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A NONAQUEOUS REPROCESSING METHOD FOR THORIUM-BASED FUELS

by

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Introduction

Programs have been active periodically to develop a thorium-based fuel cycle for increasing the nation's resource of fissile material. Part of the effort has been the investigation of nonaqueous reprocessing methods for separating thorium from uranium and the behavior of these elements in the presence of fission products and other impurities.¹ Interest in such pyrometallurgical methods and the entire thorium fuel cycle declined in the early 1970s, primarily due to the lower breeding ratio of the Th-²³³U cycle compared to that of the ²³⁸U-²³⁹Pu cycle, and the consequent effort placed on developing the PuO₂-UO₂ fuel cycle for fast breeder reactors. The recent advent of proliferation concerns has renewed the interest in the thorium fuel cycle and associated pyrometallurgical reprocessing. One reprocessing scheme which addresses the current problem is described below.

The effect of proliferation concerns on the acceptability of a fuel cycle, and the development of aqueous Civex processes designed to meet these concerns have been outlined previously.² One new criterion imposed on reprocessing by proliferation issues is that the process streams be diversion and proliferation resistant. For thorium-based fuel cycles, this means that those products containing fissile material, ²³³U or ²³⁹Pu, must be coprocessed with thorium or be denatured with ²³⁸U. In addition, reprocessing schemes must take into account special features of the thorium fuel cycle, such as the buildup of ²³³Pa which decays to ²³³U. The breeding chain for ²³³U is as follows:

Since ²³³Pa is neutron poison,³ a significant waiting period may be necessary before the reprocessed fuel would be returned to the reactor. Separation of the ²³³Pa would allow a quick return to the reactor, but would lead to a pure ²³³U product, and thus increase the proliferation risk.

Another feature of the thorium fuel cycle which affects reprocessing is the buildup of ²³²U in the irradiated fuel. Equilibrium concentrations of ²³²U may be reached in a few years during fuel irradiation but even 100 day irradiations may produce substantial concentrations of ²³²U.⁴

The decay of the short half life of ^{232}U leads to a long decay chain of nuclides which include a penetrating 2.6 MeV gamma ray. This will likely require shielding and remote handling of the fuel during all phases of reprocessing and refabrication.

A desirable feature for the reprocessing method is that it should be adaptable to various thorium fuel cycles and to several fuel types, and it must be able to produce a product with a high enough fissile content for core fuel specifications. As an example, a fuel cycle which is produced in existing light water reactors (LWR) is combined with thorium and burned in FBRs. The irradiated core fuel from the FBR would contain plutonium, uranium, and thorium while the blanket contains ^{233}U and thorium. The process for the FBR fuel must therefore meet two demands: one product stream must be suitable for HTGRs or LWR fuels and the other for return to the FBR core. The actinides in the spent FBR fuel should therefore be separated into a uranium-thorium portion (for HTGR or LWR) and a plutonium-thorium portion (for FBR core).

Process Description

A conceptual pyrometallurgical method for the reprocessing of thorium-based fuels is presented in Fig. 1. It is responsive to the constraints described previously, being operable with either oxide or metal alloy fuel, and producing product streams consisting of enriched uranium/thorium and plutonium/thorium. The process can be divided into three main steps: (1) oxide reduction or metal dissolution, (2) uranium/plutonium separation and thorium partition, and (3) product recovery. Each step is described below.

1. Reduction

Assuming the fuel to be de-clad using a method compatible with subsequent process steps, it must then be converted to metallic form. For an oxide fuel, this involves a reduction of the type

Carbides can be converted to oxides and reduced as above. Metal alloy fuels are already in suitable form and can be processed directly. Calcium is used as the reducing agent as the free energy of Reaction 1

is -6.6 kcal/mole at 1000°C. The other fuel and fission product oxides are reduced more easily than ThO_2 , thus the reduction should be complete once the thorium is reduced.

The reduction proceeds via the addition of calcium to a magnesium-based alloy which is covered with a fused salt (CaCl_2 , CaF_2). The salt wets the oxide fuel and serves as a medium for the reduction. It also dissolves the CaO produced during the reduction and takes up the alkali and alkaline earth fission products (FP-2) and also the iodine.⁵ The salt represents the major waste stream in the process and needs to be bled off because of a buildup of FP-2. High salt discard rates are not necessary because the CaO is removed by electrolysis and the calcium is recycled. The variables controlling reduction are discussed more fully later.

2. Uranium/Plutonium/Thorium Partition

After the reduction step, the metals partition according to their solubility in the magnesium alloy. Magnesium is used as the focus metal because it provides a means of separating uranium from plutonium.

The solubilities of uranium, plutonium, and thorium in magnesium at 650°C are 0.002 wt %, 55 wt %, and 44 wt %, respectively. Thus, assuming no solute interaction, uranium is essentially insoluble in magnesium, while plutonium is quite soluble and good separation can be effected. Under process conditions the amount of thorium far exceeds other elements. To obtain the necessary division of thorium between the minor uranium and plutonium constituents, only a method of controlling the quantity of thorium in solution is needed. This can be achieved by controlling the amount of liquid magnesium solvent. By limiting the volume of the liquid magnesium, thorium can be divided in a soluble and insoluble fraction. Even more control can be gained by alloying cadmium with magnesium. This alloy solvent retains the low solubility of uranium and complete solubility of plutonium but allows the thorium solubility to be varied between 5 and 42 wt %. It is also compatible with the reduction and retorting operations.

As an example, for one metric ton of plutonium/thorium (1:4) fuel with a burnup of 55 000 MWD the resulting core composition (wt %) is Th-75.5, Pu-14.6, FP-5.9, U-3.7, and Pa-0.3.⁶ Thus, to produce product streams plutonium/thorium (1:4) and uranium/thorium (1:4.5) the process requires 1600 kg of Cd-50 wt % Mg alloy at 600°C.

The necessary nonproliferation constraints are provided by the high radioactivity of each product stream, and the remote handling requirement of each process step. In addition, both the fissile uranium and plutonium are coprocessed with thorium. Pure plutonium cannot be obtained because both thorium and plutonium have a large solubility in the solvent alloy. A pure uranium could in principle be obtained by repeatedly washing the uranium-thorium precipitate with fresh liquid magnesium. However, in practice such separations have proven difficult.⁷ Finally, the protactinium, which decays to ^{233}U , remains with the uranium and does not provide a source of clean fissile material.⁸

3. Product Recovery

After the uranium/thorium precipitate has settled a solid liquid separation is effected. The remaining uranium/thorium is retorted to remove entrained solvent and the product is recovered.

The alloy in which the plutonium/thorium is dissolved also contains the soluble rare earth fission products (FP-3). A fraction of these radioactive products are selectively extracted from the alloy using a "salt-transport" process.⁹ The remainder of the FP-3 fission products stay with the plutonium/thorium stream to provide diversion resistance. The plutonium/thorium remaining in the original alloy is then recovered by retorting the alloy. The solvent in both retorting steps is recycled to the beginning of the process.

Process Chemistry

The direction of each fuel constituent and the control which can be exercised over it during the process is summarized below.

FP-1 (krypton, xenon, hydrogen)--are removed during decladding and reduction and are treated as off gases.

FP-2 (iodine, cesium, rubidium, strontium, barium, europium, samarium)--are removed during the reduction step by extraction into the salt phase. There will be an accumulation of FP-2 fission products in the salt which is controlled by a continuous salt bleed. For 1000 kg of fuel, 2000 kg of salt are required. To keep a constant level of 10% FP-2 in the salt a bleed of 200 kg of salt/batch is necessary.

FP-3 (yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, gadolinium, terbium)--are soluble (~15 wt %) in the process alloy and are removed by selective extraction into the salt after the reduction. This is a salt-transport step and is used as the method of controlling the FP-3 concentration in the process stream and of consolidating the FP-3 for waste handling. A nominal amount of FP-3 remain in the plutonium/thorium stream for diversion resistance.

FP-4 (zirconium, niobium, molybdenum, technetium, ruthenium, lead, palladium, silver, cadmium, indium, tin, antimony)--are only slightly soluble (<1 wt %) in the process alloy, thus will partition between both product streams. The process, as presented, offers no method of FP-4 removal and possibly an unwanted increase in these products would occur if the fuel were to be recycled. However, it would be possible to separate the FP-4 from the plutonium/thorium stream by recovering the plutonium/thorium by hydriding. The FP-4 do not form stable hydrides and would remain in solution.

Uranium--is very insoluble in the alloy chosen for reduction and <0.1% of the uranium in the fuel will be in the plutonium stream. Also uranium does not transfer into the salt during the FP-3 removal to a significant extent so total uranium losses should be negligible.

Plutonium--is very soluble in the process alloy so only through coprecipitation will any follow the uranium stream. There will be some plutonium loss during the FP-3 extraction but should be <0.4% with proper choice of alloy and salt.

Thorium--will not go into the salt at all and is partitioned by solubility as desired between the plutonium and uranium streams.

Protactinium--precipitates with the uranium and after about 300 days will have decayed completely into ^{233}U .

Solubility of Thorium in Cadmium/Magnesium Alloys

The key to the partitioning of thorium in the described conceptual flow sheet is the solubility in cadmium-magnesium. Experimental data associated with this problem have been obtained. The weight percent thorium in solution was determined by taking samples of the equilibrated liquid at

varying temperatures and alloy compositions. The samples were analyzed for thorium, mangesium, and cadmium using atomic absorption spectroscopy and the results are estimated to have a relative accuracy of $\pm 3\%$. Samples were taken in tantalum sampling tubes having a porous tantalum filter (35μ pore) at the end. An explanation of the sampling technique has been reported previously.¹⁰ The melts were contained in tantalum crucibles and equilibrated by stirring for 1-1/2 hours between samples. The temperatures were measured by means of a calibrated chromel-alumel thermocouple with an estimated accuracy of $\pm 1^\circ\text{C}$.

The results are shown in Fig. 3. The thorium solubility decreases uniformly as the cadmium concentration of the melt is increased or as the temperature is decreased. Samples were not taken below 550°C as melts with higher magnesium concentration are solidified.

These results compare favorably with previous data obtained for the solubility of thorium in cadmium¹¹ but indicate a much larger thorium solubility at high magnesium concentrations than had previously been reported.¹² The present results are reasonable in that the solubility of thorium in magnesium is 42 wt % at 582°C .

Electrolysis

During the reduction process, calcium oxide is generated which is collected in the salt phase. The amount of CaO in the salt can reach about 30 atom percent before the reduction rate substantially decreases. The salt can be either discarded as high level waste or processed to remove the CaO . The volume of waste salt generated for each metric ton of fuel processed would be ~ 850 L. This amount can be decreased to 8 L by using the calcium recycle process presented in Fig. 4.

This concept is based on electrolysis of CaO in a fused salt ($\text{CaCl}_2 \cdot \text{CaF}_2$). The net cell reaction is

The cathode reaction generates calcium metal for recycle and the anode reaction yields oxygen which combines *in situ* with the carbon anode to produce a mixture of CO and CO_2 . (For simplicity only CO is considered in

the mass balances.) Thus, the oxygen is removed from the oxidic fuel not as a large volume solid waste but as a common gas which can be scrubbed for release into the atmosphere.

Electrolysis of CaO has been achieved in previous studies¹³ where gram quantities of calcium metal were produced from the fused salt electrolysis of CaCl_2 containing ≤ 2 wt % CaO at $\sim 800^\circ\text{C}$. No chlorine was detected at the anode which indicated CaO rather than CaCl_2 was electrolyzed, which is consistent with thermodynamics.

To establish the feasibility of Equation 2, experiments utilizing a cell design employing a liquid metal cathode and a graphite anode are being conducted. The metal cathode serves as the collector for the calcium metal. The selected cathode metal should be more dense than the fused salt electrolyte and be compatible with the oxide reduction reaction so that the regenerated calcium can be recycled directly to the reduction step. Graphite immersed in the salt electrolyte is used as an anode. The entire cell is operated in a dry argon atmosphere.

Initial experiments utilized cadmium as the cathode CaCl_2 , 15 wt % CaF_2 , 5 wt % CaO as the salt. The cell was run at 700°C and a current density of about 0.5 /cm^2 . The cell potential was 2 volts. The reaction was monitored by taking filtered samples of the metal and salt phases and samples of the gas stream directly above the cell. The results indicate that during the electrolysis the calcium metal concentration in the cathode metal increased from 0 to 3 wt %. The CaO in the salt decreased from 5 to 1 wt % and CO_2 and CO were found in the off gas. These results indicate the electrolysis proceeds as expected and, with optimization of the operating conditions, will serve as a means of recycling calcium metal thus reducing the waste volume from the reduction step.

Reduction

As indicated in the reference flow sheet for oxide fuels (Fig. 1) the processing of the fuel constituents requires a reduction step. Pyrochemical reduction of UO_2 ,¹⁴ PuO_2 ,¹⁵ and ThO_2 ¹² has been demonstrated, but the process parameters have not been optimized for calcium reduction. These parameters include alloy and salt composition, temperature, effect of mixing, CaO and metal loading in the salt and alloy respectively, and type of oxide being

reduced. Importantly, only the reduction of powdered ThO_2 has been demonstrated. Reduction of high fired ThO_2 , as might be obtained from a reactor, has not been attempted. Preliminary experiments designed to demonstrate this reduction are reported.

Two types of high fired thoria (1700°C) were used, 200 mesh microspheres and 1/4 in. pieces of irregular shape (Cerac, 99.9% pure). The other process variables were chosen to be compatible with the flow sheet and to optimize conditions for reduction. A Cd-45 wt % Mg, 10 wt % Ca alloy was covered with premelted salt (CaCl_2 , 20 at. % CaF_2) and equilibrated at 675°C . Enough ThO_2 was added so that with complete reduction the resulting alloy would contain 5 wt % thorium. Upon addition of the ThO_2 the melt was mixed by stirring with a flat impeller located at the salt metal interface. The stirring rate was 800 rpm. The salt and alloy were sampled at the beginning of the experiment and at timed intervals up to four hours. For both types of starting material there was a decrease in the calcium concentration and an increase in the thorium concentration in the alloy indicating the reduction went to about 5% completion. A change in the CaO concentration in the salt, larger than experimental error, could not be detected.

These results indicate the reduction of high fired thoria is difficult and that an understanding of the reaction mechanism is likely to be necessary so that the optimum conditions can be identified.

Conclusions

A conceptual flow sheet for the pyrometallurgical reprocessing of thorium-based fuels has been presented which meets current concerns about nonproliferation and waste control. Preliminary results indicate the desired process streams, uranium/thorium and plutonium/thorium, can be obtained using actinide solubility differences in cadmium-magnesium alloys and that salt waste can be minimized by electrolyzing CaO produced during the reduction process and recycling the calcium. However, further optimization of conditions controlling the reduction rate must be achieved before the process can be used for oxide fuels.

Figure 1

Figure 2

Figure 3

Figure 4

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List of Figures

1. A Conceptual Flow Sheet for Thorium-Based Oxide Fuels.
2. The Solubility of Uranium, Plutonium, and Thorium in Cadmium/Magnesium Alloys.
3. The Solubility of Thorium in Cadmium/Magnesium Alloys.
4. A Schematic Representation of the Calcium Recycle Process Designed for the Reduction of Oxide Fuels.