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PROPERTIES OF POTENTIAL URANIUM PRECIPITATES
AS RELATED TO CHEMICAL PROCESSING

by

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INTRODUCTION

Physical properties of potential uranium precipitates must be known to calculate nuclear safety parameters for the chemical processing of nuclear fuels. Density and uranium content of the settled precipitate are of principle concern.

For the purpose of these studies, the term "precipitate" will be taken to include the associated water and extraneous ions as well as the actual precipitated compound. Precipitate density is defined as the weight of the precipitate divided by the volume occupied by the precipitate at 25° C. Uranium density is given as the weight of uranium per liter of precipitate at 25° C.

The volume of the precipitate at a given time is dependent upon settling characteristics. Since settling characteristics may differ between the plant and the laboratory, centrifugation has been used as a means of gaining a maximum precipitate density. It is felt that such a maximum is valid for the short term. Long term validity is questionable due to the unknown effect of radiation and long term settling. It is also assumed that supernatant liquid is always present, thus drying effects are not considered.

Both clinical and process equivalent centrifuges have been utilized. Any difference in the densities produced was less than experimental error and not discernible.

EXPERIMENTALI. Precipitation by Sodium Hydroxide(a) Sodium Polyuranate

The addition of NaOH to uranyl nitrate solution is the most likely means of uranium precipitate formation in current processing. Two insoluble polyuranates appear to be formed: $\text{Na}_2\text{U}_{16}\text{O}_{49}$ (yellow) and $\text{Na}_2\text{U}_2\text{O}_7$ (orange)⁽¹⁾. Other species are also formed as conditions vary.

A wide range of precipitate densities occur according to precipitating conditions. Table I illustrates this variance.

The maximum density of a polyuranate precipitate with associated liquid which has been achieved in the laboratory is 2.00 g/ml with the uranium density being 905 g/l.

(b) Behavior of Plutonium When Sodium Polyuranate is Precipitated

The major constituent of dissolver solution is uranyl nitrate with plutonium and fission products being present at much lower concentrations. When sodium hydroxide is added to dissolver solution, the behavior of plutonium is dependent upon the plutonium valence state.

The plutonium to uranium ratio will be higher in the precipitate than in the original solution if plutonium is in the IV valence state.

Laboratory experiments, where only a portion of the uranium is precipitated, indicate an immediate 80% plutonium enrichment in the precipitate. A prolonged digestion period considerably increases

TABLE I

	<u>Solutions</u>	<u>Initial Temp. C</u>	<u>Agitation</u>	<u>Separation</u>	<u>Density g/ml</u>	<u>U g/l</u>
1.	25 ml 2.0 <u>M</u> UNH 2.25 ml 19 <u>M</u> NaOH	25°	Stirred Constantly	Centrifuged (clinical cent.)	1.90	871
2.	same as 1.	25°	Stirred Constantly	Centrifuged (clinical cent.)	1.85	819
3.	same as 1.	25°	Stirred Slightly	Centrifuged (clinical cent.)	2.00	905
4.	same as 1.	72°	Stirred Slightly	Centrifuged 1400 gravities	1.96	835
5.	same as 1.	72°	Stirred Slightly	Centrifuged 1400 gravities	1.97	864
6.	same as 1.	100°	Stirred Slightly	Centrifuged 1400 gravities	1.80	788
7.	same as 1.	25°	Stirred Constantly	Settled by gravity-24 hrs.	1.67	538
8.	25 ml 0.25 <u>M</u> UNH 1.0 ml 19 <u>M</u> NaOH	25°	Stirred Constantly	Centrifuged (clinical cent.)	1.42	292
9.	same as 8.	25°	Stirred Constantly	Settled by gravity-24 hrs.	1.06	96
10.	same as 8.	25°	Stirred Slightly	Centrifuged (clinical cent.)	1.16	175
11.	25 ml 0.25 <u>M</u> UNH 2.5 ml 19 <u>M</u> NaOH	25°	Stirred Constantly	Centrifuged (clinical cent.)	1.37	263

this figure. Plutonium polymer formation is most likely the principle contributor to the observed enrichment. The above experiments were performed with a beginning dissolver solution temperature of 45° C. Variance in temperature could change the above figure considerably.

The opposite condition exists when plutonium is in the VI valence state. The Pu/U ratio in the precipitate is a factor of two less in the precipitate than in the original solution.

Analyses of dissolver solutions indicate that plutonium is normally present as 75-90% Pu(IV).

(c) Precipitation by Caustic Coating Waste

Another means of precipitating sodium polyuranate is by combining uranyl nitrate solution with coating waste (formed by dissolving aluminum jackets with NaOH-NaNO₃ solution).

The following compositions were used:

<u>Coating Waste</u>		<u>Uranyl Nitrate Solution</u>	
NaAlO ₂	2.38 M	UO ₂ (NO ₃) ₂	1.7 M
NaNO ₂	1.70 M	Al(NO ₃) ₃	0.2 M
NaNO ₃	0.15 M	NH ₄ F	0.06 M
NaOH	1.36 M	HNO ₃	0.58 M

One volume of coating waste will completely precipitate the uranium from 0.95 volume of the uranyl nitrate solution. The average density of the precipitate, composed of sodium polyuranate, aluminum oxide, and associated liquid with extraneous ions was 1.494 g/ml with a uranium density of 224 g/l. Since the uranium

precipitate is heavier than the aluminum precipitate, the precipitate layer is not homogeneous. Therefore, measurements were taken of approximately the bottom half of the centrifuged precipitate which yielded a density of 1.587 g/ml with a uranium density of 327 g/l.

The mechanism of reaction as uranyl nitrate solution is added to coating waste appears to be as follows: aluminum oxide forms as well as sodium polyuranate; the formation of aluminum oxide releases NaOH which is then available for additional uranium precipitation.

II. Precipitation with Sulfuric Acid

Uranyl sulfate is precipitated from aqueous solutions as the trihydrate⁽¹⁾. Moderate solubility should lessen the concern for criticality potential. Solubilities in grams per 100 cc are⁽²⁾: water, 20.5 at 15.5° C and 22.2 at 100° C; concentrated sulfuric acid, 24.3 at 13° C.

Uranyl sulfate precipitated in the laboratory by adding H₂SO₄ to uranyl nitrate solution has yielded densities up to 2.494 g/ml with a uranium density of 970 g/l. Studies have not been as comprehensive as with the polyuranate precipitates.

III. Precipitation with Oxalic Acid

The density and uranium content of various uranyl oxalate precipitates covered a wide range and varied according to the laboratory technique used to isolate the precipitate from the supernatant liquid. For practical purposes, three categories will be considered in reporting

this particular data. Definition of categories and data are as follows:

1. Precipitate properties which would be most probable on the bottom of a process vessel or centrifuge (run less than twenty minutes).

Density	1.74 g/ml
Uranium Density	637 g/l

2. The maximum density and uranium content of a wet uranyl oxalate precipitate which could occur in the Purex plant as a result of process errors.

Density	1.91 g/ml
Uranium Density	838 g/l

3. The highest values which have been obtained in the laboratory for a purified, dry uranyl oxalate precipitate. (Specific tailoring of a process would be necessary to obtain these values.)

Density	1.98 g/ml
Uranium Density	1224 g/l

Values given in category 2 were derived from numerous laboratory experiments, taking into account maximum variables in measurements and analytical results, in order that the values may be used as working figures for criticality analysis.

IV. Precipitation of Uranyl Ion by Sodium Carbonate

Scouting runs indicated that the densities of carbonate precipitates were too low to warrant comprehensive experiments. The maximum density obtained by precipitating at 25° C was 1.141 g/ml. Maximum

density by precipitating at 72° C was 1.175 g/ml with a uranium density of approximately 160 g/l.

V. Uranyl Dibutylphosphate

Uranyl dibutylphosphate as precipitated in the laboratory without any effort to purify the substance, yielded a density of 1.551 g/ml. The uranium density was 541 g/l.

VI. Uranium(IV) Precipitation by Fluoride

The hydration of uranium(IV) fluoride precipitates is dependent upon the temperature of precipitation. Table II illustrates the variation.

TABLE II

<u>Precipitation Temperature</u>	<u>Precipitate Density</u>	<u>Uranium Density</u>
25° C	1.30 g/ml	885 g/l
72° C	1.92 g/ml	
100° C	1.72 g/ml	

Additional work concerning UF_4 precipitates has been performed by T. R. McKenzie⁽³⁾. All data reported by McKenzie is less than the maximum 1.92 density reported above.

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