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PREPARATION OF CLEAR URANYL NITRATE SOLUTION BY FRACTIONAL DISSOLUTION OF SODIUM DIURANATE

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ABSTRACT

This paper describes a procedure for preparation of clear uranyl nitrate solutions by fractional dissolution of crude sodium diuranate (SDU). The raw SDU used is obtained by industrial processing of monazite sand and contains some thorium, rare earth elements, iron, silicon and phosphorus as main impurities.

With the procedure here described, clear and stable uranyl nitrate solutions having 270 to 300 g/l U and exhibiting good filtration characteristics are obtained. The procedure allows a satisfactory removal of thorium, rare earth elements, phosphorus, silicon and iron.

INTRODUCTION

The purpose of the fractional dissolution of sodium diuranate (SDU), from which approximately 95% of the total uranium were solubilized, is to obtain clear and sufficiently concentrated solutions of uranyl nitrate from which uranium can be extracted nearly quantitatively by means of an organic solvent (for instance, by the widely spread known TBP-diluent extraction), or alternatively the uranyl nitrate solution can be used to feed columns of ion exchange resins from which the purified uranium can be eluted by convenient elutriants. The prepared uranyl nitrate solutions are reasonably pure to feed tributyl phosphate extraction and ion exchange plants for preparation of nuclear pure ammonium diuranate.

To reach this end, the SDU is attacked by nitric acid,

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this operation being followed by a filtration where the insoluble residue is separated. The clear uranyl nitrate obtained by the fractional dissolution is acid deficient. To feed the ion exchange purification process, the uranium concentration is adjusted conveniently by dilution with water. For the purification of uranium by the solvent extraction process (TBP, for instance), a given quantity of nitric acid and salting agent is added to the clear uranyl nitrate.

The fractional dissolution precedure outlined here allows the preparation of a stable clear uranyl nitrate solution with the additional advantage of satisfactorily removing impurities like thorium, rare earth elements, phosphorus, silicon and iron.

The raw uranium salt used is obtained by industrial processing of monazite sand[1]. This sodium diuranate contains some thorium, rare earth elements, iron, silicon, and phosphorus as main impurities. Analysis of typical feed SDU is given in Table I[2]:

TABLE I - CHEMICAL COMPOSITION OF SODIUM DIURANATE

Element	%
U as U_3O_8	79.5
B	0.0002
Cu	0.001
V	0.004
Mo	0.0005
As	0.01
P as PO_4	0.3
S as SO_4	1.5
F	0.02
Halogens	0.015
Th as ThO_2	3.0*
Rare earths	0.2
Sm + Eu + Gd + Dy	0.02 max.
Fe	0.1
Cd	0.007
Pb	0.015
Ti	0.015
Si as SiO_2	1.4
Na as Na_2O	9.2

* Variable from 0.3 to 8.0%

DISSOLVING THE SODIUM DIURANATE

The SDU attack is carried out with concentrated nitric acid. The SDU is brought dry to the dissolution vat containing enough water to prepare a slurry, and followed by addition of sufficient concentrated nitric acid of technical grade required for dissolution of 94 to 96 percent of the total uranium.

The nitric acid (14 M HNO_3) is added slowly (one hour) to the aqueous SDU slurry, and the pH of the mixture is controlled to 1.4 to 1.6. The temperature is then raised to 80°C. At this point, powdered activated carbon is added (4-g carbon per Kg of SDU) and the mixture is maintained at this temperature under agitation for 30 minutes. The hot mixture is vacuum filtered using a canvas filter. The insoluble residue containing some uranium, thorium, rare earth elements, phosphorus, silicon, and iron is removed and set aside for further processing and recovery of uranium and thorium. The dried residue contains approximately 4 to 5 percent of the total uranium.

Laboratory experiments are run using 1-, 2-, and 4-liter beakers; and, for dissolution of 1- to 2-Kg SDU quantities, a stainless steel vessel is used.

By the procedure, clear uranyl nitrate solutions having 270 to 300 g/l U and exhibiting good filtration characteristics are easily obtained. These uranyl nitrate solutions have good stability, allowing a storage time of at least one month.

REMOVAL OF IMPURITIES

A great advantage offered by the fractional dissolution of the SDU is a satisfactory removal of thorium (ca. 50%), iron (ca. 40%), silicon (ca. 30%) and phosphorus (ca. 85%), as can be seen in Table II. A tracer technique using radio-europium showed

that some rare earth elements followed thorium:

TABLE II - PARTIAL RENOVAL OF IMPURITIES BY FRACTIONAL DISSOLUTION OF SDU WITH NITRIC ACID AT pH 1.50, 80°C, AND 30-MIN HEATING TIME

Exp No.	U Dissolved (%)	Retained in the Dried Residue			
		Th (%)	P_2O_5 (%)	SiO_2 (%)	Fe_2O_3 (%)
1	94.70	47.9	82.5	33.0	45.0
2	94.56	50.5	86.5	29.5	42.5
3	94.84	48.8	83.0	32.0	44.2
4	94.62	46.2	82.5	22.0	41.2
5	94.40	41.1	89.7	24.0	32.5
6	92.35	46.2	85.5	36.0	44.8
7	94.05	60.5	87.2	29.0	41.6

The insoluble residue also contains minor constituents like cadmium, titanium, and boron. Analysis for the quantitative determination of these and other minor constituents are being done.

Natural radioisotopes, like Th-230 (ionium) and Th-234 (UX_1), are collected and removed along with common thorium thus resulting in a further advantage.

RESULTS AND DISCUSSION

A great number of experiments were performed searching the best conditions for the fractional dissolution of the SDU.

The effect of pH has shown to be of paramount importance, as can be seen in Table III.

TABLE III - EFFECT OF pH ON THE SDU DISSOLUTION AT 80°C, HEATING TIME 30 MIN, 225 g SDU, VOLUME: 500 ml, FILTER: Ø 9.6 cm

Exp No.	pH	U Dissolved (%)	Filtration (min)	Retained in the Dried Residue			
				Th (%)	P_2O_5 (%)	SiO_2 (%)	Fe_2O_3 (%)
8	0.40	95.51	15.0	14.0	92.7	0.2	0.5
9	0.50	95.15	5.5	20.0	93.1	0.2	0.7
10	1.20	94.95	7.0	13.6	91.2	14.5	15.0
11	1.30	95.12	1.5	18.5	88.7	12.2	35.0
2	1.50	94.56	2.0	50.5	86.5	29.5	42.5
1	1.50	94.70	2.5	47.9	85.5	33.0	45.0
7	1.50	94.05	1.5	60.5	87.2	29.0	41.6

At pH 0.4 to 1.30, the filtration is poor and lengthened; the removal of thorium, silicon, and iron is lower, while the removal of phosphorus is good; and the solubilization of uranium is about the same, approximately 95 percent.

For routine work, the optimum pH is maintained in the 1.4 to 1.6 range.

The effect of temperature is of great importance. Below 70°C, the filtration is poor; some experiments have been interrupted due to a very long filtration time. From 70 to 100°C, the filtration is excellent, as can be seen in Table IV.

TABLE IV - EFFECT OF TEMPERATURE ON THE DISSOLUTION OF SDU AT pH 1.50, 225-g SDU
VOLUME: 500 ml, FILTER: Ø 9.6 cm, HEATING TIME: 30-Min

Exp No.	Temp (°C)	Filtration (min)	U Dissolved (%)	Retained in the Dried Residue			
				Th (%)	P_2O_5 (%)	SiO_2 (%)	Fe_2O_3 (%)
12	70	10.0	98.98	24.2	85.5	18.0	38.0
1	80	2.5	94.70	47.9	85.5	33.0	45.0
2	80	2.0	94.56	50.5	86.5	29.5	42.5
3	80	2.0	94.84	48.8	83.0	32.0	44.2
4	80	2.0	94.62	46.2	82.5	22.0	41.2
13	90	1.0	94.00	45.1	88.7	26.0	30.5
14	100	1.0	92.50	47.8	85.0	34.5	42.8

Heating time has little influence on the filtration. Experiments are performed with 15 to 90 min of digestion time at pH 1.50 and 80°C, as shown in Table V. Filtration time is excellent in all experiments.

Heating time of less than 30 min has some influence on the removal of some species, specially on uranyl, thorium, phosphorus, and silicon.

TABLE V – EFFECT OF HEATING TIME ON DISSOLUTION OF SDU AT 80°C, pH 1.50, 225g SDU, VOLUME: 500 ml, FILTER: ∅ 9.6 cm

Exp No.	Heating Time (min)	Filtration (min)	U Dissolved (%)	Retained in the Dried Residue			
				Th(%)	P_2O_5 (%)	SiO_2 (%)	Fe_2O_3 (%)
15	15	2.0	97.18	24.2	60.8	15.5	38.2
1	30	2.5	94.70	47.9	85.5	33.0	45.0
2	30	2.0	94.56	50.5	86.5	29.5	42.5
4	30	2.0	94.62	46.2	82.5	22.0	41.2
3	30	2.0	94.84	48.8	83.0	32.0	44.2
16	45	3.0	96.60	37.5	75.0	21.5	40.0
17	45	1.5	95.07	28.0	89.9	17.5	43.2
18	60	1.5	95.10	45.5	66.9	29.5	43.5
19	60	1.5	94.65	55.6	85.2	28.5	42.5
20	60	2.5	94.63	47.3	78.1	23.0	45.7
21	90	1.0	93.50	45.8	88.0	25.5	32.8

CONCLUSION

The fractional dissolution of SDU with nitric acid proved to be advantageous and very convenient as is described in this paper. Good results are obtained at the optimal work conditions determined, that is, controlled addition of nitric acid to keep the pH in the 1.4 to 1.6 range, with solubilization of approximately 95 percent of the total uranium and 30 min as the heating time of the mixture at 80°C. Reasonably pure uranyl nitrate solutions are prepared; the filtration is excellent; the solutions are clear and stable for at least 1 month, showing no turbidity.

Decontamination of major impurities elements specially thorium, phosphorus, rare earth elements, silicon, and iron, are very satisfactory. Further advantage is gained by the removal of natural radioactivity, mainly Th-230 and Th-234, these radioisotopes being removed along with Th-232.

Additional advantage is obtained, if it is considered that the uranyl nitrate solutions prepared by the described procedure can feed both solvent extraction (TBP) and ion exchange processes for purification of uranium concentrates to nuclear grade uranium, as it is the actual situation at the Instituto de Ener

gia Atômica where two pilot plants are installed for the purification of uranium. One of these plants, the ion exchange plant, uses an acid deficient uranyl nitrate solution requiring, thus, only a dilution step. The other plant uses TBP-diluent extraction; and, to prepare the feed solution, it is only necessary to add enough nitric acid and salting agent.

Finally, the economy of the process is improved; the dissolution is done at low temperature and with short digestion time. At the Instituto de Energia Atômica, two procedures are put in practice for dissolving the SDU. The first one[2] uses a hot, concentrated, nitric acid digestion of the SDU previously calcined at 450°C during 4 hours, being the totality of the uranium dissolved, while the digestion temperature is maintained at 120°C during 6 to 8 hours. The second one is here described and uses fractional dissolution of the SDU only, dried at 110°C.

RESUMO

Êste trabalho descreve um procedimento para a preparação de soluções clarificadas de nitrato de uranilo pela dissolução fracionada de diuranato de sódio de grau técnico. Êste diuranato de sódio é obtido pelo processamento industrial da monazita e contém tório, terras raras, ferro, silício e fósforo como impurezas principais.

Com o método aqui descrito são obtidas soluções límpidas e estáveis de nitrato de uranilo, cuja concentração varia 270 a 300 g/l U e exibindo boas características de filtração. O método possibilita uma remoção satisfatória de tório, terras raras, fósforo, silício e ferro.

RÉSUMÉ

La communication décrit un procédé de preparation de solutions claires de nitrate d'uranyl par dissolution fractionnée à partir du diuranate de sodium brut.

Cette matiere première est fabriquée industriellment par traitement des monazites et contient, comme principale impuretés, des composés du thorium ainsi que des terres rares, du fer, du silicium et du phosphore.

Par le procédé décrit on obtient des solutions limpides et stables de nitrate d' Uranyl à 270-300 gr d'U/l après filtration facile, et avec élimination de la plus grande partie des impuretés mentionees ci-dessus.

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