Separation of Metal and Metal Oxides using Ethyl Acetate & Bromine

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Abstract

In the development of techniques to treat spent fuel, a new method is coming of age. Pyroprocessing seems to be the new way of the future. A series of experiments were conducted to observe the electrolytic reduction during this process. A fuel rod was submerged into molten Lithium Chloride (LiCl) at 650^{0}C. The rod serving as a cathode and a platinum wire serving as the anode, were given an electric charge. The current passed through the anode and cathode causing the oxide fuel to be reduced to metal while oxygen was released at the anode. Analysis of the oxide fuel is the main focus of this particular experiment. Another important aspect is to determine the concentration of various constituents in the two different phases, metal and oxide. Induced Couple Plasma Mass Spectrometry (ICP-MS) will be used to analyze Uranium, Plutonium, Neptunium-237 and Americium-241. All the other constituents will be analyzed via Induced Couple Plasma Optical Emission Spectrometry (ICP-OES).

Introduction

Bench scale experiments of pyroprocessing were performed at INL in order to obtained information about the reduction process that uranium fuel rods go under. The three main objectives of these experiments are to:

1. Examine the distribution of fuel constituents.
2. Determine the extent of reduction of metal oxides in the fuel face.
3. Assess the effects of accumulated fission products.

In order to accomplish these objectives, the fuel samples need to be separated into the metal and oxide phases by a Bromine/Ethyl Acetate solution. This technique has been prepared by various INL scientists based on previous work. The following describes the operating conditions, methods and results.

Idaho National Laboratory (INL) Nuclear Reactor

Method

1. Open a sample container and immediately weigh an approximately 0.5 gram sample into a glass tare weighted beaker.
2. Cover with approx. 60 ml ethyl acetate.
3. Add a stir bar to each beaker and then add approx. 0.5 grams of magnesium oxide to each beaker.
4. Add 3 milliliters of elemental bromine to each beaker and place on a stir plate. Cover with a watch glass.
5. Stir the sample mixture for 1 1/2 hours.
6. Transfer the solution to a 50 ml centrifuge cone including the stir bar and centrifuge.
7. Pour off the supernate into a clean glass beaker.
8. Wash the solid with 20 ml clean ethyl acetate; use the stir bar to break up the cake.
9. Centrifuge and add the supernate to the first supernate.
10. Wash the solid with 20 ml of methanol.
11. Repeat step #9.
12. Wash the solid with 20 ml of nanopure water.
13. Repeat step #9.
14. Dissolve the residue left in the centrifuge cone with 10 ml nanopure water plus 2 ml of 4N HNO_3.
15. Quantitatively transfer the dissolved solid to the original beaker.
16. When the entire remaining solid is dissolved, transfer to a tared 60 ml polybottle and dilute to volume with 6N HNO_3 and reweigh.
17. To the supernate, add 10 ml of concentrated HCl and leave to air dry.
18. Add 30 ml of 8N HNO_3 to the beaker to dissolve the solid and quantitatively transfer to a tarred polybottle.
19. Submit samples for analysis.

Results

		Run #1		Run #4	
Element Name	**Symbol**	**Fuel Metal (wt%)**	**Fuel Oxide (wt%)**	**Fuel Metal (wt%)**	**Fuel Oxide (wt%)**
Uranium	U	98	2	99	1
Plutonium	Pu	87	13	96	4
Neptunium	Np-237	98	2	98	2
Americium	Am-241	68	32	84	16

		Salt Post Runs			
Element Name	**Symbol**	**1st**	**2nd**	**3rd**	**4th**
Cesium	Cs	129-150	190-231	308-354	111-119
Barium	Ba	85-140	210-220	310-330	140
Strontium	Sr	40-60	85-90	130-140	65
Rubidium	Rb	ND	ND	ND	ND
Tellurium	Te	ND	ND	ND	75
Europium	Eu	ND	ND	ND	15
Uranium	U	5-11	10-15	3-9	0.2-0.5
Plutonium	Pu	0.4-4	0.6-0.8	0.4-1.3	0.3-0.4
Neptunium	Np-237	ND	ND	ND	0.3-0.6
Americium	Am-241	ND	ND	ND	ND

Conclusion and Benefits

1. A mathematical ratio of metal to metal oxide was obtained, thus a value for efficiency could be calculated.
2. The perfection of an alternative method to recycle spent fuel that is not liquid-liquid extraction was achieved.
3. Less steps are needed in pyroprocessing, hence less waste by-products.
4. Uranium oxide reduction was estimated at 95%.

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