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Separation of Metal and Metal Oxides using Ethyl Acetate and Bromine

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ABSTRACT

The processing of nuclear material from spent fuel has been a priority of nuclear science. Scientists have come up with ingenious ideas to try to resolve this issue. One of the first ideas was the bismuth/phosphate method for reprocessing the spent fuel. This was the primary reprocessing method for a long time and it was very effective at recovering plutonium. The government needed a fast production of plutonium in order to satisfy the need for nuclear weapons. Yet this method had a mayor flaw in that it did not recover the uranium. Once the need for the fast production of plutonium passed, scientists from different parts of the nation came together to find a more effective way to process spent fuel.

In 1949, a new technology was developed at the Oak Ridge National Laboratory. It was called PUREX(2) and it revolutionized the way spent fuel was refined. This process is what is called a liquid-liquid extraction method. Even though this method is still widely used and is considered the standard, other methods have been developed in recent years. One method in particular is pyroprocessing.(7) In this method, molten salts, like potassium chloride or lithium chloride, are heated to about 650 degrees and melted to a liquid. Then, the fuel rods are inserted into the molten salt and an electric current is added. Following an electrical reaction of the uranium oxide, the uranium stays on the anode side and oxygen gas gets attached to the platinum rod. In order to determinate the amount of uranium that stayed on the rod, a series of analytical experiments needed to be conducted. Scientists at Idaho National Laboratory came up with a technique where the fuel rods are treated with a solution containing bromine in an ethyl acetate medium.(4) Followed by a series of dissolutions and centrifuging, it is possible to determinate the concentration of uranium in the rod. To do this, a rather common method of determination will be used. ICPMS was the method chosen for this experiment. This is due to its ease and ability to determinate various other elements at the same time. This report will describe all the procedures and results gained from this experiment.

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1. INTRODUCTION

Ever since large scale nuclear reactors were built, the need to separate plutonium from spent fuel has been a top priority. In the 1940s, several methods were proposed but one was a particular success in the science community. The process was called bismuth/phosphate extraction. The process developed by the Oak Ridge National Laboratory (ORNL) in 1943 was put in place to produce plutonium for evaluation and also for the use in nuclear weapons. Once bench scale experiments were performed and tested, a larger operation was started in the state of Washington at the Hanford site. Operations at Hanford started on 1944 and the bismuth/phosphate process was a success at recovering plutonium at that particular time. However, it had one major fault; it fail to recover uranium. Researchers went back to the drawing board to figure out a more efficient way to separate the plutonium. Once again, ORNL was the pioneer in the field of nuclear extraction and, in 1949, ORNL came up with the PUREX (plutonium and uranium recovery by extraction) process.(1) PUREX is now considered the standard for the separation of plutonium and uranium from fission products. PUREX follows a type of separation known as liquid-liquid separation. It works by diluting fuel rods in aqueous nitric acid and then treating it with an organic solvent composed of about 30% tributyl phosphate and kerosene. The fission products remain in the aqueous nitric phase. The plutonium and uranium are then separated by a series of chemical processes that can vary from chemical stripping to centrifuging and decanting (5, 6). Major operations in the PUREX process are shown schematically in Figure 1.

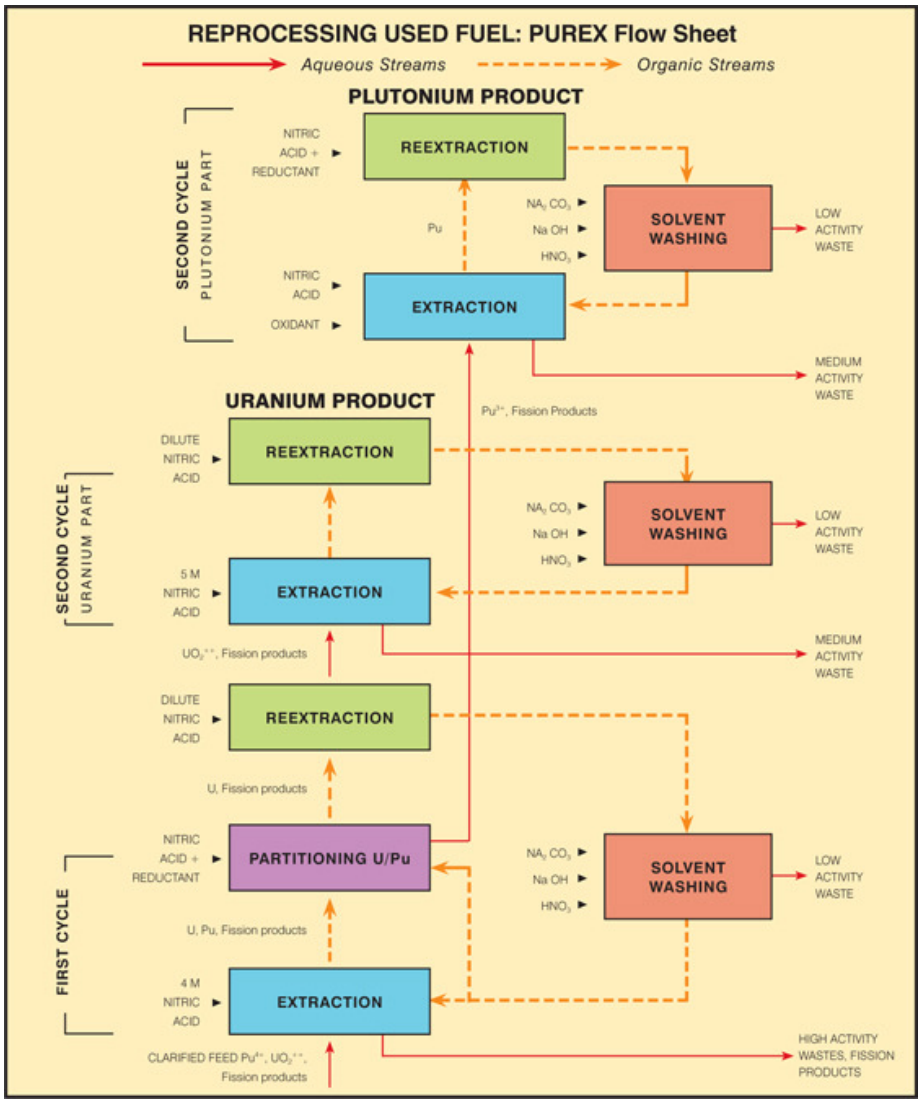

Figure 1. Schematic of the PUREX process.

Even though PUREX is the standard for reprocessing spent nuclear fuel, many other methods have been developed by scientists and researchers over the years. One of these processes is pyroprocessing. Pyroprocessing is a method for treating spent fuel through the use of a technique which is carried out in a vessel filled with molten salt. The molten salt is usually lithium fluoride (LiF). The reagent is then heated to a temperature between 550 – 650^{o}C where it becomes a molten liquid. The spent nuclear fuel is chopped into pieces and placed in a basket that is lowered into the molten salt. All of the products of the reaction dissolve in the liquid salt, thereby separating the solids. These solids include plutonium oxide (PuO_2) and the noble fission elements (Mo, Ru, Tc, Rh, Pd, and others).(7) On the other hand, the liquid salt together with the dissolved constituents are subject to hydrofluorination to convert ZrO_2 to water. To recover the uranium products, the salt bath is then treated with fluorine to yield a gaseous UF_6 product. The residual salt bath is either recycled or converted to a fluorine-based waste. The plutonium remaining in the basket can be recovered by using a plutonium recovery process. Although all the methods mentioned above are used in the nuclear industry, a new innovative method is being

developed. Since 1996 at Idaho National Laboratory, the electrometallurgical treatment of irradiated metal fuel has been an ongoing project. Electrolytic reduction of spent fuel is one of these processes. This new procedure consists of two different but simultaneous phases. First is the anodic dissolution of the fuel in molten lithium chloride/potassium chloride/uranium chloride ($LiCl/KCl/UCl_3$) and second is the cathodic deposition and recovery of the refined fuel. (7) One of the main purposes of this experiment is to extend the treatment to oxides fuels. This can be accomplished by a head-end method to reduce the oxide fuel to a metal state. In order to analyze the fuel samples, a separation of the metal and the oxide is required. (4) This can be accomplished by dissolving a fuel sample in elemental bromine in an ethyl acetate medium. The aftermath of this process shows that the bromine dissolves the metals in the fuel samples and the oxide compounds stay in the solid state. Subsequently, the solids are separated by a series of multiple centrifuging, and decanting and washing. Once separated, they are ready for constituent analysis. (5) The following sections will describe the experiment and the results.

2. EXECUTIVE SUMMARY

This research has been supported by the DOE-FIU Science and Technology Workforce Development Initiative Program. During the summer of 2009, a Florida International University (FIU) a DOE Fellow (Alex Henao) spent 10 weeks doing a summer internship at Idaho National Laboratories under the supervision and guidance of Mr. Rick Demmer. This internship was coordinated by Florida International University. The intern's project was initiated on June 6, 2009, and continued through August 20, 2009, with the objective of studying the effects of dissolving metal and metal oxides with a matrix combination of bromine and ethyl acetate.

The need to recover plutonium from spent fuel has been a top priority for scientists in the nuclear field for many years. Several methods that were invented and developed at ORNL, like the bismuth/phosphate method and the PUREX (1, 2) method are benchmarks of these processes. Yet many of these methods have their shortcomings. For example, the bismuth/phosphate method lacked the ability to recover uranium. Major breakthroughs were made after the PUREX method was developed and it is still considered the industry standard. With extensive experimentation and the need to develop new technologies for the separation of the spent fuel, an innovative method is gaining attention. Pyroprocessing seems to be the way of the future. (7) Pyroprocessing has several advantages over conventional methods. First, it is more compact than aqueous methods, thus allowing on-site reprocessing at the reactor site, which avoids transportation of spent fuel and its security issues. Second, it can separate many or even all actinides at once and produce highly radioactive fuel which is harder to manipulate for theft or making nuclear weapons. In contrast, the PUREX process was designed to separate plutonium for weapons and leaves alkaline minor actinides (americium, curium) behind, producing waste with more long-lived radioactivity. Idaho National Laboratory has been a pioneer in the pyroprocessing process, performing several bench scale experiments to showcase its benefits. The specific objectives of these demonstrations are to examine the distribution of constituents between the salt and fuel phase, to determine the extent of reduction of metal oxides in the fuel phase, and to assess the effects that accumulated fission products in the salt phase may have on the process. (3) The main focus of this paper is on the analytical results for the fuel samples and on the separation of the oxide metal phase from the metal. A fairly new method of separation will be implement using bromine in an ethyl acetate media. Once separated, a conventional method of detection, inductively coupled plasma mass spectrometry (ICPMS), will be used to identify the different constituents and their concentration. ICPMS has been chosen for its low detection limits, high selectivity and good precision and accuracy.

3. EXPERIMENTAL

All chemicals used in this experiment were American Chemical Society *(ACS)* reagent grade and handled in accordance with LWP-8000, "Environmental Instructions for Facilities, Processes, Material and Equipment."

The experiment steps were as follows:

1. Open a sample container and immediately weigh an approximately 0.5 gram sample into a glass tarred beaker.
2. Cover with about 60 ml ethyl acetate.
3. Add a stir bar to each beaker and then add about 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 one-and-a-half 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 tarred 60 ml polybottle and dilute to a volume with 6N HNO_3 and reweigh.
17. To the supernate, add 10 ml of concentrated HCl and take the solution to dryness.
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.

4. RESULTS AND ANALYSIS

After the experiment was finished, samples were submitted and analyzed by ICPMS. Below is a brief description of the instrument and its advantages over other conventional methods.

Inductively Coupled Plasma Mass Spectrometry (ICPMS)

By the early 1980s, ICPMS had grown to be one of the most important techniques in the determination of elemental analysis. This is due to its low detection limits for most elements, its high degree of selectivity and its reasonably good precision and accuracy. ICPMS works in a very peculiar way; positive metal ions, produced in a conventional ICP torch, are sampled through a differentially pumped interface linked to a quadrupole mass spectrometer. The spectra produced in this way, which compared to an ICP optical spectra, is many times simpler to analyze. The spectrum is then used for qualitative determination of the elements and also for the quantitative measurement of their amounts. Figure 2 shows a schematic of the ICPMS instrument.

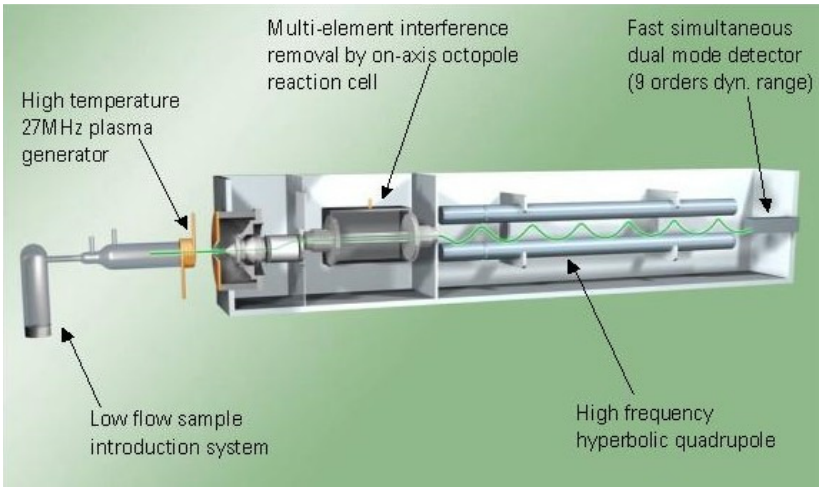

Figure 2. Schematic of ICPMS instrument.

Performance specifications for typical commercial atomic mass spectrometers equipped with an ICP torch include a mass range of 3 to 300, the ability to resolve ions differing in mass to charge ration (*M/Z*) by one, and a dynamic range of 6 orders of magnitude. Over 90% of the elements in the periodic table have been determined with this type of instrument. One of the advantages of using mass spectrometric detection with inductively coupled plasma, as opposed to optical detection, is that mass spectra are usually much simpler and easier to interpret than corresponding optical spectra. This property is particularly true for those elements such as rare earth metals that may exhibit thousands of emission lines.

Because ICPMS is easily adaptable to multi-element analysis, it is well suited to the rapid characterization and semi-quantitative analysis of various types of naturally occurring and man-made complex materials. Generally, detection limits are better than those for optical emission ICO and competes with detection limits for electro-thermal atomic absorption spectroscopy. Another additional advantage to ICPMS is the lower detection limits attainable with mass

spectrometric detection than with optical methods. Finally, the ICPMS procedure offers the great advantages of speed and multi-element capabilities.

Table 1 shows the amount in grams for each sample that was analyzed. Approximately 0.500 grams of the uranium oxide per sample was the target.

Table 1. LOUR Fuel Sample Weights

LOUR Fuel Samples			
Sample Number	Tare Weight (g)	Gross Weight (g)	Net Weight (g)
1	16.1446	16.6152	0.4706
2	16.2689	16.7926	0.5237
3	16.1592	16.5789	0.4197
4	16.2115	16.8710	0.6595
5	16.2466	16.8495	0.6029
6	16.2928	16.6774	0.3846
7	16.2594	16.7488	0.4894
8	16.3994	17.1907	0.7913
9	16.4814	17.2759	0.7945
10	16.4716	17.1508	0.6792
11	16.2763	16.4251	0.1488
13	16.1713	16.3319	0.1606
14	16.2655	16.3482	0.0827
15	16.3216	16.3954	0.0738
16	16.1567	16.5590	0.4023
17	16.2041	16.6530	0.4489
18	16.3260	16.7148	0.3888
19	16.1656	16.7268	0.5612

After the first treatment with the ethyl acetate/bromine was performed, the total weight of the metal portion of each sample was determined (Table 2).

Table 2. Metal Weight after Treatment with EtAcBr

Metal EtAcBr			
Fraction 1			
Sample Number	Tare Weight (g)	Gross Weight (g)	Net Weight (g)
1	14.8486	75.9051	61.0565
2	14.9231	78.0195	63.0964
3	14.761	75.1635	60.4025
4	14.8846	72.731	57.8464
5	14.8152	70.8741	56.0589
6	14.8959	74.4406	59.5447
7	14.7869	68.7505	53.9636
8	14.7721	65.2723	50.5002
9	14.7719	70.1222	55.3503
10	14.8645	63.3012	48.4367
11	14.7461	55.9166	41.1705
13	14.8293	49.8935	35.0642
14	14.9079	52.4964	37.5885
15	ND	ND	ND
16	14.9953	71.056	56.0607
17	14.9848	69.7941	54.8093
18	14.9809	69.2702	54.2893
19	14.9871	70.3749	55.3878

Also after the first treatment with the ethyl acetate/bromine was performed, the total weight of the oxide portion of each sample was determined (Table 3).

Table 3. Oxide Weight after Treatment with EtAcBr

Oxide after EtAcBr			
Fraction 2			
Sample Number	Tare Weight	Gross Weight	Net Weight
1	14.8133	71.6069	56.7936
2	14.8552	75.6972	60.8420
3	15.0392	74.6363	59.5971
4	14.7826	72.7142	57.9316
5	14.8369	70.4948	55.6579
6	14.7976	72.7214	57.9238
7	14.7849	59.3985	44.6136
8	14.8126	59.8736	45.0610
9	14.8156	62.5831	47.7675
10	14.7588	64.4797	49.7209
11	14.8082	52.9358	38.1276
12	14.8843	46.1359	31.2516
13	14.7797	47.1745	32.3948
14	ND	ND	ND
15	15.0159	62.0324	47.0165
16	14.9951	62.3554	47.3603
17	15.0054	62.0169	47.0115
18	14.9681	68.0629	53.0948

In Table 4, the percentage of uranium found in both phases, the metal and the oxide, is provided. Notice that there seems to be more uranium left on the oxide phase than the metal phase. Yet, on Sample 17, the results show the reverse (more uranium in the metal phase). The ICP-MS instrument was used to obtain this data.

Table 4. ICP-MS Results for Metal and Oxide Fractions

ICP-MS Results for Metal and Oxide Fractions			
Sample	Metal	Oxide	
Number	Total U	Total U	Total U
	wt%	wt%	wt. %
1	36.86	41.14	78.00
2	43.96	36.62	80.58
3	44.43	34.30	78.72
4	48.26	26.88	75.15
5	15.48	56.90	72.38
6	16.60	59.20	75.80
7	14.91	56.12	71.03
8	18.05	54.58	72.64
9	34.31	42.30	76.62
10	70.71	9.97	80.68
11	30.62	47.69	78.31
12	57.18	18.40	75.58
13	1.37	73.33	74.70
14	0.54	72.13	72.67
15	17.87	60.08	77.95
16	87.01	7.60	94.62
17	60.10	25.72	85.82

Table 5 shows the concentration of lithium and chloride for each sample. The ICP-MS instrument was used to obtain the lithium results and a chlorine probe was used to obtain the chloride results.

Table 5. ICP-AES Results for Water Fraction

ICP-AES Results for Water Fraction		
Sample Number	Li	Chloride
	µg/g	µg/g
1	23800	73761
2	20600	73852
3	25900	80085
4	21100	81568
5	19800	55504
6	22000	44914
7	27200	61341
8	29300	38825
9	29100	71774
10	26300	119241
11	23100	75729
12	13200	69935
13	11800	50613
14	15000	67879

In order to understand better the data showcased in the tables above, I will give a summary of what they mean and their importance. Table one wants to show the amount of each sampled that was analyze, we wanted to target a 0.500g of the uranium rod so we need this data for the mass balance calculations. That is also the case for the next table, after we got the sample weight; we added the 60ml of the ethyl acetate-bromine solution, this is also necessary to calculate the mass balance. The other final tables are the most importance since it shows the % of uranium in each of the two phases, the oxide phase and the metal phase. The last table shows the concentration of Lithium and Chloride left in the sample. Lithium and Chloride are present when the rods are submerged in the pyro-process and we wanted to know how much was attached to the samples.

5. CONCLUSION

As demonstrated with the series of experiments conducted at INL, we can observe several conclusions. For one, the scientists at INL have come up with a very creative and efficient way to determinate metal content in a mixed sample of metal and metal oxides. We can now obtain a mathematical ratio of metal to metal oxide; thus, a number for efficiency can also be determined. In addition, we are now perfecting a method of recycling oxide spent fuel with little to no aqueous waste, compared to the liquid-liquid methods currently used in the industry. Also, pyroprocessing can be accomplished in fewer steps than the current method of spent fuel recycling, PUREX. Yet, PUREX has been in the industry for much longer and it is viewed as the standard method by many scientists. This does not mean that PUREX is the best method, but pyroprocessing must overcome the natural inclination for scientists to stick with the method they know best. One major advantage of PUREX over pyroprocessing is that PUREX can recycle a large amount of fuel, and overall, the process has performed to expectations. More research would be needed to one day reach the same processing volume via pyroprocessing. For the near future, bench scale experimentation will continue to better understand this fascinating process.

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