Removal of Zr and Mo from the Simulated Radwaste Solution by Denitrification with Formic Acid (I)


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Abstract: The removal of Zr and Mo from a simulated radwaste solution was experimentally examined by batch denitrification with formic acid. The aims of this study were to separate Zr and Mo as precipitate and to reduce the acidity of simulated radwaste solution from 2 to less than 0.5M. Resulting from this study, it was found that the optimum conditions were the [HCOOH]/[HNO₃]=1.5 and 2.5hr denitration. Under the optimum conditions, the acidity of the denitrated solution could be reduced to less than 0.5M, and Zr and Mo could be removed over 99% and 86%, respectively. Fe could be removed about 39%. These results satisfied the requirements established in this study, except for about 86% precipitation of Mo. The cause on the decrement of Mo precipitation is mainly due to the containing the platinum group metals (PGM) such as Pd and Ru. The effects of each element on the precipitation of Mo increased in the order of Pd, Ru >> Fe > Nd. Also filterability of denitrated solutions was favorable.

Introduction

High-level liquid waste (HLW) generated from the first extraction cycle in fuel reprocessing by PUREX, contains fission products, actinides, lanthanides, corrosion products, various chemical additives and a significant amount of nitrate ion. The acidity of HLW varies between 2 and 7M HNO₃, with reprocessing operation conditions.

Generally, the management of HLW has been considered in the glass solidification, and the vitrified solids must be stored or disposed of for a long time.
time. However, high acidity of HLW and high concentration of nitrates can be the source of many problems in glass solidification[1, 2, 3]. So, the chemical denitration method is recommended to reduce the acidity of HLW and to decompose the nitrates.

On the other hand, the partitioning and transmutation concept has been recently proposed as an ultimate disposal method, particularly for reducing the long-term biological hazards of the wastes. The idea is the removal of long-lived radionuclides such as actinides, which are often referred as transuranium(TRU) elements, from the HLW, and transmutation of the nuclides to short-lived or stable nuclides in either the FBR or accelerator.

In the partitioning process, the short lived elements(Zr and Mo, etc), TRU, platinum group metals(PGM), and Cs/Sr can be separated by denitrification, solvent extraction and ion exchange methods[4]. Especially, the denitrification is one of separation processes for the removal of Zr and Mo. The denitrification of HLW can be achieved using various organic reducing agents such as formic acid, formaldehyde, sugars, etc. However only formic acid is of particular interest[5].

Therefore, this study was performed using formic acid as a reducing agent and satisfied the two different requirements needed for the process development. One was to separate Zr and Mo as precipitate. The other was to reduce the acidity of HLW from 2 to less than 0.5M. These are the most appropriate conditions for the mutual-separation of TRU/lanthanides by extraction using HDEHP[di(2-ethylhexyl)phosphoric acid] or co-precipitation of TRU/lanthanides by using oxalic acid.

The precipitation behaviors of each element after denitrification and the filterability of denitrated solutions in multicomponent system were experimentally examined with the changes of the initial stoichiometric ratio of formic acid to nitric acid(described as [HCOOH]/[HNO3]). Also the effect of each element on Zr and Mo precipitation was considered.

2. Experiment

2.1. Materials

In this study, elements such as U, Al, Ag, Cd, Cs, Sr, etc were omitted because their presence in HLW is minimal or does not affect precipitation behavior of Zr, Mo and TRU/lanthanides during denitrification. The simulated solution containing 6 elements Zr, Mo, Nd, Pd, Ru, and Fe was prepared. Nd and Pd/Ru were used to represent TRU/lanthanides and PGM, respectively. The initial acidity of HNO3 was constantly maintained at approximately 2M.

All chemicals of analytical grade formed the nitrate complex, except for Mo, were used without further purification. The chemical compositions of the simulated radwaste solution are shown in Table 1, based on the report by JAERI[6].

2.2. Denitrification

A denitrification apparatus consisted of a 500mℓ three-necked flask equipped with a reflux condenser and a heating mantle. All experiments were carried out in batch system.

After the addition of formic acid, the 50mℓ of simulated HLW was heated to 90℃ under refluxing for 5.5hr. After cooling to room temperature, the denitrated solution was filtered through the 0.2μm modified polysulfone membrane filter. The pH and total acidity of denitrated solutions were measured by pH meter and titration with NaOH. The concentration of each element in the denitrated solutions was analyzed by ICP(inductively coupled plasma

<table>
<thead>
<tr>
<th>Element</th>
<th>Compound</th>
<th>Composition(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>ZrO(NO3)2 · 2H2O</td>
<td>0.069</td>
</tr>
<tr>
<td>Mo</td>
<td>(NH4)2MoO4 · 4H2O</td>
<td>0.069</td>
</tr>
<tr>
<td>Nd</td>
<td>Nd(NO3)3 · 9H2O</td>
<td>0.127</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd(NO3)2</td>
<td>0.018</td>
</tr>
<tr>
<td>Ru</td>
<td>Ru(NO)(NO3)3</td>
<td>0.034</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(NO3)3 · 9H2O</td>
<td>0.038</td>
</tr>
<tr>
<td>H⁺</td>
<td>HNO3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 1. Chemical Compositions and Compounds Used in this Study

emission spectrophotometry).

3. Results and Discussion

3.1. Precipitation Behavior of Each Element in 6 Components System

3.1.1. Denitrification Rate

Total acidities of denitrated solution determined by titration are in error because of dilution of the sample solution with distilled water and NaOH. So, total acidity is directly expressed as a pH measured with pH meter.

Fig. 1 shows the pH of denitrated solutions with denitrification time. Under the condition of [HCOOH]/[HNO₃]=1.25, the total acidity could not be decreased to less than 0.5M, which did not satisfy the requirements noted in the previous section. The denitrification reaction proceeded remarkably during the first 0.5hr, evolving gases and rapidly reducing the acidity. The pH of the denitrated solution increased by increasing the [HCOOH]/[HNO₃]. Also, the pH changes obtained at [HCOOH]/[HNO₃] below 1.5 and over 1.75 were minimal after 2.5 or 3.5hr denitrification. From these results, it was considered that denitrification was finished by 2.5~3.5hr of heating.

3.1.2. Precipitation Fraction of Each Element After Denitrification

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Fig. 4. Effect of denitrification time on precipitation fraction of Nd at several molar ratios of [HCOOH]/[HNO₃].

Fig. 5. Effect of denitrification time on precipitation fraction of Ru at several molar ratios of [HCOOH]/[HNO₃].

Fig. 6. Effect of denitrification time on precipitation fraction of Pd at several molar ratios of [HCOOH]/[HNO₃].

Fig. 7. Effect of denitrification time on precipitation fraction of Fe at several molar ratios of [HCOOH]/[HNO₃].

Fig. 2~7 show the precipitation fraction of each element remaining in denitrified solution with denitrification time at [HCOOH]/[HNO₃] = 1.25, 1.5, 1.75, and 2.0 respectively. The meaning of 100% is equivalent to the initial amount of each element in the simulated solution. For removal of Zr and Mo, the precipitation fraction of these elements was constantly maintained after 2.5hr. So, based on the results obtained at 2.5hr denitrification, the precipitation fraction of each element will be discussed.

Regardless of [HCOOH]/[HNO₃], almost all of Zr was precipitated after 1.5hr. Therefore, Zr could be completely removed in the denitration step.

The precipitation fraction of Mo was 78% at [HCOOH]/[HNO₃]=1.25, and 86%, 91% at [HCOOH]/[HNO₃]=1.5, 1.75, respectively, and increased to 90% at [HCOOH]/[HNO₃]=2.0.

Generally, it is known that Zr and Mo tend to hydrolize and precipitate during denitration[7]. Therefore, precipitation fractions of Zr and Mo depend on the pH of denitrated solution, which increases with the increasing of [HCOOH]/[HNO₃]. From the results, the most appropriate condition for removing only Mo is [HCOOH]/[HNO₃]=2.0. However, this condition also caused the co-precipitation of other elements.

On the other hand, Nd was not precipitated at [HCOOH]/[HNO₃] below 1.5, and precipitated at 6% and 18% at [HCOOH]/[HNO₃]=1.75, 2.0, respectively. Nd behaves much like TRU chemically. Therefore, denitration at [HCOOH]/[HNO₃] over 1.75 should be avoided in the pretreatment of HLW for the partitioning which is aimed at separation of TRU from the HLW.

The precipitation fraction of Ru was about 8% at [HCOOH]/[HNO₃]=1.75, and increased to 25% at [HCOOH]/[HNO₃]=2.0. However, Ru abruptly precipitated at about 88% with increasing of denitration time at [HCOOH]/[HNO₃]=2.0. It is thought that Ru(NO)⁺⁺ is quantitatively converted into Ru(NO)(OH)₆. These results are consistent with the previous study where (Ru(OH)₃) tends to remain in colloidal solution, and the best pH for its complete precipitation is found to be 6.4[8].

Pd was not precipitated at [HCOOH]/[HNO₃] below 1.75, and 68% of Pd was precipitated at [HCOOH]/[HNO₃]=2.0. This phenomenon is due to the chemical characteristics of Pd in nitric acid. In the nitric acid solution, Pd exists in the form of Pd(OH)⁺ at pH=0.5, and Pd forms stable precipitate, Pd(OH)₆, at pH over 2.0[9]. These results on Ru and Pd show the possibility that denitration is one of the good methods for recovering the PGM

Fig. 8. Effect of molar ratio of [HCOOH]/[HNO₃] on precipitation fraction and on pH after 2.5hr denitration.

[10].

Fe affecting the 3rd phase formation in the solvent extraction process was precipitated about 7% and 39% at [HCOOH]/[HNO₃]=1.25, 1.5, respectively, and increased to 78% at [HCOOH]/[HNO₃] over 1.75. These results agree with the previous report performed under similar conditions[11], which provide a favorable condition to the next process. However, the precipitate of Fe dissolved again with the increasing of denitration time over 4.5hr. This phenomenon might be ascribed to complex formation with formic acid, although confirmation will be needed.

3.1.3. Optimum Condition

In order to confirm the optimum condition for the denitration process, we must choose the condition that only Zr and Mo precipitate and the other elements, especially Nd used as a representative of TRU/lanthanides, do not precipitate. Also the acidity can be reduced to less than 0.5M, which satisfied the acidity of the feed solution in the next process. Fig. 8 shows the precipitation fraction of each element and pH with [HCOOH]/[HNO₃] at 2.5hr denitration. From the results obtained above, the
3.2. Effect of Each Element on the Precipitation of Zr and Mo

The effect of each element on the Zr and Mo precipitation was experimentally examined on the following systems, and chemical constituents were changed stepwise from a combination Zr and Mo as basic constituents. The examined 5 systems are 1) Zr-Mo, 2) Zr-Mo-Fe, 3) Zr-Mo-Nd, 4) Zr-Mo-Pd-Ru and 5) Zr-Mo-Fe-Nd-Pd-Ru. Concentrations of each element are shown in Table 1.

Fig. 9 shows the pH of denitrated solution with denitration time at [HCOOH]/[HNO_3]=1.5. It was also found that pH recoveries are minimal after 2.5 hr denitration, and pH was somewhat increased more than that of only Zr-Mo system by adding the each element, especially Pd and Ru used as a representative of PGM, except for Fe. Generally, decomposition of metal nitrate with formic acid is known to produce the hydroxide of metals and to raise the pH of denitrated solution[12]. Also, PGM was known to catalize decomposition of formic acid[13]. Therefore, the formic acid remained after denitration may be decomposed by addition of a small amount of PGM. So, pH is somewhat increased. However, it is reported to reduce from Fe^{3+} to Fe^{2+} at low acidity solution, below 0.2M HNO_3 during denitration[1]. For this reason, pH of denitrated solution adding the Fe was relatively decreased, although the confirmation will be need.

Fig. 10 shows the precipitation fraction of Zr and Mo with the each element. Regardless of the adding elements, precipitation fraction of Zr was at over 99%. From these results, Zr as precipitate is completely removed. Precipitation fraction of Mo did not also have any significant effect in the solution adding the Fe or Nd, but that of Mo decreases to 86%, when Pd and Ru is adding. This result did not agree with that of the previous section, namely precipitation of Mo was increased by increasing the pH of denitrated solution. This phenomenon was due to the various chemical characteristics of Mo in nitric acid of pH below 1.0. Mo exists in form of MoO_4(H_2O)_3^{7+} at pH below 0.5, and HMoO_4^- at pH over 3.5, respectively.
Table 2. pH and Precipitation Fraction of Each Element

<table>
<thead>
<tr>
<th>System</th>
<th>pH</th>
<th>Zr Precipitation (%</th>
<th>Mo</th>
<th>Fe</th>
<th>Nd</th>
<th>Pd</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Mo</td>
<td>0.69</td>
<td>&gt;99</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr-Mo-Fe</td>
<td>0.45</td>
<td>&gt;99</td>
<td>96</td>
<td>37</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr-Mo-Nd</td>
<td>0.72</td>
<td>&gt;99</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr-Mo-Pd-Ru</td>
<td>0.85</td>
<td>&gt;99</td>
<td>87</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Zr-Mo-Nd-Fe-Pd-Ru</td>
<td>1.00</td>
<td>&gt;99</td>
<td>86</td>
<td>39</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Mo also forms the precipitate of H₂MoO₄ and MoO₂ in the pH range of 0.9~3.5 and that of zirconium molybdate at pH over 5[14], even if the these are not clearly known.

Table 2 shows the pH and precipitation fractions of each element remaining in denitrated solution of several systems at [HCOOH]/[HNO₃] = 1.5, 2.5hr.

3.3. Filterability of Denitrated Solutions

Filterability of denitrated solutions was one of the problems to be considered in the denitration process. Fig. 11~12 show SEM photography of the precipitate formed after 2.5hr denitration at [HCOOH]/[HNO₃]=1.5, 2.0, respectively. As a result, the particle size of precipitate was relatively small and the shape of particles was an aggregation of irregular amorphous types. Especially, particle size became larger, when an excess of formic acid was added. These phenomena may be attributed to the co-precipitation of Nd, Pd and Ru with Zr and Mo[15], although the mechanism of co-precipitation is not clearly known. Also, almost all of the denitrated solutions could be smoothly filtered during 1min. So, filterability of denitrated solutions is favorable.

4. Conclusion

Denitration was a highly acceptable method for removing the Zr and Mo. The optimum condition of denitrating was [HCOOH]/[HNO₃]=1.5 and 2.5hr. Under the optimum conditions, the acidity of denitrated solution could be reduced to less than 0.5M, which provided a favorable condition for the next process. Zr could be eliminated at more than 99% and Mo at about 86%. Also, Fe could be removed to about 39%. The above results satisfied the requirements established in this study, except for about 86% precipitation of Mo. The cause on the decrement of Mo precipitation is mainly due to the containing the PGM such as Pd and Ru. The effecting order of each element on the precipitation of Mo increased in the sequence of Pd, Ru >> Fe >> Nd.

Further investigation will be continued in order to advance the precipitation yield of Mo, and to apply
the semi-batch system, which is favourable in view of effective treatment of NO, evolved during denitrification.

References