Leaching of Yttrium and Europium from Waste CRT Phosphor by Subcritical Water Extraction

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E-waste: end of life electrical and electronic appliances

2014: 41.8 million (Mt)

2018: 50 million (Mt)

(Baldé et al., 2015)
E-waste are landfilled or incinerated

Cathode ray tube (CRT) is being replaced by new technologies (i.e. PDP and LCD) and accounts for over 70% of e-waste worldwide. (Yu et al., 2015; Singh et al., 2016)
**CRT phosphor**

CRT phosphor presents as a layer on the glass surface in CRT of display devices.

**Phosphors:**
- Red phosphor: $\text{Y}_2\text{O}_2\text{S}$-based (activated with Eu)
- Green/Blue phosphor: ZnS-based

*Figure 1. The structure of a cathode ray tube (Habib Al Razi, 2016)*
Yttrium (Y) & europium (Eu)

Rare earth metals

They are widely used in phosphor materials, magnetic substances, alloys, and catalysts.

Strategic material
\textbf{Source of waste CRT phosphor}

The waste of CRT phosphor was taken from a waste recycling company in Taichung, Taiwan, 2016.

- Amount of phosphor:
  1) 6.3 g phosphor/ CRT TV
  2) 2.8 g phosphor/ monitor

Pb-containing glass generated in the cutting unit of the recycling process.
Conventional REEs recovery methods

**Acid leaching**
- Inorganic acid.
- Time: 3~6h.
- Temperature: 70~125°C.
  (Rabah, 2008; Resende and Morais, 2010; Innocenzi et al., 2013; Yang et al., 2013)

**Solvent extraction / Precipitation**
- Traditional solvent extraction: DEHPA (Yang et al., 2016)
- Supercritical fluid extraction: TBP: HNO₃: H₂O (Shimizu et al., 2005)
- Ionic liquid extraction: DODGAA in [C4mim][Tf₂N]
  (Yang et al., 2013)
- Precipitation: Oxalic acid (Pan et al., 2013)

**Subcritical Water Extraction**

(REEs concentrate) → Calcination → (REEs oxalate)
Subcritical water extraction (SWE)

Subcritical water technology

Immobilization

Extraction

Hydrothermal synthesis

Also called superheated water extraction and pressurized hot water extraction (PHWE).
(Yoswathana and Eshtiaghi, 2013)

Enhanced mass transfer!

SWE is an environment-friendly technique that can provide higher extraction yields from solid samples.
(Abdelmoez et al., 2014)

The dielectric constant <<

The ion product of water (Kw) >>

The viscosity of water <<

(Moller et al., 2011).

Enhanced mass transfer!

Temperature: 100-374 °C

Pressure: under enough pressure to maintain the liquid phase state (usually from 10 to 60 bar)

(Mukherjee, 2016)
Objectives

✓ Recycle Y & Eu from waste CRT phosphor by **subcritical water extraction**.

✓ **Sequential extraction** is used to investigate the speciation of heavy metals in waste CRT phosphor residue.
**Experimental procedure**

- **Sieving**: (100 mesh)
- **Acid Solution**: 0.50 g of CRT phosphor with 50 mL acid solution
- **Oven**: Heating time: 40 ± 10 min
  Reaction time: 30 min
  Cooling time: 30 ± 10 min
  Pi: 10 kg/cm²
  Temperature: 100 – 150 °C stirring at 300 rpm.
- **Filtration**: Through a 0.22 μm cellulose ester membrane

Sequential extraction procedure was following Tessier et al, 1979.
**SWE apparatus**

Legend of picture:
1. Glass chamber.
3. Stirring equipment.
4. Subcritical water reactor.
5. Pressure gauge.
6. Thermocouple-controlled heating equipment.
Results and Discussion

Characteristics of waste CRT phosphor

✓ XRF result:

Table 1. Chemical compositions of waste CRT phosphor was analyzed by XRF.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content (wt%)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>42.20 ± 2.70</td>
<td>Ir</td>
<td>0.50 ± 0.42</td>
</tr>
<tr>
<td>Pb</td>
<td>11.76 ± 2.37</td>
<td>Ti</td>
<td>0.18 ± 0.31</td>
</tr>
<tr>
<td>Zn</td>
<td>11.75 ± 0.58</td>
<td>Sb</td>
<td>0.16 ± 0.025</td>
</tr>
<tr>
<td>As</td>
<td>7.82 ± 0.61</td>
<td>Cd</td>
<td>0.12 ± 0.018</td>
</tr>
<tr>
<td>K</td>
<td>7.16 ± 0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>6.49 ± 0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>3.04 ± 0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>2.65 ± 0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>2.58 ± 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>2.40 ± 0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>2.06 ± 1.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.75 ± 0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.74 ± 0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Dominant elements: Si, Pb, and Zn
2. Rare earths: Y and Eu
3. Heavy metals: Cu, Pb, Zn, Ni, As
**Total metal content:**

Table 2. The elemental content of CRT phosphor was determined by aqua-regia digestion.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content (mg/g)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>80.85 ± 1.23</td>
<td>K</td>
<td>1.19 ± 0.40</td>
</tr>
<tr>
<td>S</td>
<td>61.30 ± 1.24</td>
<td>Sb</td>
<td>1.14 ± 0.18</td>
</tr>
<tr>
<td>Y</td>
<td>44.56 ± 0.32</td>
<td>Mn</td>
<td>0.74 ± 0.04</td>
</tr>
<tr>
<td>Pb</td>
<td>40.95 ± 3.15</td>
<td>Zr</td>
<td>0.41 ± 0.03</td>
</tr>
<tr>
<td>Fe</td>
<td>15.11 ± 0.77</td>
<td>Ga</td>
<td>0.37 ± 0.01</td>
</tr>
<tr>
<td>Na</td>
<td>9.82 ± 3.03</td>
<td>As</td>
<td>0.25 ± 0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>7.23 ± 1.64</td>
<td>In</td>
<td>0.22 ± 0.15</td>
</tr>
<tr>
<td>Al</td>
<td>5.88 ± 0.54</td>
<td>Ce</td>
<td>0.15 ± 0.005</td>
</tr>
<tr>
<td>Ir</td>
<td>5.63 ± 0.61</td>
<td>Ni</td>
<td>0.09 ± 0.002</td>
</tr>
</tbody>
</table>

- The dissolution of CRT phosphor was **34.74 - 36.83%**.
- Chen and Ma (2001) reported that silicate minerals would not be digested by aqua-regia.
✓ XRD results:

**Figure 4.** XRD patterns of original waste CRT phosphor

**Figure 5.** XRD patterns of waste CRT phosphor after aqua-regia digestion

![XRD graph showing SiO₂ peaks](image)
Effect of acid type

Extraction (%) = \left( \frac{Cs}{Ct} \right) \times 100

Ct: Total concentration of metal determined by aqua-regia digestion.
Cs: Concentration remaining in the extractant.

Leaching efficiency using 0.5M acid at 100 °C of (a) Y and Eu and (b) heavy metals

\begin{align*}
\text{(a)} \\
\text{Concentration (mg/L)} & \\
\text{HCl} & (2.60\%) \\
\text{H}_2\text{SO}_4 & (22.15\%) \\
\text{HNO}_3 & (22.90\%) \\
\text{Acid} & \\
\end{align*}

\begin{align*}
\text{(b)} \\
\text{Concentration (mg/L)} & \\
\text{HCl} & (96.08\%) \\
\text{H}_2\text{SO}_4 & (9.84\%) \\
\text{HNO}_3 & (28.89\%) \\
\text{Acid} & \\
\end{align*}
Effect of acid concentration

Leaching efficiency using H₂SO₄ at 100°C of Y and Eu

- The higher concentration of acid could result in higher extraction efficiency.
Effect of reaction temperature

Temperature effect on SWE using 0.75M H₂SO₄ at 100°C to 150°C of Y and Eu

- The higher temperature results in higher extraction efficiency.
• No Y-containing compounds could be detected in the SWE residue.

**Figure 11.** XRD patterns of residue after SWE in 0.75M H$_2$SO$_4$ at 150 °C.
Sequential extraction

Figure A.1 Schematic diagram of the sequential extraction procedure.

0.3g of residue from SWE

8 mL of 1 M MgCl₂ (pH 7, 1 h, 25°C, stirring at 120rpm)
Residual

8 mL of 1 M NaOAc (pH 5, 5 h, 25°C, stirring at 120rpm)
Residual

20 mL of NH₄OH-HCl in 2.9% v/v HOAc (6h, 96°C)
Residual

Centrifugation at 10,000 rpm for 30 min between each fraction and filtrated by 13 mm syringe with 0.22 μm PVDF membrane.

Analysis

Fraction 1
Exchangeable

Fraction 2
Carbonates

Fraction 3
Fe-Mn oxides

Fraction 4
Organic matter

Fraction 5
Residual

20 mL of Aqua regia mixture
Sequential extraction

- The percentage association state of Y, Eu and Zn were stable and Pb was potentially mobile.

Fractionation of Y, Eu, Zn and Pb in original waste CRT phosphor
Figure 13. Fractionation of heavy metals in original waste and residue of SWE (a) Zn (b) Pb

Raw SWE -0.1C/T100
Raw SWE -0.1S/T100
Raw SWE -0.1N/T100
Raw SWE -0.5C/T100
Raw SWE -0.5S/T100
Raw SWE -0.5N/T100
Raw SWE -0.75S/T100
Raw SWE -0.75S/T125
Raw SWE -0.75S/T150

0 20 40 60 80 100
Zn (%)

F1- Exchangeable
F2- Carbonates bound
F3- Fe/Mn bound
F4- Organic matter bound
F5- Residue (Aqua-regia)

0 20 40 60 80 100
Pb (%)

F1- Exchangeable
F2- Carbonates bound
F3- Fe/Mn bound
F4- Organic matter bound
F5- Residue (Aqua-regia)

• SWE effectively stabilized Zn and Pb in solid residues and significantly transformed them into F4 or F5, which reduced the risk to the environment
Conclusions

• The **100% extraction** of Y and Eu could be extracted with low concentration of acid (0.75 M) compare to previous study (2.0-5.0 M).

• High efficiency and selectivity could achieved by $\text{H}_2\text{SO}_4$ in the extraction of Y and Eu.

• The extractive efficiency of Y and Eu increased with increasing **acid concentration** ($\text{H}_2\text{SO}_4$).

• Extraction efficiency of Y and Eu increased with increasing **temperature** ($\text{H}_2\text{SO}_4$).

• Heavy metals (**Zn and Pb**) in waste CRT phosphor transformed into stable phase after SWE.
Thank you very much!