SECURITY INFORMATION

SECRET

CONFIDENTIAL
mcw-5
UNCLASSIFIED

A STUDY OF THE DISTRIBUTION OF IMPURITIES

IN THE EXTRACTION OF URANYL NITRATE

WITH ETHER FROM AQUEOUS SOLUTIONS

CONFIDENTIAL
RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

UNCLASSIFIED

Classification changed to Unclassified
by authority of H.F. Carroll 2-27-57
by H. Kinser date 9-27-11
and C.M. Davenport date 9/27/11

Written by:

C. R. Conard

Work done by:

J. Boyd, C. Conard, J. Graham,
L. Kaplan, J. Ruhoff, and S. Tuthill

Contributions of:

Mallinckrodt Chemical Works
H. V. Farr, Technical Director

Contract No. W-7405-eng-1

April 1, 1946

This document is
PUBLICLY RELEASABLE

H. Kinser
Authorizing Official

Date: 9-27-11

CAUTION

This document contains restricted data as defined in the Atomic Energy Act of 1946 which restricts the transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited and may result in severe penalties under applicable Federal Laws.

P-214-1

CLASSIFICATION CANCELLED
DATE FEB 27 1957 *De*
For The Atomic Energy Commission
H. P. Canale
Chief, Declassification Branch

007122000380

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~CONFIDENTIAL~~

A STUDY OF THE DISTRIBUTION OF IMPURITIES
IN THE EXTRACTION OF URANYL NITRATE
WITH ETHER FROM AQUEOUS SOLUTIONS

I. INTRODUCTION

Early in 1942 it had been found on a laboratory scale that certain impurities such as the Rare Earths were removed by small water washes from an ether solution of Uranyl Nitrate.* It was hoped that in the large production units to be constructed that the water soluble impurities would all be washed out by the time the radioactive Thorium had been removed, so that the decrease in radioactivity could be used as an index of the amount of all kinds of impurity remaining in the ether layer. Experience has taught both the production and the laboratory chemist to view with suspicion a process which claims to separate one element from all others in the periodic system with a simple set of manipulations such as an extraction. Furthermore, there is the familiar example of iodide ion which anyone would expect to be oxidized to iodine and then be transferred almost quantitatively to the ether layer from which it would not wash out. It seemed reasonable that other elements or ions would be found which would fail to wash out of the ether layer.

* Bureau of Standards Report # A 131 a.

~~SECRET~~
DECLASSIFIED

P.274-2

Since the objective was the removal of the neutron absorbers whether their danger coefficients* were especially high or not, it became important that every possible check on the effectiveness of the extraction method was investigated. Furthermore there was a probability that the concentration of any individual impurity in different batches of raw material would vary over a wide range. The question was raised whether a large increase in the concentration of some ions would either make the washing of the ether layer unsuccessful or uneconomical.

II. DISCUSSION

As a preliminary investigation a rapid screening of a few easily accessible ions was rushed through. Even this scanning of the elements showed that the suspicions were justified and that special precautions should be developed for those elements dissolving in the ether layer to see that they were quantitatively washed out.

A more painstaking and thorough investigation** was carried out with the aid of the shotgun test, in which known amounts were introduced into a sample which went through the shotgun procedure of concentrating the impurities in a sample of material containing 10 Kg of Uranium to a button with a total weight of ten grams. The two buttons should give the same neutron absorption if the procedures

* ratio of their neutron absorbing power as compared with that for uranium.

** Dr. R. I. Martens of the Chicago Group - Report Name or No. not known.

P.274-3

[REDACTED]

wash all of the impurities out of the ether layer. The results showed that the eight elements B, N, Cl, Ru, Pd, Os, Pt and Hg, should be tested for separately, and that the others were unimportant such as carbon and oxygen, ^{vv}would be lost in processing such as iodine, or would be found in the shotgun test. This meant that the washing procedures as used in the plant were safe because in the above list the six elements B, N, Cl, Ru, Os, and Hg are lost in the shotgun due to volatility either as compounds or as the element. No reason is apparent for the failure of Pd or Pt to be separated quantitatively by the Shotgun procedures.

Before the investigation was completed by Dr. Martens, the starting material had changed from the Black Oxide U_3O_8 to Sodium DiUranate and related material which contained considerable amounts of Molybdenum and Vanadium. Since the preliminary screening tests were none too reassuring, especially with regard to Vanadium, a careful check was made on the distribution ratios of Molybdates and Vanadates in the ether and water layers obtained under conditions which would exist during plant operation.

The conclusion reached was that in batch extraction any reasonable concentrations of elements found as impurities would be removed. It should be noted, however, that appreciable concentrations of halides were removed before processing, in order to avoid corrosion of the stainless steel equipment. This fact eliminates from consideration a number of complex ions such as the iron chloride complexes and

[REDACTED]

DECLASSIFIED

P-274-4

[REDACTED]

indeed this is one of the reasons why the washing of the ether solution of Uranyl Nitrate is so effective.

III. EXPERIMENTAL

Shake Out Tests

The scanning of the available elements was done in a series of brief shake-out tests. The general plan was to introduce a known amount of an element into a funnel with hexahydrate and shake with ether. The element might appear in the water layer, in the ether layer, in a precipitate, or be distributed among these possible places. If it appeared in the ether layer in detectable amounts, the element should receive special consideration and if necessary, a means must be found for it's removal from the Uranyl Nitrate solutions before extraction.

Since Lithium, Boron, Cadmium, and Cobalt were the common elements with very high neutron absorbing capacity an experiment was done to see whether any of these elements would be transferred in appreciable quantities to the ether layer in case they were present as impurities in the molten "hex."

1 gram each of Lithium Nitrate, Boric acid, Cadmium Nitrate Tetrahydrate and Cobalt Nitrate Hexahydrate were mixed and powdered in a mortar. The resulting mixture was mixed thoroughly with 100 grams of Uranyl Nitrate Hexahydrate. The entire mixture was shaken in a separatory funnel with about 55 grams of ether and each layer was analysed for the elements added.

[REDACTED]

[REDACTED]

P.274.5

Compound	Gms. found in ether layer	Gms. found in water dryer
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	less than 0.016	.89
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	less than 0.00125	.86
$\text{Li}(\text{NO}_3)$	less than 0.05	.87
H_3BO_3	small	.87

The fact that traces of Boron were found in the ether showed the need of further screening tests to see how many common elements appeared in the ether layer. The reader should realize that these were done under pressure of great haste to locate possible sources of trouble before the plant was built and production started. A typical experiment will suffice to show the type of procedure used.

10 grams of Silver Nitrate was dissolved in distilled water and diluted to 100 cc total volume. 10 cc of this solution was added to about 100 cc of an ether solution nearly saturated with Uranyl Nitrate in a separatory funnel. The layers were separated. The water layer was made up to 50 cc, 10 cc of which titrated with N/10 NH_4SCN , required 10.55 cc. Multiplying this by the conversion factor we have, $10.55 \times 0.016989 = 0.179$ gm AgNO_3 or a total of $5 \times 0.179 = 0.895$ gm recovered in water layer. An ether layer of 98 cc was recovered, 20 cc of which was treated with about 10 cc of water and 2-3 cc of diluted HCl. The ether layer was then placed on a steam bath overnight, filtered through a tared Jena crucible, dried at 110°C and weighed again. Gain in weight = 0.0023 gm. Then $0.0023 \times 1.185 \times 98/20 = 0.0133$ grams AgNO_3 in ether layer, leaving $1 - (0.895 + 0.013) = 0.092$ grams not accounted for.

Other results obtained in these early shake-out tests are recorded in table VII. The importance of this work was in getting tangible evidence that certain elements are somewhat soluble in the ether layer and that further work should be done either to make

P-274-6

certain that they could be removed by the washing procedures finally adopted or to prove that special treatment must be resorted to be sure that they were removed before the ether extraction. This was also of importance in the Shotgun test*.

TABLE VIII

Tabular View of Shake Out Tests

Salt Added	Weight Added gms.	Found in Water layer gms.	Found in Ether layer gms.
AgNO_3	1.0	0.895	0.013
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.0	0.956	none
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1.0	1.063	none
$\text{Hg}(\text{NO}_3)_2$	1.0	.902	.0048
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1.0	1.081	none
K MnO_4		deep color	none
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	1.0	1.283	none
K Cl	1.0	.872	.021
$\text{Ce}(\text{NO}_3)_2$	1.0		small if any
K Br	1.0	.8570	.013
V_2O_5	.05	.031	Unsatisfactory

(Con't on page 7)

- * The Simplification and Improvement of the Concentration of Impurities in the "Shotgun Test." Written by C. R. Conard, Contribution of Mallinckrodt Chemical Works

DECLASSIFIED

P.274-7

Salt Added	Weight Added gms.	Found in Water layer gms.	Found in Ether layer gms.
K I	1.0	none	1.008
K ₂ SO ₄	1.	1.009	none
SbCl ₃	0.5		
Na ₂ WO ₄ ·2H ₂ O	0.5	.5456	none
Na ₂ MoO ₄ ·2H ₂ O	0.5	.50	none
K ₂ Cr ₂ O ₇	0.5	.407	none
H ₃ AsO ₄	0.5	.487	.002

Molybdenum And Vanadium

In order to get data under conditions similar to those found in plant operation (a) solubilities were measured and (b) loaded hexahydrate nearly saturated with Mo and V, prepared using procedures simulating plant methods, was extracted with ether, and the distribution ratio for each element was found.

(a) Solubility Measurements.

The solubility of ammonium molybdate and ammonium vanadate in aqueous hex solution of various concentration is given in Table I. Separate portions of pure hexahydrate solutions having compositions listed in the first column of Table I were treated with an excess of ammonium molybdate or vanadate. The mixture was mechanically stirred, heated on a steam bath for several hours, cooled to room temperature and then filtered. The clear filtrates were analyzed for molybdenum or vanadium. The results, given in columns two and three, are expressed in grams of Mo or V per hundred grams of uranium

in the filtered solution. The data suggest that the filtered hex solutions obtained in the factory will contain no more than 0.5-1.0% Mo and 0.010 - 0.020% V.

TABLE I

Solubility of Ammonium Molybdate and Ammonium Vanadate in Hex Solutions of Various Concentrations.

% Hex in Solution	gr. Mo. . 100	gr. V . 100
	gr. V	gr. V
15	0.46	0.025
25	0.48	0.016
35	0.37	0.011
50	0.8	0.010

(b) Extraction experiments

In order to determine whether hex containing Mo and V can be purified by extraction with ether, aqueous solutions containing sufficient Mo and V to nearly saturate the solutions with these two elements were prepared and their boiling points adjusted to 117-118°C. One hundred cc samples were extracted with two hundred cc of ether and, after transferring to a separatory funnel, samples of the water and ether layer were withdrawn. These samples were ignited to black oxide and analyzed for Mo or V. The Potassium ethyl xanthate method was used in the estimation of Mo and the diphenylamine method was used for V. The data obtained are listed in Tables II-A and II-B.

TABLE II-A

The Distribution of Mo Between Water and Ether Nearly Saturated With Hex.

Exp.	% Mo in black oxide Water	Ether	Ratio Water/Ether	Comment
22A	< 0.006	< 0.006	-	Blank
22A	0.20	0.01	20	Hex not filtered
22A	> 1	< 0.006	166	Hex not filtered
22C	0.7	< 0.003	233	Hex filtered

TABLE II-B

The Distribution of V Between Water and Ether Nearly Saturated With Hex

Exp.	% V in black oxide Water	Ether	Ratio Water/Ether	Comment
22B	< 0.002	< 0.002	-	Blank
22B	0.07	< 0.002	> 35	Hex not filtered
22B	0.07	< 0.002	> 35	Hex not filtered
22C	0.08	< 0.0002	> 400	Hex filtered

Columns two and three in these tables give the percent Mo or V found in the black oxide obtained from the water and ether layer respectively. Column four gives the ratio of these numbers. The hex solutions used in experiment 22A and 22B were not filtered before extracting and the water and ether layers were somewhat turbid.

P-274-10

In experiment 22C the solutions were filtered and more sensitive tests for Mo and V were used in the analysis.

This series of experiments indicated that the distribution ratios for both the Molybdates and the Vanadates were sufficiently high for satisfactory removal of these elements in the batch washing process. More recent investigations** have been carried out to study the behavior of these elements in the continuous extraction of aqueous solutions with ether and related operations.

CRC
Conard
dab

** Research Report No. 18
Research Report No. 19
Research Report No. 21
Research Report No. 23

P-274-11

DECLASSIFIED