

12-2010

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**A REVIEW OF THE BENEFITS AND APPLICATIONS OF THE
THORIUM FUEL CYCLE**

An Undergraduate Honors College Thesis

in the

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College of Engineering
University of Arkansas
Fayetteville, AR**

**by
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09-21-2010

Abstract

This paper aims to inform the reader of the benefits that can be achieved by using thorium as a fuel for nuclear power. Stages of the thorium cycle are directly compared against the current uranium based nuclear fuel cycle. These include mining, milling, fuel fabrication, use of various reactor designs, reprocessing, and disposal. Thorium power promises several key advantages over traditional nuclear power methods, namely a dramatic decrease in long lived radioactive waste, increased fuel efficiency, greater chemical stability during disposal, and higher adaptability for differing reactor designs across a wider range of the thermal neutron spectrum. Obstacles that face the thorium fuel cycle are the necessity for remote and automated reprocessing, build up of neutron poisoning and long lived ^{233}Pa in the decay chain during operation, and a large logistical shift in the way the nuclear power industry operates. By combining the thorium fuel cycle with molten salt reactor technology, the first two challenges are mitigated due to the simple reprocessing associated with the novel idea of a liquid based reactor core. Hence, an increase in public demand for thorium power will be necessary to persuade key players in the nuclear industry that the switch to thorium will be economical.

Introduction

Over the past decade, environmental, economic, and social conditions have led to expectations that a worldwide “nuclear renaissance” may soon emerge as a solution to the current energy crisis. Rising oil prices, the threat of global warming, and the growing demand for “green” energy, are considerations that have re-sparked interest in the practicality of nuclear power. However, before such a renaissance can be realized, the nuclear power industry must meet three crucial objectives on a worldwide level: the reduction of both the volume and decay life of spent fuels so as to allow for appropriate geological storage, the development of a nuclear fuel cycle that provides inherent weapons proliferation resistance, and the use of a reactor design that utilizes passive safety features to prevent the event of a nuclear accident.

The conversion from an open, solid element, uranium based fuel cycle to a closed, dissolved liquid, thorium based fuel cycle is a path that will allow such goals to be realized. The whole of the thorium fuel cycle will be discussed, from mining to disposition. The reprocessing side of the cycle will be emphasized, as the inability to adequately reprocess waste is the major drawback facing the nuclear power industry in general. In addition, the advantages, challenges, and recommendations associated with thorium power in each stage of the cycle will be highlighted.

Mining

In the earth’s crust, thorium is 3-4 times more abundant than uranium and is easily extractable. Monazite sands are the primary source for the current extraction of thorium ore. The Nuclear Energy Agency (NEA) estimates that there are a total of 6.08 million tons of thorium world reserves. A more conservative approximation, which only

considers Reasonably Assured Reserves (RAR) and Estimated Additional Reserves (EAR), predicts 4.4 million tons of thorium (*Uranium 2007* 28). Major shareholders of thorium resources include India, Brazil, Turkey, Australia, and the U.S. However, there is considerable debate among competing geological surveys as to who holds what percent of the total, and how much that total is, which will hopefully be settled once an increased demand for thorium ore provides for more in-depth investigations. Another problem, and likely one of the most impeding obstacles facing thorium power, is that though thorium is naturally more abundant in the earth's crust, identified monazite and other high concentration reserves of the element are three times lower compared to uranium. Hence, considerable exploration and prospecting for high density thorium minerals is vital to the prosperity of the thorium fuel cycle (*IAEA 90*).

Typically, monazite sands contain between 6-12% ThO₂. Heavy minerals are separated from the sands based upon physical properties such as specific gravity, magnetic susceptibility, and electrical conductivity. Up to 98% pure monazite is achievable with these procedures (*IAEA 45-46*). An advantage of thorium mining is that the overburden, the amount of soil lying above the desired ore, is much smaller compared to uranium. The radioactive waste produced from mining is also two orders of magnitude lower. This is mostly attributed to the very short half-life of thoron gas, ²²⁰Rn, produced from thorium compared to radon gas, ²²²Rn, produced from uranium. Thoron has a half-life of 56s, while radon has a half-life of 3.8 days. Most of the thoron gas never penetrates to the surface of the soil, thus the inhalation risk is considerably lower. It should be warranted however, that if inhaled, the gamma emitting decay products of thoron, ²¹²Pb and ²¹²Bi, are longer lived than those of radon, leaving more time for them

to be absorbed by vital organs (Kendall and Phipps 427-428). Yet, the open pit nature of monazite extraction provides enough air circulation so that no ventilation system is needed to limit the occupational dose. Thus, the limited risk of inhalation, smaller overburden, and natural ventilation of monazite mining makes the extraction of thorium a more favorable process than that of uranium.

Milling

After mining and purification, the monazite then undergoes a milling process to create ThO_2 powder to be used in the fuel fabrication. The monazite is first finely ground and dissolved in 50-70% NaOH solution at around 140°C . Next, it undergoes a series of chemical processes including solvent extraction and ion exchange methods to obtain thorium nitrate, which can be precipitated to form thorium oxalate. The thorium oxalate is then subject to calcination to form ThO_2 powder. The recent Thorium Retrieval, Uranium Recovery & reStorage of Thorium oxalate (THRUST) project has demonstrated complete recovery in a 99% pure thorium oxalate form. The oxalate compound is very easy to store, handle, and retrieve prior to calcination (IAEA 46). This process is comparable to traditional uranium milling procedures where the ore is ground into a fine slurry before leaching with sulfuric acid to separate the uranium from the waste rock. It is then recovered through a solvent extraction procedure and precipitated as U_3O_8 , commonly referred to as yellowcake (WNA “The Nuclear Fuel Cycle”).

Fuel Fabrication

There are numerous options for designing thorium fuel elements depending upon the type of reactor technology to be implemented. All except the Molten Salt Reactor (MSR) use either ceramic microspheres or packed pellets incased in metal cladding as solid

component fuel elements (*IAEA 48*). The powder-pellet method is the most developed of these processes. For packed pellets, ThO₂ powder from the milling process undergoes several metallurgical processes such as granulation, binder addition, pelletization, and sintering before the product pellet is formed. In order to obtain high densities from the powder, the high melting point of ThO₂ (roughly 3,350°C) requires sintering temperatures of at least 2,000°C. However, the addition of even minute amounts of sintering aids can drastically reduce the required temperature. For example, Nb₂O₅ is an aid that when applied, reduces the necessary process temperature to as low as 1,150°C. The addition of 2% U₃O₈ has provided high density pellets with theoretical smear densities of 96% and a sintering temperature of 1,100°C. This is very useful in the fabrication of thorium-uranium mixed oxide fuel elements, as no additional sintering agents are needed (*IAEA 51*). However, powder pellet fabrication involves the handling of fine radioactive powders that must be carried out in ventilated enclosures to eliminate inhalation. Also, fine powders are not free flowing, thus complicating remote and automated fabrication. This problem is mitigated with the switch to granulated powders which are free flowing. Still, microhomogeneity of the fertile and fissile species in powder form is difficult due to the limitations of mechanical mixing and sintering time to form a complete solid solution formation (*IAEA 53*).

An alternative to the powder-pellet route, which can produce free flowing microspheres without forming dust or powders, is the sol-gel process. In this procedure ammonia gas is first introduced into a rotating disperser shaft that is immersed in a heated vessel containing nitrate solutions of thorium and uranium or plutonium. The sol-gel formed from solution passes through an electromechanical vibrator and size controlling

jetting nozzle to form droplets. These droplet then pass through ammonia gas filled pipes, where they form a gel-skin coat before falling into a NH_4OH gelation bath. A washing step using 1% ammonia solution removes any ammonia nitrate present. Last, the microspheres are placed on a continuous belt drier at 200°C to form the finished product. The only waste associated with the process, is the NH_4NO_3 containing wash water which can be converted to NO_x , N_2O , N_2 , and H_2O gases or to recyclable ammonia and nitric acid (*IAEA 54*). The absence of hazardous radiotoxic dust in the sol-gel process and its free-flowing nature make it very suitable for remote and automated operations. The microhomogeneity is also superior to that obtainable in the powder-pellet process, as the constituents of the fuel element are mixed in the liquid phase. Furthermore, the uranium, plutonium, and thorium nitrate solutions used in the fabrication of sol-gel microspheres, are already end products for the reprocessing stage of the fuel cycle, allowing for reduced materials and equipment costs (*IAEA 53*). One of the disadvantages of the sol-gel process is the lower obtainable theoretical density of 90%, which limits its use in water cooled reactor systems (*IAEA 50*). Other disadvantages associated with the sol-gel process is the precision required for control of the composition, concentration, pH, and viscosity of the feed solution and the fact that the technology is not yet commercially available while the powder-pellet method is a mature procedure (*IAEA 61*).

Fuel Properties and Reactors

Thorium exists as nearly 100% fertile ^{232}Th , which in the reactor undergoes neutron capture and two series of beta decays before becoming fissile ^{233}U fuel that is capable of sustaining a nuclear reaction. This is similar to the traditional “fast-breeding”

fuel cycle where ^{238}U also undergoes neutron absorption followed by two beta decays to become fissile ^{239}Pu (IAEA 1). However, natural thorium contains almost no trace amounts of fissile isotopes that can be enriched to provide sufficient neutron flux to instigate transmutation, as does natural ^{238}U with ^{235}U . Thus, ^{232}Th must be complemented with pre-existing ^{233}U , ^{235}U , or ^{239}Pu at the start of the reaction. Yet, there are several qualities associated with thorium that make it an advantageous fuel source when compared to uranium. In the thermal neutron spectrum, where the kinetic energy of the free neutrons is approximately 0.025eV, ^{232}Th is the superior material as it has an absorption cross-section three times larger than that of ^{238}U (7.4 barns compared to 2.7 barns) which provides a higher, more efficient conversion to fissile material. Likewise, as a fissile material, ^{233}U is advantageous to ^{235}U and ^{239}Pu in the thermal spectrum. It is more adaptable to varying reactor designs due to the fact that more than 2.0 neutrons are liberated per capture over a wider range of the spectrum, than ^{235}U or ^{239}Pu . In addition, though the fissile cross section for ^{233}U , ^{235}U , and ^{239}Pu are roughly similar (525, 527, and 742 barns respectively), the capture cross-section of ^{233}U (46 barns) is much smaller than that of ^{235}U (101 barns) and ^{239}Pu (271 barns). All these factors greatly limit the occurrence of non-fissile absorption, resulting in a dramatic decrease in the presence of higher isotopes and transuranics in the spent fuel (IAEA 8).

A problem associated with the thorium fuel cycle is that the transition product ^{233}Pa , in the decay chain from ^{232}Th to ^{233}U , has a half-life of roughly 27 days compared to 2.4 days for ^{239}Np in the U-Pu decay chain. The extended presence of neutron absorbing ^{233}Pa in the reactor poses the risk of forming transuranics before it can decay to fissile ^{233}U . Therefore, removal and isolation of at least some of the ^{233}Pa for one year is

needed for a complete decay to ^{233}U , to prevent losses in the neutron economy in the reactor and recover fissile material during reprocessing (*IAEA 65*). Also, the formation of ^{231}Pa in the reactor poses a disposal problem as it is a long lived alpha emitter. Thus, the presence of protactinium is another major obstacle facing the thorium fuel cycle and is further discussed in the reprocessing section of this article.

As a solid fuel, thorium exhibits much better physical properties and characteristics suitable to the harsh environment of a nuclear reactor. ThO_2 based fuels have higher melting points, better thermal conductivity, and release less fission gas than do UO_2 based fuels (*IAEA 38*). These advantages are applicable to a variety of reactor designs. For a Light Water Reactor (LWR), replacement of UO_2 fuel assemblies with a mixture of thorium and uranium/plutonium oxides, has demonstrated in the Seed Blanket Unit (SBU) and Whole Assembly Seed & Blanket (WASB) concepts developed by the Nuclear Energy Research Initiative (NERI) a reduction in plutonium content by a factor of 3-5 and the plutonium that is produced, mostly ^{238}Pu , ^{240}Pu , and ^{242}Pu , are unfit for weapons proliferation. The SBU is a one-for-one seed and blanket replacement for a conventional PWR assembly, while the WASB is a seed and blank design where the seed and blanket each occupy one full-size PWR assembly. These once through high burn-up initiatives demonstrated improved fuel efficiency and reduced waste volume, decay heat, and toxicity (*IAEA 14*). In addition, the thorium fuel cycle can also be utilized to burn up existing plutonium reserves in a LWR. Mixed oxide (MOX) fuels containing thorium and plutonium consume roughly twice the amount of plutonium than do traditional uranium/plutonium MOX fuels. Approximately 1000 kg of reactor grade plutonium can be burned up for every 1GWyr in a thorium based LWR (*IAEA 16*). Therefore its use in

the burn-up of weapons grade plutonium could serve as a key stepping stone in the transition from the uranium to thorium based fuel cycle.

Heavy water reactor technology is at the forefront of India's campaign to switch to thorium power. The Advanced Heavy Water Reactor (AHWR) designed by Bhabha Atomic Research Center (BARC) in Mumbai has a burn-up of 20-24 MWd/kg and a power output of 920 MWt/300 MW(e), from which 75% will be contributed by thorium. Due to the higher absorption cross section of ^{232}Th to ^{238}U , fewer neutrons are absorbed by the moderator, coolant, and structural materials so that light water may be used as the coolant, with heavy water as the moderator, further improving neutron economy. The design will also provide passive safety features such as a negative void coefficient, so that reactivity responds to a negative feedback, as well as a gravity driven pool which supplies a large amount of water to submerge and pacify the core in the event of an accident (IAEA 22). India's modest supply of uranium resources and plentiful thorium reserves are likely to prompt the country to be the world leader in thorium based nuclear power in the near future.

Another drawback for the thorium fuel cycle is its limitations in the fast neutron spectrum. In this spectrum, ^{232}Th is less likely to undergo "fast" fission than does ^{238}U and the neutron economy increases much more slowly with increased energy for ^{233}U than for ^{239}Pu . However, investigations with the European Fast Reactor (EFR) showed a 35% decrease in void reactivity when the uranium MOX core was replaced with a thorium based MOX core. A larger amount of plutonium was also consumed due to the switch in fuel type. Still though, in a closed thorium fuel cycle implementing this technology requires over a 300 year doubling time, thus defeating the purpose of quickly

“breeding” fissile material that is normally the principal advantage associated with using the fast spectrum (*IAEA 31*).

Accelerated Driven Systems (ADS) are a cutting edge reactor technology which, when coupled with the benefits of thorium fuels, are capable of providing an extremely safe and sustainable power source that could also be used as means for burning and transmuting plutonium, minor actinides, and other fission products, thus vastly decreasing the need for geological waste disposal. An ADS consists of a proton accelerator which bombards a lead target, and upon impact releases 20-30 spatallion neutrons per proton. These neutrons then pass into the MOX reactor core to sustain the reaction. Liquid lead serves as both the coolant and reflector which encloses the core. Only a relatively small accelerator is needed, so that a 16mA current of 1GeV protons should be sufficient for neutron production. This system is advantageous in that it operates at sub-critical conditions so it is non-self sustaining, providing an excellent control feature dependent upon the accelerator. Most of these designs are suitable for burning and not breeding actinides in the fast spectrum. Thorium’s role in this technology will aid in avoiding the production of higher actinides and will limit the reactivity swing over the cycle (*IAEA 33*). Once this technology is further developed and made more efficient, as the cost of operation and maintenance is very high, it will deem a very effective method of waste prevention and disposal while also providing clean power.

What appears to be the most promising reactor design for the thorium fuel cycle is the one for which it originally was intended, that is the Molten Salt Reactor (MSR) or Liquid Fluoride Thermal Reactor (LFTR). Current reactor designs, typified by solid fuel elements, necessitate that the power plant be modeled as a mechanical operation, the

primary objective being the simplification of heat transfer equipment. However this is paid for by complicated fuel reprocessing. Solid fuel elements remain in the same position during their service time, accumulating fission and activation products until the fuel is so heavily poisoned that the nuclear reaction can no longer take place. The accumulation of poisons such as xenon requires the presence of more fuel than otherwise necessary, resulting in additional generation of waste. Eventually, the operation must be shutdown so that the fuel can undergo maintenance or replacement (Hron 222-223). At the least, the fuel bundles must be routinely shuffled in the core to avoid build up of neutron poisons, but this still requires downtime. Also, reprocessing is generally not economical as the solid fuel must be first converted to a liquid/gas for separations and then back to solid form for geological disposal. One alternative to this approach is a reactor with the fuel dissolved in a liquid core, modeling the facility more like a chemical plant. Such a design seeks to maximize the ease of reprocessing and recovery (Briant and Weinberg 797). The Molten Salt Reactor Experiment (MSRE) performed at Oak Ridge National Laboratory (ORNL) from the 1950's to 1970's was extremely successful and demonstrated the feasibility of the technology. The continuous and flowing nature of the process provided simple fission product removal and reprocessing. Inherent safety and proliferation resistance features were also key elements of the design. A drawback to reprocessing with a MSR is that a reprocessing plant must be collocated with each plant site, which is an added cost. However, on site reprocessing reduces proliferation threats as it decreases the need for transportation.

The MSRE was based upon the idea of dissolving the fertile and fissile materials as fluorides in a molten carrier salt, typically LiF and BeF₂. It was designed as a seed-

and blanket type reactor and was able to operate ^{233}U , ^{235}U , and ^{239}Pu as fissile fuels. The ^{232}Th - ^{233}U cycle is most applicable to a MSR, as it allows for much higher conversion in the thermal neutron spectrum, which is where the reactor operates, while the ^{238}U - ^{239}Pu cycle needs to take place in the fast spectrum to obtain complete conversion. In the original design of the MSRE, an inner spherical core contains the dissolved $^{233}\text{UF}_4$ in the fuel salt, where the nuclear reaction takes place. This is surrounded by a second vessel containing $^{232}\text{ThF}_4$ dissolved in a blanket salt. Neutron flux from the inner core passes into the blanket salt to transmute the thorium to fissile uranium. The blanket salt is continuously sent to a chemical processing plant where the thorium is returned to the blanket while the uranium is sent to the inner core fuel salt. Similarly, the fuel salt is also sent through a chemical separations procedure to remove fission products from the fuel. The rationale behind this design is due to the fact that thorium and the formed fission products are chemically similar, thus isolating the two species greatly simplifies the reprocessing procedure. The problem with this design was that the allowable critical diameter of the inner core was only 1 meter, too small to obtain sufficient power output on an industrial scale. The design was then altered so that the fluids were interlaced by an integrated plumbing scheme to provide sufficient neutron flux between the salts, while still keeping thorium separated from the fission products. However, the graphite present in the core would shrink and swell under the presence of the high irradiation, yielding a complicated and sensitive “plumbing problem”. A subsequent design was adopted that contained all the dissolved species in a single salt mixture. This design was eventually constructed and ran successfully for five years. The simplification of the reactor though, was compensated for by the difficulty in reprocessing the waste. ORNL used a Liquid

Bismuth Reductive Extraction (LBRE) process to separate the fission products from thorium, but it was a very costly, complex, and delicate process (LeBlanc “Liquid Fluoride Reactors”). Now, with the current revival of interest in nuclear power, re-investigations of ORNL’s “plumbing problem” in the two fluid design or optimization of the difficult LBRE process with current pyrochemical methods may provide an effective and economical way of closing the nuclear fuel cycle.

Construction of a two fluid MSR capable of handling the flexing problem associated with the plumbing will greatly reduce the challenge of reprocessing. For the blanket salt, bubbling F_2 gas through causes dissolved $^{233}UF_4$ to form gaseous $^{233}UF_6$, which can be easily removed, converted back to $^{233}UF_4$ by reacting with H_2 and sent to the fuel salt. Likewise, for the removal of fission products from the inner core, uranium and gaseous fission products are first removed separately from the fuel salt based upon fluoride volatility. The salt is then placed in a still to undergo vacuum distillation. The decay heat of the fission products facilitates the evaporation of the salt which is re-combined with the uranium, while leaving solid fission products behind for disposal. In addition, the two-fluid design solves the thorium fuel cycle’s protactinium problem. The risk of ^{233}Pa absorbing neutrons to form transuranic wastes is lessened because the neutron flux in the blanket salt where the protactinium is formed is much lower. Thus, ^{233}Pa can be allowed to simply remain in the salt and decay to ^{233}U (LeBlanc “Liquid Fluoride Reactors”).

Efficiency, safety, and proliferation resistance features make the MSR a viable technology. The chemical and physical stability of the salt allow the reactor to reach much higher temperatures than traditional solid fuel reactors. The MSRE, a 1000 MWe

design, demonstrated an operating temperature of 700°C, significantly higher than that of a typical LWR (~315°C). For any power cycle, higher temperatures result in higher efficiencies. A MSR could potentially allow power plants to replace steam driven turbines with the more efficient gas driven turbines (LeBlanc “Liquid Fluoride Reactors”). Today, a current 1 GW capacity nuclear plant requires up to 800,000 tons mined uranium ore to undergo milling and fuel fabrication, of which results to roughly 35-40 tons of spent fuel per year. A 1GWyr MSR however, only requires around 200 tons of thorium ore and results in about 1 ton of fission products and little to no transuranic waste due to the use of thorium as fuel. The absence of transuranics means that only 300-500 years is needed for the entirety of the fission product waste to decay to a stable and safe state. In addition, in the thermal spectrum, the best way demonstrated of obtaining complete fuel consumption is by use of a MSR run on the thorium fuel cycle. If all of the fuel from the uranium cycle is desired to be burned, the neutronic speeds must be switched to the fast, and arguably less safe, spectrum. With such efficiencies, it is possible that a thorium fueled MSR is capable of producing enough energy so that only 100 grams of pure thorium would represent the average U.S citizen’s lifetime energy consumption. In comparison 3.5kg of Lightly Enriched Uranium (LEU) would represent the same amount of energy (Sorensen “Energy from Thorium) as would 54 tons of coal (ENS “Fuel Comparison”).

The design of a MSR is also inherently safe. As the fuel salt heats up inside the core, it expands and flows out of the high neutron flux zone. This loss of fissile material in the core limits the extent of reaction and cools down the system. The process works in reverse as well when the reactor is performing below the desired output temperature, the

more dense salt allows more fissile material to flow in and increase the neutron economy. Unlike traditional pressurized water cooled designs, the liquid salt in the MSR serves as its own coolant and its high boiling point allows it to operate at low pressure. This eliminates the risk of a high pressure rupture in the system, so that no expensive containment vessels or piping and equipment designed for high pressure applications are needed. If there were however, a breach in the system, the high melting point of the salt would simply cause it to solidify upon contact with the air and possibly even seal the break. In the event of a loss of power to the system, ORNL developed a simple and effective method for cooling the reactor. Under normal operation, a fan system was used to cool and solidify a section of piping containing the salt, known as the “freeze plug”. If power was lost, the freeze plug would simply melt and the molten salt would then flow to a passively cooled containment vessel. This is much simpler than current reactor designs where emergency coolant has to be brought to the reactor and override normal operation procedures (Sorensen “Energy from Thorium”).

As a guard against weapons proliferation, the simple fact that the fuel exists as a molten liquid form with a temperature of at least 500°C makes it a difficult material to misappropriate. In addition, the use thorium fuel cycle yields ^{232}U as a side product of the burn-up chain, regardless of the reactor design, which also enhances proliferation resistance as its daughter products are strong gamma emitters that make direct handling and weapons usage difficult (*IAEA 66*). Furthermore, in the event of the security of the facility being compromised, $^{238}\text{UF}_4$ can be quickly dumped into the reactor, denaturing it to a form unsuitable for proliferation (LeBlanc “Liquid Fluoride Reactors”).

THOREX Reprocessing

The THOREX process is the most developed method for reprocessing. However, this process which utilizes a liquid-liquid extraction technique for the removal of uranium, thorium, and/or plutonium from the fission products has yet to reach the efficiency and practicality of its equivalent PUREX process (*IAEA 65*).

The first step of reprocessing solid fuel elements from a LWR is the removal of its protective cladding, commonly referred to as the head-end process. This consists of either a series of mechanical de-cladding operations or a chemical de-cladding procedure. For most Zircaloy or stainless steel clad fuel elements the mechanical option is usually implemented, and consists of cutting, grinding, shearing, and crushing away the casing. The chemical option consists of either a dry-fluorination procedure, a SULFEX solution (5 M HNO₃ + 2 M HCl and 5 M H₂SO₄) for SS removal or a ZIRFLEX solution (6 M NH₄F + 0.5 M NH₄NO₃) for Zircaloy removal (*IAEA 71*).

After the head-end process, the fuel is dissolved in the nitric acid based THOREX solution. This solution undergoes a varying degree of feed preparation, extraction, partitioning, and stripping stages depending on whether uranium, uranium and thorium, or uranium, thorium, and if present plutonium are desired to be recovered. Tributyl phosphate (TBP) dissolved in dodecane is generally used as the extractant. Control of the concentration of TBP and acidity of the scrubbing and stripping solutions permits selectivity of what actinides will be recovered (*IAEA 72*).

In the 1980's, Zimmer and Merz performed much work fine tuning the THOREX process developed by ORNL in the 1950's by adjusting and optimizing acid and TBP concentrations throughout the extraction process in order to maximize decontamination

factors and minimize precipitant crud formation. They also proposed the use of pulse columns for reprocessing thorium fuel. Compared to mixer-settlers, pulse columns provide less contact time between fission products and the organic phase, which leads to less decomposition of TBP into unwanted DBP. Also, any crud precipitation formed in the process is less likely to cause clogging than in mixer-settlers due to the increased flow velocity as well as a decrease in the occurrence of any unwanted third phase complexes associated with thorium and TBP. However, the issue of criticality should be acknowledged with pulse columns, as it was observed that the concentration of uranium in the upper part of the column in the partitioning stage is one order of magnitude higher than in the feed solution (Merz and Zimmer 338-339).

The most common method of THOREX reprocessing is the sole retrieval of uranium leaving thorium discarded in the raffinate, known as the INTERIM 23 process. 1.5% to 5% TBP is used in the extraction stage, followed by a series of scrubbing stages with 1-2 M HNO₃, and ending with a dilute nitric acid stripping stage to remove the ²³³U from the organic solvent. If further purity is desired, an anionic exchange method in HCl solution may be used. This however, presents problems as corrosion control is arduous to maintain and the resulting corrosion products lead to poor decontamination factors (IAEA 72).

When the retrieval of both uranium and thorium is desired a 30% to 43% TBP solution is capable of extracting both actinides. An acid strip greater than 0.3M HNO₃ used in the partitioning stage removes the majority of the thorium, while a very dilute acid strip removes the uranium from the organic. A problem associated with this procedure is the aforementioned formation of a third phase due to poor solubility of the

complexes formed by thorium and TBP in the dodecane diluent. Replacements for dodecane capable of sufficient loading without formation of a third phase are currently being considered such as amides and aromatic diluents (IAEA 73).

Little investigation has been undertaken in the development of a three stream process for recovering plutonium if Th-Pu MOX fuel is used. This process would theoretically combine aspects of the PUREX and THOREX processes. A 5% TBP extraction / scrubbing / stripping process will yield a U-Pu nitrate solution that can then undergo traditional PUREX processing for eventual formation of separate oxide powders. The leftover thorium contained in the raffinate will then be removed from the fission products with at 30% TBP extraction / scrubbing / stripping process followed by precipitation and calcination to form an oxide powder. A problem presented in this scheme is the formation of nitrous gases that stabilize plutonium ions, limiting their solubility in the initial 5% TBP extractant. Considerable research is needed concerning the process chemistry of this scheme before its application can be realized (IAEA 74).

If the intermediate ^{233}Pa , in the transmutation of ^{232}Th to ^{233}U , is desired for recovery and eventual conversion to ^{233}U , then considerable technological development must be undertaken. In the current THOREX process, protactinium passes through with the fission products in the raffinate waste. Not only is this a loss of the potentially re-usable ^{233}Pa as a transitional to ^{233}U , but it also means that any ^{231}Pa formed in the burn-up chain of ^{232}U will be carried with the remaining waste for permanent disposal. ^{231}Pa is an alpha emitting isotope with a long term radiological impact constituting a half-life of 3×10^4 years that is a concern regarding geological disposal. The recovery of both of these

isotopes of protactinium would limit the amount and severity of the waste product and reduce fuel consumption as both can be converted to ^{233}U in the reactor (IAEA 65-66).

An alternative to recovering ^{233}Pa from the spent fuel is to simply allow it to decay to ^{233}U before reprocessing. However, as stated early, this requires storage time of one year that can be expensive. Oddly enough, it appears that the most viable solution to solving the protactinium problem may have been already solved by ORNL in the 1960s. They were able to successfully adsorb 98% of the protactinium dissolved in THOREX solution on pulverized unfired Vycor glass. This was done by introducing agitated contact between the protactinium containing solution and the Vycor glass for 24 hours. The difference in the gross gamma count of the glass and aqueous raffinate was then used to measure the amount of adsorbed protactinium. In order to determine if this technique is transferable to an industrial process, ORNL suggested that a hot-cell experiment involving THOREX solution from spent fuel pins be performed to determine the effects of fission product concentrations on the adsorption of protactinium under normal process conditions (Moore 1-2).

It should be noted however, that the attainment of ^{233}U from ^{233}Pa from reprocessing poses a significant weapons proliferation problem. Any ^{233}U obtained from ^{233}Pa , will be considered Highly Enriched Uranium. This ^{233}U will have little of the proliferation limiting ^{232}U that it is normally associated with in the thorium burn-up chain. Thus, the Vycor adsorption process would limit the protactinium problem, so long as the protactinium recovered was sent back to the service end of the fuel cycle before conversion to ^{233}U .

In addition, the THOREX process faces another challenge concerning the role of ^{232}U . On the one hand, the ^{232}U formed by (n, 2n) reactions of ^{232}Th , ^{233}Pa , and ^{233}U in the thorium decay chain provides a natural proliferation barrier as its decay products, such as ^{212}Bi and ^{208}Tl , yield strong gamma emissions of 0.78MeV and 2.6MeV, respectively. These emissions are capable of compromising the electronic triggering components of a military weapon attempting to utilize reprocessed ^{233}U , potentially rendering such a bomb unstable or useless. The presence of such radiation will also greatly aid in the exposure of concealed nuclear weaponry due to the growing science and technology of nuclear detection systems (IAEA 9). On the other hand, the presence of ^{232}U complicates spent fuel reprocessing. It has a half-life of roughly 72 years and the radioactivity of its daughter products necessitates remote, shielded, and preferably automated reprocessing. While this may be beneficial in deterring the proliferation of the spent fuel, it is costly and complicated. This is due to the fact that both ^{232}U and its alpha decay product ^{228}Th are chemically inseparable from their respective isotopes of ^{233}U and ^{232}Th (IAEA 66). Isotopic separation of the thorium should be easily achievable with current centrifugal effect technology due to the relatively large difference in atomic mass between the isotopes. However, the very slight mass difference between the uranium isotopes may prove to be a challenge. Emerging separation technologies involving mass spectrometry or atomic laser vapor isotope separation (AVLIS) may prove applicable to this process once further developed.

If desired, the amount of ^{232}U can be minimized by controlling the neutron flux spectrum of the reactor. Higher ^{232}U concentrations are associated with fast neutron spectrums than with thermal. For a fast LWR, for example, the ^{232}U present is roughly

on the order of 2000-3000 ppm. In a thermalized PHWR, ^{232}U concentration is expected at 500-1000 ppm. However, it has been demonstrated by the BN-350 sodium cooled fast reactor in Kazakhstan, that by introducing a 15-20 cm spacing between the thorium blanket and central core, ^{232}U can be all but eliminated. The ^{232}U obtained from this design was only 2-11 ppm, proving that minimization of ^{232}U can be achieved, but this returns us to the proliferation problem of reprocessing pure ^{233}U (IAEA 66).

Unlike UO_2 and PuO_2 , ThO_2 exists in only one oxidation state, making it more stable under most storage and process conditions. While UO_2 is easily dissolved in nitric acid, mixed fuels containing over 80% ThO_2 cannot be dissolved in pure HNO_3 . A small amount of HF is needed to aid in the dissolution. The addition of HF, however, introduces a corrosion problem for stainless steel piping and equipment. These effects can be mitigated with the addition of aluminum nitrate, which complexes with excess free fluoride ions that would otherwise instigate corrosion. In the 1950's ORNL developed a process using the following dissolved acid: 13M HNO_3 +0.05 M HF+0.1M $\text{Al}(\text{NO}_3)_3$ which is now the accepted THOREX solution formula and has served as the best medium for dissolving ThO_2 to date. ThO_2 is dissolved in THOREX solution at $\sim 120^\circ\text{C}$ and ambient pressure, while coupled with agitation. Increasing the temperature and pressure to $\sim 200^\circ\text{C}$ and 9 atm greatly increases the dissolution rate, but of course increases safety risk as well. It has been also demonstrated that irradiated fuel dissolves more readily in solution than fresh fuel. This is most likely attributed to disturbances formed in the crystal structure of the spent fuel during the service period. Recent experiments performed with un-irradiated fuel have also shown that the addition of roughly 1.5%

MgO during the pellet fabrication stage and replacement of HF with NaF in the THOREX solution lead to increased dissolution rates (*IAEA 66*).

Disposal

The direct disposal of spent thorium fuels would be anticipated to be very similar to that of uranium. Currently, different countries have adopted different methodologies for disposing of nuclear waste. In the U.S, civilian waste remains on-site in large cooling ponds. These large concrete structures serve to provide radiation protection and remove heat generated from radioactive decay. It is intended that after sufficient cooling time, the waste from these pools will be encapsulated and transported to a permanent geological repository such as Yucca Mountain in Nevada or the Waste Isolation Pilot Plant in New Mexico (WNA “Waste Management”). In Canada, long term waste management plans involve placement of the waste in corrosion resistant containers enclosed by a clay-based buffer barrier. These containers are then set into a deeply excavated granite vault for permanent disposal (*IAEA 76*). In Europe, much of the spent fuel is actually reprocessed in either the UK or France. The recovered fuel is returned to the plants, while the waste is vitrified, sealed in stainless containers, and either stored at the reprocessing facility or returned as well. Eventually, the waste will also be sent to permanent geological disposal (WNA “Nuclear Waste Management”). Thus, regardless of when and how the waste gets there, a geological repository is the final step in waste management for all countries. It is here where thorium based fuels hold the advantage over traditional uranium fuels. The high chemical stability of ThO_2 and its very low solubility in groundwater aids in its retention of harmful fission products, making it suitable for direct geological disposal. Also, it has been shown that fission gas release

from defected thorium fuel elements is 1 to 2 orders of magnitude lower than that of uranium and that release of Br, Cs, and Rb from the fuel matrix is much slower as well (IAEA 78). In the event of a rupture of the casing material during permanent disposal, a gas leak containing radioactive material would pose safety and logistics issues, which a thorium fuel cycle would moderate.

Conclusion

A dramatic renovation in the operation and protocol of the nuclear power industry must be undertaken in order for the thorium fuel cycle to be utilized. This will be an extremely difficult task, as a whole new nuclear infrastructure will have to be installed and will be in direct competition with very strong and influential enterprises that already have a reliable and profitable system established. Thus, the only way for thorium power to be economically accessible, is for an increased public awareness of the benefits it can provide, so as to feed demand. Thorium is capable of fixing the negative stigma associated with nuclear energy by providing a sustainable, safe, and weapons resistant form of power. When coupled with MSR technology, the thorium fuel cycle will be capable of producing little to no long lived transuranic waste, will have a natural negative void coefficient during service end operation, and will deter weapons proliferation with the presence of ^{232}U and ease of denaturing. The more minds that are aware of and insist upon the use of thorium power, the sooner it will be economically realizable and available to the public as a very clean form of energy.

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