CO₂ MINERAL CARBONATION BY OIL SHALE WASTES FROM ESTONIAN POWER PRODUCTIONS

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1. Background

**CO\textsubscript{2} atmospheric concentration**
- 280 ppm (pre industrialization) → 384 ppm (2007)
- Annual growth rate 2 ppm since the year 2000

Meeting the challenge of anthropogenic climate change:

**Adaption**

**Mitigation:**
- **Counter measures:** natural fixation into biomass, dissolution into ocean
- **Direct reduction:**
  - **Improved efficiency**
  - **Fuel switching:** lower C/H ratio, nuclear power, renewable energy
  - **CO\textsubscript{2} capture and storage:** geological storage, ocean storage,

**CO\textsubscript{2} sequestration by mineral carbonation**

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CO₂ sequestration by mineral carbonation

- Waste residues (from power sector, steel industry and cement industry)

  + Usually situated near the CO₂ emission source
  + Main reactive species are Ca-silicates, CaO, Ca(OH)₂
  - Limited storage capacity

  No mining, low transport costs!
  More reactive towards CO₂!
  Not enough for serious reduction of CO₂ emissions!

Extra value:
+ Stabilization of waste material
+ By-products with high commercial value (PCC)
Heat and power production in Estonia is based on combustion of oil shale:

Since 1959 pulverized firing (PF). Since 2004 also the circulating fluidized bed combustion (CFBC).

Accompanied by:

1. High CO₂ emissions
   + mineral CO₂ from carbonate decomposition
   Total: 948 – 1199 t CO₂/GWh

2. Formation of alkaline ash
   ~ 5 million tons annually
   (Ash content of oil shale is 42 – 48%)

- Ash contains up to 25% of free CaO which strongly basifies (pH 13) transportation waters formed during hydraulic transport of ash.
- Ca- and Mg-oxides and silicates could in certain conditions be the binders of CO₂.

Emissions and waste flows from energy production

![Emissions and waste flows from energy production](image)

Oil shale opencast, N-E Estonia

Oil shale seam, underground mine, N-E Estonia

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Estonian oil shale is a carbonaceous fine-grained sedimentary rock of Ordovician age containing 10–60\% kerogen (solid organic matter), 20–70\% carbonates represented by limestone, or more rarely by dolomite, and 15–60\% siliciclastic minerals.

During combustion of one tonne of oil shale 450-550 kg of ash is produced (in case of mineral coal only 100 kg of ash is produced).
2. Characterization of ashes

Circulated fluidized bed combustion (CFBC)

- BA (bottom ash) ~30%
- INT (Intrex ash) ~11%
- ECO (economizer ash) ~6%
- PHA (air preheater ash) ~3%
- ESPA ~50%

Pulverized firing (PF)

- BA (bottom ash) ~15%
- SHA (superheater ash)
- ECO (economizer ash) ~15%
- CA (cyclone ash) ~60%
- ESPA (electrostatic precipitator ash) ~10%

\[ t = \text{720-800°C, } k_{\text{CO}_2} = 0.75-0.85 \]
\[ t = \text{1250-1400°C, } k_{\text{CO}_2} = 0.97 \]
## Phase composition

<table>
<thead>
<tr>
<th></th>
<th>CFBC ash</th>
<th>PF ash</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lime CaO</strong></td>
<td>3.2-19.9%</td>
<td>14.3-29.3%</td>
</tr>
<tr>
<td><strong>Periclase MgO</strong></td>
<td>3.3-7.0%</td>
<td>3.8-7.9%</td>
</tr>
<tr>
<td><strong>Melilite (Ca,Na)(_2)(Mg,Al)(Si,Al)(_3)O(_7)</strong></td>
<td>1.0-3.6%</td>
<td>3.2-18.9%</td>
</tr>
<tr>
<td><strong>Merwinitie Ca(_3)Mg(SiO(_4))(_2)</strong></td>
<td>3.0-5.2%</td>
<td>6.5-13.2%</td>
</tr>
<tr>
<td><strong>Belite Ca(_2)SiO(_4)</strong></td>
<td>4.6-7.3%</td>
<td>12.3-20.3%</td>
</tr>
<tr>
<td><strong>Wollastonite CaSiO(_3)</strong></td>
<td>1.4-3.4%</td>
<td>0.7-2.6%</td>
</tr>
<tr>
<td><strong>Orthoclase, KAlSi(_3)O(_8)</strong></td>
<td>1.3-15.6%</td>
<td>1.7-9.7%</td>
</tr>
<tr>
<td><strong>Quarz SiO(_2)</strong></td>
<td>5.6-17.7%</td>
<td>1.6-10.4%</td>
</tr>
<tr>
<td><strong>Calcite CaCO(_3)</strong></td>
<td>4.0-34.8%</td>
<td>2.0-7.6%</td>
</tr>
<tr>
<td><strong>Anhydrite CaSO(_4)</strong></td>
<td>8.8-29.9%</td>
<td>4.6-24.1%</td>
</tr>
</tbody>
</table>

Quantitative XRD performed at Institute of Geology, UT

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Morphology

**CFBC ash**
- Irregular shape;
- Porous and uneven surface;
- The glassy phase is not formed.

**PF ash**
- Regular spherical shape;
- Smooth surface;
- The glassy phase is formed.

SEM analysis performed by Dr. V. Mikli at Center of Material Research, TUT
3. Concept of CO₂ mineralization

- The amount of CO₂ emitted during oil shale-based heat and power generation could be diminished by intensification of natural CO₂-binding process occurring during ash transportation and deposition.
- At the same time the alkaline effect of waste ashes is reduced.
4. Reaction Mechanism

In the context of CO₂ sequestration and ash stabilization, the availability of lime for hydration and carbonation reactions is of key importance.

- Impact of solution composition
- Impact of specific surface area
Ca-Mg-silicates in aqueous carbonation process

- $Ca/Mg$-silicate (s) + 2$H^+$ (aq) $\rightarrow$ $(Ca/Mg)^{2+}$ (aq) + $SiO_2$ (s) + $H_2O$ (l)
- $CaSiO_3 + 2H^+ (aq) \rightarrow Ca^{2+} (aq) + SiO_2(s) + H_2O(l)$
- $Ca_2SiO_4 + 4H^+ (aq) \rightarrow 2Ca^{2+} (aq) + SiO_2(s) + 2H_2O(l)$
- $Ca_3Mg(SiO_4)_2 + 8H^+ (aq) \rightarrow 3Ca^{2+} (aq) + Mg^{2+} + 2SiO_2(s) + 4H_2O(l)$
- $Ca^{2+} (aq) + HCO_3^- (aq) \rightarrow CaCO_3 (s) + H^+ (aq)$
- $Mg^{2+} (aq) + HCO_3^- (aq) \rightarrow MgCO_3 (s) + H^+ (aq)$

Oil shale ashes contain also $Ca$-$Mg$-silicates ($CaSiO_3$, $Ca_2SiO_4$, $Ca_3Mg(SiO_4)_2$). $CO_2$ dissolves in water to form carbonic acid which dissociates to $H^+$ and $CO_3^{2-}$. The $H^+$-ions react with the $Ca$-($Mg$)-silicates, liberating $Ca^{2+}$ (and $Mg^{2+}$)-ions, which in turn react with $HCO_3^-$-ions to form solid carbonate.
5. Direct aqueous carbonation of oil shale ash

1. Batch process:

\[
\begin{align*}
&\text{Model gas: } CO_2 (10-15\%) + \text{air} \\
&\text{pH, EC} \\
&\text{Solid product} \\
&\text{Liquid phase} \\
&\text{Separation}
\end{align*}
\]

\[
\begin{align*}
&\text{pH}=11.5-12 \\
&Ca^{2+}=1.1-1.5g/L \\
&CaCO_3=18-36\% \\
&CaO_{\text{free}}=4-15\%
\end{align*}
\]

\[
\begin{align*}
&\text{pH}=10-11.5 \\
&Ca^{2+}=0.8-1.1g/L \\
&CaCO_3=27-43\% \\
&CaO_{\text{free}}=2-5\%
\end{align*}
\]

\[
\begin{align*}
&\text{pH}=7.5-9 \\
&Ca^{2+}=0.4-0.7g/L \\
&CaCO_3=34-45\% \\
&CaO_{\text{free}}=0.6-2\%
\end{align*}
\]

\[
\begin{align*}
&\text{pH}=6.5-7 \\
&\text{Carbonation of } Ca-Mg-silicates
\end{align*}
\]

2. Continuous flow process:

\[
\begin{align*}
&\text{Off gas analysis: } CO_2; H_2S; SO_2; O_2 \\
&\text{Liquid phase} \\
&\text{Solid product}
\end{align*}
\]

\[
\begin{align*}
&\text{pH}=11.5-12 \\
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&\text{pH}=6.5-7 \\
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\end{align*}
\]

**Ashes:**
- **PF ash** CaO$_r$~22.4%
- **CFBC ash** CaO$_r$~12.4%

**Conditions:** P~1 atm, t~20°C; S/L=0.1w/w
Direct aqueous carbonation of oil shale ashes

By extending the carbonation treatment (up to 1 hour) at lower pH region (pH~7) it is possible to increase the amount of CO₂ bound on account of Ca-silicates (an example based on PF ash):

Free CaO
16.15 g CO₂/100 g PFA
CaO, Ca(OH)₂
~56% of the total CO₂ bound

Ca-silicates:
9.61 g CO₂/100g PFA
Predominantly Ca₂SiO₄
~33% of the total CO₂ bound

Other (Mg, K compounds):
3.1 g of CO₂/100g PFA
~11% of the total CO₂ bound

Total amount of CO₂ bound by PFA:
29 g CO₂/100 g PFA

Theoretical CO₂ binding ability:
35 g CO₂/100g PFA

<table>
<thead>
<tr>
<th>Carbonated ashes</th>
<th>CaO, %</th>
<th>CO₂, %</th>
<th>BD&lt;sub&gt;CO₂&lt;/sub&gt;, %</th>
<th>CO₂,kg/ash,t (bound)</th>
<th>pH of aqueous solution of solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFBC ashes</td>
<td>&gt;1</td>
<td>20</td>
<td>87</td>
<td>100</td>
<td>9.0</td>
</tr>
<tr>
<td>PF ashes</td>
<td>1-2.9</td>
<td>17-20</td>
<td>65</td>
<td>160</td>
<td>11.0</td>
</tr>
</tbody>
</table>
6. Indirect aqueous carbonation of oil shale ash

Step 1. Reactive component (Ca\(^{2+}\)ion) is extracted from the feedstock (ash).

Step 2. Reactive component (Ca\(^{2+}\)ion) is reacted with CO\(_2\) to form solid carbonates.
- \( \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \)
- \( \text{CO}_2 (g) + \text{OH}^-(aq) \rightarrow \text{HCO}_3^-(aq) \)
Characterization of solid product (PCC):

- $\text{CaCO}_3 = 94-96\%$
- Rhombohedral crystal structure
- Brightness ISO 2470:1999 93%
- Homogeneous particle size distribution $d_{\text{mean}} = 4-8\mu m$
7. A new method for eliminating CO$_2$ from flue gases by Ca-containing waste material

The process includes contacting the aqueous suspensions of Ca-containing waste material with CO$_2$-containing flue gas in two steps:

1. **First step**: keeping the pH levels in the range of 10–12.
   The water-soluble components such as *free lime* are carbonated in the *first step*.

2. **Second step**: keeping the pH levels in the range of 7–8.
   The components of low water-solubility, in which *Ca is generally contained in the form of silicates*, are carbonated in the *second step*.

**Conditions**: atmospheric pressure, room temperature
As another process route:

1. Separating *free lime* from ash by leaching it into the aqueous solutions in order to produce precipitated calcium carbonate (PCC) as a commercial product.

2. The lime depleted residue (LDM) is able to bind an additional amount of CO₂ on account of *Ca-silicates*.
The amount of CO₂ bound per 1 million ton of ash:

1. By ash transportation water 52,000 t
2. By ash deposits 60,000 t
3. By carbonation of ash suspensions 140,000 t
4. Sum of technological abatement 192,000 t

10.3% from total CO₂ emitted
62.7% from mineral CO₂ emitted

Per 1 year: 0.9 – 1.0 million t (at production level 2006)

By 1 million m³ of alkaline ash transportation water

- CO₂ captured: 950 - 1000 t
- PCC formed: 2200 - 2300 t
9. Conclusions

- The concept of CO$_2$ mineral sequestration *by* ashes from Estonian power production has been worked out.
- Ashes from oil shale combustion have been characterized as sorbents for CO$_2$ binding from flue gases in aqueous mineral carbonation processes.
- CO$_2$ fixation from model gas via direct and indirect aqueous carbonation of oil shale ash at mild operating conditions has been demonstrated:
  - The CO$_2$ binding potential of various ash components has been evaluated.
  - Indirect aqueous carbonation of oil shale ash could provide a waste valorization option by production of precipitated CaCO$_3$.
  - Based on multifaceted studies related to carbonation of oil shale ash, a new method for eliminating CO$_2$ from flue gases by Ca-containing waste material has been proposed.

The total amount of CO$_2$ bound averaged to **190-210 kg/t ash** or 10-11% and 60-65% of the total and mineral carbon content, respectively.
10. Publications of mineral carbonation
by Laboratory of Inorganic Materials, Tallinn University of Technology

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Thank You very much!
About 77% of the mined oil shale with lower calorific value is used as boiler fuel in large power plants. During combustion of oil shale CO₂ is formed not only as a burning product of organic carbon, but also as a decomposition product of the ash carbonate part. Therefore the total content of carbon dioxide increases up to 15% in flue gases of oil-shale. Oil shale ash contains up to 20-25% free Ca-Mg oxides. Portlandite Ca(OH)₂ forming from free lime during hydraulic transportation and wet deposition of ash can bind CO₂ also from air. Natural weathering process could be accelerated by simple methods. It has been demonstrated by batch and continuous mode experiments, that by processing of the ash – water suspension by flue gases, the CO₂ binding ability of ash could be utilized completely. The results of these experiments show that watered oil shale ash can bind 80-160 kg and more of CO₂ per one tonne of ash, and 30-80 kg CO₂ could be bound by alkaline wastewater used for transportation of one tonne of ash [6]. From annual production of about **16.3 mln tonnes of oil shale in Estonia in 2007, 14.3 mln t (88%)** are the share of oil shale combustion by Energy Sector. Taking into account that 450-550 kg of ash is produced from every one tonne of combusted oil shale, about **7 mln tonnes of ash was produced in 2007**. The amount of CO₂ bound by oil shale ash in wet mineralization process by flue gas could reach 560 – 1120 thousand tones and by alkaline wastewater neutralization process in reactor 210– 560 thousand tonnes. The maximum amount of CO₂ bound with flue gas could be summarized as 770 – 1680 thousand tonnes. Taking into account that big industrial Energy enterprises using mainly oil shale produced 14.5 million tonnes CO₂ in 2007, the CO₂ amount which is possible to bind with oil shale ash and transportation water by flue gas could reach 10-12% of emitted by power plants CO₂ [6, 7]. There exist some prerequisites that carbonates formed as result of the binding process could be separated and used as independent by-product, but more useful is to store them in the closed oil-shale mines. The last solution will permit to fill underground mining cavities and to prevent environmental problems arising from ash heaps.

Remark 2:

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