Cement Kiln and Waste to Energy Incineration of Spent Media
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THERMAL TREATMENT OF PFAS
STATE OF THE SCIENCE WORKSHOP

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Project Focus: Incineration of PFAS-laden Ion Exchange Resins with a Lime Sludge Additive

- PFAS removal from water by ion exchange resins
  *Management of spent PFAS-laden resins*

- Rotary kilns (e.g., cement kilns) for solid waste and waste to energy incineration

- Incineration of PFAS-laden resin in rotary kilns
  - *HF capture after incineration is needed*
  - *Calcium additive can capture fluorine*

- Lime sludge reuse as a low cost additive for fluorine capture during incineration

PFAS Removal from Water

- Ion exchange and activated carbon adsorption are identified as the most mature and feasible technologies for PFAS removal.
- Anion exchange resins can be used as a stand-alone treatment or in combination with GAC.
- Anion exchange resins have shown excellent performance for PFAS removal at relatively low EBCTs when compared to GAC.

Options for Management of the Spent Resins

- Regeneration with brine solutions: Not recommended due to the fate and liability of concentrated PFAS residuals in wastewater.
- Offsite incineration of single use anion exchange resins
  - Waste-to-Energy Incinerators
  - Cement Kiln Incinerators

Source: Paul Chaplin, The Patriot-News/file

Source: journal-news.net
Case Studies from Resin Manufacturers (Kuraray, Formerly Calgon Carbon)

- Spent resin in North Carolina (~70 cubic feet) was sent to a waste-to-energy incinerator in Virginia.
- Spent resin in Colorado (~425 cubic feet) was sent to a waste-to-energy incinerator in California.
- New resin water treatment installations are planned in Colorado (14.5 MGD) and New Jersey (3 MGD) in 2020. This equates to ~2,700 cubic feet and ~540 cubic feet of spent resin that will be incinerated at the end of their service lives at least two years from now.
Select cement kilns have incinerated waste resins from Purolite’s production plant in Philadelphia.

Not all cement kilns are set up to dry feed resins or similar media.

Each pound of resin will generate about 12,000 BTUs of energy making resin a useful fuel supplement for the cement kilns.

The temperature at which the cement kilns operate (1400°C-2000°C) allows for full destruction of PFAS compounds.

The recoverable energy is also helpful from a sustainability standpoint.
Rotary kilns are used for various manufacturing, calcination, thermal processing, and incineration applications including:
- GAC reactivation
- Cement production
- Waste incineration

Rotary kilns can be operated in co-current or counter-current modes.

Rotary kilns can be operated under different operating conditions:

- Gas temperature up to ~2,000 °C
- Gas residence times of up to 10 sec
- Solid residence time of up to 30 min

### Table 3: Typical Combustion Zone Conditions in Cement Kilns vs. Hazardous Waste Incinerators

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical Cement Kiln</th>
<th>Typical Hazardous Waste Incinerator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Gas Temperatures</td>
<td>&gt; 2200°C¹</td>
<td>≤ 1480°C</td>
</tr>
<tr>
<td>Maximum Solid Temperatures</td>
<td>1420°-1480°C</td>
<td>≤ 1370°F</td>
</tr>
<tr>
<td>Gas Retention Times at ≥ 2000°F</td>
<td>6-10 seconds</td>
<td>0-3 seconds</td>
</tr>
<tr>
<td>Solid Retention Times at ≥ 2000°F</td>
<td>20-30 minutes</td>
<td>2-20 minutes</td>
</tr>
<tr>
<td>Oxidizing Conditions Turbulence (Reynolds’ number)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>&gt; 100,000</td>
<td>&gt; 10,000</td>
</tr>
</tbody>
</table>

Rotary Kilns for Municipal or Industrial Waste Incineration

- Solid or liquid waste is injected co-currently with fuel on one side
- Organic waste combustion provides additional heat, lowering the fuel consumption and energy input
- A second burner burns the residual organic contaminants in the flue gas
- Heat is recovered and converted to steam/power
- Filtration and scrubbing systems clean the flue gas before sending it to the stack

Incineration of PFAS-laden Media

- Ion exchange resins saturated with PFAS compounds can be incinerated in rotary kilns with gas temperatures of up to ~2,000 °C.
- PFAS compounds decompose at < 700 °C and generate different free radicals and unstable fragments of original PFAS molecules, and finally form stable fluorocarbon compounds such as CF₄ and C₂F₆.
- Higher temperatures (1,000-1,600 °C) may be needed to break very stable C-F bonds without a catalyst (e.g., calcium), complete oxidation reactions, and finally form HF that requires post-combustion treatment with a caustic medium such as Ca(OH)₂.
- A conventional cement kiln with post-combustion treatment unit can effectively incinerate PFAS-laden media and capture HF from combustion flue gas.
- However, there are several research data gaps such as information about optimized temperature and residence time requirements for destruction of various PFAS compounds.

Sources:
Several researchers have reported effective PFAS destruction and capture by using a mixture of PFAS and excess amounts of CaO, CaCO₃, or Ca(OH)₂.

Incineration of a mixture of PFAS-laden media and a calcium sorbent can lower the total energy requirement (by lowering the incineration temperature).

Different free radicals and unstable fragments generated during the decomposition stage of PFAS compounds (at < 700 °C) react with a calcium additive to form stable calcium fluoride mineral before forming stable organic fluorocarbon compounds (e.g., CF₄) that require very high temperature (up to 1,600 °C) for decomposition.

Lime as a Low Cost Additive for Fluorine Capture during PFAS Incineration

- Similar to conventional incineration of PFAS-laden materials, there are major research gaps in understanding the temperature and residence time requirements for incineration of PFAS-laden media and calcium additive mixtures.
- Utilization of low-cost calcium materials such as lime softening sludge as a replacement for CaCO₃, CaO, or Ca(OH)₂ in PFAS incineration has not been explored.

Lime sludge is precipitated calcium carbonate produced during the lime softening process at water treatment plants.

Lime sludge is a highly reactive form of calcium carbonate with a BET surface area of up to 12 m²/g, about one order of magnitude higher than the surface area of limestone or reagent CaCO₃.

In the US, ~3.2 million tons of lime sludge is generated per year with an estimated disposal cost of ~$90 million.

Generated lime sludge is currently managed by disposal in landfills that may add up to 10% to the overall cost of the water treatment.

Beneficial reuse of lime sludge can reduce disposal costs and generate revenue.

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Questions?

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