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Deep Eutectic Solvents for Potential Selective Removal of Toxic Metals From Spent Uranium Catalysts

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1. Introduction

The use of uranium-based catalysts in acrylonitrile production has led to the accumulation of radioactive and toxic spent catalysts, presenting significant waste management challenges. These catalysts contain uranium (U), antimony (Sb), tellurium (Te), and iron (Fe) in mixed oxide forms ($USbFeO_x$) with low solubility in conventional acids and alkalis. By 2004 in South Korea, approximately 7,000 drums of spent uranium catalysts had accumulated, with disposal costs reaching 17 million KRW per drum[1]. Japan stored around 200 tons by 2011 without a clear disposal strategy[2].

The primary challenge is that these spent catalysts cannot meet the strict Waste Acceptance Criteria (WAC) of the Gyeongju disposal site, which imposes specific limits on free-standing water, radioactivity, particulate fines, and Sb oxidation state. Conventional hydrometallurgical processes using strong acids or alkalis are ineffective for $USbFeO_x$ treatment, potentially generate secondary waste through silica dissolution, and may alter Sb's oxidation state, making these catalysts non-compliant with disposal regulations.

This study aims to develop an environmentally friendly method using Choline Chloride-based deep eutectic solvents (ChCl-based DESs) to effectively dissolve and extract problematic metals like Sb, Te, and U from spent catalysts, enabling the remaining catalyst residue to meet WAC requirements for safe disposal. Simultaneously, the extracted valuable metals could be recycled, creating economic value.

DESs offer an environmentally friendly alternative with low toxicity, biodegradability, and cost-effectiveness compared to conventional ionic liquids[3]. ChCl-based DESs enable selective dissolution capabilities, minimizing toxic byproduct generation[4]. ChCl:p-toluenesulfonic acid (ChCl:pTSA) has demonstrated effective dissolution of Sb_2O_5 and TeO_2. Additionally, ChCl:pTSA (2:1) achieved 100% dissolution of UO3 within 4 hours and high solubility for UO_2 (84.39%) and U_3O_8 (47.06%)[5].

This study examines uranium-free spent catalysts (UFSC) and key metal and metalloid oxides in ChCl-based DESs. Given ChCl:pTSA's high viscosity, hydration at 5, 10, 20 wt.% is introduced to investigate its effects on viscosity reduction and dissolution efficiency. The addition of water helps reduce viscosity, improving mixing and mass transfer for practical application.

The research specifically evaluates whether ChCl-based DESs can selectively dissolve metals from spent catalysts while preserving the silica support structure, thereby meeting disposal requirements and achieving both safe disposal and resource recovery objectives.

2. Methodology

To investigate the dissolution behavior of UFSC and individual metal oxides, various DESs were synthesized using ChCl with ethylene glycol (ChCl:EG, 1:2 molar ratio), urea (ChCl:Urea, 1:2 molar ratio), and pTSA (ChCl:pTSA, 1.5:1 molar ratio). The ChCl:pTSA system was further mixed with 5 wt. %, 10 wt. %, and 20 wt. % water to examine hydration effects on metal dissolution efficiency.

Before conducting UFSC leaching, individual metal oxides (Sb_2O_5, Sb_2O_3) were tested separately to evaluate their dissolution behavior in DESs. For each leaching experiment, a mixture containing 0.1 g of the target material (consisting of one metal oxide or the UFSC) was combined with 6 g of DES, then stirred at 60 °C for 24 hours.

Synthesized DESs were characterized to assess hydrogen bond formation using Fourier-transform infrared attenuated total reflectance (FTIR-ATR) and thermal stability using thermogravimetric analysis (TGA). UFSC characterization included morphological analysis using scanning electron microscopy (SEM), chemical composition analysis inductively coupled plasma optical emission spectroscopy (ICP-OES) digestion coupled with energy-dispersive X-ray spectroscopy (EDS), and phase identification using X-ray diffraction (XRD). Leaching efficiency for individual metal and metalloid oxides as well as UFSC was determined using ICP-OES.

3. Results and Discussion

3.1. Characterization of Deep Eutectic Solvents (DESs)

Hydrogen bonding interactions in DESs were analyzed using FTIR-ATR. In ChCl:EG, the OH stretching peak of EG at 3287 cm^{-1} shifted to 3300 cm^{-1} (**Fig 1(a)**). In ChCl:Urea, the N-H stretching peak at 3320 cm^{-1} shifted to a lower frequency (**Fig 1(b)**). In ChCl:pTSA, a broad OH-stretching band was observed between 1600–2500 cm^{-1} (**Fig 1(c)**). These spectral shifts confirmed hydrogen bond formation in each DESs.

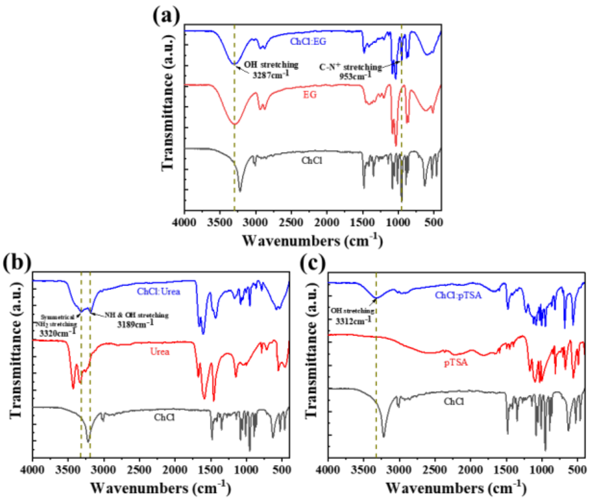

Fig 1. FT-IR spectra of ChCl:EG (a); ChCl:Urea (b); ChCl:pTSA (c).

Thermal stability was assessed using TGA in both dynamic and isothermal modes. Dynamic TGA was conducted from 40 °C to 400 °C at a heating rate of 5 °C/min. The total mass loss at 400 °C was 99.68 % for ChCl:EG, 90.6 % for ChCl:Urea, and 84.77 % for ChCl:pTSA, with ChCl:pTSA showing the lowest mass loss.

Isothermal TGA, performed at 60 °C for 24 hours, showed mass losses of 8.04 % for ChCl:EG, 6.36 % for ChCl:Urea, and 1.70 % for ChCl:pTSA. ChCl:pTSA exhibited the lowest mass loss in both dynamic and isothermal conditions, suggesting it maintains sufficient stability under the planned leaching conditions, with no significant decomposition expected to interfere with the metal extraction process.

3.2. Characterization of Uranium-Free Spent Catalysts

Surface morphology and particle size distribution were analyzed using SEM and laser diffraction analysis. SEM imaging revealed both near-spherical and irregularly shaped particles (**Fig 2**).

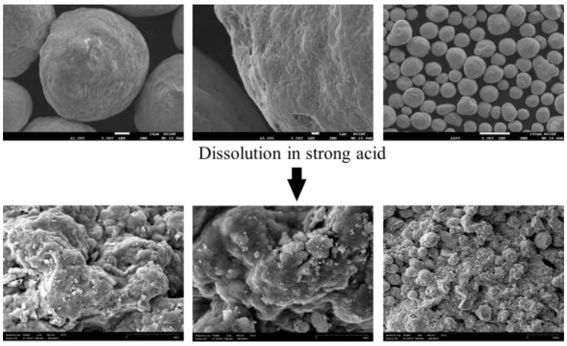

Fig 2. SEM image of UFSC before & after dissolution in HF and aqua regia.

Elemental composition analysis of UFSC was attempted using wet ICP digestion methods, but complete dissolution could not be achieved even with strong acids including hydrofluoric acid (HF) and aqua regia. The dissolution rate of UFSC in HF and aqua regia was approximately 50%, with the remaining 50% analyzed using EDS (**Table 1**). Based on **Table 1**, the significant Si content suggests that a large portion of the spent catalyst consists of silica-based support, which is expected to remain largely undissolved during leaching.

Table 1. Elemental content of the UFSC by ICP digestion coupled with EDS

Element	**Content (wt %)**
Sb	48.7
Si	22.8
Fe	15.7
Te	5.92
Cu	3.89
W	1.36
Mo	1.26
Ni	0.3

Phase identification and oxidation states were assessed using XRD, which revealed $FeSbO_4$ as the dominant crystalline phase, with Sb as Sb^{5+} and Fe as Fe^{3+} (**Fig 3**). The presence of a strong Fe-Sb-O bonding network suggests that $FeSbO_4$ may hinder the dissolution of Sb and Fe, potentially limiting leaching efficiency.

These characterization results indicate that selective leaching conditions must be optimized to efficiently extract valuable metals such as U, Sb and Te for recycling and resource recovery, while ensuring that any remaining waste materials comply with disposal regulations.

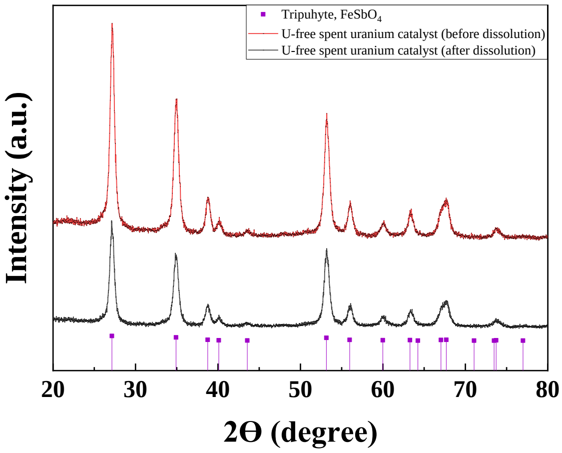

Fig 3. XRD pattern of UFSC before and after dissolution.

3.3. Leaching of Individual Metal and Metalloid Oxides

The ChCl:pTSA system demonstrated superior extraction efficiency for Sb oxides compared to 2M HCl, with notable differences in extraction behavior between oxidation states. Sb^{3+} exhibited higher extraction rates than Sb^{5+}, reflecting their distinct extraction mechanisms - Sb^{3+} was predominantly extracted through chloride coordination, while Sb^{5+} mobilization occurred via solvation and hydrolytic processes, as shown in **Fig 4**.

With the addition of 5% water to the ChCl:pTSA system, changes in Sb extraction behavior were observed. The extraction efficiency of Sb^{5+} showed an increasing trend with water addition, suggesting that even small amounts of water promote the formation of hydrated Sb^{5+} species, enhancing extraction.

In contrast, Sb^{3+} extraction remained relatively unaffected by variations in water content. This suggests that at 5% water addition, the Sb^{3+} extraction mechanism continues to rely primarily on chloride coordination, with water presence having minimal impact on this process.

These findings indicate that the addition of small amounts of water to ChCl:pTSA can enhance the selective extraction efficiency of Sb oxides, particularly for Sb^{5+}. This differential extraction behavior between Sb oxidation states could be advantageously utilized in developing selective separation and recovery strategies based on oxidation state.

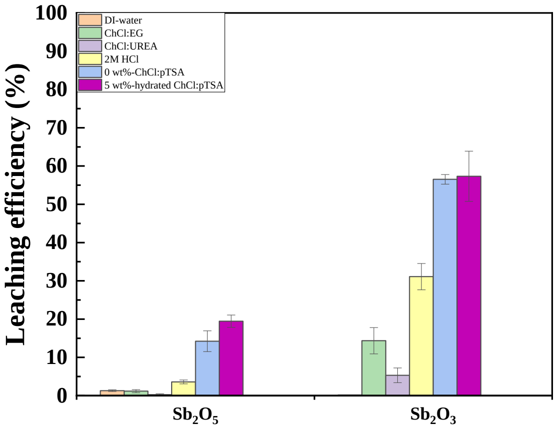

Fig 4. Leaching efficiency of Sb_2O_5, Sb_2O_3 in different solvents at 60°C, 24 hours, 400 rpm.

3.4. Leaching of Uranium-Free Spent Catalysts

The extraction efficiency from UFSC was significantly lower than from isolated oxide compounds, particularly for antimony, as shown in **Fig 5**. This reduced performance can be attributed to the robust $FeSbO_4$ crystalline structure with resilient Fe-Sb-O bonds that resist solubilization. The thermal conditions during catalyst operation likely enhanced $FeSbO_4$ crystal formation and structural integrity.

The addition of water to the ChCl:pTSA system produced contrasting effects on different elements. Tellurium extraction showed a modest increasing trend with higher water content, while antimony mobilization exhibited a declining trend, as illustrated in **Fig. 5**. These observations suggest that water incorporation may reinforce $FeSbO_4$ stability while facilitating Te solubilization through enhanced solvation mechanisms.

Consistent with earlier findings, silica mobilization remained negligible during UFSC processing. This limited SiO_2 extraction proves advantageous for selective metal recovery since silica constitutes a substantial portion of the UFSC matrix by both mass and volume.

Although ChCl:pTSA demonstrated superior performance compared to traditional acidic media and other DES types, it proves inadequate as a standalone system for efficient antimony recovery from UFSC. This highlights the necessity for supplementary processing approaches, potentially including reductive extraction protocols, stronger complexing agents, or thermal/mechanical preprocessing to facilitate the breakdown of the persistent $FeSbO_4$ phase.

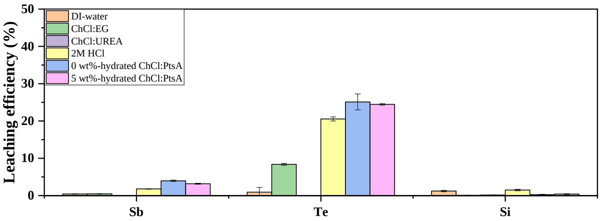

Fig 5. Leaching efficiency of the UFSC in different solvents at 60°C, 24 hours, 400 rpm.

4. Conclusion

This study showed that ChCl-based DESs, particularly ChCl:pTSA, demonstrated effective leaching capabilities for individual metal oxides but showed limited effectiveness when applied to actual catalyst material. While individual Sb oxides achieved high dissolution rates, their recovery from UFSC was significantly lower due to the stable $FeSbO_4$ crystalline structure. Hydration effects were metal-specific and insufficient to overcome these structural barriers. These findings suggest that while DESs show promise for selective metal recycling with reduced environmental impact, additional processing strategies are necessary to meet WAC requirements and achieve economically viable recovery rates. Future work should explore combining DES leaching with mechanical pretreatment, reductive agents, or advanced dissolution techniques to effectively disrupt the resistant $FeSbO_4$ phase while maintaining selective recovery of valuable U, Sb, and Te.

5. Acknowledgement

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