초임계이산화탄소를 이용한 방사성 금속이온 추출
The Extraction of Metal Contaminants using Supercritical CO2

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요약
원자력발전 등에 기인한 방사성 오염물질들은 대부분 제염과정을 통하여 방사능과 그 부피를 줄이는데, 물을 주로 사용하는 기존의 방사성 물질 제염방법은 많은 양의 2차 폐기물을 발생시킨다. 본 연구에서는 용매로 이산화탄소의 특성을 이용하여 폐기물 저감에 효과적인 제염 방법을 적용해보았다. 이를 위해 본 연구에서는 우선 원자력 오염물질의 제염 대상을 금속 이온, 금속과 금속산화물로 분류하여 두 가지 방법을 적용하였다. 전자의 경우 계면활성제 킬레이트법을 이용하여 제염하였다. 제염대상 핵종으로는 Sr, Co, Nb, Zr을 선정하였다. Sr과 Co는 각각 핵분열 생성물과 방사화 부식 생성물의 대표 핵종이고 Nb와 Zr은 오염된 방호복에서 가장 많은 방사능을 차지하는 핵종이다. Static Extraction을 통하여 Sr은 최고 97%, Nb과 Co, Zr은 각각 79%, 73%, 64%의 추출율을 얻었다.

Abstract
Conventional decontamination methods utilize water–based systems, which generate high amounts of secondary wastes. Herein, we describe an environmentally benign decontamination method using liquid and supercritical CO2. The use of CO2 as a solvent affords effective waste reduction by its ability to be recycled, thereby leaving be hind only the contaminants upon its evaporation. In this study, a CO2 solution process was assessed using t–salen(t–butylsalen), DC18C6 (dicyclohexano–18Crown6), 8–HQN(8–hydroxyquinoline), NEt4PFOSA(perfluoro–1–octanesulfonic acid tetra–ethyl ammonium salt), and NEt4PFOA(pentadecafluorooctanoic acid ammonium salt) to extract spiked radioactive contaminants(Nb,Zr,Co,Sr) from an inert sample matrix, namely filter paper. With the static extraction method, Sr was extracted with a maximum extraction rate of 97%, and Nb was extracted with a maximum extraction rate of 75%. Additionally, we were also able to extract Co and Zr with maximum extract ion rates of 73% and 64%, respectively.

I. INTRODUCTION
Disposal and handling of industrial wastes imposes high costs and efforts on the society. For nuclear power industries in particular, it is quite expensive and difficult to process the waste products, as they
are often radioactive. Because nuclear power plants use aqueous solutions for the decontamination of items such as clothing, hats, shoes, tools, and other parts, there exists a problem of producing secondary radioactive waste, such as contaminated radioactive water. Therefore, it is necessary to develop a new technology through which the decontamination solvent can be recycled, thereby reducing costs. Recently, we have seen vast improvements in metal extraction technology using supercritical fluid.

A supercritical fluid is any substance above its critical temperature and critical pressure. The critical temperature is the highest temperature at which a gas can be converted into a liquid by increasing pressure. The critical pressure is the highest pressure at which a liquid can be converted to a gas by an increase in temperature. Supercritical state is only one state-of-the-fluid and possesses both gas-like and liquid-like properties[1].

As mentioned above, supercritical fluids based on CO2 are gaining popularity as alternative, environmentally friendly process solvents as CO2 is non-toxic, non-flammable, and inexpensive. Its critical conditions are easily achievable with existing process equipment. Also, this unique combination of physical, chemical and economic properties of Supercritical CO2 has prompted research on its use as a replacement of process solvents currently used in many commercial applications, including extraction of natural products, separation of fats or oils, cleaning of organic material, and decontamination of radioactive components[1].

As most radioactive wastes contain metal compounds, it is possible to decontaminate radioactive waste with supercritical CO2. If we extract metals using CO2 as a solvent, we can then easily separate CO2 from the extracted metals through vaporization, and these parted CO2 can subsequently be reused in the extraction process. Typically, metal extraction using CO2 is known to be a nontoxic, nonflammable, and environmentally benign process. Furthermore, this method of employing supercritical CO2 is energy efficient, is applicable to low temperature processes, and can be employed to processes containing real-short materials. However, CO2 (which is a non-polar compound) has difficulty dissolving metals, which are polar. Therefore, extracting agents are required to extract metals when CO2 is used as a solvent[1-5]. [Table 1] displays a summary of radioactive nuclides that typically exist in contaminated clothing at nuclear power plants. All radioactive nuclides mentioned in the table, except I, are metal nuclides. Of them, Nb and Zr exhibit high radioactivity values in contaminated clothing. Therefore, in this investigation, we selected Zr, Nb, Co (the strongest -emitter of all corrosion products), and Sr (a representative nuclide of a fission product) as the nuclides to be subjected to decontamination[7-14].

Table 1. Radiation of various nuclides found in clothing contaminated at a nuclear power plant

<table>
<thead>
<tr>
<th>Nuclides</th>
<th>Radioactivity (Bq/g)</th>
<th>Half Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-95</td>
<td>3.167E+02</td>
<td>35 d</td>
</tr>
<tr>
<td>Zr-95</td>
<td>2.452E+02</td>
<td>64 d</td>
</tr>
<tr>
<td>Zr-97</td>
<td>5.016E-01</td>
<td>17 h</td>
</tr>
<tr>
<td>Co-60</td>
<td>1.424E+00</td>
<td>5 y</td>
</tr>
<tr>
<td>Cr-51</td>
<td>4.024E+01</td>
<td>28 d</td>
</tr>
<tr>
<td>Zn-65</td>
<td>2.702E+00</td>
<td>244 d</td>
</tr>
<tr>
<td>I-131</td>
<td>5.975E-01</td>
<td>8 d</td>
</tr>
<tr>
<td>Cs-137</td>
<td>5.789E-01</td>
<td>30 y</td>
</tr>
<tr>
<td>Ba-140</td>
<td>3.744E+00</td>
<td>13 d</td>
</tr>
</tbody>
</table>

Figure 1. Property of Supercritical fluid
We used chemical species that are soluble in CO₂ and have been used in conventional solvent extractions as the extracting agents. In order to neutralize the complexes of the metal ion-chelating agents, NEt₄PFOA (pentadecafluorooctanoic acid ammonium salt) and NEt₄PFOSA (perfluoro-1-octanesulfonic acid tetra-ethyl ammonium salt) were used as counter anions. Table 2 summarizes the solubilities (in liquid and supercritical CO₂) of the extracting agents used in this investigation [5][6].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Extracting Agents</th>
<th>Pressure (Mpa)</th>
<th>Temp. (℃)</th>
<th>Solubility (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>8-HQN</td>
<td>11.0</td>
<td>50</td>
<td>6.890×10⁻³</td>
</tr>
<tr>
<td>Co</td>
<td>t-Salen</td>
<td>7.0</td>
<td>20</td>
<td>1.814×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.0</td>
<td>60</td>
<td>1.325×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.0</td>
<td>60</td>
<td>1.325×10⁻⁴</td>
</tr>
<tr>
<td>Nb, Sr</td>
<td>DC18C6</td>
<td>9.1</td>
<td>20</td>
<td>2.684×10⁻²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.6</td>
<td>60</td>
<td>2.684×10⁻²</td>
</tr>
<tr>
<td></td>
<td>NEt₄PFOA</td>
<td>8.8</td>
<td>20</td>
<td>2.853×10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.2</td>
<td>60</td>
<td>2.853×10⁻³</td>
</tr>
<tr>
<td></td>
<td>NEt₄PFOSA</td>
<td>21.0</td>
<td>20</td>
<td>3.178×10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.0</td>
<td>60</td>
<td>7.944×10⁻⁴</td>
</tr>
</tbody>
</table>

II. EXPERIMENTAL PROCEDURES

In this investigation, 1.08×10⁻³M of Nb, 1.08×10⁻³M of Zr, 1.69×10⁻³M of Co, and 1.14×10⁻³M of Sr in AAS (atomic absorption standard) aqueous solutions were used as the metals to be extracted. DC18C6 (Dicyclohexano-18Crown6), t-salen (t-buty1salen), and 8-HQN (8-hydroxyquinoline) were used as the metal chelates. NEt₄PFOSA and NEt₄PFOA were used as the counter anions. The extracting agents were dissolved in methanol before use. For the experimental specimens, 10×10mm filter papers (Whatman No.2) were spiked with 50µL of each AAS solution and then dried. 10mL of the solution containing the extracting agent solution was poured into a reactor, and subsequently dried. After drying, 10µL of H₂O, a stirrer, and an experimental specimen were then added to the reactor. In order to avoid direct influence of the stirrer, the specimens were always placed above the stirrer using a tripod. We then placed the reactor in a water bath to maintain the desired temperature [Figure 2]. 20min of static extraction was applied for each experiment. Liquid CO₂ was used at 20℃ whiles supercritical CO₂ was used at 60℃, each under 10MPa of pressure. CO₂ pressure was applied using a 260D syringe pump (ISCO), and the results were analyzed by inductively coupled plasma (ICP, LeemanLab).

III. RESULTS

1. Sr EXTRACTION

In general, there are three possible ways to extract the metal ion. The first extraction method is to use a chelating agent. Because metal ions form complexes with chelating agents, these complexes can be extracted. In such cases, the complexes are insoluble in CO₂. The second method is the extraction of counter anion/metal ion complexes. The third method involves the extraction of the compound containing the metal ion, chelating agent, and the counter anion. Most metals are extracted using the third method. In this case, the rate of extraction depends on the solubility of the counter anion. [Figure 3] and [Figure 4] display the results of the Sr ion extraction using
DC18C6 in liquid CO₂, where NEt₄PFOA and NEt₄PFOSA, respectively, were used as the counter anions. When NEt₄PFOA was used, the extraction rate increased as the molar ratio of DC18C6 and NEt₄PFOA increased [Figure 4]. However, when NEt₄PFOSA was used, an increase in the extraction rate was not observed, because the change in the solubility of metal complex depends on the counter anion [Figure 5]. For the Sr ion, when the molar ratio of the various chemical entities were Sr : DC18C6 : NEt₄PFOA = 1 : 10 : 50, the extraction rate exhibited a maximum value of 97%.

Figure 3. The result of Sr extraction using DC18C6 and NEt₄PFOA in liquid CO₂

Figure 4. The result of Sr extraction using DC18C6 and NEt₄PFOSA in liquid CO₂

Figure 5. The result of Sr extraction in supercritical CO₂

2. ANION EFFECT

[Figure 6] displays the effects of NO₃ and Cl counter anions on the extraction of the nuclide, when they are introduced into the solution containing the nuclide to be extracted. When Sr : NEt₄PFOA = 1 : 1, with a counter anion of Cl, the extraction rate was very low, which is most likely a result of Cl interfering with the formation of the PFOA metal complex. However, if the molar ratio of the Sr ion to NEt₄PFOA is increased by a sufficient amount, then the effects of the counter anion were no longer observable [6].

Figure 6. The result of Sr extraction using DC18C6 and NEt₄PFOA in liquid CO₂

3. Nb EXTRACTION

[Figure 7] and [Figure 8] display the results of the Nb ion extraction in liquid and supercritical CO₂, respectively. When liquid CO₂ was used as the solvent, and the molar ratio of the Nb ion to the
various chemical additives was Nb : DC18C6 : NEt4PFOA = 1 : 1 : 10, the maximum extraction rate obtained was 68%. When supercritical CO2 was used as the solvent and the molar ratio of the Nb ion to the various chemical additives was Nb : DC18C6 : NEt4PFOA = 1 : 50 : 10, we were then able to obtain a maximum extraction rate of 79%. Furthermore, both DC18C6 and NEt4PFOA worked individually as extractant, even when used independently, in the extraction of Nb in both liquid and supercritical CO2. This result is caused by the metal complex of Nb and DC18C6 and the metal complex of Nb and PFOA both being soluble in CO2 to some extent. For the solution containing Nb, the extraction rate also increased as the amount of DC18C6 and NEt4PFOA increased.

Figure 7. The result of Nb extraction in liquid CO2

Figure 8. The result of Nb extraction in supercritical CO2

4. Co EXTRACTION

[Figure 9] displays the results of the Co ion extraction in liquid CO2 using t-salen and NEt4PFOA. [Figure 9] confirms that there was no apparent improvement of the extraction rate when the molar ratio(NEt4PFOA/Metal ion) was 1:10, but the extraction ratio greatly improved when the molar ratio was 1:50. In particular, when the ratio of the Co ion to the chemical additives was Co:t-salen: NEt4PFOA=1:10:50, the extraction rate exhibited a maximum value of 73%. However, even with a similar molar ratio, the extraction rate in supercritical CO2 was only 8%. This phenomenon is likely a result of the fact that t-salen has very low solubility in supercritical CO2.[Table 2].

Figure 9. The result of Co extraction using t-Salen in liquid and supercritical CO2

5. Zr EXTRACTION

[Figure 10] displays the results of the Zr ion extraction in supercritical CO2. 8-HQN and NEt4PFOA were used as the metal chelate and counter anion, respectively. For the Zr ion, as with the Sr and Nb ions, an extraction rate of 28% was obtainable only with NEt4PFOA. It was also observed that the extraction rate increased as the molar ratio of 8-HQN to NEt4PFOA increased. When the ratio of the Zr ion to the chemical additives was Zr:8-HQN: NEt4PFOA=1:10:50, the extraction rate exhibited a maximum value of 64%. However, even with the same molar ratio, the extraction rate in liquid CO2 was only 21%, which is a result of the pH being a
critical factor for 8-HQN to act as a metal chelate. 8-HQN works effectively as a metal chelate at neutral pH, but loses its ability to act as a metal chelate in acidic conditions. Additionally, the pH of CO₂ in the presence of H₂O and under the same pressure, increased as the temperature increased. Therefore, the extraction rate significantly decreased as liquid CO₂ is more acidic than supercritical CO₂.

**Figure 10. The result of Zr extraction using 8-HQN in liquid and supercritical CO₂**

### IV. CONCLUSION

In the present investigation, we selected Nb, Zr, Co and Sr as the subject nuclides to be extracted, and performed decontamination experiments with these nuclides in both liquid and supercritical CO₂ using a static extraction system. In all cases, a single extraction could extract more than 60% of the target nuclides. Additionally, upon performing additional extractions, we were able to extract more than 90% of the target nuclides. Therefore, we could verify the feasibility of the decontamination of radioactive contaminants with liquid and supercritical CO₂. We plan to apply this technology to future decontamination experiments using actual radioactively contaminated specimens.

Supercritical fluid systems are expensive, the set up of Supercritical fluid systems including recycling system costs from over 100 million won. However, D&D(decontamination and decommissioning) costs are lower than competing cleaning system that require the disposal of spent solvent or 2nd-wastewater, since the waste residue is 100% contaminant. It is expected that disposal costs increase gradually as environmental regulations are tighten. Therefore, supercritical fluids system can reduce substantially disposal costs.

**참 고 문 헌**


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