

Reprocessing of Ceramic and Molten Salt Nuclear Fuels

NE551 - Nuclear Reactor Fuels

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1 Introduction

Nuclear reactors are messy. They produce power by splitting a fissile atom, most commonly ^{235}U into countless exotic nuclides, many of which are highly radioactive and some which negatively contribute to the neutron economy in the core. Further, the neutron fluence through the heavy metal fuels produces transuranic isotopes, which also can be radiological hazards [1], but can be useful, as they (particularly ^{239}Pu) can themselves serve as fission fuel.

An entire field of nuclear engineering, called reprocessing and recycling is focused on this issue [2, Ch. 7]. In addition, reprocessing can be used to give new life to used fuel [3, Ch. 10], since the reactor does not run to completion - fissile and fertile species remain. Nearly all commercial reactors are solid fueled, so recycling and reprocessing can only be performed after the fuel is removed from the reactor. Some reactor concepts, like the molten salt reactor (MSR) utilize a liquid fuel which circulates with the coolant between the core and the primary heat exchange system [4, Ch. 2]. This opens the door to online refining which extends the lifetime of the fuel by stripping out poisons such as ^{135}Xe and ^{149}Sm , restoring excess reactivity to the core.

2 Overview of the Nuclear Fuel Cycle

Like any raw material, nuclear fuel begins in the ground. Its destination, too, is in the ground. It is almost always inert before processing, with a notable exception at the Oklo mine in Gabon [5]. This paper is focused primarily on nuclear fuel reprocessing and recycling, with an extra look into molten salt refining, but it is still worth briefly discussing how we turn bedrock into electricity to better understand where the material we are reprocessing comes from. Similarly, it is important to understand what happens downstream from the reprocessing facility to show why it is important.

2.1 Mining and Milling

An ore-bed is first identified, often by finding locations with higher than normal background radiation [2, Ch. 2]. The ore, containing U_3O_8 , is then taken out of the ground by open pit

mining, underground mining, or *in-situ* leaching, where a leachant is pumped into the ground to extract the ore without digging. In the particular case of underground mining, precautions must be taken to prevent long-term exposure to radon and uranium dust from harming workers [6]. The ore is then concentrated to yellow-cake uranium by a series of steps, beginning with comminution and roasting to a size small enough to be effectively leached (note: This step is not required when uranium is mined by *in-situ* leaching.) in an acidic and oxidizing solution. Tailings are thickened and stored in waste ponds, which contain radium and other decay products and require proper radiological management [2, Ch. 2]. Organic solvent extraction and ammonium chloride stripping purify the U_3O_8 , which can be precipitated using ammonia and dried into a powdered concentrate.

2.2 Conversion and Enrichment

The powdered concentrate is purified using a solvent extraction process, either organic or peroxide based. It is then converted by a two step process [2, Ch. 3]: 1) hydrofluorination to uranium tetrafluoride ($U_3O_8 + 4HF \rightarrow UF_4 + 2H_2O$); and 2) fluorination to uranium hexafluoride ($UF_4 + F_2 \rightarrow UF_6$), which is a gas. The ratio of ^{235}U to U [238] can be increased in a centrifuge, which spins to separate the species by weight [3, Ch. 14]. After many stages, the enriched UF_6 is pressurized to deposition so it can be stored and shipped as a solid.

2.3 Fuel Design and Fabrication

Enriched uranium is converted from UF_6 into the desired form (metallic or ceramic) UO_2 is the most common fuel, and is formed by: 1) bubbling the gas through water ($UF_6 + H_2O \rightarrow UO_2F_2$); 2) precipitating as ammonium diuranate (ADU) with ammonia; 3) calcining to U_3O_8 and reducing to UO_2 with hydrogen; and 4) powdering, binding, pressing, and sintering to form pellets. These pellets are placed in cladding tubes with room for fission gasses. The cladding is often made from zirconium alloys, or Zircalloys [7, Ch. 1]. Zirconium ore always contains hafnium, a notable neutron absorbing material, so proper separation is required to ensure the cladding has good neutronic properties [3, Ch. 7]

2.4 Storage

After fuel rods are taken out of the reactor, they are placed in a spent fuel pool on-site to cool down [1, 8, Ch. 4]. These have limited capacity, hence the need to reprocess spent fuel and prepare for long-term storage. Reprocessed waste could be casked and buried forever in a well-characterized geologic storage such as Yucca Mountain [9] in Nevada (development on this site has been tabled indefinitely), or Onkalo in Finland [10].

3 Reprocessing and Recycling

After light water reactor (LWR) fuel is removed from the reactor, it still contains as much as 33% of fissile atoms (^{235}U plus transuranics like ^{239}Pu) that it began with [2, Ch. 7]. By reprocessing the spent fuel, these nuclides can be isolated and recovered. They can then be recycled into new fuel, such as MOX, or mixed oxide fuel, which appropriately consists of a mixture of UO_2 and PuO_2 . This is like burning a gallon of gas in our car, catching the combustion gasses, and using them to drive another 10 miles. Unfortunately, the processes outlined below are not allowed in the power reactor fuel cycles due to non-proliferation concerns.

3.1 PUREX Process

Among the most prevalent reprocessing methods is the PUREX process; a liquid-liquid extraction process that manipulates valence states to selectively extract U and Pu into an organic solvent (tri-*n*-butyl phosphate (TBP) blended with kerosene), and then strip it back into the aqueous phase for recovery [2, Ch. 7]. The fuel is broken into pieces and dissolved into nitric acid, then extracted into the organic phase by forming a +2 oxidation complex with TBP [11]. The ^{239}Pu is then reduced to plutonium (III) using hydrazine and (historically) ferrous sulfamate so that it can be stripped into fresh water while leaving the uranium in the solvent. This pure stream of plutonium is what threatens non-proliferation. The uranium is recovered in a similar manner, by stripping with copious amounts of hot dilute nitric acid so the organic solvent can be re-utilize [12].

3.2 Recycling

The most common use for the plutonium recovered by fuel reprocessing is to make MOX by combining it with depleted uranium [2, Ch. 7]. The uranium recovered is converted from uranyl nitrate to UF_6 for enrichment, or, in the case of reprocessing a highly enriched fuel [13] (such as those from decommissioned nuclear weapons) it may instead be converted to UF_4 , a common fuel for circulating molten salt reactors (MSRs) [14, 15]. As was alluded earlier, plutonium is not the only transuranic element produced in a nuclear reactor. isotopes of neptunium, americium, curium, berkelium, californium, einsteinium, and fermium are also produced. These so-called *minor actinides* are left in the initial aqueous phase in the PUREX process and can also be recycled, primarily as a disposal means. Many of the aforementioned species are radioactive with exceptionally long half-lives. If they are diverted from disposal streams into the fuel stream of MSRs, they may be burned (a term commonly used to describe endothermic fission of undesirable nuclides) to decrease the activity, persistence, and stock-pile of high-level waste [16].

4 Molten Salt Electrorefining

Another reprocessing method is under development at Argonne National Lab [2, Ch. 7] which takes advantage of the conductivity of molten salts to supply the required redox potential with electricity rather than expensive and toxic chemical reagents. This is by nature also a pyrometallurgical process at 500 degrees Celcius. The electrorefiner is composed of a steel cathode, an anode basket into which used fuel is loaded, and a molten halide salt electrolyte [16]. The fuel dissolves into the solution, and the uranium deposits on the cathode alongside rare-earths; the plutonium does not deposit due to ionic complexes with the halides in solution. This process has the advantage of keeping the minor actinides with the plutonium so they can be easily burned rather than disposed of with high-level waste.

5 MSR Online Reprocessing

Liquid fueled molten salt reactors (MSRs) provide a distinct advantage over solid fueled reactors on the topic of reprocessing - The fuel, as well as minor actinides and fission products, circulate, spending time outside of the core during operation. This means that the fuel can be reprocessed, removing fission gasses and soluble poisons on the fly without the need for recycling. First, xenon, krypton, helium-3, helium-4, and tritium are stripped from solution by bubbling helium gas through the salt [17]. Then, noble and semi-nobel metals, are precipitated on a nickel filter before lanthanides, soluble fission products, and corrosion impurities are selectively extracted by liquid metals such as cadmium, zinc, and bismuth. These processes combine to remove entrained negative reactivity from the fuel and increase its lifetime, allowing a significantly higher burn-up fraction to be attained.

Thorium based MSRs utilize nuclide separation when the salt is outside of the core as well. These reactors operate by breeding ^{233}U ; a step in this process includes the beta decay of proactinium-233, which has a halflife two orders of magnitude longer than the other steps in the process. As such, it may be separated from the rest of the salt mixture either by electroseparation or by fluoride volatilization until it decays into the fissile uranium-233 [18].

6 Conclusions

Nuclear fuel reprocessing and recycling is an important field with exciting advances on the horizon. It shows the potential to improve uranium utilization in the fuel cycle by up to 25% at manageable energy costs. Unfortunately, at least in this country, political concerns stand in the way of taking advantage of this technology at a consequential scale. As such, we are left with a sub-optimal fuel cycle and unnecessarily enduring waste. With some luck, we may see these restrictions loosened to take full advantage of Gen IV MSRs' rise to prominence.

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