
Chlorine-37 Fuel Cycles for Molten-Chloride Fast Reactors (MCFRs)

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Summary

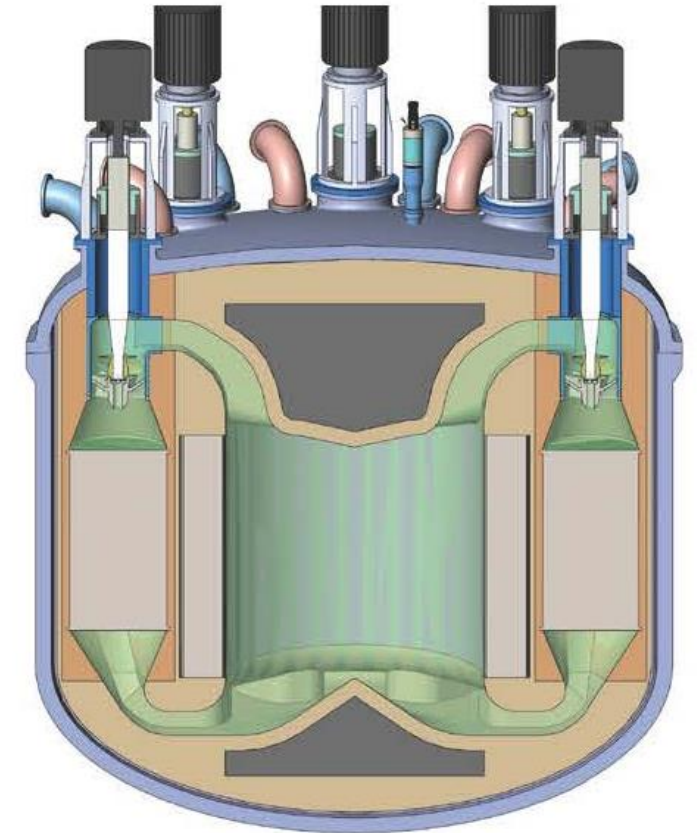
- Using ^{37}Cl in molten chloride fast reactors (MCFR) rather than natural chlorine has two advantages
 - Better neutron economy
 - Better repository performance
- Creates economic and environmental incentives for enriching ^{37}Cl for fuel and recovery with recycle of ^{37}Cl from wastes back to MCFRs

Molten Chloride Fast Reactor Characteristics

- Fuel dissolved in a chloride salt (Uranium, Sodium, etc.)
- Very hard neutron spectrum that enables in some designs “breed and burn” fuel cycles
 - Startup core with plutonium or enriched uranium
 - Refuel by adding depleted uranium to fuel with direct disposal of fraction of fuel with uranium and plutonium
 - Simplest possible fuel cycle
- Two isotopes of chlorine—chlorine-35 consumes more neutrons so better performance with chlorine-37

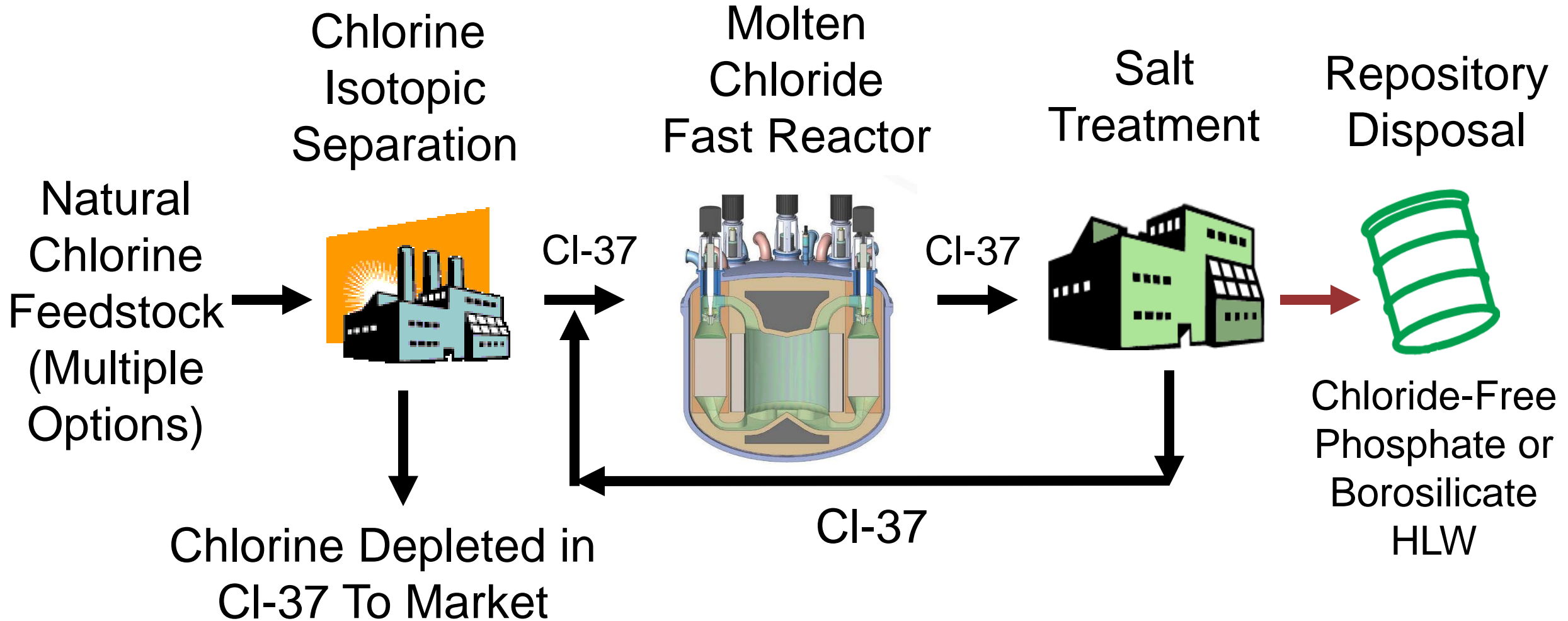
Two Classes of MCFRs Being Developed

- MCFR with the reactor being a wide space in the loop
 - TerraPower/Southern with Pu/U fuel
 - Elysium with Pu/U fuel
 - SINAP (China) with $^{233}\text{U}/\text{Th}$ fuel
- Molten chloride fuel salt in tubes with clean fluoride salt coolant: Moltex
 - Clean salt coolant loop
 - Similarities to sodium fast reactor except simple to process fuel—pour out of tubes



TerraPower/Southern

The Chlorine-37 Fuel Cycle



Why Use Chlorine-37 in a Molten Chloride Fast Reactor

Natural Chlorine: 76 % ^{35}Cl and 24 % ^{37}Cl (Molar Ratios)

Incentives for Isotopic Separation

- Using ^{37}Cl in MCFR avoids two ^{35}Cl reactions
 - Neutron, gamma
 - Neutron, proton (significant nuclear cross section uncertainties)
- Enables harder neutron spectrum—chlorides are the largest fraction of the fuel salt
- For U/Pu MCFRs, reduce ^{35}Cl by an order of magnitude but no large incentive for very highly enriched ^{37}Cl

Isotopically Separating Chlorine-37 from Chlorine-35

Multiple Isotopic Separation Options

- No public detailed review of options
- Likely near-term option is gas centrifuge using existing (uranium) enrichment plants
- Need chloride-containing gas
 - Cl_2 gas complicates enrichment because three component separation: $^{35}\text{Cl}\text{-}^{35}\text{Cl}$, $^{35}\text{Cl}\text{-}^{37}\text{Cl}$ and $^{37}\text{Cl}\text{-}^{37}\text{Cl}$
 - **Potential gaseous compounds with single chloride atom to avoid three component separation: methyl chloride (CH_3Cl) and hydrogen chloride (HCl)**

Low-cost Commercial Feedstock Has Economic Implications

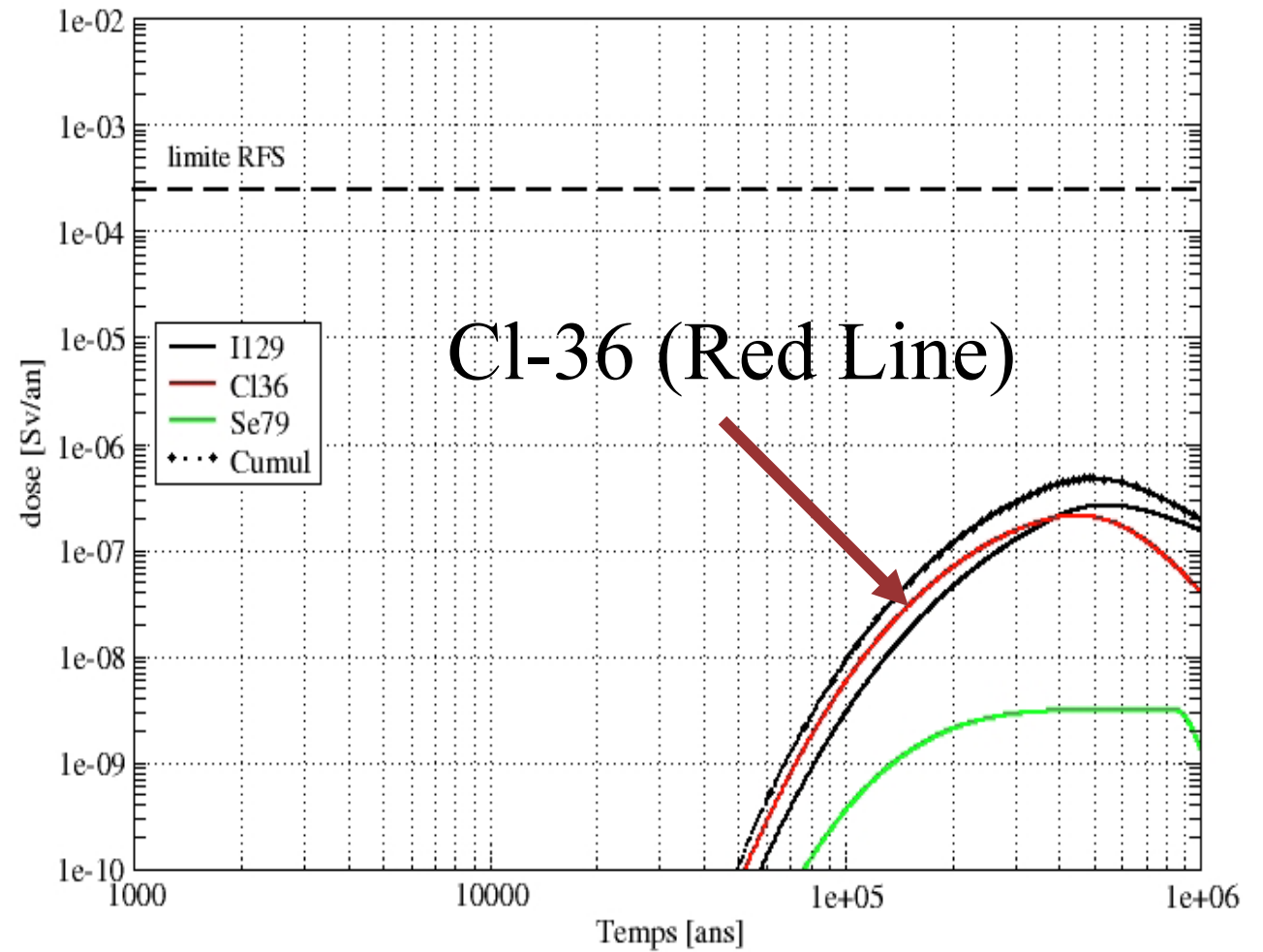
- Unlike natural uranium, **very low-cost chlorine feedstock options**
- Cheap feedstock implies no need to maximize extraction of ^{37}Cl so less enrichment required. Assume: Nominal 90% ^{37}Cl product and Nominal 15% ^{37}Cl tails
- **Relative enrichment required**

Tails Assay (% ^{37}Cl)	Relative SWU
15	1
10	1.17
5	1.46
1	2.17
0.5	2.5

Recycle of Chlorine-37 from Waste while Producing High-Quality High-Level Waste

In Repositories, Chlorine-36 is a Risk Contributor

- Chemistry determines what can escape from a repository
- Fission products, not actinides, control risk in most repositories
- Chlorides are soluble in water, that is why the ocean is full of salt (NaCl)
- If no ^{35}Cl in reactor, no ^{36}Cl in waste



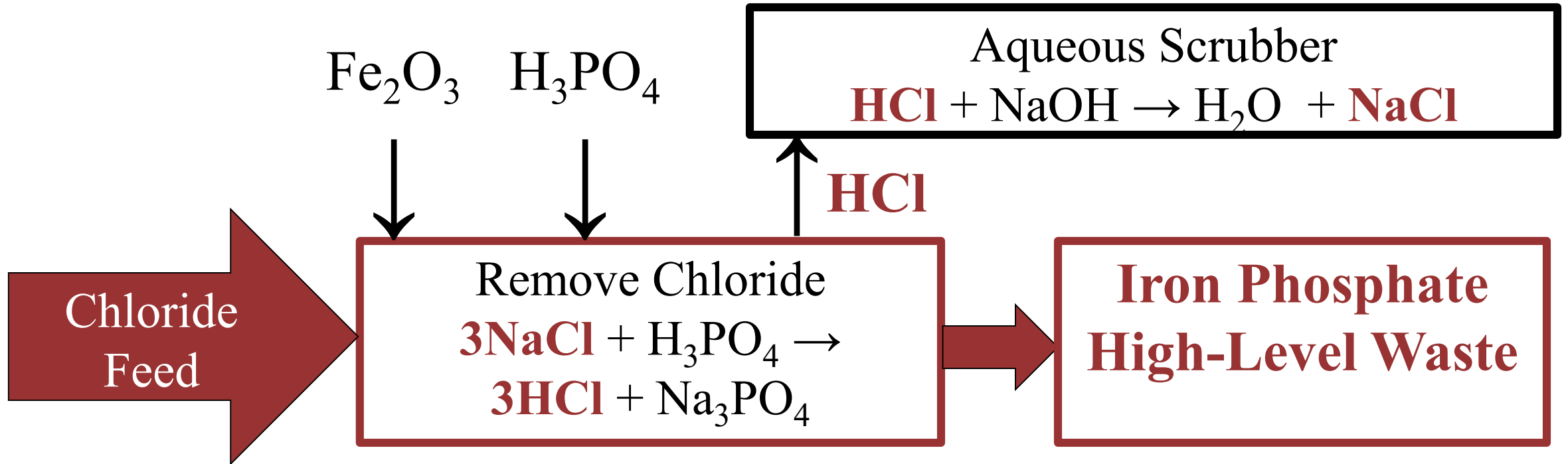
Large Incentives to Remove Chlorides from Waste

- Chloride waste forms have low performance compared to phosphate and borosilicate waste forms because of tendency of chlorides to dissolve in water.
- **Incentives to remove chlorides from waste—even if there was no radioactive form of chlorine**
- Added advantage for MCFR with ^{37}Cl to recover valuable isotopically-separated ^{37}Cl .

Process Options to Remove Chloride from Waste

- Convert to generally-accepted high-level-waste form
 - Iron Phosphate
 - Borosilicate glass.
- Add compound to convert from chloride to oxide waste form with volatile chloride existing to off-gas system
 - HCl
 - PbCl_2
- Recover volatile chloride in off-gas system as sodium chloride and recycle to MCFR

Example: Convert Waste to Phosphate Waste Form



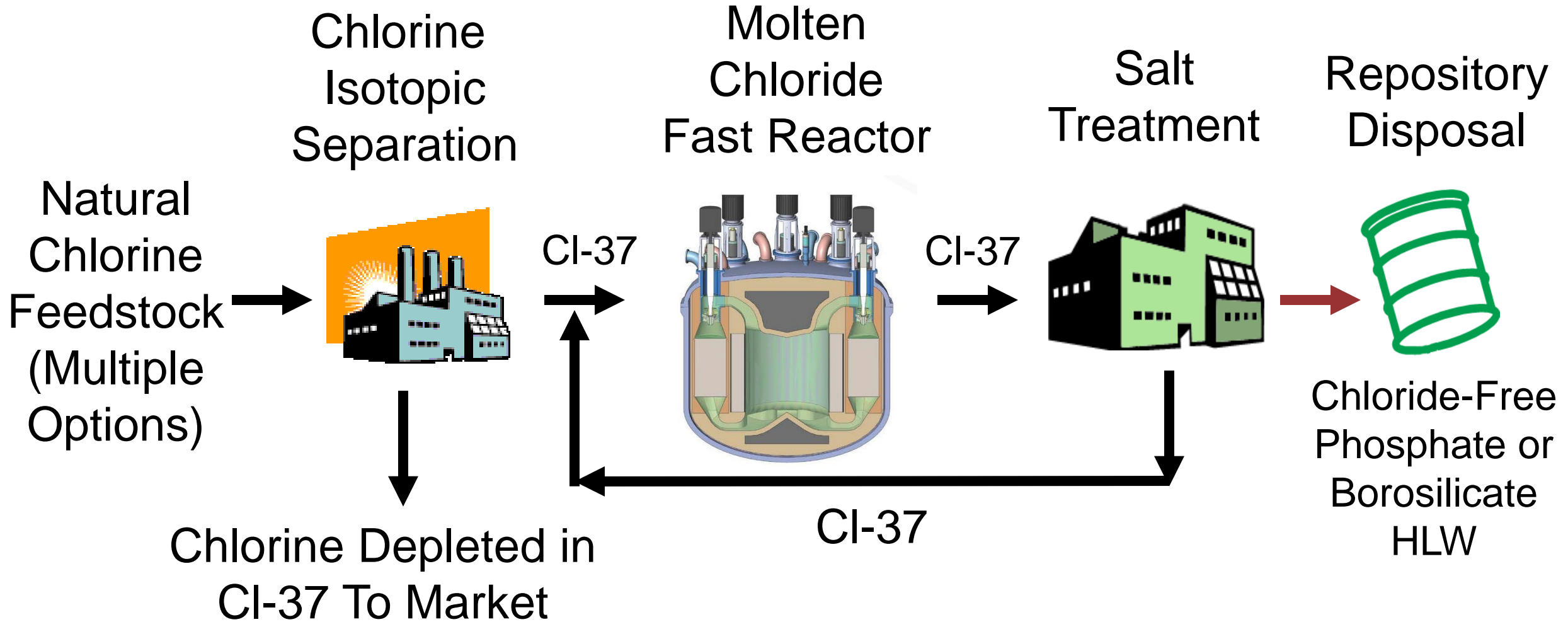
Relatively Simple Process

Conclusions

Conclusions

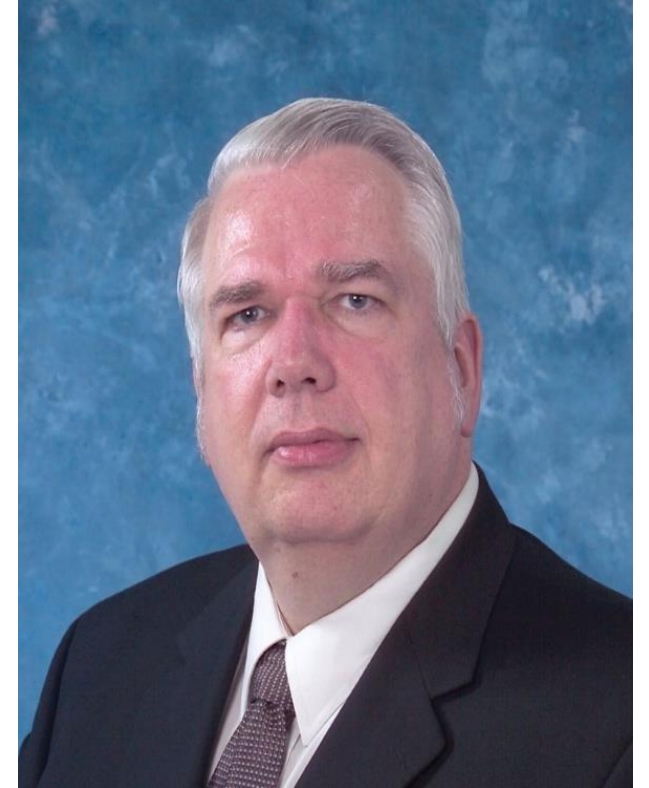
- Large incentives for Chlorine-37 fuel cycle in MCFR
 - Higher breeding ratio in the reactor and smaller fissile inventory
 - Reduce inventory of chlorine-36 in the repository that may control long-term repository risk
 - Better final repository waste forms by conversion to oxide forms
- Multiple isotopic separation technologies for chlorine isotopes
 - Gas centrifuge is the near-term option
 - No systematic study of options in public literature
- Large incentives to use demonstrated and accepted waste forms where processes enable recycle of chlorine-37

Questions

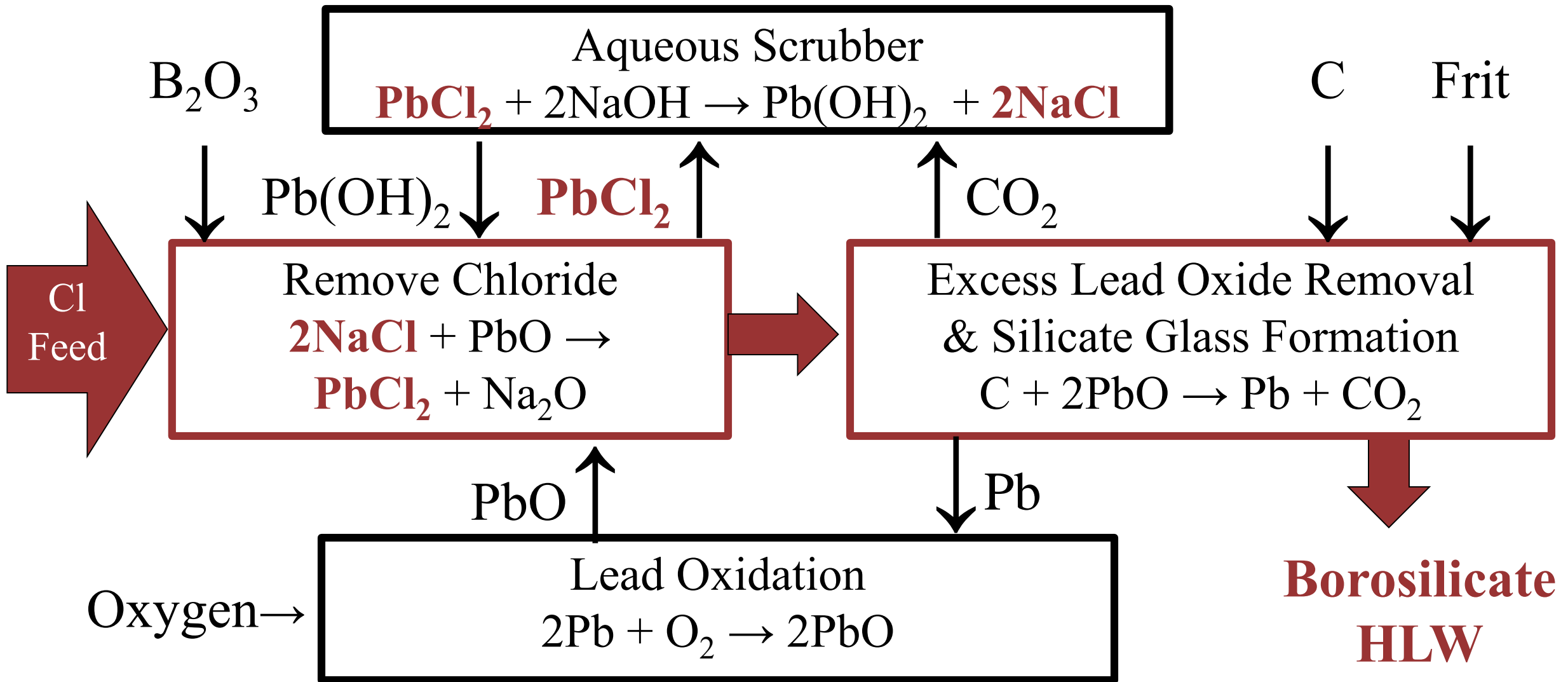


Biography: Charles Forsberg

Dr. Charles Forsberg research areas include Fluoride-salt-cooled High-Temperature Reactors (FHRs) and utility-scale heat storage including Firebrick Resistance-Heated Energy Storage (FIRES). He teaches at MIT the fuel cycle and nuclear chemical engineering classes. Before joining MIT, he was a Corporate Fellow at Oak Ridge National Laboratory. He is a Fellow of the American Nuclear Society, a Fellow of the American Association for the Advancement of Science, and recipient of the 2005 Robert E. Wilson Award from the American Institute of Chemical Engineers for outstanding chemical engineering contributions to nuclear energy, including his work in waste management, hydrogen production and nuclear-renewable energy futures. He received the American Nuclear Society special award for innovative nuclear reactor design and is a Director of the ANS.. Dr. Forsberg earned his bachelor's degree in chemical engineering from the University of Minnesota and his doctorate in Nuclear Engineering from MIT. He has been awarded 12 patents and published over 300 papers.



Convert Waste to Borosilicate Glass



Market Basis for All Salt Systems: Higher Temperature Delivered Heat to Power Cycle

Coolant	Average Core Inlet Temperature (°C)	Average Core Exit Temperature (°C)	Ave. Temperature of Delivered Heat (°C)
Water	270	290	280
Sodium	450	550	500
Helium	350	750	550
Salt	600	700	650

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INTRODUCTION

Several companies [1, 2] are developing molten-chloride fast reactors (MCFRs). In these reactors the fissile isotopes, fertile isotopes and fission products are molten chloride salts. These reactors will function using normal chlorides. However, the breeding ratio [3, 4] is much better if isotopically-separated chlorine-37 (Cl-37) is used because of neutron adsorption associated with chlorine-35.

For breed-and-burn MCFRs, the chlorine must be over 75% Cl-37. Normal chlorine contains 75.77% Cl-35 and 24.23% Cl-37. In a breed-and-burn reactor with a once-through fuel cycle, the reactor starts up with enriched uranium or plutonium and is refueled with natural or depleted uranium. The fuel utilization can be 30 times better than a light-water reactor. It results in a radically simplified fuel cycle with no need for uranium enrichment or reprocessing except for the initial reactor core. Most work on breed-and-burn reactors has been with sodium-cooled traveling-wave reactors with a uranium alloy metallic fuel [5]. There is now an increased interest in MCFRs as breed-and-burn reactors. For MCFRs with fuel recycle, there are large incentives for Cl-37 to boost the breeding ratio and reduce the uranium enrichment or plutonium content of the fuel.

There is a second benefit of using isotopically separated Cl-37. When irradiated, Cl-35 produces long-lived Cl-36 with a half-life of 301,000 years. The use of Cl-37 minimizes production of Cl-36 in the reactor and thus simplifies waste management.

We examine the fuel cycle for use of Cl-37 that includes (1) isotopic separation of the chlorine isotopes and (2) recovery of the valuable Cl-37 when converting chloride wastes into high-level waste (HLW) forms. Removal of the chloride from the final waste form also results in an improved waste form. There is a parallel interest in converting wastes from MSRs using fluoride salts into HLW forms without fluorides to improve waste form performance. The same waste solidification processes can be used. This paper is a first look at the chlorine fuel cycle.

MOLTEN-CHLORIDE FAST REACTORS AND RELATIONSHIP TO TRADITIONAL CHLORIDE SALT PROCESSING OF METALLIC FUEL

There are two classes of MCFRs. The traditional design [1] is a pot, piping, pump and heat exchanger where the reactor core has no internal components. The fluid chloride salt flows around a loop and becomes critical in the reactor

core where the change in geometry enables nuclear criticality. The design has many similarities to other molten salt reactors.

The alternative design by Moltex [2] has fuel assemblies with liquid chloride salt in fuel pins. The fuel assemblies are cooled by a second clean fluoride salt coolant. The pins are vented to avoid pressurization of the fuel pin by fission gases. Filters in the pins limit releases to the coolant—primarily to chemically-inert krypton. The slow circulation of the molten chloride salt in the pin allows uniform fuel composition in the pin over its length when in the core. The liquid fuel avoids solid-fuel pellet-clad interactions. There is a negative reactivity feedback by thermal expansion of the salt with temperature. The fuel pins add complexity to the reactor core but simplify the primary loop that has a clean coolant. To recycle the fuel, the liquid chloride salt is poured from the tubes after the end is cut off—simpler than the front end reprocessing of solid fuel pins. Filling new pins with liquid salt is much simpler than fabrication pins with solid fuel.

The chloride salt will contain fissile and fertile chlorides, fission product chlorides and other salts such as sodium chloride used to lower the melting point and adjust other physical properties of the liquid salt.

MCFRs can have fuel recycle or a once-through fuel cycle. If the chloride fuel salt is recycled, there will be two product streams—a chloride salt returned to the reactor with high uranium and plutonium content and a chloride waste salt with fission products but relatively low concentrations of actinides. The fuel product is a chloride salt—not metal fuel. With once-through fuel cycles the chloride waste includes uranium and plutonium chlorides.

The development of a MCFR once-through or recycle fuel cycle has potentially major implications for the traditional sodium fast reactor fuel cycle with metallic fuel that uses a chloride-salt reprocessing flowsheet. Chlorides make poor waste forms relative to traditional borosilicate and phosphate HLW glasses because chlorides are generally more soluble in water. That is why the ocean is full of chloride salts. The MCFR fuel cycle creates large incentives to recover the Cl-37 from the HLW that enables production of higher-quality chloride-free borosilicate or phosphate HLW forms. That same technology becomes directly applicable to converting wastes from the traditional chloride-salt reprocessing flowsheets for metallic SFR fuel.

ISOTOPIC SEPARATION OF CHLORINE ISOTOPES

Unlike heavy-water enrichment for CANDU reactors, there appear to be no large incentives for very pure Cl-37 [3,

4]. This implies lower requirements for isotopic separation of chlorine isotopes. In a fast neutron spectrum, the primary reaction of concern is Cl-35 (n,p), not the (n,γ) reaction that produces Cl-36. It is likely that the goal will be to increase the Cl-37 enrichment from 24% to somewhere between 90 and 95% Cl-37. Such enrichments would reduce the Cl-35 concentration by about an order of magnitude lowering neutron losses and the production of Cl-36. With no requirement for high enrichments, the enrichment requirements measured in Separative Work Units (SWUs) are reduced.

Because natural chlorine compounds are cheap, there is no incentive to strip most of the Cl-37 from the Cl-35. This is in contrast to uranium where the tails assay of depleted uranium is typically between 0.2 and 0.3% U-235. Because of the higher cost of natural uranium, one wants to extract as much U-235 from the depleted uranium as possible. Consider separating chlorine into a product assay of 90% Cl-37 and a tails assay of 15%. In terms of SWUs, if the tails assay is 15% Cl-37, the relative number of SWUs for 15%, 10%, 5%, 1% and 0.5% Cl-37 tails assay are 1, 1.17, 1.46, 2.17 and 2.50. The cheap feedstock implies the need for fewer SWUs.

Different chlorine compounds can be used for isotopic separation. Chlorine (Cl₂) is unlikely to be used because it exists in three forms: ³⁵Cl-³⁵Cl, ³⁵Cl-³⁷Cl and ³⁷Cl-³⁷Cl. If use chlorine, a three component separation is required that complicates separations and increases costs. The most likely compounds to be used in an isotopic separation process are compounds such as HCl and CH₃Cl in gaseous forms with a single chlorine isotope. These compounds are cheap and commercially available in large quantities because of their use in many industrial applications. Hydrogen chloride is corrosive and when combined with water forms a strong acid. Methyl chloride is used as a chemical reagent in several industries and has been used as a refrigerant—thus there is massive industrial experience in the handling methyl chloride.

Hydrogen in nature contains ¹H and ²H. Carbon in nature contains ¹²C and ¹³C. Isotopic separation of chlorine isotopes with these chemical compounds will result in the Cl-37 compound enriched the heavy isotopes of whatever other elements are in the chlorine compound. It is unclear if the value of these isotopes would have any significant economic implications. No use for isotopically-separated Cl-35 has been identified.

There are many processes to separate chlorine isotopes. We are not aware of systematic study of the options. What is required is a systematic assessment of options such as has been done for uranium isotopic separation in the past [6]. Herein we describe several of the leading candidates but this should not be considered a definitive list of options.

All of these compounds can be separated by gas centrifuge where the separation in practical machines depends upon the square of the mass difference of the two isotopes [7]. Existing gas centrifuges used for uranium

enrichment are also used to separate many stable isotopes. The main question is whether the existing materials of construction are chemically compatible with these compounds. One could custom-build centrifuges for this separation but that would only be justified if there is a large market. In this context, there are significant differences in the details of designs of Urenco (Europe), Russian, U.S. and other centrifuges. This may result in favoring particular suppliers. There is currently a surplus of centrifuge capacity; thus, the potential for industrial quantities of Cl-37.

The capacity of a centrifuge depends upon what is being separated. Separative capacity is roughly proportional to (1) the square of the mass difference times (2) the density times (3) the coefficient of self-diffusion times (4) a set of terms that describe the specific machine. The density times the coefficient of self-diffusion is a constant for any gas. The SWU capacity of a machine for some chlorine compounds is expected to be within a factor of two or three of its uranium SWU rating.

These compounds have low molecular weights where distillation and similar physical processes are potential candidates for isotopic separation. Distillation is used for separation of other light isotopes and depends upon the difference in the vapor pressure of the two compounds. All the candidate chemical compounds have critical points below room temperature and thus cryogenic distillation would be required. There are also many processes based on sorption kinetics on various resins and other materials as well as chemical kinetics of different chemical reactions.

There are multiple laser processes. Laser processes depend upon the chemistry of the specific chemical reaction. It is not possible to make generic statements about the economics of laser processes relative to other processes or make comparisons with uranium enrichment processes.

CONVERSION OF CHLORIDE WASTE INTO SOLIDIFIED HIGH-LEVEL WASTE WITH CHLORIDE RECOVERY

There are large incentives to convert chloride wastes into a borosilicate or phosphate HLW form with recovery of the Cl-37. These are the only two HLW forms where there is large-scale industrial experience, massive data bases of their performance and regulatory acceptance. Qualifying other waste forms would involve significant resources in time and money. Both processes described below can accept wastes with or without uranium, plutonium and minor actinides. The processes enable recovery of Cl-37.

It is highly desirable to remove the chloride from the waste because chloride waste forms tend to be more soluble and have lower performance than other waste forms. The oceans are salty because of chloride salts that are soluble in water, are leached out of soils and flow via rivers to the oceans. This is independent of the economic incentives for recovery of Cl-37

There are multiple phosphate processes [8, 9, 10] but all have many similarities. We describe the process demonstrated by Siemer [9]. The chloride waste is melted with ferric oxide and concentrated phosphoric acid in a stir melter. The phosphoric acid reacts with the chloride releasing hydrogen chloride (HCl) to the off-gas. In the off-gas system the HCl would be scrubbed using an alkaline hydroxide solution such as sodium hydroxide producing sodium chloride (Cl-37) and water. The alkaline hydroxide would be chosen to match the chloride salt required for the MCFR fuel salt. A high-quality iron phosphate glass is produced. All of the steps have been demonstrated in the laboratory and most

of the steps are used in different industries. The chemistry is well understood.

An alternative process (11, 12) is the Glass Material Oxidation and Dissolution System (GMODS) that produces borosilicate glass. The chemistry is demonstrated; but, the process is much earlier in development. Figure 1 shows the equipment and process flowsheets. The waste is mixed in a melter with lead oxide and boron oxide. Lead oxide is a powerful oxidizer and oxidizes any non-fully-oxidized materials producing lead metal that separates as a liquid at the bottom of the melter. The boron oxide is a powerful dissolution agent for any oxide; thus if solids form protective oxides, the boron oxide removes the protective oxide layer.

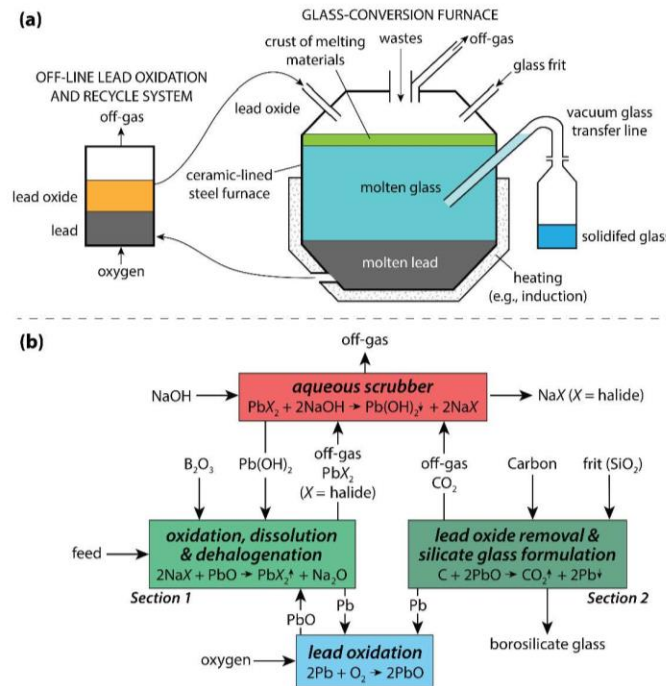


Figure 1. GMODS process showing (a) a schematic [11] and (b) a flow diagram of the process [12].

Halides are converted to volatile lead halides that are sent to the off-gas system and fission product or actinide oxides dissolve in the boron oxide melt. In the off-gas system the lead halide is reacted with an alkaline sodium hydroxide solution creating a soluble chloride salt and an insoluble lead hydroxide. The lead hydroxide is returned to the melter to oxidize any other components.

After dissolution of the wastes, carbon is added to convert excess lead oxide into lead metal that separates from the glass and carbon dioxide that exits to the off gas. Silica is added with other glass formers to produce the HLW form.

There is a variant [13] of GMODS process designed to recover fissile materials using aqueous processes. Chlorides or fluorides or other feedstocks with fissile material are processed through GMODS except for the last step where

glass formers are added. The boron fusion melt is sent to a conventional aqueous process for recovery of fissile material with the aqueous wastes sent to a borosilicate glass plant.

These flowsheets can be modified for variations in the chloride waste stream from the MCFR or from a chloride-salt reprocessing plant for metallic fuel from a SFR. Significant development work is required for the GMODS process.

MOLTEN-SALT-REACTOR FLUORIDE WASTES

The chloride treatment processes, with relatively minor changes, will also convert fluoride wastes from MSR into borosilicate or phosphate waste forms with separation of the fluoride into the off-gas system. That is relevant because fluoride wastes near room temperature in the presence of radiation fields will generate free fluoride [14]. In this context, development of any of these processes may be highly beneficial in the development of better (higher performance, cheaper) waste processes for fluoride-salt MSRs.

CONCLUSIONS

The performance of MCFRs can be improved if the chloride is Cl-37. Generation of radioactive Cl-36 is minimized. Waste form performance is improved by removal of chlorides from the waste. This creates incentives to isotopically separate Cl-37 and recycle Cl-37 during waste solidification—creating a Cl-37 fuel cycle. There are multiple enrichment and waste treatment processes but insufficient work has been done to determine the preferred processes. There are many isotopic separation options. The waste treatment choices with Cl-37 recovery are limited by the economic and environmental incentives to produce a proven borosilicate or phosphate waste form. Recycle of Cl-37 from wastes reduces enrichment costs.

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