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PRECIPITATION OF NEPTUNIUM PEROXIDE

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by

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ABSTRACT

Optimum conditions were determined for the precipitation of neptunium(IV) peroxide from nitric acid solutions. The results indicate that the precipitation could be applied successfully on a plant scale.

Data are presented for the solubility of neptunium peroxide in solutions of nitric acid and hydrogen peroxide. The solubility is less than $10^{-4}M$ in 1.5 to 2.5M nitric acid containing 4.5M hydrogen peroxide. Two crystalline modifications of the peroxide were prepared; these two crystalline structures were similar to structures previously reported for plutonium peroxide.

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PRECIPITATION OF NEPTUNIUM PEROXIDE

INTRODUCTION

Neptunium may be isolated from nitric acid solutions by a variety of routes. The precipitation of neptunium(IV) oxalate is an attractive method that has been explored thoroughly and applied successfully on a plant scale⁽¹⁾. In contrast, the precipitation of neptunium(IV) peroxide has not been extensively studied, although the analogous plutonium system has received considerable attention and the method has been applied on a production scale⁽²⁾.

La Chapelle, Magnusson, and Hindman⁽³⁾ reported that a colorless-to-white flocculent precipitate of neptunium(IV) with a solubility of 100 mg of neptunium per liter was formed in 0.8M HNO₃ - 3M H₂O₂ solution. However, when a solution of neptunium(VI) in 0.5M HNO₃ was made 1.5M in H₂O₂, the neptunium(VI) was rapidly reduced to (V), but reduction to (IV) did not take place and no precipitation occurred. Katz and Seaborg⁽⁴⁾ observed that neptunium solutions form an insoluble precipitate upon addition of peroxide, but they assumed that this precipitate was a derivative of the (VI) rather than the (IV) state.

This study was undertaken to elucidate the chemistry of neptunium peroxide formation and to evaluate the precipitation as a plant process. For this application optimum conditions were sought for producing a solid that would filter easily and have a minimum solubility.

SUMMARY

Neptunium(IV) peroxide was precipitated readily from solutions containing Np(IV), (V), or (VI) in 3M nitric acid by the addition of hydrogen peroxide. The higher valence states were rapidly reduced to the (IV) state, which was precipitated by the hydrogen peroxide in the strong acid solutions. The precipitate was gray-purple, and the precipitation did not progress through the highly colored, soluble peroxy complexes that are characteristic in the formation of plutonium peroxide⁽⁵⁾.

Two crystalline forms of neptunium(IV) peroxide were prepared that were quite similar to the two forms of plutonium peroxide found under similar conditions⁽⁶⁾. The crystalline form derived from solutions of low acidity (1M) was face-centered cubic ($a = 17\text{\AA}$), while the structure formed at higher acidity (4M) was nearly identical with the hexagonal form of plutonium peroxide.

The solubility of neptunium peroxide at 23°C varied as a function of the concentration of nitric acid and hydrogen peroxide. A minimum solubility of approximately 10^{-4}M neptunium occurred in solutions containing 1.5 to 2.5M HNO₃ and 4.5M H₂O₂.

Neptunium(IV) peroxide with good filtration characteristics was formed with losses of less than 0.2% of the neptunium to the filtrate when the acid concentration, the mixing efficiency, and the peroxide addition rate were controlled.

The precipitation of neptunium peroxide did not effectively separate neptunium from plutonium, protactinium, zirconium, or niobium.

DISCUSSION

EXPERIMENTAL PROCEDURE

PREPARATION OF REAGENTS

A stock solution of neptunium-237 was prepared by anion exchange. The anionic nitrate complex of neptunium(IV) was absorbed from 8M nitric acid on a column of "Dowex" 1-X4 resin, and the resin was then washed with ten bed volumes of 3M nitric acid. Solutions of neptunium(IV) were obtained by eluting neptunium from the column with 0.35M nitric acid that contained 0.05M hydrazine as an antioxidant. Neptunium(V) was obtained by eluting with 0.35M nitric acid and heating the eluate to 55°C for 30 minutes. The valence state of neptunium in each solution was verified by spectrophotometric examination⁽⁷⁾.

A 30% solution of reagent grade hydrogen peroxide that was stabilized with sodium stannate was used for all experiments except in one precipitation for which a 55% solution was used.

The hydrazine used was a 35% aqueous solution produced by Fetz Laboratories and marketed under the trade name "Hyzeen".

SOLUBILITY STUDIES

Precipitates of neptunium peroxide were prepared by adding aliquots of neptunium(IV) solution to mixtures of nitric acid and hydrogen peroxide. The precipitate was removed by filtration, washed with alcohol, and air dried. The peroxy-oxygen content of the precipitates was determined by iodometric titration.

Each solubility value was determined several times, starting with the solid precipitate or with a solution of Np(IV). Results from the two methods agreed. Equilibrium was reached in less than 20 hours starting with solutions of neptunium, and in less than 6 hours starting with solid precipitates. For the determinations a solution was prepared with the desired concentration of hydrogen peroxide and nitric acid. Enough neptunium stock was added to give the solution the composition desired after precipitation, or enough solid neptunium peroxide was added to ensure an excess during equilibration. The sample was held at 23°C and agitated. Each sample was centrifuged at regular intervals, then an aliquot of the supernate was analyzed for neptunium, hydrogen

peroxide, and nitric acid. The concentration of neptunium was determined by alpha counting. The concentration of H_2O_2 was determined by titrating with standard $KMnO_4$ solution, and the concentration of HNO_3 was determined by titrating with standard NaOH solution.

PRECIPITATION STUDIES

In studying the effect of variables in the precipitation, the anion exchange eluate was adjusted to 35 grams of neptunium per liter and to the desired acid concentration by adding nitric acid. Other reagents were added as required and the temperature was adjusted to the desired value; then an equal volume of 30% hydrogen peroxide was added to the agitated neptunium solution. After addition of hydrogen peroxide, the slurry was digested at a controlled temperature and filtered through a medium porosity fritted glass disc. The temperature and the times were varied for addition of hydrogen peroxide and for digestion.

The filtration characteristics of the precipitates were compared by measuring "filtration factors". The filtration factor was defined as the ratio of the time required to filter a given slurry through a given filter to the time required to pass an equal volume of water through the same filter under the same conditions.

NATURE OF THE PRECIPITATE

Preliminary studies showed that the neptunium(IV) peroxide precipitate was gray-purple, and that the precipitation did not progress through the highly colored, soluble peroxy-complexes that are characteristic of the formation of plutonium peroxide⁽⁵⁾.

Two crystalline forms of neptunium peroxide were prepared that were quite similar to the two forms of plutonium peroxide⁽⁶⁾. The crystals formed in solutions of low acidity, about 1M, were shown by X-ray diffraction to be face-centered cubic with a unit cell dimension $a_0 = 17\text{\AA}$. The crystals formed in solutions of high acidity, about 4M, were nearly identical with the hexagonal form of plutonium peroxide.

The peroxy-oxygen to neptunium ratio was 2.9 for the cubic form, and 3.3 for the hexagonal form. The values reported for the two forms of plutonium peroxide were 3.04 and 3.34, respectively⁽⁶⁾.

SOLUBILITY OF NEPTUNIUM PEROXIDE

The solubility of neptunium peroxide at 23°C varied as a function of the concentrations of nitric acid and hydrogen peroxide. The solubility curve as a function of acid concentration is shown in Figure 1; the curve may be considered to consist of three parts. Between 0.1 and 1.0M nitric acid, the solubilities are difficult to reproduce, but appear to decrease with approximately an inverse first-power dependence on acid concentration. Between 1.0 and 2.5M nitric

acid, the solubility is essentially independent of the acid concentration. At acid concentrations greater than 3M, the solubility increases with an approximate fourth-power dependence on acid concentration.

FIG. 1 SOLUBILITY OF NEPTUNIUM PEROXIDE AS A FUNCTION OF NITRIC ACID CONCENTRATION

Only at acid concentrations greater than 2.5M were the solubilities readily reproducible. In the concentration range of 3 to 5M acid, the following reaction describes the approximate fourth-power acid dependence.

The experimental data for this range of acid concentration are consistent with the expression

$$S = 9.93 \frac{[\text{H}^+]^4}{[\text{H}_2\text{O}_2]^2}$$

where S is neptunium concentration in milligrams per liter, and $[\text{H}^+]$ and $[\text{H}_2\text{O}_2]$ are hydrogen ion and hydrogen peroxide concentrations expressed in molarity. In nitric acid solutions more concentrated than 2.5M, only the hexagonal modification of neptunium peroxide was formed. In fact it was shown that the low-acid, or cubic form, when added to 2.5 to 5M acid was converted to the hexagonal form in less

than 24 hours, the time of equilibration in the solubility determinations. Thus, the solubility measurements in 2.5 to 5M acid were not complicated by the presence of more than one crystalline form. Furthermore, at these higher acidities reduction of Np(VI) and Np(V) to Np(IV) by hydrogen peroxide was quite rapid and complete. For this reason, the solubility measurements were also not complicated by the presence of traces of the higher valence states of neptunium. A comparison of experimental and calculated solubilities at the higher acid strengths is shown in the table.

Solubility of Np Peroxide at 23°C

<u>HNO₃, M</u>	<u>H₂O₂, M</u>	<u>Solubility, mg Np/l</u>	
		<u>Experimental</u>	<u>Calculated</u>
2.57	4.6	30	21
3.09	4.6	46	43
3.62	4.6	72	79
3.84	4.6	108	98
4.68	4.6	218	229
5.00	4.6	282	293
2.5	1.8	113	120
2.5	2.8	54	49
2.5	3.7	32	28
2.5	4.7	21	18
2.5	6.5	11	9

Below 2M acid concentration, the measured solubilities were erratic and difficult to reproduce. It was demonstrated that the hexagonal form of neptunium peroxide, when added to 1M acid, was not completely converted to the cubic form in 24 hours. Thus, there is the possibility that both cubic and hexagonal forms of the peroxide were present at the lower acid concentrations and that the mixed crystal forms may have contributed to the erratic solubility data. Another potential difficulty in achieving reproducible results was the slow reduction of Np(V) to Np(IV) by hydrogen peroxide at low acid strength. The neptunium measured in the solution after equilibration may have contained Np(V) as well as Np(IV). The solubility data shown in Figure 1 in the acid range from 0.1 to 2.5M are minimum values; experimental values were often two to three times greater than the values given.

The solubility of neptunium peroxide decreases with increasing concentrations of hydrogen peroxide. There is approximately an inverse 1.84-power dependence on hydrogen peroxide concentration in 2.5M nitric acid. The data are shown in Figure 2.

FIG. 2 SOLUBILITY OF NEPTUNIUM PEROXIDE AS A FUNCTION OF HYROGEN PEROXIDE CONCENTRATION

STUDIES OF VARIABLES IN THE PRECIPITATION

EFFECT OF ACID CONCENTRATION AND VALENCE STATE OF NEPTUNIUM

In the precipitation, the optimum final acidity for low solubility and good filtration characteristics was 1.5 to 2.5M; this is consistent with the equilibrium solubility measurements described above. Some typical data for precipitations at different acidities are shown in the following table. In the optimum range of acidity, the losses of neptunium to the filtrate were near the equilibrium solubility values.

Effect of Acid Concentration on Solubility and Filtration Characteristics

Feed: 35 mg Np(V)/ml in varying concentrations of HNO₃
 Conditions: An equal volume of 30% H₂O₂ added at a
 controlled rate over 2 hours at 23°C -
 Digestion at 5°C for 30 minutes

Concentration of HNO ₃ in Filtrate	Filtration Factor ^(a)	Concentration of Np in Filtrate, mg/l
0.7	7.0	710
1.2	5.0	93
1.8	6.8	27
2.2	5.7	34
2.8	8.8	40
3.6	5.5	92

(a) A filtration factor less than about 10 is adequate for operation on a production scale.

The solubility of neptunium and the filtration characteristics of the precipitate were not dependent on the valence state of neptunium in the feed solution, as long as the acid concentration was in the optimum range. This may be seen by comparing the results in the above table where the feed contained Np(V), with the results in the following table, where stabilized Np(IV) was present in the feed. In the two experiments at acidities less than 1M, the loss of neptunium to the filtrate was higher when the feed was Np(V) because of incomplete reduction to the (IV) state.

Effect of Np Valence on Solubility

Feed: 35 mg Np(IV)/ml - 0.04M N_2H_4 in varying concentrations of HNO_3 .

Conditions: Same as in previous table

<u>Concentration of HNO_3 in Filtrate</u>	<u>Filtration Factor</u>	<u>Concentration of Np in Filtrate, mg/l</u>
0.8	9.5	101
1.2	6.3	77
2.25	8.5	42
3.4	5.7	71

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION

The solubility of neptunium peroxide in 2.2M nitric acid was decreased approximately 30% by increasing the concentration of hydrogen peroxide from 4.6 to 6.9M. The two concentrations of hydrogen peroxide were attained by adding 30% hydrogen peroxide for the lower concentration and 50% hydrogen peroxide for the higher concentration.

Effect of Hydrogen Peroxide Concentration on Solubility and Filtration Characteristics

Feed: 35 mg Np(IV)/ml in HNO_3

Conditions: An equal volume of H_2O_2 added at a controlled rate over 2 hours at 23°C -
Digestion at 5°C for 30 minutes

<u>Composition of Filtrate</u>	<u>Filtration Factor</u>	<u>Concentration of Np in Filtrate, mg/l</u>
4.6M H_2O_2 - 2.2M HNO_3	5.6	39
6.9M H_2O_2 - 2.2M HNO_3	7.3	26

EFFECT OF SULFATE

The addition of 0.05M sulfate to the neptunium nitrate feed solution improved the filtration characteristics of the precipitate and decreased the time required for filtration by approximately 40%. This same effect has been observed in the precipitation of plutonium peroxide. Addition of sulfate did not appreciably effect the solubility of neptunium.

Effect of Sulfate on Solubility and Filtration Characteristics

Feed: 35 mg Np(V)/ml in HNO_3
Conditions: An equal volume of 30% H_2O_2 added at a controlled rate over 2 hours at 23°C

<u>Feed Composition</u>	<u>Digestion Conditions</u>	<u>Filtration Factor</u>	<u>Concentration of Np in Filtrate, mg/l</u>
3M HNO_3 - 0.05M SO_4	30 min at 23°C	3.6	38
3M HNO_3 - No SO_4	30 min at 23°C	5.7	44
3M HNO_3 - 0.05M SO_4	30 min at 5°C	3.8	25
3M HNO_3 - No SO_4	30 min at 5°C	6.8	32
4M HNO_3 - 0.05M SO_4	30 min at 5°C	4.0	41
4M HNO_3 - No SO_4	30 min at 5°C	5.7	34

EFFECT OF IRON

Since the reduction of neptunium(V) to (IV) with ferrous sulfamate is rapid and quantitative in 3 to 4M nitric acid, an attempt was made to decrease the solubility of neptunium peroxide by adding this reductant. The filtrate losses were in actuality higher in the precipitations in which ferrous sulfamate was added. This is possibly explained by the catalytic oxidation of Np(IV) to the more soluble Np(V) by iron(III), which is produced by the oxidation of iron(II) by hydrogen peroxide. Some typical data are given in the following table.

Effect of Iron on Solubility and Filtration Characteristics

Feed: 35 mg Np/ml in HNO_3
Conditions: Equal volume of 30% H_2O_2

<u>Feed Composition</u>	<u>Precipitation Conditions</u>	<u>Filtration Factor</u>	<u>Concentration of Np in Filtrate, mg/l</u>
Np(IV) in 3M HNO_3 - 0.05M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$	H_2O_2 addition: 30 min at 17°C	6.1	47
Np(IV) in 3M HNO_3 - No $\text{Fe}(\text{NH}_2\text{SO}_3)_2$	Digestion: 30 min at 17°C - Cooled to 5°C for filtration	5.7	28
Np(V) in 4M HNO_3 - 0.2M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$	H_2O_2 addition: 2 hours at 23°C	6.5	71
Np(V) in 4M HNO_3 - No $\text{Fe}(\text{NH}_2\text{SO}_3)_2$	Digestion: 30 min at 5°C	5.7	34

EFFECT OF TEMPERATURE

The solubility of neptunium peroxide was decreased approximately 25% by digesting and filtering at 5°C rather than at 23°C. The filtration characteristics of the precipitate were not significantly affected by varying the temperature of digestion of the slurry.

Effect of Temperature on Solubility and Filtration Characteristics

Feed: 35 mg Np(V)/ml

Conditions: An equal volume of 30% H₂O₂
added over 2 hours at 23°C

<u>Feed Composition</u>	<u>Digestion Conditions</u>	<u>Filtration Factor</u>	<u>Concentration of Np in Filtrate, mg/l</u>
3M HNO ₃	30 min at 23°C	5.7	44
3M HNO ₃	30 min at 5°C	6.8	32
4M HNO ₃	30 min at 23°C	6.7	43
4M HNO ₃	30 min at 5°C	5.7	34

PURIFICATION OF NEPTUNIUM BY PEROXIDE PRECIPITATION

The purification of neptunium that is attainable by peroxide precipitation was not studied extensively. It is expected that the separation from a number of cationic impurities, such as iron, would be excellent, as it is in the case of plutonium peroxide precipitation. The separation of neptunium from plutonium, zirconium, niobium, and protactinium was measured and found to be poor. Plutonium was carried completely with the precipitate. Pa²³³, the daughter product of Np²³⁷ alpha decay, was carried to the extent of about 90% when present in equilibrium quantities. About 30% of the Zr⁹⁵-Nb⁹⁵ present in tracer quantities was carried by the peroxide precipitate.

CONCLUSIONS

Precipitation of neptunium(IV) peroxide is an adequate method for plant use. Hydrogen peroxide conveniently reduces neptunium to the proper valence state for precipitation. When the acidity, the rate of peroxide addition, and the degree of mixing are carefully controlled, the properties of neptunium peroxide are quite similar to those of plutonium peroxide. The loss of neptunium to the filtrate approximates 10^{-4} molar.

RECOMMENDED PROCEDURE FOR PRECIPITATION OF NEPTUNIUM PEROXIDE

The following procedure is recommended for the precipitation of neptunium peroxide:

Feed Preparation: Adjust the acid concentration to 3 to 4M
No valence adjustment is necessary.

Precipitation: Maintain adequate mixing. Add an equal volume of 30% hydrogen peroxide at a controlled rate over a period of 90 minutes. Maintain the temperature of the slurry at 18-25°C.

Digestion: Cool the slurry to 8°C and hold at this temperature for 30 minutes.

Filtration: Filter as rapidly as possible through a frit with a mean pore size of approximately 8 to 10 microns.

Wash: Wash the precipitate as required for subsequent processing with a mixed nitric acid - hydrogen peroxide solution.

Drying: Dry as required for subsequent processing.

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