Solidification/stabilization of hazardous materials for recycling the industrial wastes

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Categories of wastes in Korea

Wastes
- household waste
- General industrial waste
- Industrial waste
- Construction waste
- Sewage sludge
- Hazardous industrial waste

By generated field & industry

Wastes
- Waste with high heavy metal content
  - Recover potential energy value from the wastes
  - Enhance process efficiency
- Waste with low heavy metal content

→ Need to new recycling field for the consumption of the wastes
Many countries recognize that although the recycling is the best solution in their disposal, it may not be viable, economically or due to the fact that recycling also generates further wastes.
The co-incineration technique consists of partial substitution of raw materials or fuel for waste in a high temperature industrial process in such a manner that the waste is destroyed, the generated ash is incorporated in the product, and the product quality is not affected.

The co-incineration process provides an economy to the process in addition to providing a hazardous waste treatment method.
### Comparison cement kiln with incinerator

#### Cement Industry
- **Temperature**: above 1,450°C → decomposition of hazardous substances
- **Residence time**: 5 sec
- **Residue**: None → zero pollution
- **Remarks**: • need for homogenizing of components  
  - control of heavy metals  
  - control of volatile components  
  • use of present facilities  
  • mass treatment

#### Incinerator
- **Temperature**: above 850°C
- **Residence time**: 2 sec
- **Residue**: 20-30 wt.% of raw waste
- **Remarks**: • high volume and weight reduction  
  • generation of residues  
  • secondary pollution

### Detailed Comparison

<table>
<thead>
<tr>
<th>Item</th>
<th>Cement kiln</th>
<th>Incineration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>above 1,450°C → decomposition</td>
<td>above 850°C</td>
</tr>
<tr>
<td>Residence time</td>
<td>5 sec</td>
<td>2 sec</td>
</tr>
<tr>
<td>Residue</td>
<td>None → zero pollution</td>
<td>20-30 wt.% of raw waste</td>
</tr>
</tbody>
</table>
| Remarks             | • need for homogenizing of components  
  - control of heavy metals  
  - control of volatile components  
  • use of present facilities  
  • mass treatment | • high volume and weight reduction  
  • generation of residues  
  • secondary pollution |
Recycling amount of wastes in cement industry

- **Sludge & dust, slag etc**
  - '99: 0.1
  - '03: 0.4

- **Sewage sludge**
  - '99: 0.1
  - '03: 0.4

- **Coal ash**
  - '99: 1.5
  - '03: 2.6

- **MSWI ash**
  - '99: 0.0
  - '03: 0.0

Increase rate for waste application in cement industry: about 10%, annually

To increase ratio of recycling amount, the studies on how to reuse as raw material in cement industry

Especially, municipal solid wastes have to be used in cement industry
Emerging Technologies for Environmental Friendly Materials

- Sludge & dust, slag etc
- Sewage sludge & Construction waste
- Fly & bottom ash

Manufacture Tec.:
- Ordinary Portland Cement
- Special cement (CSA cement) (Calcium sulfo-aluminate)
- Eco-cement (CCA cement) (Calcium chroline-aluminate)

Control wastes Tech.:
- Mixing & Crushing
- Separation
- Content of water
- Storage of wastes

Volatilization/condensing of volatile substances
Heat distribution change in kiln
Incomplete sintering/yellow clinker

Discharge of hazardous substances
- Dioxin
- CO gas
- SO₂ & NOₓ gas

Envir. Stability of Products

Storage of wastes

Korea Institute of Geoscience and Mineral Resources
Emerging Technologies for Environmental friendly Materials in Korea

- **Treatment Tec.**
  - Control wastes Tech.
    - Mixing & Crushing
    - Separation
    - Content of water
  - Storage of wastes

- **Manufacture Tec.**
  - Volatilization/condensing of volatile substances
  - Heat distribution change in kiln
  - Incomplete sintering/yellow clinker

- **Products**
  - Ordinary Portland Cement
  - Special cement (CSA cement) (Calcium sulfo-aluminate)
  - Eco-cement (CCA cement) (Calcium chroline-aluminate)

- **Protect Env.**
  - Discharge of hazardous substances
    - Dioxin
    - CO gas
    - SOx & NOx gas
  - Envir. Stability of Products

**Content of our research**

- Slag & Dust from POSCO
- MSWI bottom ash

- Behavior of chlorine & volatile substance in Kiln
- Produce OPC in Plant

- Calcium sulfo-aluminate cement synthesis from slag from iron making industry
- Calcium chroline-aluminate cement synthesis from MSWI ash
- Ordinary Portland cement Manufacturing from inorganic wastes

- Behavior of circulation of toxic gas
- Estimation of discharge gas for air environment

Applying waste as the raw material to cement industry, it is possible to influence to the cement products and process.

→ To use wastes in cement industry, it is necessary to research on the behavior of heavy metals and alkali chlorine, and influence on the cement properties.
A Pretreatment for Cl Removal and Stabilization of Heavy Metal to Recycle Municipal Solid Waste Incineration Bottom Ash
- Generation of municipal solid waste in 2003: about 15 million tons
### Category of municipal solid waste incineration ash

<table>
<thead>
<tr>
<th>Ash Category</th>
<th>Location</th>
<th>Korea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>Material discharged from the bottom of incinerator</td>
<td>Bottom ash</td>
</tr>
<tr>
<td>Grate Siftings or Riddlings</td>
<td>Material dropped through grate</td>
<td></td>
</tr>
<tr>
<td>Grate Ash</td>
<td>Material remaining after excluding grate siftings from bottom ash</td>
<td></td>
</tr>
<tr>
<td>Heat Recovery Ash(HRA)</td>
<td>Particulate material collected from the heat recovery system</td>
<td></td>
</tr>
<tr>
<td>Fly Ash</td>
<td>Particulate material transported to the top of the incinerator and removed from flue gas.</td>
<td>Fly ash</td>
</tr>
<tr>
<td>APC Residue</td>
<td>Mixed material collected from APC system including fly ash, injected adsorbent, flue gas condensate</td>
<td></td>
</tr>
</tbody>
</table>
Environmental hazardousness - dioxin

Amount of dioxins and furans in bottom ash in various countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Facility</th>
<th>Total Dioxins (PCDD)</th>
<th>Total Furans (PCDF)</th>
<th>1/TEQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>GVRD</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PEI</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>LVH</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SWARU</td>
<td>&lt;2.0*10^-3</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>QUC</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>Germany</td>
<td>A</td>
<td>3.6<em>10^-3, 3.9</em>10^-3</td>
<td>9.6*10^-3</td>
<td>1.8*10^-3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4.1<em>10^-4, 4.8</em>10^-3</td>
<td>9.1*10^-3</td>
<td>2.0*10^-3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>2.5<em>10^-2, 2.9</em>10^-3</td>
<td>9.4*10^-4</td>
<td>0.8*10^-3</td>
</tr>
<tr>
<td>USA</td>
<td>Mid-Corn</td>
<td>4.0<em>10^-3, 3.1</em>10^-3</td>
<td>1.000-500</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dry Scrubber1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dry Scrubber2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dry Scrubber3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Guidelines for soil pollution of dioxin in various countries

<table>
<thead>
<tr>
<th>Countries</th>
<th>Objects</th>
<th>(Pg-TEQ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>playground</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>residential district</td>
<td>1,000</td>
</tr>
<tr>
<td></td>
<td>park</td>
<td>1,000</td>
</tr>
<tr>
<td></td>
<td>commercial and industrial area</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td>farm land</td>
<td>5-40</td>
</tr>
<tr>
<td>Netherlands('97)</td>
<td>town</td>
<td>1,000</td>
</tr>
<tr>
<td>Sweden('96)</td>
<td>Residential district, farm land, playground</td>
<td>10</td>
</tr>
<tr>
<td>USA</td>
<td>EPA('98)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>residential district</td>
<td>1,000</td>
</tr>
<tr>
<td></td>
<td>Commercial and industrial area</td>
<td>5,000 ~ 20,000</td>
</tr>
<tr>
<td>HHS/ATSDR('97)</td>
<td>town</td>
<td>1,000</td>
</tr>
</tbody>
</table>

● Amount of dioxin in bottom ash satisfies environmental guidelines for soil pollution of dioxin

Amount of dioxins in bottom ash of Korea

<table>
<thead>
<tr>
<th>2,3,7,8-sustritution</th>
<th>Bottom ash I</th>
<th>Bottom ash D</th>
</tr>
</thead>
<tbody>
<tr>
<td>pg-TEQ/g</td>
<td>pg-TEQ/g</td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-TCDF</td>
<td>0.44</td>
<td>0.00</td>
</tr>
<tr>
<td>1,2,3,7,8-PCDF</td>
<td>0.14</td>
<td>0.02</td>
</tr>
<tr>
<td>2,3,4,7,8-PCDF</td>
<td>3.65</td>
<td>0.92</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDF</td>
<td>0.41</td>
<td>0.09</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.87</td>
<td>0.14</td>
</tr>
<tr>
<td>2,3,4,6,7,8-HxCDF</td>
<td>1.14</td>
<td>0.22</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.18</td>
<td>0.24</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.53</td>
<td>0.03</td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDF</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>OCDF</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>PCDFs</td>
<td>7.44</td>
<td>1.70</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>0.77</td>
<td>0.00</td>
</tr>
<tr>
<td>1,2,3,7,8-TCDD</td>
<td>0.96</td>
<td>0.00</td>
</tr>
<tr>
<td>1,2,3,4,7,8-TCDD</td>
<td>0.26</td>
<td>0.18</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>0.76</td>
<td>0.29</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.58</td>
<td>0.21</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.53</td>
<td>0.04</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>PCDDs</td>
<td>3.99</td>
<td>0.72</td>
</tr>
<tr>
<td>PCDDS/DFs</td>
<td>11.43</td>
<td>2.42</td>
</tr>
</tbody>
</table>
Removal & Solidification of chloride in MSWI bottom ash

- Synthesis of calcium chlorine-aluminate cement (CCA cement) -
Environmental harmfulness of chloride

**Municipal solid waste**
- battery
- ceramics
- vinyl
- food waste

**Volume-rate garbage disposal system**

**incineration**

**poisonousness**
- Chloroform
- Chlorite
- Chlorate

→ synthesis

**Soil**

 Adsorption
- clay
- Fe/Mn Oxide
- organic matter

→ soil pollution

**incineration**

**chloride and salts**
- NaCl
- KCl
- CaCl₂·6H₂O

**ionization**
- Cl⁻

**heavy metals and its compound**
- Metal Oxide
  - Cd²⁺
- Metal Hydroxide
  - Zn²⁺
- M(III)³⁺

**Adsorption**
- clay
- Fe/Mn Oxide
- organic matter

→ soil pollution

**Soil**

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→ soil pollution

**Soil**

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- KCl
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- Metal Hydroxide
  - Zn²⁺
  - M(III)³⁺

**Adsorption**
- clay
- Fe/Mn Oxide
- organic matter

→ soil pollution

**Soil**
Removal of chloride

- Chloride removal of above 85% within 30 minutes
- Residual chloride content of bottom ash: 0.2-0.3%

(L/S ratio: 10, Temp.: 20°C)
Characteristics of CCA cement

Calcium-chloroaluminate (11CaO·7Al₂O₃·CaCl₂) cement

- Incineration ash utilised as a "fill-in" material in the cement composition.

The sintering temperature of CCA clinker:
- Ordinary cement: approximately 1,450°C
- Ecocement: approximately 1,350°C

Reduction of CO₂ emission

Application: Soil stabilization projects

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>Ig.Loss</th>
<th>Insol</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>R₂O</th>
<th>Cl</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecocement</td>
<td>0.8</td>
<td>0.2</td>
<td>15.2</td>
<td>10.2</td>
<td>1.9</td>
<td>60.3</td>
<td>1.4</td>
<td>8.8</td>
<td>0.7</td>
<td>0.5</td>
<td>100.0</td>
</tr>
<tr>
<td>Ordinary cement</td>
<td>0.6</td>
<td>0.1</td>
<td>22.2</td>
<td>5.1</td>
<td>3.2</td>
<td>65.1</td>
<td>1.4</td>
<td>1.6</td>
<td>0.7</td>
<td>0.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical properties (%)</th>
<th>CsS</th>
<th>C₆S</th>
<th>C₆A</th>
<th>C₁₁A₇·CaCl₂</th>
<th>C₄AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecocement</td>
<td>68.1</td>
<td>4.5</td>
<td>—</td>
<td>24.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Ordinary cement</td>
<td>52.7</td>
<td>23.5</td>
<td>8.2</td>
<td>—</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Main components of incineration ash: Al₂O₃, SiO₂, Fe₂O₃, CaO.

Incineration ash contains the main components that are necessary to produce ordinary cement.
# Application field of CCA cement

## Solidification agents

### Building construction
- **Soil stabilisation**
- **Solidification of dredged and excavated materials.**

### Concrete structures / products

#### Building construction
- Concrete blocks
- Hollow blocks
- Cemented board using wood
- Cemented board: Autoclaved Lightweight Concrete panel

#### Civil engineering
- Interlocking blocks
- Concrete blocks
- Tetrapods and other marine structures

### Images
- Interlocking blocks
- Concrete blocks
- Cemented board: using wood
Chemical composition of Municipal solid waste incineration bottom ash

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>ZnO</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom ash I</td>
<td>24.70</td>
<td>10.27</td>
<td>1.07</td>
<td>8.78</td>
<td>2.21</td>
<td>23.29</td>
<td>3.47</td>
<td>1.65</td>
<td>0.21</td>
<td>5.75</td>
<td>1.10</td>
<td>2.7</td>
</tr>
<tr>
<td>Bottom ash D</td>
<td>27.50</td>
<td>8.50</td>
<td>0.98</td>
<td>9.48</td>
<td>2.20</td>
<td>25.49</td>
<td>2.50</td>
<td>2.00</td>
<td>0.25</td>
<td>4.70</td>
<td>1.20</td>
<td>2.5</td>
</tr>
</tbody>
</table>

XRD patterns of (a) bottom ash I and (b) bottom ash D with various temperatures

Synthesis of calcium chloroaluminate: above 1,000°C
<table>
<thead>
<tr>
<th>Additive ratio of CCA(%)</th>
<th>Curing time(day)</th>
<th>Concentration of heavy metal in leaching (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>Cu</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0.010</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.028</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.037</td>
<td>ND</td>
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<tr>
<td>5</td>
<td>1</td>
<td>0.028</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.011</td>
<td>ND</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0.027</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.015</td>
<td>ND</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0.041</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.03</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.028</td>
<td>ND</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>0.037</td>
<td>ND</td>
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<td>28</td>
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<tr>
<td>15</td>
<td>1</td>
<td>0.031</td>
<td>ND</td>
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<tr>
<td></td>
<td>28</td>
<td>0.011</td>
<td>ND</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0.030</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.012</td>
<td>ND</td>
</tr>
</tbody>
</table>

Environmental criteria

It satisfies the environmental standard and regulation
Solidification & stabilization of heavy metals in MSWI bottom ash
Environmental harmfulness of chloride

- Chloride and salts
  - NaCl
  - KCl
  - CaCl₂·6H₂O

- Ionization
  - Cl⁻

- Poisonousness
  - Chloroform
  - Chlorite
  - Chlorate

- Synthesis

- Heavy metals and its compound
  - Metal Oxide
  - Metal Hydroxide
  - Al(Mn, Fe)²⁺ M(Ⅱ⁺) Oxide

- Soil
  - Adsorption
    - Clay
    - Fe/Mn Oxide
    - Organic matter
  - Soil pollution

- Incineration
  - Volume-rate garbage disposal system
Objectives
- Stabilization of soluble salts
- Stabilization of hydrogen-forming metals (such as aluminum)
- Proper maintenance of moisture
- Control of pH by carbonization reaction and stabilization of heavy metals
- Time requirement for 3-6 months

Aging requirement of bottom ash for road materials

- U.S
  - ageing for 60 days for using as aggregates of concrete
  - ageing for 30 days for using as pavement materials

- France
  - ageing for 3-6 months

- Germany
  - ageing for 3 months for recycling of bottom ash

- England
  - ageing for 3-6 months for using as aggregates of concrete
Stabilization/conversion of bottom ash during aging

Quenching of bottom ash - Unstable -

- CaO + H₂O → Ca(OH)₂
  Calcium oxide          Portlandite
- CaSO₄ + 1/2H₂O → CaSO₄·1/2H₂O
- Dissolution of salts

Ageing for 3 months - Semi-stable & stable -

- Ion solidification
- Ca(OH)₂ + CO₂ → CaCO₃
  Portlandite          Calcite
- Fe₂O₃ → Y - Fe₂O₅ → α - Fe₂O₃
- Expansion of aluminum

Ageing for several years - Stable -

- Ion solidification
- CaSO₄·1/2H₂O + 1/2H₂O
  → CaSO₄·2H₂O
  Gypsum
- α - Fe₂O₃ → FeOOH
- Feldspars → Kaolinite

Quenching of bottom ash - Unstable -

- CaO + H₂O → Ca(OH)₂
  Calcium oxide          Portlandite
- CaSO₄ + 1/2H₂O → CaSO₄·1/2H₂O
- Dissolution of salts

Ageing for 3 months - Semi-stable & stable -

- Ion solidification
- Ca(OH)₂ + CO₂ → CaCO₃
  Portlandite          Calcite
- Fe₂O₃ → Y - Fe₂O₅ → α - Fe₂O₃
- Expansion of aluminum

Ageing for several years - Stable -

- Ion solidification
- CaSO₄·1/2H₂O + 1/2H₂O
  → CaSO₄·2H₂O
  Gypsum
- α - Fe₂O₃ → FeOOH
- Feldspars → Kaolinite
Carbonation for Fixation of Metals in MSWI Bottom Ash

\[
\text{Cd}^{2+} + \text{CO}_2 \rightarrow \text{CdCO}_3 \quad K_{sp} = 2.6 \times 10^{-1}
\]

\[
\text{Zn}^{2+} + \text{CO}_2 \rightarrow \text{ZnCO}_3 \quad K_{sp} = 2.4 \times 10^{-1}
\]

\[
\text{Pb}^{2+} + \text{CO}_2 \rightarrow \text{PbCO}_3 \quad K_{sp} = 3.8 \times 10^{-2}
\]

\[
\text{Cu}^{2+} + \text{CO}_2 \rightarrow \text{CuCO}_3 \quad K_{sp} = 7.5 \times 10^{-1}
\]
Solubility product constant of heavy metals compound (25°C)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Phosphate</th>
<th>Hydroxide</th>
<th>Sulfide</th>
<th>Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr²⁺</td>
<td>CrPO₄</td>
<td>Cr(OH)₂</td>
<td></td>
<td>7.1×10⁻⁷</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>2.5×10⁻⁷</td>
<td>Cr(OH)₃</td>
<td></td>
<td>6.3×10⁻⁴</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Mn(OH)₂</td>
<td>MnS</td>
<td>MnCO₃</td>
<td>2.3 10⁻²</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>2.3</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Pb₃(PO₄)₂</td>
<td>Pb(OH)₂</td>
<td>PbS</td>
<td>PbCO₃</td>
</tr>
<tr>
<td></td>
<td>2.3×10⁻⁴</td>
<td>7.1×10⁻²</td>
<td>2.1×10⁻⁶</td>
<td>3.8×10⁻²</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Cd₃(PO₄)₂</td>
<td>Cd(OH)₂</td>
<td>CdS</td>
<td>CdCO₃</td>
</tr>
<tr>
<td></td>
<td>4.1×10⁻²</td>
<td>1.1</td>
<td>2.5×10⁻⁹</td>
<td>2.6×10⁻¹</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Hg₂HPO₄</td>
<td>Hg₂S</td>
<td>Hg₂CO₃</td>
<td>5.4×10⁻¹ⁱ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Hg(OH)₂</td>
<td>HgS</td>
<td></td>
<td>2.4×10⁻¹</td>
</tr>
<tr>
<td></td>
<td>CuOH</td>
<td>Cu₂S</td>
<td></td>
<td>8.1×10⁻¹³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.2×10⁻¹¹</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Cu₃(PO₄)₂</td>
<td>Cu(OH)₂</td>
<td>CuS</td>
<td>CuCO₃</td>
</tr>
<tr>
<td></td>
<td>3.1×10⁻³</td>
<td>1.1×10⁻²</td>
<td>1.6×10⁻¹¹</td>
<td>7.5×10⁻¹</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Zn₃(PO₄)₂</td>
<td>Zn(OH)₂</td>
<td>ZnS</td>
<td>ZnCO₃</td>
</tr>
<tr>
<td></td>
<td>3.0×10⁻²</td>
<td>5.2×10⁻¹</td>
<td>4.3×10⁻¹</td>
<td>2.4×10⁻¹</td>
</tr>
</tbody>
</table>

Solubility of heavy metals hydroxides
### pH change

<table>
<thead>
<tr>
<th>Samples</th>
<th>Aging period(month)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>bottom ash I</td>
<td></td>
<td>12.3</td>
<td>11.5</td>
<td>11.3</td>
<td>11.1</td>
<td>9.4</td>
</tr>
<tr>
<td>bottom ash D</td>
<td></td>
<td>12.5</td>
<td>12.2</td>
<td>12.0</td>
<td>11.8</td>
<td>10.2</td>
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</table>

### Leaching concentration of heavy metals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging period (month)</th>
<th>pH</th>
<th>Cr</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>bottom ash I</td>
<td>0</td>
<td>12.3</td>
<td>0.13</td>
<td>3.26</td>
<td>0.06</td>
<td>ND</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.4</td>
<td>0.03</td>
<td>1.73</td>
<td>ND</td>
<td>ND</td>
<td>0.06</td>
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<tr>
<td>bottom ash D</td>
<td>0</td>
<td>12.5</td>
<td>0.15</td>
<td>4.41</td>
<td>0.05</td>
<td>ND</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>10.2</td>
<td>0.10</td>
<td>1.8</td>
<td>0.02</td>
<td>ND</td>
<td>0.05</td>
</tr>
</tbody>
</table>

| Leaching criteria of Korea | 1.5 | 3.0 | 1.5 | 0.3 | 3.0 |
### Leaching of heavy metals with pH

#### bottom ash I

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>12.94</td>
<td>141.75</td>
<td>27.6</td>
<td>0.976</td>
<td>1.73</td>
</tr>
<tr>
<td>4.0</td>
<td>1.80</td>
<td>32.37</td>
<td>4.4</td>
<td>0.710</td>
<td>0.84</td>
</tr>
<tr>
<td>6.8</td>
<td>0.0043</td>
<td>3.68</td>
<td>0.6</td>
<td>0.150</td>
<td>0.34</td>
</tr>
<tr>
<td>8.3</td>
<td>0.27</td>
<td>3.40</td>
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<td>0.59</td>
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<td>9.4</td>
<td>0.48</td>
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<td>ND</td>
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<td>ND</td>
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<td>0.50</td>
<td>5.26</td>
<td>ND</td>
<td>ND</td>
<td>2.83</td>
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Criteria of leaching: 1.5 | 3.0 | 1.5 | 0.3 | 3.0

#### bottom ash D

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>3.57</td>
<td>94.45</td>
<td>30.0</td>
<td>1.26</td>
<td>1.98</td>
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<tr>
<td>3.8</td>
<td>0.30</td>
<td>17.12</td>
<td>5.4</td>
<td>0.90</td>
<td>0.90</td>
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<tr>
<td>5.7</td>
<td>ND</td>
<td>2.97</td>
<td>3.3</td>
<td>0.34</td>
<td>0.44</td>
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<td>7.7</td>
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<td>1.67</td>
<td>1.6</td>
<td>0.0016</td>
<td>0.51</td>
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<td>9.1</td>
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<td>1.77</td>
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<td>ND</td>
<td>0.25</td>
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<tr>
<td>12</td>
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<td>2.45</td>
<td>ND</td>
<td>ND</td>
<td>0.67</td>
</tr>
<tr>
<td>13</td>
<td>0.3</td>
<td>3.49</td>
<td>ND</td>
<td>ND</td>
<td>5.49</td>
</tr>
</tbody>
</table>

Criteria of leaching: 1.5 | 3.0 | 1.5 | 0.3 | 3.0
## Concentration of leached heavy metals with pH change by carbonation

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu</th>
<th>Pb</th>
<th>Cr</th>
<th>Cd</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.3</td>
<td>5.1</td>
<td>0.6</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>11</td>
<td>4.0</td>
<td>0.5</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>1.3</td>
<td>0.5</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>9</td>
<td>1.1</td>
<td>0.5</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>1.3</td>
<td>0.7</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>criteria</td>
<td>3.0</td>
<td>3.0</td>
<td>1.5</td>
<td>0.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

- pH 10-8 satisfied the environmental standards and regulation
Cu leaching by carbonation
- diminishment above 50% (3.7ppm $\rightarrow$ 1.3ppm)
Comparison of natural weathering and carbonation

**Carbonation**

<table>
<thead>
<tr>
<th>Aging period (month)</th>
<th>pH</th>
<th>Cu</th>
<th>Pb</th>
<th>Cr</th>
<th>Cd</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12.3</td>
<td>5.1</td>
<td>0.6</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>4.0</td>
<td>0.5</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1.3</td>
<td>0.5</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>1.1</td>
<td>0.5</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>1.3</td>
<td>0.7</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>criteria</td>
<td></td>
<td>3.0</td>
<td>3.0</td>
<td>1.5</td>
<td>0.3</td>
<td>1.5</td>
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</table>

**Natural weathering**

<table>
<thead>
<tr>
<th>Samples</th>
<th>pH</th>
<th>Aging period (month)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>I bottom ash</td>
<td></td>
<td>11.7</td>
</tr>
<tr>
<td>D bottom ash</td>
<td></td>
<td>12.3</td>
</tr>
</tbody>
</table>

**Leaching of heavy metals**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging period (month)</th>
<th>pH</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>I bottom ash</td>
<td>0</td>
<td>12.3</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.4</td>
<td>0.03</td>
</tr>
<tr>
<td>D bottom ash</td>
<td>0</td>
<td>12.5</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>10.2</td>
<td>0.10</td>
</tr>
<tr>
<td>criteria</td>
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<td></td>
<td>1.5</td>
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</table>
## Characteristics of wastewater after treatment

<table>
<thead>
<tr>
<th>Sample Items</th>
<th>Waste water</th>
<th>criterion</th>
<th>Sample Items</th>
<th>Waste water</th>
<th>criterion</th>
<th>Sample Items</th>
<th>Waste water</th>
<th>criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>T–N</td>
<td>12.1</td>
<td>&lt;60</td>
<td>Zn</td>
<td>0.03</td>
<td>&lt;5</td>
<td>F</td>
<td>0.30</td>
<td>&lt;15</td>
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<tr>
<td>T–P</td>
<td>7.03</td>
<td>&lt;8</td>
<td>Cu</td>
<td>0.05</td>
<td>&lt;3</td>
<td>Color</td>
<td>42</td>
<td>&lt;400</td>
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<tr>
<td>Phenol</td>
<td>ND</td>
<td>&lt;5</td>
<td>Hg</td>
<td>ND</td>
<td>&lt;0.005</td>
<td>ABS</td>
<td>0.56</td>
<td>&lt;5</td>
</tr>
<tr>
<td>N–hexane extracts</td>
<td>ND</td>
<td>M*: &lt;5</td>
<td>Organophosphorus</td>
<td>ND</td>
<td>&lt;1</td>
<td>E.Coli</td>
<td>&lt;2</td>
<td>&lt;3,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O**: &lt;30</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>0.002</td>
<td>&lt;1</td>
<td>As</td>
<td>0.001</td>
<td>&lt;0.5</td>
<td>PCB</td>
<td>ND</td>
<td>&lt;0.003</td>
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<tr>
<td>BOD</td>
<td>42.5</td>
<td>&lt;30</td>
<td>Pb</td>
<td>0.09</td>
<td>&lt;1</td>
<td>TCE</td>
<td>ND</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>COD</td>
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<td>&lt;40</td>
<td>Cr</td>
<td>ND</td>
<td>&lt;0.5</td>
<td>PCE</td>
<td>ND</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>0.05</td>
<td>&lt;10</td>
<td>Mn</td>
<td>0.02</td>
<td>&lt;10</td>
<td>pH</td>
<td>9.5</td>
<td>5.8–8.6</td>
</tr>
</tbody>
</table>

* : Mineral oil  
** : Oil and fat of animals and plants

- Quality of wastewater satisfies the environmental standard and regulation
Carbonation process for capsulation

- Increase of volume/gravity: \( \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \): 11.8% (\( \text{Ca(OH)}_2 \) gravity(volume) : 2.24g/mol(33.0ml), \( \text{CaCO}_3 \) gravity(volume) : 2.71(36.9ml)

- Decrease of porosity, enhancement of strength: formation of C–S–H gel, Calcite, ettringite

- Decrease of pH: pH of lowest solubility for metal hydroxides(pH 8–9.5)

- Formation of stable heavy metal compounds
  - Pb: formation of PbCO\(_3\)
  - Cd: formation of hydroxicarbonates
  - Ni, Co: substitution of Ca in C–S–H
  - Ba: formation of BaCO\(_3\), BaSO\(_4\)

- Capsulation effect: immobilization of heavy metals
## Chemical composition of bottom ash

### The content of Cu and Pb in bottom ash

<table>
<thead>
<tr>
<th>size (mm)</th>
<th>Cu (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cr (ppm)</th>
<th>Ni (ppm)</th>
<th>Cd (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Over 4.75</td>
<td>2938</td>
<td>618</td>
<td>333</td>
<td>112</td>
<td>12</td>
</tr>
<tr>
<td>2.36-4.75</td>
<td>2592</td>
<td>880</td>
<td>327</td>
<td>133</td>
<td>28</td>
</tr>
<tr>
<td>1.18-2.36</td>
<td>3511</td>
<td>1849</td>
<td>496</td>
<td>171</td>
<td>22</td>
</tr>
<tr>
<td>0.6-1.18</td>
<td>2299</td>
<td>1412</td>
<td>442</td>
<td>145</td>
<td>24</td>
</tr>
<tr>
<td>0.3-0.6</td>
<td>2592</td>
<td>1202</td>
<td>489</td>
<td>167</td>
<td>33</td>
</tr>
<tr>
<td>0.15-0.3</td>
<td>1818</td>
<td>1075</td>
<td>378</td>
<td>135</td>
<td>35</td>
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<tr>
<td>Under 0.15</td>
<td>1602</td>
<td>985</td>
<td>394</td>
<td>137</td>
<td>43</td>
</tr>
</tbody>
</table>

### Chemical composition and pH in fresh and carbonated bottom ash

<table>
<thead>
<tr>
<th>Size (mm)</th>
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<th>Al(%)</th>
<th>Zn(%)</th>
<th>Na(%)</th>
<th>Cu</th>
<th>Pb</th>
<th>Cr</th>
<th>Ni</th>
<th>Cd</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18-2.36</td>
<td>17.4</td>
<td>4.55</td>
<td>0.6</td>
<td>4.35</td>
<td>3511</td>
<td>1849</td>
<td>496</td>
<td>171</td>
<td>22</td>
<td>11.74</td>
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</tbody>
</table>
Carbonation reactor

Reactor of carbonation process

● Condition of dry carbonation

- CO₂ flow rate: 1.0 L/min
- Water content: 20%

● Condition of wet carbonation

- Liquid/Solid: 10
- CO₂ flow rate: 1.0 L/min
# Leaching amount of Heavy metals & pH according to wet/dry carbonation

<table>
<thead>
<tr>
<th></th>
<th>fresh bottom ash (St. Limited)</th>
<th>bottom ash after wet carbonation</th>
<th>bottom ash after dry carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (ppm)</td>
<td>3.26(3.0)</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>1.54(3.0)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>pH</td>
<td>11.74</td>
<td>7.96</td>
<td>9.02</td>
</tr>
</tbody>
</table>

- Leaching amounts of Cu and Pb decrease with the wet/dry carbonation
- pH of MSWI bottom ash also decreases via the wet/dry carbonation
# Change in surface area, volume, and pore size of MSWI bottom ash via wet/dry carbonation

<table>
<thead>
<tr>
<th></th>
<th>Fresh Bottom Ash</th>
<th>Bottom Ash after Wet Carbonation</th>
<th>Bottom Ash after Dry Carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>1.2233</td>
<td>3.5269</td>
<td>2.3892</td>
</tr>
<tr>
<td>Volume (m²/g)</td>
<td>0.1047</td>
<td>0.7587</td>
<td>0.3317</td>
</tr>
<tr>
<td>Pore Size (cm³/g)</td>
<td>0.00046</td>
<td>0.000401</td>
<td>0.000154</td>
</tr>
</tbody>
</table>

- Surface area, and volume increase with the wet/dry carbonation
- Pore size decreases via the wet/dry carbonation
- In particular, the pore size is drastically decreased by dry carbonation
Surface Analysis of MSWI bottom ash with SEM

- Without carbonation
- With wet carbonation
- With dry carbonation

- Capsulation effect: immobilization of heavy metals
- Wet carbonation < Dry carbonation

- Products (Calcium carboantes)
- Capsulation effect: immobilization of heavy metals
- Wet carbonation < Dry carbonation

Carbonated zone

Products: Calcium carboantes
Stability of Heavy metals

Wet carbonation system

- Carbonation process effects the pH of solution: 11.9 → 7.9
- Change in solubility of Cu and Pb
- Leaching amounts of Cu and Pb decrease

with dry carbonation

- Carbonation process forms carbonates on the surface of MSWI bottom ash
- Capsulation effect
- Leaching amounts of Cu and Pb decrease

A Long term stability

Wet carbonation < Dry carbonation
Pretreatment using in U.S and European countries

Problems in recycling of bottom ash

- leaching of Cu, Pb, Cd
- instable physical properties (expansion)
- high chloride content

Weathering

- Stabilization of heavy metals
- Stable properties

Need of long period for 3-6 months
- Lack of stockpile
- Low effect of chloride removal

Developing technology

Weathering effect

- Stabilization of heavy metals
- Stable properties

- Shortening of stabilization period
- Chloride removal

Korea Institute of Geoscience and Mineral Resources
Pilot scale (60L)

1. Treatment of wastewater
2. Agitator type
3. Rotation type
Lay-out of pilot plant

Capacity : 100kg/hr

- Incineration plant
- Vibrating screen
- Magnetic separator
- Feed hopper
- Non-ferrous separator
- Rotary kiln
- Trommel
- Coarse aggregate silo
- Equipment for Fixation of heavy metals & Removal of Cl
- Wastewater treatment
- Fine aggregate silo
Solidification of Heavy metals in Cement industry

- Clinkering Reaction
- Hydration Reaction
Solidification of Heavy metals in Cement industry

- Clinkering Reaction
- Hydration Reaction
Main minerals of clinker

- $C_3S$ : Tricalcium Silicate – Alite
  \((Ca_{0.98}Mg_{0.01}Al_{0.0067}Fe_{0.0033})3(Si_{0.97}Al_{0.03})O_5\)
- $C_2S$ : Dicalcium Silicate – Belite
  \(Ca_2Fe_{0.05}Al_{0.05}Si_{0.90}O_3.95\)
- $C_4A$ : Aluminate Phase
  \(K_{0.05}Na_{0.05}Ca_{0.76}Mg_{0.08}Ti_{0.01}(Fe_{0.22}Al_{1.60}Si_{0.18})O_6\)
- $C_2AF$ : Ferrite Phase – Celite
  \(Ca_3AlFe_{0.8}Mg_{0.2}Si_{0.15}Ti_{0.05}O_5\)

Clinkering reaction in kiln

- **Breakdown of clays and iron ore**
  - Kaolinite + CaCO$_3$ → $C_3S$ + CA + H$_2$O + 5CO$_2$
  - 2CaCO$_3$ + Fe$_2$O$_3$ → C$_2$F + CO$_2$

- **Liq. formation**
  - 2CaO + SiO$_2$ → C$_2$S
  - CaO + C$_2$S → C$_3$S
  - 2CaO + C$_2$F → C$_4$AF

- **Carbonation of SiO$_2$ + CaO**
  - 800 ~ 1000 °C

- **Carbonate dissociation**
  - 700 ~ 900 °C

- **Release of SiO$_2$, Al$_2$O$_3$ of clays**
  - 350 ~ 900 °C

- **Formation of $C_3S$**
  - 900 ~ 1200 °C

- **Cooling zone**: 1450 °C

- **Sintering zone**: 12 min

- **Transition zone**: 15 min

- **Preheater**: < 1 min
Solidification of heavy metals in Clinkers

**Tricalcium silicate (Alite)**

\[
Ca_{106}Mg_2(Na_{0.25}K_{0.25})Fe_{0.5}(Al_2Si_{34})O_{180}
\]

Alite containing small amounts of iron, magnesium, potassium, sodium, aluminum and titanium occurs in Portland cement

- **Substitution of Si\(^{4+}\) ion by Ti\(^{4+}\) in tetrahedral site**
  

- **Substitution of Zn\(^{2+}\) for Ca\(^{2+}\) site**
  

- **Substitution of Cr\(^{3+}\) for Ca\(^{2+}\) site**
  

**Dicalcium silicate (Blite)**

\[
Ca_{87}MgAlFe(Na_{0.25}K_{0.25})Al_2Si_{42}O_{180}
\]

Blite containing small amounts of magnesium, aluminum, iron, sodium, and potassium occurs in Portland cement clinker

- **Calcium silicate networks** retain large amount of Cd, Pb, Cr and Zn
  
  [M. A. Trezza et al., Cem. Con. Res. 30 (2000) 137-144]
Result of EDX experiment

- **MgO**
- **Al**
- **Ca**
- **S**
- **CuCr PbZn**
- **Mg**
- **Cr**
- **Ca**
- **Si**
- **CrZn**
- **Al**
- **Ca**
- **Fe**

Chemical compounds:
- **4CaO·3Al_2O_3·SO_3**
- **2CaO·SiO_2**
- **4CaO·Al_2O_3·Fe_2O_3**

Micrographs and EDX spectra.
Changes in crystal structure via substitution of each heavy metal

- Especially, the change in 211 plane
- As addition of heavy metal, the crystal structure of CSA was slightly distorted
- In case of Pb is added, a big change at 1,100°C
- Crystal shrinkage occurred by the vaporization of Pb at 1,100°C.
In this research, chose the calcium sulfoaluminate, because it can produce ettringite by self-hydration reaction.
Solidification of Heavy Metals in hydrates; Ettringite & Tobermorite (C-S-H)

- **Substitution of SO$_4^{2-}$ ion by CrO$_4^{2-}$ or SeO$_4^{2-}$** in tetrahedral site
- **Substitution of Al$^{3+}$ ion by Cr$^{3+}$** in Octahedral site

Ettringite [3CaO•Al$_2$O$_3$•3CaSO$_4$•32H$_2$O]

- **Ca/Si ratio increase**
  - Paired Si tetrahedron
  - Bridging Si tetrahedron
  - Interlayer Ca$^{2+}$
  - Ca-O sheet: sevenfold-coordinated Ca-O polyhedron

However, it does not make completely fixation because C-S-H itself is known as very unstable hydrates.
The crystals have two distinct structural components:
Columns, \(\{\text{Ca}_6[\text{Al(OH)}_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}\), and Channels, \(\{(\text{SO}_4)^3 \cdot 2\text{H}_2\text{O}\}^{-}\).

- **Column structure**
  - Substitution of \(\text{Al}^{3+}\) ion by \(\text{Cr}^{3+}, \text{Ni}^{3+}, \text{Mn}^{3+}\) or in octahedral site
  - Substitution of \(\text{Ca}^{2+}\) ion by \(\text{Pb}^{2+}, \text{Cd}^{2+}, \text{Co}^{3+}\) or in polyhedral site

- **Channel structure (intercolumnar)**
  - Substitution of \(\text{SO}_4^{2-}\) ion by \(\text{CrO}_4^{2-}, \text{AsO}_4^{3-}\) or \(\text{SeO}_4^{2-}\) in tetrahedral site
To extent the immobilization potential of ettringite in the field under specific conditions

competing ion effect

The degree of the substitution of oxyanions into the ettringite structure depends largely on competing effects between oxyanions
**Synthesis of Cr\textsuperscript{III} or VI-Ettringite**

\[ 6\text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 + 36\text{H}_2\text{O} \rightarrow \text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O} \]

**In distilled water with Cr \textsuperscript{3+}**

- Ultrasonic transducer
- Sonic horn
- \text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}

**In distilled water with Cr \textsuperscript{6+}**

- Ultrasonic transducer
- Sonic horn
- \text{Ca}_6[\text{Al(OH)}_6]_2(\text{CrO}_4)_3 \cdot 26\text{H}_2\text{O}

- \text{Cr}^{3+} \rightleftharpoons \text{Al}^{3+}

- Competing ions

- \text{Cr}^{3+}: 300\text{mg/kg}
- \text{Cr}^{6+}: 300\text{mg/kg}

- \text{CrO}_3 \text{ or } \text{CrCl}_3 (0.005)

Ettringite is the main phase in the products of all synthesis systems.

But, in the case containing Cr(III) monosulfate formed together with ettringite.
Ettringite is only shown with the column-crystalline in distilled water and in the solution containing Cr(VI).

But monosulfate with plate shape is found to be formed together with that of ettringite in solution containing Cr(III).

This results well agree with that of XRD measurement.
Cr\(^{3+}\) is almost substituted during the reaction, but in case of Cr\(^{6+}\), a large amount of chrome ions are detected in solution after reaction.

This results means that a fixed quantity of Cr\(^{6+}\) is only substituted into ettringite crystal, and most of them did not participate into the reaction.
FT-IR spectrum of ettringite synthesized in solution containing Cr\textsuperscript{6+} are very similar to that of ettringite in distilled water.

Especially, absorbance peak attributed to CrO\textsubscript{4} vibration did not shown at 867-902cm\textsuperscript{-1}.

But the absorbance peak at 785.325 closely matched the peak attribute to Cr\textsuperscript{3+}-compounds in the spectrum of ettringite synthesized in solution with CrCl\textsubscript{3}.

- **Cr(VI) (CrO\textsubscript{4})**: 886cm\textsuperscript{-1}, 867-902cm\textsuperscript{-1}
- **Cr(III)**: 750-850cm\textsuperscript{-1}, 798cm\textsuperscript{-1}
In distilled water

\[ 6 \text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 + 36 \text{H}_2\text{O} \rightarrow \text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 26 \text{H}_2\text{O} \]

In solution with Cr(III)

\[ 6 \text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 + m \text{CrCl}_3 + 36 \text{H}_2\text{O} \]

\[ \rightarrow (1-n)\{\text{Ca}_6[\text{Al}(1-m\cdot\text{Cr}^{m/2(1-n)})(\text{OH})]_2(\text{SO}_4)_3 \cdot 26 \text{H}_2\text{O}\} + n(2-m)\text{Al}^{3+} + m\text{Cl}^{-} + 6n\text{Ca}^{2+} + 3n(\text{SO}_4)^{2-} + m\text{H}_2\text{O} \]

\[ \rightarrow (1-n)\{\text{Ca}_6[\text{Al}(1-m\cdot\text{Cr}^{m/2(1-n)})(\text{OH})]_2(\text{SO}_4)_3 \cdot 26 \text{H}_2\text{O}\} + n\{\text{Ca}_4[\text{Al-OH}]_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}\} + 2n\text{CaSO}_4 + 2nm\text{Al(OH)}_3 + m\text{Cl}^{-} \]

Ettringite  \[ n<<1 \]  Monosulfate

In solution with Cr(VI)

\[ 6 \text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 + n \text{CrO}_3 + 36 \text{H}_2\text{O} \]

\[ \rightarrow (1-m)\text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 26 \text{H}_2\text{O} + m\text{Ca}_6[\text{Al(OH)}_6]_2(\text{CrO}_4)_3 \cdot 26 \text{H}_2\text{O} \]

\[ \rightarrow (1-m)\text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 26 \text{H}_2\text{O} + m\text{Ca}_6[\text{Al(OH)}_6]_2(\text{CrO}_4)_3 \cdot 26 \text{H}_2\text{O} + n-m\text{Cr}^{6+} +(\text{OH}) + \text{H}_2\text{O} \]

Ettringite  \[ m: \text{not much} \]
Thank You!