**CHOLINE-CHLORIDE BASED DEEP EUTECTIC**

**SOLVENTS AS AN ALTERNATIVE**

**DECONTAMINATION AGENT FOR**

**RADIOACTIVE METAL WASTE**

NAYOUNG KIM

WONSEOK YANG

SUNGYEOL CHOI

KAIST

Daejeon, Republic of Korea

Email: [nayoung\_kim@kaist.ac.kr](mailto:nayoung_kim@kaist.ac.kr)

JAMES AMPHLETT

Seaborg

Copenhagen, Denmark

**Abstract**

Deep eutectic solvents (DES) are a mixture of a hydrogen bond acceptor (HBA), commonly quaternary ammonium salt, and a hydrogen bond donor (HBD), such as a carboxylic acid or alcohol. These solvents are readily synthesized from easily accessible materials. DES are characterized by their low cost, melting point, flammability, toxicity and wide electrochemical windows. Chemical and physical properties of DES can be tuned through judicious choice of HBA and HBD such as acidic HBD’s which readily dissolves metal oxides. This illustrates novel advantages over currently used or proposed decontamination agents such as ionic liquid, molten salts or strong acids. In this research, we tested the feasibility of DES synthesized from choline chloride (ChCl) and p-toluenesulfonic acid (PtsA) as a decontamination agent. ChCl:PtsA was selected owing to its high metal oxide solubilizing power. Metal oxides such as Fe3O4, CoO, Cr2O3, and NiO present in the contaminated layer of stainless steel 304 were studied and were shown to have good solubilities in ChCl:PtsA. The effect of adding water to the solvent on the metal oxide solubility was studied. The work proposes and proves the possibility of using ChCl:PtsA as a decontamination agent.

1. INTRODUCTION

Decontamination of structural materials from nuclear power plants is vital to reduce cost of disposal by reducing the waste volume and recycling. Stainless steel 304 (SS304) is of concern especially because it is widely used in pressurized water reactors (PWR) for primary piping and core structures [8]. The contaminant layer consists primarily of magnetite, Fe3O4, but the protective Cr2O3 layer and embedded corrosion products such as Co complicate the decontamination process [1-2].

Conventional decontamination methods focused on the treatment of the passive layer using strong acids, which pose concerns for secondary waste generation, toxicity and cost of processing [3-4]. Chemical or electrochemical processes utilizing strong acids yield high decontamination factor of 5~100 [5]. However, strong acids and their substitutes like ionic liquids or molten salts are concerned with their toxicity, high flammability, expensive costs and complex production processes. To overcome such limitations, deep eutectic solvents (DES) which have favorable characteristics and excellent metal oxide solubilizing power are considered as an alternative decontamination agent.

In this paper, viability of DES as a decontamination agent was assessed by investigating the solubilities of CoO, Cr2O3, Fe3O4 and NiO in the DES formed from choline chloride (ChCl) and p-toluenesulfonic acid monohydrate (PtsA). The metal oxide solubilities in ChCl:PtsA were compared to those in aqueous solutions of HCl [7] and PtsA and other common DES [7]. The effects of addition of water on the metal oxide solubilities were studied.

1. EXPERIMENTAL

ChCl:PtsA was synthesized from choline chloride (≥ 98%) and p-toluenesulfonic acid monohydrate (≥ 99.9%) purchased from Sigma Aldrich. ChCl was dried in the vacuum oven at 80 °C overnight before stored in the glovebox under argon atmosphere with [O2] ≥ 1 ppm and [H2O] ≤ 0.2 ppm. PtsA was used as received. ChCl and PtsA were mixed at a molar ratio of 2:1 out on the bench. ChCl was weighed out in the glovebox, and PtsA was weighed out on the bench. Their mixture was stirred until a clear transparent liquid was formed. To produce hydrated ChCl:PtsA, deionized water was added to the formed DES and stirred further. Every DES was synthesized freshly before each experiment to prevent any degradation.

Samples for solubility investigation were prepared by dissolving metal oxides in ChCl:PtsA. CoO (≥ 99.99%, trace metals basis), Cr2O3 (99.9%, trace metals basis), Fe3O4 (97%, trace metals basis) and NiO (99.99%, trace metals basis) were also purchased from Sigma Aldrich. Metal oxide powders were dried and stored similar to ChCl. Metal oxide was added to ChCl:PtsA and hydrated ChCl:PtsA and allowed to dissolve at 60 °C for 48 hours on the bench. Small increments of metal oxide powders were added to the solvent and stirred until no more dissolved and particles remained. The supersaturated solvents were then centrifuged using Labogene centrifuge at 13.5 rpm for 30 minutes. The liquid was extracted and ran through centrifugation again at 13.5 rpm for 30 minutes to remove further excess powders. The final saturated liquid was extracted and diluted in 10% HNO3 for Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS). ICP-OES was performed using Agilent ICP-OES 5110, and ICP-MS was done using iCAP RQ from Thermofisher Scientific.

1. RESULTS AND DISCUSSION

Solubility of CoO, Cr2O3, Fe3O4, and NiO in ChCl:PtsA and other solvents are shown in Fig 1. Aqueous solutions of hydrochloric acid ([HCl] = 3.14 M [7]) and p-toluene sulfonic acid ([PtsA] = 2.4 M) were used to compare. [PtsA] in the DES is also 2.4M. Filled bars represent the values obtained in this paper, and the empty bars are from literatures [6-7].

Solubility of each metal oxide in ChCl:PtsA was analyzed. CoO dissolved up to 32960 ppm ± 1846 ppm in ChCl:PtsA. Such high solubility value for CoO in ChCl:PtsA and hydrated ChCl:PtsA is significant in that 60Co is one of the main radioisotopes from nuclear power plants. Its effective removal from structural materials and the reduction of radioactivity of structural materials yield high decontamination factor and allow the reuse of materials. Cr2O3, which exists as the passive layer on the surface, dissolved readily in ChCl:PtsA which is expected to ease the decontamination process. The solubility of Cr2O3 in ChCl:PtsA was 4.844ppm ± 0.455 ppm. The protective layer of Cr2O3 is imperative to remove as it is commonly resistant and insoluble in acids. Fe3O4 dissolved up to 43180 ppm ± 605 ppm. Because the contaminant layer of SS304 is primarily Fe3O4, the dissolution of Fe3O4 is fundamental. Sufficient dissolution of Fe3O4 will allow other less soluble, embedded corrosion products to be removed from the stainless steel surfaces. NiO had the solubility of 2281 ppm ± 84 ppm in ChCl:PtsA. Although the percentage of NiO in the oxide layer is not the largest, it is a significant metal oxide that is produce from nuclear power plant and concerns diverse industrial processes.

For all metal oxides, the solubility was higher in ChCl:PtsA than in PtsA by few orders of magnitude and was, and for most metal oxides, ChCl:PtsA had comparable solubility to HCl. CoO dissolved 22 times more in ChCl:PtsA than in PtsA, and Cr2O3 dissolved 17 times more. Fe3O4 was twice more soluble in ChCl:PtsA than in PtsA and NiO was almost 400 times more soluble. Substantially high solubility of metal oxides in ChCl:PtsA compared to PtsA corroborates that the interaction between ChCl and PtsA is responsible for the dissolution of metal oxides. ChCl:PtsA had lower solubility than 3.14 M HCl for CoO, Cr2O3, and NiO, but this may due to the higher concentration of acid in 3.14 M HCl. Their solubilities may be analogous to each other for 2.4 M HCl.

|  |
| --- |
| (a) |
| (b) |
| (c) |
| (d) |

*FIG 1. Metal oxide solubilities of (a) CoO, (b) Cr2O3, (c) Fe3O4, and (d) NiO in 3.14M HCl [7], 2.4M PtsA, ChCl:EG [7], ChCl:MA [7], ChCl:PtsA and 10wt% hydrated ChCl:PtsA (Data were reported without error bars in the literature [6-7])*

For all metal oxides, ChCl:EG and ChCl:MA showed significantly low solubilities. ChCl:PtsA has few orders of magnitude higher solubilities. As hypothesized, acid-based DES, ChCl:MA and ChCl:PtsA, showed higher solubilities than alochol based DES, ChCl:EG. The exceptionally high metal oxide solubility of ChCl:PtsA may stem from the strong acidity of PtsA. While the pKa of MA is 2.85, that of PtsA is –2.8. The innate acidity of HBD is expected to result in a more acidic DES, which consequentially give high metal oxide solubility. The difference in solubilities is especially significant for Fe3O4.

Water was added to ChCl:PtsA to investigate its effects, and desirable trends were observed for most metal oxides, except for Cr2O3. For CoO and NiO, the solubility increased upon the addition of water. The solubility of Fe3O4 decreased with the addition of water, but the extent is insignificant. Therefore, for those three metal oxides, the addition of water did not ruin the principle mechanism by which ChCl:PtsA dissolves them. However, the solubility of Cr2O3 dropped significantly, by 89 times, with hydration. This may be due to the substantial amount of water in the solvent. 10 wt% hydration of ChCl:PtsA can be converted into 57 mol% of H2O in the solvent, which is considerably high. For industrial application, ChCl:PtsA with lower molar percentage may be sufficient, which then would not compromise Cr2O3 solubility significantly.

The compatibility of ChCl:PtsA as a decontamination agent is promising, but the decrease in Cr2O3 solubility with the addition of water needs to be contemplated. ChCl:PtsA showed sufficient solubilities for all metal oxides that were comparable to strong acids. Strong acids or other solvents with such high solubilities usually have concerns regarding toxicity or environmenal hazards. However, while DES has good solubilizing power, its threats to the surroundings are insignificant. While it is inevitable to mix water for realistic industrial application, Cr2O3 solubility is compromised. To apply hydrated ChCl:PtsA to the decontamination process, pre-treatment of stainless steel structures, such as oxidation of Cr3+ to Cr6+, may be required.

1. CONCLUSION

The solubilities of CoO, Cr2O3, Fe3O4, and NiO in ChCl:PtsA were obtained and compared to other solvents while the effect of addition of water was investigated to assess the viability of ChCl:PtsA as a decontamination agent. CoO, Cr2O3, Fe3O4, and NiO dissolved up to 32960 ppm ± 1846 ppm, 4.844 ppm ± 0.455 ppm, 43180 ppm ± 605 ppm, and 2281 ppm ± 84 ppm, respectively in ChCl:PtsA. The hydration of ChCl:PtsA had minimal or positive impacts on CoO, Fe3O4 and NiO, but significantly lowered Cr2O3 solubility. The obtained solubilities manifested that ChCl:PtsA is a promising decontamination agent, but the need for pre-treatment of contaminated samples needs to be considered to deal with Cr2O3.

This research will be developed by investigating the speciation of metals in ChCl:PtsA and simulating the decontamination process with oxidized SS304 specimens. Understanding the metal speciation in ChCl:PtsA will help analyzing the solubility data of different metal oxides. Oxidized stainless steel samples will be leached in the solvents, and the metal oxide behaviors will be monitored over time. The effectiveness or trends will be evaluated among different solvents in different experimental conditions. Leaching of specimens from real nuclear power plants will be followed.

1. AUTHOR AFFILIATIONS

NAYOUNG KIM

KAIST

Daejeon, Republic of Korea

Email: [nayoung\_kim@kaist.ac.kr](mailto:nayoung_kim@kaist.ac.kr)

JAMES AMPHLETT

Seaborg

Copenhagen, Denmark

Email: [j.amphlett@kaist.ac.kr](mailto:j.amphlett@kaist.ac.kr)

WONSEOK YANG

KAIST

Daejeon, Republic of Korea

Email: [abw94@kaist.ac.kr](mailto:abw94@kaist.ac.kr)

SUNGYEOL CHOI

KAIST

Daejeon, Republic of Korea

Email: [sungyeolchoi@kaist.ac.kr](mailto:sungyeolchoi@kaist.ac.kr)

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