Utilization of Al-/Fe-/Si- Ceramic Matrices for Cadmium Detoxification in Wastes

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Comprehensive

Being to be High-level

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Main routes for entry of cadmium into the food chain and uptake by human. (Vromman, V., et al., 2008)

- Kidney damage
- Skeleton deformation
- Lung cancer

Since 1990s, Cd was classified as a group 1 carcinogen (Program 2014)
Cadmium Production and Utilizations


World cadmium refinery production (ton)
(Data in metric tons of cadmium content unless otherwise noted—USGS, 2014)

<table>
<thead>
<tr>
<th>Country</th>
<th>2012</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>380</td>
<td>380</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>Canada</td>
<td>1,100</td>
<td>800</td>
</tr>
<tr>
<td>China</td>
<td>7,300</td>
<td>7,400</td>
</tr>
<tr>
<td>India</td>
<td>620</td>
<td>630</td>
</tr>
<tr>
<td>Japan</td>
<td>1,800</td>
<td>1,900</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>1,300</td>
<td>1,400</td>
</tr>
<tr>
<td>Korea, Republic of</td>
<td>3,000</td>
<td>3,900</td>
</tr>
<tr>
<td>Mexico</td>
<td>1,624</td>
<td>1,630</td>
</tr>
<tr>
<td>Netherlands</td>
<td>560</td>
<td>560</td>
</tr>
<tr>
<td>Peru</td>
<td>684</td>
<td>685</td>
</tr>
<tr>
<td>Poland</td>
<td>530</td>
<td>400</td>
</tr>
<tr>
<td>Russia</td>
<td>700</td>
<td>850</td>
</tr>
<tr>
<td>Other countries</td>
<td>880</td>
<td>870</td>
</tr>
<tr>
<td><strong>World total (rounded)</strong></td>
<td><strong>20,900</strong></td>
<td><strong>21,800</strong></td>
</tr>
</tbody>
</table>

Batteries
Pigments
Coating
Stabilizer
Alloys and solar cell

20 tons of cadmium discharged into the Liujiang River (Guangxi, China) by a mining plant, causing severe cadmium pollution affecting up to 4 million people. (Reported in January, 2012)

A ¥ 40.7 billion project (began in 1979) to restore cadmium contaminated farmland in the Jinzu River basin, Japan. (Reported in March, 2012)
Common Treatment of Cadmium Bearing Waste

- Solidification/stabilization (S/S) process
  - Bauxite (Miller, B. B., et al., 2004)
  - Kaolin (Yao, H., et al., 2005)
  - Montmorillonite (MMT) and silica (Lee, M.-H., et al., 2005)
  - Calcium oxide (Miller, B. B., et al., 2006)
  - Alumina (Kuo, J.-H., et al., 2009)
  - Cement based wastes forms (Polettini, A., et al., 2002)

Drawbacks:
The need of additional stabilization due to the weak binding ability of sorbents by physical or chemical adsorption.
Proposed Technology for Cadmium Stabilization

Techniques

Ceramic Sintering Process (CSP)

Environmentally Friendly

Waste-to-Resources

Thermally converting them into non-hazardous / less hazardous products.

Aluminum-rich materials

Or

Iron-rich materials

Sintering

Ceramic products

With high acidic resisting ability

Equilibrium Diagrams of Cd-Al-O and Cd-Fe-Mg-O Systems

Cd-Al-O system (Colin, 1968)

Cd-Fe-Mg-O system (Bashkirov and Kornilova 1980)

% of elements in the Earth’s Crust

- Oxygen: 46%
- Silicon: 28%
- Aluminum: 8%
- Iron: 6%
- Calcium: 4%
- Sodium: 8%
- Potassium: 6%
- Titanium: 4%
- Others: 8%
Sample Preparation, Characterization and Evaluation

CdO

Mixtures

Stoichiometric ratios of Cd/Al and Cd/Fe.

Matrices

Fired pellets

SEM/TEM

CPLT + ICP

Major characterization and analysis techniques

Microstructure observation

Qualitative analysis

Quantitative analysis

Stabilization effect evaluation

Milled & Dried

Pelletized at ~250 Mpa

Sintering

Cd-Al-O phase

Ground

Powder

γ-Al₂O₃

γ-Al₂O₃

CdO + γ-Al₂O₃
Quantification Quality Evaluation for QXRD analysis

"R-pattern", \( R_p \), \( R_p = \frac{\sum |Y_{o,m} - Y_{c,m}|}{\sum Y_{o,m}} \)

"R-weight pattern", \( R_{wp} \), \( R_{wp} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{w_m Y_{o,m}^2}} \)

"R-expected", \( R_{exp} \), \( R_{exp} = \sqrt{\frac{\sum M - P}{\sum w_m Y_{o,m}^2}} \)

"Goodness of fit", GOF, \( GOF = \chi^2 = \frac{R_{wp}}{R_{exp}} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{M - P}} \)

Incorporation Efficiency Evaluation

\[
TR(\%) = \frac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite}} \times \frac{\text{wt.\% of CdO}}{\text{MW of CdO}} + \frac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite}}
\]

Leached Metals Normalization

\[
NLC_{d_{SA}} = 10^{-6} \times \frac{n}{k} \times \frac{C_{Cd} \times AW_{Cd}}{SW \times SA \times MW_{Phase}}
\]
CdO + 2γ-Al₂O₃ → CdAl₄O₇ (Monoclinic structure)

CdO + α-Fe₂O₃ → CdFe₂O₄ (Spinel)

Incorporation Efficiency

Transformation ratios

\[
TR(\%) = \frac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite} + \text{wt.\% of CdO}} \times \frac{\text{MW of CdO}}{\text{wt.\% of Aluminate or Ferrite}}
\]

The transformation ratios (TR, %) for cadmium incorporation into CdAl₄O₇ monoclinic structure and CdFe₂O₄ spinel.
Leachability of CdAl\(_4\)O\(_7\) and CdFe\(_2\)O\(_4\)

Leached at constant pH 4.0.

\[
\text{CdO} (s) + 2H^+_{(eq)} \rightarrow \text{Cd}^{2+}_{(eq)} + H_2O
\]

\[
\text{CdAl}_4\text{O}_7(s) + 14H^+_{(eq)} \rightarrow \text{Cd}^{2+}_{(eq)} + 4\text{Al}^{3+}_{(eq)} + 7H_2O
\]

\[
\text{CdFe}_2\text{O}_4(s) + 8H^+_{(eq)} \rightarrow \text{Cd}^{2+}_{(eq)} + 2\text{Fe}^{3+}_{(eq)} + 4H_2O
\]

Formation of robust crystalline structures

\[
\text{CdO} + 2\gamma-\text{Al}_2\text{O}_3 \rightarrow \text{CdAl}_4\text{O}_7 (\text{Monoclinic structure})
\]

\[
\text{CdO} + \alpha-\text{Fe}_2\text{O}_3 \rightarrow \text{CdFe}_2\text{O}_4 (\text{Spinel})
\]

Detoxification of the hazardous wastes
Leaching Behavior of CdAl₄O₇ and CdFe₂O₄

The soluble Cd and Al concentrations in the leachates of CdAl₄O₇ monoclinic structure and (b) the soluble Cd and Fe concentrations in the leachates of CdFe₂O₄ spinel.

<table>
<thead>
<tr>
<th>Molar Ratios of [Al]/[Cd] in CdAl₄O₇ Leachates</th>
<th>Molar Ratios of [Fe]/[Cd] in CdFe₂O₄ Leachates</th>
</tr>
</thead>
<tbody>
<tr>
<td>At pH 4.0</td>
<td></td>
</tr>
<tr>
<td>[Al]$^{3+}_{(aq)}$ should be 6.3×10⁻² M (1701 mg/L),</td>
<td>[Fe]$^{3+}_{(aq)}$ should be 1.05×10⁻⁵ M (0.59 mg/L),</td>
</tr>
<tr>
<td>The [Al]/[Cd] molar ratios in CdAl₄O₇ leachates and</td>
<td></td>
</tr>
<tr>
<td>[Fe]/[Cd] molar ratios in CdFe₂O₄ leachates.</td>
<td></td>
</tr>
</tbody>
</table>

Incongruent dissolution

The (a) soluble Cd and Al concentrations in the leachates of CdAl₄O₇ monoclinic structure and (b) the soluble Cd and Fe concentrations in the leachates of CdFe₂O₄ spinel.
Cadmium-hosting Product Phase Formation via Sintering with Si-rich Ceramic Matrices

CdO + SiO₂ → CdSiO₃
2CdO + SiO₂ → Cd₂SiO₄
3CdO + SiO₂ → Cd₃SiO₅

XRD patterns of sintered (a) CdO + silica fume and (b) CdO + α-quartz samples with various Cd/Si molar ratios (Cd/Si molar ratio = 1.0, 2.0, and 3.0) at 950 °C for 3 h.

Views of sintered CdO + silica fume and CdO + α-quartz samples with Cd/Si molar ratios (Γ = 1.0, 2.0, and 3.0) at 950 °C for 3 h.
Efficiency of Cadmium Incorporation into Cadmium Silicates

- With silica fume
  \( \text{Cd/Si} = 1.0 \)

- With quartz
  \( \text{Cd/Si} = 1.0 \)

- With silica fume
  \( \text{Cd/Si} = 2.0 \)

- With quartz
  \( \text{Cd/Si} = 2.0 \)

- With silica fume
  \( \text{Cd/Si} = 3.0 \)

- With quartz
  \( \text{Cd/Si} = 3.0 \)
Leachability of CdO, CdSiO$_3$, Cd$_2$SiO$_4$ and Cd$_3$SiO$_5$
A successful reduction of cadmium under acidic environments, identifying a promising and safe avenue for cadmium-laden sludge treatment.

\[
\text{CdO} + 2\gamma-\text{Al}_2\text{O}_3 \rightarrow \text{CdAl}_4\text{O}_7 \text{ (Monoclinic structure)}
\]

\[
\text{CdO} + \alpha-\text{Fe}_2\text{O}_3 \rightarrow \text{CdFe}_2\text{O}_4 \text{ (Spinel)}
\]
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Thanks!