1958

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Recommended Citation

Cobb, John E.. (1958). *Separation of fission products from irradiated uranium by peroxide precipitation*. University of the Pacific, Thesis. https://scholarlycommons.pacific.edu/uop_etds/1374

SEPARATION OF FISSION PRODUCTS FROM IRRADIATED URANIUM BY PEROXIDE PRECIPITATION

Thesis
Presented to
the Faculty of the Department of Chemistry
College of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by
John E. Cobb
June 1958

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The basic constituent in the propagation of the fission process in nuclear reactors is uranium. More explicitly, uranium enriched in the isotope 235. Reactors may be fueled, however, with any one of the heavy elements having a large fission cross section and a high ratio of fissions per neutron absorption. This limitation leaves only three logical choices, either U_{233}, U_{235} or Pu_{239}. Since Pu_{239} is artificially produced by neutron capture in U_{238} and is yet not a commercial reactor fuel, the chemistry of fuel element purification is restricted, in this paper, to the isotopes of uranium.

Reactor fuel, after a predetermined exposure, must be reprocessed regardless of the fuel type. The circumstances necessitating fuel removal and reprocessing are different for various types of reactors. In solid fuel reactors the fuel itself most likely becomes physically damaged and changes dimensions before reactivity is limited by the actual burnup of fissionable material. Reactors employing homogeneous solutions or molten salt suspensions lose their ability to sustain the chain reaction due to the depletion of the fissionable material. In either of the mentioned reactor types, or in any chain reacting nuclear system, the accumulation of fission products and non fission capture reactions will continually decrease the reactivity of the system until the concentration of parasitic atoms completely poisons the reaction. Characteristically at this time only a small portion of the fissionable atoms have been utilized and the spent fuel still contains a large amount of fissionable material. Therefore, fuel processing must be carried out in such a manner that essentially all of the remaining fissionable species are recovered.

Recovery of the fissionable species is hampered by the intense radiation of the fission products and heavy element buildup. Some 200 separate isotopes have been detected as primary fission particles and beta decay daughter products of the unstable fission particles. These 200 isotopes represent about thirty different elements. Since the chemistry of element separation is not dependent upon the number of isotopic species, the list of thirty elements can be divided into eight groups for separation purposes. The degree of radioactivity in irradiated fuel is dependent upon the length of fuel exposure and the cooling off time allowed before purification is commenced. A one hundred day cooling time allows ample decay of most short lived radioactive species and allows equilibrium formation of heavy elements which are produced by parasitic capture in the fissionable species and fertile material; even then several curies per gram of activity still persists.

There are two primary reasons for fuel purification; these are elimination of poisons and restoration of fuel physical properties. Only a few fission products are severe poisons while others are extremely radioactive. These two main species must be removed while low concentrations of the other fission products are quite tolerable. This requires that a rating as to the objectionability of each isotope must be determined. The time which may be allowed for fuel cooling is limited by the hold up of both fissionable and fertile material. Economic reasons demand that fuel charges continue even when the fuel is not being irradiated. An economic balance is thereby required to determine the most desirable time for processing.

Fuel element purification has been necessary since CP-1 was constructed in the latter part of World War II; however an acceleration of the reactor program and the economic entrance of nuclear power has taxed the technology available for fuel purification. The methods employed to date include ion exchange, fractional distillation of the fluorides, pyrometallurgical techniques, solvent extraction and precipitation. CPP at Arco, Idaho presently purifies 90% of the United States fuel by the solvent extraction method. If nuclear systems are to play an important role in the near future, the fuel cycle cost must be improved. The solvent extraction method is very expensive and invites improvement in cycle costs from any one of the above mentioned methods.

An especially attractive method for uranium purification lies in the perfection of the aqueous peroxide percipitation of uranium from the uranyl nitrate solution as uranium peroxide. Feed preparation is immensely simplified and exceptional separation coefficients have been obtained for most fission products and cladding materials. The end product is essentially identical to the end product of the solvent extraction process and must be reduced to the metal if metallic elements are required. Uranium dioxide is rapidly replacing metal as a fuel. Uranium dioxide may be dissolved directly in nitric acid to produce the feed and uranium peroxide is reduced directly back to uranium dioxide above 600°C making an extremely simple single stage purification cycle. Fuel hold up and cycle time may be materially reduced by such a scheme. Achieving the optimum cycle process should cut equipment and chemical cost and substantially reduce purification cycle cost.

OBJECTIVES

Aqueous precipitation of uranium as the peroxide has been used as a purification procedure since the early days of the Manhattan Project. The procedure has successfully produced an extremely pure product when handled in small batches. Heretofore peroxide precipitation has been utilized for relatively pure fuel from gaseous diffusion plants or in purifying column extraction product from salvage processes. A search of the unclassified literature had rendered no information upon the feasibility of separating fission products and fuel cladding materials by selective precipitation of uranium peroxide.

The primary objective of this research was to produce a uranium oxide which is suitable free from nuclear poisons so that the uranium may immediately be refabricated for use as reactor fuel. The purified product must be decontaminated with respect to the radioactive impurities so that fuel fabrication may proceed with the use of standard fabrication techniques. The product of precipitation, uranium peroxide, should settle at a rate which will allow a continuous processing method to be employed.

A secondary objective was to discover a technique which would improve the existing purification procedures presently in use substituting one precipitation where two or more are presently required. The effect of organic complexing on the settling rate of the precipitate was studied in an effort to improve the technology of single stage purification.

PROCEDURE

Uranium forms a peroxide which is precipitated by the addition of hydrogen peroxide to dilute acid solutions of uranyl nitrate. The resulting precipitate may vary in color from an orange yellow to a light creamy yellow and in texture from a dense crystalline mass which settles rapidly to a suspension which is almost colloidal in its nature. The basic reaction producing the uranium peroxide precipitate is:

$$UO_2(NO_3)_2 + H_2O_2 \longrightarrow UO_4\downarrow + 2HNO_3$$

The characteristics of the uranium peroxide produced from the above reaction are strongly dependent upon the acidity of the solution as is its reversibility. In order to determine the effect of acidity on the reaction, the pH was held constant by the addition of ammonium hydroxide. In the course of several hundred standard runs it was determined that in addition to pH nine other variables affected the characteristics of the precipitate and its purity. They are in order of their effect except for the last.

1. Temperature of solution
2. Uranium concentration
3. Hydrogen peroxide addition rate
4. Mixing rate
5. Impurity level

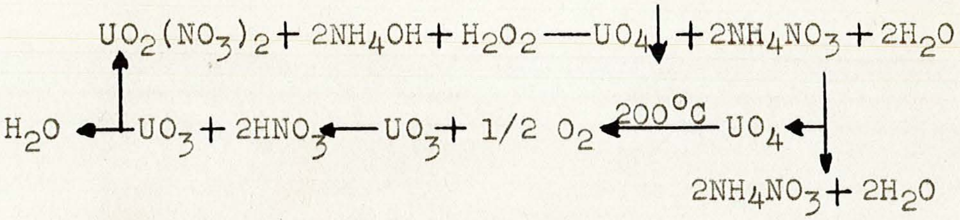
6. Ammonium hydroxide strength

7. Digestion time

8. Hydrogen peroxide strength

9. Reagent addition

Uranyl nitrate feed solutions are prepared by dissolving U_3O_8 and uranium metal in fifteen normal nitric acid. If the solutions are prepared from recycle batches the cycle is:



Uranium peroxide may also be dissolved in hot concentrated nitric acid, however any organic reagents present remain in solution.

The first series of determinations established the effect of pH on uranium peroxide density and purity. Uranyl nitrate solutions containing 250 grams of uranium per liter were prepared in 200 ml portions by dissolving uranyl nitrate hexahydrate in water. The pH was adjusted by addition of 14.8 normal (concentrated) chemically pure ammonium hydroxide. Two fifty ml burets were placed in position above the 400 ml beaker of uranium solution. The beaker was placed on a Magne-Stir magnetic mixer and the entire apparatus was located adjacent to a portable Beckman pH meter. The pH was measured with standard calomel and glass electrodes. See FIGURE 1.

Hydrogen peroxide was added at a constant rate of four ml per minute and the pH was kept constant by addition of concentrated ammonium hydroxide from the adjoining buret. Determinations were performed at pH 3.5, 3.0, 2.5, 2.0 and 1.5. See FIGURE 2. This range was selected due to the formation of ammonium diuranate at and above a pH of 3.5 and colloidal uranium peroxide formation at and below a pH of 2.0. Preliminary chemical analysis indicated very poor purification coefficients for this set of determinations. The best purity level is achieved at a pH of about 2.2.

In an effort to complex iron in the solution, citric and malonic acids were added. An immediate improvement in the precipitate characteristics and purity level was noted. The first set of determinations was reperformed with the addition of one gram of citric and one gram of malonic acid. The results caused an additional determination to be performed at a pH of 1.0. This last run was the only one where a colloidal suspension was noted. The runs at 1.5 were marginal.

Several determinations were performed at a pH of 1.8. The uranium peroxide was allowed to settle and the supernatant liquid removed by vacuum. The precipitate was

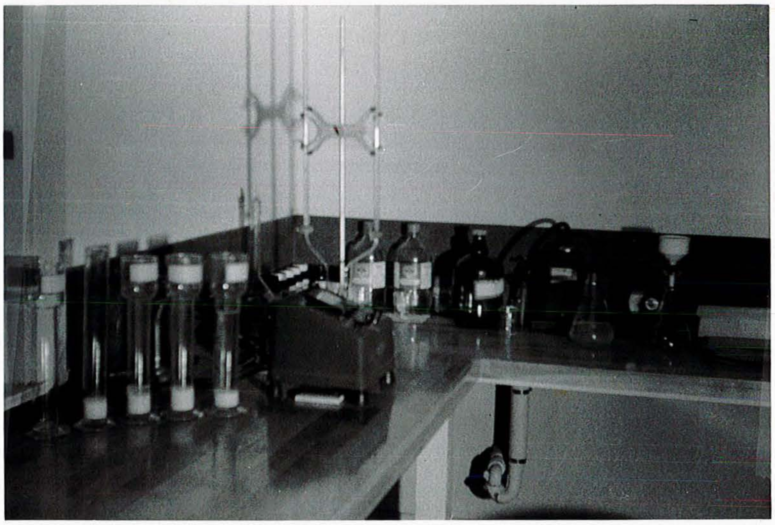


FIGURE 1

ARRANGEMENT OF EQUIPMENT

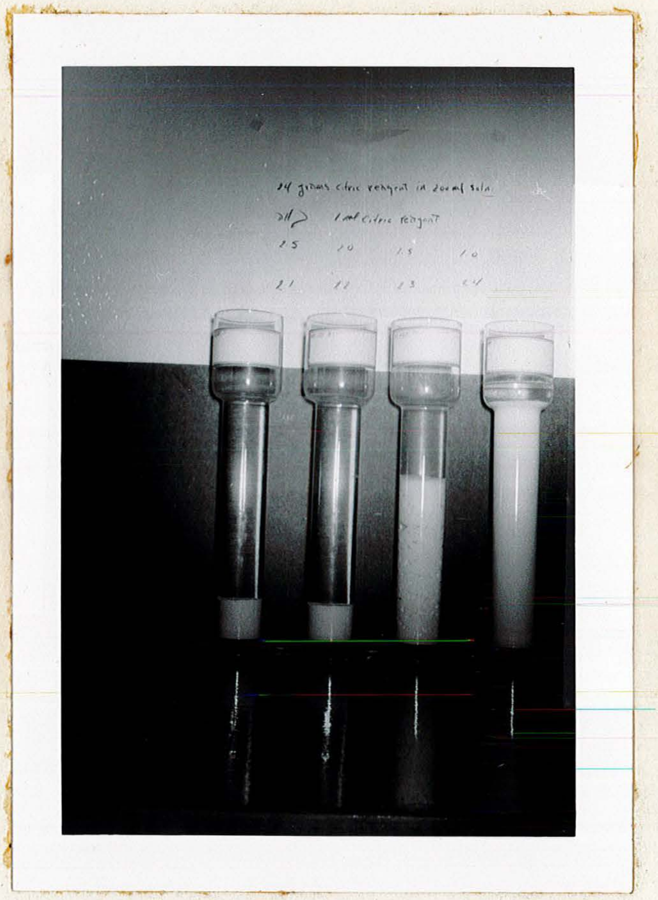


FIGURE 2

EFFECT OF pH ON PRECIPITATE DENSITY

washed two times with distilled water and filtered in a fritted glass filter of fifteen to twenty micron porosity. A fluorometric analysis of the filtrate yields a typical analysis of .01 ppm of uranium. Emission spectrographic analysis of the uranium peroxide cake yielded the following results in parts per million: (typical)

TABLE I

Li	.1	Be	.2	B	.2	Na	5	Mg	3	Al	3	Si	1
K	1	Ca	2	V	1	Cr	4	Mn	.2	Fe	1.5	Co	2
Ni	.5	Cu	.3	Sr	1	Zr	1	Mo	.3	Cd	.2	Sn	1

In most cases this represents a purification factor of 10^3. For Mg, Al and Ca purification coefficients of 10^4 are often obtained.

Variations in citric acid concentration, solution temperature and pH at which the determinations were performed were noted to give large differences in the precipitate appearance and purity. A basic relationship relating precipitate density and purity was derived from observation of results from eight hundred determinations. Precipitations carried out below a pH of 2.5 give a product whose purity is directly related to the uranium peroxide cake density and inversely proportional to the pH of the determination.

Using the above relationship the remainder of the research was devoted to the production of dense precipitates at the lowest possible pH.

Effect of Complexing Agent Concentration. The first analysis in this series was determination of the effect of variation of citric and malonic acids. Fifty grams of uranyl nitrate was dissolved in 300 ml of distilled water. The solution was placed in a 400 ml beaker and heated to 60°C. One gram of malonic acid was added to the solution. The pH was adjusted to 2.0. The stirring rate was set at 6.5 on the Magne-Stir and hydrogen peroxide addition was commenced. The pH was maintained at 2.0 ±.1 by ammonium hydroxide addition. Eleven ml of 35% hydrogen peroxide was added in three minutes and the precipitate was allowed to digest for an additional three minutes. The precipitate and solution was transferred to a 500 ml bell top cylinder and the settling rate observed. This procedure was repeated for solutions containing 200 grams uranium per liter with the addition of .5, 2, 7 and 15 ml of citric acid reagent. The observed settling rates indicated that citric reagent addition at this pH had relatively little effect, however the determination with only malonic acid failed to settle. The blank run likewise failed to settle. Evidently citric acid is required for satisfactory precipitation at this pH but only small amounts are necessary. See FIGURE 3.

A graphical representation of the results relating

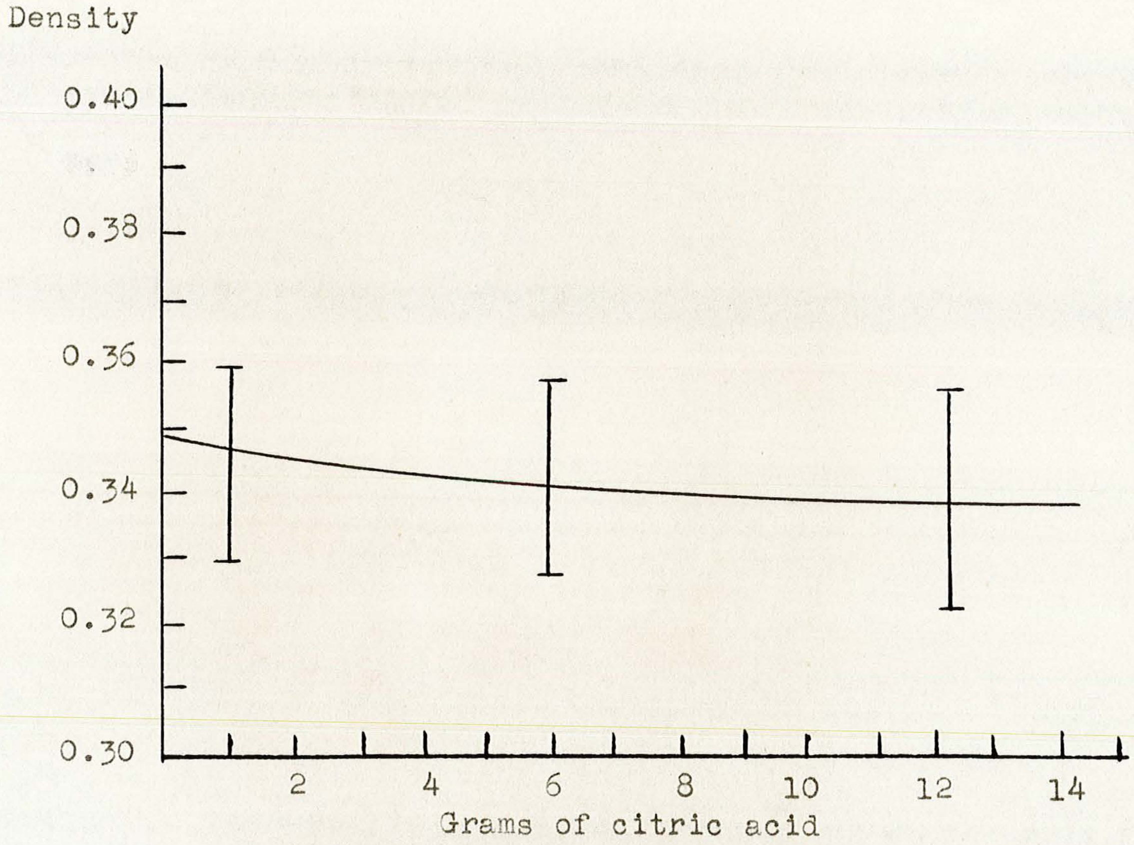


FIGURE 3

CITRIC ACID EFFECT ON PRECIPITATE DENSITY

PRECIPITATION CONDITIONS

1. pH 2.0
2. Temperature 60°C
3. 125 grams uranium per liter
4. Four minutes precipitation time
5. Concentrated reagents
6. Settling time ten minutes

the uranium density in the precipitate to the method of precipitation is given for each set of determinations. The volume of precipitate was measured after ten minutes; this volume is the reference in calculating the uranium density. The density, ρ, is:

$$\rho = \frac{\text{Uranium weight in precipitation}}{\text{Measured volume}}$$

Effect of Temperature. The effect of temperature upon precipitation of uranium peroxide was determined by holding nine of the ten variables constant and altering temperature. The selection of values of the nine variables used was one that had given good results in past precipitations but was near the borderline pH. It was difficult to constantly produce good precipitates below a pH of 2.0. The selected range should magnify effects of temperature variation. The results are shown in FIGURE 4.

Effect of Uranium Concentration. The effect of uranium concentration in solution was determined by holding all factors constant and precipitating the uranium peroxide utilizing information gained in the first two sets of determinations. Again a pH of 2.0 was chosen for the first set of concentration determinations so that the variation effects would be magnified. See FIGURES 5 and 6.

Hydrogen ion concentration has proven to be the

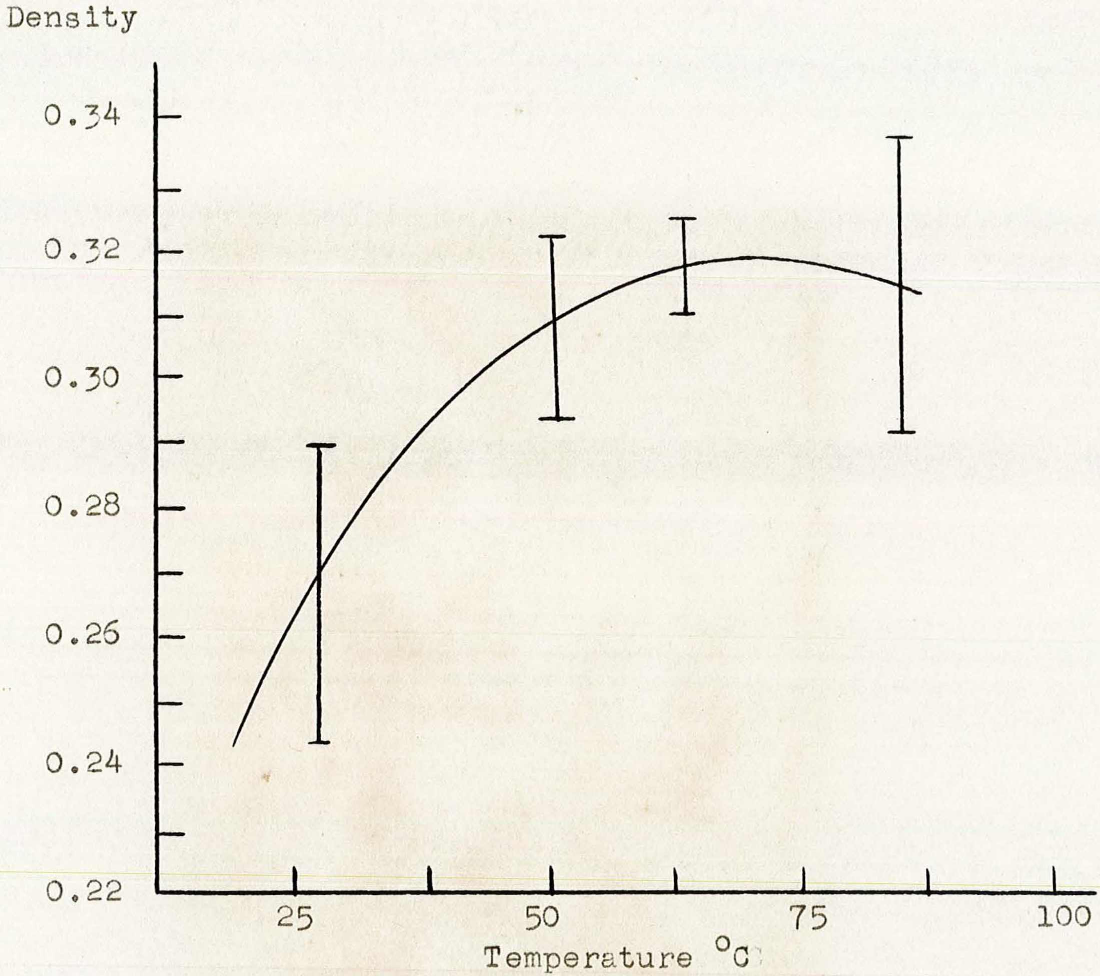


FIGURE 4

TEMPERATURE EFFECT ON PRECIPITATE DENSITY

PRECIPITATION CONDITIONS

1. pH 2.0
2. 165 grams uranium per liter
3. Four minute precipitation time
4. Concentrated reagents
5. .2 grams citric acid added
6. Settling time ten minutes

FIGURE 5

EFFECT OF CONCENTRATION ON SETTLING

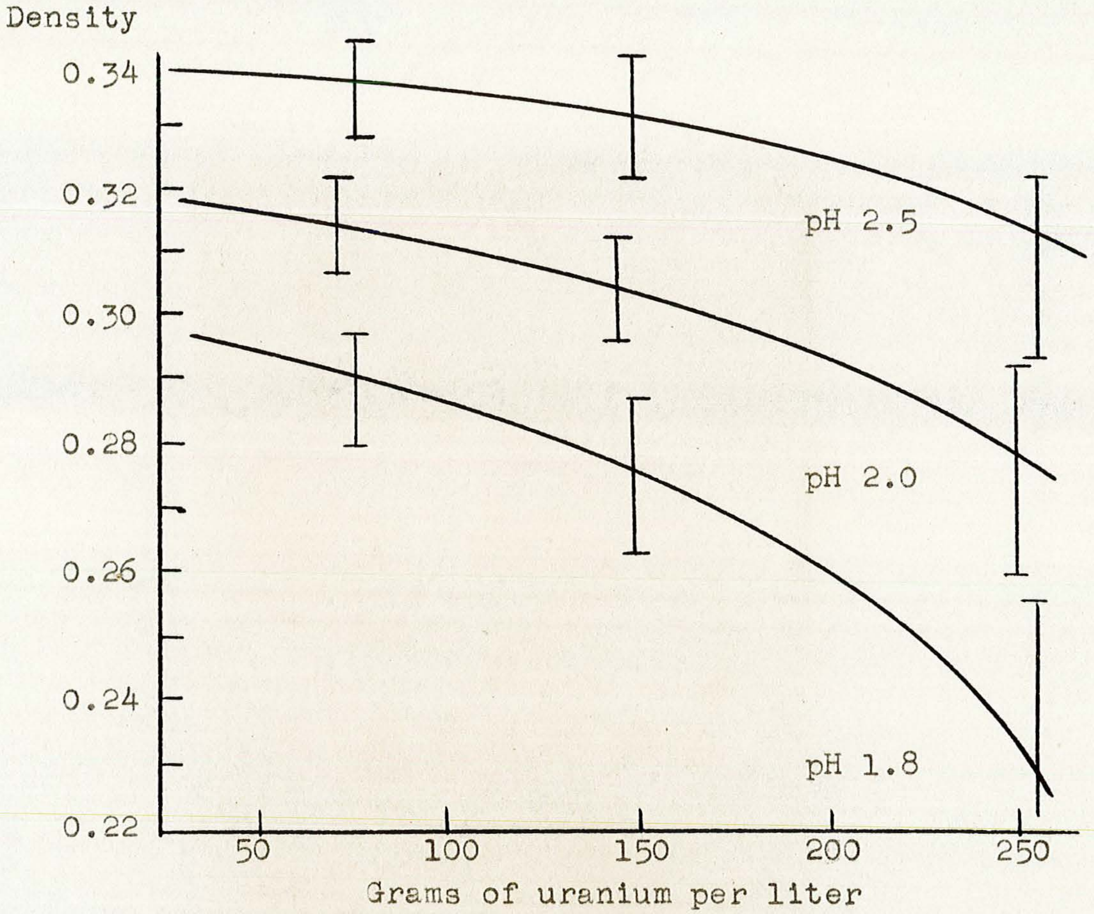


FIGURE 6

CONCENTRATION EFFECT ON PRECIPITATE DENSITY

PRECIPITATION CONDITIONS

1. Temperature 50°C
2. Four minute precipitation time
3. Concentrated reagents
4. One ml citric acid reagent
5. Stirring rate 6.5 (Magne-Stir)
6. Settling time ten minutes

variable most seriously affecting uranium peroxide density and purity. Although the precipitate characteristics are strongly affected by pH, selection of the organic reagent and its concentration may be more important as the solution acidity is increased. More work will be performed on pH effect as the precipitation characteristics develop during the course of the experimental program. See FIGURE 7.

The Effect of Reagent Concentration. The effect of peroxide and ammonium hydroxide concentration on the precipitate density was not distinguishable as long as the addition time is maintained nearly constant. Very slow or very fast addition rates resulted in poorer precipitations. Very fast addition rates resulted in local precipitation of ammonium diuranate which became occluded and was carried down with the hydroxide impurities. Slow stirring rates also result in agglomeration of impurity hydroxides while fast stirring rates result in a shearing action which breaks up the precipitate. The effect of precipitation rate is a major factor only when the rate is very slow or very fast. Temperature and pH affect precipitation rate so strongly that they must be investigated simultaneously. See FIGURE 8.

Effect of H_2O_2 Addition Rate. Addition rates faster than six ml of 35% hydrogen peroxide per minute cannot be controlled manually. Considerable ammonium diuranate is

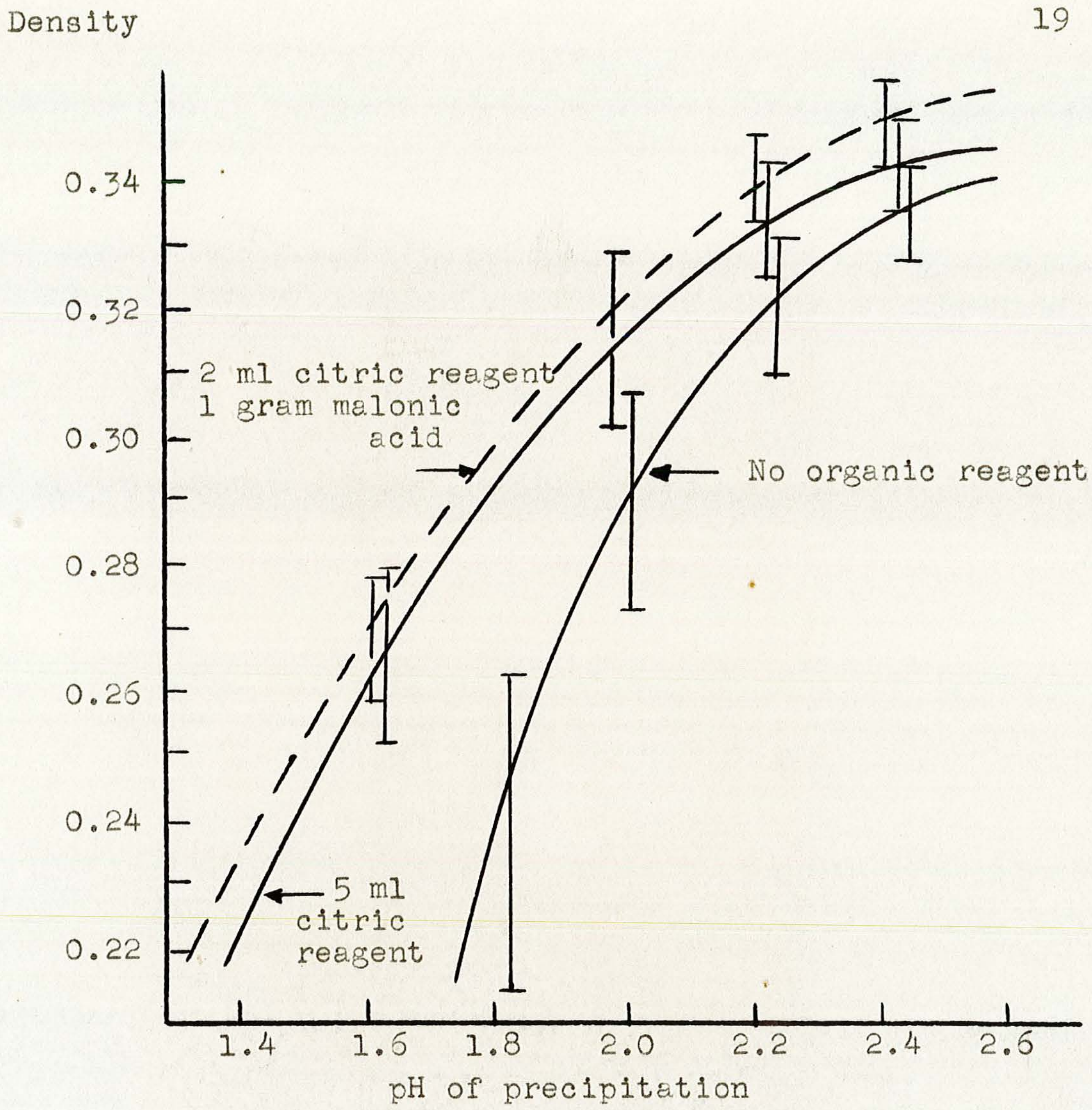


FIGURE 7

pH EFFECT UPON PRECIPITATE DENSITY

PRECIPITATION CONDITIONS

1. Temperature 50°C
2. 125 grams uranium per liter
3. Four minute precipitation time
4. Concentrated reagents
5. Organic reagents as listed
6. Settling time ten minutes

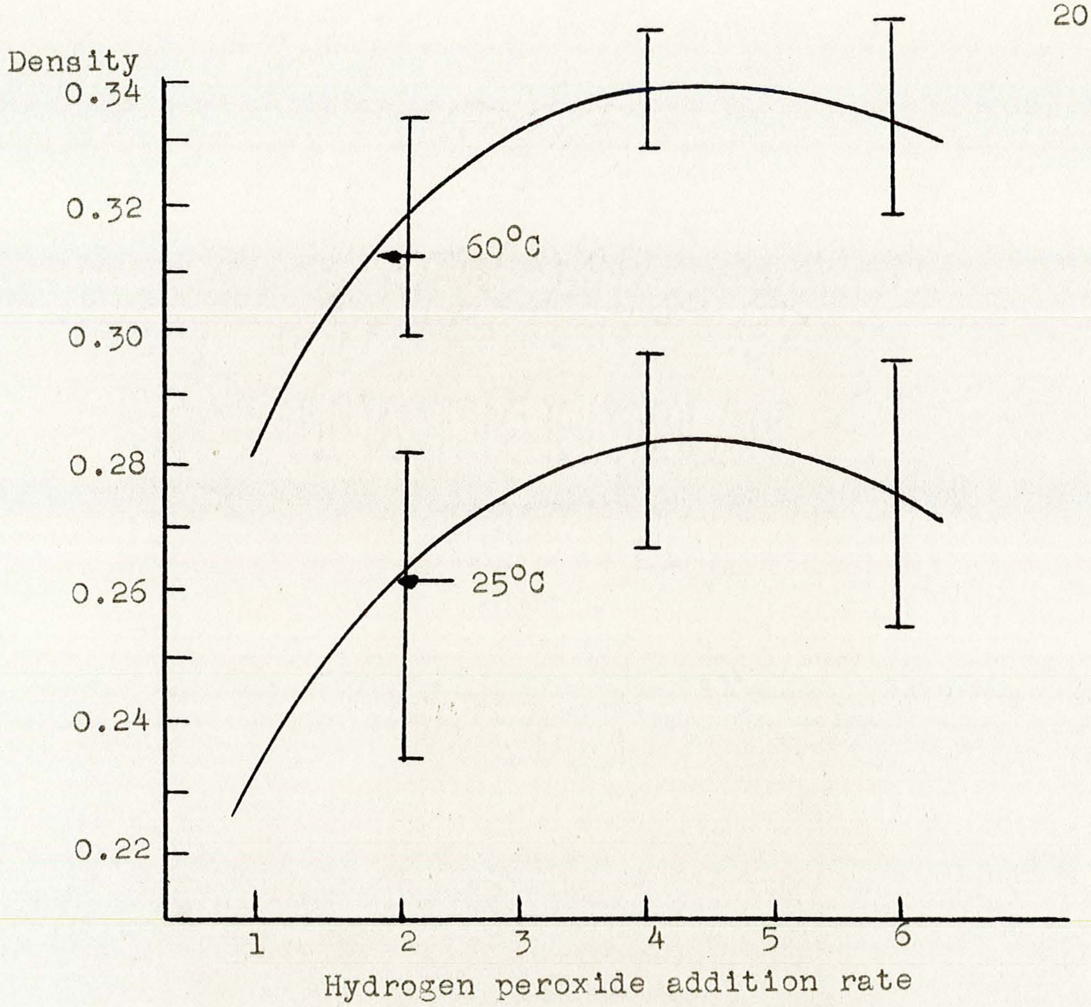


FIGURE 8

PRECIPITATION RATE EFFECT UPON PRECIPITATE DENSITY

PRECIPITATION CONDITIONS

1. pH 2.0
2. Temperature as listed
3. 125 grams uranium per liter
4. Four minute precipitation time
5. Five ml citric acid reagent added
6. Ten minutes settling time

present throughout the precipitate for the six ml per minute rate.

The impurity level affected the precipitation characteristics when those elements which decompose hydrogen peroxide, such as iron, are present in concentrations greater than approximately 40,000 parts per million. Rapid precipitation rates are required for solutions with high impurity levels; this coupled with a minimum digestion time has produced the best precipitates from high impurity solutions.

In an effort to increase precipitate density and settling rate, various surface active agents such as Separan I and II have been employed both during and upon completion of the precipitation to coagulate the colloidal particles. No apparent effect was noted; however malonic acid in addition to citric acid gave an increase in precipitate density while exhibiting no effect when used by itself.

By selecting the best results obtained in the research program, a precipitate density of .37 grams of uranium per cc was obtained by precipitation of uranium peroxide with the addition of citric acid and malonic acid. A survey of parameters producing this precipitate quality is given in TABLE II. Using the .37 grams per cc precipitate density and determination pH of 2.0 as a reference, a survey of other possible uranium complexing agents was commenced. See FIGURE 9 and FIGURE 10.

TABLE II

PRECIPITATION CHARACTERISTICS

pH	2.0±.1
Temperature	60°C
Uranium concentration	125 grams per liter
Hydrogen peroxide addition rate ..	4 ml per minute
Mixing rate	6.5 Magne-Stir
Impurity level (approximate)	1500 ppm total impurities
Ammonium hydroxide strength	Concentrated ammonium hydroxide and distilled water 1:1
Digestion time	1 minute
Hydrogen peroxide strength	17.5%
Reagents used	2 grams citric acid 2 grams malonic acid

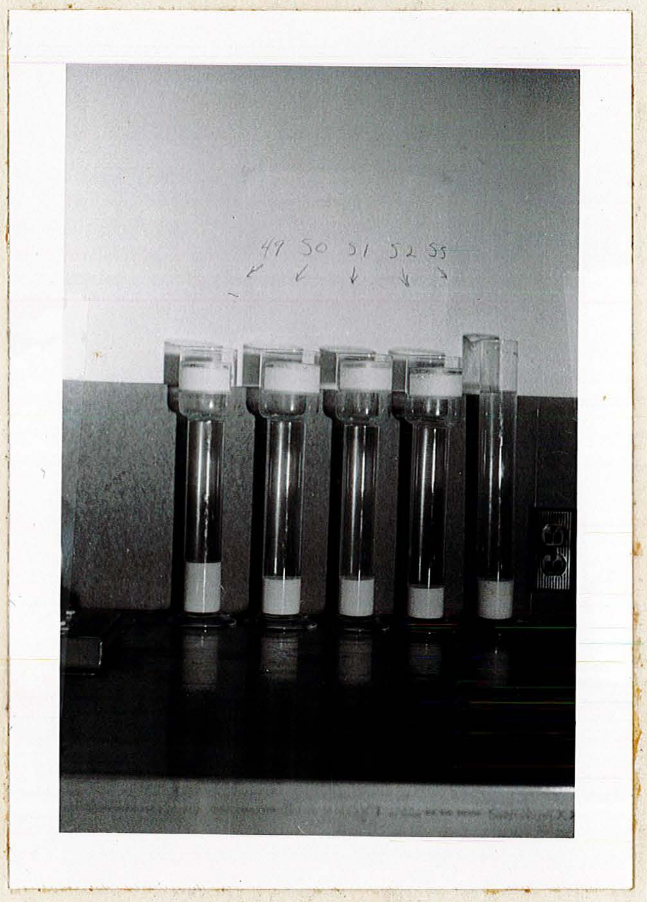


FIGURE 9

EFFECT OF ORGANIC REAGENT VARIATION (1)

FIGURE 10

EFFECT OF ORGANIC REAGENT VARIATION

Use of Other Complexing Agents. The success with polycarboxylic acids dictates the field of greatest interest. Aromatic compounds were eliminated early in the search due to their limited solubility in water and relatively negligible effect as complexing agents. Alcohols, ketones and aldehydes were investigated next. The polysubstituted reagents gave the best results; however some improvement was noticable for additions of each reagent. As expected, polycarboxylic acids gave the best results. Small additions of itaconic acid showed definate improvement in precipitate density and quality. The precipitate density was steady at .39 grams per cc from the solution described in TABLE II.

The additive reagent which achieved the sought after effect was ethylenediaminetetraacetic acid (EDTA). The acid was prepared by addition of concentrated hydrochloric acid to a concentrated solution of the tetrasodium salt of ethylenediaminetetraacetic acid (versene). The acid, slightly soluble in cold water, was washed several times with dilute hydrochloric acid solution to remove residual sodium. Upon addition to the uranium nitrate solution EDTA was first dissolved and then appears to coagulate with the uranium, possibly as a large complex molecule. Stirring tends to break up the mass. Several runs were performed with EDTA addition. The results of the versene program are given in FIGURE 11.

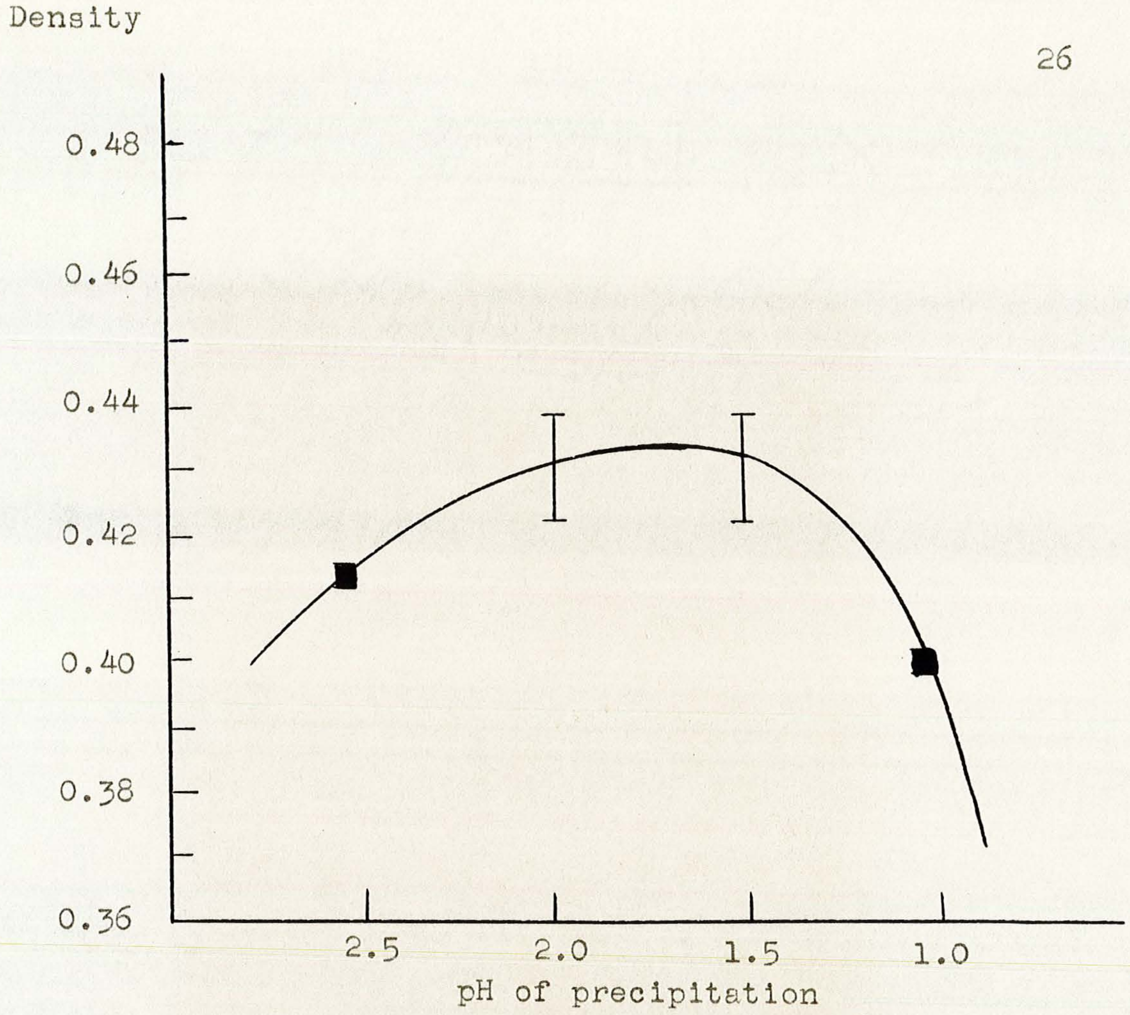


FIGURE 11

EDTA EFFECT ON PRECIPITATE DENSITY

PRECIPITATION CONDITIONS

1. Temperature 50°C
2. 125 grams uranium per liter
3. Four minute precipitation time
4. Concentrated reagents
5. 1 gram EDTA
6. Settling time ten minutes

EDTA became less soluble as the acidity of the uranium solution increased. The utility of EDTA below a pH of 1.5 was questionable although considerable effect was still noticable. An additional dividend was gained in the use of EDTA; the precipitate was so dense that complete settling was accomplished in four minutes rather than the ten minutes accorded to the best precipitations completed with addition of citric acid. See FIGURE 12.

Additional precipitations were performed with combinations of organic reagents giving the best results. The combination of one half gram each of citric, malonic, itaconic acid and EDTA gave a precipitate density of .48 grams per cc with the settling complete in four minutes. The determination variables used for the above precipitation are the same as those used for the precipitation at pH of 1.6 in FIGURE 11. See FIGURE 12 for results of EDTA and multiple reagent precipitations.

Recovery of UO_3. At the termination of the research program, the uranium was recovered from the solutions and precipitates and stored as the trioxide. The method for converting to the trioxide follows: The precipitates were dissolved in boiling concentrated nitric acid. The nitrate solution was evaporated to dryness yielding yellow hexahydrate crystals. The hexahydrate is placed in a furnace and dried at 120°C for four hours. Uranium hexahydrate becomes

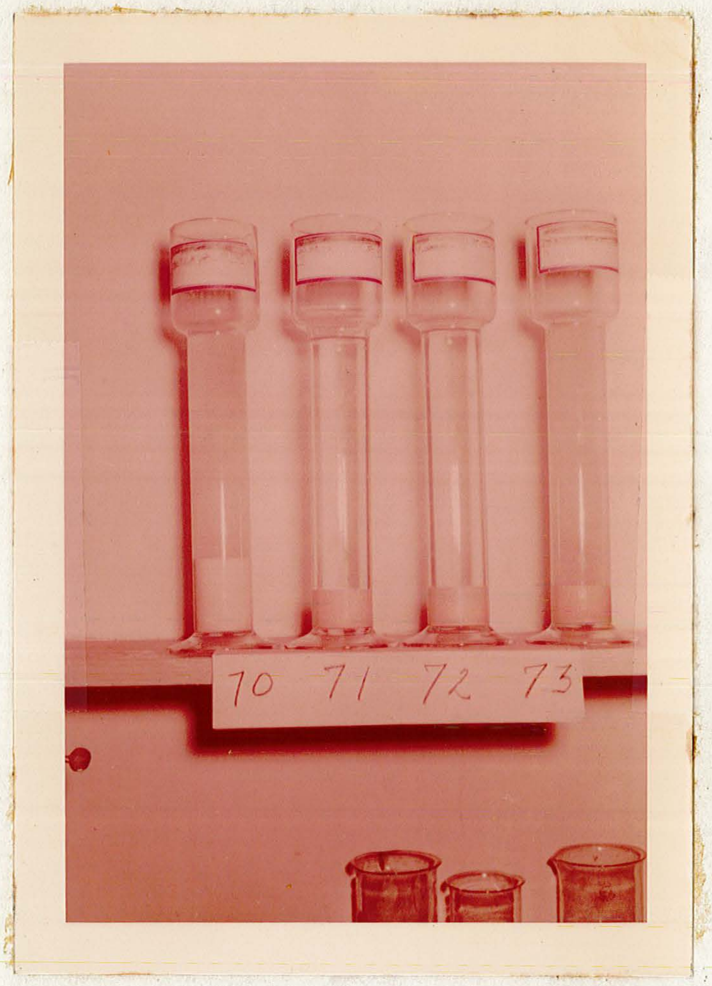


FIGURE 12

EFFECT OF MULTIPLE REAGENT ADDITION

molten above 60°C with some evolution of nitric oxide fumes. After the molten uranyl nitrate solidified, the temperature was raised to 210°C where conversion to uranium trioxide was completed in two hours.

THEORY

Build-up of radioactive impurities occurs from the fission and parasitic capture of neutrons in uranium 235 and uranium 238 by the following scheme:

$$_{92}U^{235} + n \left\langle \begin{array}{l} \xrightarrow[\text{107 barns}]{\text{capture}} {}_{92}U^{236} \xrightarrow[\text{6 barns}]{(n,\gamma)} {}_{92}U^{237} \xrightarrow[\text{6.75 days}]{\beta^-} {}_{93}Np^{237} \\ \xrightarrow[\text{580 barns}]{\text{fission}} \quad F_p\ (200\%) + 2.46\ \text{neutrons} \end{array} \right.$$

$$_{92}U^{238} \xrightarrow[\substack{\text{2.75 barns} \\ \text{and resonance} \\ \text{capture}}]{(n,\gamma)} {}_{92}U^{239} \xrightarrow[\text{23.5 min.}]{\beta^-} {}_{93}Np^{239} \xrightarrow[\text{56 hours}]{\beta^-} {}_{94}Pu^{239}$$

Fuel element processing must be delayed beacuse of induced activity of uranium 237 contributing more than allowable tollerances of gamma radiation. The same statement may be made for the shorter half life neptunium 239. Plutonium 239 is a valuable fissionable isotope with both a military and reactor application which commands a high price when extracted from irradiated fuels. Insufficient cooling off time will allow some loss of this isotope. Plutonium is important in the separation chemistry of uranium due to the chemical similarity and formation of an insoluble peroxide.

The relative production of fission products is given in FIGURE 13. More than 300 separate nuclides occur (Glasstone 1955) from fission of uranium 235. Many have such

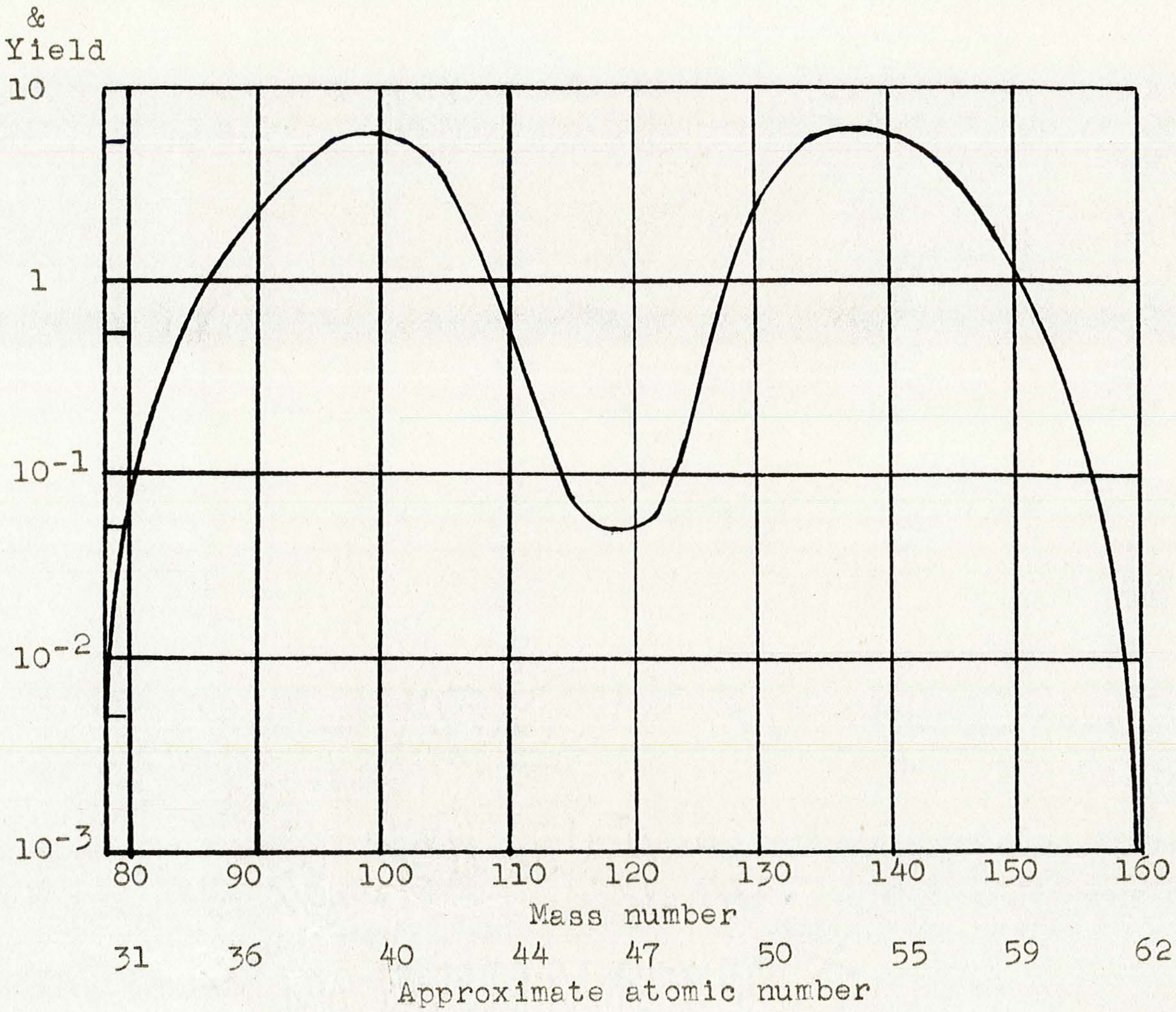


FIGURE 13

ISOTOPE YIELD FROM SLOW NEUTRON FISSION OF U^{235}

Short half lives that these may not be accurately measured. Each nuclide exhibits a different problem to cope with in separation chemistry. Even though neutrons are liberated in fission, the average fission product is overly rich in neutrons and progresses toward a more stable state by successive beta decay. In most instances, the beta decay is accompanied by one or more gamma emissions of various energies. Other isotopes exhibit an ability to parasitically absorb neutrons thereby poisoning the nuclear reaction. The relative objectionability of a particular isotope was determined by weighting the production, radioactivity and neutron absorption cross section and combining into one factor. The objectionability factor, OF, was computed by the following procedure for this research:

$$OF = \frac{\text{grams of isotope}}{\text{fission}} \times \frac{\log_{10}\text{ curies}}{\text{gram}} \times \frac{\log_{10}\text{ barns}}{\text{atom}}$$

An example using Samarium 149 is:

$$OF_{(Sm\ 149)} = .013 \times 1 \times 4.3 = .056$$

Other fission products exhibiting high objectionability factors are given in TABLE III.

The estimated curie level of one gram of mixed fission products is 471 curies. (Benedict, 1957) According to the above reference, a decontamination factor of 5×10^6 is required before the fuel may be reprocessed by ordinary

TABLE III

OBJECTIONABLE FISSION PRODUCTS

Neutron Absorbers

Technetium	99	Samarium	149, 151
Rhodium	103	Europium	155
Xenon	131, 133, 135	Gadolinium	155
Neodymium	143, 145		

Radioactive Isotopes

Krypton	85	Iodine	129, 131
Strontium	89, 90	Xenon	133
Yttrium	90, 91	Cesium	137
Zirconium	95	Barium	140
Niobium	95	Lanthanum	140
Molybdenum	99	Cerium	141, 144
Technetium	99	Praseodymium	143, 144
Ruthenium	103, 106	Neodymium	147
Rhodium	106	Promethium	147
Tellurium	129		

fabrication techniques. Since the twenty two elements listed in TABLE III contribute almost all of the objectionable characteristics, the decontamination program may be tailored to their removal. Of the twenty two elements listed, four are gaseous at some phase of feed preparation leaving eighteen remaining elements, five are lanthanides and exhibit almost identical chemical characteristics leaving thirteen separate elements. These thirteen elements may be divided into five groups and treated independently as such. The peroxide precipitation process is successful in removing these groups in varying rations.

Uranium is removed from fission products by precipitation of uranium peroxide from dilute acid solution of uranyl nitrate. Some fission products form insoluble hydroxides or ammonium complexes in a dilute acid solution. Although the ammonium complexes and hydroxides may be soluble at the pH of the precipitation, they are formed locally when reaction acid is neutralized by ammonium hydroxide and resist dissolution. The heavy uranium peroxide precipitate occludes the impurity thereby seriously imparing the purification coefficient of the occluded group. Various methods may be employed to break up or prevent formation of the local impurity precipitates; these are: increased stirring rate, higher temperature, increased acidity and decrease of precipitation rate. Each of the above, except temperature, hampers the precipitation of uranium. The two most effective methods of dissolving local impurity precipitates are by increasing temperature and decreasing pH.

Uranium has three stable oxidation states. They are compared with other lanthanides and actinides in TABLE IV. (Seaborg, 1954) The most stable oxidation states of the elements listed in TABLE IV are underlined. The expected oxidation state of uranium in an oxidizing solution then is six. The tendency of a given atom, M, toward hydrolysis for various oxidation states, and within the same chemical series, increases according to

$$MO_2^+ < M^{3+} < MO^{2+} < M^{4+}$$

A pertinent example is the precipitation of the hexavalent uranium ion, UO_2, as the diuranate above a pH of 3.6. The acidity at which the precipitation of uranium peroxide is carried out must be considerably less than 3.6 since certain tetravalent lanthanides and actinides hydrolyze below uranium.

The characteristics and purity of uranium peroxide precipitates are closely related to solution acidity. Uranium peroxide, UO_4, carries two molecules of water to form a stable crystal. Loss of the water of hydration results in decomposition of the UO_4 to a compound $UO_{3.5}$. (Seaborg, 1954) Tridot (same reference) suggests that the uranium peroxide should be formulated, $(UO_2)_2UO_8 \cdot 9H_2O$, however due

TABLE IV

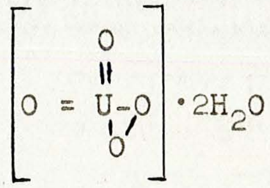
LANTHANIDE OXIDATION STATES

Atomic number	57	58	59	60	61	62	63	64	65	66
Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
Oxidation states						2	2			
	3	3	3	3	3	3	3	3	3	3
		4	4						4	

ACTINIDE OXIDATION STATES

Atomic number	89	90	91	92	93	94	95	96	97	98
Element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
Oxidation states	$\underline{3}$	3	3	3	3	3	3	3	3	3
		$\underline{4}$	4	4	4	$\underline{4}$	4		4	
			$\underline{5}$	5	$\underline{5}$	5	5			
				$\underline{6}$	6	6	6			

to an almost exact mole to mole ratio of hydrogen peroxide to uranium required for precipitation a more plausible formula would be $UO_4 \cdot 2H_2O$ with a structure



where the peroxide linkage is transferred directly upon reaction with the divalent uranyl nitrate complex.

The effect of solution acidity in the role of uranium peroxide purity is well defined; as the acidity is increased hydrolysis of the metal ions in solution decreases. Local centers of ammonium diuranate break up more rapidly and the impurity precipitates are not carried down by the heavy uranium pricipitate. Uranium, as the pH of the solution is decreased below 2.5, forms a finely divided precipitate which resists settling; when the fine precipitate is filtered (with difficulty) the impurities are absorbed on the spongy precipitate surfaces giving poor decontamination. The effect of acidity upon the lanthanide elements is noted; above a pH of 2.0 some cloudiness occurs upon addition of excess hydrogen peroxide. Below a pH of 2.0 this cloudy suspension dissipates returning the clear light yellow solution characteristic of the investigated lanthanides. Upon addition of ammonium hydroxide, a deep brown precipitate occurs and is dissipated only when the pH is returned to a value below 2.0. An increase in temperature speeds up disipation of the hydrolyzed lanthanides.

An increase in solution temperature tended to dissipate local formation of hydroxides, thereby preventing occlusion of impurities in the rapidly settling uranium precipitate. The precipitate, in addition to being of greater purity, tended to increase in density as the temperature of the determination was increased to approximately 60°C and then was retarded for higher temperatures. This effect is explained by the formation rate of uranium peroxide and may be compared with the effect of hydrogen peroxide addition rates. As the reaction rate is retarded, the number of precipitate formation centers increases. When the reaction is complete, the centers of precipitation no longer grow; water of hydration becomes attached and the centers do not congeal. Above 60°C, the hydrogen peroxide tended to decompose causing visual damage to the precipitate. The concentration of uranium in solution and strength of the hydrogen peroxide also effected the precipitate characteristics by a similar mechanism involving crystal formation centers. The uranium peroxide dihydrate has a definite crystal structure when a rapidly settling precipitate occurs but does not when colloid size particles are formed.

The appearance of a deep orange color was noticed at the end of each determination. This color, although is does not persist except locally below a pH of 3.0, is attributed to the formation of an ammonium peruranate complex with a formula $(NH_4)_2UO_4$. The color was dissipated rapidly with mixing but serves as an excellent end point indicator.

The contribution of organic complexing agents in uranium peroxide precipitation and purification is one of utmost importance. In addition to holding impurity ions in solution, the organic complexing agents materially improved the uranium peroxide precipitate density.

The tendency of metal ions to form stable complexes in solution is in general directly proportional to the ionic charge and inversely proportional to the atomic volume. This relationship coupled with the fact that the actinides and lanthanides contract in volume as the charge increases indicates that both groups tend to complex. Ions which exist in solution with greater ionic charges would tend to complex more readily, however they also tend to hydrolyze and generally form ions such as UO_2. These ions also may form stable complexes and in the instance of UO_2, behave as if the charge is between three and four. The tendency to form complexes as the oxidation state of an actinide element decreases is:

$$M^{+4} > MO_2^{+2} > M^{+3} > MO_2^{+}$$

for a given anion.

Examination of the effect of the anion on the complexes formed by a specific cation shows a rough similarity between the stability of the complex and the weakness of the acid formed by the anion. The anions of dibasic acids carry a double negative charge and therefore generally form more stable complexes than do singly charged anions. The anions of weak organic acids therefore generally form stable neutral complexes with the actinides and to a lesser degree the lanthanides.

At low acidities hydrolysis of the actinides increases and the normal equilibrium is shifted to the right. Due to the hydrolysis of highly charged positive ions in solutions of low acidity, precipitation of a basic salt or a complex cation containing one or more hydroxide groups occurs. This precipitate is insoluble in water but frequently remains in solution as a colloidal suspension, particularly at lower concentrations. In the presence of anions which form complexes, the tendency for hydrolysis to occur at a given acidity is decreased.

When the oxidation or reduction process involves a change in the number of hydrogen ions, the potentials are affected by the acidity of the solution. Since uranium is already in its highest oxidation state in a uranyl nitrate solution, the only consideration is keeping other ions in solution. Increased acidity tends to make the oxidation reduction potential more positive. When oxidation occurs the atoms tend to complex and remain in solution rather than form insoluble hydroxides or colloidal solutions.

The uranyl ion complexed in solution resists formation of uranyl peroxide. As the amount of peroxide is increased local centers of crystaline uranium peroxide are formed. Once this formation commences, the crystal grows rapidly as the uranium peroxide dihydrate. The formation of fewer crystal centers allows growth of larger crystals and provides a denser precipitate.

The tetrabasic EDTA forms very stable complexes with uranium allowing formation of large crystal centers. The complex is probably four uranium atoms per EDTA molecule. The formation of a hexadentate is unlikely due to steric hindrance. Excessive addition of organic acids may retard uranium peroxide formation to such a degree that the precipitation center effect is lost as was evidenced during the research program.

Uranium has an orbital electron configuration: $5f^3$, $6d^1$, $7s^2$. In the hexavalent state all of the electrons are utilized. The uranyl ion forms covalent bonds with oxygen giving a probable arrangement:

5f ● ● ● O O O O
6d ● O O O O
7s O

for UO_2. The complexing action for complete utilization of the characteristic six complexing number of uranium is probably:

5f ⦶ ⦶ ⦶ ⊘ ⊘ ⊘ ⊘

6d ⦶ ⊘ ⊘ O O

7s O

where the 5f orbitals are filled first.

CONCLUSIONS AND RECOMMENDATIONS

This research program was successful in determining the precipitation characteristics of uranium peroxide from dilute acid solutions of uranyl nitrate. Since the precipitate density and purity is a function of nine separate variables including reagents, rates and concentrations, an optimum precipitation condition may be determined. These nine variables, however, are a function of a tenth which is the organic complexing agent added to the solution before precipitation.

The precipitate, uranium peroxide, accepts two moleclues of water of hydration. These molecules may not be separated from the uranium peroxide without decomposing the precipitate to a lower oxide state. It is assumed, then, that these hydration molecules are necessary for crystal formation. It was noted that uranium peroxide dominated the precipitate below a pH of 3.5 but did not completely replace the diuranate formation until the precipitation was performed below a pH of 2.5. Local areas of diuranate formation caused hydrolysis of foreign ions which precipitate with the diuranate giving an impure precipitate. These localized areas of diuranate are broken up by increased temperature, stirring rate and acidity. The optimum stirring rate was determined to be 6.5 to 7.0 on the Magne-Stir magnetic stirrer. The determination temperature must be kept below 70°C due to hydrogen peroxide decomposition; the optimum temperature is between 60°C and 70°C. The use of organic complexing agents allowed the precipitation pH to be lowered to 1.8 in the case of citric or itaconic acid and to 1.6 with the addition of EDTA. The precipitate densities at the given pH was increased to 0.35 and 0.45 respectively which is a gain of 50% in the latter case. These are density increases at lower pH levels and produce a superior uranium final product both from a purity and processing standpoint.

Although this program determined the basic characteristics of uranium precipitated from acid solutions as the peroxide, time did not allow extensive analytical work on the final product. Future work should determine the purification coefficient for each of the objectionable fission products and the more common cladding and alloy materials. Work should also be commenced to determine the exact degree for which the oxidation states of uranium and impurity atoms are stabilized by addition of various organic polycarboxylic complexing agents. The mechanism by which precipitation centers are formed and the manner in which the uranium peroxide dihydrate crystal grows will require further research. A greater understanding of these phenomena will undoubtedly allow further purification to be achieved.

SUMMARY

Uranium 235, upon exposure to a flux of thermal neutrons, fissions liberating two to three neutrons and in general two fission particles. The fission particle spectrum lies between atomic numbers thirty four and sixty four. Most are radioactive undergoing first beta and then gamma transformation to achieve a stable state. Eleven of the fission particles are serious neutron absorbers and will poison the nuclear reaction if their concentration is allowed to increase indefinitely. In addition to the above reasons for reprocessing, the fuel also changes its physical characteristics when irradiated for long periods.

Fission products may be removed by selective precipitation of uranium peroxide from a dilute acid uranyl nitrate solution. The precipitation was performed by addition of hydrogen peroxide to the uranyl nitrate solution. The formation of uranium peroxide liberates two molecules of nitric acid; this acid is neutralized by addition of ammonium hydroxide in order to maintain a constant pH. Build-up of acid in the solution during the precipitation results in an impure colloidal suspension of the uranium peroxide.

The purity of the uranium from the precipitation is a function of nine variables inherent to the precipitation. Each of these variables was examined with respect to the others to determine the optimum selection of precipitation variables which will produce the highest quality precipitate.

Certain organic acids effect the quality of the precipitate; a survey of these acids was performed.

The addition of certain polycarboxylic organic acids gave a very improved precipitate even from solutions precipitated at a higher acidity. The addition of EDTA at a solution pH of 1.6 gave a precipitate a factor 1.5 denser than precipitation without any organic complexing reagent and an improvement of 1.3 better than solutions with citric acid added.

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