Decontamination of Cementitious Waste Using Deep Eutectic Solvents

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1. Introduction

As of December 31st 2017 there are 139 nuclear reactors undergoing decommissioning globally [1]. This decommissioning process results in the production of large amounts of waste that has been contaminated with radioactive material. Directly disposing of this waste in the same manner as other industrial waste poses hazards to the environment and public, therefore it must be managed and disposed of in a safe and secure way. Removal of radionuclides during the decommissioning process is a way of managing these wastes. Not only does this remove the hazardous radioactive material, it can also concentrate it, whereby reducing the volume of and reducing disposal costs. This is an important factor to consider, as disposing of radioactive waste is expensive. For example, there is an estimated £250 billion set to be spent on global decommissioning projects, and it costs £9360 m⁻³ for radioactive waste disposal in the UK [2], [3].

The two major material wastes from nuclear sites are concrete and steel. Concrete makes up the majority of this, accounting for just over 70% by volume [4]. Concrete has been used so widely not only for its structural properties, but for its radiation shielding properties as well. Using concrete as radiation shielding causes it to become radioactive through the process of neutron capture. Trace contaminant elements in the raw materials used to make the cement such as Eu, Co, Ba, Cs, Mn and Zn are responsible for this, these form ¹⁵²Eu, ¹⁵⁴Eu, ⁶⁰Co, ¹³³Ba, ⁵⁴Mn and ⁶⁵Zn, respectively [5]. As well as neutron activation, concrete can become contaminated with radionuclides through contact with other active materials, causing surface contamination. As there are many reactors in the world scheduled for shut down and decommissioning, the volume of waste produced is going to increase [4]. This will require effective, safe and sustainable decommissioning technologies to cope with managing this increase in hazardous radioactive waste.

There are many potential technologies for decommissioning cementitious waste from nuclear sites. Generally, scarification is used initially to remove the surface layer of the concrete, as this is most likely to be where the majority of the contamination resides [6]. Ideally this results in a smaller volume of waste which can either be disposed of as radioactive waste, or further treated, while the bulk can be disposed of as nonradioactive waste or recycled. Chemical techniques can also be used for the decontamination process, proposed technologies include bio-decontamination via the action of bacteria and fungi, supercritical CO_2 , chemical gels, polymeric superadsorbents, leaching with acids and treating the resultant effluent with molecular extractants, and electrochemical methods [4], [7]–[10].

Though these methods can be effective, they all produce secondary wastes, some use hazardous chemicals (conc. acid), and often use expensive and/or novel chemicals which will impact upon the viability of using these in large scale industrial processes. An ideal decontamination technology would produce little to no secondary waste, be capable of large waste volume reductions, be biologically and environmentally nonhazardous, be cheap and use common bulk chemicals, and ideally selectively remove target elements.

A family of chemicals, which have never been tested in nuclear waste decontamination are deep eutectic solvents (DES). These are a new class of ionic liquid analogues, composed of a salt (generally a quaternary ammonium salt; QAS) and a hydrogen bond donor (HBD; alcohol, amide or carboxylic acid) [11]. When mixed together at set ratios they form a eutectic mixture with a lower freezing point than the two individual components. They have many of the favorable properties of ionic liquids, such as low vapour pressure, high conductivity, wide liquid range, and are non-flammable [11], [12]. However, they are composed of cheap, bulk chemicals, unlike traditional ionic liquids. For example, one of the most well studied DES is a mixture of choline chloride and urea, both produced globally on a massive scale (Fig. 1) [12]. It is possible that they are able to fulfil the requirements of a decontamination technology detailed in the previous paragraph, however, not enough is known about their behavior yet to make such a conclusion.



Figure 1. Chemical structures of choline chloride and urea.

It is known that DES are able to dissolve metal oxides, with a wide range of oxides having been studied [13], [14]. However, they have never been applied to concrete decontamination. In this work, initial studies have focused on determining the ability of a set of DES (Fig. 2) to dissolve metal oxides, producing solubility



Figure 2. Chemical structures of selected hydrogen bond donors in the studied DES (1 = ethylene glycol, 2 = oxalic acid, 3 = urea, 4 = glycerol, 5 = malonic acid, 6 = n-methylurea).

values. Following this, decontamination experiments are being performed on simulant cementitious waste samples. It is hoped that this work will act as a proof of concept for the use of DES in decontamination technologies that can be built on to produce effective decommissioning flowsheets.

2. Methods

2.1 Equipment and Reagents

NiO, CoO, CeO₂, Eu₂O₃ and Dy₂O₃ were all purchased from Sigma-Aldrich (all 99.9% or above), Nd₂O₃ was purchased from Alfa-Aesar (99.997%). Choline chloride (99%) was purchased from Acros Organics, ethylene glycol (99.8%), oxalic acid (99%+), urea (99.5%), n-methylurea (97%) and glycerol (99.5%) were purchased from Sigma-Aldrich and malonic acid (99.5%) was purchased from Alfa Aesar. Nitric acid (conc. 70%, ≥99.999% purity trace metals basis) was purchased from Sigma Aldrich. Cement samples doped with CoCl₂ and EuCl₃ (300 ppm) were kindly provided by the Korea Atomic Energy Research Institute (KAERI). All work (apart from ICP-OES sample preparation) was carried out in a glovebox with an Ar atmosphere, H₂O and O₂ concentrations were maintained below 2ppm at all times. Chemicals were dried overnight in a vacuum oven at a minimum of 80°C before being transferred to the glovebox. Metal analysis was carried out by ICP-OES using an Agilent ICP-OES 5110.

2.2 DES Production

DES were produced by mixing choline chloride and a hydrogen bond donor at the appropriate molar ratio (Table 1) on a heating mantle at 50°C overnight, whereupon a clear liquid was produced. The DES were stored in glass bottles until they were required for experiments.

2.3 Metal Oxide Dissolution Studies

A known amount of metal oxide (ca. 0.1 g) was added to a glass vial, followed by DES (ca. 4 g). Vials were left heating for at least 2 weeks at 50°C using a

Table 1. Ratio of choline chloride (QAS) to selected hydrogen bond donors (HBD) used in this work.

HBD	QAS : HBD
Ethylene glycol	1:2
Glycerol	1:2
Oxalic acid	1:2
Malonic acid	1:2
Urea	1:1
N-methylurea	1:1

Daihan MaXtable HM dry heating block. Samples were not removed for analysis if there was a visible concentration gradient up the vial (done by eye, only possible for NiO and CoO experiments). Samples were then removed from the heating block and 3 samples of loaded DES (*ca.* 0.5 g) were taken from each. These samples were removed from the glovebox, dissolved in 10 mL of deionized water (> 18 M Ω) and filtered using a Whatman 0.45 µm filter. Aliquots of solution from these samples were then diluted with HNO₃ (10%) to make ICP-OES samples for analysis.

2.4 Concrete Decontamination Studies

The same general procedure was followed as in section 2.1.2. However, *ca*. 0.5 g of concrete was added to each vial with DES and the experimental duration was 1 week.

3. Results and Discussion

3.1 Metal Oxide Dissolution Studies

Table 2 shows the determined solubility values for the studied metal oxide/DES systems. Current results show that the metal oxides are more soluble in the malonic acid than the ethylene glycol or glycerol DES. This is likely due to the presence of an

acidic proton on the malonic acid moiety participating in a standard acid base reaction. If this is the case it has implications for process design, as it means the solvent will degrade.

Table 2. Solubilities of metal oxides in DES. Errors are reported as one standard deviation.

Solubility / mg kg ⁻¹			
	ChCl - MA	ChCl - EG	ChCl - G
NiO	814 ± 25.7	2.35 ± 0.305	< 1
CoO	23600 ± 1550	150 ± 8.76	59.9 ± 3.92
CeO ₂	15.1 ± 0.787	1.16 ± 0.092	< 1
Nd ₂ O ₃	1530 ± 355	101 ± 5.97	43.9 ± 9.15
Eu ₂ O ₃	-	84.0 ± 5.68	$38.6\ \pm 4.36$
Dy ₂ O ₃	4760 ± 119	26.6 ± 7.79	-

Changing the HBD from glycerol to ethylene glycol increases the ability of the DES to dissolve metal oxides. The reasons for this are unknown, but may be due to solvent polarity and/or its ability to form stable soluble complexes with the dissolved metal cations. There have been attempts to measure DES polarity, but quantification and the production of a "polarity series" has proved challenging [15]. Ethylene glycol has been reported to bind to Ni²⁺ in a bidentate motif in a choline chloride DES using EXAFS spectroscopy. This complexation may help promote solubility, though more experiments are needed to confirm this.

In all studied DES CoO is much more soluble than NiO (2 orders of magnitude). This is behavior that has been reported previously in a choline chloride malonic acid DES [13]. It is unclear as to why this is the case currently. Differences in ionicity of the metal oxide are unlikely to be important factors, so it may be due to the stability of the formed solution species. Co²⁺ readily forms complexes in aqueous solutions containing Cl-([CoCl₂], [CoCl₃]⁻, [CoCl₄]²⁻), whereas Ni²⁺ prefers to form hydrated species [16]. This enhanced ability of Co^{2+} to form stable chloride complexes may explain the difference in solubility. Deducing this will require further work utilizing techniques such as UV/Vis spectroscopy and EXAFS. Additionally, the solubility values for both CoO and NiO determined in this work are much higher than in the work by Abbot et.al. [13]. It is likely that this is due to differences in methodology. Their work only performed the dissolution experiment for 2 days, whereas here we tested for two weeks. This means that they may not have reached metal saturation in their experiment.

CeO₂ is the least soluble lanthanide oxide studied. In acidic solutions CeO₂ is dissolved via a reduction mechanism, forming Ce³⁺ [17]. This may explain its higher solubility in the malonic acid than the alcoholic DES. As the other Ln oxides do not have to undergo this process they are more soluble. The other Ln oxides show the same behavior as the transition metals, a higher solubility in the malonic acid DES. This enhanced solubility may be due both to the action of acidic dissolution and the ability of the malonic acid molecule to bind to dissolved metal species, stabilizing them in solution.

3.2 Concrete Decontamination Studies

Experiments are currently ongoing with results expected by the end of March. Once the results are collected we will be able to determine the most effective DES studied for concrete decontamination. This will take into account both the ability to solubilize contaminant radionuclides and how much of the concrete matrix is codissolved.

Following this, more focused studies targeting the selected DES will be performed. It will be important to collect data regarding solubility kinetics and the effect of temperature, as well as methods for recovering the dissolved radionuclides. Options for radionuclide recovery include burning the DES to leave the solid oxides behind, vacuum distillation of the DES, a solvent extraction method and electrochemical recovery. Once the most adequate method has been identified they will be combined to produce a proof of concept decontamination process.

4. Conclusions

The choline chloride - malonic acid DES is more effective at dissolving metal oxides than the ethylene glycol and glycerol versions. This agrees with published work and is thought to be due to their acidic nature, with the protons participating in acid – metal oxide neutralization reactions [13].

Large differences in solubility between NiO and CoO have been attributed to stabilization of the solution species. This needs to be confirmed by further work to determine the solution species. This theory may also explain the observed higher Solubilities of metal oxides in choline chloride – ethylene glycol than in choline chloride – glycerol.

Though using malonic acid as the HBD results in the highest Solubilities and therefore the most promising concrete decontamination factors, the likely dissolution mechanism causes irreversible solvent degradation. This has implications for the design of a decontamination process, as the solvent will need to be replaced. It may be more viable to use a different HBD, such as ethylene glycol and continuously recover the dissolved metal species.

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