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- Out-of-date explosives, rocket fuel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
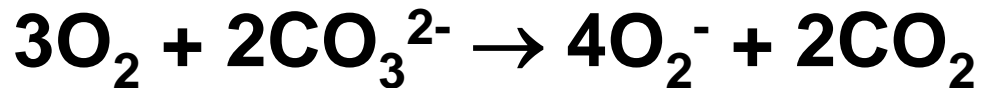
Answer: Generate these ions *in situ* at high temperatures

Question: How?

Answer: Use a molten carbonate exposed to air

Question: How does this work?

Answer: $O_2 + 2CO_3^{2-} \rightarrow 2O_2^{2-} + 2CO_2$

Oxygen is soluble in molten carbonates, dissolving *chemically*, not physically, to form peroxide. Superoxide ions can in principle also be generated
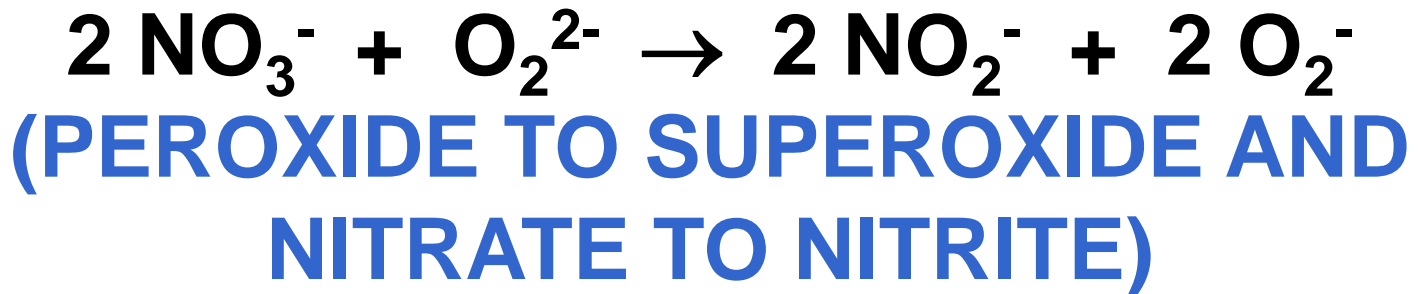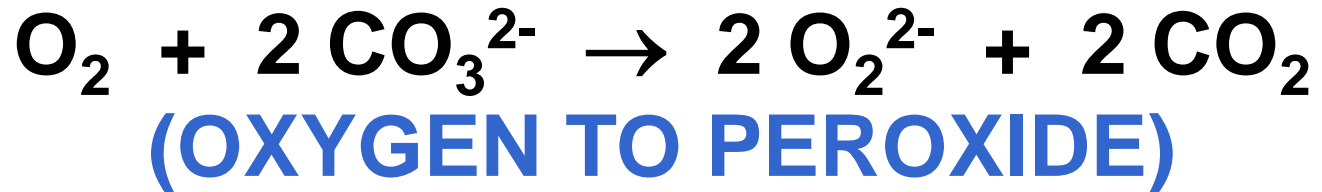
$$3O_2 + 2CO_3^{2-} \rightarrow 4O_2^- + 2CO_2$$

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)

$$O_2 + 2 CO_3^{2-} \rightarrow 2 O_2^{2-} + 2 CO_2$$
(OXYGEN TO PEROXIDE)
$$2 NO_3^- + O_2^{2-} \rightarrow 2 NO_2^- + 2 O_2^-$$
(PEROXIDE TO SUPEROXIDE AND NITRATE TO NITRITE)
$$NO_2^- + O_2^{2-} \rightarrow NO_3^- + O^{2-}$$
(NITRITE BACK TO NITRATE)
$$2 NO_2^- + O_2 \rightarrow 2 NO_3^-$$
(NITRITE BACK TO NITRATE)
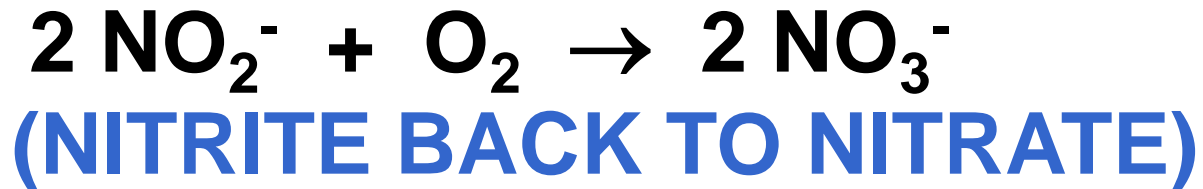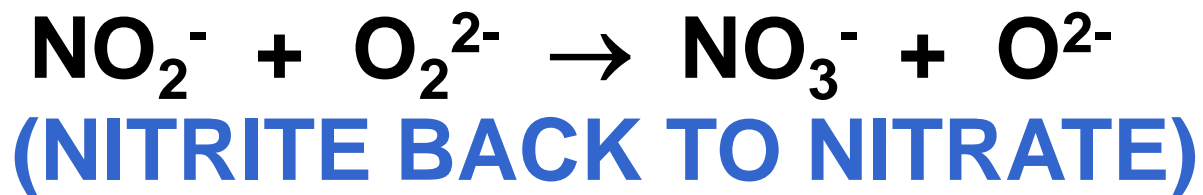
MOLTEN SALT OXIDATION

OPTIMISE CONDITIONS

PREVIOUSLY

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

NOW

Ternary eutectic $(Li,Na,K)_2CO_3$ at 550°C

Air bubbled at 2 l/min

Semi-empirical DFT calculations

Adduct intermediates: Nitrate-O_2^{2-} adduct

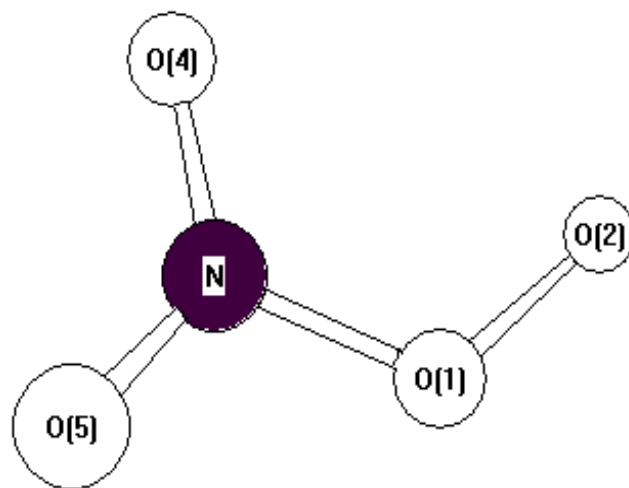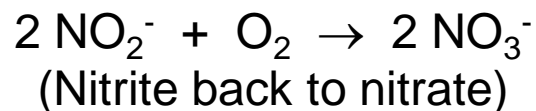$$2\ NO_3^- + O_2^{2-} \rightarrow 2\ NO_2^- + 2\ O_2^-$$

(Peroxide to superoxide and nitrate to nitrite)

NO_5^{3-}
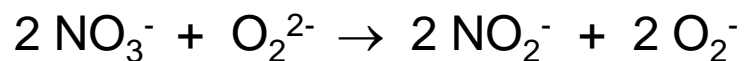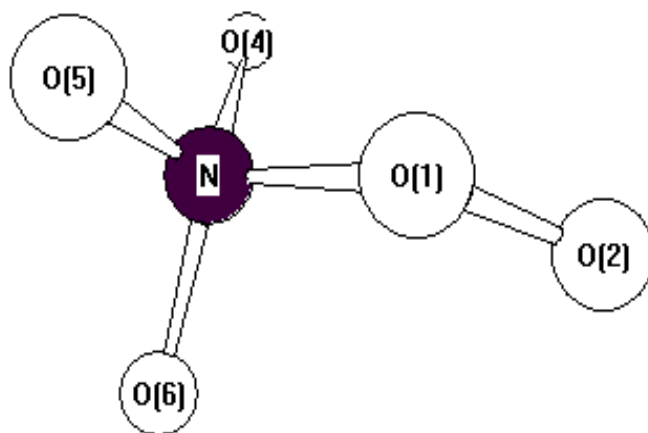
N-O4,O5,O6,O1 = 1.324, 1.342, 1.324, 1.583 Å   O1-O2 = 1.329 Å
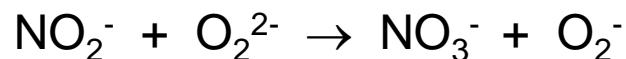
Semi-empirical DFT calculations
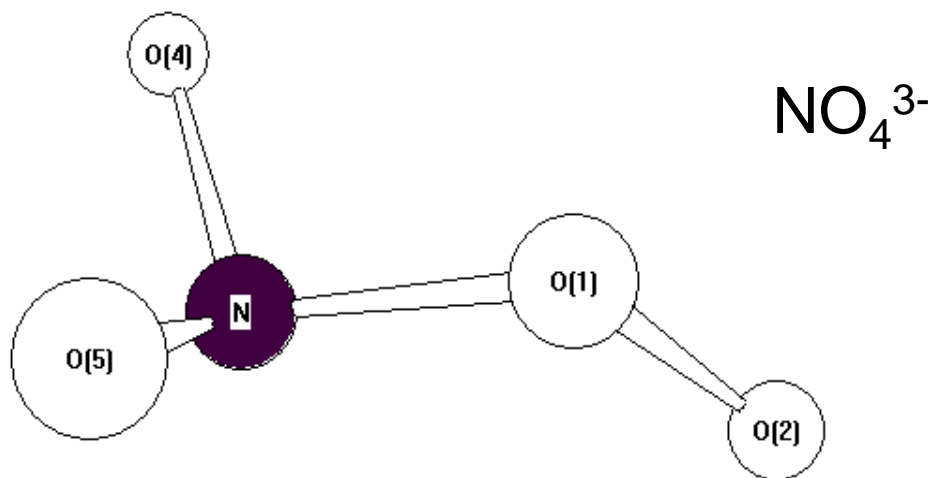
Adduct intermediates: Nitrite-O_2 adduct

$$2\,NO_2^- + O_2 \rightarrow 2\,NO_3^-$$
(Nitrite back to nitrate)

NO_4^-

N-O4,O5,O1 = 1.220, 1.230 1.412 Å   O1-O2 = 1.282 Å

Semi-empirical DFT calculations
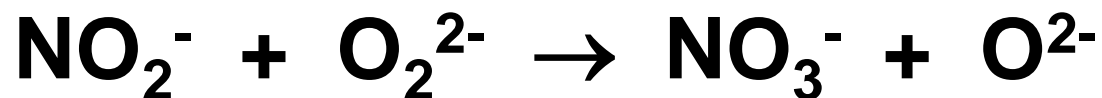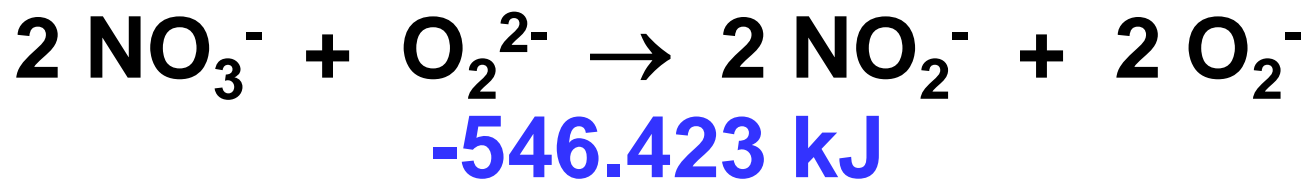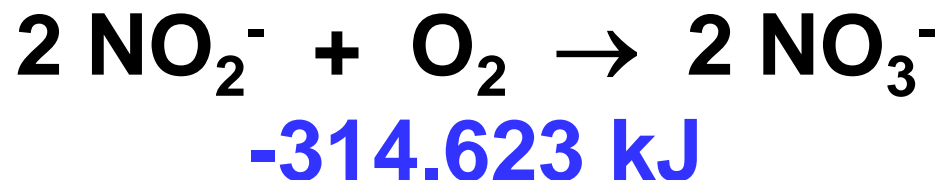
Adduct intermediates: Nitrite-O_2^{2-} adduct

$$NO_2^- + O_2^{2-} \rightarrow NO_3^- + O_2^-$$

(Nitrite back to nitrate)

NO_4^{3-}

N-O4,O5,O1 = 1.320, 1.324, 1.621 Å   O1-O2 = 1.351 Å

Calculated ΔH (kJ)$_{Reaction}$ at 600°C

$$2\ NO_3^-\ +\ O_2^{2-}\ \rightarrow\ 2\ NO_2^-\ +\ 2\ O_2^-$$

-546.423 kJ

$$NO_2^-\ +\ O_2^{2-}\ \rightarrow\ NO_3^-\ +\ O^{2-}$$

361.890 kJ X

$$2\ NO_2^-\ +\ O_2\ \rightarrow\ 2\ NO_3^-$$
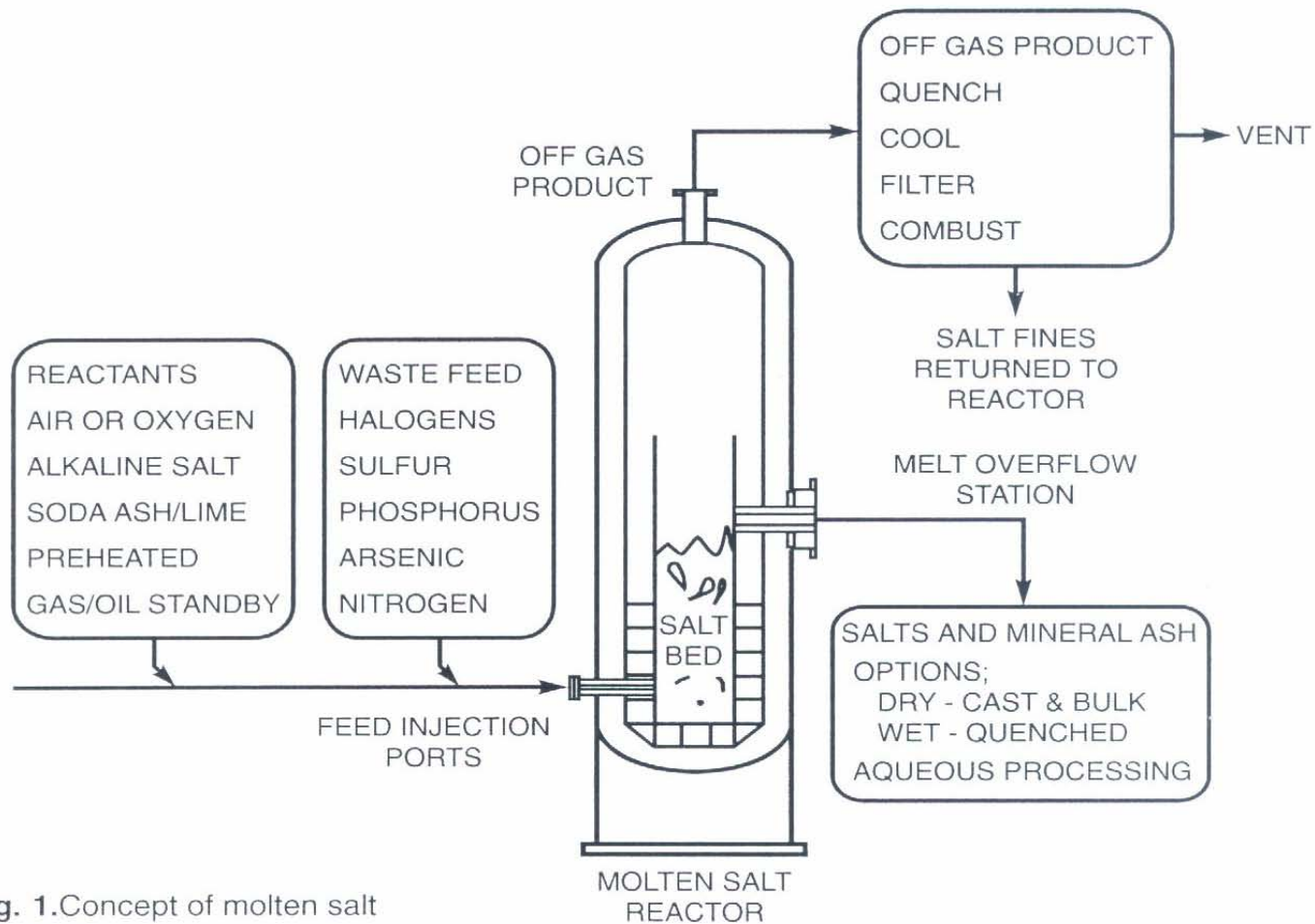
-314.623 kJ

MOLTEN SALT OXIDATION
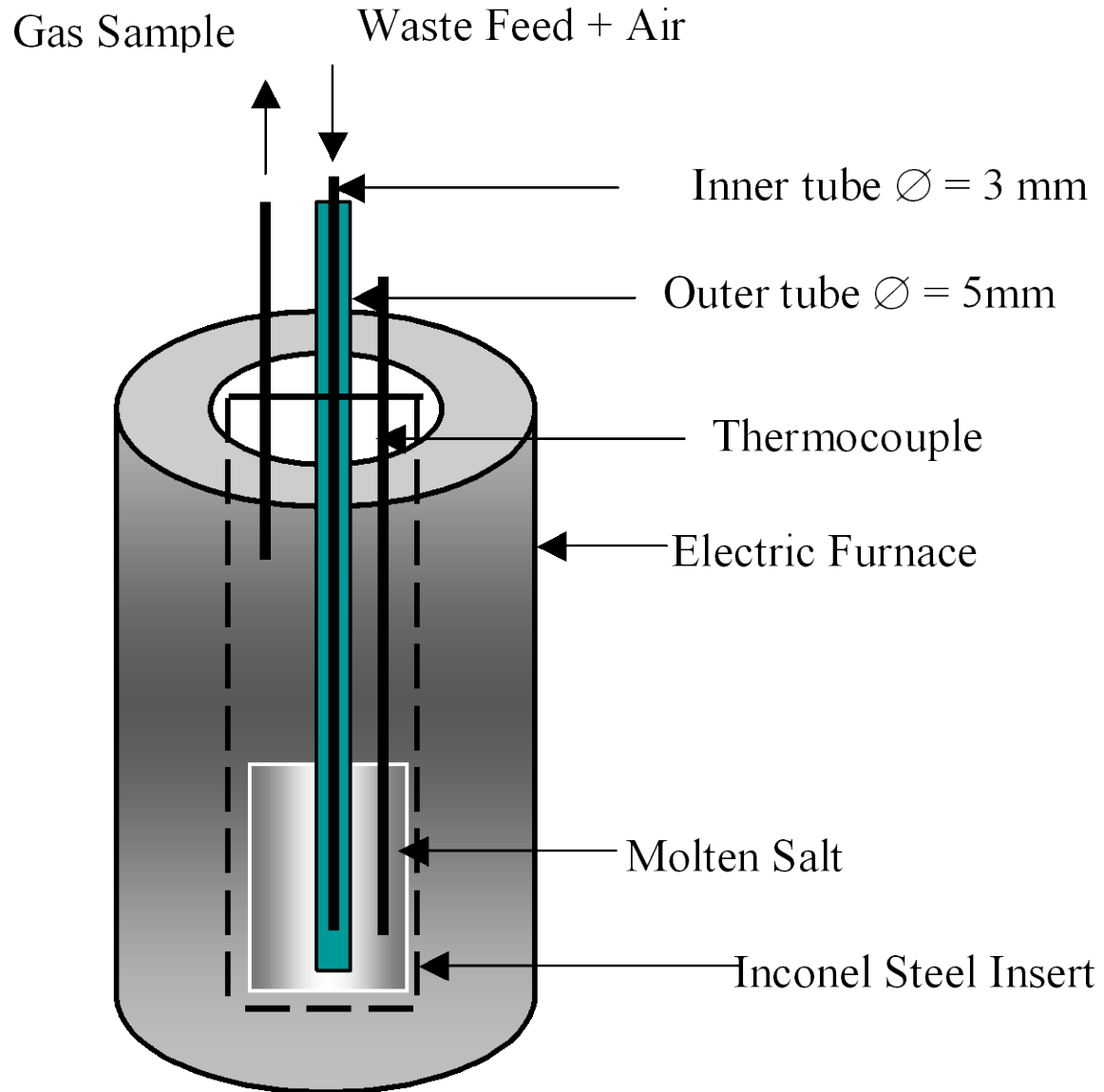
Fig. 1.Concept of molten salt

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

Waste description	Destruction efficiency	Comments
Ion exchange resins	Complete	Nitrogen and phosphates
Chemical warfare agents	>99.9999 @ 925ºC	US Army data
Trichlorobenzene	>99.9999% @ 900ºC	Liquid chlorinated hydrocarbon
PCB's	>99.9999% @ 1000ºC	No Cl_2 or phosgene
Hexachlorobenzene	>99.9999% @ 925ºC	Solid chlorinated hydrocarbon
Chlordane	>99.9999% @ 925ºC	Mix of chlorinated products
Various industrial wastes	Complete, no PIC's*	Contained N, S and Cl
Aqueous cyanide	>99.99%	Aqueous waste
Silicon carbide	Complete	Difficult inorganic
Leaded gloves	Complete	Metallic lead retained in salt

Mixed wastes and their destruction efficiency by Molten Salt Oxidation

| Waste description	Test results	Comments
Pu contaminated waste	>99.9% Pu in melt	Pu in first pre-filter only
Simulated fission products	>99.9% in melt	Sr, Eu, Cs in melt
Simulated low level glove box waste	Complete destruction	7 day pilot plant test
Perchloroethylene	Complete, no PIC's*	Feed contained 550 ppm U
Conc. aqueous slurry ($NaNO_3$)	Smooth operation	No NOx
Solid nitrates and nitrites	No NO_3^- or NO_2^- in the melt	NOx as low as 26 ppm

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.
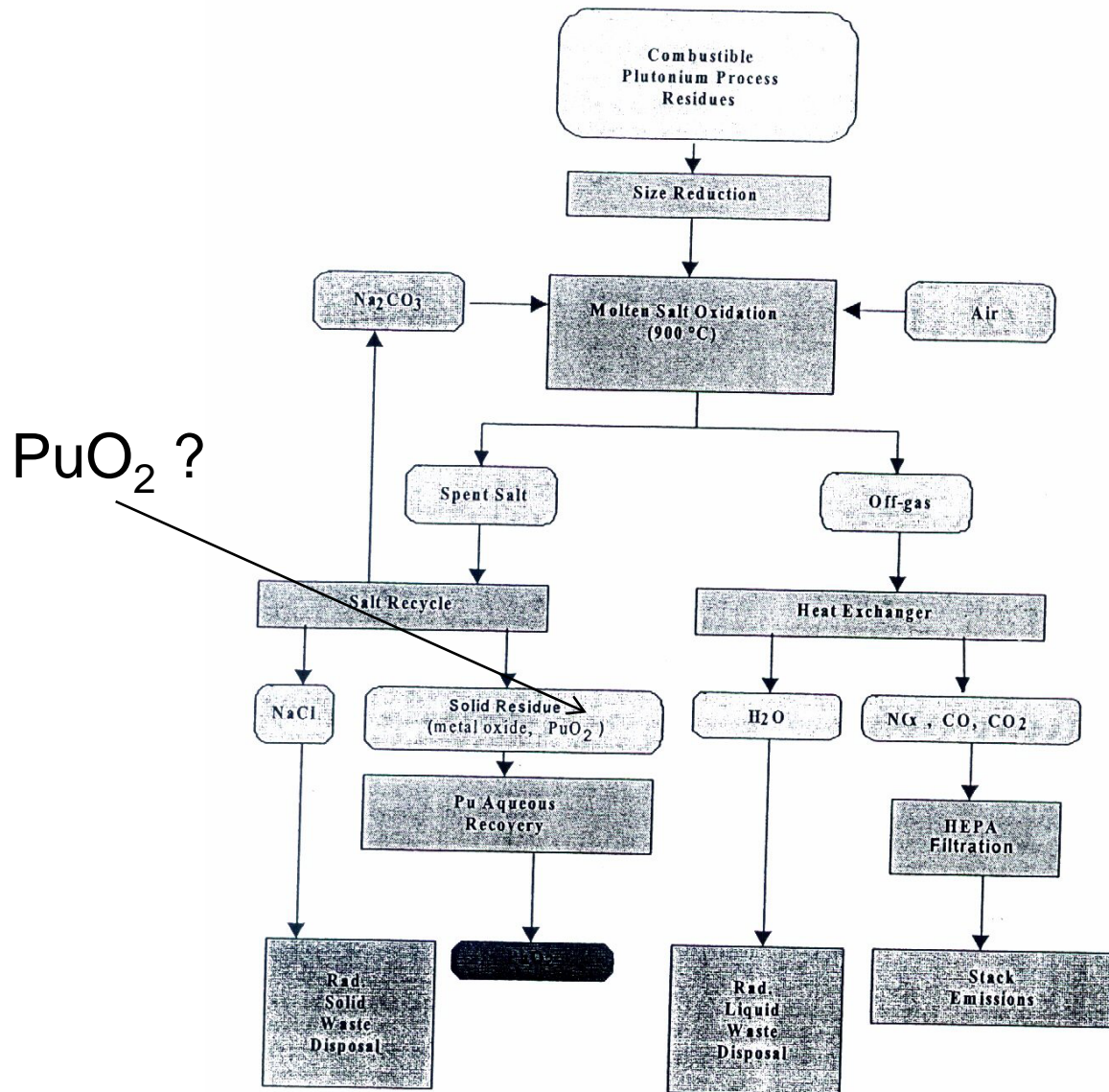
Proposed plutonium recovery process, but using sodium carbonate at 900°C

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 550ºC for 2h by MSO using a ternary eutectic melt containing added nitrate and air sparged at 2 l/min**

MOLTEN SALT OXIDATION

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

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**
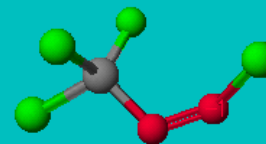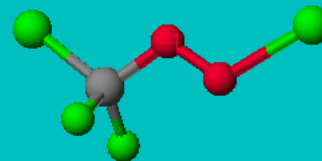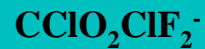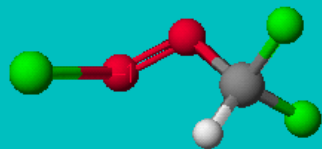
MOLTEN SALT OXIDATION
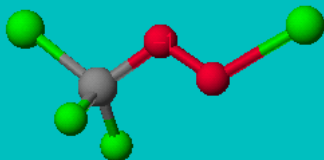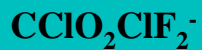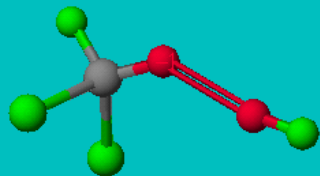
Freons and superoxide

- **Theoretical calculations for O_2^- insertion**
- **Semi-empirical and "ab initio" methods**
- **Five most common Freons examined**
- **CCl_2F_2, CCl_3F, $CClF_2H$, CCl_2FCF_2Cl and $CClF_2CClF_2$**
- **Superoxide-chlorofluorocarbon adduct**
- **Enthalpies of formation and reaction exothermic so Freons "fall apart" to form F^- and Cl^- ions in carbonate melt**
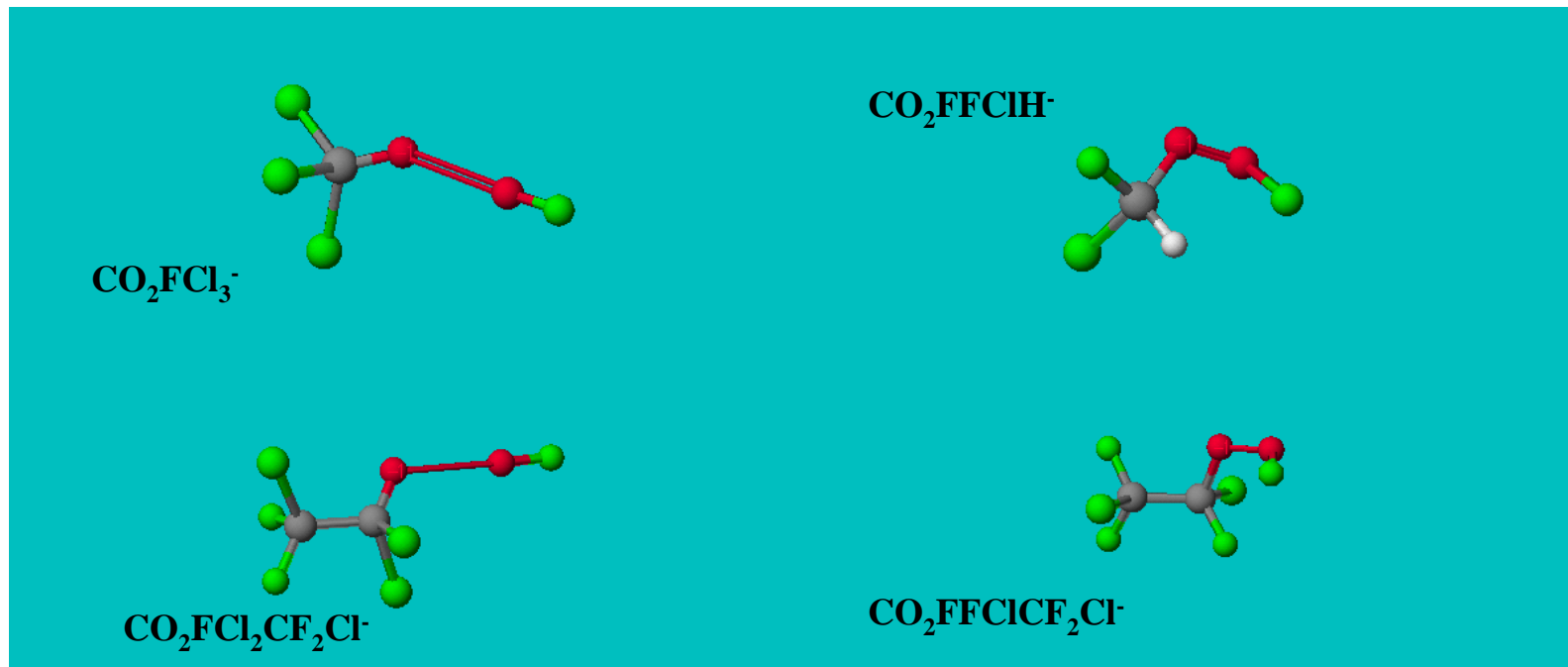
MOLTEN SALT OXIDATION

Method of Calculation and ΔH_{form} (kcal/mol)			
Compound	AM1	PM3	PM5
Superoxide	-22.7092	-13.2868	-50.1116
CCl_2F_2	-107.0450	-116.0771	-113.6517
$CClO_2ClF_2^-$	-143.2701	-199.7412	-208.5044
ΔH_{react} (kcal/mol)	-13.5159	-70.3773	-44.7411

MOLTEN SALT OXIDATION

$CClO_2ClF_2^-$

$CO_2ClClFCF_2Cl^-$

$CClO_2ClF_2^-$

$CO_2ClCl_2F^-$

$CO_2ClF_2H^-$

$CO_2FFCl_2^-$

MOLTEN SALT OXIDATION
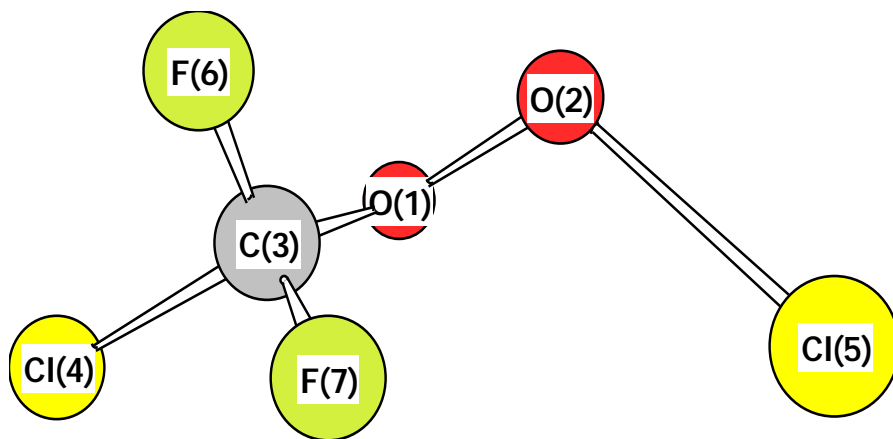

$CO_2FCl_3^-$

CO_2FFClH^-

$CO_2FCl_2CF_2Cl^-$

$CO_2FFClCF_2Cl^-$
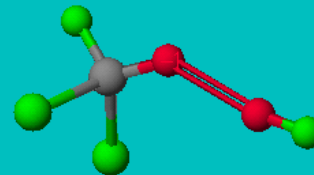
AM1 versions

MOLTEN SALT OXIDATION


Molecular Structure of $CO_2ClClF_2^-$

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

Figure   Flowsheet for Aqueous Processing of Spent Salt
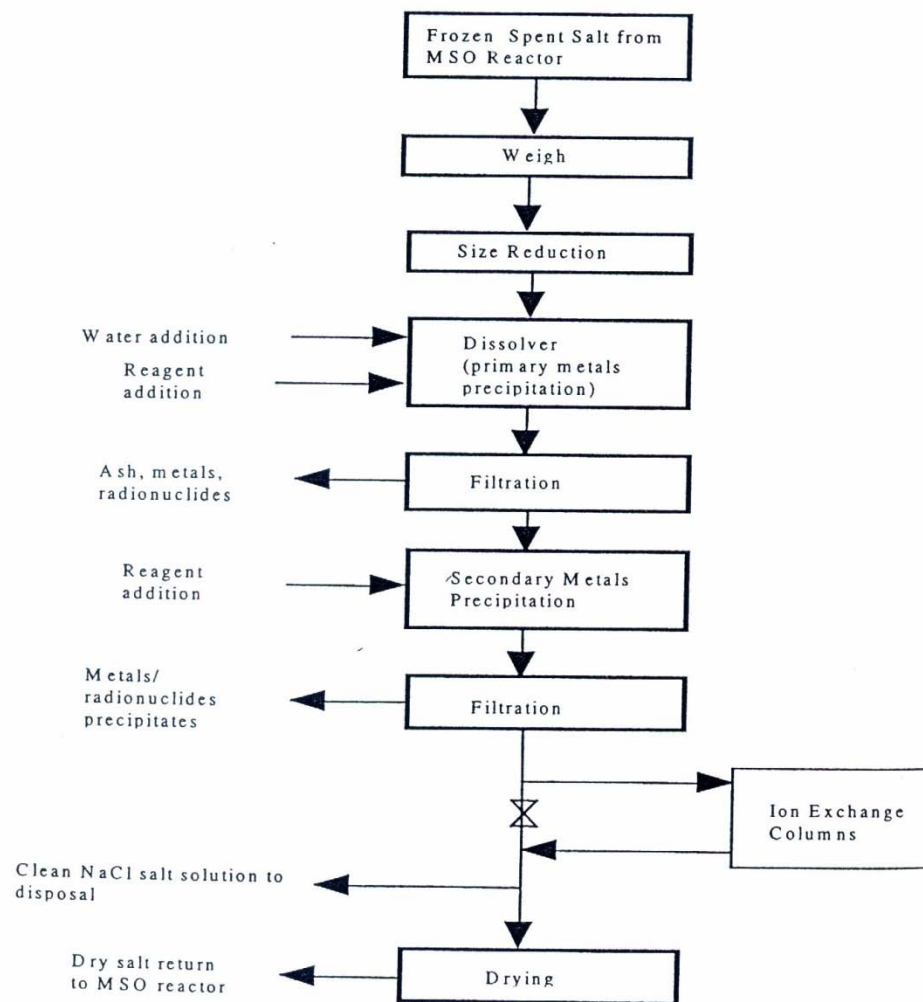
**Proposed purification of sodium carbonate for recycling
Similar process for a ternary carbonate**

Table .. MSTF design features and typical process conditions

Element	Characteristic	Value
Containment Vessel	Diameter (OD)	86 cm
	Length	5.5 m
	Wall thickness	1.6 cm
	Material	Nickel alloy
Heat removal system	Air-blast with fins	380 kW
Reference feed material (PCB waste)	Carbon	49 wt.%
	Hydrogen	1 wt.%
	Chlorine	50 wt.%
	Heating value	17,400 kJ/kg
Feed rates (for oxygen-enriched air)	PCB waste	100 kg/h
	Air	140 kg/h
	Oxygen	105 kg/h
	Sodium carbonate	100 kg/h
Melt composition	Sodium carbonate	25 wt.%
	Sodium chloride	75 wt.%
Melt temperature (nominal)		900 C
Destruction and removal efficiency (DRE)		99.9999%

Technical details MSO plant design but for use with Na_2CO_3 under more aggressive conditions
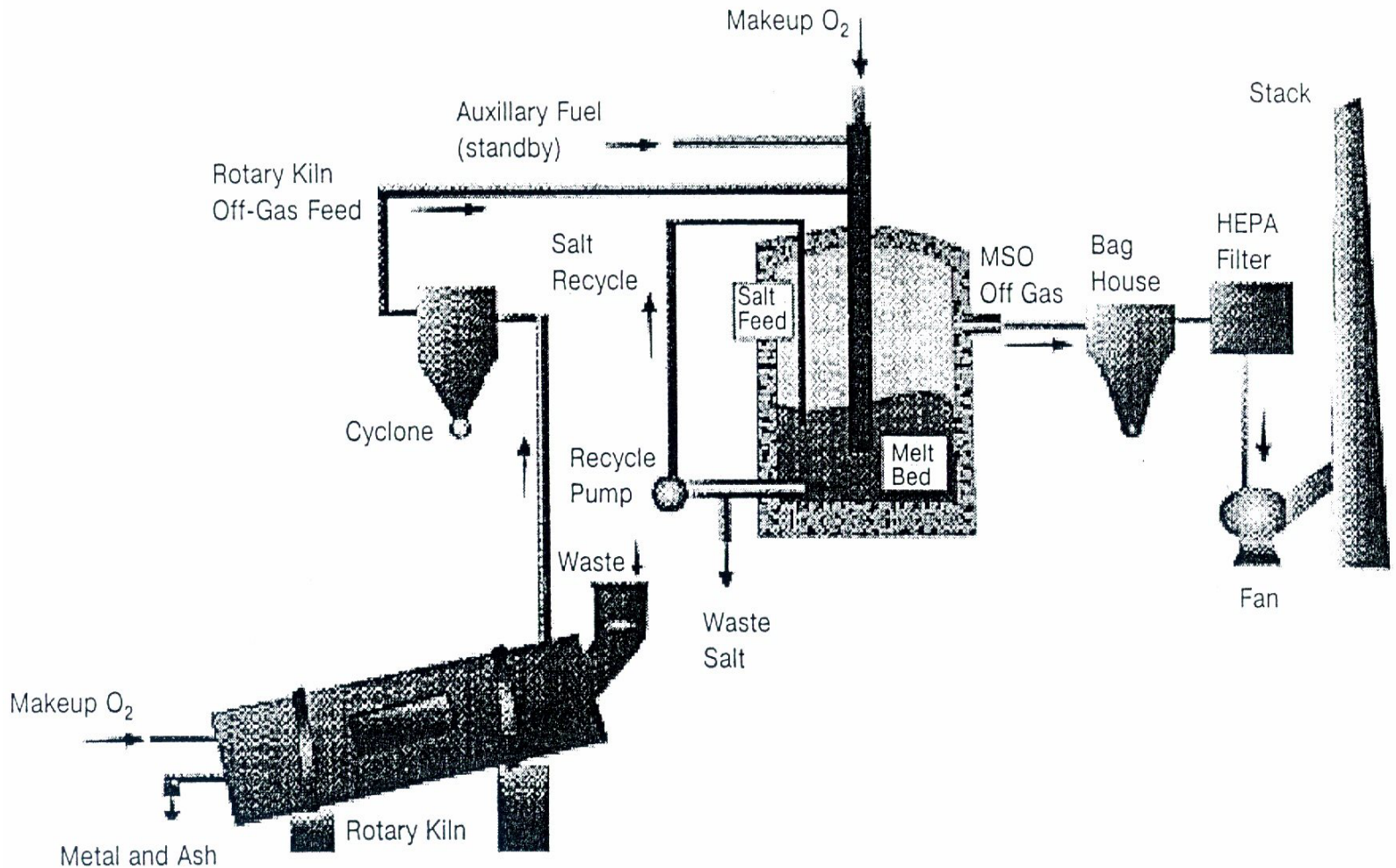
Proposed MSO for secondary treatment stage for incinerator off-gases to replace conventional wet-scrubbing

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.)