Cleanse Electrolyte
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Abstract

Present methods to separate caesium and strontium from other fission products use expensive and hazardous solvents such as calixarene ethers, bis-1,2-dicarbollyl cobalt titanium in nitrobenzene, and an aqueous phase containing polyethelene glycol and 1,2-cyclohexyldiaminetetraacetic acid. A simple aqueous process can separate caesium and strontium from other fission products that remain in electrolyte after pyroelectric refining. All steps operate at atmospheric pressure. Chemical steps operate at room temperature. The only consumed inputs are heat and ammonium sulfate. Inexpensive initial inputs are required, but they are conserved. There are no hazardous or expensive solvents, and no wastes other than fission products. The final waste forms have significantly higher fission-product density than in the zeolite waste form produced at Experimental Breeder Reactor II. Essentially all electrolyte is recovered. The objective is not to obtain pure caesium and strontium, but rather to produce other waste forms that do not contain them. Whether this process is useful depends upon the relationship of its expense to the cost savings that result from storing caesium and strontium separately from other fission products.

1 Introduction

After using the pyroelectric method developed at EBR-II to process one tonne of 5.218%-burnup metallic nuclear reactor fuel that had been stored for ten years, then drawing out trivalent lanthanides [10], and drawing down actinides below 100 ppm [10], eutectic KCl-LiCl electrolyte would contain the amounts of fission products shown in Table 1, according to output from the ORIGEN-2 computer program [1]. This assumes that sodium-soluble fission products such as barium, caesium, iodine, rubidium, strontium, and tellurium have not diffused into bond sodium and then been removed by other means [8].

Element	Element Grams	wt. %	Chloride Grams	Power Watts (th)	Radiotoxicity Sieverts	$T_{1/2}$
Antimony (III)	29.06	0.246	54.40	5.218	6.77×10^4	2.759 y
Arsenic	0.2982	2.41533	0.72	0	0	∞
Barium	2776	23.5	4212.49	0	0	2.552 m
Beryllium	2.29×10^{-4}	1.90×10^{-6}	1.87×10^{-3}	5.338×10^{-9}	1.809×10^{-4}	1.6 My
Caesium	3680	31.2	4653.29	709.8	6.745×10^7	30.04 y
Carbon	4.02×10^{-5}	3.41×10^{-7}	4.41×10^{-4}	52.53×10^{-9}	3.844×10^{-3}	5700 y
Europium (II)	233.4	1.98	341.68	73.35	6.241×10^5	8.593 y
Gallium	7.93×10^{-6}	6.72×10^{-8}	2.01×10^{-5}	0	0	∞
Germanium	0.9951	8.43×10^{-3}	2.87	0	0	∞
Indium	2.892	2.45×10^{-2}	5.58	$<1 \times 10^{-12}$	1.998×10^{-8}	441 Ty
Iodine	357.6	3.03	357.6	22.33×10^{-6}	196.6	16.1 My
Lithium	2.57×10^{-5}	2.18×10^{-7}	1.57×10^{-4}	0	0	∞
Rubidium	524.5	4.44	735.08	26.47×10^{-9}	1.758×10^{-3}	48.1 Gy
Samarium (II)	1284	10.9	1894.60	65.21×10^{-3}	2017	90 y
Selenium	84.68	0.718	159.09	153.9×10^{-6}	66.32	377 ky
Silver	115.4	1.01	153.03	4.922×10^{-3}	30.38	249.8 d
Strontium	1135	9.78	2040.96	562.84	8.697×10^7	28.79
Tellurium (IV)	749.1	6.35	1572.27	0.3411	1.307×10^4	57.4 d
Tin	139.9	1.19	221.68	2.076×10^{-3}	213.9	230 ky
Yttrium	676.2	5.73	1486.14	0	0	2.671 d
Zinc	9.72×10^{-3}	8.24×10^{-5}	0.02	0	0	∞
Total	11810		17867	1351.5	15.51×10^7	
Gases	8558	Not in electrolyte				
Other FP	31812	Remain in anode or removed by third cathode				

There are radioactive isotopes with varying half lives, and nonradioactive isotopes, for most of the elements shown in Table 1. Only the half life of the most radiotoxic isotope is shown.

Whether a high-level waste product contains 1% low-level waste is not important. A low-level waste product containing more than 100 ppm high-level waste is not acceptable. The goals are:

- Process small amounts continuously to maintain desired concentration as fuel is processed.
- Recover essentially all electrolyte in sufficient purity for re-use.
- Produce a harmless barium product with less than 100 ppm caesium, strontium or actinides.
- Produce a caesium product with only small amounts of electrolyte and other products.
- Produce an europium product with less than 100 ppm caesium, strontium or actinides.
- Produce a strontium product with only small amounts of other products.
- Produce a final form of the other fission products with less than 100 ppm caesium, strontium or actinides.
- Maximize storage density.
- Minimize consumed materials.
- No waste other than fission products.
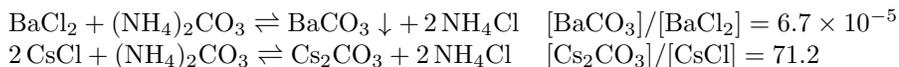- No hazardous or expensive materials.

2   Method

The method shown in Figure 1 is described in succeeding paragraphs.

Figure 1: Separating fission products
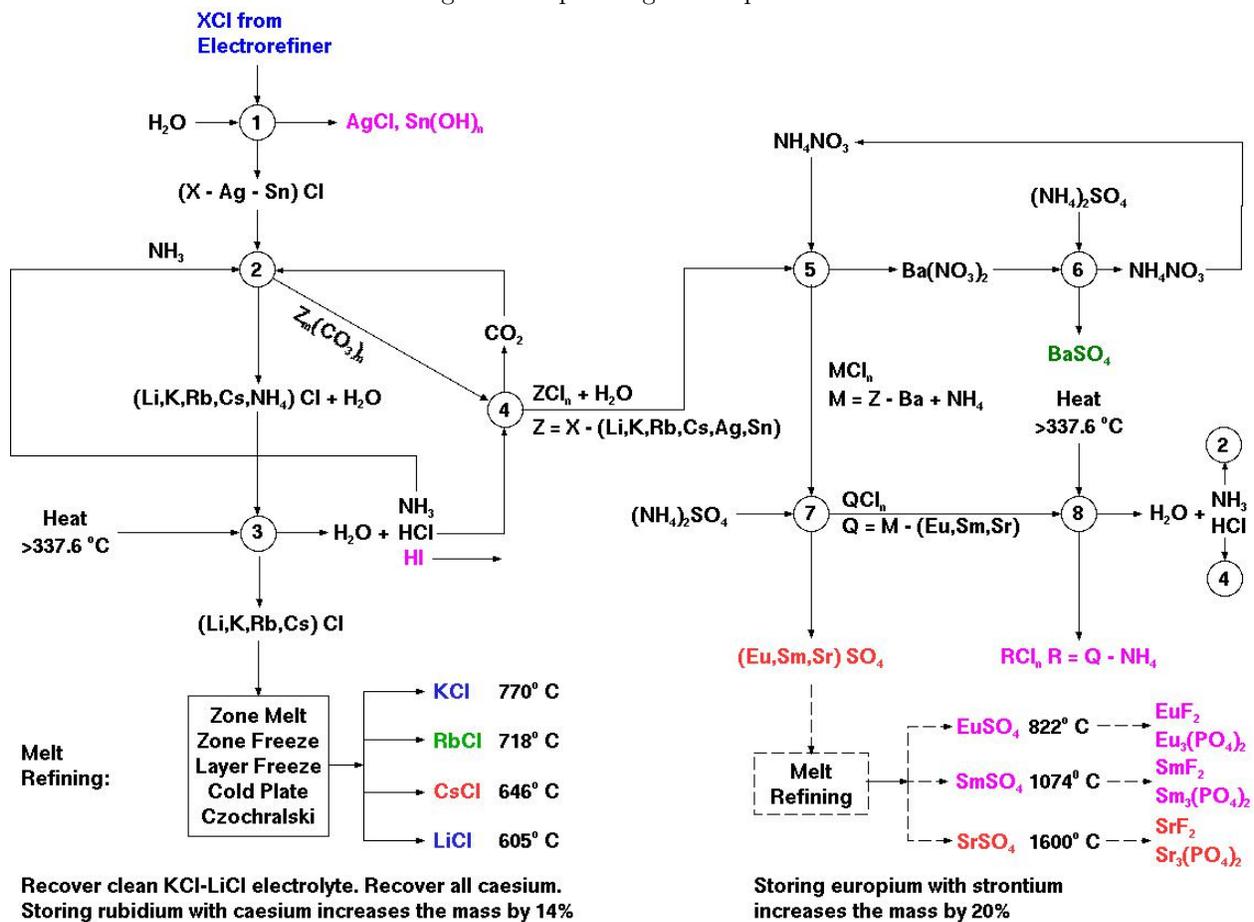
1. Dissolve contaminated electrolyte in water. Remove precipitates of AgCl, and precipitates of $Sn(OH)_n$ that result from hydrolysis of $SnCl_n$. Reduce water to saturate remaining solution.

2. To start the process, Add $(NH_4)_2CO_3$. After the process is running, add NH_3 from steps 3 and 8 and CO_2 from steps 3 and 4 to form $(NH_4)_2CO_3$. Metals other than those in group Ia form insoluble carbonates, but group Ia carbonates are all soluble, e.g. reactions such as,

$$BaCl_2 + (NH_4)_2CO_3 \rightleftharpoons BaCO_3 \downarrow + 2\,NH_4Cl \quad [BaCO_3]/[BaCl_2] = 6.7 \times 10^{-5}$$
$$2\,CsCl + (NH_4)_2CO_3 \rightleftharpoons Cs_2CO_3 + 2\,NH_4Cl \quad [Cs_2CO_3]/[CsCl] = 71.2$$
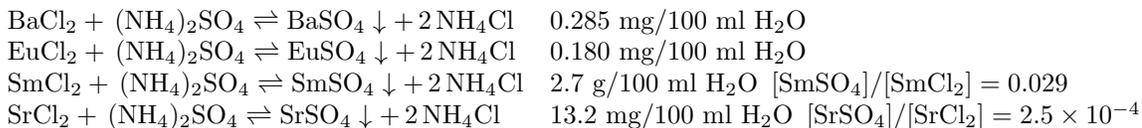
   remove essentially all group Ia salts. Small amounts of other fission product carbonates and chlorides in filtrate with group Ia salts are acceptable. The objective is to remove essentially all group Ia metals, not to obtain them in pure form.

3. Add HCl to filtrate from step 2 as necessary to convert any carbonates to chlorides. Save CO_2 for use in step 2. Evaporate water, then heat to decompose NH_4Cl to NH_3 and HCl ($337.6°C$). Save the NH_3 for use in step 2. Save HCl for use in this step and step 4. If NH_4I is decomposed to NH_3 and HI ($404.7°C$), and HI is used with HCl in step 4, iodine will appear in the final product in step 8. The residue consists almost entirely of group Ia chlorides, and their iodides, depending upon the extent to which iodine appears as NH_4I that is not decomposed.

4. Add HCl from steps 3 and 8 to carbonate residue from step 2. Save CO_2 for use in step 2. All carbonates are converted to soluble chlorides, except AgCl and $Sn(OH)_n$ if they are not removed in step 1. E.g.,

$$BaCO_3 \downarrow + 2HCl \rightarrow BaCl_2 + CO_2 \uparrow + H_2O$$

5. Add sufficient NH_4NO_3 to solution from step 4 to cause most $Ba(NO_3)_2$ to precipitate. $Ba(NO_3)_2$ is slightly soluble (9.02 g/100 ml H_2O at $20°C$). The next least soluble nitrate is $Sr(NO_3)_2$ (70.8 g/100 ml H_2O at $20°C$). Reduce water and separate the $Ba(NO_3)_2$ precipitate. Wash to remove $SrCl_2$ and $Sr(NO_3)_2$, but not enough to dissolve significant amounts of $Ba(NO_3)_2$. The objective is to obtain most of the barium as $Ba(NO_3)_2$ with $[Sr(NO_3)_2]/[Ba(NO_3)_2] < 10^{-4}$, not to obtain all barium.

6. Add sufficient water to dissolve the $Ba(NO_3)_2$ precipitate from step 5. Add $(NH_4)_2SO_4$. Separate the $BaSO_4$ precipitate for disposal. Use less than the stoichiometric amount of $(NH_4)_2SO_4$ so that all sulfate is removed as $BaSO_4$, and no strontium is removed as $SrSO_4$. Use the resulting NH_4NO_3 solution in step 5. If sulfate remains, step 5 will create $EuSO_4$ and $SrSO_4$ precipitates along with $Ba(NO_3)_2$. Recirculating small amounts of $Ba(NO_3)_2$ to step 5 is not harmful.

7. Add $(NH_4)_2SO_4$ to filtrate from step 5. Sulfates of barium, europium, and strontium are the least soluble. The next least soluble sulfates are $SmSO_4$ (2.7 g/100 ml at $20°C$) and $In_2(SO_4)_3$ (53.92 g/100 ml). Do not precipitate excessive amounts of samarium (there is 13% more samarium than strontium, and 5.5 times more than europium). Small amounts of samarium are acceptable. The objective is to concentrate europium and strontium, and to leave very small amounts in solution, not to obtain them as pure compounds. Separate sulfate precipitates.

$$BaCl_2 + (NH_4)_2SO_4 \rightleftharpoons BaSO_4 \downarrow + 2\,NH_4Cl \quad 0.285 \text{ mg/100 ml } H_2O$$
$$EuCl_2 + (NH_4)_2SO_4 \rightleftharpoons EuSO_4 \downarrow + 2\,NH_4Cl \quad 0.180 \text{ mg/100 ml } H_2O$$
$$SmCl_2 + (NH_4)_2SO_4 \rightleftharpoons SmSO_4 \downarrow + 2\,NH_4Cl \quad 2.7 \text{ g/100 ml } H_2O \; [SmSO_4]/[SmCl_2] = 0.029$$
$$SrCl_2 + (NH_4)_2SO_4 \rightleftharpoons SrSO_4 \downarrow + 2\,NH_4Cl \quad 13.2 \text{ mg/100 ml } H_2O \; [SrSO_4]/[SrCl_2] = 2.5 \times 10^{-4}$$

   It might be possible to remove europium, barium, strontium, and samarium sequentially, without using steps 5 and 6, by careful control of the rate of addition of $(NH_4)_2SO_4$. $EuSO_4$ and $SrSO_4$ can be converted to less soluble EuF_2 and SrF_2 using NH_4F, or to $Eu_3(PO_4)_2$ or $Sr_3(PO_4)_2$ using $(NH_4)_3PO_4$. Phosphates generally make good glass. Molten $EuCl_2$ and $SrCl_2$ are immiscible [7, p. 170]. Their sulfates can be converted to chlorides by way of carbonates, which might be justified if separating their chlorides is sufficiently less expensive than separating their sulfates.

8. Evaporate water from filtrate chlorides from step 7 and heat sufficiently to decompose NH_4Cl. Save NH_3 for use in step 2. Save HCl for use in step 4.

The only consumed input is $(NH_4)_2SO_4$, or NH_4F or $(NH_4)_3PO_4$ if sulfates are converted to less soluble fluorides or phosphates. There are no hazardous or expensive solvents.

3   Group Ia chlorides

Chlorides from step 3 are almost all in group Ia. Metals from other groups appear to the extent their carbonates are soluble.

All group Ia chlorides form binary eutectics at around 50 wt.% [7]. It is therefore not possible to perform complete separations using zone melt refining, layer freezing, or a clean cold surface. Williams et al [9] reported recovering 89% of electrolyte from a CsCl-LiCl-KCl mixture. Cho et al [5] reported recovering > 90% of LiCl from a CsCl-SrCl-LiCl mixture..

Assuming optimistically that 97.5% of electrolyte is separated, in a mixture of 50 wt.% KCl-LiCl, 43.5 wt.% CsCl, and 6.5 wt.% RbCl, fission products constitute 40 wt.%. In pure CsCl, the density of fission-product caesium is 79.2 wt.%.

Borho et al proposed an alternative to vacuum distillation to separate eutectic mixtures [4]:

1. Coat a clean surface with pure crystals of the highest melting point component of the eutectic.
2. Flow or trickle molten eutectic over the surface, maintained at a temperature between the melting points of components to be separated.
3. When the surface is sufficiently laden with product, wash it to remove eutectic, but not sufficiently to remove the product.
4. Remove the product by melting or washing.

To separate an eutectic that has more than two components, either a series of devices can be used, or the same device can be used for successive separations by cleaning the surface between separations. If a surface is always used only to separate a single product, it is not necessary to clean it between successive uses.

The Borho et al process cannot be used on electrolyte without first doing steps 2 and 3 because the melting points of some chlorides are above the boiling points of others, e.g., $BaCl_2$ melts at $962°C$, but $TeCl_4$ boils at $380°C$, and some have nearly identical melting points, e.g., YCl_3 melts at $721°C$ and RbCl at $718°C$.

Iodine should be recovered in step 3. Otherwise, it will appear with caesium and lithium chlorides in outputs from the Borho process. Seven surfaces instead of three would be necessary to separate it.

Melting points °C

KCl 779	RbCl 737	KI 681	CsCl 646	RbI 642	CsI 621	LiCl 614	LiI 469

4   Other chlorides

After actinides are drawn out of electrolyte using a third cathode process, about 100 ppm (0.01 wt.%) remain. Actinide carbonates are insoluble, so their chlorides will appear in the output from step 8. If electrolyte is cleansed when the load of fission products reaches 5 wt.%, actinide concentration is 0.2 wt.% after step 2. If sarmarium is removed as sulfate before step 8, the concentration of actinides among the final chlorides is about 1.1 wt.% (as chloride). These actinides should be separated, and returned to the electrorefiner to "fertilize" the next processing operation. The goal is not to recover them as useful fuel, but to allow to store the remainder as low-level waste. Storing all chlorides from step 8 with caesium as high-level waste would increase the weight by 170%. Storing all the chlorides resulting from step 3 together, instead of removing barium, europium, strontium, and maybe samarium, would increase the weight by 380% compared to storing caesium separately.

Even if an immiscible solvent process such is PUREX or TRUEX is necessary for the final actinide separation, the device would be very small because after step 8 only 3.3 kilograms of chlorides remain (assuming samarium is not removed), per tonne of 5.2%-burnup fuel processed.

5 Final waste form

Zeolite-A is used to cleanse electrolyte at Experimental Breeder Reactor II (EBR-II). Ackerman and Johnson [3, p. 5] reported that zeolite includes "significant amounts of occluded and adhered electrolyte" but did not quantify "significant amounts." They also remarked "it appears that Cs and I are also removed, although less strongly." Contaminated zeolite is then mixed with glass frit and compression melted to make a final waste form consisting of glass and sodalite. The method proposed here would put less electrolyte into the final waste form, and less caesium and iodine back into the electrorefiner.

After processing one tonne of 5%-used spent fuel, caesium and strontium must be stored as high-level (154 MSv) high-heat (1273 watts) long-duration (300 y) waste. Europium is medium-level (624 kSv) medium-heat (73.74 watts) medium-duration (85 y) waste. The output from step 8 can be stored as low-level (83 kSv) low-heat (4.8 watts) waste, some of very long duration and therefore very low activity. ^{90}Y is the decay product of ^{90}Sr. After strontium is removed, ^{90}Y in the output from step 8 quickly decays to non-radioactive ^{90}Zr.

The final waste form produced at EBR-II contained 4 wt.% of fission products [2, p. 141]. Table 3 shows that storing europium and strontium as sulfates, fluorides, or phosphates increases storage density compared to storage in zeolyte. Chlorides, including caesium, have been successfully stored in hastalloy containers at Hanford [6]. Forsberg [6] concluded that storing different categories of wastes separately reduces total storage cost. The decision whether to separate fission products depends upon whether the reduction in storage cost offsets the increase in processing cost.

Table 3: Fission product densities, wt.%

Element	Sulfate	Fluoride	Phosphate	Chloride
Caesium				79.2
Europium	61.3	80.0	70.6	
Strontium	47.7	69.6	55.8	

6 Processing rate

For burnup B, the mass of fission product metals that appear in electrolyte is $F = 11.81B/0.05218 = 226.33\,B$ kilograms per tonne of fuel.

The amount of contaminated electrolyte containing weight fraction R of fission-product metals (not chlorides) is $C = F(1 - R)/R$ kilograms per tonne of fuel.

Assuming that fissioning one tonne of heavy metal produces one tonne of fission products and one GWe-year of electricty, with power output P in gigawatts, the rate of fission product production is $D = 0.6197\,P$ kilograms per day. The amount of electrolyte that must be processed per day is $A = D\,(1 - R)/R$ kilograms per day.

A 300 MWe plant produces $D = 186$ grams per day of fission product metals that must be removed from electrolyte after the actinide and lanthanide drawdown steps.

Maintaining a weight fraction $R = 0.05$ of fission-product metals (not chlorides) in electrolyte requires processing $A = 3.532$ kilograms of contaminated electrolyte per day, and maintaining $R = 0.1$ requires processing $A = 1.673$ kilograms per day.

7 Conclusions

The process as described separates caesium, and then europium and strontium, from other fission products. Europium can be easily separated from strontium if desired. Innocuous barium is obtained with less than 100 ppm caesium or strontium. After removing those, the final waste form contains less than 100 ppm caesium or strontium, and very little electrolyte. The original 100 ppm actinide concentration in electrolyte

is concentrated to 1.1 wt.% in the final chloride form, from which actinides ought to be separated. All final waste forms have significantly higher fission-product densities than their density in zeolite as used at Experimental Breeder Reactor II.

The process operates at atmospheric pressure. The chemical steps are aqueous steps that operate at room temperature. The only consumed inputs are heat, ammonium sulfate, and ammonium phosphate or fluoride depending upon the final form chosen for europium and strontium. There are no expensive or hazardous solvents. There are no wastes other than the fission products' final forms.

Whether this process is useful depends upon the relationship between its expense and the cost savings that result from storing fission products having different hazards in different repositories.

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