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Modified Sodium Diuranate Process for the Recovery of Uranium from Uranium Hexafluoride Transport Cylinder Wash Solution

by

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ABSTRACT

Uranium hexafluoride (UF_6) containment cylinders must be emptied and washed every five years in order to undergo recertification, according to ANSI standards. During the emptying of the UF_6 from the cylinders, a thin residue, or heel, of UF_6 is left behind. This heel must be removed in order for recertification to take place.

To remove it, the inside of the containment cylinder is washed with acid and the resulting solution generally contains three or four kilograms of uranium. Thus, before the liquid solution can be disposed of, the uranium must be separated. A modified sodium diuranate (SDU) uranium recovery process was studied to support development of a commercial process. This process was sought to ensure complete uranium recovery, at high purity, in order that it might be reused in the nuclear fuel cycle. An experimental procedure was designed and carried out in order to verify the effectiveness of the commercial process in a laboratory setting.

The experiments involved a small quantity of dried UO_2F_2 powder that was dosed with 3wt% FeF_3 and was dissolved in water to simulate the cylinder wash solution. Each experiment series started with a measured amount of this powder mixture which was dissolved in enough water to make a solution containing about 120 gmU/liter.

The experiments involved validating the modified SDU extraction process. A potassium diuranate (KDU) process was also attempted. Very little information exists regarding such a process, so the task was undertaken to evaluate its efficacy and determine whether a potassium process yields any significant differences or advantages

as compared to a sodium process. However, the KDU process ultimately proved ineffective and was abandoned.

Each of the experiments was organized into a series of procedures that started with the UO_2F_2 powder being dissolved in water, and proceeded through the steps needed to first convert the uranium to a diuranate precipitate, then to a carbonate complex solution, and finally to a uranyl peroxide (UO_4) precipitate product. Evaluation of operating technique, uranium recovery efficiency, and final product purity were part of each experiment. Evaluation of a technique for removing fluoride from the diuranate precipitation byproduct filtrate using granular calcite was also included at the end of the uranium recovery testing.

It was observed that precipitation of sodium diuranate (SDU) was very nearly complete at a pH of 11-12, using room temperature conditions. Uranium residuals in the filtrate ranged from 3.6 – 19.6 ppm, meaning almost complete precipitation as SDU. It was postulated and then verified that a tailing reaction occurs in the SDU precipitation, which necessitates a digestion period of about 2 hours to complete the precipitation. Further, it was shown, during this phase of the process, that a partial precipitation step at pH 5.5 did not adequately separate iron contamination due to an overlap of uranium and iron precipitations at that condition.

Carbonate extraction of the SDU required an extended (3-4 hours) digestion at 40°C and pH 7-8 to complete, with sodium bicarbonate found to be the preferred extractant. The carbonate extraction was also proven to successfully separate the iron contamination from the uranium.

Potassium-based chemistry did produce a potassium diuranate (KDU) analogue of SDU, but the subsequent carbonate extraction using either potassium bicarbonate or potassium carbonate proved to be too difficult and was incomplete. The potassium testing was terminated at this step.

The uranyl peroxide precipitation was found to operate best at pH 3.5 – 4.0, at room temperature, and required an expected, extended digestion period of 8 -10 hours. The reaction was nearly complete at those conditions, with a filtrate residual ranging from 2.4 to 36.8 ppmU. The uranyl peroxide itself was very pure, with impurity averages at a very low 0.8 ppmNa and 0.004 ppmFe. ASTM maximum levels are 20 ppmNa and 150 ppmFe.

Fluoride removal from the SDU precipitation filtrate required multiple passes of the solution through a calcite bed with acid additions to adjust the pH back down to below 6 before each pass to allow the removal reaction to proceed. This result was a modification of the single pass technique that was planned due to the apparent shutdown of the NaF/calcite reaction at pH above about 10.

Conclusions drawn from the testing were that the results demonstrated a workable and effective series of processing steps. Techniques developed from the tests will make uranium recovery viable when transferred to the commercial process design.

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LIST OF ABBREVIATIONS

ADU	Ammonium Diuranate
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
CFR	Code of Federal Regulations
KDU	Potassium Diuranate
LEU	Low Enriched Uranium
SDU	Sodium Diuranate

CHAPTER 1: INTRODUCTION

Uranium hexafluoride (UF_6), known in the nuclear industry as “hex,” is a chemical compound used in the conversion, enrichment, transportation, and storage of uranium. It is an incredibly useful compound because it has a unique triple point, which makes it perfectly suited for most applications. The triple point of UF_6 lies at a mere 64.05°C (147°F) and just above standard atmospheric pressure—at about 20 psia (1). Thus, it can readily be converted between its solid, liquid, and gas phases, making it easy to handle, transport, enrich, and store.

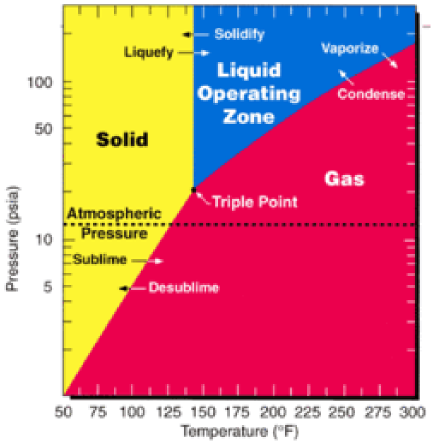

Figure 1.1 – UF_6 Phase Diagram (2)

UF_6 is usually transported as a solid and then quickly converted to liquid or gas for removal from its transport container. It can then be easily put to use, most often for enrichment at gaseous diffusion or centrifuge enrichment facilities (3). Also, because there are not many uses for the large amounts of depleted uranium generated at this time, UF_6 is used as a chemical means to store it long-term.

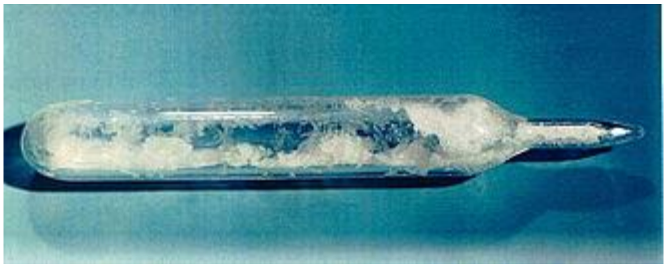

Figure 1.2 – UF_6 crystals in a small glass ampoule (4)

As a solid, UF_6 is a white, crystalline material. It is inert in dry air and will not react with oxygen, nitrogen, or carbon dioxide. However, it is highly corrosive and exceptionally reactive with water—the humidity in the air being enough for it to react. As UF_6 reacts with water, it is quickly converted to uranyl fluoride (UO_2F_2) and hydrogen fluoride (HF). In aqueous solution, whether in water or even humid air, hydrogen fluoride forms hydrofluoric acid, which is incredibly toxic and extremely corrosive, even in low concentrations. This means that stringent measures must be taken when transporting UF_6, not only to protect the public from the radiation and toxicity hazards inherent with uranium, but also from the health hazards of HF. (5)

To mitigate these risks and make the transport of UF_6 safe, easy, and cost-effective, special containment vessels have been designed for its shipment. These containers come in a variety of sizes depending on the enrichment of the UF_6 being transported and the needs leading to its use. The smallest certified containers are only 1.5 inches in diameter, hold a maximum of 1lb of UF_6, and are made of nickel or nickel-copper alloy. The largest containers are 48 inches in diameter, can hold upward of 14 metric tons of UF_6, and are made of stainless steel (6). The two basic sizes that have been developed over the years to transport commercial quantities of UF_6 are a 30 inch diameter cylinder that holds about 2.25 metric tons of solid UF_6 (30B container), and a 48 inch diameter cylinder that holds either 10 metric tons (48X container) or 14 metric tons (48Y container) of UF_6, depending on its length. The current predominant designs are the 30B and 48Y containers.

Figure 1.3 – 48Y UF_6 Container (7)

No matter the size, each of the container designs is a metal cylinder, with rounded ends, specially designed to hold solid UF_6 for decades. They are designed to meet or exceed very strict ANSI regulations, and during transportation they are fitted with overpacks to help protect them in case of fire (8).

The expected, worldwide uranium requirements for “commercial nuclear generating capacity and reactor-related uranium requirements” for 2011 were 65,180 metric tons of natural uranium, and that number is expected to increase to somewhere between 69,000 and 76,000 metric tons by 2015 (9). All of this uranium must be converted, enriched, and fabricated into fuel before it can be used, and the only way to transport it currently is in the described containment cylinders. Thousands of metric tons of UF_6 are handled and transported on a yearly basis (3).

About 6,600, 30B cylinders, containing low enriched uranium (LEU, <5 wt% 235U), are transported each year, moving UF_6 from enrichment plants to fuel fabrication plants, where the UF_6 is converted into UO_2 for power reactor fuel. About 9,100, 48X and 48Y cylinders each year are used each year to transport natural UF_6 from UF_6 conversion plants to enrichment plants (10). About 90,000 48X, 48Y and 48G (a thinner-walled version of the 48Y) cylinders are used for long-term storage of depleted UF6 tailings from enrichment plants. Many of this last group of cylinders have long exceeded their transport certification limit and cannot be moved out of their storage sites without special dispensation by government authorities or recertification.

The UF_6 being transported is highly corrosive and poses serious health risks should it be released to the environment. So, the transport cylinders must be inspected regularly—at “intervals not to exceed 5 years”—to ensure that there are no “leaks, corrosion, cracks, bulges, dents, gouges, defective valves, damaged stiffening rings or skirts, or other conditions that, in the opinion of the qualified inspector, render it unsafe or unserviceable in its existing condition” (11). Thus, in order to maintain the credentials required for continued use as a transportation container, each of these cylinders must be recertified every five years, using a series of physical tests designed to demonstrate the integrity of the cylinder. Successful completion of the physical testing recertifies the cylinder for five additional years of service.

When the time comes for a container's recertification, it is first heated in order to vaporize the UF_6 within so that it can be extracted from the container. Empty cylinders contain a small residue of UF_6, called a "heel," which must be washed from the cylinder before testing can begin. This heel is usually 3-4 kg—though regulations allow for up to 22.7 kg—of solid UF_6 that has adhered to the cylinder walls due to corrosion. Many different techniques, operating procedures, additives, and approaches to cylinder washing have been developed and are in use throughout the world, with varying degrees of efficacy. Most of these approaches involve the use of a caustic chemical wash that pulls the uranium off of the inside of the container. The wash solution must then be stripped of uranium so that it can meet disposal standards.

This study was conducted to evaluate the efficacy of a sodium diuranate process that was designed to completely remove the uranium from a cylinder wash solution, and recover it as highly pure, solid uranyl peroxide, which can be put back into the nuclear fuel cycle.

CHAPTER 2: LITERATURE REVIEW

Title 49 of the Code of Federal Regulations, Part 173.420 (49CFR173.420) establishes the guidelines for the transportation of UF_6 in the United States. This section requires that packages for the transport of UF_6 must conform to American National Standard N14.1 (ANSI N14.1) (12), which sets standards for all aspects of UF_6 transportation cylinders, covering everything from cylinder design and materials, to testing, certification, and transportation.

ANSI N14.1, Section 6.3.2 requires that “all cylinders shall be periodically inspected and tested throughout their service life at intervals not to exceed 5 years” and that “cylinders shall not be refilled [after each five-year interval] until they are properly reinspected, retested, and restamped.” This required, periodic inspection includes internal and external examinations of the cylinder, hydrostatic strength testing, and air leak testing. Should anything about a cylinder be “found to…, in the opinion of [a] qualified inspector, render it unsafe or unserviceable,” it must be removed from service for repair or replacement. (11)

Section 8.1.2 of ANSI N14.1 allows for the transport of empty UF_6 cylinders that contain less than a specified weight of UF_6 residue, or heel. This allowed weight varies according to container size and percent enrichment, but does not exceed a heel of 50 lbs at 4.5 wt% U235—the weight allowed to be transported in 48X and 48Y containers (13). This information is given in Table 2.1.

Table 2.1 – Maximum Heel Allowed by Cylinder Type

Cylinder Model Number	Heel (lb)	Heel (kg)	Max U235, wt%
5A or 5B	0.1	0.045	100
8A	0.5	0.227	12.5
12A or 12B	1	0.454	5
30B	25	11.3	5
48X	50	22.7	4.5
48Y	50	22.7	4.5
48G, 48H, 48O, 48OM	50	22.7	1
Allied or 48T	50	22.7	1

However, when the time comes for recertification, the inside of the container must be thoroughly cleaned and the heel must be removed, so that the cylinder can be fully, properly, and safely inspected. The uranium heel is removed with an acidic solution, which must then be processed to recover the uranium, which can afterward be processed into a form and purity that will allow it to be reused in the nuclear fuel cycle.

Many milling processes use an acidic solution to leach uranium from its ores so that it can be processed into yellow cake. The acidic solution is treated with an alkaline solution to strip the uranium and convert it into an alkali form, which is then processed with more acid and precipitated with hydrogen peroxide into a uranium oxide yellow cake (14).

A similar process is used to convert the uranium oxide to UF_6. To produce UF_6, the yellow cake is dissolved in nitric acid, forming a uranyl nitrate solution. A selective solvent extraction is used to remove impurities, and the resulting, purified uranyl nitrate can then be precipitated with an alkaline solution (ammonium hydroxide, sodium hydroxide, potassium hydroxide, etc.) to form an alkali diuranate. This substance is then calcined, reduced, hydrofluorinated, and fluorinated in order to produce UF_6. (15)

The process to recover uranium from a UF_6 solution as a usable uranium oxide works much like the conversion process in reverse, and uses similar techniques to the milling process. A liquid, acidic UF_6 solution is treated with an alkali solution to form an alkali diuranate solid. This diuranate goes through a carbonate solvent extraction, wherein the diuranate solid is mixed with a carbonate solution, to strip the uranium from any present impurities. The resulting uranyl carbonate complex can then be precipitated with hydrogen peroxide as uranyl peroxide (16), which can be calcined into usable yellow cake.

There are many processes available to convert uranium into an alkali form, but according to Murty, et al., the ammonium diuranate (ADU) process “has been the most intensively followed and investigated” (17). Sodium diuranate (SDU) processes have also been widely used, but have generally been discarded because of the potential for sodium contamination. Murty, et al., and Manna, Roy and Joshi, point out that the properties of the diuranate precursor, which are gained from the processes that make it, are passed on to the final uranium dioxide product (17, 18).

Since SDU and ADU are chemically analogous, it is of great benefit to understand the importance of ADU in the nuclear fuel cycle. ADU is an intermediate compound in the milling and conversion of uranium. It is generally produced by either a uranyl nitrate or a uranyl fluoride process, where the uranyl compound is reacted with a gaseous ammonia or an aqueous ammonium hydroxide. The ADU solid formed can then be filtered, dried, and calcined in air to form UO_3 or U_3O_8 (18), which can then be more readily converted into UF_6 for storage and transport or reduced to UO_2 for fuel fabrication. The only thing necessary to produce SDU instead of ADU, is the use of sodium compounds as opposed to ammonium compounds (i.e. NaOH instead of NH_4OH).

The Triple Altura Laboratory (LTA) in Argentina uses a sodium diuranate process to recover uranium from scrap that has been generated by the manufacture of uranium/aluminum alloy fuel elements. In order to recover the nuclear material from the scrap, LTA uses a three-step process. First, the material from which the uranium is to be recovered is dissolved using $NaNO_3$ and NaOH solutions. This alkaline dissolution converts the aluminum to soluble sodium aluminate and the uranium to insoluble sodium diuranate ($Na_2U_2O_7$). The second step is to separate the sodium diuranate from the liquid via filtration, and then eliminate any excess aluminum with a wash each of NaOH and deionized water. The solid is then, finally, dissolved with HNO_3 to form an aluminum-free, uranyl nitrate solution. The process researched follows steps very similar to those used by LTA, in that an alkaline dissolution would be used to separate the impurities and uranium from the initial solution, and then a carbonate (rather than nitrate) extraction dissolution would be used to recover the uranium from the SDU. (19)

In order for uranium oxides to be used for direct hydrogen reduction to nuclear grade uranium dioxide, they must conform to the standards set forth in ASTM C1348. Table 1 of ASTM C1348 gives a list of impurity elements and their maximum allowable concentrations in the uranium if it is to be used for eventual fuel fabrication (20). This list is shown in Table 2.2.

Table 2.2 – Impurity Elements and Maximum Concentration Limits

Element	Maximum Concentration Limit of Uranium, µg/gU
Aluminum	50
Barium	5
Beryllium	100
Bismuth	3
Calcium + Magnesium	100
Carbon	100
Chlorine	100
Chromium	100
Cobalt	80
Copper	100
Fluorine	100
Iron	150
Lead	40
Manganese	50
Molybdenum	200
Nickel	80
Phosphorus	100
Silicon	200
Sodium	20
Tantalum	200
Thorium	10
Tin	50
Titanium	50
Tungsten	100
Vanadium	10
Zinc	20

The limit for sodium contaminants is 20 µg/gU, and must be held below this level because sodium contamination can cause cracking in reactor fuel. As SDU processes use large amounts of sodium, they typically have to be carried out more slowly and have to be more carefully monitored than ADU processes in order to ensure an acceptable final product. Thus, most of the current processes use ammonia to form ADU. Since fuel conversion and fabrication facilities generally shoulder the burden of washing UF_6

cylinders and use ammonia in their processes, an ADU process is also used to recover uranium from the UF_6 cylinder wash solution.

An SDU process was designed that would recover all of the uranium from the cylinder wash solution, separate all of the iron contamination from the recovered uranium, and allow ensure sodium content less than 20 µg/gU in the final uranium oxide, meeting the requirements of ASTM C1348. In this process, a cylinder wash solution would be titrated with sodium hydroxide (NaOH) to a pH of 4.5-5.5, in order to remove iron contaminants. The iron would precipitate out of solution as solid ferric hydroxide ($Fe(OH)_3$), which usually precipitates at about pH 3.5 (21). Literature indicates that the uranium should not fully precipitate as SDU ($Na_2U_2O_7$) until around pH 12.0 (22, 23), allowing for full removal of the iron and subsequent precipitation of the SDU with the addition of more NaOH. This SDU would undergo a carbonate solvent extraction with a sodium carbonate/sodium bicarbonate solution, in order to strip the uranium from any sodium impurities, as a uranyl carbonate complex solution (24). The uranium would then be precipitated out of the solution as uranyl peroxide solid ($UO_4{\cdot}nH_2O$), by titrating it with hydrogen peroxide (H_2O_2) and nitric acid (HNO_3), which is used to keep the pH in the range of 2.5-5.5, which the literature suggests is the optimal range for the reaction (16, 25).

Since the uranyl peroxide from this process is precipitated as a hydrate, water trapped in the final solid could result in an incorrect calculation of recovered uranium if a simple mass balance is used. Thus, measures other than simply weighing, or air drying and then weighing, would have to be taken to verify complete uranium recovery, either by baking the solid product or converting it into a different, non-hydrated uranium oxide.

Both measures were used in order to determine the mass of uranium recovered. While a temperature of 400-450C was chosen to dry the uranyl peroxide, work by Morais, et al., and Bonini, et al., showed that a temperature of at least 800°C was necessary to fully calcine the $UO_4 \cdot nH_2O$ and convert it to U_3O_8 (19, 25). Thus it was calcined at 1000°C for 6 hours.

CHAPTER 3: METHODOLOGY

A modified sodium diuranate (SDU) process was designed to extract the uranium from UF_6 cylinder wash solution, carry it through a purification and conversion process, and then recover it as uranyl peroxide (UO_4) solid. An experimental procedure was developed and carried out in order to study the process and evaluate its efficacy in a laboratory setting.

The process was designed to first use sodium hydroxide to precipitate any iron contamination from the wash solution, according to Eqn. 3.1, which iron would then be filtered from the solution.

$$FeF_3 + 3NaOH \rightarrow Fe(OH)_3\ (s) + 3NaF \tag{3.1}$$

Then more sodium hydroxide would be used to precipitate the uranium out of the solution as solid SDU, following the reaction given in Eqn. 3.2.

$$2UO_2F_2 + 6NaOH \rightarrow Na_2U_2O_7\ (s) + 4NaF + 3H2O \tag{3.2}$$

The intermediary precipitation of the iron was thought to be possible because the iron should react and precipitate at a much lower pH than the uranium. The SDU would go on to be mixed with a sodium carbonate/bicarbonate solution to extract the uranium as a uranyl carbonate complex solution (“uranyl carbonate” and “UCO_3” are used as shorthand notations for “uranyl carbonate complex solution throughout the study), as shown below in Eqn. 3.3.

$$Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O \rightarrow 2Na_4UO_2(CO_3)_3 + 6NaOH \tag{3.3}$$

The uranium would then be precipitated out of the carbonate solution with nitric acid and hydrogen peroxide, as solid UO_4.

$$Na_4UO_2(CO_3)_3 + 6HNO_3 \rightarrow UO_2(NO_3)_2 + 3CO_2 + 3H_2O + 4NaNO_3 \tag{3.4}$$

$$UO_2(NO_3)_2 + H_2O_2 + nH_2O \rightarrow UO_4 \cdot nH_2O\ (s) + 2HNO_3 \tag{3.5}$$

The process was developed to extract all of the uranium from the wash solution and carry it through to the production of UO_4, and the UO_4 should be devoid of any iron or sodium contamination. Figure 3.1 outlines this process.

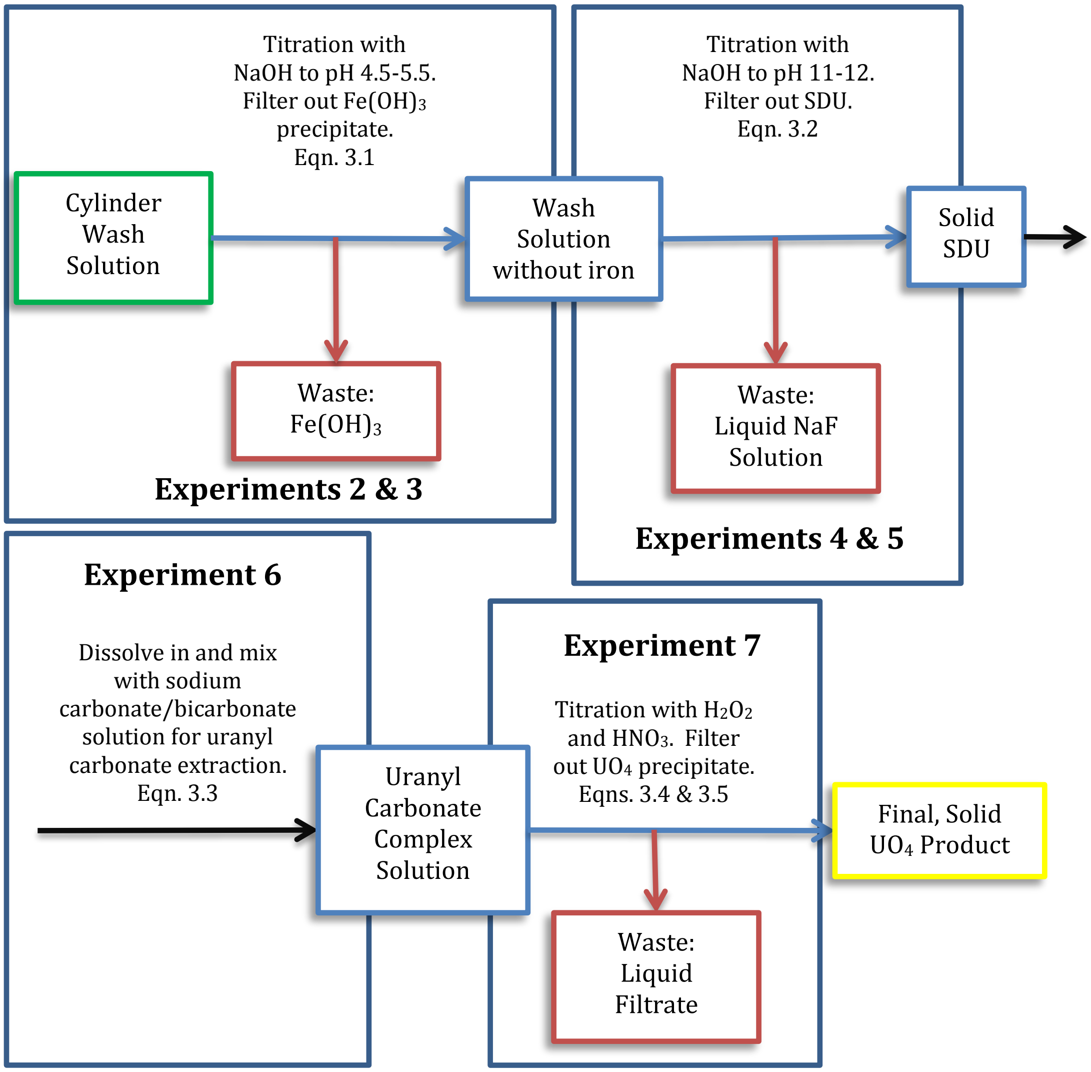

Figure 3.1 – SDU Process for recovering uranium from UF_6 containment cylinder wash solution

A similar, potassium diuranate (KDU) process was also investigated, using potassium hydroxide instead of sodium hydroxide to form KDU instead of SDU, and using potassium carbonate/bicarbonate to extract the uranium as uranyl carbonate. Experimentation was carried out to see if this would make a viable recovery process.

Nine experiments were developed to evaluate these processes and gauge key information, such as precipitate settling rates and titration curves. Each experiment involved an initial quantity of dried UO_2F_2 powder that was dosed with 3wt% FeF_3 and was dissolved in water to simulate the cylinder wash solution. Each experimental series started with a measured amount of this powder mixture which was dissolved in enough water to make a solution containing about 120 g uranium per liter of solution.

All of the experiments proceeded from the preparation of simulated cylinder wash solution through the steps needed to first convert the uranium to a diuranate precipitate, then to a carbonate complex solution, and finally to a UO_4 precipitate product. Evaluation of operating technique, uranium recovery efficiency, and final product purity were part of each experiment. Evaluation of a technique for removing fluoride from the diuranate precipitation byproduct filtrate using granular calcite was also included at the end of the uranium recovery testing. The nine experiments are described thusly:

Experiment One

The first experiment was to be used to develop a titration curve for the SDU precipitation reaction, and to exercise the laboratory setup and equipment for the first time. The simulated wash solution would be prepared and placed in a magnetically-stirred polyethylene beaker. The solution would then be slowly titrated with 24% NaOH solution, dispensed as droplets from a 100 mL burette that was positioned over the beaker. The pH of the mixture would be periodically measured with p-Hydrion paper strips as the titration progressed, at room temperature, and it would be titrated with NaOH from a pH of about 1 to a pH of 11-12. The data would be collected, and a curve prepared.

Experiment Two

The second experiment was designed to begin a run-through of the full recovery process, by first titrating the simulated wash solution to a pH of 4.5. This was to be done to evaluate a partial precipitation technique for separating the iron from the uranium in the mixture. In theory, the FeF_3 solid and any dissolved iron would be immediately converted to $Fe(OH)_3$ solid at the first addition of NaOH and would remain insoluble at a pH lower than that at which the uranium would begin to precipitate as SDU, and this separation of the iron from the uranium was thought to be possible at a pH of about 4.5. A new batch of simulated wash solution would be prepared, and the same set-up was to be used as that for the first experiment, except an 8% NaOH solution was used for titration, to allow for a slower approach toward the pH of 4.5. After the target pH of 4.5 was reached, the third experiment was to begin.

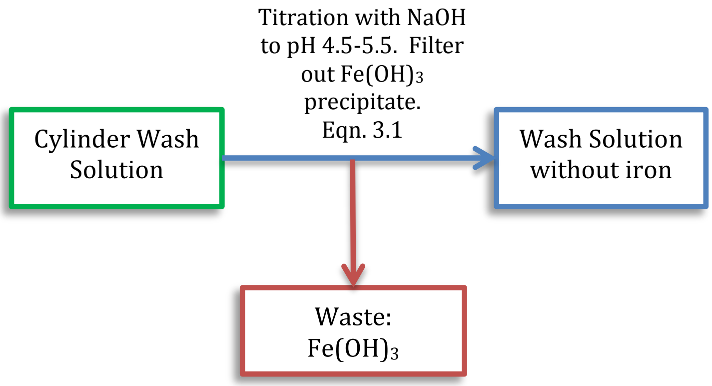

Figure 3.2 – Experiments 2 & 3

Experiment Three

The third experiment was a settling test to determine the volume of $Fe(OH)_3$ precipitate generated in Experiment Two, and the time it takes to settle out of solution. Thus, the solution from the second experiment would be poured into a graduated cylinder and allowed to settle for two hours. During these two hours, the demarcation level between the sediment and the clear, supernate liquid above it would be recorded at specific time intervals. The solution would then be allowed to sit overnight, and the final demarcation would be recorded.

Experiment Four

The fourth experiment was to precipitate the uranium out of the remainder of the wash solution (now devoid of iron) as solid SDU precipitate. First, a vacuum transfer apparatus would be assembled by connecting a vacuum pump to a polypropylene Erlenmeyer flask with a bit of tubing. The first flask would serve as an overflow flask to protect the vacuum pump, and it would be connected to a second, capture flask by more tubing. The second flask would be attached to a dipping tube, which would be dipped into the clear supernate solution to draw it into the flask. This set up is shown in Figure 3.3.

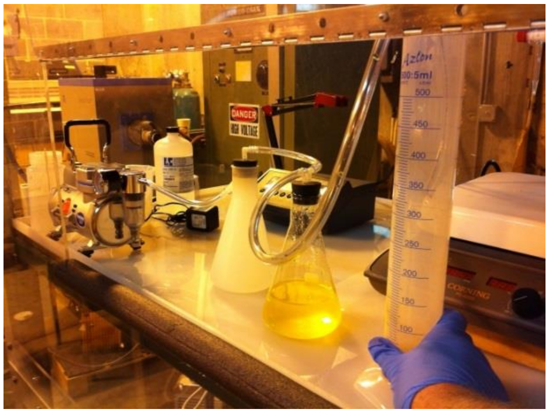

Figure 3.3 – Vacuum apparatus system

This vacuum apparatus would be used to remove the clear supernate liquid from the top of the Experiment Three settling test, and, afterward, the solid precipitate would be filtered from the dregs, leaving a brilliant yellow, partially titrated wash solution, now containing no iron. This solution would be put in a new beaker and further titrated with 8% NaOH, to a pH of 11-12, to form the solid SDU precipitate. An electronic pH sensor was to be used to record the pH during this titration, and a reading would be taken at regular intervals to form a titration curve. After the pH reached about 12, the magnetic stirrer would be stopped and initial settling observations would be made. After these observations had been made, the stirrer would be started again, a temperature sensor would be lowered into the solution, and the hot plate would be turned on. The solution was then to be heated to 35-40°C, and allowed to stir slowly for two hours, to see if heat and a digestion period increase particle size and speed precipitate settling. After the two hour digestion time passed, the hot plate and stirrer would be turned off and Experiment Five would immediately begin.

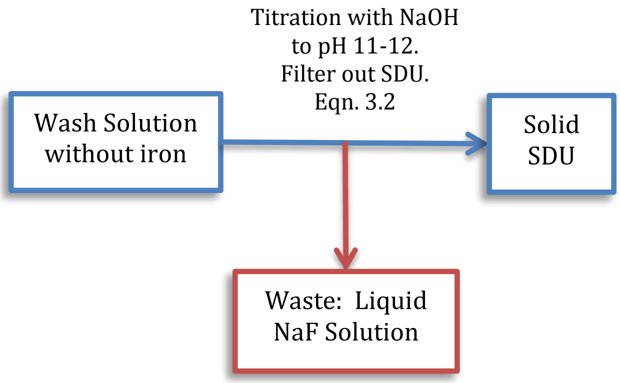

Figure 3.4 – Experiments 4 & 5

Experiment Five

The fifth experiment was to be used to observe the settling behavior of the SDU precipitate formed in Experiment Four. The final solution from the fourth experiment would be poured into a graduated cylinder and the demarcation between the supernate liquid and solid precipitate was to be recorded, at regular intervals, as in Experiment Three.

Experiment Six

Once full separation between the SDU precipitate and the liquid waste had been achieved, Experiment Six would begin. This experiment would be used to extract the uranium from the SDU precipitate in the form of a carbonate complex solution. This would start with a filtering of the solution to separate out the SDU. The liquid filtrate would be set aside for further testing to measure residual uranium content. The SDU filter cake and filter paper would be removed from the vacuum filtration system and the SDU scraped into a beaker. A sodium carbonate/sodium bicarbonate solution would be made by mixing together 240 mL of saturated $NaHCO_3$ solution and 60 mL of 10% Na_2CO_3 solution. The filter paper would be washed into the SDU beaker with a bit of this solution and the rest would be poured into the beaker as well. The magnetic stir bar would then be added and the stirrer turned on to thoroughly mix the SDU and carbonate solution, forming a bright yellow/orange uranyl carbonate solution.

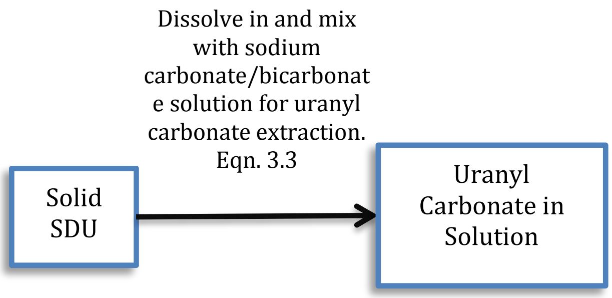

Figure 3.5 – Experiment 6

Experiment Seven

Experiment Seven was designed to precipitate the uranium out of the carbonate solution and into a UO_4 solid. A 50 mL portion of the UCO_3 solution would be poured into a beaker with the stir rod. Two 100 mL burettes would be mounted and positioned above the beaker, one filled with 100 mL of additional UCO_3 solution, and the other filled with 100 mL of 35% H_2O_2. A small squeeze bottle would be filled with 20% HNO_3, to be used throughout the experiment. The temperature and pH sensors would be extended into the beaker and preliminary measurements made. Enough HNO_3 would be gradually added to the uranyl carbonate solution in the beaker until the pH dropped to 3, and then titration would begin. A slow drip of H_2O_2 would be started, and when yellow UO_4 crystals began to form in the solution, a slow drip of UCO_3 would be started as well. The pH meter reading would be closely monitored at this point, and the flow rates would be adjusted, and HNO_3 would be added, a little at a time, to hold the pH of the solution at 4. The precipitation would be continued until all of the UCO_3 had been used, pausing to refill burettes as needed. Once all of the UCO_3 had been added the burettes would be removed and the final pH and volumes recorded. The mixture would stir slowly overnight, to allow for a complete reaction and crystal growth.

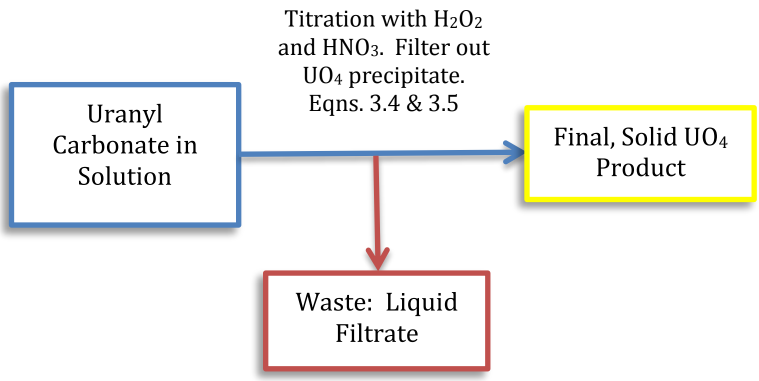

Figure 3.6 – Experiment 7

Experiment Eight

Experiment Eight was a settling test for the UO_4 precipitate produced in Experiment Seven. After being allowed to stir all night, the mixture from the seventh experiment would be poured into a graduated cylinder and observed as in the third and fifth experiments. After full settling had taken place, the solution would be filtered, separating the UO_4 precipitate from the $NaNO_3$ solution filtrate. The liquid filtrate was stored for further analysis and the solids were set aside for drying and subsequent analysis.

Both the liquid and solids were analyzed by on a Thermo Scientific Element II high –resolution inductively coupled plasma mass spectrometer (ICP-MS). The liquids were analyzed for uranium content in parts per million (ppm) and the solids were analyzed for Na and Fe contamination in ppm. Each liquid sample was collected and diluted by a factor of 100, and each solid sample was made by dissolving about 1 mg of solid UO_4 in 100 mL of 5% HNO_3 solution. The ICP-MS was calibrated by analyzing a blank rinse of 2% distilled nitric acid five times, then, each sample was run through the machine and the data was collected. The concentrations of the contaminants in question were calculated based on a linear regression. Special thanks must be given to Elizabeth Bair and the Center for Elemental Mass Spectrometry at the University of South Carolina for running these tests and analyzing the data.

Experiment Nine

The ninth and final experiment was designed to evaluate a process for the removal of fluoride from the NaF solution generated in Experiment Four and filtered in Experiment Five. This was to be accomplished by filling a Sentry RC-100 column with calcite granules and capping it. The bottom end would be attached to the vacuum apparatus and the top connected to a length of tubing which was to be used to draw the NaF solution into the column.

The NaF solution would be poured in a glass beaker, placed on the hot plate, and heated to about 70°C, then enough 20% HNO_3 would be added to drop the pH to about 5. This heated, pH-modified solution would be drawn out of the beaker and run through the column slowly—in increments of about 5mL each—until it had all passed through the column. The NaF solution, at a pH of about 5, reacts with the calcite to form sodium carbonate and calcium fluoride according to the reaction noted in Equation 3.6.

$$2NaF + CaCO_3 \rightarrow CaF_2 + Na_2CO_3 \tag{3.6}$$

Should multiple passes be required, the solution exiting the column would be collected and have its pH checked and modified as necessary. It would then be heated and run through the column again.

These nine experiments came together into five test series. The first test series dealt only with experiment one. The second test series followed the complete sodium process from experiment two through experiment eight. The results of the second test series led to the development of modifications to the process, which had to be tested, and an auxiliary test was devised to do this using the combination SDU/$Fe(OH)_3$ precipitate in NaF solution that was the product of the first test series. This modified process was altered to forego the partial precipitation step in experiments two and three, and separated the iron from the wash solution during the carbonate extraction in experiment six, also changing the carbonate extraction process to use only water and $NaHCO_3$. This test series was named "Auxiliary Tests on First Test Series SDU." The modified process is shown in Figure 3.3.

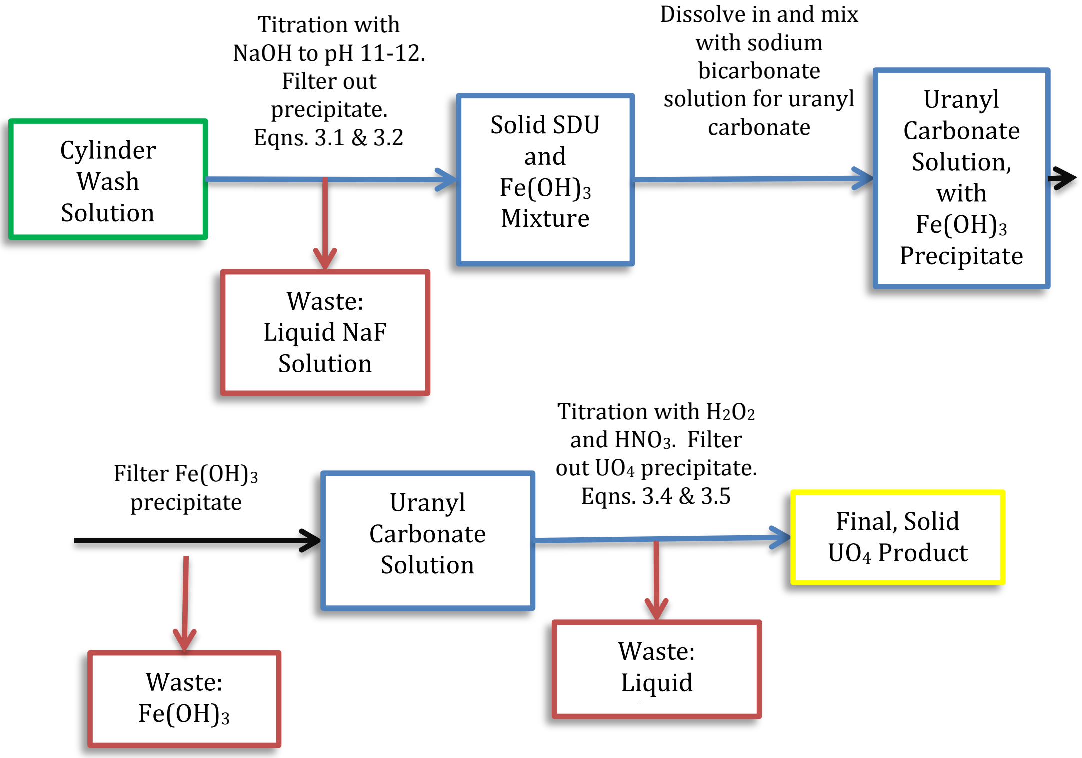

Figure 3.7 – Modified Recovery Process

The third and fourth test series ran through the potassium-analogous process, going from experiments two through eight, as modified in Figure 3.3, using KOH in place of NaOH, $KHCO_3$ in place of $NaHCO_3$, and K_2CO_3 in place of Na_2CO_3. The fifth and final test series was used as a verification run for the modified recovery process, going through the entire procedure from the second to ninth experiments, again, as modified.

CHAPTER 4: RESULTS AND DISCUSSION

First Test Series

The first test series was used to develop a precipitation curve for the initial reagents. A UO_2F_2 solution was prepared by dissolving 16 g of the UO_2F_2 powder mix into 100 mL of water, and this mixture was titrated with 24 wt% NaOH solution. A magnetically stirred polyethylene beaker was the reaction container and the NaOH solution was dispensed as droplets from a 100 mL burette positioned over the beaker. The pH of the mixture was periodically measured with p-Hydrion paper strips as the titration progressed, at room temperature. Table 4.1 following depicts the results of the titration.

Table 4.1 – First Test Series, SDU Precipitation

NaOH added (total mL)	pH	Comments
0	1.0	Solution light green color
1.8	3.0	Local precipitation, re-dissolved
2.6	3.5	
4.6	5.5	Precipitation persisting more
5.6	5.5	Tan/yellow precipitate forming
7.5	6.5	Precipitating heavily
9.2	7.0	
12.6	8.0	
17.8	10.0	Precipitation complete
20.6	12.0	

The data are displayed graphically in Figure 4.1 below. Test photos are also shown in Figure 4.2 and 4.3.

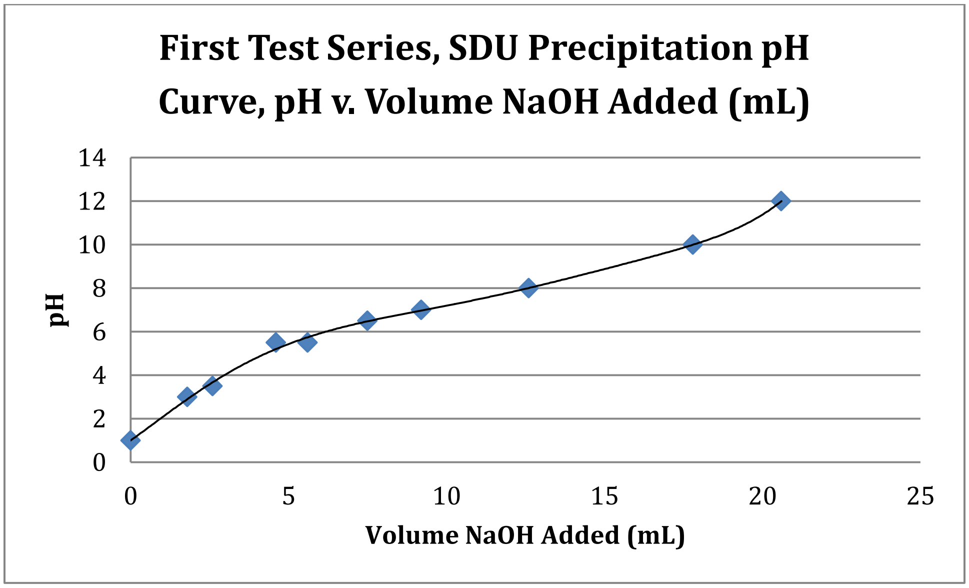

Figure 4.1 – Graph of First Test Series, SDU Precipitation pH Curve, pH v. Volume NaOH Added (mL)

Figure 4.2 – Powdered UO_2F_2 dosed with 3wt% FeF_3, and the powder dissolved in water

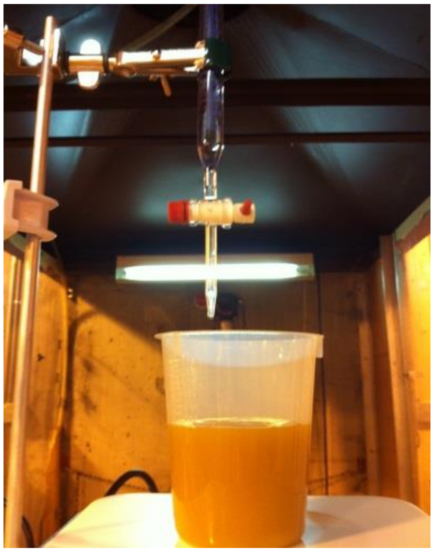

Figure 4.3 – Titration with NaOH

One item of test observation was that the magnetic mixing system was having difficulty dispersing first additions of NaOH with the result that localized precipitation formations took several seconds to re-dissolve and stabilize in the solution. As a result, a decision was made to dilute the NaOH solution with water from 24% to 8% on subsequent test series, in order to better control the uniformity of the precipitations.

After the pH of the slurry of precipitated SDU/$Fe(OH)_3$ reached 12.0, it was transferred to a storage bottle and left overnight to settle. The next morning the solids had settled to one-third of the original slurry volume, with the remaining two-thirds of the volume consisting of a clear supernate liquid. The settled mixture was held for additional testing, described later in this chapter, in the section "Auxiliary Tests on First Test Series SDU".

Figure 4.4 – First Test Series SDU
after overnight settling

Second Test Series

The second test series started with 50 g of the UO_2F_2 powder dissolved in 300 mL of water. The precipitation setup was the same as it was for the first test series, except 8% NaOH solution was loaded into the titration burette. The purpose of the first step of this series was to evaluate a partial precipitation technique for separating the iron from the uranium in the mixture. In theory, the FeF_3 solid and any dissolved Fe would be immediately converted to $Fe(OH)_3$ solid at the first addition of NaOH and would remain insoluble at a pH lower than where the uranium would begin to precipitate as SDU. A physical separation of the iron from the uranium at pH of about 4.5 was thought to be possible. As the titration began, a rust colored precipitate soon formed, so it looked as if the reaction was following the prediction. As the titration reaction progressed, however, some yellowing occurred in the precipitate. After a slow addition of 17.6 mL of NaOH, the pH measured 4.5. The titration was stopped and the mixture was transferred to a graduated cylinder for a settling test.

The settling test data are shown in Table 4.2 following. The starting volume of the mixture was 315 mL on the graduated cylinder.

Table 4.2 – Second Test Series, Partial Precipitation of Iron Sediment Settling

Settling Time (min)	Volume of Supernate Liquid (mL)	Volume of Slurry (mL)	Comments
10	305	10	Murky supernate
20	307.5	7.5	
30	307.5	7.5	Some clearing
40	307.5	7.5	Clear
50	307.5	7.5	
60	307.5	7.5	
80	307.5	7.5	
100	307.5	7.5	
120	307.5	7.5	
Overnight	307.5	7.5	Clear*

*Had a slight haze to about 15 mL above slurry

The result of the settling was a very rapid separation to a fixed fraction of solids and liquid that did not change even with extended settling. A yellowish caste remained in the precipitate indicating some SDU had precipitated with the iron.

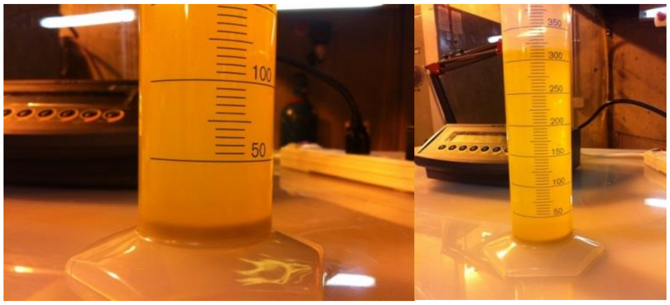

Figure 4.5 – Settling of $Fe(OH)_3$ Solid

The purpose of the next steps of this series was to filter the mixture to separate the iron precipitate and then set up the filtrate to complete the precipitation of SDU.

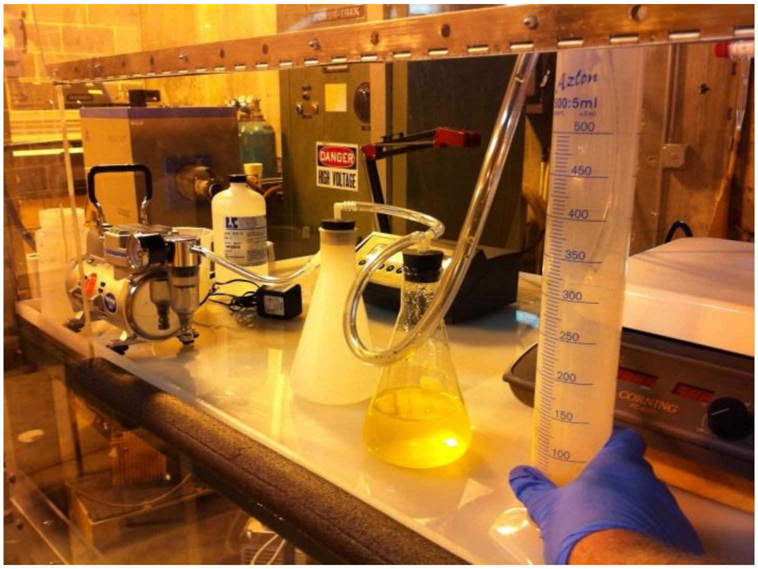

Figure 4.6 – Siphoning off supernate liquid before filtering out $Fe(OH)_3$ solids

The filtration yielded 265 mL of filtrate which was put into a beaker for titration with additional 8% NaOH solution. The filtrate volume had been reduced by the solids removal and some evaporation losses during the previous overnight settling test. The Hanna electrical pH meter was set up for the first time and its probe was submerged in the beaker of filtrate before the titration began. It took about 20 minutes for the pH meter to stabilize at a starting reading of 5.05 (versus pH 4.50 by p-Hydrion paper measurement at the end of the previous day). Table 4.3 and Figure 4.7 show the SDU precipitation data and the pH readings on the Hanna instrument.

Table 4.3 – Second Test Series, SDU Precipitation

Time	mL NaOH Added	pH Meter Reading	Comments
9:30	0	5.05	
9:45	6.5	5.34	Precipitation starting
10:00	17.2	5.58	Additional precipitate
10:10	24.2	5.81	
10:22	36.0	6.38	
10:30	43.4	6.91	
10:40	50.0	7.37	Heavy precipitation
10:50	60.0	7.87	
11:00	74.0	8.38	
11:10	86.0	8.74	Precipitation about done
11:20	98.5	9.19	
11:25	100.0	9.22	Stop and reload burette
11:35	107.5	9.50	Precipitation done
11:45	114.0	10.08	
11:55	121.2	10.90	
12:05	128.8	11.63	
12:07	129.5	11.62	Stopped titration

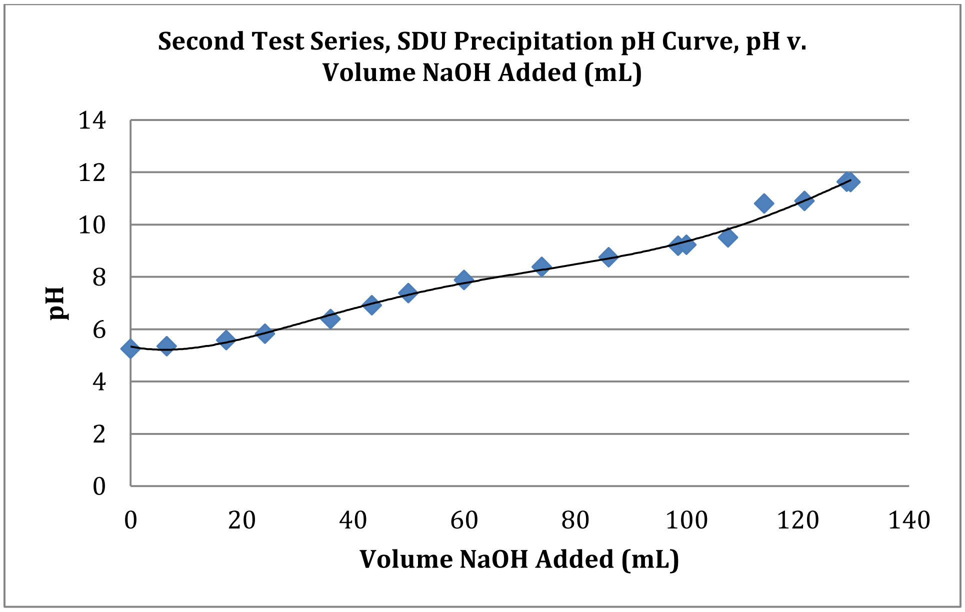

Figure 4.7 – Graph of Second Test Series, SDU Precipitation pH Curve, pH v. Volume NaOH Added (mL)

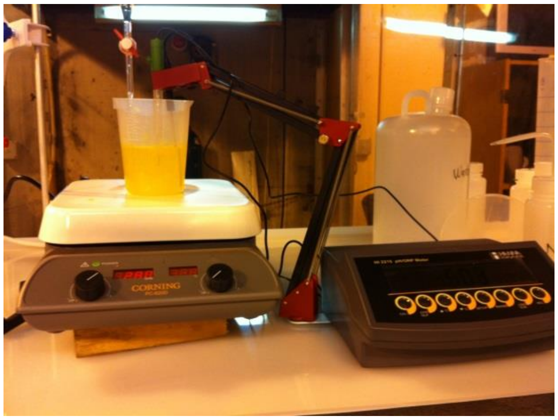

Figure 4.8 – Titration set-up

The magnetic stirring was stopped to install the temperature probe into the beaker. Just after the stirring stopped, preliminary observations of the settling characteristics were noted. The estimated supernate volume in the beaker for each time period is shown in Table 4.4 below, as a prior-to-digestion settling data set.

Table 4.4 – Second Test Series, SDU Settling, No Digestion Period

Time	Estimated Supernate Volume (% of total volume)
12:11	0
12:16	50
12:21	70
12:31	73
13:35	73

These data indicated that even without a heated digestion period to promote particle size growth, the solids settled into the bottom 27% of the beaker within 20 minutes.

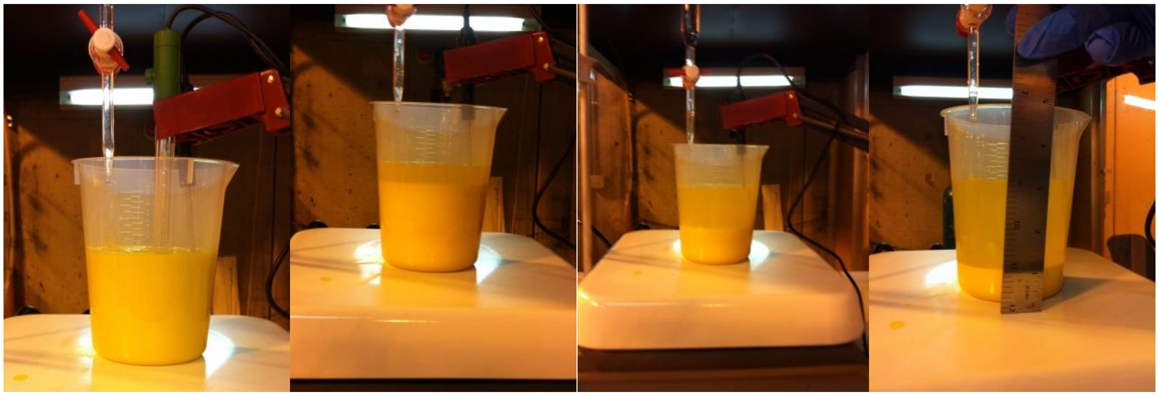

Figure 4.9 – SDU settling, no digestion period

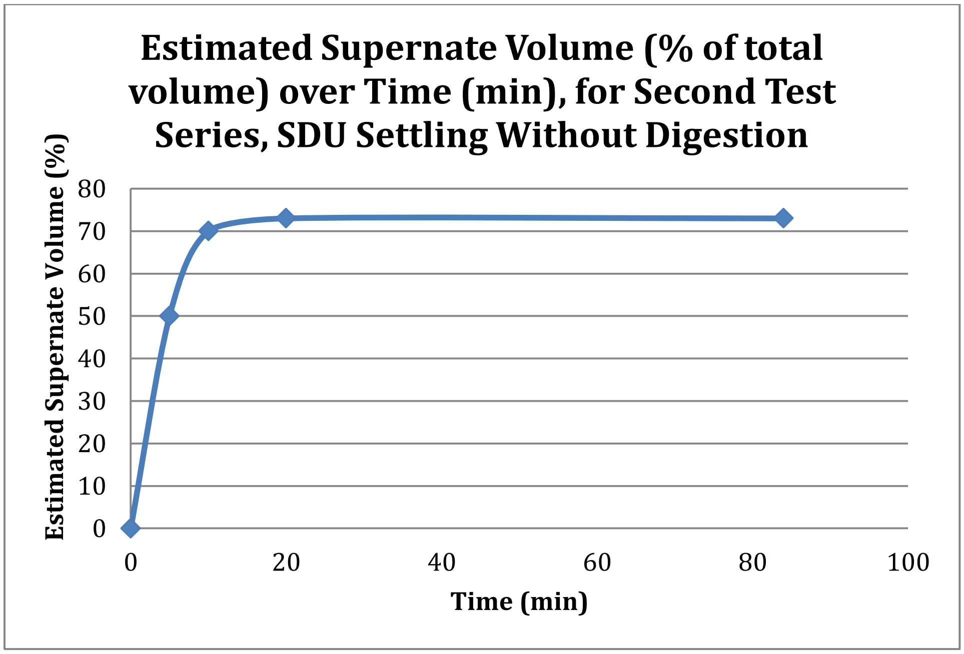

Figure 4.10 – Graph of the Estimated Supernate Volume (%) over Time (min) for Second Test Series, SDU Settling, Without a Digestion Period

At 13:40 the magnetic stirrer was re-started and the heating plate under the beaker was turned on. The temperature of the slurry was elevated to 35-40°C and held there for about 2 hours to give the mixture a digestion period. Next, the mixture was poured into a graduated cylinder along with about 5 mL of water used to rinse out the beaker. The settling test data for the 400 mL of digested slurry follows in Table 4.5.

Table 4.5 – Second Test Series, SDU Settling, With Digestion Period

Time	Supernate Volume (mL)	Slurry Volume (mL)
15:45	0	400
15:50	160	240
15:55	240	160
16:00	275	125
16:05	290	110
16:10	300	100
16:15	310	90
16:20	315	85
16:25	315	85
16:30	315	85
Overnight	317.5	82.5

An interesting observation of the data in Table 4.4 and Table 4.5 shows that a twenty minute settling gives almost exactly the same sediment volume fraction (about 27%), indicating that heated digestion at about 40°C does not improve settling rates of the slurry sediment—at least not in the early stages of the settling. A graph display of the data and photos follow.

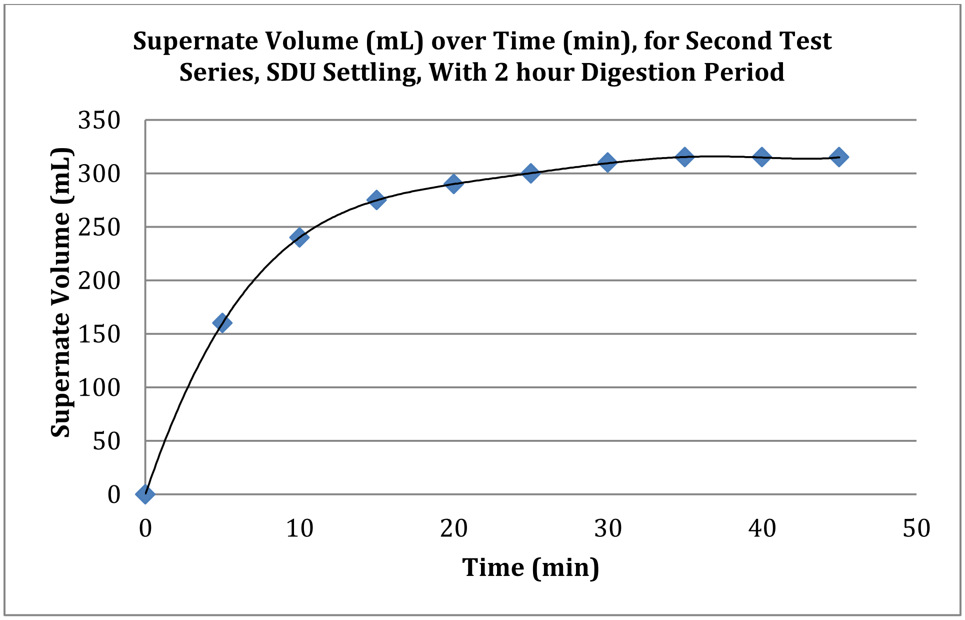

Figure 4.11 – Graph of the Supernate Volume (mL) over Time (min) for Second Test Series, SDU Settling, With 2 hour Digestion Period

Figure 4.12 – Second Test Series, SDU settling after 2 hour digestion

The next step in this series was used to convert the solid SDU into a solution of uranyl carbonate and further remove any carryover iron contamination. This was accomplished by mixing the SDU with a solution of Na_2CO_3 and/or $NaHCO_3$ at a pH of about 10.1. The two carbonate reagents used were 10% Na_2CO_3, which measured at a pH of 11.84, and saturated $NaHCO_3$, which measured at a pH of 8.27.

The settled mixture from the graduated cylinder in the previous test was filtered to separate the SDU from the NaF solution present at that stage of the process. The SDU filter cake was recovered from the filter paper and put into a beaker with 300 mL of 10% Na_2CO_3 solution. This mixture was stirred for 45 minutes to break up the SDU filter cake, then heated to 35°C for one hour while stirring. The mixture was then poured into a storage bottle and allowed to settle overnight. The next day the mixture had separated into about two-thirds clear yellow solution and one-third tan colored sediment. The tan sediment color (instead of a bright yellow) indicated that some iron was still present, and because of the sizeable amount of sediment, not all of the SDU had been converted into soluble uranyl carbonate complex. The pH of the mixture was also high, at 11.83.

Figure 4.13 – Filtration set-up, SDU Filter Cake, SDU filtrate (NaF Solution)

Figure 4.14 – SDU Filter Cake in Beaker, Sodium Carbonate/Bicarbonate mixture (pH=10), Slurry of SDU and 300 mL of 10% Na_2CO_3 solution

Figure 4.15 – Uranyl Carbonate Solution after overnight settling. Yellow sediment at the bottom shows that not all of the SDU has been converted.

These results led to a decision to re-treat the mixture with additional carbonate this time using the 8.27 pH, $NaHCO_3$ solution as the carbonate source in order to lower the pH of the mixture toward the target of 10.1. First, 50 mL of water was added and the pH was checked again. It was measured at 11.81, which was almost exactly the same.

Next, 100 mL of the $NaHCO_3$ solution was loaded into a burette and slowly added to the mixture. The pH decreased to 10.45. Another 100 mL increment was similarly added and the pH decreased to 10.12. By this time the 600 mL beaker being used was nearly full, so the mixture was split into two portions with one portion placed into a storage bottle for an extended settling period and the other portion returned to the beaker for additional processing.

Addition of another 50 mL of $NaHCO_3$ to the beaker decreased the pH to 9.95, at which point no further $NaHCO_3$ was added. The mixture was then heated to 40°C and poured into a storage bottle. The final pH of the heated mixture was 9.84. After overnight settling both halves of the mixture had light brown flocculent precipitates with the volume of precipitate in the heated portion about half the volume in the unheated portion.

Figure 4.16 – Final UCO_3 Products. Clear, yellow uranyl carbonate solution, with thin layers of brown sediment (most likely iron carryover).

The continuing presence of the light brown flocculent precipitate indicated that there was some iron carryover from the earlier pH 4.5 separation step. That, coupled with the indication that some uranium also precipitated around the pH 4.5 region, pointed to a precipitation overlap, and suggested that the anticipated clean separation of the two elements at that condition does not occur. With that being the case, a decision was made to modify the process to completely precipitate the iron and uranium together at pH 11 – 12, then use the carbonate extraction of the uranium step to separate the two elements.

The purpose of the next test in the second series was to separate the uranium from the solution of residual sodium compounds. The technique was to precipitate the uranium as uranyl peroxide, perform a settling test on the peroxide crystals, and then physically separate the peroxide crystals from the solution mixture of sodium compounds.

To begin, the first half of the sodium uranyl carbonate solution produced in the previous test was filtered to remove the iron precipitate remnant. A 50 mL portion of the filtrate (pH 10) was then put in a beaker to serve as the initiation solution. A total of 25 mL of 20% nitric acid was slowly added to the carbonate until the pH was reduced to 2.0. Bubbles of CO_2 formed and dissipated as the acid reacted with the carbonate. One burette was filled with 100 mL of 35% H_2O_2 and another burette was filled with 100 mL of the carbonate filtrate. Both burettes were mounted above the beaker of starter solution. A 125 mL squeeze bottle of 20% nitric acid was on standby.

A slow drip of H_2O_2 was started and immediately a pale yellow (almost white) precipitate began forming in the starter solution. Next a drip of the carbonate solution was started and the heating plate was turned on. The pH gradually started to increase and when it reached 7.0, nitric acid was added from the squeeze bottle to bring it back down. The two burette drips and intermittent squirts of nitric acid were continued with frequent pH checks attempting to hold the pH in the desired 3.5 – 4.5 range during the reaction. At the beginning there were both high and low excursions out of the desired pH range as the flows were juggled, but as experience developed, better pH control resulted. The additions continued until all of the carbonate solution had been used up. The final tally of inputs was: 230 mL carbonate solution, 35.6 mL 35% H_2O_2, and 95 mL 20% HNO_3. The mixture was stirred while heated to 45°C for 1.5 hours, then the heat was turned off and the mixture was left stirring slowly for 72 hours, to allow the peroxide precipitation to complete. The pH after the heating had fallen to 3.0, evidence of a continuing peroxide precipitation reaction.

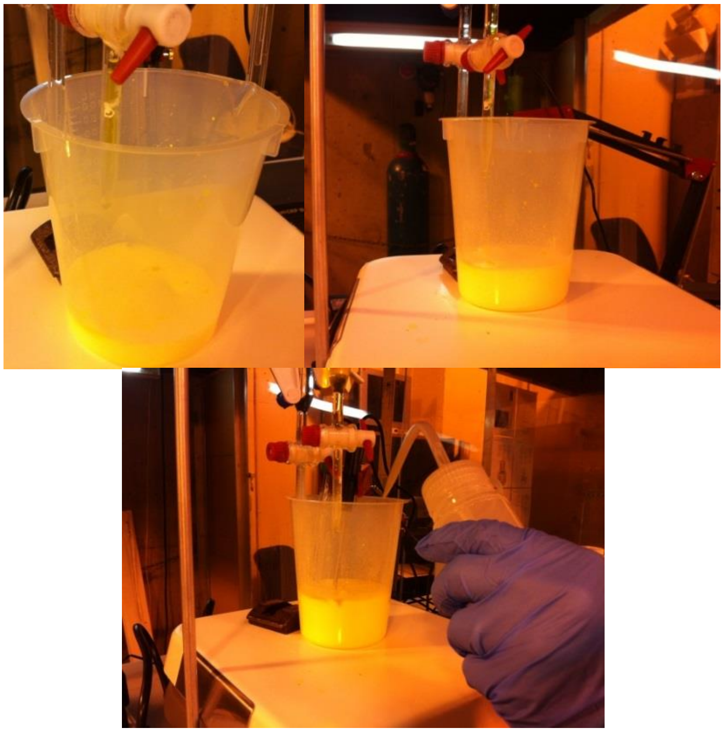

Figure 4.17 – UO_4 Precipitation

After the 72-hour stirring period, the pH had fallen further to 1.5, so some extra Na_2CO_3/$NaHCO_3$ mix was added to bring the pH back up to 4.0. During the 72-hour period, there had also been a substantial evaporation loss from the beaker such that only 195 mL remained of what had started out as 360 mL. The mixture was poured into a graduated cylinder for a settling test, which test data can be found in Table 4.6.

Table 4.6 – Second Test Series, First Half, UO_4 Settling Test

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	195
10	5	190
20	5	190
30	10	185
60	15	180
80	20	175
100	22	173
120	25	170
2 days	42	153

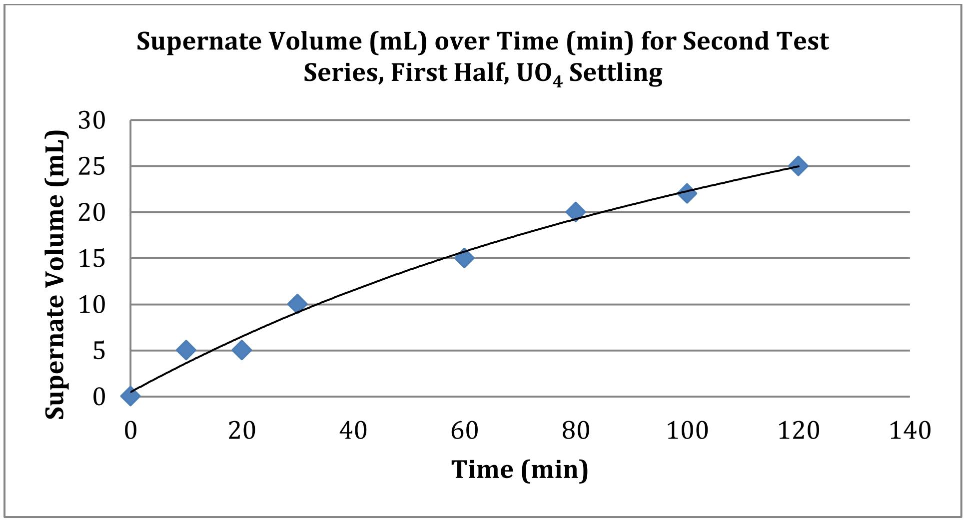

Figure 4.18 – Graph of Supernate Volume (mL) over Time (min) for Second Test Series, First Half, UO_4 Settling

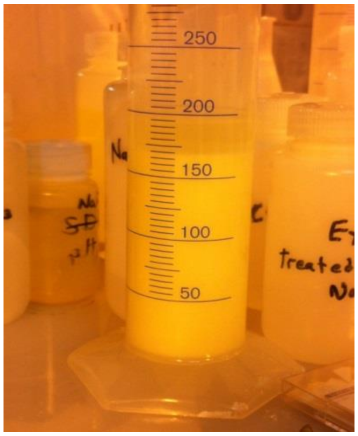

Figure 4.19 – Settling of Second
Test Series, First Half, UO_4

The settling data indicated that the peroxide particle size was very small and that separation may be quite difficult. This was not the case, however, as the subsequent filtration required only 23 minutes. The peroxide crystals were scraped off the filter paper and placed in an open container in the process hood to air dry. The dried crystals were placed in a tared sample bottle, and had a net weight of 30.24 g $UO_4 \cdot nH_2O$. The filtrate was a clear solution and a portion of it was also placed in a sample bottle for subsequent analyses.

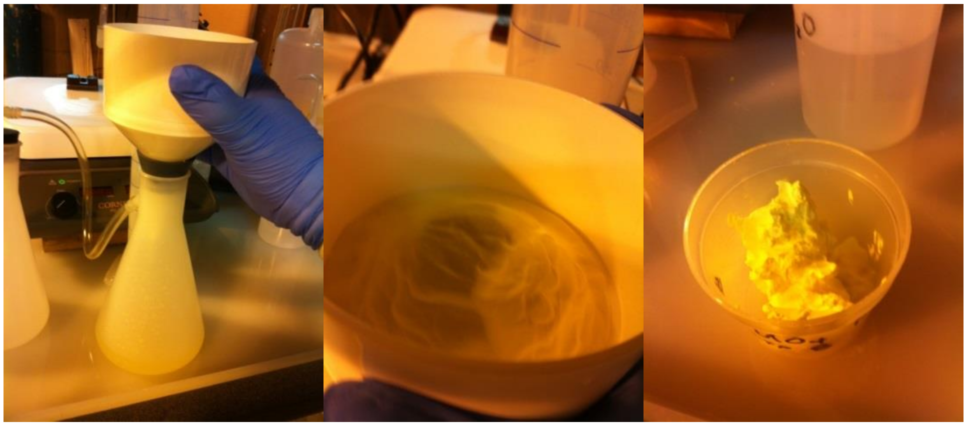

Figure 4.20 – Filtration of Second Test Series, First Half, UO_4. From left to right: filtration apparatus, UO_4 filter cake, UO_4 in container to air dry.

The second half of the second series carbonate extract solution was then filtered to remove the trace of $Fe(OH)_3$ solid and was transferred to a beaker. The solution was precipitated with hydrogen peroxide using the same burette setup and titration technique described previously for the first half to completely precipitate the UO_4 from the solution. The total reagents used were 394 mL carbonate solution, 65.6 mL 35% H_2O_2, and 156 mL 20% HNO_3. The final slurry was put into a graduated cylinder for a settling test with the results in Table 4.7, below.

Table 4.7 – Second Test Series, Second Half, UO_4 Settling Test

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	500
10	452	48
20	460	40
30	460	40
40	470	30
50	470	30
60	470	30

The settling data showed very rapid initial settling and a very complete separation of 6% slurry and 94% supernate liquid, after 40 minutes. The mixture was then filtered, along with the remaining slurry that would not fit into the settling test cylinder and the UO_4 cake was air dried for one week. The air-dried cake weighed 27.82 g.

Auxiliary Tests on First Test Series SDU

An auxiliary series of processing was carried out using the SDU/$Fe(OH)_3$ co-precipitate slurry made from the first test series. The purpose of these tests was to evaluate an iron-uranium separation after a complete co-precipitation of both had been done. Since an iron separation on this slurry had not been attempted, it was ideal to use it to test the concept of making the iron separation at the carbonate extraction step rather than at the pH 4.5 partial precipitation step used in the Series 2 sequence. Also, since the Na_2CO_3/$NaHCO_3$ mixture used in the Series 2 carbonate extraction yielded such a high final pH (11.84), it was decided to use only $NaHCO_3$ (pH 8.27) as the extractant in the auxiliary test. Processing at room temperature (no heating) was a third variant added to the test technique.

The SDU/$FeOH_3$ slurry from the Series 1 precipitation was filtered and the solids were scraped off the filter paper into a beaker. A 50 mL allotment of water was used to help wash off the filter paper, and was added to the beaker and stirred to re-slurry the SDU/$FeOH_3$ solids. The pH of the mixture was 7.6.

A burette was filled with 100 mL of the saturated $NaHCO_3$ solution and a drip was started, adding $NaHCO_3$ solution to the SDU/$FeOH_3$ slurry. The beaker was not heated during this test. The pH measured 7.5 after 50 mL of the carbonate solution was added and 7.7 after 100 mL was added. Addition of carbonate solution was halted at this point and the mixture was put into a storage bottle and left to settle. After settling, the solids had almost completely dissolved leaving a bright yellow solution over a thin, dark-brown sediment layer.

This mixture was filtered to remove the dark-brown iron sediment, and 50 mL of the filtrate was put into a small container as a starter solution.

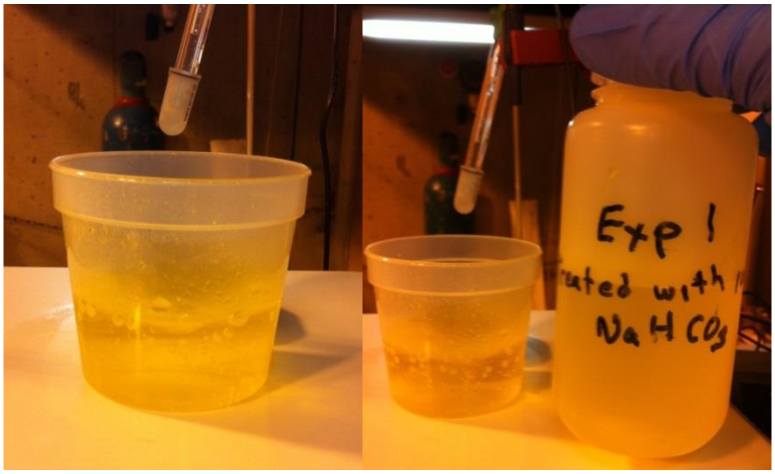

Figure 4.21 – Uranyl Carbonate Solution prepared from First Test Series SDU and $NaHCO_3$, then filtered. This is the 50mL put into a small container that served as a starter solution.

A burette was filled with 100 mL of the filtrate, and was mounted above the small starter solution container, along with a second burette containing 35% H_2O_2. To begin the uranyl peroxide precipitation, 18.4 mL of 20% HNO_3 plus 1.6 mL of 35% H_2O_2, plus an additional 20 mL of the filtrate were added to the container, at which point the mixture was transferred to a 600 mL beaker. Additional carbonate, acid and peroxide were slowly added in proportions to keep the pH in the 3.0 – 4.0 range. Once again the beaker was not heated. The tally of reagents at the end of the precipitation was 194 mL carbonate solution, 32.1 mL 35% H_2O_2, and 27.3 mL 20% HNO_3. The final pH was 3.5. The mixture was poured into a graduated cylinder for a settling test, with data shown in Table 4.8, below.

Table 4.8 – First Test Series, Auxiliary Testing, UO_4 Settling

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	235
10	10	225
20	14	221

30	25	210
40	40	195
50	57	178
60	85	150
80	97	138
100	105	130
120	110	125
2 days	155	80

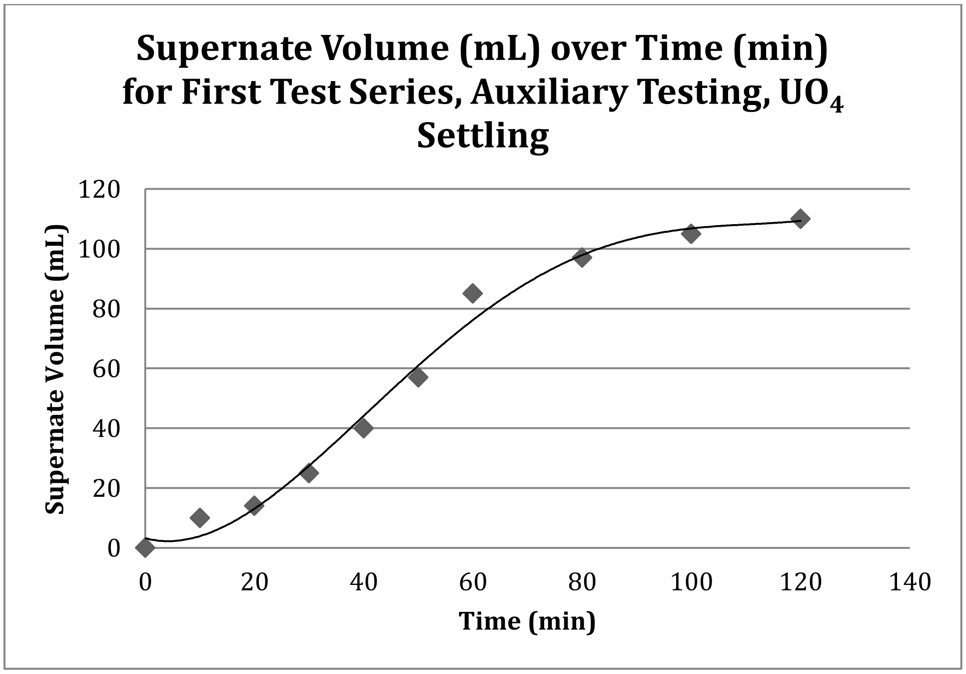

Figure 4.22 – Graph of Supernate Volume (mL) over Time (min) for First Test Series, Auxiliary Testing, UO_4 Settling

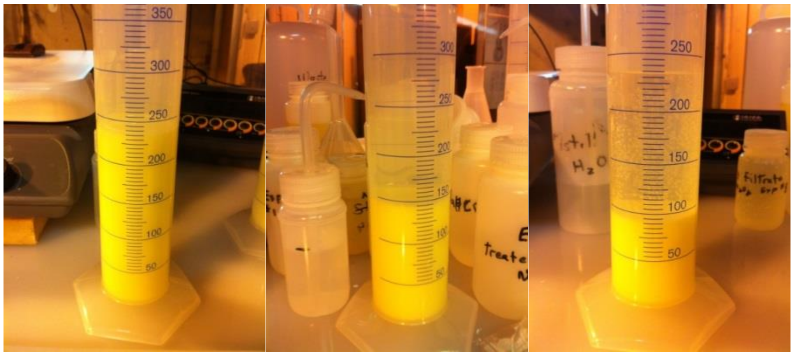

Figure 4.23 – First Test Series, Auxiliary Testing, UO_4 Settling

It is noteworthy that the settling results for the room temperature tests in the auxiliary and second half of Series Two portions were considerably better than the results of the same settling test in the first half of the Series Two work, indicating that larger particle sizes resulted from room temperature reaction conditions.

After 48 hours of settling, the mixture was filtered and the $UO_4 \cdot nH_2O$ crystals were scraped off the filter paper and put into an open container in the work hood. After air-drying for 48 hours, the crystals were put into a tared sample bottle, and the net weight of the dried crystals was 17.76 g. A uranium material balance calculation on this weight, however, indicated some water was still present in the crystals so a heated re-drying was planned for later. A sample bottle of the filtrate was also collected for analysis.

Figure 4.24 – First Test Series, Auxiliary Testing, UO_4 (yellow solids) and filtrate (clear liquid)

Third Test Series: KDU Testing with Potassium Bicarbonate

A third test series was done using analogous potassium compounds in place of sodium compounds as the reagents. The purpose of this series was to identify process differences and detect any possible advantages for using potassium compounds. Very little information exists regarding the use of potassium compounds in uranium processes so another goal was to expand the knowledge of what results can be expected. The experiment protocols used were, for the most part, the same as those used for the sodium tests, but followed the modified recovery process outlined at the end of Chapter 3, and in Figure 4.7.

The first test started with 50 g of the UO_2F_2 powder dissolved in 300 mL of distilled water. That mixture was titrated using a burette filled with 100 mL of 15% KOH solution, and a KDU/$Fe(OH)_3$ mixture was produced. The titration was done very slowly, with heating, to observe any differences and keep the reaction mixture close to equilibrium. Table 4.9 below shows the data collected.

Table 4.9 – Third Test Series, KDU Precipitation

Vol. KOH Added (mL)	pH	Temp. (°C)	Comments
0	1.0	22	Clumps of precipitate, redissolved
4	1.5	30	
6	2.0	32	
8	3.5	35	
10	3.5	36	
12	4.0	37	
14	4.0	38	Clumps more persistent
16	4.5	39	Color darkening yellow/brown
18	5.0	39	
20	5.0	39	
24	5.5	39	Clumps stopped forming
28	6.0	39	Persistent yellow/brown precipitate
32	6.5	39	Precipitate more grainy
36	6.5	39	Precipitate getting uniform
40	7.0	39	
44	7.0	39	
49	7.0	39	
57	7.5	39	Precipitate very uniform
67	7.5	39	
77	8.0	39	

87	9.0	39	
100	9.5	38	Precipitation appears complete

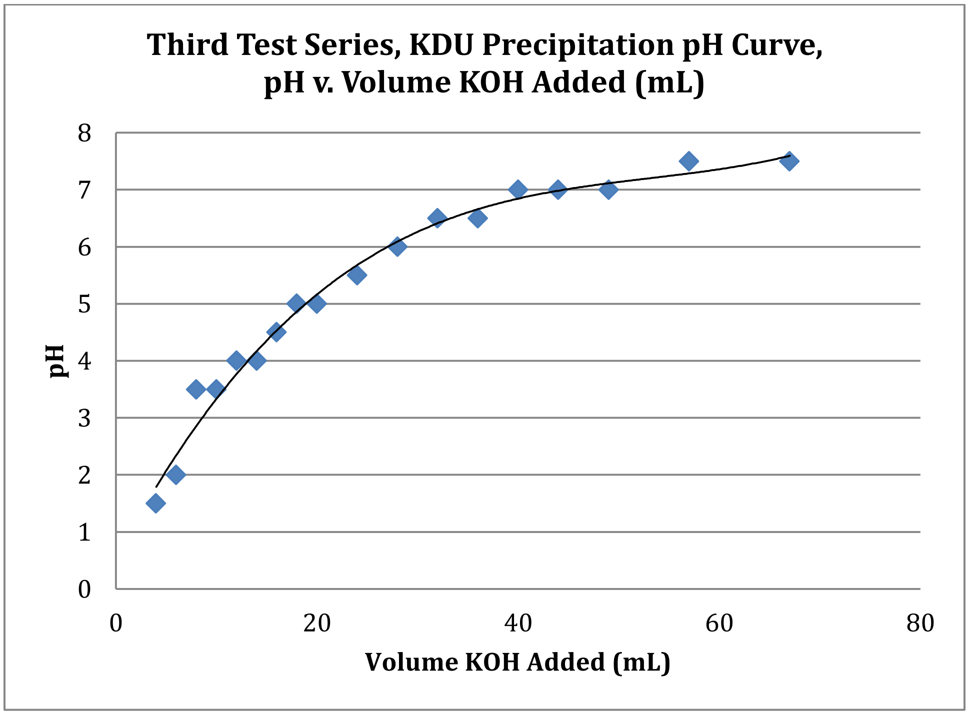

Figure 4.25 – Graph of pH v. Time (min) for Third Test Series, KDU Precipitation

The KDU mixture was poured into a graduated cylinder for a settling test. Of the 400 mL of liquid titrated, 20 mL were lost to evaporation during the 2 hour titration so the volume for the settling test was 380 mL. Table 4.10, below, shows the settling data.

Table 4.10 – Third Test Series, KDU Settling

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	380
10	95	285
20	160	220
30	200	180
40	225	155
50	240	140

60	245	135
80	255	125
100	255	125
120	257.5	122.5
2 days	260	120

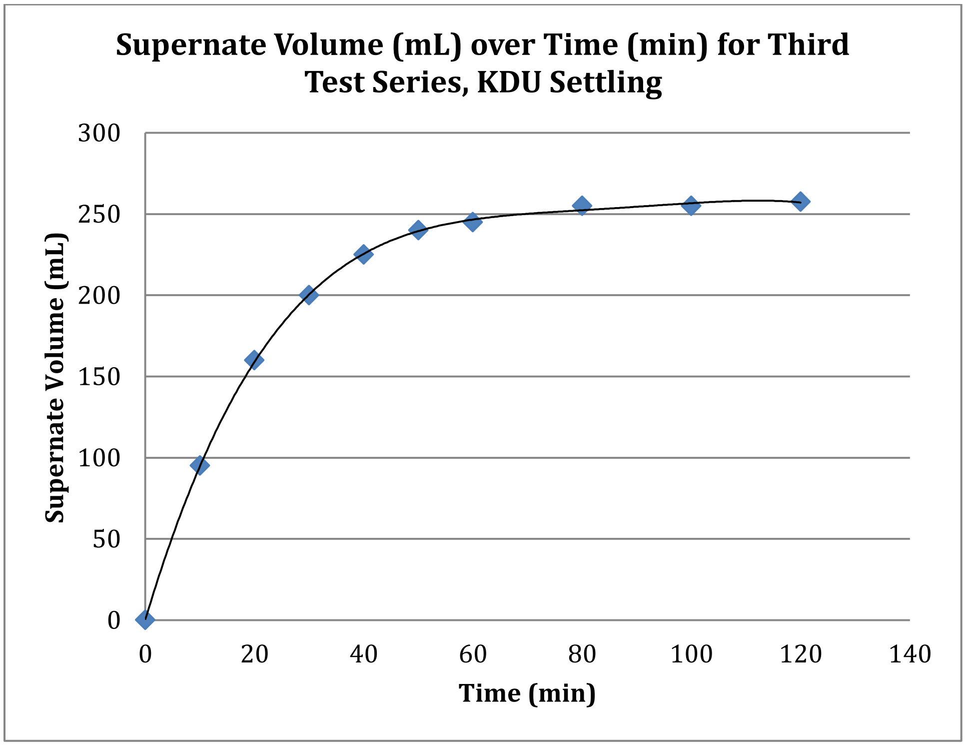

Figure 4.26 – Graph of Supernate Volume (mL) over Time (min) for Third Test Series, KDU Precipitate Settling

After 7 days, the settled mixture was filtered to recover the precipitate. An additional 13 mL of evaporation loss had occurred from the graduated cylinder, so a total of 367 mL of mixture plus a few mL of water used to rinse out the graduated cylinder were filtered. The filter cake was scraped of the filter paper, was re-slurried in 50 mL of water, and was put in a storage bottle. The filtrate had a pH of 7.0, indicating that the precipitation reaction had continued after the titration had stopped causing the pH to decrease from 9.5 to 7.0. A few drops of KOH solution were added to the filtrate, resulting in more precipitate forming in the filtrate, so the decision was made to resume the titration on the filtrate. Two 10 mL portions of KOH were then added to the filtrate. The first raised the pH to 8.5 and the second raised the pH to 11.5. A moderate amount of additional precipitate formed in the filtrate, so the 395 mL of mixture was heated to 40°C for a one-hour digestion, and was then poured back into a graduated cylinder for a settling test, the data of which is shown in Table 4.11.

Table 4.11 – Third Test Series, Additional KDU Settling

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	395
10	75	320
20	135	260
30	185	210
40	220	175
50	245	150
60	265	130
2 days	332	63

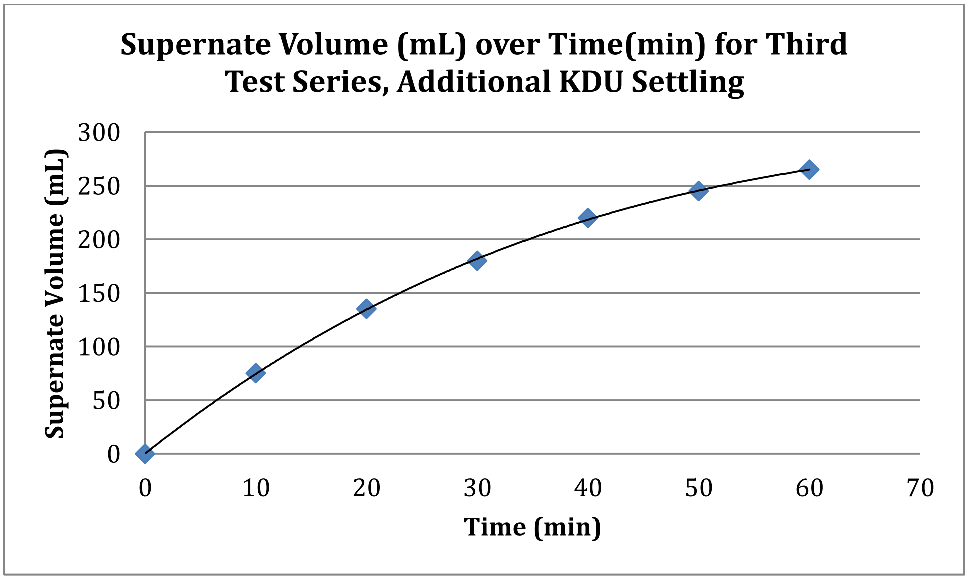

Figure 4.27 – Graph of Supernate Volume (mL) over Time (min) for Third Test Series, Additional KDU Settling

Figure 4.28 – Third Test Series
KDU Extraction after settling.

After two days the settled mixture was filtered and the filter cake was re-slurried in 50 mL of water and put into a storage bottle. The filtrate test pH 11.5 indicating the precipitation reaction had gone to completion in the second titration. The filtrate was saved in a storage bottle for later analysis.

The next step was to set up for carbonate extraction of the KDU filter cakes. Because of the good results using $NaHCO_3$ as the extractant in the auxiliary series above, it was decided to use its analog, $KHCO_3$, for the first potassium-based carbonate extraction. A solution of $KHCO_3$ could not be obtained, so a crystalline solid version of the compound was procured, and a solution was prepared by dissolving 90 g of the $KHCO_3$ crystals in 300 mL of distilled water. This solution tested at pH 7.5, somewhat lower than the 8.27 measured for the $NaHCO_3$ solution. The filter cakes from the two KDU/$Fe(OH)_3$ filtrations, 100 mL of water, and the filter paper rinse waters were combined in a beaker and stirred to re-slurry the solids. The combined mixture volume was 175 mL. A burette was filled with 100 mL of the $KHCO_3$ solution, as prepared above, and was mounted over the beaker. The titration data is shown in Table 4.12.

Table 4.12 – Third Test Series, First Uranyl Carbonate Extraction Titration

Time (min)	Vol. $KHCO_3$ Added (mL)	pH	Comments
0	0	7.0	
4	10	7.0	
13	20	7.0	
19	30	7.0	
22	40	7.0	Beginning to see bubbles
25	50	7.0	
28	60	7.0	More vigorous bubbles
31	70	7.0	
33	80	7.0	
37	90	7.0	
39	100	7.0	Stopped to reload burette
43	-	-	Started back up
46	110	7.0	Getting brown color in slurry
49	120	6.7	Stopped titration

The slurry was then poured into a graduated cylinder to start a settling test. Bubbles continued to form but no settling was observed, so the settling test was aborted and the mixture was put back into a beaker and placed on the stir plate. The heater was turned on and the mixture was warmed to 40°C. Once this temperature was reached, an additional 40 mL of $KHCO_3$ solution was slowly added, which generated even more bubbles, indicating that the pH was so low that the carbonate was breaking down into CO_2. At a low enough pH, the carbonate reacts with the nitric acid before it can react with the uranium and following reaction takes place before the uranyl carbonate can form.

$$KHCO_3 + HNO_3 \rightarrow CO_2 + H_2O + KNO_3 \tag{4.1}$$

To counteract this, a 4 mL allotment of 15% KOH solution was added to the mixture to pull the pH back up, and the bubbling stopped. The mixture was poured back into the graduated cylinder, but no immediate settling occurred. The mixture was left in the graduated cylinder for 72 hours, after which the solids slurry had settled to 190 mL supernate liquid and 145 mL of combination KDU/$Fe(OH)_3$ solids. The mixture was filtered and the filter cake was scraped off the filter paper into a beaker. The yellow colored filtrate was put into a storage bottle as the first carbonate extraction.

Figure 4.29 – Third Test Series, First Carbonate Extraction. High volume of solids on filter led to the belief that not all of the uranium had been extracted, so a second attempt was made.

The substantial amount of solids left after the first uranyl carbonate extraction indicated that a significant amount of KDU did not dissolve as carbonate complex, so the cake in the beaker was mixed with 120 mL more $KHCO_3$ solution. That mixture was stirred and heated to 40°C for one hour and was then poured back into a graduated cylinder for four days. The mixture pH was 9.0. After four days, the mixture was filtered and the yellow colored filtrate was put into a storage bottle as the second carbonate extraction. The filter cake was scraped off the filter paper, re-slurried in water and put into a storage bottle.

Figure 4.30 – Re-slurried solids from Third Test Series, first carbonate extraction

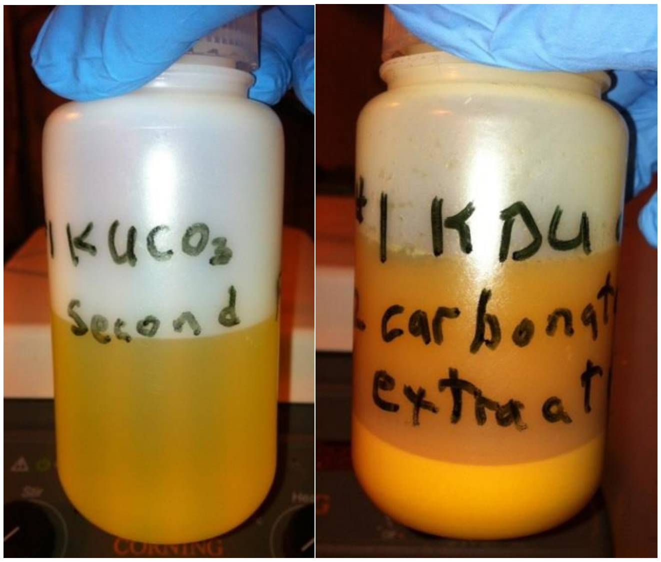

Figure 4.31 – Left to right: Third Test Series, second carbonate extraction filtrate; Solids from second carbonate extraction, re-slurried in water.

Three days later, the slurry in the storage bottle was put back into a beaker and a third carbonate extraction was done. The mixture was heated to 40°C and 100 mL more of $KHCO_3$ was slowly added. The pH of the mixture started at 8.0 and remained at 8.0 throughout the carbonate addition. No evolution of bubbles occurred. The heat was turned off and filtering preparations were started. Before filtration was started, however, the mixture separated quickly into a dark brown slurry above a tan sediment, as shown in Figure 4.32.

Figure 4.32 – Attempted third carbonate extraction

When filtration was started the slurry portion easily separated from the sediment layer so it was decanted off the top, through the filter. Nearly all of the dark brown material decanted off the sediment so the filtration was stopped at the end of the decanting. The filtered solid was a grainy, almost black material on the filter paper. The filter paper was set aside to air dry and the sediment slurry was poured back into its storage bottle with enough $KHCO_3$ solution to fill the bottle. The filtrate was put in a separate storage bottle and set aside as the third carbonate extraction.

Figure 4.33 – Third Test Series, Third Carbonate Extraction filtration.
Dark brown solids on filter are mostly iron; the yellow solids indicate the presence of even more uranium. It was determined that the potassium series made total uranium extraction too difficult. The yellow liquid on the left is the third carbonate extraction filtrate.

With the result so far that the KDU was substantially too resistant to the $KHCO_3$ extraction attempts, the decision was made to abandon further efforts on this approach. One final idea for using a potassium-based reagent was to repeat the carbonate extraction attempts with K_2CO_3 solution in place of $KHCO_3$ solution.

Fourth Test Series: KDU Testing with Potassium Carbonate

The fourth test series was put forth to duplicate the KOH precipitation sequence, then attempt to extract the uranium from the KDU with K_2CO_3 solution, while heating the reactions to about 40°C. The batch size was reduced to half, so the series started with 25 g UO_2F_2 dissolved in 150 mL water. This solution was titrated with 15% KOH and Table 4.13 below shows the titration results.

Table 4.13 – Fourth Test Series, KDU Precipitation

Time	Vol. KOH Added (mL)	pH	Temp. (°C)
1:52	0	1.0	22
1:56	10	3.5	35
2:01	20	5.0	37
2:06	30	6.5	38
2:12	40	7.0	39
2:18	50	7.5	40
2:24	60	8.0	40
2:28	65	9.0	40
2:33	70	9.5	40
2:38	75	10.0	40

The mixture was held at 40°C for one hour and was then poured into a graduated cylinder. After four days, the pH of the mixture had decreased to 7.0, so 3 mL of KOH solution were added to bring the pH up to 12. The mixture was filtered and the KDU cake was mixed with water and put into a storage bottle.

A solution of 150 g K_2CO_3 in 300 mL water was prepared which measured pH 12. The water slurry of KDU was put in a beaker and titrated with the prepared K_2CO_3 solution. A total of 200 mL of carbonate solution were added to the mixture while holding the temperature at 40°C, then the heat was turned off and the mixture was continually stirred for 72 hours as a digestion step. Even after the extended digestion time there was still substantial un-dissolved KDU remaining in the mixture, so further efforts were abandoned, and this concluded the study of potassium-based reagents. The conclusion drawn from the testing was that while the KDU precipitation is just as adequate as the SDU precipitation, subsequent complete recovery of soluble uranyl carbonate from the KDU is much more difficult and not practical.

Fifth Test Series: Modified SDU Confirmation

A final uranium test series was performed as a confirmation run of the SDU techniques developed from the results of the first and second test series. The tests started with 50 g of UO_2F_2 powder dissolved in 300 mL water which was put into a beaker and titrated with 8% NaOH, at room temperature. The titration is recorded in Table 4.14 below.

Table 4.14 – Fifth Test Series, SDU Precipitation

Time	Vol. NaOH Added (mL)	pH	Comments
9:23	0	1.0	Light green solution
9:27	20	4.5	Local precipitate clumps, dark color
9:32	40	5.0	More persistent precipitate
9:37	60	7.0	More persistent heavy precipitate
9:41	80	8.0	Heavy precipitate, dark yellow
9:45	100	8.0	
9:52	120	8.0	
9:56	130	8.5	
10:02	140	9.0	
10:07	150	9.0	
10:11	160	9.5	
10:16	170	10.0	
10:19	180	11.0	
10:20	180	11.0	Started one-hour digestion
11:20	180	8.0	Still heavy precipitate, but low pH
11:21	185	9.0	
11:22	190	9.5	
11:23	195	9.5	
11:24	200	9.5	
11:25	205	9.7	
11:26	210	10.0	
11:26	215	11.0	Started second hour-long digestion
12:26	215	9.5	
12:27	225	11.0	Precipitation complete

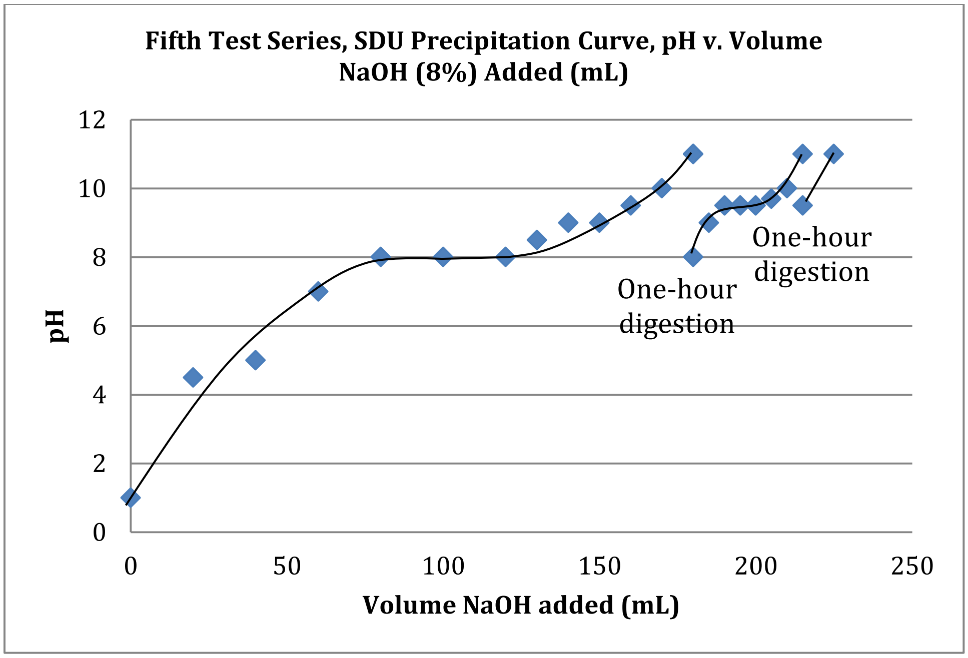

Figure 4.34 – Graph of Fifth Test Series, SDU Precipitation pH Curve, pH v. Volume NaOH Added (mL)

Figure 4.35 – Fifth Test Series SDU Precipitation

The precipitation slurry and a small amount of rinse water were transferred to a graduated cylinder for a settling test. Results of that test are in Table 4.15.

Table 4.15 – Fifth Test Series, SDU Settling

Time	Supernate Volume (mL)	Slurry Volume (mL)
12:42	0	528
12:52	63	465
13:02	108	420
13:12	153	375
13:22	191	337
13:32	228	300
13:42	253	275
13:52	298	230
14:02	318	210
14:12	328	200
14:22	343	185
14:32	358	170
14:42	363	165
Overnight	383 (pH=10.5)	145 (27.5% of total volume)

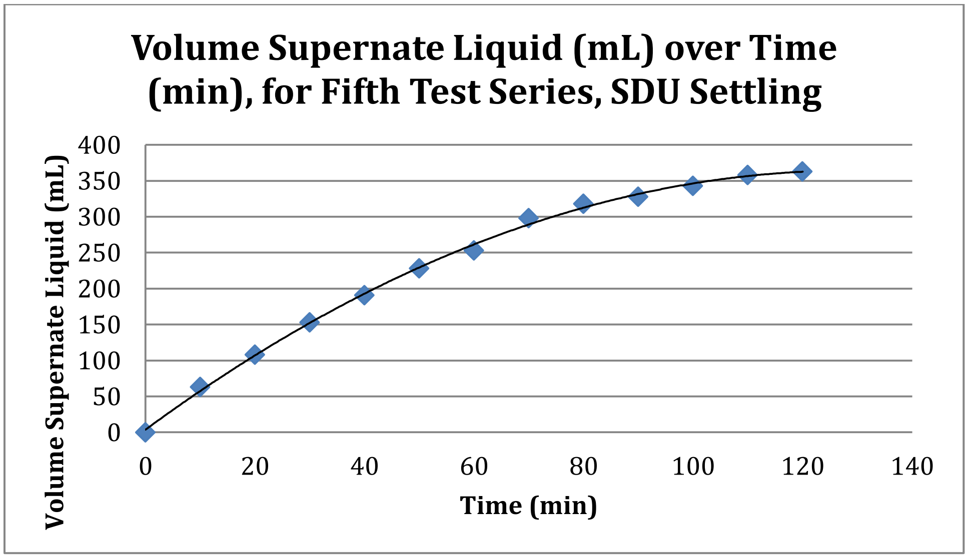

Figure 4.36 – Graph of Volume Supernate Liquid (mL) over Time (min) for Fifth Test Series, SDU Settling

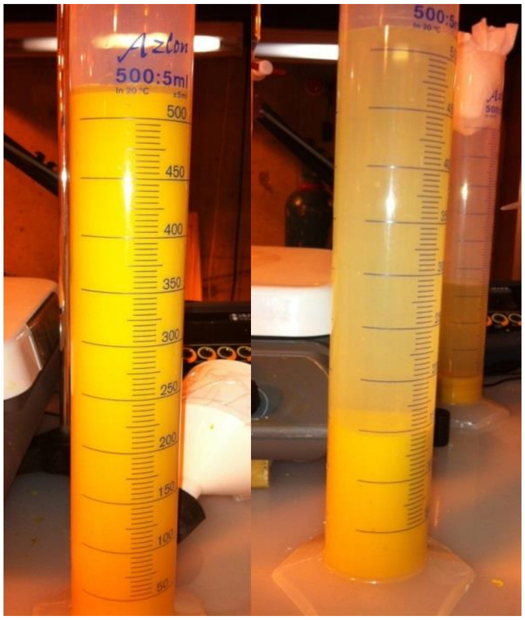

Figure 4.37 – Fifth Test Series SDU Settling

The mixture in the graduated cylinder was then filtered (filtration time = 14 minutes) and the filter cake was scraped into a beaker where 200 mL of saturated $NaHCO_3$ solution was added. The mixture was stirred for about 15 minutes then another 100 mL of $NaHCO_3$ and 150 mL water was added. The mixture was stirred for another hour, and the stirring was stopped and the slurry was allowed to settle for 15 minutes, so that the color intensity of the supernate liquid might be observed. The color was only moderately intense, indicating that not much uranyl carbonate had been produced, so the stirring was resumed and the heater was turned on. The slurry was heated to 40°C and stirred for an additional hour after which it was poured into a graduated cylinder for a settling test. The settling was slow with only 21% supernate separation after one hour of settling. The mixture was then filtered (filtration time = 1 hour 35 minutes). The filtrate, which was the first carbonate extraction for this series, was put into a storage bottle. The filter cake was re-slurried in 250 mL water (slurry pH 10) and put into a storage bottle overnight.

The next day, the slurry was put back into a beaker and 8 mL of 20% HNO_3 was added to decrease the pH to 8.0. 100 mL of saturated $NaHCO_3$ solution was added and the mixture was stirred at room temperature for one hour, and then poured back into a graduated cylinder. Settling was observed to be once again very slow, so the mixture was put back into a beaker and another 8 mL of acid was added to decrease the pH to 7.5. The heater was turned on and the mixture was stirred for one hour at 40°C. The volume of mixture at that point was 290 mL, which was poured back into a graduated cylinder and kept there overnight.

The next day, the mixture had settled to 200 mL supernate liquid and 90 mL slurry, with a pH of 7.5. It was filtered, and the intensely colored filtrate was designated as the second carbonate extraction. The filter cake was re-slurried in 100 mL water and 100 mL saturated $NaHCO_3$. It was then stirred and heated to 40°C for 1 hour 35 minutes, and then poured into a graduated cylinder. The 220 mL of mixture had completely separated into 200 mL of intensely colored supernate liquid and 40 mL of a dark brown slurry after one hour. The final pH was 8.0. After filtering, the filtrate was designated as the third carbonate extraction and the brown filter cake was placed in a small container to air dry. After 72 hours of drying, the brown residue net weight was 2.157 g. The theoretical residue weight from 50 g of starting material dosed with 3% FeF_3 would be about $0.03 \times 50 = 1.5$ g $Fe(OH)_3$, so the maximum SDU carryover possible is 0.657 g or $0.657/49.92 \times 100 = 0.013$ or 1.3% of the original SDU in this series. Un-evaporated water likely contributed some to the residue weight so the actual SDU carryover loss was likely less than 1%.

Figure 4.38 – Fifth Test Series SDU Carbonate Extraction 1. Residual solids are on the left, re-slurried in water. Carbonate extraction is on the right.

Figure 4.39 – Fifth Test Series SDU Carbonate Extraction 2. Residual solids on the left and carbonate extractions #2 and #1 on the right.

Figure 4.40 – Fifth Test Series SDU Carbonate Extraction 3.
The final bit of deep brown residue is on the left and all three carbonate extractions are on the right.

The three carbonate extractions totaled more than the capacity of the processing beaker, so they were peroxide precipitated in three batches comprised as follows:

1. Batch 1 was the entire first carbonate extraction
2. Extractions 2 and 3 were combined, then divided in half to make Batch 2 and Batch 3 for the peroxide precipitation.

The data for each of the batches follows.

Batch 1

First, 100 mL of extract starter solution was added to a beaker, and 20% HNO_3 was added slowly to reduce the pH to 3.5. Then the combined slow addition of H_2O_2, extract solution, and acid commenced. The data is shown in Table 4.16 below.

Table 4.16 – Fifth Test Series, Batch 1, UO_4 Precipitation

Volume Carbonate (mL)	Volume H_2O_2 (mL)	Volume HNO_3 (mL)	pH
100	0	0	11.5
100	0	2	7.5
100	0	4	7.0
100	0	15	6.0
100	0	17	5.0
100	0	20	5.0
100	0	21	4.5
100	0	22	3.5
200	26	42	3.5
300	55	64	2.5
400	82	83	4.0
412	84	87	3.5

Figure 4.41 – Fifth Test Series, Batch 1, UO_4 precipitation.

The mixture was stirred overnight, then put into a graduated cylinder for a settling test. The data from the settling test is shown in Table 4.17.

Table 4.17 – Fifth Test Series, Batch 1, UO_4 Settling

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	550
10	180	370
20	235	315
30	305	245
40	365	185
50	400	150
60	425	125
80	450	100
100	455	95
120	455	95 (17.2% of total volume)

The mixture was then filtered, and the filter cake was scraped into a container for air drying. The filtrate was put into a storage bottle.

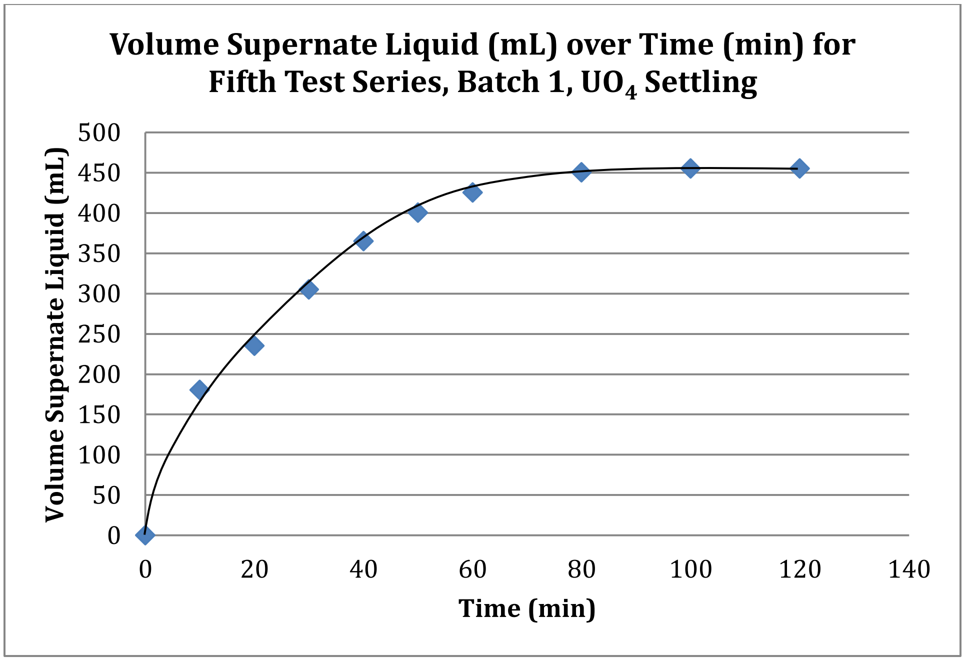

Figure 4.42 – Graph of Volume Supernate Liquid (mL) over Time (min) for Fifth Test Series, Batch 1, UO_4 Settling

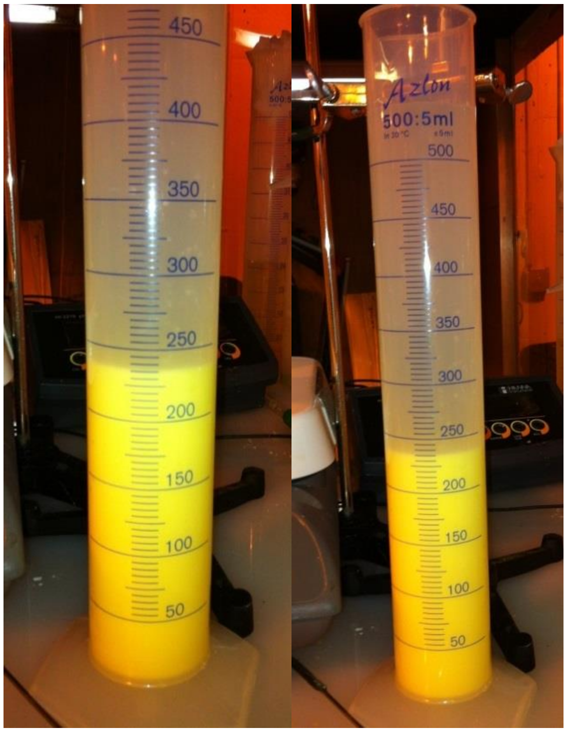

Figure 4.43 – Fifth Test Series, Batch 1, UO_4 settling.

Figure 4.44 – Fifth Test Series, Batch 1, UO_4 filter cake (left) and filtrate (right).

Batch 2

The peroxide precipitation technique was the same as Batch 1 and the data is in Table 4.18.

Table 4.18 – Fifth Test Series, Batch 2, UO_4 Precipitation

Volume Carbonate (mL)	Volume H2O2 (mL)	Volume HNO3 (mL)	pH
100	0	0	8.8
100	0	10	6.0
100	0	12	3.5
200	26	26	3.5
300	50	40	4.0

The mixture was stirred for 1.5 hours and then poured into a graduated cylinder for a settling test. Table 4.19 shows the settling data.

Table 4.19 – Fifth Test Series, Batch 2, UO_4 Settling

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	360
10	30	330
30	100	260
40	130	230
50	160	200
60	190	170
80	230	130
100	265	95
120	265	95

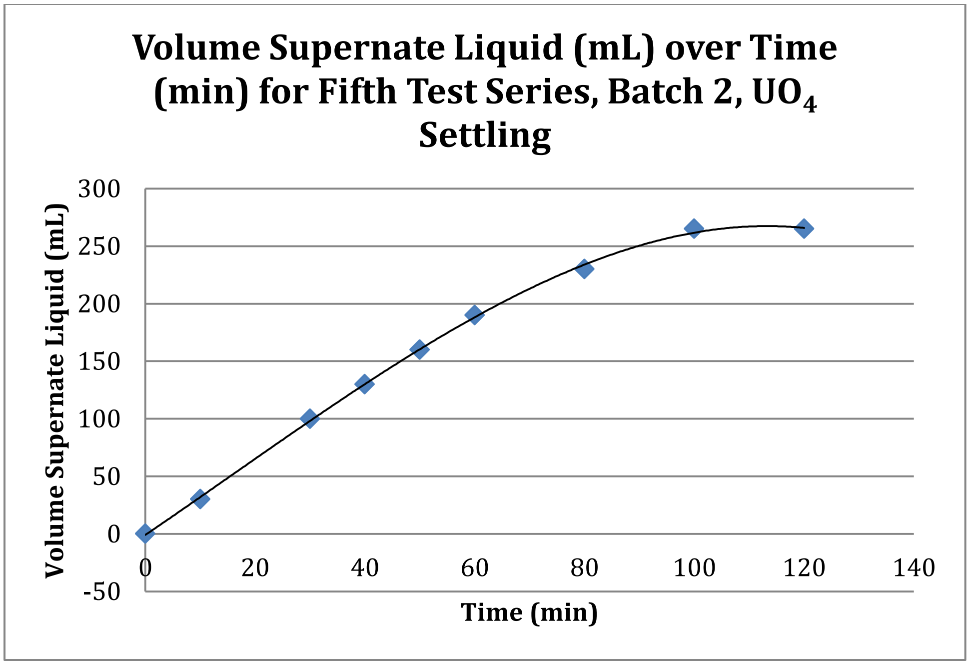

Figure 4.45 – Graph of Volume of Supernate Liquid (mL) over Time (min) for Fifth Test Series, Batch 2, UO_4 Settling

The mixture was then filtered, and the filter cake was scraped into a container for air drying. The filtrate was put into a storage bottle.

Figure 4.46 – Fifth Test Series, Batch 2, UO_4 filter cake (left) and filtrate (right).

Batch 3

Peroxide precipitation technique was the same as Batches 1 and 2, and the data is in Table 4.20.

Table 4.20 – Fifth Test Series, Batch 3, UO_4 Precipitation

Volume Carbonate (mL)	Volume H_2O_2 (mL)	Volume HNO_3 (mL)	pH
100	0	0	8.0
100	0	11	3.0
200	28	26	3.5
221	34	29	4.0

The mixture was stirred overnight then poured into a graduated cylinder for a settling test. Table 4.21 below shows the settling data.

Table 4.21 – Fifth Test Series, Batch 3, UO_4 Settling

Time (min)	Supernate Volume (mL)	Slurry Volume (mL)
0	0	253
10	43	210
20	88	165
30	126	127
40	163	90
50	178	75
60	183	70
80	183	70
100	183	70
120	183	70 (27.7% of total volume)

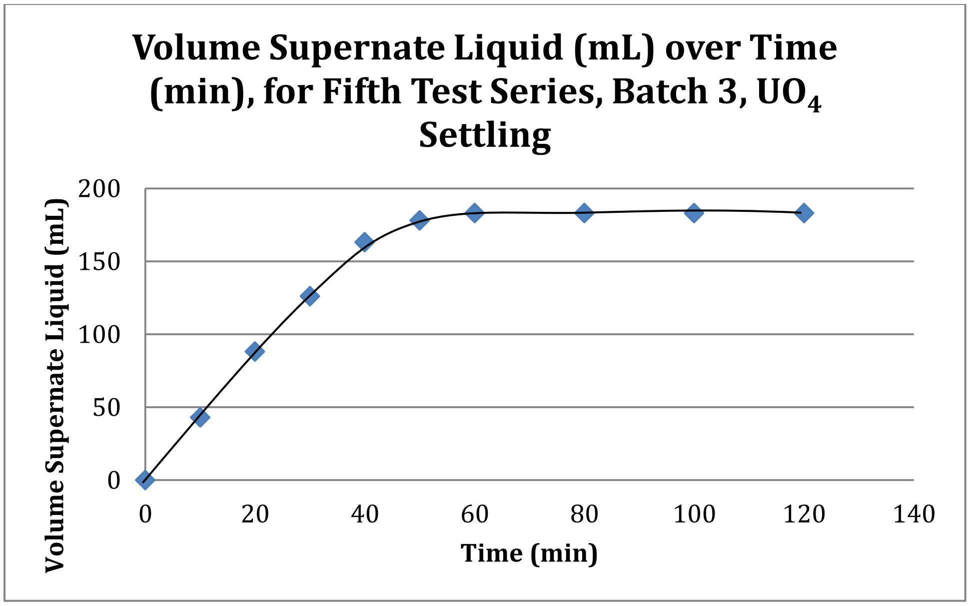

Figure 4.47 – Graph of Volume of Supernate Liquid (mL) over Time (min) for Fifth Test Series, Batch 3, UO_4 Settling

The mixture was then filtered, and the filter cake was scraped into a container for air drying. The filtrate was put into a storage bottle.

Figure 4.48 – Fifth Test Series, Batch 3, UO_4 filter cake (left) and filtrate (right).

Removal of Fluoride Using a Calcite Bed

The sodium fluoride (NaF) solution recovered from the filtration of the Series Five SDU slurry was heated to 70°C and percolated through a 2.54 cm diameter column, partially filled with a 0.04 cm sized granular calcite ($CaCO_3$), in order to test the ability of the calcite to capture the fluoride and remove it from the solution.

Figure 4.49 – Calcite column apparatus.

The reaction involved was the formation of CaF_2 within the calcite crystal structure via the reaction given in Eqn. 3.6 and reiterated below.

$$2NaF + CaCO_3 \rightarrow CaF_2 + Na_2CO_3$$

Literature information indicated it was necessary to lower the pH of the solution from the original pH of 11 to about 6 or less, in order for the reaction to proceed. Early expectations were that a single pass of the solution through the calcite bed would remove nearly all the fluoride. The actual testing, however, showed this was not the case because, as the reaction progressed, the Na_2CO_3 produced quickly raised the pH back up to 11 and stopped the reaction long before all the fluoride was captured. To counter that situation, a technique was developed to collect the solution after each pass and re-acidify it back to below pH 6. A series of nine consecutive passes were performed using this technique, generating the following data:

Table 4.22 – pH Change with Each Pass through Calcite Column

Pass Number	Volume 20% HNO_3 Added (mL)	pH In	pH Out
1	37	5	11
2	18	5	11
3	12	5	10
4	8	4	9
5	2	5	8
6	1.5	4	7
7	1	3	6.75
8	0.4	4	6.5
9	0.2	5	6.5

The data showed that after the seventh pass, the pH was stabilizing, indicating that nearly all the fluoride had reacted. The slight pH movement on pass 8 and 9 were likely a reaction of the acid present with the calcite itself rather than the formation of Na_2CO_3. Confirming fluoride analyses on samples of solution from each pass were not available due to a lack of analytical means for that element. The samples were saved for later analysis, if needed. Figure 4.49 displays a graph of the data.

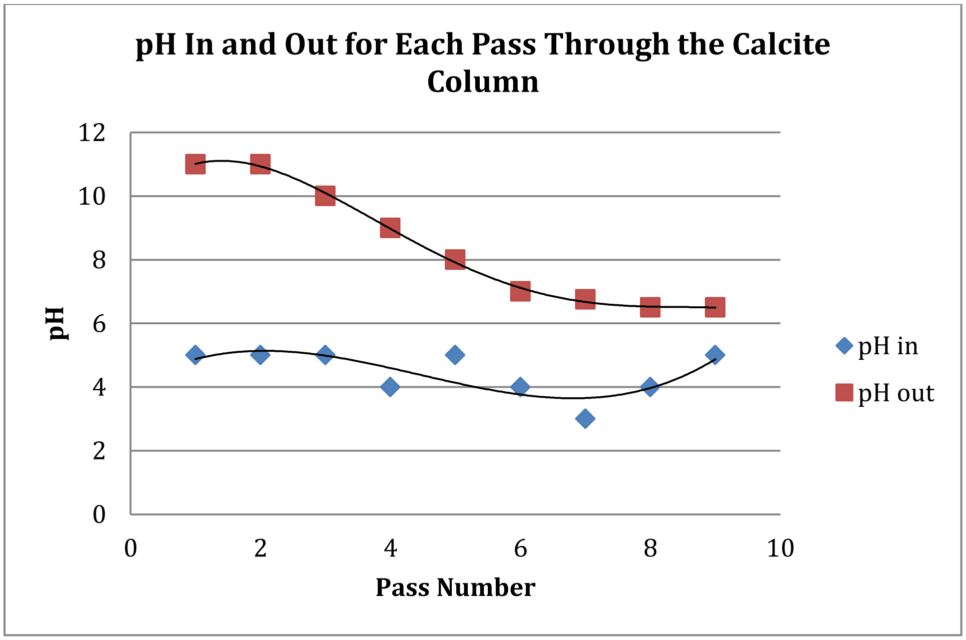

Figure 4.50 – Graph of pH In and pH Out for each pass through the calcite column.

UO_4 and Filtrate Analysis

The $UO_4 \cdot nH_2O$ product collected from each portion of the precipitation test was first air dried at room temperature, then weighed on an analytical balance in order to project a material balance for each series of experiments. Preliminary calculations using the air-dried weights, however, gave uranium recoveries in excess of 100% so an add-on drying procedure was implemented in an attempt to remove as much excess water as possible. Each batch of filter cake was re-dried at 180°C for 1.5 hours then cooled and re-weighed. The results were then compared with the stoichiometric prediction from the precise weight of the starting feed material. The results are shown in Table 4.23 below. Note that the starting material UO_2F_2 actual weight was decreased by the known 3% of FeF_3 that was added to simulate cylinder wash solution.

Table 4.23 – Mass $UO_4 \cdot nH_2O$ from Each Series

Series Number	Net wt. (g)	UO_2F_2 wt. (g)	UO_4 predicted (g)	$UO_4 \cdot nH_2O$ actual (g)
1 (“Aux”)	15.8142	15.3398	15.9375	16.4086
2 (Combined)	50.2060	48.6998	50.5972	50.9737
5 (Confirm)	50.0920	48.5892	50.4823	52.1118

The results showed consistently more recovery than what was predicted from stoichiometric calculations indicating that there was likely still some water trapped in the matrix of the material.

To better evaluate the uranium recovery, samples of $UO_4 \cdot nH2O$ were taken from the second and fifth test series and were dried to remove the water from the UO_4. This was done using a Netzsch TG 409 CD thermobalance. The initial mass was taken for a sample, it was loaded into the machine, and it was dried in an argon environment at 420-450°C, for 2-3 hours. After drying, the mass of each sample was taken to determine the percentage of mass lost, and this data was used to determine the amount of uranium recovered.

First, the mass of UO_2F_2 powder, dosed with 3 wt% FeF_3, was corrected for just the UO_2F_2 mass. This was then multiplied by the mass fraction of U in UO_2F_2, to obtain the initial mass of uranium present in each series. This data is shown in Table 4.24.

Table 4.24 – Mass of Uranium before Recovery Process

Series Number	Mass UO_2F_2 (g)	Mass Fraction U in UO_2F_2	Initial Mass U (g)
1	15.3398	0.772727	11.8535
2	48.6998	0.772727	37.6317
5	48.5892	0.772727	37.5462

Next, a small sample of $UO_4{\cdot}nH_2O$ was taken from each series, and was dried in the thermobalance, which recorded the change in mass over time, while the drying took place. This allowed for a mass reduction percentage to be calculated, as seen in Table 4.25.

Table 4.25 – Drying Data

Series Number	Initial Mass UO_4 (g)	Drying Temp (°C)	Time Dried (minutes)	Mass UO_4 After Drying (g)	% Reduction in Mass
2	1.0364	420	120	0.7941	23.3790
5	1.1681	450	180	0.9029	22.7035

The mass reduction percentage of each sample was extrapolated to the entire mass of $UO_4{\cdot}nH_2O$ for its respective series, in order to calculate the final mass of UO_4 from the series. The mass fraction of U in UO_4 was calculated and the mass of UO_4 was multiplied by this fraction to determine the mass of uranium recovered from the process, for each series. This was then used to determine the percentage of uranium recovered in each series. This data can be seen in Table 4.26

Table 4.26 – Mass of Uranium Recovered

Series Number	Mass $UO_4{\cdot}nH_2O$ (g)	Mass Reduction Fraction During Drying	Mass UO_4 (g)	Mass Fraction U in UO_4	Mass U Recovered (g)	% Uranium Recovered
2	50.9737	0.766210	39.0566	0.788079	30.7797	81.7919
5	52.1118	0.772965	40.2806	0.788079	31.7443	84.5473

A sample of the UO_4 produced by the first test series auxiliary testing was calcined using the same Netzsch TG 409 CD thermobalance, to see if different results were obtained. It was ground with a mortar and pestle to maximize the reaction surface area, and was then loaded into the thermobalance and calcined at 1000°C, for 6 hours, in air, to convert it to U_3O_8. The same mass analysis was performed to determine how much uranium was recovered. This data is shown in Tables 4.24, 4.27, and 4.28.

Table 4.27 – Calcining Data

Series Number	Initial Mass UO_4 (g)	Mass U_3O_8 After Calcining (g)	% Reduction in Mass
1	0.56577	0.40813	27.8629

Table 4.28 – Mass of Uranium Recovered through Calcination

Series Number	Mass $UO_4 \cdot nH_2O$ (g)	Mass Reduction Fraction During Calcination	Total Mass U_3O_8 (g)	Mass Fraction U in U_3O_8	Mass U Recovered (g)	% Uranium Recovered
1	16.4086	0.721371	11.8367	0.847981	10.0373	84.6780

The calcining did not show any significant change in results from the drying. Therefore, this testing suggested that 81-85% of the initial uranium was recovered as uranyl peroxide through the modified process.

Liquid filtrates from both the SDU and UO_4 filtrations were also analyzed to determine how much residual uranium was left behind during precipitation and filtration. These samples were analyzed by Dr. Elizabeth Bair and the Center for Elemental Mass Spectrometry at the University of South Carolina, using a Thermo Scientific Element II high-resolution inductively coupled plasma mass spectrometer (ICP-MS). Data from the ICP-MS analysis shows that a very high uranium recovery was experienced for the SDU and UO_4 precipitations. Table 4.29 shows this data.

Table 4.29 – Residual Uranium Content in SDU and UO_4 Filtrates

Series Number	SDU Filtrate Uranium Content (ppm)	UO_4 Filtrate Uranium Content (ppm)
1 (“Aux”)	19.6	25.0
2 (Combined)	16.2	6.3
5 (Confirm)	3.6	19.6 (avg. of 2 filtrations)

Uranium recovery from both the SDU precipitation step and the uranyl peroxide precipitation step were nearly complete as indicated by the filtrate uranium measurements after the mixtures were filtered. However, the drying and calcination data shows that only about 81-85% of the uranium was carried through the entire process from the wash solution to the UO_4 product. This was a significant amount of loss, that had to be accounted for somewhere in the process other than the precipitation steps.

First, a detailed isotopic analysis of the UO_2F_2 powder, dosed with 3 wt% FeF_3, was never obtained, so the purity of the material could not be determined. This fact likely accounts for the majority of the recovery discrepancy. Also, during experimentation, the uranium precipitates tended to be very sticky and would adhere to gloves, instruments, and the sides of the beakers and graduated cylinders, resulting in mass lost from the system throughout the procedure. The removal of $Fe(OH)_3$ during the process lead to a bit of uranium loss from the system. For example, during the second test series, a small amount of uranium was lost during the attempted partial precipitation of $Fe(OH)_3$, prior to SDU precipitation, and in the fifth series some losses occurred when filtering out the $Fe(OH)_3$ precipitate after carbonate extraction. Error could also appear through the fact that small samples of each UO_4 batch were taken for drying and calcination, which data may not be wholly applicable to the entire batch.

The $UO_4 \cdot nH_2O$ product was also analyzed via ICP Mass Spectrometry for sodium and iron content, and was found to have much less than ASTM limits for both elements, verifying a very high purity for the material. Maximum limits in ASTM C1348 for mixed oxides are 20 ppm Na and 150 ppm Fe. Table 4.30 below shows that data.

Table 4.30 – Sodium and Iron Contaminant Concentrations in UO_4 Product

Series Number	Product Na (ppm)	Product Fe (ppm)
1 (“Aux”)	1.5	0.002
2 (Sample A)	0.4	0.002
2 (Sample B)	0.7	0.004
5 (Sample A)	1.1	0.004
5 (Sample B)	0.7	0.006
5 (Sample C)	0.2	0.007

These impurity results are much less than the ASTM nuclear grade standards of 20 ppm for Na maximum and 150 ppm maximum for Fe and are conclusive evidence of the uranium-selective capability of the peroxide precipitation process.

CHAPTER 5: CONCLUSIONS

During the first, second, and fifth test series, it was observed that precipitation of sodium diuranate (SDU) was very nearly complete at a pH of 11-12, using room temperature conditions. ICP-MS analysis of the NaF solution filtered from the SDU showed that residual uranium levels ranged from 3.6 – 19.6 ppm, meaning almost complete precipitation of the uranium as SDU. It was postulated that a tailing reaction occurs during SDU precipitation, which necessitates a digestion period of about 2 hours to complete the precipitation, this was verified during experimentation. Further, it was shown in the second test series that a partial precipitation step to precipitate $Fe(OH)_3$ at pH 5.5 did not adequately separate iron contamination due to an overlap of uranium and iron precipitations at that condition.

Carbonate extraction of the uranium from the SDU required an extended (3-4 hours) digestion at 40°C and pH 7-8 to complete. Sodium bicarbonate was found to be the preferred extractant because of its lower pH, which helped drop the pH of the reaction solution and allow for continued uranyl carbonate formation. During the second and fifth test series, the carbonate extraction was proven to successfully separate the iron contamination from the uranium, since the iron remained in solid precipitate form after the uranium had been converted into a liquid uranyl carbonate solution.

Potassium-based chemistry did produce a potassium diuranate (KDU) analogue to SDU, but the subsequent carbonate extraction using either potassium bicarbonate or potassium carbonate could not be completed fully. More research will need to be done to find out exactly why this reaction did not work, but the potassium carbonate and bicarbonate simply could not strip the uranium from the KDU and form a uranyl carbonate complex solution. The potassium testing was terminated at this step.

The uranyl peroxide precipitation was found to operate best at pH 3.5 – 4.0, at room temperature, and required an extended digestion period of 8 -10 hours. The reaction was nearly complete at those conditions, and ICP-MS analysis showed a filtrate residual ranging from 2.4 to 36.8 ppmU, with an average of 17.625 ppmU. The uranyl peroxide itself was very pure, with impurity averages at a very low 0.8 ppmNa and 0.004 ppmFe. ASTM maximum levels are 20 ppmNa and 150 ppmFe, so the uranyl peroxide produced met and exceeded those standards, and could be reintroduced to the nuclear fuel cycle if all other standards were met, as they were assumed to be throughout experimentation. Drying and calcination of the $UO_4 \cdot nH_2O$ showed that 81-85% of the uranium present in the simulated wash solution was recovered by the process.

Fluoride removal from the NaF solution that was a product of the SDU precipitation step required multiple passes of the solution through a calcite bed. Each pass required acid addition to adjust the pH back down to below 6 and heating to 70°C before each pass to allow the removal reaction to proceed. This result was a modification of a single pass technique that was initially hypothesized and attempted due to the apparent shutdown of the NaF/calcite reaction at a pH above about 10.

Conclusions drawn from the testing were that the results demonstrated a workable and effective series of processing steps. The process successfully removes the uranium and iron from cylinder wash solution through a co-precipitation of SDU and $Fe(OH)_3$. It then separates out the iron contaminants during uranyl carbonate extraction with sodium bicarbonate. Highly pure, solid uranyl peroxide can be precipitated from the uranyl carbonate complex solution, nearly completely recovering the initial amount of uranium. Techniques developed from the tests will make uranium recovery viable when transferred to a commercial process design.

REFERENCES

1. "Uranium hexafluoride" *Wikipedia: The Free Encyclopedia.* Wikipedia, n.d. Web. Accessed 31 Oct. 2013. <http://en.wikipedia.org/wiki/Uranium_hexafluoride>
2. Figure from "Depleted UF_6 Production and Handling Slide Presentation, Slide 22: UF_6 Phase Diagram." *Depleted UF_6 Management Information Network.* Argonne National Laboratory (for the U.S. DOE Office of Environmental Management). Web. Accessed 31 Oct. 2013. <web.ead.anl.gov/uranium/guide/prodhand/sld022.cfm>
3. "Uranium Hexafluoride (UF6)." *URENCO.* URENCO Limited, n.d. Web. 31 Oct. 2013. <http://www.urenco.com/page/58/Uranium-Hexafluoride-UF6.aspx>
4. Figure from "Depleted UF_6 Production and Handling Slide Presentation, Slide 19: UF_6." *Depleted UF_6 Management Information Network.* Argonne National Laboratory (for the U.S. DOE Office of Environmental Management). Web. Accessed 31 Oct. 2013. <web.ead.anl.gov/uranium/guide/prodhand/sld019.cfm>
5. "Transport." *URENCO.* URENCO Limited, n.d. Web. Accessed 31 Oct. 2013. <http://www.urenco.com/page/21/Transport.aspx>
6. *Packaging of Uranium Hexafluoride for Transport.* ANSI Standard N14.1-2001 Table 1. Accessed 31 Oct. 2013. <http://archive.org/stream/gov.law.ansi.n14.1.2001/ansi.n14.1.2001#page/n13/mode/2up>
7. Figure from "Uranium Hexafluoride (UF6) Monitoring Needs, Slide 1." Presentation by Eccleston, George, and Ed Wonder. Presented at NMMSS Users Group Meeting, Las Vegas, NV, 18 May 2010. <http://nnsa.energy.gov/sites/default/files/nnsa/inlinefiles/Monitoring_UF6_Cylinders.ppt>
8. "Uranium Hexafluoride (UF_6)." *Depleted UF_6 Management Information Network.* Argonne National Laboratory (for the U.S. DOE Office of Environmental Management). Web. Accessed 31 Oct. 2013. <http://web.ead.anl.gov/uranium/guide/uf6/>
9. OECD Nuclear Energy Agency. *Uranium 2011: Resources, Production and Demand.* OECD Nuclear Energy Agency, 2011. Online PDF Copy. < http://www.oecd-nea.org/ndd/pubs/2012/7059-uranium-2011.pdf>
10. Eccleston, George, and Ed Wonder. "Uranium Hexafluoride (UF6) Monitoring Needs, Slide 6: Illustrative Worldwide Cylinder Numbers and Flows." Presented at NMMSS Users Group Meeting, Las Vegas, NV, 18 May 2010. <http://nnsa.energy.gov/sites/default/files/nnsa/inlinefiles/Monitoring_UF6_Cylinders.ppt>
11. *Packaging of Uranium Hexafluoride for Transport.* ANSI Standard N14.1-2001, Section 6.3.2 "Periodic Inspections and Tests." Accessed 31 Oct. 2013.

<http://archive.org/stream/gov.law.ansi.n14.1.2001/ansi.n14.1.2001#page/n15/mode/2up>

12. "Uranium hexafluoride (fissile, fissile excepted and non-fissile)." Title 49 *Code of Federal Regulations*, Pt. 173.420. 2013 ed.
13. *Packaging of Uranium Hexafluoride for Transport.* ANSI Standard N14.1-2001, Section 8.1.2 "Empty Cylinders." Accessed 31 Oct. 2013. <http://archive.org/stream/gov.law.ansi.n14.1.2001/ansi.n14.1.2001#page/n43/mode/2up>
14. Walters, Marten, Thomas Baroody, and Wes Berry. *Technologies for Uranium Recovery from Phosphoric Acid.* Presented at AIChE Central Florida Section 2008 Clearwater Convention. 7 June 2008. < http://www.aiche-cf.org/Clearwater/2008/Paper1/8.1.4.pdf>
15. "Depleted UF_6 Production and Handling Slide Presentation, Slide 6: Conversion of Yellow Cake to UF_6." *Depleted UF_6 Management Information Network*. Argonne National Laboratory (for the U.S. DOE Office of Environmental Management). Web. Accessed 31 Oct. 2013. <web.ead.anl.gov/uranium/guide/prodhand/sld006.cfm>
16. Hardwick, Thomas J. (1982). *U.S. Patent No. 4,428,911*. Washington, DC: U.S. Patent and Trademark Office.
17. Murty, B. Narasimha, et al. "Influence of temperature of precipitation on agglomeration and other powder characteristics of ammonium diuranate." *Powder Technology* 115 (2001): 167-183. Print.
18. Manna, Subhankar, Saswati B. Roy and Jyeshtharaj B. Joshi. "Study of crystallization and morphology of ammonium diuranate and uranium oxide." *Journal of Nuclear Materials* 424 (2012): 94-100. Print.
19. Bonini, A., et al. *Nuclear Fuel Cycle Head-Enriched Uranium Purification and Conversion Into Metal.* Presented at The 1998 International Reduced Enrichment for Test Reactor Conference, Sao Paulo, Brazil. 18-23 October 1998. Web. <http://www.rertr.anl.gov/Fuels98/Bonini.pdf>
20. *Standard Specification for Blended Uranium Oxides with ^{235}U Content of Less Than 5% for Direct Hydrogen Reduction to Nuclear Grade Uranium Dioxide.* ASTM C1348-01 (2008). Table 1.
21. "Overview of Chemicals Available to Treat AMD (Active)." *LEO EnviroSci Inquiry.* Lehigh Environmental Initiative at Lehigh University, n.d. Web. Accessed 8 Nov. 2013. <http://www.ei.lehigh.edu/envirosci/enviroissue/amd/links/chem1.html>
22. Slama, Elshafeea H. Y. Abow, Etemad Ebraheem, and Adam K. Sam. *Precipitation and purification of uranium from rock phosphate.* Sudan Atomic Energy Commission, n.d. Web. Accessed 8 Nov 2013. <http://indico.cern.ch/getFile.py/access?contribId=189&sessionId=3&resId=0&materialId=poster&confId=117934>
23. Schnell, Henry. "The Trekkopje Project, Slide 25: MINI – SDU Precipitation." Presented at the IAEA Technical Meeting on Low Grade Uranium Ore. By Areva. 29-31 March, 2010. Web. Accessed 8 Nov. 2013 <http://www.iaea.org/OurWork/ST/NE/NEFW/documents/RawMaterials/TM_LGUO/4b_Sch.pdf>

24. Ikeda, Atsushi, et al. "Comparative Study of Uranyl(VI) and –(V) Carbonato Complexes in an Aqueous Solution." *Inorganic Chemistry* 46 (2007): 4212-4219. Print.
25. Morais, C. A., et al. "Uranium stripping from tertiary amine by sulfuric acid solution and its precipitation as uranium peroxide." *Minerals Engineering* 18 (2005): 1331-1333. Print.