MOLTEN CARBONATE TREATMENT OF ION-EXCHANGE RESINS AND OTHER WASTES

(Or the best oxidising system - ever!)

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MOLTEN CARBONATES
AND MOLTEN SALT
OXIDATION

SUMMARY OF MSO

What it is
How it works (technically)
What it can do
Advantages
MOLTEN SALT OXIDATION

What it is

Molten salt oxidation is a thermal, non-flame, process capable of oxidising (destroying) the organic constituents of radioactive wastes, mixed wastes, hazardous wastes and energetic materials while retaining inorganic and radioactive constituents in the salt, molten carbonate.
MOLTEN SALT OXIDATION

How it works (technically)

Waste, together with excess air, is injected into a bath of molten carbonate and the only off-gases are steam and CO$_2$, plus nitrogen and oxygen. All other gases, in their highest oxidation state, are acidic and thus react with and remain in the carbonate melt.
MOLTEN SALT OXIDATION

What it can do

Efficient destruction of:

- **RADIOACTIVE WASTE**
  - Ion exchange resins, reprocessing spent fuel, radiochemicals, contaminated clothing, etc.

- **MEDICAL WASTE**
  - Hospital pathogens, plastics, paper

- **MUNITIONS**
  - Out-of-date explosives, rocket fuel

- **HAZARDOUS CHEMICALS**
  - Nerve gases, rubber tires, Freons
MOLTEN SALT OXIDATION

Advantages

- LOWER TEMPERATURES
- MSO - 550°C (FLAME > 1000°C)
  Clean off-gas (NOx, dioxins, etc.)
- SELF SUSTAINING
- Exothermic reactions, no additional fuel
- VERY EFFICIENT
- Generally > 99.9999%
- OXIDISE DANGEROUS WASTES
- Radiochemicals, Pathogens, Explosives, Propellants, Plastics, Freons
- ON-SITE CAPABILITY
MOLTEN SALT OXIDATION

BACKGROUND

- The process was developed nearly 40 years ago by Rockwell International, now part of the Boeing company.
- Initially for coal gasification but they also showed its effectiveness for destroying hazardous organics such as polychlorinated biphenyls (pcb’s), poison gases, pesticides and for the recovery of silver, antimony, aluminium and tin.
- Molten salt oxidation was largely abandoned about twenty years ago but our new understanding and developments have made it much more efficient.
MOLTEN SALT OXIDATION

The technology was not then deployed because hazardous waste incineration, the alternative treatment, was allowed and less expensive.

Lawrence Livermore National Laboratory (LLNL) has built an integrated pilot-scale MSO treatment system, including off-gas treatment, a salt recycle system, feed preparation equipment, and equipment for preparing ceramic final waste forms.

Oak Ridge National Laboratory (ORNL) later built a bench-scale apparatus to destroy hazardous chlorinated organics. Funding was withdrawn some twenty years ago and research stopped.

The Naval Surface Warfare Center (NSWC) Indian Head Division has used MSO to destroy energetic and inert waste materials, including composite and double base propellants, oils, carbohydrates, paints, cellulose, solvents and diesel fuel, and is still be doing so.
MOLTEN SALT OXIDATION

HOW IT WORKS (chemically)

THE CARBONATE MELT IS *NOT*

A CATALYST FOR THE PROCESS

Early and previous reports had not understood the interaction of oxygen with molten carbonate
MOLTEN SALT OXIDATION

Most powerful chemical methods for oxidising materials need high temperatures and peroxide and superoxide ions.

Problem: High temperatures decompose these ions
Answer: Generate these ions \textit{in situ} at high temperatures

Question: How?
Answer: Use a molten carbonate exposed to air

Question: How does this work?
Answer: \( \text{O}_2 + 2\text{CO}_3^{2-} \rightarrow 2\text{O}_2^{2-} + 2\text{CO}_2 \)

Oxygen is soluble in molten carbonates, dissolving \textit{chemically}, not physically, to form peroxide. Superoxide ions can in principle also be generated

\[ 3\text{O}_2 + 2\text{CO}_3^{2-} \rightarrow 4\text{O}_2^{-} + 2\text{CO}_2 \]
MOLTEN SALT OXIDATION

Can this process be improved?

- **Answer 1**: Yes, by bubbling in air or oxygen to increase peroxide concentration.
- **Answer 2**: Yes, even more, by adding sodium peroxide or potassium superoxide.
- **Answer 3**: Yes, for maximum effect, by adding a soluble nitrate. This generates superoxide ions by a catalytic cycle when simultaneously peroxide ions are continuously generated, continuing the oxidation.
CATALYST ENHANCED MOLTEN SALT OXIDATION (CEMSO)

\[ \text{O}_2 + 2 \text{CO}_3^{2-} \rightarrow 2 \text{O}_2^{2-} + 2 \text{CO}_2 \]
(OXYGEN TO PEROXIDE)

\[ 2 \text{NO}_3^- + \text{O}_2^{2-} \rightarrow 2 \text{NO}_2^- + 2 \text{O}_2^- \]
(PEROXIDE TO SUPEROXIDE AND NITRATE TO NITRITE)

\[ \text{NO}_2^- + \text{O}_2^{2-} \rightarrow \text{NO}_3^- + \text{O}_2^- \]
(NITRITE BACK TO NITRATE)

\[ 2 \text{NO}_2^- + \text{O}_2 \rightarrow 2 \text{NO}_3^- \]
(NITRITE BACK TO NITRATE)
MOLTEN SALT OXIDATION

OPTIMISE CONDITIONS

PREVIOUSLY

Sodium carbonate melt at 900-1100°C and air bubbling

NOW

Ternary eutectic \((\text{Li,Na,K})_2\text{CO}_3\) at 550°C

Air bubbled at 2 l/min
Semi-empirical DFT calculations

Adduct intermediates: Nitrate-O$_2^{2-}$ adduct

\[ 2 \text{NO}_3^- + \text{O}_2^{2-} \rightarrow 2 \text{NO}_2^- + 2 \text{O}_2^- \]

(Peroxide to superoxide and nitrate to nitrite)

\[ \text{NO}_5^{3-} \]

N-O4,O5,O6,O1 = 1.324, 1.342, 1.324, 1.583 Å  
O1-O2 = 1.329 Å
Semi-empirical DFT calculations

Adduct intermediates: Nitrite-O$_2$ adduct

\[ 2 \text{NO}_2^- + O_2 \rightarrow 2 \text{NO}_3^- \]  
(Nitrite back to nitrate)

\[ \text{NO}_4^- \]

N-O4,O5,O1 = 1.220, 1.230, 1.412 Å  
O1-O2 = 1.282 Å
Semi-empirical DFT calculations

Adduct intermediates: Nitrite-O$_2$$^{2-}$ adduct

\[ \text{NO}_2^- + \text{O}_2^{2-} \rightarrow \text{NO}_3^- + \text{O}_2^- \]

(Nitrite back to nitrate)

N-O$_4$,O$_5$,O$_1$ = 1.320, 1.324, 1.621 Å  
O$_1$-O$_2$ = 1.351 Å
Calculated $\Delta H$ (kJ)$_{\text{Reaction}}$ at 600°C

\[ 2 \text{NO}_3^- + \text{O}_2^{2-} \rightarrow 2 \text{NO}_2^- + 2 \text{O}_2^- \]
\[-546.423 \text{kJ}\]

\[ \text{NO}_2^- + \text{O}_2^{2-} \rightarrow \text{NO}_3^- + \text{O}_2^- \]
\[361.890 \text{kJ} \quad \text{X}\]

\[ 2 \text{NO}_2^- + \text{O}_2 \rightarrow 2 \text{NO}_3^- \]
\[-314.623 \text{kJ}\]
Schematic of Molten Salt Oxidation operation
Integrated MSO system showing reaction vessel, off-gas treatment system, salt recycle system, feed preparation equipment and ceramic final waste forms immobilization system.
Top view of a unit to be used for demilitarisation of obsolete US munitions in Korea
## MOLTEN SALT OXIDATION

<table>
<thead>
<tr>
<th>Waste description</th>
<th>Destruction efficiency</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion exchange resins</td>
<td>Complete</td>
<td>Nitrogen and phosphates</td>
</tr>
<tr>
<td>Chemical warfare agents</td>
<td>&gt;99.9999% @ 925°C</td>
<td>US Army data</td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>&gt;99.9999% @ 900°C</td>
<td>Liquid chlorinated hydrocarbon</td>
</tr>
<tr>
<td>PCB’s</td>
<td>&gt;99.9999% @ 1000°C</td>
<td>No Cl₂ or phosgene</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>&gt;99.9999% @ 925°C</td>
<td>Solid chlorinated hydrocarbon</td>
</tr>
<tr>
<td>Chlordane</td>
<td>&gt;99.9999% @ 925°C</td>
<td>Mix of chlorinated products</td>
</tr>
<tr>
<td>Various industrial wastes</td>
<td>Complete, no PIC’s*</td>
<td>Contained N, S and Cl</td>
</tr>
<tr>
<td>Aqueous cyanide</td>
<td>&gt;99.99%</td>
<td>Aqueous waste</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>Complete</td>
<td>Difficult inorganic</td>
</tr>
<tr>
<td>Leaded gloves</td>
<td>Complete</td>
<td>Metallic lead retained in salt</td>
</tr>
</tbody>
</table>
Mixed wastes and their destruction efficiency by Molten Salt Oxidation

<table>
<thead>
<tr>
<th>Waste description</th>
<th>Test results</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu contaminated waste</td>
<td>&gt;99.9% Pu in melt</td>
<td>Pu in first pre-filter only</td>
</tr>
<tr>
<td>Simulated fission products</td>
<td>&gt;99.9% in melt</td>
<td>Sr, Eu, Cs in melt</td>
</tr>
<tr>
<td>Simulated low level glove box waste</td>
<td>Complete destruction</td>
<td>7 day pilot plant test</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>Complete, no PIC’s*</td>
<td>Feed contained 550 ppm U</td>
</tr>
<tr>
<td>Conc. aqueous slurry (NaNO₃)</td>
<td>Smooth operation</td>
<td>No NOx</td>
</tr>
<tr>
<td>Solid nitrates and nitrites</td>
<td>No NO₃⁻ or NO₂⁻ in the melt</td>
<td>NOx as low as 26 ppm</td>
</tr>
</tbody>
</table>
TBP and Kerosene Waste

Tests with mixtures of TPB and kerosene in our Molten Salt Oxidation furnace showed that complete oxidation had taken place and that the phosphorus was retained as phosphate.

Thus if spent mixtures containing radionuclides were treated by MSO the metallic elements would be retained in the carbonate melt as phosphates.

Phosphates are essentially insoluble in molten carbonate and hence these fission product phosphates can be separated off, ready for vitrification, etc.
Proposed plutonium recovery process, but using sodium carbonate at 900°C
MOLTEN SALT OXIDATION

- Incomplete and slow oxidation of paper, cotton and plastics
- Need to increase oxidising power by adding nitrate to carbonate
- Results of oxidation of paper, cloth and plastic at 550°C for 2h by MSO using a ternary eutectic melt containing added nitrate and air sparged at 2 l/min
## MOLTEN SALT OXIDATION

<table>
<thead>
<tr>
<th>Material</th>
<th>KNO$_3$/wt %</th>
<th>Method</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tissue paper</td>
<td>0</td>
<td>On surface</td>
<td>Immediate surface flame</td>
</tr>
<tr>
<td></td>
<td></td>
<td>On bottom</td>
<td>Later paper pieces and ash on surface. Much later, only some paper at bottom</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0</td>
<td>On surface</td>
<td>Immediate flame and black smoke</td>
</tr>
<tr>
<td>Tissue paper</td>
<td>1</td>
<td>Plunged in</td>
<td>Initial small flame then all oxidised</td>
</tr>
<tr>
<td>Cotton</td>
<td>2</td>
<td>As above</td>
<td>As above but carbon traces in melt</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>Cotton</td>
<td>3</td>
<td>Released under melt</td>
<td>Complete oxidation, clear melt</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3</td>
<td>As above</td>
<td>As above, no flame if material always in melt</td>
</tr>
</tbody>
</table>
MOLTEN SALT OXIDATION

- Munitions: Asia, America and Europe
- Millions of tons past their “use by” date
- Removing chemicals from containers possible for some explosives
- Adding to MSO bath: never an incident
- Bath needs some external cooling
- Slow, only one private doing this!
MOLTEN SALT OXIDATION

FREONs

- Associated with ozone hole and banned
- In refrigerators and their insulation
- Disposal difficult: white mountains
- Legislation ahead of built plant
- Destruction of Freon molecules almost impossible since particularly stable
- Alternative to storage desired
Freons and superoxide

- Theoretical calculations for $O_2^-$ insertion
- Semi-empirical and “ab initio” methods
- Five most common Freons examined
  - $CCl_2F_2$, $CCl_3F$, $CCIF_2H$, $CCl_2FCF_2Cl$ and $CCIF_2CCIF_2$
- Superoxide-chlorofluorocarbon adduct
- Enthalpies of formation and reaction exothermic so Freons “fall apart” to form $F^-$ and $Cl^-$ ions in carbonate melt
# MOLTEN SALT OXIDATION

## Method of Calculation and $\Delta H_{\text{form}}$ (kcal/mol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>AM1</th>
<th>PM3</th>
<th>PM5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superoxide</td>
<td>-22.7092</td>
<td>-13.2868</td>
<td>-50.1116</td>
</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>-107.0450</td>
<td>-116.0771</td>
<td>-113.6517</td>
</tr>
<tr>
<td>CClO$_2$ClF$_2^-$</td>
<td>-143.2701</td>
<td>-199.7412</td>
<td>-208.5044</td>
</tr>
<tr>
<td>$\Delta H_{\text{react}}$ (kcal/mol)</td>
<td>-13.5159</td>
<td>-70.3773</td>
<td>-44.7411</td>
</tr>
</tbody>
</table>
MOLten SALT Oxidation

\[ \text{CClO}_2\text{ClF}_2^- \]

\[ \text{CO}_2\text{ClClFCF}_2\text{Cl}^- \]

\[ \text{CClO}_2\text{CIF}_2^- \]

\[ \text{CO}_2\text{ClCl}_2\text{F}^- \]

\[ \text{CO}_2\text{CIF}_2\text{H}^- \]

\[ \text{CO}_2\text{FFCl}_2^- \]
MOLTEN SALT OXIDATION

AM1 versions
MOLTEN SALT OXIDATION

Molecular Structure of CO₂ClClF₂⁻

DFT (Density Functional Theory) *ab initio* calculation

Atomic charges are: O₁ = -0.250356; O₂ = -0.221893; C₃ = 0.912681;
Cl₄ = -0.253582; Cl₅ = -0.613403; F₆ = -0.303597; F₇ = -0.269849
for a total of –1.000

Bond distances are: Cl₄-C₃ = 1.844; F₆-C₃ = 1.348; F₇C₃ = 1.331;
C₃-O₁ = 1.341; O₁-O₂ = 1.427; O₂-Cl₅ = 2.482 Å.

Bond Angles are: O₂-O₁-C₃ = 107.45; O₁-O₂-Cl₅ = 112.99;
O₁-C₃-Cl₄ = 105.83; O₁-C₃-F₆ = 113.79; O₁-C₃-F₇ = 115.15;
Cl₄-C₃-F₆ = 106.94; Cl₄-C₃-F₇ = 107.75; F₆-C₃-F₇ = 106.94
Proposed purification of sodium carbonate for recycling
Similar process for a ternary carbonate
Technical details MSO plant design but for use with Na₂CO₃ under more aggressive conditions
Proposed MSO for secondary treatment stage for incinerator off-gases to replace conventional wet-scrubbing
CEMSO – *Way to Go!*

- For separating inorganics from organics
- Converting organics to CO$_2$ and steam
- Retaining radionuclides in molten carbonate
- Then precipitating them as phosphates
- Universal application, especially for ion-exchange resins and down-sizing contaminated waste stores

(Review on carbonate reprocessing of SNF Griffiths and Volkovich, Nucl. Tech. 163, 382, 2008.)