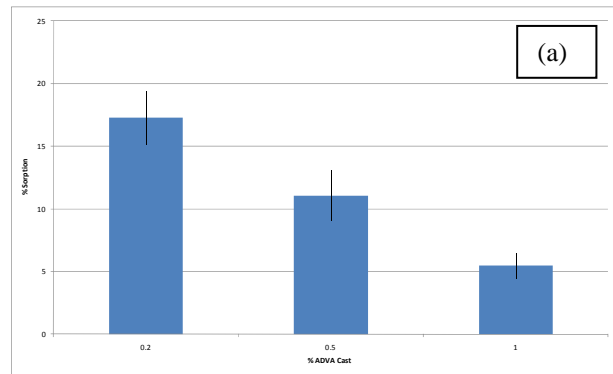


Figure 1 Percentage Sorption of ADVA Cast 551 to (a) BFS:OPC grout, (b) PFA:OPC grout and (c) OPC powder

The results show that OPC is the major ADVA Cast 551 sorbing component in the cement matrix. This is because the highest % sorption was observed with OPC powder alone, followed by PFA:OPC grout which is prepared with a PFA to OPC ratio of 3:1 and then finally BFS:OPC which is prepared at a ratio of 9:1. There is therefore a larger amount of OPC in the PFA grout proportionally.

Sorption is highest at the lowest concentration of ADVA Cast 551. This is likely to be because of the nature of the interactions between the side chains of the polymer. Steric hindrance between these chains will mean that once one mono-layer of polymer has sorbed to the surface, it is not favourable for another layer to sorb on top of that.

CONCLUSION

There is a significant increase in the solubilities of Ni(II) and Eu(III) in the presence of ADVA Cast 551. This increase however is dependent on the test solution investigated. The pH and temperature of all samples was the same for each solution and also constant throughout the experiments. The observed differences in the solubilities of the metals in different solutions is because of differences in the composition of the solutions.

The sorption of ADVA Cast 551 is highest to OPC powder and when OPC is absent i.e. in the PFA and BFS powder samples, sorption was not observed at all. The percentage of sorption is greatest when there is a lower amount of ADVA Cast 551 in solution. This is likely to be due to the steric hindrance affects from the side chains of the ADVA Cast 551 polymer.

Together, the solubility results and the sorption results are promising since they suggest that if the ADVA Cast 551 enters into solution and binds to a metal there is a high probability that it will sorb again to cement materials it comes into contact with and therefore remove the metal from solution

FUTURE WORK

The solubility study should be extended further to include Th(IV) to ensure a wide range of metal cation solubilities are investigated in the presence of ADVA Cast 551.

Degradation of ADVA Cast 551 is ongoing by thermal, chemical and radiolytic degradation. The solubility of the metal cations in the presence of the degradation products of the polymer should be conducted to compare to the fresh ADVA Cast 551 results.

Investigations into the complexation of the metal to the superplasticiser should be conducted in order to try to understand the binding mechanisms in solution. This may be done by measuring the stability constants of the metals to the ADVA Cast 551 polymer. It is important to understand the binding mechanism in order to be able to predict the fate of the metal in solution should it bind to ADVA Cast 551.

The results for the sorption study would be enhanced by understanding the reversibility of the sorption of the ADVA Cast 551 and also whether if a metal was bound to the ADVA Cast, the polymer would the polymer sorb to cement materials in the same way.

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