Nitric Acid Leaching of Base Metals from Waste PDP Electrode Scrap
and Recovery of Ruthenium Content from Leached Residues

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Nitric acid leaching of waste plasma display panel (PDP) electrode scrap was investigated as a part of development for a pre-treatment process to increase Ru content in the scrap. Leaching performance was evaluated in terms of different experimental parameters such as nitric acid concentration, reaction temperature and time.

An aqueous nitric acid leaching solution with a concentration range of 1.5 M–3.0 M at 60°C and 1.5 M–4.2 M at 75°C demonstrated as the most effective condition for the selective removal of Pb and Ba from waste PDP scrap powders with about 90% of Pb and 95% of Ba leached in 30 min. The rate of dissolution decreased after a certain level of HNO₃ concentration due to formation of Pb(NO₃)₂, which has limited solubility in the aqueous solution. Other impurities such as Bi, Zn, Ag and Co were dissolved at the level of 75%–90% at all the leachant concentrations, leaching time and temperatures applied, while Si, Al and Fe showed a poor leachability with only 7%, 30% and 40% dissolution, respectively. Ru and Zr were almost insoluble in an aqueous nitric acid solution. The total concentration of Ru in the undissolved residue (27.96%) of the scrap powder after nitric acid leaching was brought up to 93.8% from the initial concentration (14.43%) of the scrap in the final process. The precipitation behavior of Pb(NO₃)₂ as well as the solubility of SiO₂ were also investigated. [doi:10.2320/matertrans.M2010417]

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Keywords: ruthenium, nitric acid leaching, lead nitrate, solubility, scrap

1. Introduction

Increasing demand for electronic products has generated an increased amount of waste materials, and their disposal problem has necessitated their recycling. Because of their specific physical and/or chemical properties, many essential constituents of electronic components in these waste scraps consist of precious metals, such as Au, Ag, Pt, Pd and Ru. There have been a number of reports¹,² describing the recovery process of precious metals including Ru in the platinum group metals, from these electronic waste scraps. Ruthenium was mainly used as a black pigment in the PDP black electrode paste scrap consisting of non-conducting oxide powder (ruthenium oxides), inorganic binder (fritted glass for adhesion) and organic binder agents. There have also been reports³,⁴ regarding the recovery method of Ru (ruthenium) for a basic hydrometallurgical procedure. However, no details of applicable pre-treatment procedures are available for processing the waste PDP (plasma display panel) black electrode paste scrap that contains Ru together with various other base metals. Because of the low Ru content in these waste PDP scraps, the initial scrap materials need to be firstly concentrated by leaching away the base metals prior to Ru recovery process.

The waste scraps incinerated to remove plastics were usually in the form of ash powder with the ignited paste residues. An appropriate leaching method for these powder residues may be necessary. The recovery of Ru in an acid leaching solution has been described as a difficult process due to its low solubility in acidic solution. The recovery of Ru from these electronic scraps by dissolution process has been reported in the presence of mixture of an oxidizing agent (NaOCl) and chlorine gas (Cl₂), and in case of Ru oxides by alkali fusion.³ In general, the dissolution of ruthenium bearing waste scraps has involved complicated recovery procedures because of a large amount of various metal impurities contained in the scraps. Therefore, to increase the effectiveness of the overall recovery process, a pre-treatment process for the removal of the metal impurities is necessary to increase the ruthenium content in the scrap.

In this work, the leaching behavior of the base metals has been investigated as the first step for Ru recycling from the waste PDP scraps. Nitric acid was selected as the lixiviant since it dissolves most of the base metals, but not Ru.

2. Experimental

Powder samples of typical PDP electrode scrap were prepared through a process involved with a thermal treatment at about 400°C in flowing air in order to remove the plastic material constituents, followed by high speed vibration crushing with a 250 mesh wire separator screen. The average metal composition of the powder scrap thus prepared is shown in Table 1. The leaching experiment with 250 g/L pulp density of the scrap was carried out in a laboratory flask.

Table 1 Elemental composition of as-incinerated sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ru</th>
<th>Pb</th>
<th>Bi</th>
<th>Al</th>
<th>Ba</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>14.43</td>
<td>47.26</td>
<td>0.75</td>
<td>1.70</td>
<td>0.92</td>
<td>28.75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ag</th>
<th>Co</th>
<th>Zn</th>
<th>Fe</th>
<th>Zr</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>0.55</td>
<td>0.49</td>
<td>0.27</td>
<td>0.30</td>
<td>0.27</td>
<td>5.31</td>
</tr>
</tbody>
</table>

Others: Mg, P, Cl, Ca, Ti, Ni, Cu, Hg, etc.
equipped with a thermometer and a reflux condenser by adding the given amount of the sample to the leaching solution. The whole process was agitated for a period of prerequisite time. Then, the solid residue was filtered out and the metal concentrations in the solution as well as the residue were determined by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES). The residue contained lead (Pb) as the major component whilst the other metals, except Si and Ru, were present at very low concentrations each with less than 1%. It is important to increase the ruthenium content in the residue as high as possible for the development of a subsequent overall metal recycling process.

3. Results and Discussion

The performance of leaching with an aqueous nitric acid solution for the dissolution of base metal elements, such as Pb, Ba, Si, Ag, Al, Zn, Bi, Co, and Zr, from the electronic PDP scrap was investigated. HNO₃ is a strong oxidizing reagent that dissolves most base metals present in the scrap. It is worth noting that the dissolution properties of nitric acid has considerable merits over other strong acids that may produce a strong form of precipitates. Furthermore, it can be recovered and recycled.

During the leaching, lead reacts to form soluble lead nitrate according to the following reaction:

\[
Pb + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2 \quad (1)
\]

Barium is also dissolved by nitric acid to form soluble barium nitrate by the following reaction:

\[
Ba + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2 \quad (2)
\]

Similarly, the other base metals such as zinc, silver, bismuth, cobalt, aluminum and iron can also react with nitric acid to form respective nitrates.

Zinc forms zinc nitrate:

\[
3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 4H_2O + 2NO \quad (3)
\]

Silver is oxidized to silver nitrate:

\[
2Ag + 2HNO_3 \rightarrow 2AgNO_3 + H_2 \quad (4)
\]

Cobalt dissolves to form cobalt nitrate:

\[
3Co + 8HNO_3 \rightarrow 3Co(NO_3)_2 + 2H_2O + 2NO \quad (5)
\]

Bismuth also reacts to form bismuth nitrate:

\[
Bi + 4HNO_3 \rightarrow Bi(NO_3)_3 + 2H_2O + NO \quad (6)
\]

Aluminum and iron also form nitrates:

\[
Al + 4HNO_3 \rightarrow Al(NO_3)_3 + 2H_2O + NO \quad (7)
\]

\[
Fe + 4HNO_3 \rightarrow Fe(NO_3)_3 + 2H_2O + NO \quad (8)
\]

Analysis of X-ray diffraction patterns (XRD) for the PDP scrap powder before and after leaching was carried out as shown in Fig. 1. The incineration ash showed only various small peaks belonging to metal compounds due to the presence of a large amounts of non-crystalline elements, while the leach residues (at 60°C) depicted very sharp and strong peaks which were identified mainly as Ru, RuO₂, Pb₂Ru₂O₆, and SiO₂. The scanning electron micrographs (SEM) of the PDP scrap powders before and after leaching were also conducted as shown in Fig. 2. The incineration ash powder showed somewhat irregular morphologies with large agglomerates compared with the leach residues which are small uniform particles with round honeycomb shape formed during decomposition process of metal leaching.

The formation of metal nitrates during the leaching with HNO₃ was also investigated by a precipitation method of

![Fig. 1 XRD patterns of the PDP scrap powders before and after leaching.](image1.jpg)

(a) before  (b) after

![Fig. 2 SEM images of the PDP scrap powders before and after leaching.](image2.jpg)
soluble metal nitrates those extracted from the leaching solution. Figure 3 exhibited the SEM micrographs of the lead nitrate crystals together with the XRD patterns of Pb(NO$_3$)$_2$ and Ba(NO$_3$)$_2$. The result indicated that along with lead and barium nitrates, there might be some other base metal nitrates those formed during leaching process. Thus, an additional analysis for the nitrates was also conducted by the wave length dispersive X-ray spectroscopy (WDX) as shown in Fig. 4. It clearly showed the presence of other various base metals in the nitrates such as, Zn, Co, Fe, Ag, Si, Al, and Bi.

3.1 Effects of nitric acid concentration on dissolution behavior of metals

The leaching behavior of various metals was investigated by varying nitric acid concentration in the range of 0.5–12 M at two different temperatures 60°C and 75°C. Temperature was varied to generate leaching data for different solubility limits of Pb(NO$_3$)$_2$. The metal nitrate phases were precipitated out at room temperature.

The dissolution behavior of major elements Pb, Si, and Ru and that of minor elements such as; Bi, Zn, Ag, Ba, Co, Al, Fe, and Zr present in the scrap at different nitric acid concentration was shown in Fig. 5. As observed from the figure, the dissolution of Pb, Ba, Ag, Zn, Bi and Co were generally high with a range of 80%–90% where Pb and Ba leaching increased up to 4.0 M HNO$_3$ concentration. While Al and Fe showed only about 30% and 40%, respectively, indicating no significant effect of higher concentration of HNO$_3$. Similarly, Si showed low dissolution with maximum recovery amount of 7% at 2.2 M HNO$_3$ concentration. Meanwhile, among all the elements, Ru and Zr were observed to dissolve in less quantity, 0.3% and 0.5%, respectively, at all the nitric acid concentrations studied.

The dissolution behaviors of Pb, Ba, and Si increased with increase of nitric acid concentration and reached maximum value within HNO$_3$ concentration of 1.0–3.5 M and then decreased rapidly to about 10% dissolution for Pb, 2% for Ba, and 0.1% for Si at 11.0 M HNO$_3$. This indicated that the limited solubility of other metal ions present in the aqueous medium did not affect dissolution of these metals significantly.

The final content of metals in the scrap residues after dissolution with 2.2 M HNO$_3$ at 60°C for 60 min is shown in Table 2. This resulted in an increase of Ru content from 14.43% to 27.96% in the residue.

Subsequently, an alkali fusion of the residue was carried out with a mixture of Na$_2$O$_2$ and NaOH, and then the product was dissolved in water. After filtration, the solution was again mixed with HCOOH to form ruthenium hydroxide. A black precipitate containing mainly ruthenium chloride was obtained by treating the ruthenium hydroxide with chlorine in
the presence of NaOCl and NaOH. The content of Ru in the precipitate was analyzed to be 86.6% of the total base metals (Table 3). This indicated that some other base metals in the precipitates are also present in the form of metal chloride particles.

3.2 Effect of lead nitrate solubility on dissolution of Pb, Ba, and Si

To understand the dissolution behavior of Pb, Ba and Si, the change in solubility limit of ionic lead nitrate in an aqueous nitric acid solution was formulated. Data for the solubility of lead nitrate in water can be obtained from the thermodynamic relationship of ‘differential enthalpy of solution’ (9) and experimental data (10).

The changes in solubility limit of ionized lead nitrate with increasing HNO₃ concentration for a saturated solution are estimated from the changes of solubility product from equilibrium constants according to the principle of Le Chatelier-Brown:

The solubility product (Kₛₚ) derived from the equilibrium relationship includes the associated NO₃⁻ and as well as unassociated Pb²⁺ ions in the solution:

$$K_{s_p} = [\text{Pb}^{2+}][\text{NO}_3^-]^2$$

(9)

The dissolution of Pb at 60°C can be compared with the estimated data derived from the solubility product of equilibrium constants as shown in Fig. 6. Also shown is a comparison with 45°C at which the samples are extracted from solution for analysis, along with the variation of [Pb²⁺] ion concentration in the low concentration region. The figure can be explained based on the following criteria: (a) is the leaching extent calculated based on all (NO₃⁻) being used for dissolution, (b) is the predicted complete dissolution of Pb, (c) is the solubility limit line of Pb(NO₃)₂ at 60°C (leaching temperature) and (d) is the solubility limit line of Pb(NO₃)₂ at 45°C (sample extraction temperature for chemical analysis). The overall trends of the calculated and experimental results are similar, with some noticeable differences in the intermediate HNO₃ concentration range. The dissolution of Pb was lower than the estimated values over a wide range of leaching times from 30 to 120 min. This may be because of the decrease in nitric acid concentration due to the formation of complex-metal ions by the presence of high [H⁺] activity (up to 1.0 M). Complex ions formed not only with Pb but also with other metals having high ionic activities (except Ag, all other metals in the scrap are more anodic in electrode potential than Pb). This is also in agreement with the observation of lead oxide compound (Pb₂Ru₂O₆) formation in the solid residues (11).

The dissolution data for Pb in the high concentration region of 3.5–11.0 M showed a reasonable agreement with the results from the solubility data of lead nitrate, which predicted a rapid decrease of the solubility with increasing nitric acid concentration. Such substantially lower dissolution rate, which can be compared with the solubility data at high HNO₃ concentrations, resulted from the difference between the leaching temperature and the sample extraction temperature for chemical analysis by 15°C. The dissolution data of Pb obtained at 75°C also showed a significant dependence on temperature, as shown in Fig. 7. As observed from the figure that at 75°C and 1.5 M HNO₃, Pb dissolution already reached more than 90%, compared with 80% at 65°C.

### Table 2 Elemental composition of HNO₃ leaching residues. (Temperature: 60°C, leaching time: 3600 s)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ru</th>
<th>Pb</th>
<th>Bi</th>
<th>Al</th>
<th>Ba</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>27.96</td>
<td>9.18</td>
<td>0.05</td>
<td>2.12</td>
<td>0.32</td>
<td>50.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ag</th>
<th>Co</th>
<th>Zn</th>
<th>Fe</th>
<th>Zr</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>0.34</td>
<td>0.27</td>
<td>0.17</td>
<td>0.38</td>
<td>0.52</td>
<td>8.38</td>
</tr>
</tbody>
</table>

### Table 3 Elemental composition of ruthenium chloride precipitates.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ru</th>
<th>Pb</th>
<th>Bi</th>
<th>Al</th>
<th>Ba</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>86.60</td>
<td>5.45</td>
<td>0.14</td>
<td>0.57</td>
<td>0.29</td>
<td>0.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ag</th>
<th>Co</th>
<th>Zn</th>
<th>Fe</th>
<th>Zr</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>0.06</td>
<td>0.09</td>
<td>0.43</td>
<td>0.57</td>
<td>0.92</td>
<td>4.31</td>
</tr>
</tbody>
</table>
The Pb dissolution rate started to decrease at 4.2 M HNO₃, compared with (a) leaching extent calculated based on all (NO₃⁻) being used for dissolution, (b) predicted complete dissolution of Ba, and (c) solubility limit line of Ba(NO₃)₂ for 60 °C (leaching temperature) and (d) for 45 °C (sample extraction temperature for chemical analysis).

The Pb dissolution rate started to decrease at 4.2 M HNO₃, whereas in case of 65 °C it started to decrease at 3.3 M.

The dissolution behavior of Ba was also very similar to that of Pb in which the dissolution rate depended on the solubility limit of lead nitrate in HNO₃ aqueous solution. Barium as an impurity with only 0.97% in the total initial metal content of the scrap was also analyzed for solubility dependence of HNO₃ leaching. Thus, the following formula was also used for Ba:

The solubility product \( K_{sp} \) is derived from the equilibrium reaction involved with remaining nitric acids in solution:

\[
K_{sp} = [\text{Ba}^{2+}][\text{NO}_3^-]^2
\]  

According to the above data of solubility product the dissolution of Ba analyzed as shown in Fig. 8, similar to that of Pb, is in better agreement with that of solubility data for actual sampling temperature of 45 °C compared with the leaching temperature of 60 °C. The Ba dissolution at 75 °C, as shown in Fig. 9, also showed a similar behavior. However, it is worth noting that at high HNO₃ concentration region, the Ba dissolution is substantially lower than that derived from solubility data. This result indicated that a fully saturated solution with lead ions may have inhibited Ba for further dissolution into aqueous solution.

Data for the Si dissolution, expressed as the weight percentage of Si dissolved, at different HNO₃ concentrations and leaching times at 60 °C and 75 °C are shown in Fig. 10. Although Si is known to have no direct reaction with HNO₃, the present data for Si showed about 7% dissolution at about 2.2 M HNO₃ concentration. The dissolution behavior of silica in acid solution has been reported,12,13) which indicates formation of amorphous SiO₂, monosilicic acid Si(OH)₄ in an aqueous acidic solution according to:

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4
\]  

It is interesting to note that a similar dissolution trend to that of Pb and Ba depending on the solubility of lead nitrate was obtained in the case of Si above 2.2 M HNO₃. There was appreciable decrease in Si dissolution with increase of HNO₃ concentration. Thus, the dissolution behavior of Si was also affected by the solubility limit of lead nitrate in the aqueous solution. Therefore, lead silicates in the scrap dissolved by removing lead atoms resulted in releasing SiO₂ groups as Si(OH)₂. The silica dissolution is thus related to the leaching behavior of lead.

### 3.3 Variation of [H⁺] during leaching

The variation of [H⁺] concentration reduced by the dissolution of metals from the scrap materials was derived from pH measurement during leaching at 30 min, 60 min, 120 min and for four different concentrations of HNO₃ (1.1, 1.5, 2.1, and 3.3 M), as shown in Fig. 11. It revealed that [H⁺] in solution rapidly decreased during leaching at all four concentrations for an initial time of 30 min and then stabilized till 120 min. Decrease in [H⁺] due to metal oxidation reactions for different concentrations is also plotted in Fig. 12. The amount of [H⁺] involved in the dissolution of metals increased with increasing time and reached more than 90% of the total initial content after 30 min for both 1.1 M and 1.5 M, 120 min for 2.1 M and 3.3 M HNO₃.
generally increased with increasing HNO$_3$ indicated that the reaction time for dissolution of metals was lower than about 1.5 M HNO$_3$ compared with leaching by a solution with a concentration higher than about 1.5 M proceeded at a much slower pace. This suggested that the other impurity metals of about 9.5% observed was only with a less than about 90% dissolution. The overall dissolution behavior of metallic elements in the scrap has generally been characterized on the bases of the following three parameters: (1) solubility limit of the nitrate formed, (2) concentrations of dissolved metals in solution and (3) leaching time.

(1) The dissolution rate of Pb, Ba, and Si are sharply reduced resulting in lead nitrate solubility in solution, while those of Pb and Ba for all their contents in the scrap. The dissolution of Pb and Ba was highly dependent upon the HNO$_3$ concentration in the leaching solution because their properties depended upon the solubility of Pb(NO$_3$)$_2$ in aqueous HNO$_3$ solution. As expected in leaching reactions of base metals mentioned earlier, Pb, Ba, Ag, Zn, Bi and Co were highly reactive with HNO$_3$ resulting in 80–90% dissolution, while Al and Fe were much less reactive with HNO$_3$ resulting in only 30–40% dissolution. Ru and Zr were very little dissolved in HNO$_3$ showing 0.3 and 0.5% dissolution levels, respectively. By dissolving the base metals present in the scrap, the overall ruthenium content was raised to about 28% from about 15% in the starting material. It is thus concluded that nitric acid is an appropriate leaching reagent for the first step toward Ru recovery from waste PDP scraps.

The overall dissolution behavior of metallic elements in the scrap has generally been characterized on the bases of the following three parameters: (1) solubility limit of the nitrate formed, (2) concentrations of dissolved metals in solution and (3) leaching time.

(2) Among the base metals in the scrap, Pb, Ba, Ag, Zn, Bi and Co are highly reactive with HNO$_3$ whilst Al and Fe are not reactive with it having only 30–40% of dissolution. Ru and Zr showed no reactive with HNO$_3$ solution. Silicon does not directly react with HNO$_3$, but is involved in indirect dissolution of SiO$_2$ to form Si(OH)$_4$ in an acidic solution. The dissolution of SiO$_2$ was also influenced by lead nitrate solubility. The lead silicates in the scrap dissolved by removing lead atoms resulted in releasing Si(OH)$_4$. The silica dissolution is thus related to the leaching behavior of lead.

(3) The most effective leaching conditions for Pb and Ba are 60°C, 1.0–1.5 M HNO$_3$ concentration and a reaction time of 30–60 min.

Nitric acid in the concentration range 1.5–3.0 M at 60°C, as well as 1.5–4.0 M at 75°C was considered to be effective for dissolution of both Pb and Ba for all their contents in the scrap. The reaction of [H$^+$] in solution would be sufficient for all of the Pb leached, but on the contrary to what observed was only with a less than about 90% dissolution. Since the equivalent concentration of [H$^+$] in HNO$_3$ solution for dissolution of all the Pb content from the scrap materials is 1.2 M, the amount of [H$^+$] for reaction in solution would be sufficient for all of the Pb leached, but taken 120 min of leaching to reach more than 1.2 M. It is considered that a result of much slow leaching process due to the saturation of complex ions in solution lowering in solubility.

The overall dissolution behavior of metallic elements in the scrap has generally been characterized on the bases of the following three parameters: (1) solubility limit of the nitrate formed, (2) concentrations of dissolved metals in solution and (3) leaching time.

(1) The dissolution rate of Pb, Ba, and Si are sharply reduced by an increase in HNO$_3$ concentration resulting from a decrease in lead nitrate solubility in solution, while those of the rest of the base metals in the scrap were not affected by the solubility reduction of lead nitrate.

(2) Among the base metals in the scrap, Pb, Ba, Ag, Zn, Bi and Co are highly reactive with HNO$_3$ whilst Al and Fe are not reactive with it having only 30–40% of dissolution. Ru and Zr showed no reactive with HNO$_3$ solution. Silicon does not directly react with HNO$_3$, but is involved in indirect dissolution of SiO$_2$ to form Si(OH)$_4$ in an acidic solution. The dissolution of SiO$_2$ was also influenced by lead nitrate solubility. The lead silicates in the scrap dissolved by removing lead atoms resulted in releasing Si(OH)$_4$. The silica dissolution is thus related to the leaching behavior of lead.

(3) The most effective leaching conditions for Pb and Ba are 60°C, 1.0–1.5 M HNO$_3$ concentration and a reaction time of 30–60 min.

Based on the data of HNO$_3$ leaching experiments conducted as the first step for pre-treatment process of Ru recovery from waste PDP electrode scraps, the following conclusions can be drawn:

4. Concluding Remarks

Fig. 11 The variation of [H$^+$] in leaching solution as a function of time.

Fig. 12 The decrease in [H$^+$] in leaching solution as a function of time.

Fig. 13 The average rate of [H$^+$] depletion up to 30 min as a function of nitric acid concentration.
Acknowledgement

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REFERENCES