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January 1, 1952 to March 31, 1952

MATERIALS CHEMISTRY DIVISION

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Subject Category: Metallurgy - Raw Materials

PROGRESS REPORT

URANIUM CHEMISTRY OF RAW MATERIALS SECTION

JANUARY 1, 1952 to MARCH 31, 1952

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May 23, 1952

MATERIALS CHEMISTRY DIVISION
G. H. Clewett, Division Head

OAK RIDGE NATIONAL LABORATORY

Operated by

CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation

Oak Ridge, Tennessee

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URANIUM CHEMISTRY OF RAW MATERIALS

K. B. Brown

INTRODUCTION AND SUMMARY

The Uranium Raw Materials program at Oak Ridge National Laboratory during the first quarter of 1952 has, as previously, been concerned with studies of uranium chemistry and with the development of processes for recovering uranium (and byproducts) from various types of ores.

The uranium chemistry program has included (1) investigations of the solvent extraction of uranium and thorium from aqueous nitrate, sulfate, phosphate, and fluoride solutions through the use of organic complexing agents, (2) precipitation of uranium and thorium from aqueous solutions with organic compounds, (3) studies of the behavior of hexavalent uranium in phosphate solutions, (4) reduction of uranium in sodium carbonate solutions, and (5) studies with ion exchange resins.

Process development work has been devoted to the following projects: (1) uranium recovery from the Florida leached zone, (2) recovery of uranium from Dakota lignite, (3) precipitation of uranium from carbonate and basic phosphate solutions, (4) vanadium and uranium recovery from carnotite ores, (5) recovery of uranium from Marysvale type ores, and (6) uranium recovery from metal production salvage.

In the search for organic reagents capable of extracting uranium, certain heterocyclic chelating agents have shown appreciable extractions from uranyl nitrate solutions; but their ability to compete with other anions has not yet been shown. Most of the effort has been directed toward synthesis and investigation of organophosphorus acids which have been shown to possess high extraction abilities in acidic phosphate, sulfate and fluoride solutions. Limited correlation of complexing ability and structure of the organic compounds has been made in the case of phosphinic acids. Detailed studies are being made with compounds representative of the phosphinic, phosphonic and alkyl phosphoric acids to determine the nature of the complex extracted, its stability,

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concentrations required to extract uranium and the selectivity for uranium in the presence of other cations.

Several of the organophosphorus compounds have been used very effectively in separating thorium from the rare earths. Thorium has been almost completely extracted in a single stage from sulfuric acid solutions of monazite sand using petroleum ether solutions of monooctyl phosphate which contained only about 6 moles of reagent per mole of thorium. The presence of cerium or other rare earths in the organic phase has not been detected by ordinary spectrographic means.

Fairly complete precipitation of thorium has been obtained from sulfuric acid solutions of monazite sand with benzene phosphonic acid and with dibutyl phosphate, using only small quantities of reagent. The rare earth contents of the precipitates have not been determined.

Initial extraction experiments with a new group of organic compounds, secondary and tertiary amines, have given encouraging results. Uranium has been extracted from sulfuric acid solutions of uranium sulfate and from a sulfuric acid leach of LZ (Florida leached zone) material using a 1% mixture of methyl dioctyl amine in chloroform. Primary amines have not been tested. A more intensive survey of the applicability of these reagents to raw material processing will be carried out during the next quarter.

Continued investigations of the solubility behavior of $UO_2HPO_4 \cdot 4H_2O$ in 0.02 to 5.5M H_3PO_4 solution indicates the existence in solution of the complex, $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)_2H_3PO_4$. An extension of the spectrophotometric studies to solutions of lower acidity (i.e., from 1M to 0.1M perchloric acid) shows that $UO_2H_2PO_4^+$ is still the predominant uranium complex.

Preliminary studies of the solubility of uranium in basic phosphate solutions has indicated that there are regions of appreciable solubility in this system. The uranium can be reduced and precipitated from the solutions with small amounts of sodium hydrosulfite if the surrounding atmosphere is inert.

Spectrophotometric measurements have indicated the formation of a soluble U(IV) complex when sodium hydrosulfite is added to sodium carbonate solutions of pH$\approx$9. In more basic solutions (e.g., pH=11), the uranium is reduced and precipitated. Essentially complete precipitations have been obtained using only 1 mole of hydrosulfite per mole of uranium if an inert atmosphere is provided.

Very preliminary tests have indicated that reasonable uranium extractions from the Florida leached zone can be obtained with less acid if anion exchange resin is present during the leaching step. Further tests are being made with samples of different varieties of leached zone material.

Multicolumn anion exchange sorption of uranium from low sulfate LZ liquor has shown satisfactory pickup and loading. Eluents have averaged above one gram of uranium per liter. Reduction-precipitation tests from the same low-sulfate liquor gave 98% recovery in cakes containing about 1% uranium. Good extraction of uranium was also obtained from nitric acid leach liquor and from reduced sulfuric acid leach liquor of LZ ore with di(2-ethylhexyl)phosphinic acid in carbon tetrachloride.

Sink-float tests with raw crushed Dakota lignite have shown that over 50% of the total inorganic constituents may be discarded as a sink product. This fraction contained only 3-8% of the total carbon and apparently only 10-20% of the total uranium. Chemical processing studies of the lignite have been started and will be conducted during the next quarter.

Direct dissolution of vanadium from carnotite ores by sodium carbonate leaching has been increased from a few percent to more than 60% by pressure leaching (200 psi) at higher temperatures (200°C) in the presence of an oxidant ($KMnO_4$). Above 200°C the dissolution of uranium is decreased possible due to the instability of uranium-bearing carbonate solutions at high temperatures.

Only a small amount of work has been carried out during the quarter with Marysvale type ores and with the metal production salvage. The subsequent discussions of the work with ion exchange resins are also quite brief since a separate report (ORNL-1264) is being issued covering the studies with phosphate-sulfate and phosphate-nitrate solutions.

URANIUM CHEMISTRY

Organic Reagents for Solvent Extraction and Precipitation of Uranium (and Thorium)

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The investigation and evaluation of solvent extraction as a method for removing uranium and other metal ions from various types of aqueous solutions have been continued according to the general outline presented in previous reports.[1,2] The experiments fall naturally into the following categories: (1) the selection and preliminary examination of certain organic compounds for their ability to complex uranium in acid media; (2) the further testing of promising reagents in solutions containing appreciable amounts of the common anions ($SO_4^{=}$, $PO_4^{=}$, F^-) and cations other than uranium (Fe, Al, Ca); (3) the correlation of extraction data with the structure of the organic complexing agent and the synthesis of compounds likely to have desirable extraction properties; (4) determination of the nature and stability of the complexes formed with uranium and other metal ions, the concentrations required to effect extraction, methods of recovering the uranium from the organic phase, and the physical properties of the more promising reagents; (5) the extraction of thorium from solutions containing large amounts of cerium and the rare earths.

The problem of removing uranium from aqueous solutions containing small concentrations of uranium and relatively large amounts of other material is receiving emphasis elsewhere in the Raw Materials program, and it is possible that solvent extraction may provide a suitable means of recovering uranium from several of these solutions. Preliminary results using phosphinic acids to complex the uranium from leached zone process liquors look promising. Dow Chemical Company has reported[3] successful extractions of uranium from concentrated phosphoric acid using inexpensive reagents.

Before the general applicability of a solvent extraction process to liquors which vary widely in anion, cation, and uranium composition can be known, there are many problems which must be studied, a few of these being: (1) ability of the agent to compete for the uranium with other uranium complexers present, (2) the relative strengths of the complexes formed by the reagent with uranium and other metal ions,

(3) precipitation or emulsification during extraction, (4) reagent loss to raffinate, (5) extraction rate, (6) the factor by which the uranium may be concentrated across the system, (7) the stripping cycle, (8) the recycle of reagent, (9) choice of solvent, etc.

It is possible that certain processes, after combination of the best answers to these problems, will not be able to compete economically with other recovery schemes for treating solutions where the metal values are very dilute. The same process may still play an important role, however, in treating liquors of higher concentration where the reagent cost per unit of recovered values may be relatively low. The extractions, reported here, of thorium from solutions of monazite sand are for this reason of special interest. Additional tests are being conducted also on liquors of the type resulting from leaching of ores obtained in the Marysvale, Utah, district. The strong complexing reaction of some of the compounds being studied with the tetravalent metal ions suggests other applications for these reagents, such as the separation of zirconium and hafnium.

It is the intent of the following experiments to provide, in part, answers to the problems presented above.

Screening of Possible Organic Complexing Agents

Additional organic compounds have been selected, fitted into the classification scheme proposed in a previous report[1] and tested for their ability to extract uranium from dilute uranyl nitrate solutions having a pH range of from 1 to 2. The method of testing and the results are presented in Table 1.

Extraction by Neutral Compounds

Of the neutral compounds screened, only certain of the amides and esters extract uranium from nitrate solutions and these reagents shown no ability to compete for uranium with added phosphate ion.

Extraction by Basic Compounds

Certain of the basic compounds (octadecyl betaine, phenylbiguanide and guanidine stearate) precipitated appreciable amounts of uranium, but in each case, the pH change taking place during extraction is so large that hydrolytic precipitation of the uranium has probably taken place.

Table 1

SCREENING OF POSSIBLE ORGANIC COMPLEXING AGENTS

Screening Procedure

Equal volumes of organic and aqueous phases (50 ml).
Concentration of organic compound in organic solvent = 0.1M.
Solvent used dependent upon solubility of organic compound (Typical solvents: toluene, n-butylether, butylacetate, chloroform, isoamyl alcohol, carbon tetrachloride).
Concentration of uranium(VI) in aqueous phase = 0.004M.
Uranium present as $UO_2(NO_3)_2$, phosphate added as phosphoric acid.
Initial pH (adjusted with HNO_3) as indicated.
Contact time one hour, mechanical agitation.
Analysis of uranium in aqueous phase made by fluorimetric methods. Extractions of less than 15% have doubtful significance.

A. Neutral Compounds

1. Solvents	Percent Extraction From $UO_2(NO_3)_2$, pH=1
Butyl acetate	0
Hexone	0
Chloroform	0
Trichlorethylene	0
Dibutyl carbitol	0
Penta ether	0
Toluene	0
n-Butyl ether	0

2. Amides	% Extraction From Solutions Containing $UO_2(NO_3)_2$ pH=1	$UO_2(NO_3)_2$ pH=2	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2
Acetoacetanilide	12	1	--	--
Benzoylpiperidine	3	--	--	--
N, N-dibutylacetamide	0	--	--	--
Tri-n-butylphosphoramide	79	91	4	0
Hexaethylphosphoramide	47	48	--	1

	% Extraction From Solutions Containing			
	$UO_2(NO_3)_2$		1.5M $PO_4^{\equiv}$	
3. Esters	pH=1	pH=2	pH=1	pH=2
Butyl dibutylphosphinate*	75	64	--	0
Ethyl dithioöxalate	--	0	--	--
Tributyl phosphite	0	2	--	--
Tetraethyl methanediphosphonate	2	--	--	--
Dibutylbenzenephosphonate	0	28	--	3
4. Thiocyanates				
Ethylene thiocyanate	0	--	--	--
5. Oxides				
Tributylphosphine oxide*	98	98	--	0

B. Basic Compounds

1. Quaternary Salts				
Tetra-n-butylammonium iodide	9	--	--	--
Tetra-n-butylammonium nitrate	--	33	--	--
Quinoline ethiodide	0	--	--	--
Octadecyl betaine	77a	--	--	3

2. Amines	Percent Extraction From $UO_2(NO_3)_2$, pH=1
Phenyl-ß-naphthylamine	0
Phenyl-α-naphthylamine	0
Hydrazobenzene	0
2, 4-Diaminodiphenylamine	2
3. Ketazines	
4-methyl-2-pentanone ketazine	0
4. Amidines	
Lauramidine-HCl	0
5. Substituted Ureas	
Guanylurea·H_3PO_4	0
Guanylurea·H_2SO_4	25

* Prepared and donated by Dr. Willis H. Baldwin, Chemistry Division, ORNL.

a Precipitation and emulsification.

5. Substituted Ureas (Cont.)	Percent Extraction From $UO_2(NO_3)_2$, pH=1
Phenylthiourea	10
Phenylbiguanide	97[b]
Guanidine stearate	96[b]
Di-n-butylthiourea	3
Phenylsemicarbazide	12
Sodium diethyldithiocarbamate	0

C. Acidic Compounds

1. Carboxylic Acids	Percent Extraction From $UO_2(NO_3)_2$	
	pH=1	pH=2
m-Cresoxyacetic acid	0	--
Salicylic acid	0	--
1-Hydroxy-2-naphthoic acid	--	3
3-Hydroxy-2-naphthoic acid	--	12
Ethylthioglycolic acid	--	11
3-Phenylsalicylic acid	--	5
2. Phenols		
0-Nitrophenol	0	--
Sodium nitrosoresorcinol	38[a]	--
Curcumin	10	--
Acetyl-0-aminophenol	10	00
3. Hydroxamic Acids		
Benzohydroxamic acid	0	--
Caprohydroxamic acid	22	--
Caprylohydroxamic acid	0	--
Laurohydroxamic acid	0	--
Benzensulfohydroxamic acid	--	28
4. Diketones		
Acetylbenzoyl	0	--
Acetylcaproyl	0	--
Acetylacetone	0	--
Curcumin	10	--
Acetoacetanilide	12	0
Dibenzoylmethane	--	20

a Precipitation
b Large rise in pH during extraction leading to hydrolytic precipitation.

	% Extraction From Solutions Containing			
	$UO_2(NO_3)_2$		1.5M $PO_4^{\equiv}$	
5. Unsaturated Ketones	pH=1	pH=2	pH=1	pH=2
Cinnamalacetophenone	--	0	--	--
Salicylalacetone	--	1	--	--
Dibenzal acetone	--	0	--	--
6. Hydroxyl Amines and Oximes				
α-Benzoin oxime	1	--	--	--
α-Isonitrosopropiophenone	--	8	--	--
7. Arsonic and Arsinic Acids				
Phenylarsonic acid	--	99[a]	--	--
Phenoxarsinic acid	100[a]	--	0	--
8. Sulfonic Acids				
Biphenyl-p, p'-disulfonic acid	--	3	--	--

D. Amphoteric Compounds

1. Amino Carboxylic Acids				
N, N'-dibenzylethylene diamine N, N' diacetic acid (Na salt)	0	--	--	--
N-amylanthranilic acid	0	0	--	--
N, N'-Hexamethylenebis-ß-alanine	0	--	--	--
Octadecyl betaine	77[a]	--	--	3
Guanidine stearate	96[b]	--	--	--
Phenylguanidine stearate	99[b]	--	--	--
Quinaldinic acid	92[a]	--	--	0

2. Amino Sulfonic Acids	Percent Extraction From $UO_2(NO_3)_2$	
	pH=1	pH=2
o-Aminobenzenesulfonic acid	0	--
N,N-dibutyltaurine	0	--
4, 4'-Diaminostilbene-2, 2'-disulfonic acid	0	--
3. Amino Arsonic Acids		
Arsanilic acid	--	98[a]
O-Aminophenylarsonic acid	41	--

a Precipitation
b Large rise in pH during extraction leading to hydrolytic precipitation.

4. Amino Phenols	Percent Extraction From $UO_2(NO_3)_2$	
	pH=1	pH=2
o-Aminophenol	--	7
Acetyl-0-aminophenol	10	--
5, 7-dibromo-8-hydroxyquinoline	0	81[a]
2-dimethylaminomethyl-4-(t-butyl) phenol	13	--
2, 4, 6-Tris(dimethylaminomethyl) phenol	10	--

[a] Precipitation

Extraction by Acidic Compounds

None of the reagents listed in this part of the table show removal of uranium from solution with the exception of the nearly complete precipitation obtained with the arsonic and arsinic acids. This behavior has been noted before. By far the most promising acidic reagents discovered thus far are the organophosphorus acids which are discussed in later sections.

Extraction by Chelating Agents

Through the kindness of Dr. Robert Levine, samples of heterocyclic chelating agents prepared at the University of Pittsburgh have been made available for the screening program. The names of the compounds and the results of the extractions are shown in Table 2.

Though exact reasons for the large differences in extraction obtained with various solvents (isoamyl alcohol and carbon tetrachloride, in particular) are not known, certain correlations between structure and behavior may be made. In two cases, isobutyl-2-picolyl ketone and ethyl quinaldyl ketone, there is essentially no difference in extractions with either solvent while in all other cases where this pair of solvents is used there are large differences in favor of isoamyl alcohol. It should be noted that the two compounds named are simple ketones while all of the others are diketones. Use of isoamyl alcohol to extract the two other simple ketones, phenyl quinaldyl ketone and phenyl-2-picolyl ketone would be of interest.

Due to the limited supply of reagent, tests were not made in other uranium solutions (i.e., sulfate and phosphate). Additional quantities of the reagents which gave the best extractions are being obtained for further testing.

The rather low extractions obtained with chelating agents as a class (see also "Diketones," Table 1) may result from the fact that these compounds are very weak acids; so weak that uranyl ion cannot compete with hydrogen ion in the acid solutions. When the chelating reagent is made more acid by the substitution of hydrogen with fluorine, e.g., 3-methyl-2-thenoyl-n-heptafluoro-butyryl methane, the extraction increases. Dr. Levine has agreed to synthesize chelating agents which are stronger acids in the hopes of obtaining a better extractant.

Anion Exchange Solvent Extraction

The idea of using solvent extraction to remove anionic complexes from solution is an interesting one from several

Table 2

SCREENING OF CHELATING AGENTS SYNTHESIZED AT THE UNIVERSITY OF PITTSBURGH*

Screening Procedure

Equal volumes of organic and aqueous phase (10 ml).
Concentration of organic compound in organic solvent=0.1M.
Solvents as indicated.
Concentration of uranium as $UO_2(NO_3)_2$ in aqueous phase=0.004M.
Initial pH adjusted with HNO_3 to 2.2.
Contact time 3 minutes in separatory funnel..Agitation by hand.
Analysis of uranium in aqueous phase made by fluorimetric methods. Extractions of less than 15% have doubtful significance.

Complexing Compound	Final pH	Solvent	% Ext.
Isobutyl-2-picolyl ketone	3.52	CCl_4	27
		Isoamyl alcohol	23
2-Thenoyl-heptafluoro-n-butyryl methane	2.00	CCl_4	33
2-Furoyl-2-picolyl ketone	2.20	Ø-Cl	28
		Isoamyl alcohol	41
Ethyl Quinaldyl ketone	3.20	CCl_4	17
	2.98	Isoamyl alcohol	8
Caproyl-2-thenoyl methane	2.08	CCl_4	8
	2.03	Isoamyl alcohol	42
Caproyl-2-furoyl methane	1.90	CCl_4	17
	1.97	Isoamyl alcohol	47
n-Butyryl-2-thenoyl methane	2.12	CCl_4	17
	1.99	Isoamyl alcohol	45
3-Methyl-2-thenoyl-n-hepta-fluoro-butyryl methane	2.07	CCl_4	42
	2.20	Isoamyl alcohol	81
Phenyl quinaldyl ketone	2.25	CCl_4	5.2
	2.14	BuOAc	18
Isonicotinoylbenzoyl methane	2.00	BuOAc	30
Nicotinoylthenoylmethane	2.10	ø-Cl	99[a]
Phenyl-2-picolyl ketone	2.64	Hexone	13
	2.68	BuOAc	8.7
Picolinoylbenzoyl methane	2.21	CCl_4	0
	1.96	Isoamyl alcohol	67
Dithenoylmethane	1.78	Hexone	40
	1.78	BuOAc	43
3-Thianaphthenoyl-n-butyryl methane	2.15	CCl_4	6
	1.93	Isoamyl alcohol	79

a Precipitation and emulsification
* Prepared and donated by Dr. Robert Levine

standpoints. The selectivity for a particular complex may be high, for one example, and the recovery or elution of the desired complex may be relatively easy, for another. Some exploratory work was done some time ago in this laboratory, using long-chain polyamines and valeric acid, but further experiments were deferred with the initiation of the present solvent extraction program. Recently, extractions of inorganic acids by the tertiary amine, methyldioctylamine in chloroform solution,[4] have caused some interest. Further tests by F. L. Moore of the ORNL Analytical Division, have shown extractions of polonium, plutonyl, and uranyl from acid solutions; and separations of columbium from tantalum, protactinium from thorium, and zirconium from hafnium.

Qualitative tests in this laboratory showed sufficient extraction of uranium from solutions resembling leach liquors to warrant quantitative tests, which have been started. Results with sulfate solutions, given in Table 3, show good uranium extractions by the methyldioctylamine and also by a secondary amine, di(2-ethylhexyl)amine. In a single test, about 70% of the uranium was extracted from a low-sulfate LZ leach liquor (BC-41, 70 ppm U) by an equal volume of 0.06 M methyldioctylamine in chloroform.

Qualitative tests showed rapid and complete stripping of uranium from the amine-chloroform solution by 0.9M NaCl - 0.1M HCl solution and by dilute nitric acid.

The foregoing results are all analogous to results obtained with weak-base, ion-exchange resins. Further tests are being made to determine the nature of the extraction and to examine the applicability to certain process problems.

Extraction by Organophosphorus Compounds

The results of screening various organophosphorus acids are included in the next section of this report.

Detailed Study of the Organophosphorus Acids

Twenty-five organophosphorus acids in a nearly pure state have been synthesized, some of them several times. As a class of compounds they have proved to be the best uranium extracting agents yet shown by the screening procedure. In addition to preparing new compounds the synthesis program has undertaken to provide several homologous series of compounds so that the effect of structure on extraction may be studied. This is particularly true of the phosphinic acids and the results of screening these acids are presented in the following discussion in such a way as to show this effect.

Table 3

EXTRACTION OF URANYL SULFATE BY AMINES IN CHLOROFORM

A. Methyldioctylamine

Test No:	JGM31-1	JGM31-2	JGM31-3	JGM31-4
Concn. of amine, M:	0.04	0.004	0.04	0.04
Concn. of SO_4, M:	0.05	0.05	0.05	1.0
pH, Initial:	1.1	1.1	1.8*	1.1
pH, Final:	1.4	1.2	3.6	1.2
% Extraction of U:	98	31	96	90

B. Di(2-ethylhexyl)amine

Test No:	JGM32-1	JGM32-2	JGM32-3	JGM32-4
Concn. of amine, M:	0.04	0.004	0.04	0.04
Concn. of SO_4, M:	0.05	0.05	0.05	1.0
pH, Initial:	1.1	1.1	1.8*	1.1
pH, Final	1.4	1.2	3.3	1.2
% Extraction of U:	99	34	99	91

* pH adjusted with sodium hydroxide.

Conditions: Initial uranium concentration, 0.00095M, as neutral uranyl sulfate. pH adjusted to about 1 with sulfuric acid. Additional sulfate added as Na_2SO_4. Equal volumes of aqueous and chloroform solutions used, with contact time of five minutes.

Screening of Phosphinic Acids and Correlation of Structure with Extraction Ability

A series of the normal phosphinic acids has been prepared from the di-n-butyl to di-n-decyl. All extract uranium extremely well from nitrate solutions, and in the few tests conducted, from 0.5M phosphate and sulfate solutions. Extraction from 1.5M phosphate improves with increasing chain length, reaching a maximum at diheptyl or dioctyl, and then decreasing. The data are summarized in Table 4.

It has been shown[5] in the case of the acid phosphates, the branching the chain of the alkyl group will improve extraction. This also proves true with phosphinic acids as the data in Table 5 show. The normal, secondary and isobutyl and amyl compounds show identical patterns of behavior. In each case, the secondary structure is preferable to the iso form which is only slightly better than the normal compound. The effect of increased chain length is enhanced in these tests and is particularly obvious in the case of the 2-ethylhexyl and 2-ethylbutyl compounds. The substitution of the ethyl group on the carbon atom twice removed from the phosphorus atom seems to be favorable for extraction of uranium from phosphate solutions.

It is possible that the increased effectivenss of the branched-chain compounds may result from favorable steric properties. From geometrical considerations alone, it is reasonable to expect that these rather bulky compounds will complex ions of different sizes and charges with varying ease. There are indications in experiments described later that the uranium specificity of a reagent may be helped considerably by giving it a suitable geometric configuration.

A combination of steric and possible electrostatic effects may be observed in a series of aromatic phosphinic acids. The proximity of the benzene ring to the phosphorus of the acid in the case of diphenyl phosphinic acid results in the formation of an insoluble compound with uranium. Unfortunately, the dibenzyl compound is not appreciably soluble in any common organic solvent so extractions have not been made using it, but the di(α-phenylethyl)phosphinic acid has been prepared and found to be a poor uranium extractor. Having the benzene ring on the favored β carbon atom, as in the case of di(β-phenyl)phosphinic acid results in good extraction even in phosphate. The di(γ-phenylpropyl) phosphinic acid, in which the aromatic ring is on the γ carbon atom, and in which the steric effect will be smaller, shows lower extractions of uranium. Table 6 shows these results.

Table 4

EXTRACTION OF URANIUM WITH NORMAL PHOSPHINIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	% Extraction From Solutions Containing 0.004M U and 0.008M NO_3^- pH=1	0.008M NO_3^- pH=2	0.5M PO_4 pH=1	1.5M PO_4 pH=1	1.5M PO_4 pH=2	0.5M SO_4 pH=1
Dibutyl	100	100	--	29	35	98
Diamyl	100	100	--	31	50	--
Dihexyl	100	100	--	28	60	--
Diheptyl	100	100	--	48	60	--
Dioctyl	100	100	91	38	67	98
Didecyl	100	100	--	23	52	--

Table 5

EXTRACTION OF URANIUM WITH BRANCHED-CHAIN PHOSPHINIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	% Extraction from Solutions Containing 0.004M U and 0.008M NO_3^- pH=1	0.008M NO_3^- pH=2	0.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2	0.5M $SO_4^{\equiv}$ pH=1
Di-n-butyl	100	100	--	29	35	98
Di-sec-butyl	100	100	84	45	58	--
Di-iso-butyl	100	100	89	31	58	--
Di-n-amyl	100	100	--	31	50	--
Di-sec-amyl	96	100	91	64	84	--
Di-iso-amyl	100	100	89	52	67	--
Di-n-hexyl	100	100	--	28	60	--
Di(2-ethylbutyl)	100	100	--	93	98	--
Di-n-octyl	100	100	91	38	67	98
Di(2-ethylhexyl)	100	100	94	79	91	97

Table 6

EXTRACTION OF URANIUM WITH AROMATIC PHOSPHINIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	% Extraction From Solutions Containing 0.004M U and 0.008M NO_3^- pH=1	0.008M NO_3^- pH=2	0.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2	0.5M $SO_4^{=}$ pH=1
Diphenyl	100% Ppt'n.		--	20% Ppt'n.		--
Dibenzyl	Insoluble		--	--	--	--
Di(α-phenylethyl)	15	8	7	8	8	--
Di(β-phenylethyl)	100	100	99	66	88	--
Di(γ-phenylethyl)	100	100	--	45	81	100

Table 7

EXTRACTION OF URANIUM WITH CYCLOHEXYL PHOSPHINIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	% Extraction From Solutions Containing 0.004M U and 0.008M NO_3^- pH=1	0.008M NO_3^- pH=2	0.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2
Di(n-hexyl)	100	100	--	28	60
Dicyclohexyl	100	100	99	60	93
3,5,5-Trimethyl hexyl	92	91	--	92	90
3,5,5-Trimethyl cyclohexyl	95	65	9	26	--

The introduction of the cyclohexyl ring structure into these compounds again shows the effect of configuration. The dicyclohexylphosphinic acid is appreciably better than the di(n-hexyl) compound, but subsequent addition of methyl groups as in di(3,5,5-trimethylcyclohexyl)phosphinic acid apparently causes such a large steric hindrance that complexing is very poor. The electrostatic effect of diphenylphosphinic acid is lacking in the case of dicyclohexylphosphinic acid. These data are presented in Table 7.

Screening of Phosphonic Acids

Table 8 shows the results of extractions using an homologous series of phosphonic acids. All extract uranium quite well, even in 3.0 molar phosphate, but emulsification is in evidence in nearly all cases with the particular solvents used. Hexane and octane phosphonic acids are the most promising and modification of their alkane groups may result in more desirable extraction properties.

Screening of Alkyl Phosphoric Acids

Of the alkyl phosphates described in Table 9, only monoctyl phosphate has the ability to extract a large percentage of uranium from phosphate solutions while dioctyl phosphate, surprisingly, is very poor in these same solutions.

Extraction of Iron, Aluminum and Calcium by Organophosphorus Acids

Since most of the Raw Materials process liquors contain appreciable amounts of iron, aluminum and calcium, any complexing agent, to be satisfactory in organic extractions, should show selectivity for uranium. Accordingly, extractions of these cations from pure solutions have been studied. Examination of Tables 10 and 11 shows that the phosphinic acids as a class cause less emulsification and extract less aluminum than do the alkyl phosphates and the phosphonic acids, the behavior of the latter group being particularly bad on both counts.

In iron(III) solutions precipitation and emulsification occur with all three classes of compounds, being extremely troublesome in tests using phosphonic and alkyl phosphoric acids. The branched-chain phosphinic acids, di(2-ethylhexyl) and dicyclohexyl, show less extraction, especially in 1.5M phosphate, than do any of the other acids tried. Reduction of the iron to Fe(II) reduces extraction in all cases. These data are presented in Tables 12 and 13.

Table 8

EXTRACTION OF URANIUM(VI) FROM VARIOUS SOLUTIONS WITH PHOSPHONIC ACIDS

Phosphonic Acid (0.1M in CCl_4)	% Extraction From Uranium(VI) Solutions Containing ~0.008M NO_3^- pH=1	~0.008M NO_3^- pH=2	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2	3.0M $PO_4^{\equiv}$ pH=1	3.0M $PO_4^{\equiv}$ pH=2
Hexanephosphonic	100*	100*	90	98*	58	92*
Octanephosphonic	100*	100*	95*	99*	72*	93*
Decanephosphonic	100*	100*	93*	98*	47*	98*
Dodecanephosphonic[a]	100*	100*	78*	97*	29*	75*

* Emulsification
[a] Limit of solubility in CCl_4 is 0.05M.

Test Conditions: [U] = 0.004 molar.
Equal volumes of organic aqueous phases.
Carbon tetrachloride used as organic solvents
Contact time = 1 hour.

Table 9

EXTRACTION OF URANIUM(VI) FROM VARIOUS SOLUTIONS WITH ALKYL PHOSPHATES

Alkyl Phosphate (0.1M in CCl_4)	% Extraction From Uranium(VI) Solutions Containing ~0.004M NO_3^- pH=1	~0.004M NO_3^- pH=2	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2	3.0M $PO_4^{\equiv}$ pH=1	3.0M $PO_4^{\equiv}$ pH=2	0.5M $SO_4^{\equiv}$ pH=1	0.05M F^- pH=1
Monobutyl	Ppt'n.		--	--	--	--	--	--
Dibutyl	100	100	34	63	0	31	--	--
Diisoamyl	96	95	31	62	0	25	--	--
Monoctyl	100	100	89	96	62	84	100	100
Dioctyl	96	100	8	24	0	0	--	--
Mono and di-lauryl	*	*	82*	91*	20	*	--	--

* Emulsification

Test Conditions: Same as for Table 8.

Table 10

EXTRACTION OF ALUMINUM FROM VARIOUS SOLUTIONS

WITH PHOSPHINIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	Percent Removal from Solutions Containing $Al(NO_3)_3$ pH=1	$Al(NO_3)_3$ pH=2	$Al_2(SO_4)_3$ pH=1	$Al_2(SO_4)_3$ pH=2	$AlPO_4$ pH=1	$AlPO_4$ pH=2	1.5M $PO_4^{\equiv}$ pH=1	1.5M $PO_4^{\equiv}$ pH=2
Dibutyl	3	28*	6	39*	13	15	65	40
Diamyl	15	21	19	13	0	0	0	0
Dihexyl	2	30*	6	23*	2	13	6	6
Diheptyl	0	0	0	15	15	37	46	35
Dioctyl	5	17	8	21	3	7	0	0
Didecyl	10	23	0	8	0	7	0	2
Di(2-ethylbutyl)	8	12	10	22	12	21	34	37
Di(2-ethylhexyl)	9	13	11	22	0	4	0	10
Di cyclohexyl	7	6	8	16	10	2	25	4
Di-γ-phenyl propyl	9	12	6	21	16	--	21	53

* Partial precipitation.

Test Conditions: [Al] = 0.08 molar.
Equal volumes of organic and aqueous phases (20 ml).
Carbon tetrachloride used as organic solvent.
Contact time 3 minutes in separatory funnel.

Table 11

EXTRACTION OF ALUMINUM FROM VARIOUS SOLUTIONS

WITH PHOSPHONIC AND ALKYL PHOSPHORIC ACIDS

Phosphonic Acid (0.1M in CCl_4)	Percent Removal from Solutions Containing							
	$Al(NO_3)_3$		$Al_2(SO_4)_3$		$AlPO_4$		1.5M $PO_4^{\equiv}$	
	pH=1	pH=2	pH=1	pH=2	pH=1	pH=2	pH=1	pH=2
Hexane	55	64	49	64	76	81	11	46
Octane	43	57	45	72	33	73	27	48
Decane	29	40	27	39	77	65	56	41

Partial precipitation and emulsification in all cases.

Alkyl Phosphate (0.1M in CCl_4)								
Dibutyl	37*	41*	30*	52*	17*	48*	--	--
Diisoamyl	29*	43*	15*	42*	15	67*	15	48*
Monoctyl	39	44	37	54	32	64	24	40
Dioctyl	7	11	14	18	24	20	21	15

* Partial precipitation

Table 12

EXTRACTION OF IRON FROM VARIOUS SOLUTIONS

WITH PHOSPHINIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	Percent Removal from Solutions Containing							
	$Fe(NO_3)_3$		$Fe_2(SO_4)_3$		$FeSO_4$		0.005M $PO_4^{\equiv}$	1.5M $PO_4^{\equiv}$
	pH=1	pH=2	pH=1	pH=2	pH=1	pH=2	pH=1	pH=1
Dibutyl	88	97	97	93	0	9	51	41
Diamyl	85	89	88	87	--	--	51	19
Dihexyl	65	82	41	62	--	--	39	24
Diheptyl	71	64	45	52	--	--	64	28
Dioctyl	79	77	--	99	8	20	--	8
Didecyl	78	65	72	62	--	--	50	29
Di(2-ethylbutyl)	77	90	69	85	0	5	37	8
Di(2-ethylhexyl)	49	59	38	57	14	17	25	7
Di cyclohexyl	70	86	2	62	0	1	29	0
Di-γ-phenyl propyl	88	96	90	99	0	0	51	16

Partial precipitation in every case with the exception of Fe(II) tests and those using di(2-ethylbutyl), di(2-ethylhexyl) and di cyclohexyl phosphinic acids.

Test Conditions: [Fe] = 0.06 molar.
Equal volumes of organic and aqueous phases (20 ml).
Carbon Tetrachloride used as organic solvent.
Contact time 3 minutes in separatory funnel.

Table 13

EXTRACTION OF IRON FROM VARIOUS SOLUTIONS

WITH PHOSPHONIC AND ALKYL PHOSPHORIC ACIDS

Phosphinic Acid (0.1M in CCl_4)	Percent Removal from Solutions Containing *							
	$Fe(NO_3)_3$		$Fe_2(SO_4)_3$		$FeSO_4$		0.005M $PO_4^{\equiv}$	1.5M $PO_4^{\equiv}$
	pH=1	pH=2	pH=1	pH=2	pH=1	pH=2	pH=1	pH=1
Hexane	100	100	100	100	0	46	82	53
Octane	100	100	100	100	--	--	95	63
Decane	78	100	97	100	--	--	86	61

* Partial precipitation and emulsion in all cases

Alkyl Phosphate (0.1M in CCl_4)								
Dibutyl	87+	88+	91+	85+	0	2	49+	35+
Diisoamyl	99+	100+	92+	96+	--	--	62+	44+
Monoctyl	100	100	100	100	31	36	89	39
Dioctyl	31	18	26	21	0	0	32	4

\+ Partial precipitation.

Test Conditions: [Al] = 0.08 molar.
[Fe] = 0.06 molar.
Equal volumes of organic and aqueous phases (20 ml).
Contact time 3 minutes in separatory funnel.

Preliminary treatment of calcium solutions with di(2-ethylhexyl)phosphinic acid shows little, if any, extraction of the calcium.

Concentrations of Typical Organophorus Acids Required to Extract Uranium from Various Solutions

The variation of extraction coefficients with changes in reagent concentration is of general importance in extraction procedures. In order to characterize this behavior for the organophosphorus compounds, reagents thought to be typical of each class have been selected for detailed investigation. The phosphinic acids chosen were dibutyl, dioctyl and di(2-ethylhexyl), these compounds showing the effect of increase in chain length and branching the chain. Octane phosphonic acid was chosen as were dibutyl phosphate, monoctyl phosphate and dioctyl phosphate. These reagents are being tested in uranium solutions of 0.008M NO_3^-, 0.5M F^-, 0.5M $SO_4^=$, 0.5M $PO_4^{\equiv}$, 1.5M $SO_4^=$, and 1.5M $PO_4^{\equiv}$. Since previous data have shown that extraction invariably increased with pH, and since the purpose of these experiments is to determine reagent properties alone, the acidity of the solutions has been adjusted to pH = 1.1. Reagent concentrations are varied so that the uranium extractions cover a range of from 20 to 90%. Similar studies are planned with aluminum and iron.

It is hoped that application of the theory of solvent extraction to the data will then yield information about the nature of the complexes extracted and about the relative stabilities of these complexes.

Data are presented on Figures 1, 2, and 3 showing extractions with dioctyl phosphinic, di(2-ethylhexyl) phosphinic and monoctyl phosphate, respectively. Extraction coefficients (ratio of uranium concentration in organic phase to that in the inorganic phase) are plotted against the initial mole ratio of complexing agent to uranium. The curves show the relative importance of fluoride, sulfate, and phosphate ion in inhibiting the uranium extractions. The decrease in extraction with increase in sulfate concentration is nearly linear, but in phosphate solutions there is an initial sharp drop in extraction and then a more gradual decrease with increasing phosphate concentration. Considering uranium extraction alone and neglecting selectivity behavior, monoctyl phosphate will extract more uranium at lower reagent concentrations than will either of the phosphinic acids, with di(2-ethylhexyl)phosphinic acid, in turn, being better than dioctyl phosphinic acid. Comparisons of the extracting ability of the three reagents have been made in Tables 14, 15, 16, and 17. Studies with the other reagents are not yet complete.

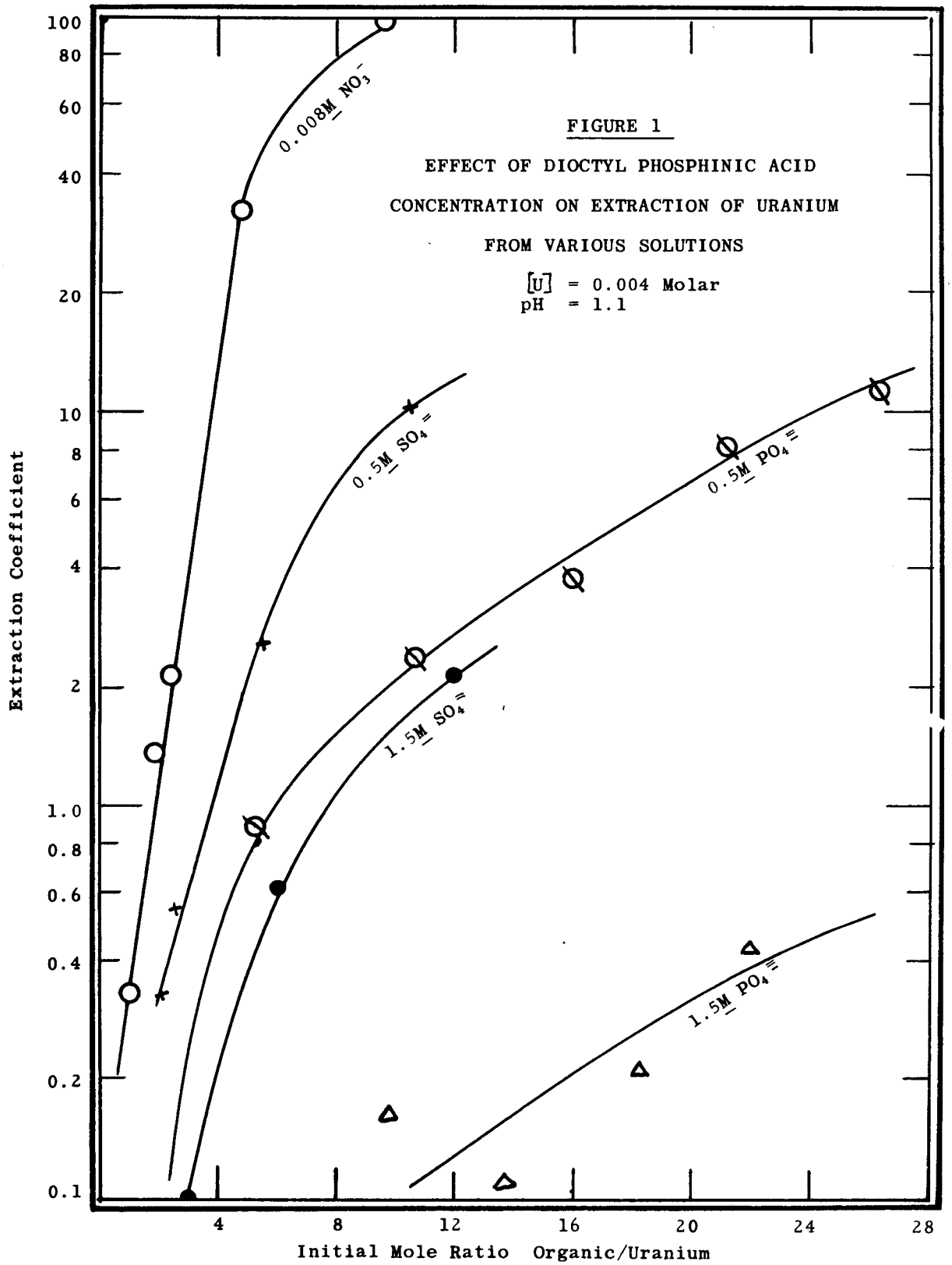


FIGURE 1
EFFECT OF DIOCTYL PHOSPHINIC ACID
CONCENTRATION ON EXTRACTION OF URANIUM
FROM VARIOUS SOLUTIONS
[U] = 0.004 Molar
pH = 1.1
0.008M NO3-
0.5M SO4=
0.5M PO4=
1.5M SO4=
1.5M PO4=
Extraction Coefficient
100
80
60
40
20
10
8
6
4
2
1.0
0.8
0.6
0.4
0.2
0.1
4
8
12
16
20
24
28
Initial Mole Ratio Organic/Uranium

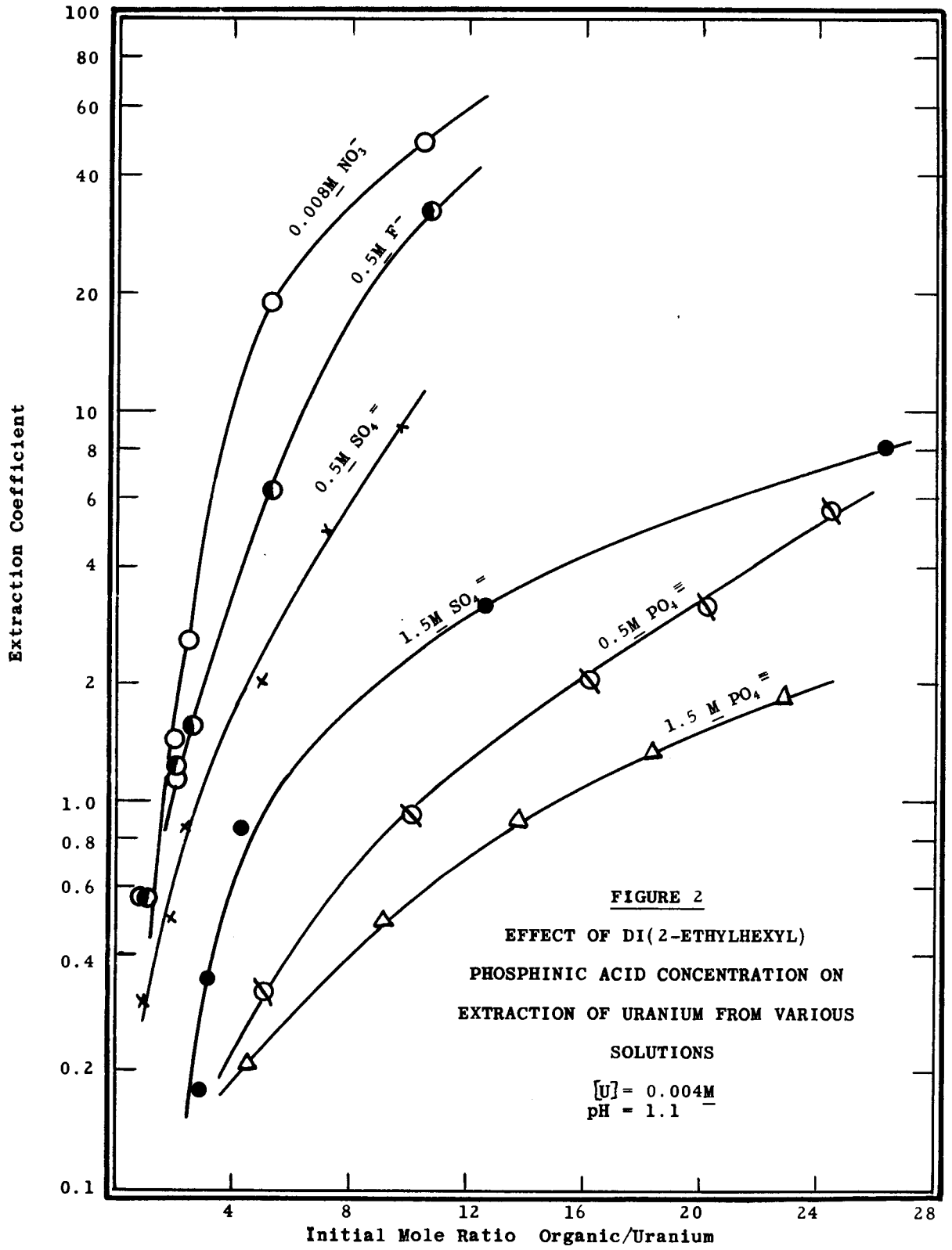


FIGURE 2

EFFECT OF DI(2-ETHYLHEXYL) PHOSPHINIC ACID CONCENTRATION ON EXTRACTION OF URANIUM FROM VARIOUS SOLUTIONS

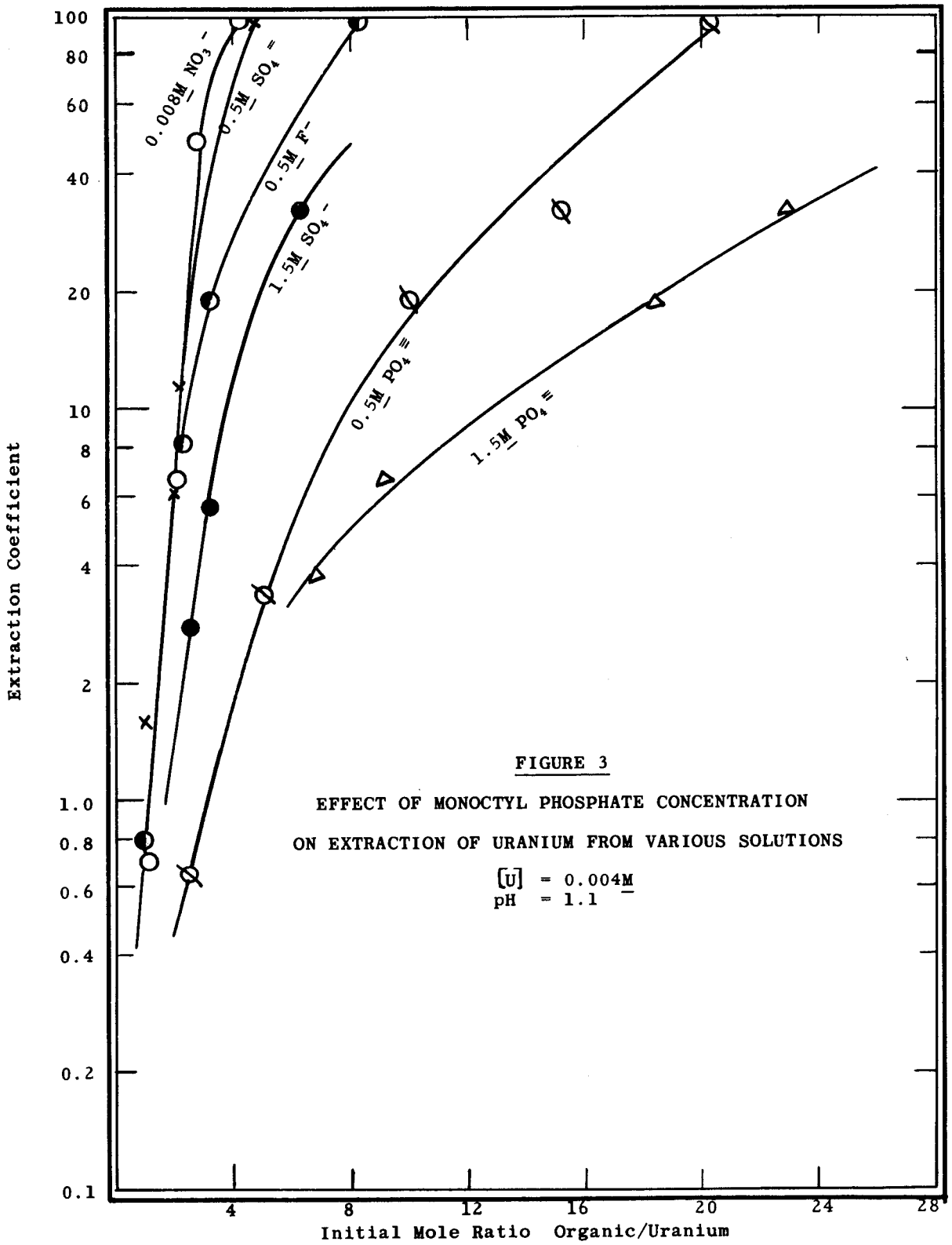


FIGURE 3

EFFECT OF MONOCTYL PHOSPHATE CONCENTRATION

ON EXTRACTION OF URANIUM FROM VARIOUS SOLUTIONS

[U] = 0.004M
pH = 1.1

Table 14

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN NITRATE SOLUTIONS WITH ORGANOPHOSPHORUS ACIDS

[U] = 0.004 molar
pH = 1.1
$[NO_3^-]$ 0.008 molar

Mole Ratio Organic/U	Monoöctyl Phosphate	Dioctyl Phosphinic	Di(2-ethyl) hexyl Phosphinic
1	0.8	0.3	0.5
2	6	1.2	1.1
4	97	13	13
6	>100	52	23
8	--	80	35

Table 15

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN PHOSPHATE SOLUTIONS

WITH ORGANOPHOSPHORUS ACIDS

[U] = 0.004 Molar
pH = 1.1

Mole Ratio Organic/U	0.5M $PO_4^{\equiv}$ Monooctyl Phosphate	0.5M $PO_4^{\equiv}$ Dioctyl Phosphinic	0.5M $PO_4^{\equiv}$ Di(2-ethyl) Hexyl Phosphinic	1.5M $PO_4^{\equiv}$ Monooctyl Phosphate	1.5M $PO_4^{\equiv}$ Dioctyl Phosphinic	1.5M $PO_4^{\equiv}$ Di(2-ethyl) Hexyl Phosphinic
4	1.9	0.4	0.1	--	--	0.2
8	11	1.6	0.7	5	--	0.4
12	25	2.7	1.3	9	.1	0.7
16	46	4.2	2.1	14	.2	1.1
20	95	6.9	3.4	23	.3	1.5
24	7100	10.5	5.2	35	.4	2.0

Table 16

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN SULFATE SOLUTIONS

WITH ORGANOPHOSPHORUS ACIDS

[U] = 0.004 Molar
pH = 1.1

Mole Ratio Organic/U	0.5M SO_4			1.5M $SO_4^{=}$		
	Monooctyl Phosphate	Dioctyl Phosphinic	Di(2-ethyl) Hexyl Phosphinic	Monooctyl Phosphate	Dioctyl Phosphinic	Di(2-ethyl) Hexyl Phosphinic
1	0.8	0.1	0.2	0.4	--	0.1
2	6.2	0.3	0.5	1.3	0.1	0.1
4	95	1.2	1.7	13	0.2	0.6
6	100	3.4	3.6	31	0.6	1.2
8	--	6.2	6.4	50	1.0	1.8

Table 17

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN FLUORIDE SOLUTIONS WITH ORGANOPHOSPHORUS ACIDS

[U] = 0.004 Molar
pH = 1.1
F = 0.5 Molar

Mole Ratio Organic/U	0.5M F^-		
	Monooctyl Phosphate	Dioctyl Phosphinic	Di(2-ethyl Hexyl phosphinic
1	0.8		0.6
2	6.7		1.1
4	30		3.8
6	58		8
8	95		16

Maximum Loading of Uranium Possible with Organophosphorus Acids

Preliminary experiments to determine the loading possible with di(2-ethylhexyl) and di(2-ethylbutyl) phosphinic acids have been made in which solutions of the acids in CCl_4 have been contacted several times with successive fresh portions of 0.004 M uranium nitrate and phosphate solutions. After several passes, the mole ratio of organic reagent to uranium in the organic phase becomes constant at a value of from three to four. These values are not to be interpreted as being the combining ratios of the extractable complexes since the concentration of uranium in the aqueous phase is much too low to cause complete saturation of the organic phase.

Saturation Experiments

In an attempt to determine the actual combining ratio of the extractable uranium complexes, saturation experiments are being run in which the organic phase is contacted with a series of solutions having uranium concentrations increasing to relatively high levels. If the complex is strong the asymptote of the curve obtained by plotting the mole ratio of complexing agent to uranium in the organic phase against the aqueous uranium concentration will indicate the complex existing in solution with the lowest combining ratio. Analytical data for these tests are not yet available.

Stripping Uranium from the Organic Phase

Little work has been done as yet on the very important phase of solvent extraction in which the uranium is recovered from the organic extract. Because of the strong complex which uranium(VI) forms in acid fluoride systems,[6] some experiments have been made in which the organic extract containing di(2-ethylhexyl) phosphinic acid is contacted with dilute (3%) HF solutions having a pH of 1.5. The data of Table 18 and Figure 4 show that nearly complete removal of the uranium is made from the organic into the aqueous phase. (Compare this behavior with the extraction into the organic phase from 0.5M F^- solutions at pH = 1 shown in Figure 2.) Moreover, the organic phase has been recycled six times to fresh uranium solution without any drop in extraction ability beyond that shown in the second extraction. Further studies in this and other possible stripping cycles are being made.

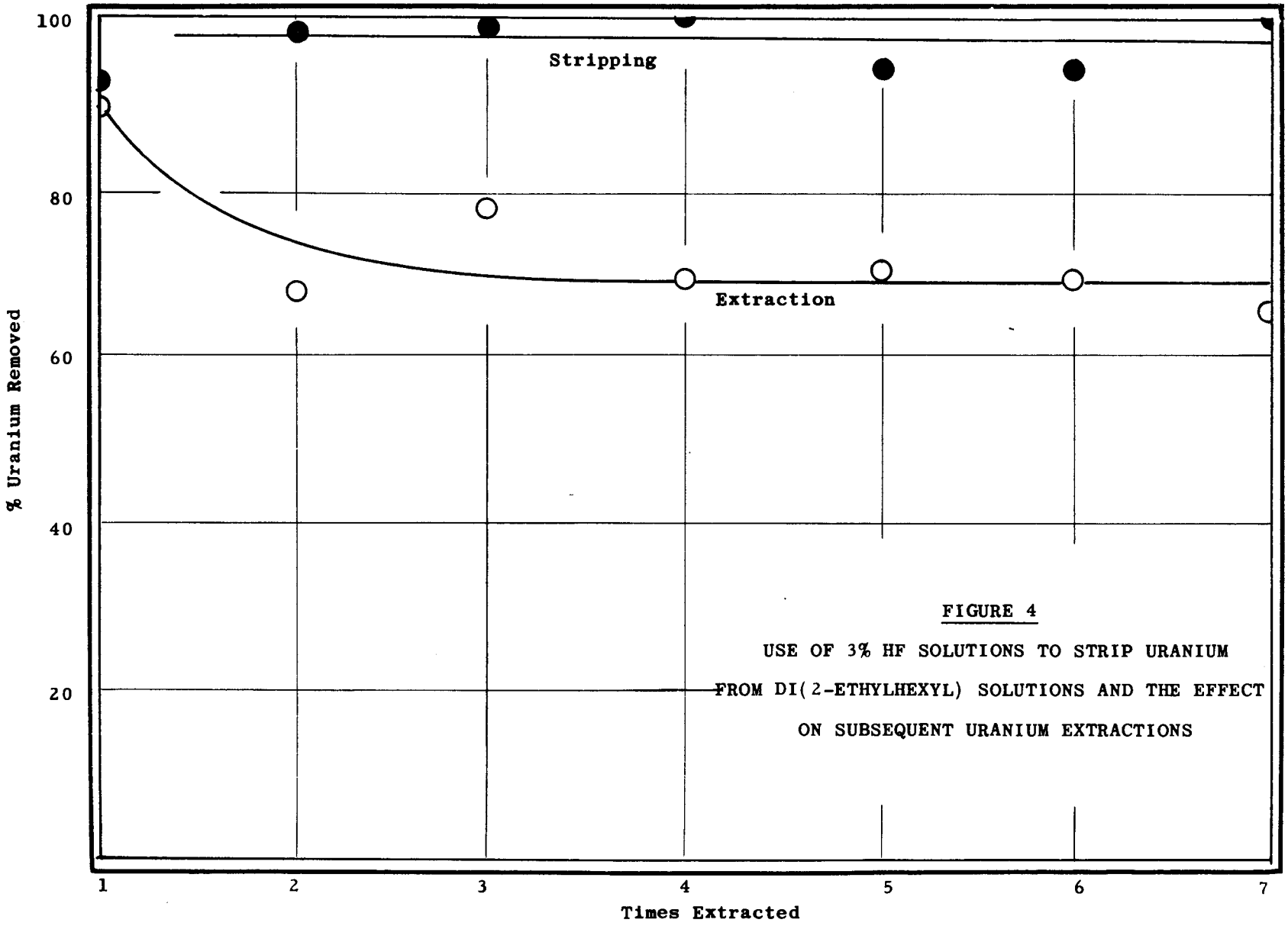


FIGURE 4

USE OF 3% HF SOLUTIONS TO STRIP URANIUM FROM DI(2-ETHYLHEXYL) SOLUTIONS AND THE EFFECT ON SUBSEQUENT URANIUM EXTRACTIONS

Table 18

STRIPPING OF URANIUM FROM ORGANIC PHASE WITH 3% HF SOLUTIONS

Conditions: 3% HF solution, pH=1.5 contacted with organic phase (20 ml each)
Concentration of organic reagent equals 0.016M in CCl_4.
Organic reagent = Di(2-ethylhexyl)phosphinic acid.
Stripped organic phase used to re-extract fresh aqueous uranium.
Concentration of uranium in aqueous phase = 0.004M.
Mole ratio of organic reagent to uranium = 4:1.

Times Extracted	% Uranium Extracted from Aqueous Phase	% Uranium Stripped from Organic Phase
1	89	92
2	67	98
3	77	99
4	69	100
5	70	94
6	69	94
7	65	100

Physical Properties of the Organophosphorus Acids

Table 19 presents as many of the physical properties of the organophosphorus compounds as are known at the present time. Since much of the fundamental work in this program depends heavily upon the purity of the reagents, a method for further purifying the non-distillable reagents has been developed. The distillable acid chloride of the phosphorus compound is formed and after two distillations the acid chloride is hydrolyzed to yield the original acid. It is hoped that this method will improve the purity of the very interesting branched-chain phosphinic acids. The solids described in the table are all quite pure having been recrystallized several time. The figures listed under the heading "Analysis" are based on total carbon analysis, while those under "Titration" are based upon potentiometric titrations with sodium hydroxide.

Synthesis Program

The synthesis of the phosphinic acids described in the preceding sections has been according to the following general method:

$$R\text{-}Br + Mg \xrightarrow[\text{Ether}]{\text{Dry}} R\text{-}Mg\text{-}Br$$

$$2R\text{-}Mg\text{-}Br + C_5H_5N\cdot POCl_3 \rightarrow R_2\text{-}PO_2H + 2MgClBr + C_5H_5N\cdot HCl$$

In a 1-liter, 3-necked flask equipped with stirrer, condenser, dropping funnel, and inlet for dry nitrogen, are placed 24.3g (1 g-atom) of magnesium, 100 ml of dry ether, and 10 ml of alkyl bromide. After reaction begins, 100 ml of dry ether is added and the mixture is treated with a solution of alkyl bromide (1 mole minus the 10 ml previously added) in 300 ml of dry ether. The rate of addition is such that the reaction does not become too vigorous. After addition is complete, the mixture is refluxed until all or nearly all of the magnesium has reacted.

In a 3-liter, 3-necked flask equipped with stirrer, condenser, dropping funnel, and inlet for dry nitrogen, are placed 77g (0.5 mole) of phosphorus oxychloride and 250 ml of dry ether. The solutions is treated dropwise with 39.5g (0.5 mole) of dry pyridine. The resultant mixture is then immediately treated slowly with the solution of Grignard reagent just prepared. After addition is complete (about 1 hour) the

Table 19

PHYSICAL PROPERTIES OF ORGANOPHOSPHORUS ACIDS

Name	M.W.	Description	(°C) M.P. or B.P	(%) Estimated Purity Anal.	Titrn.	H_2O Solvent (ppm)
Dibutyl Phosphinic	178	Wh. cryst. solid	58-61	--	--	
Diamyl Phosphinic	206	"	56-57	99	--	
Dihexyl Phosphinic	234	"	78-79	99	--	51
Diheptyl Phosphinic	262	"	71-73	99	87	26
Dioctyl Phosphinic	290	"	73-75	100	--	48
Didecyl Phosphinic	346	"	85	99	--	23
Di-2-butyl Phosphinic	178	Non-distillable liquid		--	--	--
Di-2-amyl Phosphinic	206	"		90	101	--
Di(2-ethylhexyl)Phosphinic	290	"		90	91	35
Di(2-ethylbutyl)Phosphinic	234	"		--	--	--
Diisobutyl Phosphinic	178	"		--	103	--
Diisoamyl Phosphinic	206	"		--	65	--
Diphenyl Phosphinic	218	Wh. cryst. solid	191-193	--	--	--
Dibenzyl Phosphinic	246	"	175-180	90	--	--
α-phenylethyl Phosphinic	274	"	114-116	--	--	--
β-phenylethyl Phosphinic	274	"	83-85	--	--	--
γ-phenylpropyl Phosphinic	302	"	100-1004	97	--	38
Dicyclohexyl Phosphinic	262	"	136-141	95	--	--
Di(3,5,5)Trimethyl cyclohexyl Phosphinic	314	"	168-170	99	--	--
Di(3,5,5)Trimethyl hexyl Phosphinic	318	Non-distillable liquid		--	109	--
Hexane Phosphonic	166	Wh. cryst. solid	103-105	--	--	--
Octane Phosphonic	194	"	98-100	--	--	--
Decane Phosphonic	222	"	94-98	--	--	--
Dodecane Phosphonic	250	"	90-95	--	--	--
Hexadecane Phosphonic	306	"	94-96	--	101	--

Table 19 (contd.)

Name	M.W.	Description	(°C) M.P. or B.P.	(%) Estimated Purity Anal.	Titrn.	H_2O Solvent (ppm)
Monobutyl Phosphate	155	Lt.-yellow liquid	--	--	92	--
Dibutyl Phosphate	210	"	--	--	99	220
Monoisoamyl Phosphate	168	"	--	--	95	--
Diisoamyl Phosphate	238	"	--	--	98	--
Monoctyl Phosphate	210	"	--	--	96	200<<400
Dioctyl Phosphate	322	"	--	--	94	62

mixture is stirred 2 hours longer, then decomposed by the slow addition of 300g of ice water. Usually an oil separates. It may be extracted with ether and (if solid) crystallized from an appropriate solvent (e.g., dilute alcohol).

The phosphonic acids have been prepared according to the following method:

$$R\text{-}Br + P(OEt)_3 \xrightarrow{160^\circ} R\text{-}\overset{O}{P}(OEt)_2 + Et\text{-}Br$$

$$R\text{-}\overset{O}{P}(OEt)_2 + 2H_2O \xrightarrow{HCl} R\text{-}\overset{O}{P}(OH)_2 + 2EtOH$$

An equimolar mixture of alkyl halide and triethyl phosphite (Organic Synthesis, Vol. 31) is heated at 160° for 3 or 4 hours in a flask surmounted by an air condenser so that the reactants reflux and the ethyl halide escapes.

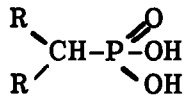
The resultant mixture is distilled in vacuo; usually a rather low pressure is desired (1 mm), but this depends on the compound being prepared. Distillation of the diethyl ester may be omitted, but ordinarily the final product is more easily purified if the ester is distilled before hydrolysis.

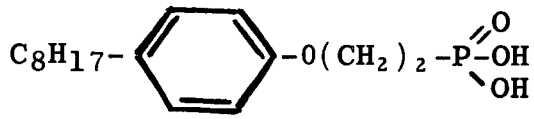
The ester is hydrolyzed by refluxing with about 4 volumes of concentrated hydrochloric acid. The resultant oil may be extracted with ether and, if the compound is solid, crystallized from an appropriate solvent (e.g., ligroin).

Effort will be spent in future synthesis work on preparation of the following general types of compounds.

1. Additional phosphinic acids to test further the effect of the configuration of the acid. Among others, phosphinic acids are to be prepared from butyl cellosolve and butyl carbitol.

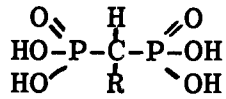
2. Additional phosphonic acids with the hope of finding some with more desirable solvent extraction properties than those already tested. In view of their remarkable extraction ability more emphasis will be placed on these compounds. One compound to be synthesized is 2(4-octylphenoxy)ethane phosphonic acid.





3. Bi-dentate phosphorus acids. It is possible that one such molecule will provide all the complexing groups necessary to extract uranium and at the same time make difficult the complexing of three-valent ions, iron and aluminum.

(a) Diphosphonic acids of the type

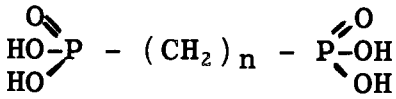


Where R is $\begin{cases} H \\ \text{alkyl} \\ \text{aryl} \end{cases}$

will be prepared.

(b) The above compounds will be alkylated at the α-hydrogen to produce compounds having low water solubility.

(c) Polymethylene diphosphonic acids



Where $n=2-6$

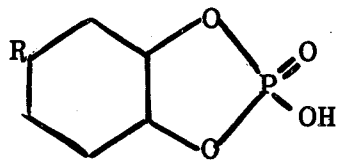
4. Thiophosphoramides of the type, tributylthio phosphoramide

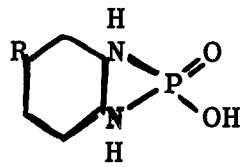
$$(BuN)_3\ P{=}S$$

5. Quaternary salts of phosphorus compounds such as tetrabutyl phosphonium chloride

$$(Bu)_4\ P^+Cl^-$$

6. Cyclic phosphate esters and amides having one acidic hydrogen atom





Recovery of Thorium from Monazite Sand Using Solvent Extraction

Continued work on the separation of thorium from rare earths by extraction of the organophosphorus complexes has been encouraging. Essentially complete extractions of thorium have been obtained in single stage extractions using small amounts of reagents; whereas the presence of rare earths in the organic phase has not been detected by ordinary spectrographic means. This is a somewhat better picture than presented last quarter where attempts were made to determine the tiny (if any) extraction of rare earths by analyzing the concentrated aqueous solutions before and after extraction (Table 9, ORNL-1220).

Preparation of Solutions

Two different solutions containing mixtures of thorium and rare earths were prepared. The first was made up by treating monazite sand directly with sulfuric acid, and the second by treating with sulfuric acid an oxalate precipitate of thorium and rare earths which was obtained some time ago during the processing of monazite for other purposes.

Solution of Monazite Sand. Fifty grams of monazite sand were heated with 100 ml of concentrated H_2SO_4 for 7 hours on a hot plate at low heat and for 8 hours at high heat, during which time most of the excess H_2SO_4 was destroyed. The resulting cake was leached with water and the insoluble material was filtered off and retreated with H_2SO_4. After the second treatment only 2 g of material remained undissolved and this appeared to be silica. The aqueous solution was treated with H_2SO_4 so that the estimated free acid concentration was about 10%. The total volume at this point was 800 ml. Thorium and rare earth contents of the solution are shown in Table 20.

Solution of Oxalate Precipitate. The oxalate precipitate was prepared some time ago by treating monazite sand with NaOH, leaching with water to remove the phosphates, dissolving the hydrous oxides in HCl, and precipitating the thorium and rare earths with oxalic acid. One-hundred grams of this precipitate was heated with 50 ml of concentrated H_2SO_4 and 180 ml of concentrated HNO_3 was added slowly to destroy the oxalic acid. The slurry was heated at a high temperature for 8 hours during

Table 20

ANALYSES* OF SOLUTIONS CONTAINING THORIUM AND RARE EARTHS

Constituent	Approximate Conc. (mg/ml) R. E. Solution	Monazite Solution
Th	5	4.5
Ce	17	17
La	6.5	6
Pr	2	1.7
Y	0.2	0.2
Sm	1.5	1.1
Gd	<5 (4)	<5 (4)
Dy	0.2	0.2
Yb	0.2	0.2

* Thorium was obtained by chemical analyses, others were determined spectrographically.

which time most of the excess H_2SO_4 was decomposed. The resulting cake was leached with dilute sulfuric acid and the insoluble material was filtered off and retreated with H_2SO_4 and HNO_3. Essentially all of the material was dissolved after the second treatment. The aqueous solution was about 10% in excess H_2SO_4 and the final volume was 1000 ml. Thorium and rare earth contents are given in Table 20.

Analytical

Thorium and the individual rare earths were determined spectrographically in most cases. As a check, chemical analyses were also made when possible for thorium, cerium, and total rare earth oxides.

Spectrographic analyses of rare earth solutions are usually made on aqueous samples and the limit of detection by the method routinely employed in the ORNL Y-12 Spectrochemical Laboratory is about 100 ppm. To determine whether important differences might arise in the analyses of organic solutions a series of solutions of Ce(IV) in a monoöctyl phosphate, carbon tetrachloride mixture were prepared and submitted for both chemical and spectrographic analyses. The comparative results were as follows:

Chemical (ppm of Ce)	Spectrographic (ppm of Ce)
660	780
140	200
40	100

The results are in fair agreement and, from the limited data, it is indicated that the spectrographic limit of detection may be lower than expected. Cerium can apparently be detected in concentrations as low as 40 ppm.

Extraction Results

As shown in Tables 21 and 22, the extractions of thorium from monazite sand solutions are very good using solutions of monoöctyl phosphate in petroleum ether or carbon tetrachloride. Over 90% of the thorium was extracted in a single stage using only about 6 moles of the monoöctyl phosphate per mole of thorium. The separations of phases were for the most part clear and reasonably rapid. Under the conditions tested,

Table 21

EXTRACTION OF THORIUM FROM SOLUTIONS CONTAINING RARE EARTHS

Solution Extracted[1]	Extractant[1] 0.1M	Th Extd. (%)	R.E. Content of Organic* (Spectrographic)					Remarks
			Ce	La	Nd	Pr	Sm	
Monazite	Monoöctyl phosphate in petroleum ether	>93	ND	ND	ND	ND	ND	Clear separation
R.E.		>94	ND	ND	ND	ND	ND	Clear separation
Monazite	Monoöctyl phosphate in CCl_4	88	ND	ND	ND	ND	ND	Organic cloudy-- aqueous clear
R.E.		87	ND	ND	ND	ND	ND	"
Monazite	Dihexyl Phosphinic acid in CCl_4	24	ND	ND	ND	ND	ND	Very slight ppt. at interphase
R.E.		32	ND	ND	ND	ND	ND	Clear separation.

1 20 ml of aqueous and 20 ml of organic were used for all tests.

* ND means "not detectable." In normal practice this means that the concentration of each rare earth must be less than 100 ppm.

Table 22

EXTRACTION OF MONAZITE SOLUTION* WITH VARYING CONCENTRATIONS OF MONOOCTYL PHOSPHATE IN PETROLEUM ETHER

MOP Conc.** (M)	Th Removed from Aqueous (%)	Remarks
0.02	25	***
0.04	50	***
0.06	65	***
0.08	75	***
0.10	94	***

* For analyses of monazite solution see Table 20.

** 25 ml of aqueous and 25 ml of organic were used in each test.

*** A gummy solid collected between the two phases and upon analysis was found to contain significant amounts of thorium. This material was not noticed in any of several tests when the MOP/Th ratio was 5 or greater.

dihexylphosphinic acid seemed to be inferior to monoöctyl phosphate as a complexing agent for thorium, and carbon tetrachloride appears to be less acceptable than petroleum ether as a solvent.

The factor for the separation of thorium from rare earths by this method is apparently very large. None of the organic extracts shown in Table 21 contained detectable quantities of the major constituents of monazite sand, i.e., Ce, La, Nd, Pr, and Sm, using the usual spectrographic method.

The rare earths were still not detected in a more concentrated sample of the organic extract. In this test, 180 ml of 0.1 M monoöctyl phosphate in petroleum ether was used to extract 180 ml of monazite sand solution. The organic phase was evaporated and ignited to drive off organic matter and the solids were redissolved in 50 ml of dilute sulfuric acid. Spectrographic examinations of the 50 ml concentrate showed over 10,000 ppm Th but no detectable quantities of Ce, La, Pr, Nd, or Sm. Assuming the detection limit at 100 ppm this means that there was less than 28 ppm of the individual elements in the original organic phase. Thorium was not detected in the aqueous raffinate, indicating a single stage extraction of over 99%.

Other organophosphorus compounds would be expected to react with thorium and several new reagents are being tested. Arrangements are also being made to obtain more accurate analyses for rare earths in the thorium product.

Removal of Thorium from the Organic Phase

Only limited studies have been made of methods for separating thorium from the organic phase. Moderate success has been obtained by treating the petroleum ether solutions of monoöctyl phosphate with sodium hydroxide to form thorium hydroxide (solid) and sodium octyl phosphate which is soluble in the aqueous phase. About 80% of the octyl phosphate has been recovered by acidifying the caustic solution and extracting with fresh petroleum ether.

Oxalic acid, hydrofluoric acid, and strong sulfuric and phosphoric acid treatments of the organic extract are being studied.

Precipitation of Thorium with Organophosphorus Compounds

Of the compounds tested, benzene phosphonic acid and dibutyl phosphate have given fairly complete precipitation of the thorium from the monazite and rare earth solutions described

in Table 20. Only small amounts of reagent have been required.

Analyses of the precipitates for rare earth content are not complete. It has been observed, however, that benzene phosphonic acid readily precipitates Ce(IV) but gives only a slight turbidity when added to a solution of Ce(III), possibly due to the presence of Ce(IV).

Further studies of the precipitation of thorium with reagents of this kind are being made.

Studies of the Uranyl Phosphate System

J. M. Schreyer, C. F. Baes, J. M. Lesser

The investigation of uranyl phosphate solutions described in the last report (ORNL-1220) has been continued.

Analytical

In this investigation, initial attempts to apply the method recommended by Kolthoff and Lingane[7] to the analysis of uranium(VI) solutions containing phosphate were unsuccessful because of the precipitation of uranium(IV) phosphate in the Jones reductor. It has been found that precipitation can be avoided by adjusting the acidity of the solution to 4.5 M in sulfuric acid.

In a series of experiments to determine the extent of reduction of uranium-phosphate solutions in the Jones reductor, excellent agreement in analysis was obtained between aerated and non-aerated samples of known stock solutions. It was further found that uranium(III) phosphate solutions were quantitatively oxidized to uranium(IV) solution when passed through the reductor.

The procedure currently used includes the modifications of increased acidity to prevent the precipitation of uranium (IV) phosphate and the omission of the aeration step.

Analytical Procedure

Introduce a sample (free of nitrate) containing approximately 2 millimoles of uranium into a 150 ml beaker. Add 20 ml of concentrated sulfuric acid and 20 ml of 85% phosphoric acid. Dilute with water to 75 to 80 ml and cool. Using gentle suction, pass the cold uranium(VI) solution through the reductor at a rate of about 30 ml per minute.

Wash the reductor with four 40 ml portions of 7.5% sulfuric acid and one 40 ml portion of water, adding the washings to the reduced solution. The reduced solution should have a light bluish-green color characteristic of uranium(IV) in phosphoric acid solutions. Add 30 ml of ferric chloride solution (100g/l), swirl, and let stand for 5 to 10 minutes, or until the solution becomes distinctly yellow. Add 15 ml of 85% phosphoric acid and 8 drops of sodium diphenylamine sulfonate indicator. Titrate immediately with standard 0.1N dichromate solution to a sharp purple end point. The indicator blank is negligible.

Solubility Measurements

Measurements in Phosphoric Acid

The solubility of $UO_2HPO_4 \cdot 4H_2O$ in phosphoric acid solutions has been measured in the range, 0.22-6.03 molar total phosphate, at 25°C. The results are presented in Figure 5 and in Curve I of Figure 6. The coordinates of each point in these figures represent the total analytical concentration of uranium and of phosphate in the corresponding saturated solution. Included in Figure 5 are some data reported by G. R. Leader[8] which are in satisfactory agreement with the present more extensive data.

Controlled Acidity Measurements

The solubility measurements of $UO_2HPO_4 \cdot 4H_2O$ in 1M perchloric acid solutions at 25°C have been extended both in the region of excess uranyl perchlorate and, in particular, in the region of excess phosphoric acid. All the data obtained thus far in this series of measurements, along with the data of G. R. Leader in 1M nitric acid[8] are plotted in Curve II of Figure 6.

These data have been corrected for acidity changes accompanying solution of the salt in accordance with the following equilibria:

(1) $$UO_2HPO_4 + 2H^+ = UO_2^{++} + H_3PO_4$$

$$K_S = \frac{[UO_2^{++}]\,[H_3PO_4]}{[H^+]^2} = .0017$$

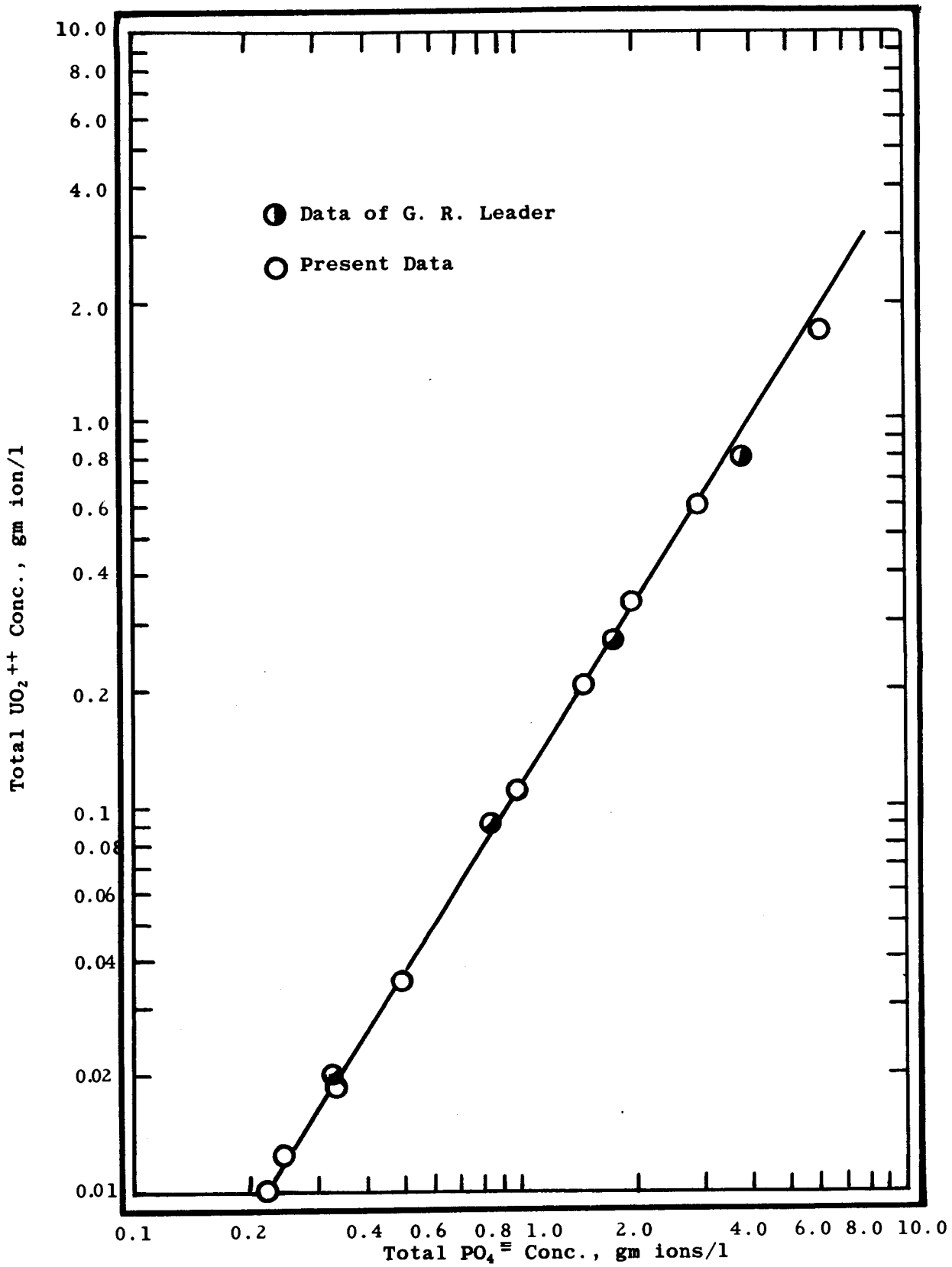


Figure 5

SOLUBILITY OF $UO_2HPO_4 \cdot 4H_2O$ IN H_3PO_4

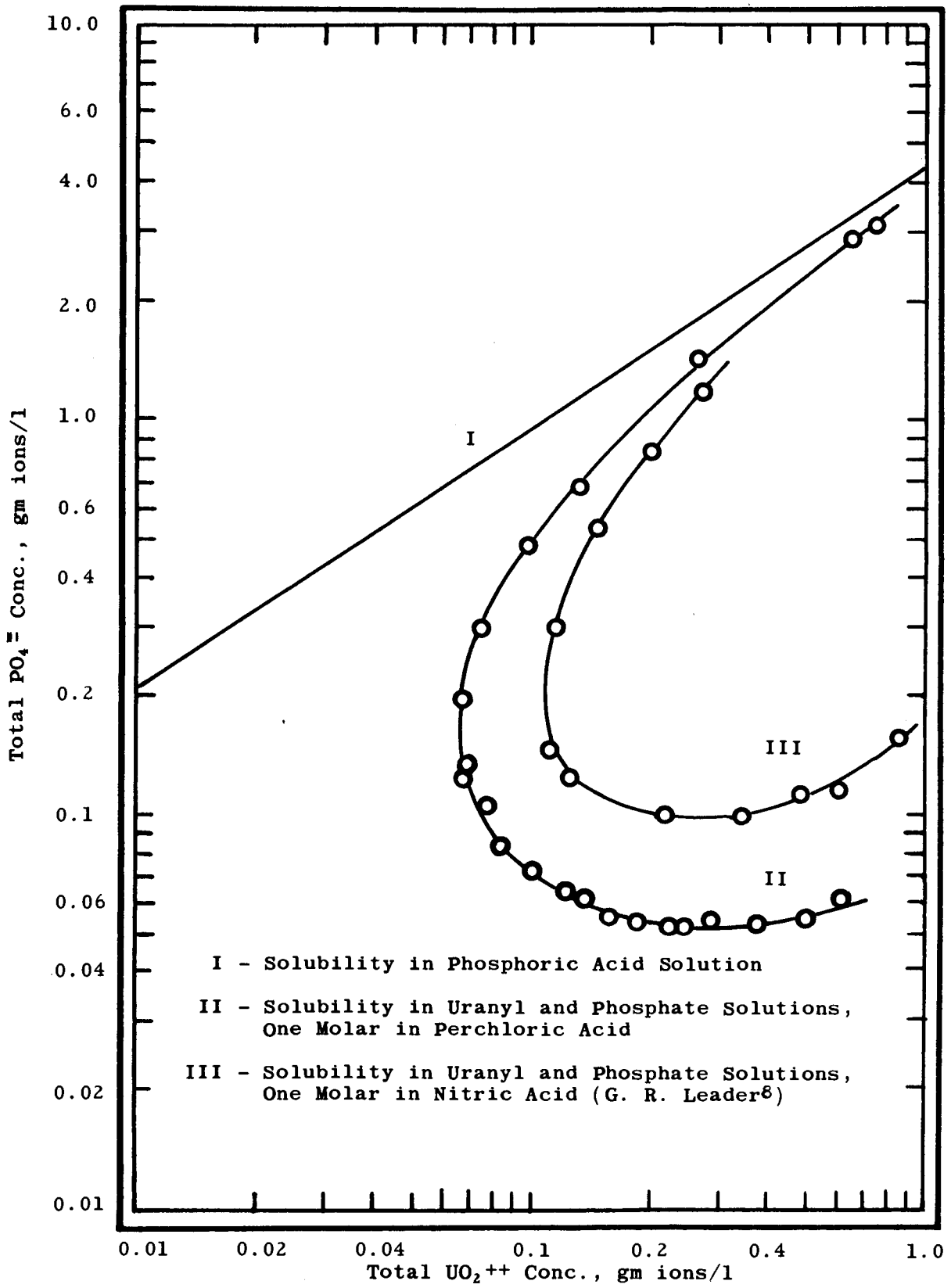


Figure 6

SOLUBILITY BEHAVIOR OF $UO_2HPO_4 \cdot 4H_2O$

(2) $$UO_2HPO_4 + H^+ = UO_2H_2PO_4^+$$

$$K_1 = \frac{[UO_2H_2PO_4^+]}{[H^+]} = 0.05$$

(3) $$UO_2HPO_4 + (n-1)H_3PO_4 = UO_2(H)_{3n-2}(PO_4)_n$$

$$K_n = \frac{[UO_2(H)_{3n-2}(PO_4)_n]}{[H_3PO_4]^{n-1}}$$

The evidence for equilibria (1) and (2) was presented in the previous report (ORNL-1220). It is apparent that K_1 is equal to the limiting solubility of UO_2HPO_4 in excess uranyl perchlorate (ca. 0.05M). The K_s value is obtained from K_1 using the previously reported stability constant for the one to one complex;

$$K = \frac{[UO_2H_2PO_4^+]\,[H^+]}{[UO_2^{++}]\,[H_3PO_4]} = 20\text{-}35$$

Several of the solubility runs in both phosphoric acid and perchloric acid are being repeated with longer shaking times to test whether or not equilibrium has been reached. Rate of solution studies in 1M perchloric acid alone indicate that equilibrium is established within the first 30 minutes of shaking. Chemical analysis of slurry samples as well as x-ray powder pattern measurements are as yet incomplete, but results obtained thus far indicate no change in the solid phase.

The rapidly increasing solubilities of $UO_2HPO_4.4H_2O$ in excess phosphoric acid shown by Curves I and II of Figure 6 indicate the presence of complex ions in which the phosphate to uranium ratio is greater than unity. Furthermore, the solubility of the salt becomes less dependent on the acidity with increasing phosphoric acid concentration, as indicated by the convergence of Curves I, II, and III. This result suggests that the most abundant complexes present in excess phosphoric acid are neutral, of the type indicated in equation (3) above, since alternative forms of the dissolution

reaction involve hydrogen ions. The solubility data in Figure 5 were fitted satisfactorily in the range 0.2-1.5M total phosphate, by a solubility curve calculated from the additional assumed equilibria:

(4) $$UO_2HPO_4 + H_3PO_4 = UO_2(H_2PO_4)_2$$

$$K_2 = \frac{[UO_2(H_2PO_4)_2]}{[H_3PO_4]} = \text{Ca. } 0.01$$

(5) $$UO_2HPO_4 + 2H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4)$$

$$K_3 = \frac{[UO_2(H_2PO_4)_2(H_3PO_4)]}{[H_3PO_4]^2} = 0.28$$

wherein the values of K_2 and K_3 were chosen to yield the best fit to the data.

In the present range of the solubility data in phosphoric acid alone, the 3:1 complex appears to be by far the most abundant uranyl species, permitting the estimation of K_3 to a few percent.

pH Measurements

In order to investigate further the hydrogen-ion dependence of the dissolution of $UO_2HPO_4 \cdot 4H_2O$ in phosphoric acid, the following pH measurements were carried out.

In a preliminary experiment, employing a Beckman pH meter, the pH of a 2M phosphoric acid solution was measured before and after it had been saturated with $UO_2HPO_4 \cdot 4H_2O$. Because of the limitations of the glass electrode in this pH range, a similar measurement was made with a quinhydrone-saturated NaCl, calomel cell, in which the 2M H_3PO_4 was brought to 0.2M in $UO_2HPO_4 \cdot 4H_2O$. In a third experiment, 2M phosphoric acid was brought to 0.5M in $UO_2(ClO_4)_2$, and the pH change measured. The results of these experiments are summarized in Table 23.

Table 23

pH MEASUREMENTS IN 2M H_3PO_4

Exp.	pH Electrode	Initial pH	Final pH	Final U Concentration
1	Glass	0.75	0.7	$0.5(UO_2HPO_4)$
2	Quinhydrone	0.8	0.8	$0.2(UO_2HPO_4)$
3	Quinhydrone	0.8	0.0	$0.5(UO_2(ClO_4)_2)$

The pH values listed in experiments 2 and 3 were obtained with the use of a calibration curve prepared from potential measurements of a series of 2M H_3PO_4 solutions containing known amounts of perchloric acid.

In view of the large acid and salt concentrations involved, these pH values are only approximate. They are sufficiently accurate, however, to indicate the hydrogen ion dependence of the dissolution reaction. For example, if one mole of hydrogen ion were consumed for each mole of salt that dissolved, the final pH values in experiments 1 and 2 would be approximately 1.5 and 1.2, respectively. If a mole of hydrogen ion were liberated, the values would be approximately 0.3 and 0.5, respectively. Thus it may be concluded from the results of these two experiments that a reaction of the type shown in equation (3) occurs, resulting in the formation of a neutral complex. In the case of experiment 3, the reaction may be written

$$UO_2^{++} + nH_3PO_4 = UO_2(H)_{3n-2}(PO_4)_n + 2H^+$$

leading to a final solution which is one molar in hydrogen ion, in agreement with the observed final pH.

Spectrophotometric Studies

The method of continuous variation has been applied to a series of uranyl phosphate solutions in which the acidity was adjusted to approximately 0.1M with perchloric acid. The ionic strength of these solutions was held constant at $\mu = 0.142$ through addition of sodium perchlorate. The amount of sodium perchlorate added was adjusted to compensate for the change in concentration of the complex, $UO_2H_2PO_4^+$,

calculated from the following equilibrium expression:

$$K = \frac{[UO_2H_2PO_4^+][H^+]}{[H_3PO_4][UO_2^{++}]} = 30$$

The sum of the analytical concentration of uranyl ion and phosphoric acid was equal to 0.014M. The measurements were made in the region of the ultra-violet because the higher extinction coefficients which were found in this region are more convenient for measurements in these dilute solutions. The curves in Figure 7 were obtained by plotting Y, the difference between the observed absorbance value and that which would be given by the uranyl species, if no complexing occurred, versus the ratio,

$$\frac{[PO_4^{\equiv}]}{[PO_4^{\equiv}] + [UO_2^{++}]}$$

where $[PO_4^{\equiv}]$ and $[UO_2^{++}]$ represent the analytical concentrations. These data indicate the presence of a complex species in which the ratio of uranium to phosphorous is one. This is in agreement with the results of the previous study in 1M perchloric acid.

The results of both of these series of measurements are not inconsistant with equilibria (4) and (5), since the relative abundance of the more highly complexed species in these solutions may be shown to be small. Thus, from equilibria (1), (2), (4) and (5), one may write,

(6) $$UO_2^{++} + H_3PO_4 = UO_2(H_2PO_4)^+ + H^+$$

$$\frac{[UO_2H_2PO_4^+][H^+]}{[UO_2^{++}][H_3PO_4]} = \frac{K1}{K_S} = 30$$

(7) $$UO_2^{++} + 2H_3PO_4 = UO_2(H_2PO_4)_2 + 2H^+$$

$$\frac{[UO_2(H_2PO_4)_2][H^+]^2}{[UO_2^{++}][H_3PO_4]^2} = \frac{K_2}{K_S} = 6$$

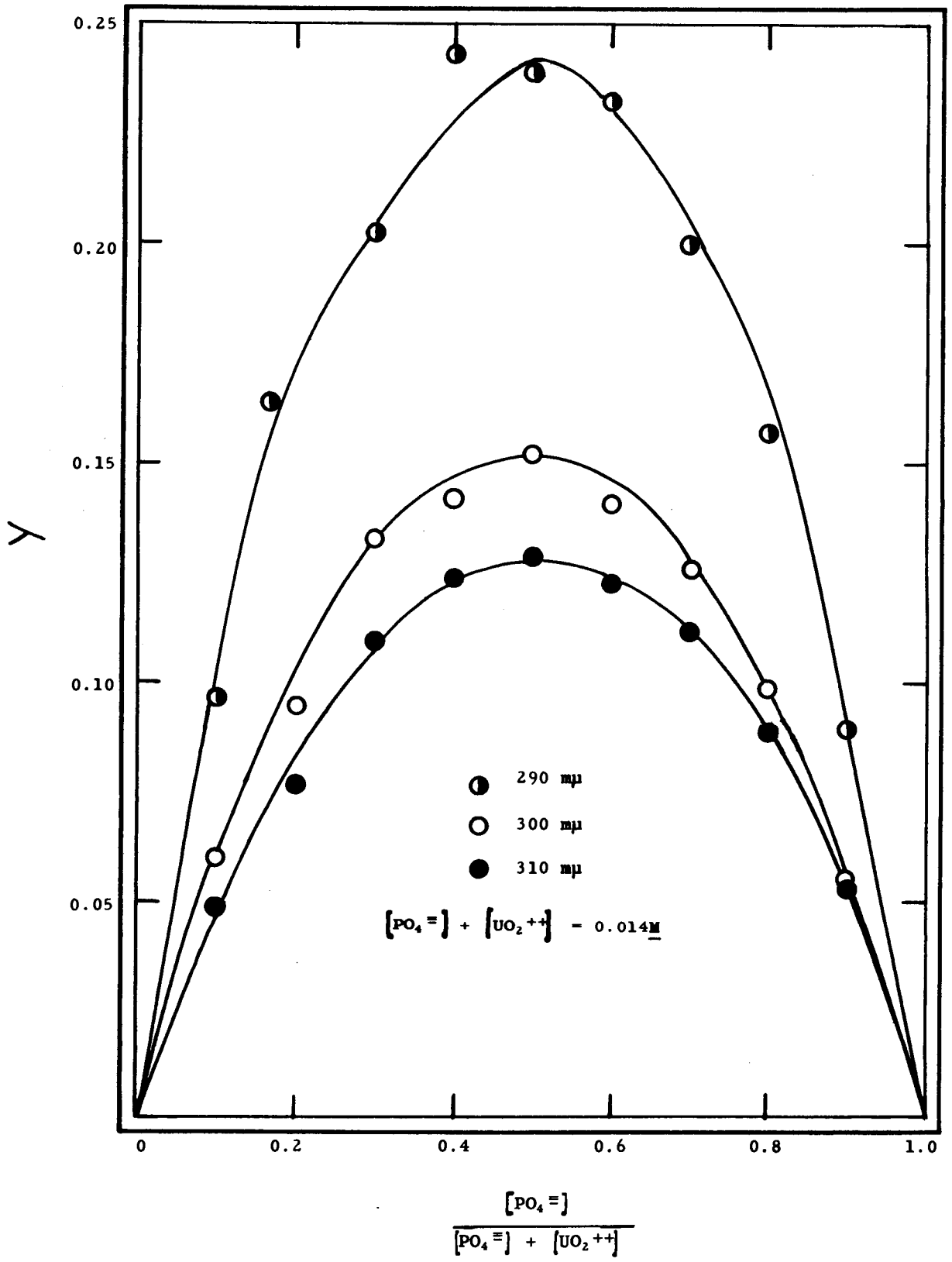


Figure 7

CONTINUOUS VARIATION METHOD APPLIED TO URANYL PHOSPHATE SOLUTIONS, 0.1 MOLAR IN PERCHLORIC ACID

(8) $$UO_2^{++} + 3H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4) + 2H^+$$

$$\frac{[UO_2(H_2PO_4)_2(H_3PO_4)][H^+]^2}{[UO_2^{++}][H_3PO_4]^3} = \frac{K_3}{K_S} = 160$$

The relative abundance of each of these assumed complexes in both series of solutions has been calculated using the above equilibrium constants. The results are listed in Table 24.

Reduction of Uranium in Sodium Carbonate Solutions with Sodium Hydrosulfite ($Na_2S_2O_4$)

F. J. Hurst and C. A. Blake

Spectrophotometric absorption measurements were reported last quarter (ORNL-1220) for a solution having the following composition:

Solution HS-15

$Na_4UO_2(CO_3)_3$	0.008 molar
Na_2CO_3	1.046 "
$Na_2S_2O_4$	0.080 "
Total Carbonate	1.070 "
pH	9.2

Additional measurements have been made on a similar solution (HS-17) in which the spectra was studied over a greater range of wave lengths (350-730 mμ). Figure 8 shows the change in the visible spectrum of the solution at room temperature 24 hours after the addition of $Na_2S_2O_4$. The spectra of a solution of UO_2HPO_4 before and after reduction to the (+4) state in a Jones reductor are shown for comparison. The shifting of the peaks in the carbonate solution in a manner similar to the shift in the phosphate solution as a result of the reduction ($U^{+6} \rightarrow U^{+4}$) strongly indicates that a soluble U^{+4} complex has been formed in the carbonate liquor.

Table 24

CALCULATED RELATIVE ABUNDANCE OF URANIUM PHOSPHATE COMPLEXES IN CONTINUOUS VARIATION SOLUTIONS

$\frac{[PO_4^{\equiv}]}{[UO_2^{++} + PO_4^{\equiv}]}$	% $UO_2H_2PO_4^+$	% $UO_2(H_2PO_4)_2$	% $UO_2(H_2PO_4)_2(H_3PO_4)$
	1M $HClO_4$; $[UO_2^{++}] + [PO_4^{\equiv}] = 0.137M$		
0.20	99.8	0.15	0.029
0.40	99.2	0.45	0.27
0.60	97.7	0.97	1.28
0.80	94.3	1.70	4.0
	0.1M $HClO_4$, $[UO_2^{++}] + [PO_4^{\equiv}] = 0.014M$		
0.20	99.8	0.15	0.0003
0.40	99.5	0.45	0.0027
0.60	99.0	1.00	0.013
0.80	98.2	1.79	0.044

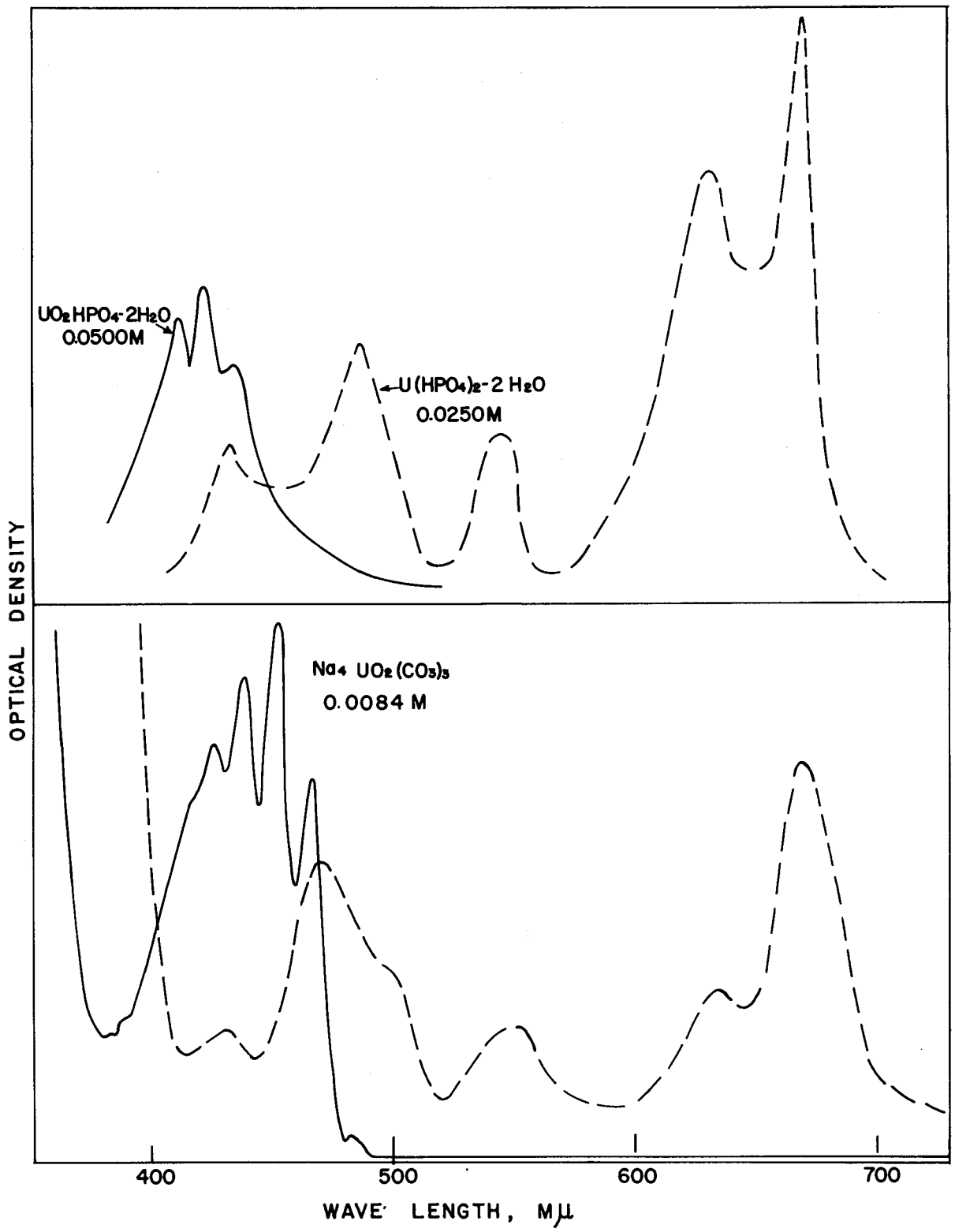


FIGURE 8. ABSORPTION SPECTRA FOR PHOSPHATE AND CARBONATE SYSTEM

As time permits, further tests will be made to determine the extent of reduction.

Studies with Ion Exchange Resins

V. S. Coleman, J. G. Moore, C. F. Coleman

Sorption of Uranium from Phosphate-Sulfate and Phosphate-Nitrate Solutions

The following report is being issued describing the results obtained to date in these systems.

ORNL-1264, "Anion Exchange Sorption of Uranium from Acid Solutions: Phosphate-Sulfate and Phosphate-Nitrate," J. G. Moore, E. Virginia Spivey, and C. F. Coleman.

Tests of a Phosphate Acid Resin

A sample was obtained from the Chemical Process Company of "Duolite C-60 Phosphonic Cation Exchanger." This resin was examined for possible sorption of uranium from acid solutions under conditions suggested by the successful liquid-liquid extraction of uranium with phosphonic acids. The pickup was zero within analytical accuracy from LZ sulfate leach liquor (60 ppm U, pH 0.7) or from uranyl nitrate, phosphate or sulfate solutions (about 0.2% U, pH about 2). The uranyl nitrate test was repeated with addition of benzene phosphonic acid and of hexane phosphonic acid (about 100 ppm) to test the possibility of sorption as a mixed complex, but the sorption was still essentially zero.

Similar tests were made with carbonate solutions at pH 11.1 (carbonate plus hydroxide), 10.8 (carbonate), and 8.4 (bicarbonate). Only the last showed any sorption, with about 8% pickup by 3.7 meq of resin from 100 ml of solution containing 0.23% uranium.

Since little is known of the configuration of this "Phosphonic Cation Exchanger," it is not possible to correlate the results obtained in experiments using this resin with those in which pure phosphonic acids were used. Liquid-liquid extractions described in another section of this report indicate that for each uranium atom extracted there may be at least two phosphorus atoms entering the extractable complex. Thus, a possible wide spacing of resin active centers or a special limitation imposed by the resin configuration could make it nearly impossible for complexing of uranium to take place with this particular resin.

Liquid-liquid extractions also show that the nature of the alkyl or aryl group constituting a part of the organophosphorus acid has a real effect upon the extraction power of that acid.

The inability of this one resin to extract uranium from aqueous solution does not preclude the possibility that some such resin may perform favorably. As a result of the investigations in liquid-liquid media it may be possible to incorporate the organophosphorus acids in a resin capable of selective uranium sorption.

PROCESS DEVELOPMENT

Recovery of Uranium from the Florida Leached Zone

D. J. Crouse
J. G. Moore
G. R. Peterson
L. R. Phillips
F. G. Seeley
V. S. Coleman
C. F. Coleman

Work has been continued on the extraction of uranium from the -200 mesh fraction of Florida Leached Zone material ("Bartow Clay") and on recovery of uranium from the resulting liquors.

Three samples of LZ concentrate (nominal -200 mesh) have now been received from the International Minerals and Chemical Company. The chemical analyses are compared in Table 25.

A sample of BC-0* was also given to Dr. T. N. McVay for examination by petrographic methods. Dr. McVay reported the following heavy minerals besides collophane as present in the fine fraction: tourmaline, sillimanite, staurolite, epidote, zircon, rutile, kyanite, garnet, and titanite. Monazite and xenotime were absent. The wavellite seemed to be present as extremely tiny crystals, too small for positive identification by microscopic examination.

After recent discussions with Mr. Z. S. Altschuler of the U. S. Geological Survey, it has been concluded that the samples of LZ material described in Table 25 are not necessarily representative of the average minable material. Arrangements are being made with the Survey to obtain samples of wavellitic sand which bear inappreciable amounts of other phosphatic minerals, as well as samples which contain varying quantities of wavellite, pseudowavellite and apatites. Arrangements are also being made with TVA at Wilson Dam to obtain a sample from the carload of material sent to them from International Minerals and Chemical Company. From visual observation this shipment appeared to contain a large amount of clay and greater than average quantities of iron oxides.

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* A sample of LZ material as dug, presumably corresponding to concentrate sample BC-1.

Table 25

HEAD ANALYSES

Percent

	BC-1	BC-2	BC-3
U	0.055	0.036	0.033
Ca	12	12	4
Al	13	10	16
PO_4	36	31	20
SiO_2	12	11	32
F	1	1	1
Fe	2	2	1
Mg	0.2	0.3	
Na	0.4	0.5	
K	0.3	0.4	
Ti	0.8	0.07	
CO_2	0.7		
SO_4	0.08		

Acid Leaching

Leaches of LZ concentrate BC-3 show less than 40% acid soluble material as compared with over 80% acid soluble in batch BC-1. The insoluble material appears to include both silica and clay (see Table 25). A large bench scale nitric acid leach, 1750 pounds HNO_3 per ton for five hours at 80°C, 15% pulp density, showed dissolution of 33% of the solids, yielding a liquor 70 ppm in uranium. Analyses are not sufficiently complete to calculate percent extraction.

Small bench scale leaches of BC-3 have been made corresponding to the leaches previously reported for batch BC-1, using nitric, sulfuric, and phosphoric acids. Sufficient analyses are not yet available to determine the differences that may exist between these two samples in their amenability to the extraction methods.

Table 26 shows the results of a large bench scale leach with a minimum amount of sulfuric acid. The conditions were similar to those reported for leach BC-32 (ORNL-1220, p. 46) except that the washings were not combined with the pregnant liquor.

Resin in Pulp

Tests have been continued of low-sulfuric acid leaching in the presence of anion exchange resins. The uranium recovery compares well with that obtained by low-sulfuric leach, filtration, and anion exchange sorption for the liquor. Table 27 shows essentially constant recovery by two resin stages over the short range of acid concentrations tested. Analyses are not complete for tests with less acid. Table 27 shows a slight decrease of uranium in the first resin stage as the acidity was increased (with compensating increase in the second stage), probably because of slight decrease of sorption efficiency with the increased acidity and increased sulfate concentration.

Table 28 shows nearly identical results with three types of resins, and appreciably better results with sulfate than with chloride resins The latter effect can be expected to decrease if the relative quantity of resin used is decreased.

Table 29 shows essentially constant results over the range of resin quantities included. Results with a much lower ratio of resin per stage are shown in Table 30, which also shows that 6 mg U per meq resin is probably close to the maximum loading that can be expected in a countercurrent leach with this ore and acid quantity.

Table 26

LOW-SULFATE LEACH BC-41

Ore:	8 kg (d.b.) Batch BC-2
H_2SO_4	2.4 kg (600 lb/ton)
Leach Conditions:	16 Hours at R.T., 20% Pulp density
Volume:	23 liters of filtrate recovered, with no washing.

Pregnant Liquor:

U	0.007%
Al	.30
Fe	.06
Ca	.06
SiO_2	.015
PO_4	3.4
SO_4	2.7
F	.21
pH	0.9

Table 27

RESIN-IN-PULP LEACHES

20g (d.b.) BC-2 treated with acid for 6 hours at R.T. Two resin stages, each with 7.2 meq Dowex-2-SO_4 for 16 hours at R.T. Initial pulp density 20%; final, 5-10%

Test No.	Acid Used lb/ton	Uranium Distribution, %*				Balance %**
		1st Resin Stage	2nd Resin Stage	Slurry Filtrates	Tailings	
LZS-2	400	69	5	2	24	102
-4	500	65	8	1	25	105
-1	575	65	10	1	25	108
-5	600	61	13	2	24	104
-6	600	65	10	1	24	112

* Based on uranium found in each test.

** Based on head analysis.

Table 28

RESIN-IN-PULP LEACHES

20g (d.b.) BC-2 treated with acid (600 lb. H_2SO_4/ton) for 6 hours at room temperature (R.T.). Two resin stages, each with 4.0 meq for 16 hours at R.T. Initial pulp density 20%, final 3%.

		Uranium Distribution, %*		
Test No.	Resin Used	1st Resin Stage	2nd Resin Stage	Slurry Filtrate
LZS-11	IRA-400-Cl	52	12	4
LZS-12	Dowex-1-Cl	50	12	4
LZS-13	Dowex-1-SO_4	61	12	-
LZS-14	Dowex-2-Cl	51	14	6
LZS-15	Dowex-2-SO_4	59	15	-

* Based on head analysis.
Tailings analyses not complete.

Table 29

RESIN-IN-PULP LEACHES

2-g (d.b.) BC-2 treated with acid (600 lb. H_2SO_4/ton) for 6 hours at R.T. Two resin stages with Dowex-2-SO_4, each for 16 hours at R.T. Initial pulp density 20%; final 40%.

		Uranium Distribution, %*				
Test No.	Meq Resin/ Stage	1st Resin Stage	2nd Resin Stage	Slurry Filtrate	Tailings	Balance %**
LZS-7	3.6	63	8	2	28	111
LZS-5	7.2	61	13	2	24	104
LZS-6	7.2	65	10	1	24	112
LZS-8	10.9	66	4	1	29	107
LZS-9	14.5	66	4	1	29	107
LZS-10	18.1	66	4	1	30	105

* Based on uranium found in each test.

** Based on head analysis.

Table 30

RESIN-IN-PULP LEACHES

200g (d.b.) BC-2 treated with acid (600 lb. H_2SO_4/ton) for 6 hours at R.T. Four resin stages, each with 2.0 meq Dowex-1-SO_4, pH 1.5 to 1.6 (Test No. LZS-16).

Resin Stage No.	Resin Contact Time, Hours	Pickup, %* per Stage	Pickup, %* Cumulative	Loading mg U/meq R
1	20	15	15	5.4
2	24	16	31	6.0
3	24	11	42	4.0
4	96	10	52	3.5

* Based on Head Analysis.

Other tests, not shown in the tables, have suggested that reasonable uranium extractions can be obtained at higher pH values, and with less acid consumption, if the resin is present during the operation. Further tests of this possibility are being made with different samples of leached zone material. Possible methods for treating the acid pulp by solvent extraction techniques are also being examined.

Leaching with Organic Reagents

It was previously reported[2] that up to about 40% of the uranium could be extracted from LZ by dibutylphosphate in inert solvents. Since 60 to 70% of the uranium was extracted by acid leaching when most of the calcium and little of the aluminum were dissolved, the results with DBP suggested that it might be specifically attacking the aluminum minerals and releasing the associated uranium. However, the following two tests appeared to contradict this hypothesis.

In the first test, samples of acid-leached tailings (from low-sulfate leach BC-32, v. ORNL-1220, p. 46) still containing about 45% of the original uranium were leached with DBP in benzene, with extraction of less than an additional 5% of the original uranium content. The results were similar for wet, oven-dried, and acetone-dried samples.

In the second test, a fresh sample of LZ (BC-1) was treated as follows:

1.	Washed with acetone to remove water.	
2.	Leached with DBP in benzene	31% of uranium
3.	Washed with benzene	
4.	Washed with acetone	
5.	Leached with acid (500 lb H_2SO_4/ton)	30%
6.	Washed with water	
	Residue:	29%
	Material Balance:	90%

These tests show that the fraction of the uranium readily available to low-acid leaching includes the smaller fraction of the uranium available to DBP leaching.

Table 31 shows the results of further leaching tests with DBP. The head ore was filtered to 65% solids, and the solvent used was a mixture of 3.5 ml diethyl ether and 1.5 ml ethyl alcohol per gram (dry basis) of ore. This

Table 31

ORGANIC LEACHING: DIBUTYLPHOSPHATE

10g (d.b.) LZ containing 5.7g water leached for 2 hours with 40 ml of ether-alcohol mixture (5:3) containing reagents as listed.

Test No.	HNO_3 lb/ton	DBP ml/40 ml Solvent	Uranium Extraction %
B-151	0	0	<1
B-182	0	2	3
183*	0	2	10
169	0	5	28
153	0	10	17
184*	0	10	13
154	0	15	4
155	0	20	8
170	0	30	22
171	0	40	42
159	50	0	1
160	100	0	5
161	200	0	19
162	400	0	33
163	600	0	45
164	50	10	25
165	100	10	25
166	200	10	31
167	400	10	25
168	600	10	33
175	600	5	19
176	600	10	22
177	600	20	31
178	600	40	25

* Leached for 24 Hours.

mixture dissolved the water present and also the nitric acid used without formation of a separate liquid phase. Various combinations of DBP and nitric acid were tested without any improvement over the best of the previously reported results. The reproducibility of the tests using DBP was much poorer than that of straight acid leaches.

Organic leaching tests have been started with some of the reagents found promising in the screening study of organic reagents (v, ORNL-1220, p. 13ff; pp.20-23 of this report). Table 32 shows the results which have been reported for tests with di(2-ethylhexyl)phosphinic acid in carbon tetrachloride. The quantities and conditions were based on those arbitrarily chosen for the screening tests. A single leach test with hexanephosphonic acid, under the same conditions as tabulated for Test No. BC-50-2, gave 20% extraction.

Uranium Recovery from Solution

Recovery studies have been continued on the low-sulfate liquors (BC-32, ORNL-1220, p. 46, and BC-41, this report, p.69). Tests have been started on nitrate liquors.

Precipitation Tests

Tables 33 and 34 summarize the results of hydrolytic precipitations of uranium from reduced low-sulfate liquors. Complete precipitation is possible in low-grade cakes containing about 1% uranium. A test similar to No. BC-44-1B (Table 33), except that the liquor was not reduced, precipitated only 65% of the uranium with a cake grade of 0.3%.

Bismuth nitrate was added to produce a bismuth phosphate carrier in two tests, giving complete precipitation of uranium at both pH 0.8 and 1.8. Both cakes contained 0.5% uranium. The bismuth was not completely precipitated.

Two cakes have been upgraded by caustic leach (10% NaOH, 80°C) with the following results:

Table 32

ORGANIC LEACHING: PHOSPHINIC ACID

25g water-free LZ leached with 100 ml of CCl_4 0.1M in di(2-ethylhexyl)phosphinic acid, washed with CCl_4 to final volume of 150 ml

Test No.	Stage No.	HNO_3 lb/ton	Time Hours	U Distribution, %* Solution	U Distribution, %* Residue	U Balance,%*
BC-50-1	1	0	0.5	23	72	95
-2	1	0	3	17	83	100
-3	1	400	3	53	44	97
-4	1	800	3	49	67**	116
BC-51	1	0	0.5	28		
	2	0	0.5	7		
	3	0	0.5	4	63	102

* Based on head analysis.

** Solid material formed into a gummy mass and could not be dispersed in the solvent.

Table 33

HYDROLYTIC PRECIPITATION OF REDUCED SULFATE LIQUOR

Reductant - Zinc amalgam

Test No.	Liquor	Base	pH	Temperature Pptn.	Temperature Filtn.	U pptn. %	Cake Grade % U (Calc)
BC-42-1A	BC-41	NH_4OH	2.2	Hot	R.T.	48	1
-42-1B	"	"	2.4	"	"	99+	0.4
BC-43-1*	"	"	2.4	"	"	99+	0.6
-40-4	BC-32	"	2.7	R.T.	"	98	1
-40-1	"	"	2.8	Hot	Hot	65	5
-42-1C	BC-41	"	2.9	"	R.T.	99+	0.3
-40-7A	BC-32	MgO	2.75	"	"	95	2
-44-1A	BC-41	"	2.8	R.T.	"	94	1
-44-1B	"	"	2.25	"	"	98	0.4
-44-1C	"	"	3.7	"	"	99+	0.3
-40-7B	BC-32	"	3.9	Hot	R.T.	99+	0.4
-44-2A	BC-41	$MgCO_3$	2.6	R.T.	"	23	2
-44-2B	"	"	2.7	"	"	77	1
-44-2C	"	"	2.8	"	"	93	0.9
-44-2D	"	"	2.9	"	"	63	0.5

* Reduced with iron instead of zinc.

Table 34

HYDROLYTIC PRECIPITATION OF REDUCED SULFATE LIQUOR

Reductant - Zinc Amalgam
$Na_2S_2O_4$ added
pH adjusted with NH_4OH

Test No.	Liquor	Conc. $Na_2S_2O_4$ g/l	pH	Temperature Pptn.	Temperature Filtn.	U Pptn. %	Cake Grade % U (Calc)
BC-40-3	BC-32	1	1.8	Hot	Hot	33	4
-40-5	"	1	2.4	R.T.	R.T.	73	9
-42-2A	BC-41	2	1.6	Hot	"	18	18
-42-2B	"	2	2.2	"	"	71	2
-42-2C	"	2	2.4	"	"	99+	0.6
-42-2D	"	2	2.7	"	"	98	0.4
-42-2E	"	2	3.1	"	"	99+	--

Test No.	pH	% U pptd.	Cake Grade % U (Calc)	U Leached % of Tot.	U in Prod. % of Total	Prod. Grade % U (Calc)
BC-45	1.8	74	2	29	45	12
BC-46	2.3	88	0.9	30	58	23

Anion Exchange

Saturation and elution of exchange columns in series has been studied, with the results shown in Figures 9, 10, and 12. Low-sulfate leach liquor BC-32[2] was used for these tests, after adjustment of the pH to 2 with sodium hydroxide. Each column was about 4 mm by 75 mm, containing 1.0 meq of Dowex-1-SO_4, with a settled volume of about 1 ml. Samples were removed from between column units by means of a stainless steel hypodermic needle. For the saturation tests shown in Figure 9, the flow was manually controlled and varied greatly, but was not allowed to increase above 0.1 ml per minute. The beginning and ending of each curve shows when the column unit was added to or removed from the series. In the series shown in Figure 10, the flow was maintained at 1 ml per minute by a squeegee pump, and all columns were present throughout the portion of the run which is shown. Curves for four of the ten units are shown.

Figure 11 shows elution of a single column unit by chloride solution (0.1M HCl, 0.9M NaCl). This was column I of Figure 9. The flow was limited to 0.1 ml per minute (retention time of at least 5 minutes), but should have been slower, as shown by the high samples obtained after overnight stoppages.

On the basis of the single-column test, a series elution test was set up as shown in Figure 12. The same chloride solution was used as eluent. The test was started with three column units in series, and the other columns were added at arbitrary intervals. (Four of these column units had been loaded in the test shown in Figure 9, the other two in a similar loading test.)

FIGURE 9

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

SATURATION OF COLUMNS IN SERIES

Slow Flow
(Retention Time 5 Min. or More)
Liquor BC-32, pH 2.0
Dowex 1 Sulfate
VS-268

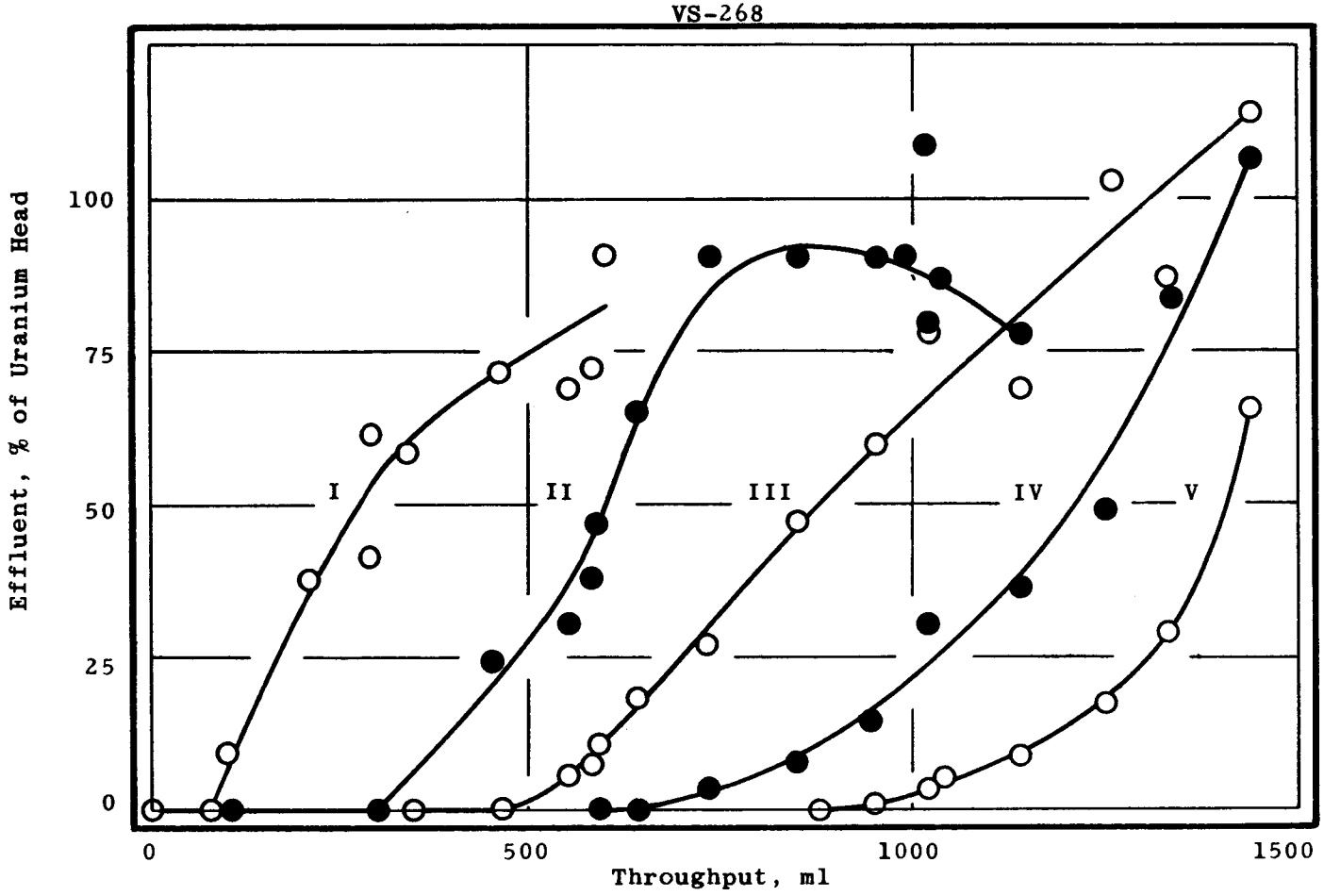


Figure 10

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR
SATURATION OF COLUMNS IN SERIES

Fast Flow
(Retention Time 0.25 Min.)
Liquor BC-32, pH 1.7
Dowex 1 Sulfate
VS-271
(Smoothed Curves)

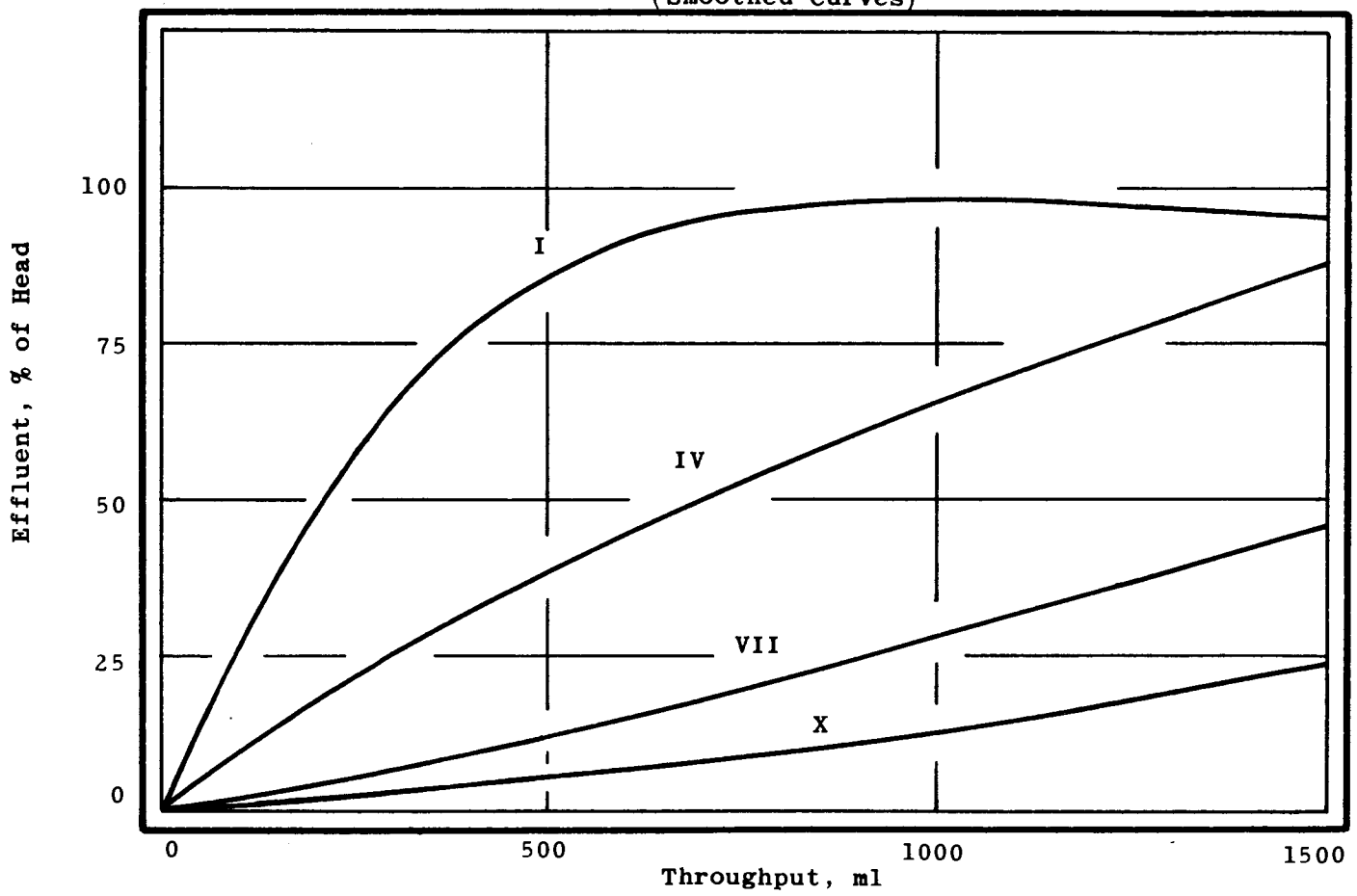


FIGURE 11

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

ELUTION OF SINGLE COLUMN

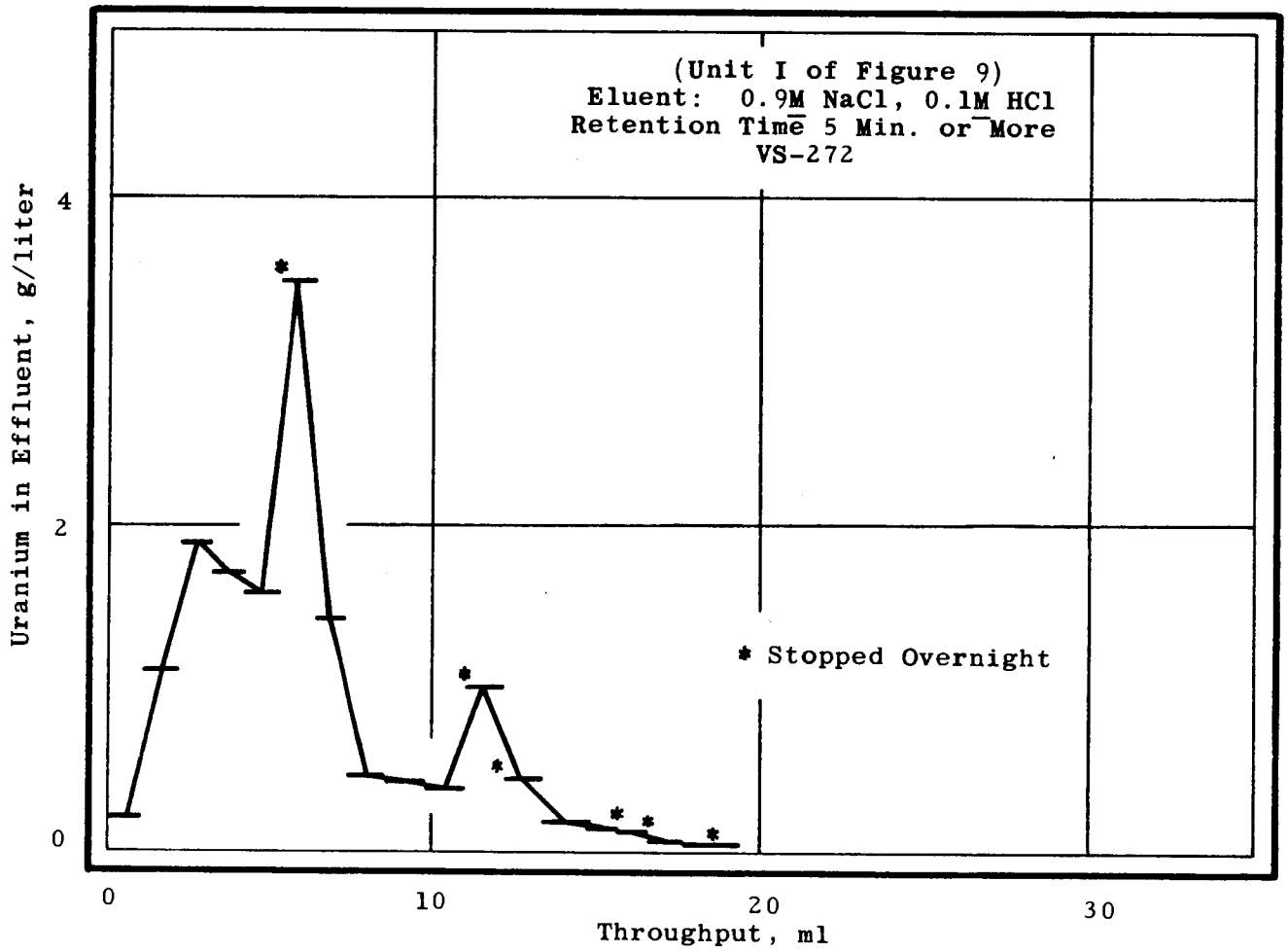
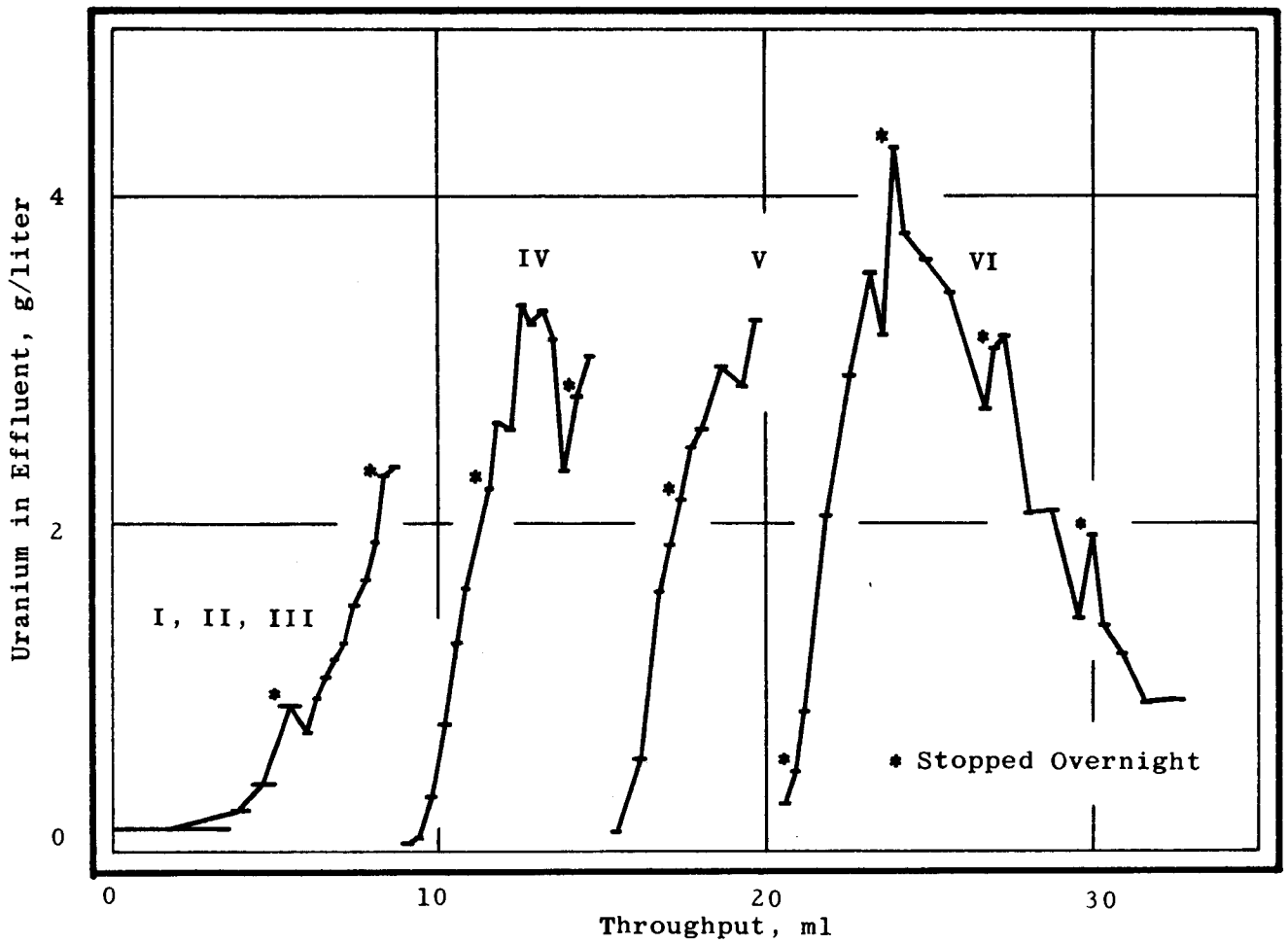


FIGURE 12

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR
ELUTION OF COLUMNS IN SERIES

Eluent: 0.9M NaCl, 0.1M HCl
Intermittent Flow
VS-273



The uranium curve dropped to zero after each column was added, as the barren liquor already in the column was displaced. Instead of attempting to maintain a very slow flow for this test, an intermittant flow was used: samples of approximately 0.3 ml (less than the void space in the resin bed of each unit) were withdrawn at intervals of not less than one hour. The resulting concentration built up too high for the acidity of the eluent, and before the test was completed a precipitate formed in each of the last three columns.

Figure 13 repeats the last section of Figure 12, showing how the uranium elution was suppressed until most of the sulfate and phosphate were removed. This accounts for the relatively slow rise of the uranium concentration in each section of Figure 12, and suggests a possible advantage in collecting separately two types of eluent, one containing most of the phosphate and sulfate, the other high in uranium and low in phosphate.

Figure 14 shows that the chloride ion (after elution) was readily removed by a small fraction of the barren liquor from the original saturation of the column unit.

Liquid-Liquid Extraction

Results are presented in Table 35 for the extraction of uranium from HNO_3 leach liquors with di(2-ethylhexyl)phosphinic acid in CCl_4. Extractions up to 99% were obtained with good selectivity; the bulk of the contamination in all cases was due to iron. Increase in pH favored higher extractions without appreciably effecting the contamination ratio. Separations of the phases was rapid and distinct, but slight amounts of precipitate were noted in some cases.

North Dakota Lignite

R. C. Nelson

History of Lignite Sample

The sample of North Dakota lignite received at this laboratory was taken from a steep bank in an area being investigated by Howard Zeller of the U. S. Geological Survey. The outcropping was stripped clean of weathered material and a 25-foot section of the freshly exposed lignite was sampled in four places. The sample cuts were approximately 3-feet long, 8 to 10-inches high, and 20-feet deep.

The samples were immediately sealed in drums and sent to Denver, Colorado, where they were crushed to minus 3/8" in a

FIGURE 13

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

RELATIVE ELUTION OF URANIUM, IRON, SULFATE, AND PHOSPHATE

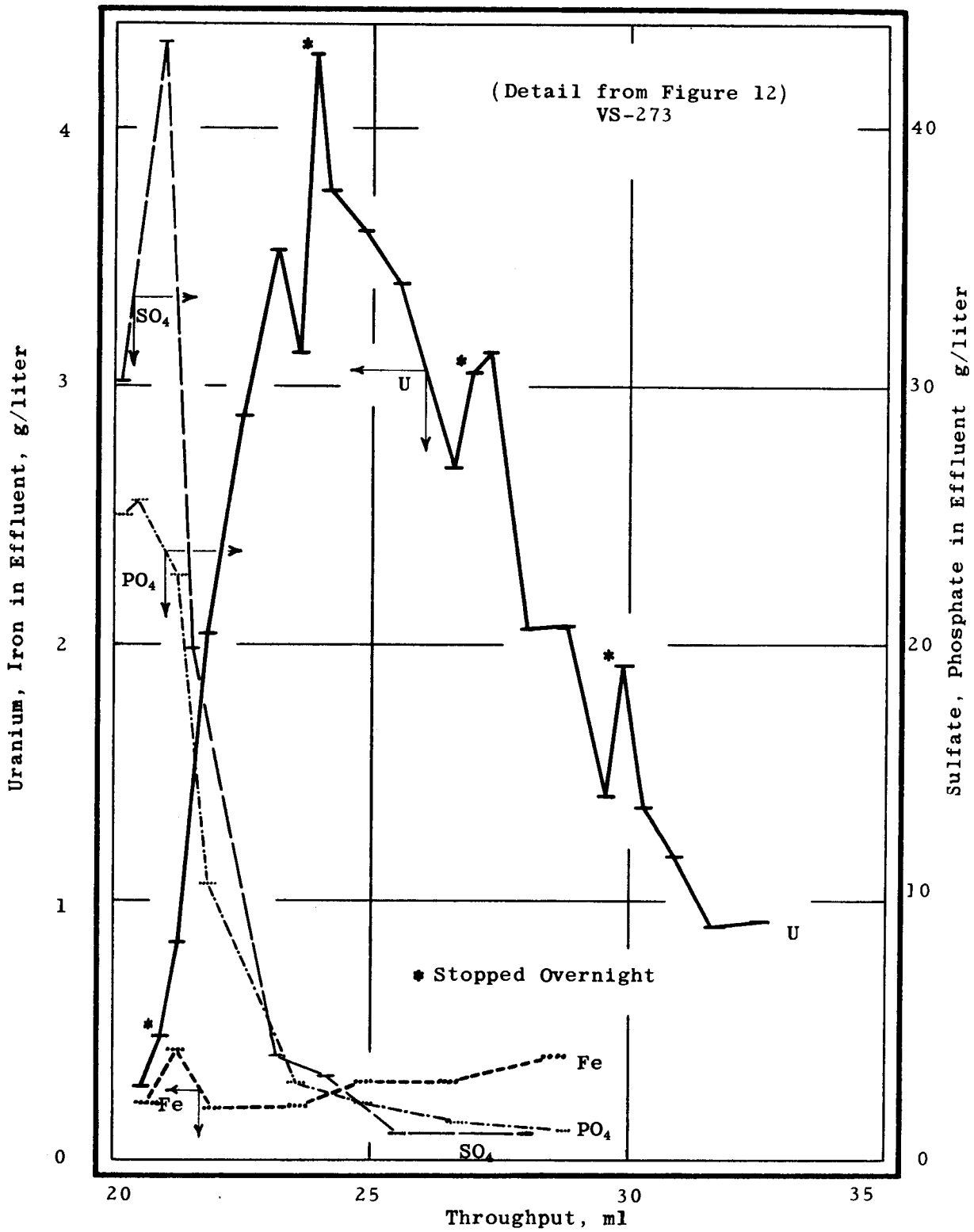


FIGURE 14

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

REGENERATION OF ELUTED RESIN BY BARREN LIQUOR

(VS-268)

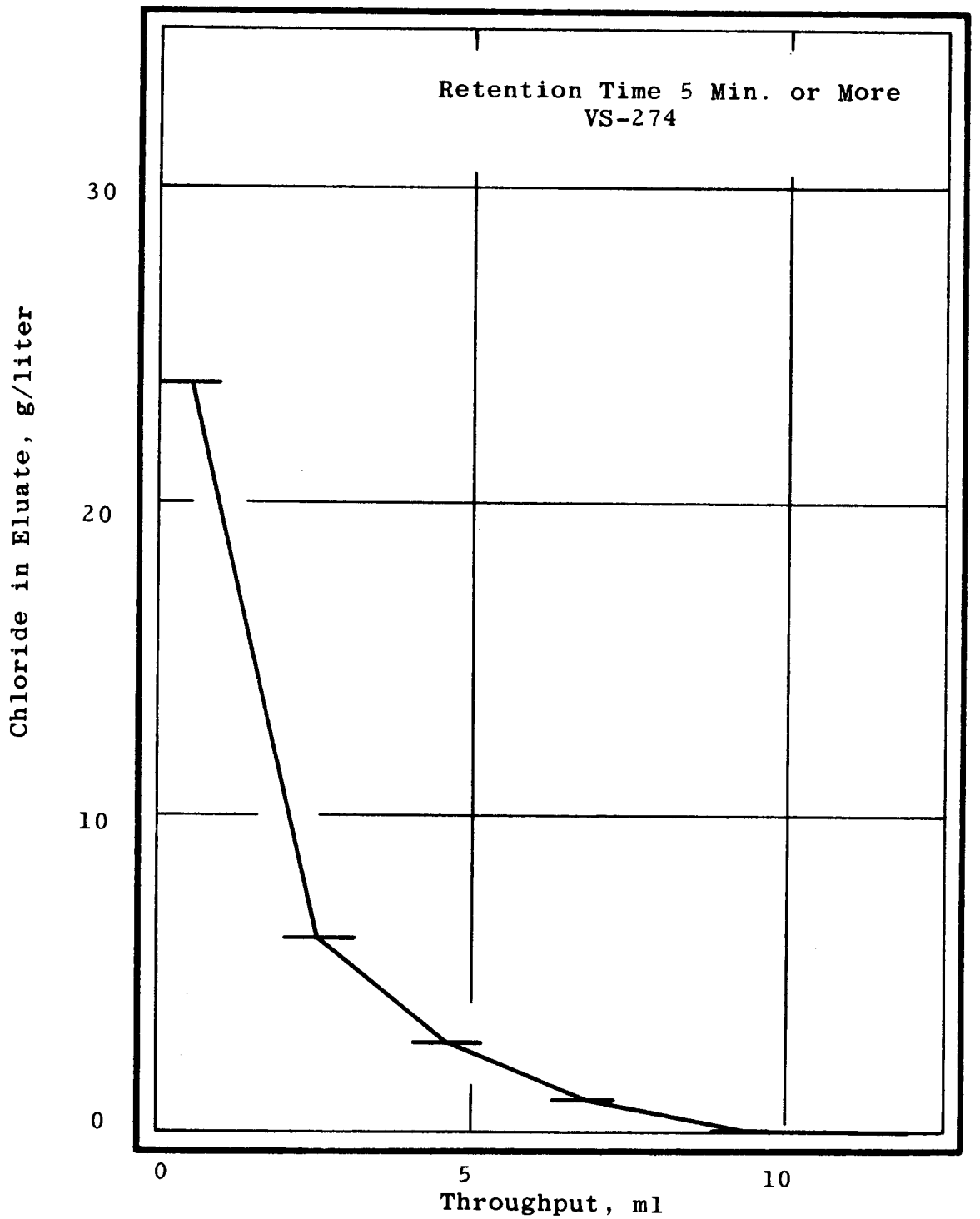


Table 35

LIQUID-LIQUID EXTRACTION FROM HNO_3 LIQUOR WITH DI(2-ETHYLHEXYL)PHOSPHINIC ACID IN CCl_4

Extraction: Aqueous - 50 ml HNO_3 liquor (LZP-3), U = 55 ppm.
Organic - 50 ml CCl_4 containing indicated quantity of extraction (90% pure).
Contact Time - 15 minutes.

Exp. No.	Molarity of Extractant	pH* of Leach Liquor	Appearance: Aqueous Phase	Appearance: Organic Phase	% U Extrn.	Contaminants Ratio**
BC-53-1	.002	<0.0	Clear	Clear	10	1.0
BC-53-2	.002	0.7	"	"	15	.6
BC-53-3	.002	1.05	Cloudy	"	28	.4
BC-53-4	.01	<0.0	Clear	"	76	.6
BC-53-5	.01	0.7	"	"	77	.9
BC-53-6	.01	1.05	Slight Precip.	"	90	.6
BC-53-7	.05	<0.0	Clear	"	96	1.3
BC-53-8	.05	0.7	"	Slightly Cloudy	95	1.2
BC-53-9	.05	1.05	Cloudy	" "	99	.9

* pH adjusted with concentrated NaOH.

** Weight ratio of Fe + Al to U in organic phase (ratio in head liquor = 313).

jaw crusher, and the crushed product was separated mechanically, by means of an automatic sampler, into two portions. The samples were mixed by bedding and coning. The samples were sealed in drums, 300 pounds being kept in reserve in Denver, and 500 pounds being shipped to ORNL.[9] The sample was taken on October 6, 1951, shipped from Denver to ORNL on October 17, 1951, and received at ORNL October 29, 1951.

Sampling Procedure

The lignite from one drum (approximately 60 pounds) was riffled into four parts and these four parts were cross-riffled four times. Portions of each of the final four riffle products were then obtained (by riffling) and combined for a head sample. The remaining lignite was stored in two quart Mason jars and sealed against moisture loss.

In its as-received condition the lignite was too wet for both screening and grinding. The material coated the grinding media during grinding and clogged the screen openings during screening. Therefore, to prepare samples for analysis, a portion of the head sample was oven-dried at 104-120°C for 5-1/4 hours, air-dried at room temperature for approximately 65 hours, and stage crushed to minus 60 mesh. Three fractions were taken for chemical, spectrochemical, and x-ray analyses.

A sample of the as-received material with no prior screening or drying was submitted for determination of moisture content.

Analytical Results

The weight loss at 110°C gave a moisture content for the lignite of 42.6% in the as-received condition.

Spectrographic Analysis

Two sets of spectrographic analyses were obtained. One sample was submitted expressly for such analyses, and one was submitted by the Analytical Chemistry Division to be used as a guide for their chemical analyses. These two sets of data are compared in Table 36.

Chemical Analysis

A sample of partially dried lignite was submitted for chemical analyses. Results from these analyses are shown in Table 37. Calculations were made of the chemical composition of the lignite in a dry and in an as-received condition.

Table 36

SPECTROGRAPHIC ANALYSES OF LIGNITE SAMPLES

Element	Head Sample	Analyt. Chem.	Element	Head Sample	Analyt. Chem.
Ag	<0.04	<0.01	Mn	0.01	0.02
Al	1.0	*	Mo	0.15	0.18
B	0.02	0.01	Na	0.3	*
Ba	0.08	0.04	Ni	<0.08	<0.02T
Be	<0.001	<0.0003	Pb	<0.04	<0.01
Ca	2.0	*	Si	10	*
Cd	<0.04	<0.01	Sn	<0.02	<0.006
Co	<0.04	<0.01	Sr	<0.1	--
Cr	<0.04	<0.01T	Ta	<1	<0.3
Cu	0.04	0.02	Ti	0.2	0.06
Fe	10	*	U	<0.04	<0.01T
K	0.08	*	W	<1	<0.3
Li	0.01	0.003	Zn	<0.3	<0.1
Mg	0.3	*	Zr	<0.08	0.02

* Chemical analyses in Table 37

Table 37

CHEMICAL COMPOSITION OF LIGNITE SAMPLE

Constituents	Sample as Submitted	Percent by Weight Dry Basis	Percent by Weight As-rec'd. Condition
Loss at 110°C (H_2O)	5.6	0.0	42.6
Volatile matter	59.3	62.8	36.0
Fixed carbon	6.3	6.7	3.85
Total carbon	33.4	35.4	20.3
Nitrogen	0.46	0.49	0.28
Total sulfur (SO_4)	12.8	13.6	7.81
Sulfate sulfur (SO_4)	10.8	11.4	6.54
Carbonate (CO_3)	0.08	0.085	0.049
Ash	28.8	30.5	17.5
Uranium	0.044	0.047	0.027
Aluminum	1.69	1.79	1.03
Calcium	2.82	2.99	1.72
Iron	5.98	6.33	3.63
Potassium	0.17	0.18	0.10
Magnesium	0.30	0.32	0.18
Sodium	0.74	0.78	0.45
Silicon	3.40	3.60	2.07

Screen Analysis

Screen analyses were made on a representative portion of the lignite which had been oven-dried at 104-118°C for 5 hours. Prior to the actual screen analysis, the material was screened dry, and then wet through a 325 mesh screen to remove the fines present. The minus 325 mesh wet material was filtered and dried and added to the minus 325 mesh material from the screen analysis. The plus 325 mesh fraction was oven-dried overnight at 104-118°C and then screened for 15 minutes in a nest of (Tyler Series) 8, 12, 20, 35, and 60 mesh screens. The minus 60 mesh lignite was then screened for 20 minutes in a nest of (Tyler Series) 80, 100, 200, and 325 mesh screens.

The results of the screen analysis as given in Table 38 show no significant differences in the uranium or carbon analyses of the various fractions with the exception of the plus 8 mesh material which has a high ash content and is low in both uranium and carbon.

Mineral Identification and Liberation

Upon completion of the screen analysis a bright-yellow mineral was noticed in fairly large amounts in the plus 8 mesh fraction. Brief chemical testing would tentatively identify the material as jarosite ($K_2O.Fe_2O_3.4SO_3.6H_2O$).

Excessive drying revealed the presence of a white mineral which was segregated by hand-picking and submitted for chemical analysis. Results showed the mineral to be 85% $CaSO_4$ with 0.09% Na, 0.82% Al, and 1.5% Si. The mineral was probably gypsum or anhydrite containing a small amount of analcite.

Microscopic examination of the various screen fractions showed the carbonaceous material to be relatively free of inorganic material in the minus 20 and 35 mesh fraction and the condition steadily improved with the finer screen sizes. The inorganic minerals were never completely freed of the organic material, however, even at minus 325 mesh. Due to the small size of the lignite particles in the as-received condition no mounted specimens were prepared for microscopic study.

Sink-Float Experiments

Two sink-float experiments have been made using different screen fractions of the oven-dried lignite. Aqueous zinc chloride solutions of varying concentrations were used as the heavy liquid separation media.

Table 38

SCREEN ANALYSIS OF LIGNITE SAMPLE L-1

Screen Size	Chem. Analysis (As Submitted)				Screen Analysis (Dry Basis)		% Distribution		
	% Moist.	% Tot. C	% Ash	% U	Wt. % Ret.	Cum. Wt. % Ret.	Tot. C	Ash	U
+8	2.97	7.31	66.7	0.0080	3.12	3.12	0.74	7.20	0.53
+14	5.81	32.3	29.9	0.046	9.09	12.21	9.75	9.69	9.09
+20	6.06	39.4	26.6	0.046	14.23	26.44	18.68	13.53	14.28
+35	6.23	24.0	24.7	0.049	18.94	45.38	15.17	16.76	20.30
+60	6.21	32.5	23.5	0.051	12.49	57.87	13.55	10.51	13.92
+80	4.95	36.3	24.8	0.054	6.11	63.98	7.30	5.36	7.12
+100	4.93	30.6	26.1	0.046	3.92	67.90	3.95	3.61	3.89
+200	4.35	31.2	27.8	0.049	11.20	79.10	11.47	10.93	11.76
+325	4,34	32.1	26.5	0.052	4.82	83.92	5.06	4.48	5.37
-325	6.55	26.6	31.0	0.039	16.09	100.00	14.34	17.92	13.74

Each test was initiated by adding 100 gm of lignite to a zinc chloride solution of specific gravity 1.7. The material was stirred in the beaker until all of the particles had been wetted and the solution was then allowed to stand until the particles were no longer in motion, i.e., the upward and downward movement had ceased and a definite float product and a definite sink product were obtained. The float product was then skimmed off using an ordinary soup strainer, and the lignite was transferred to the solution of next lowest specific gravity (1.65). This operation was repeated on down to a specific gravity of 1.15. The float product at 1.15 was kept as a separate product. After thorough washing and drying, the products were ground to at least minus 60 mesh and submitted for determination of their carbon, ash, moisture and uranium content.

Due to their acidity at high concentrations, the zinc chloride solutions were not particularly desirable as the separation media but were the only ones readily available. Analyses of the solutions after use, however, have shown negligible leaching of the uranium values.

Test Results

Test No. 1, using -8 to +20 mesh lignite, is described by the results in Table 39. It may be noted that separations at a specific gravity of 1.7 gave a sink product which was 21% of the total weight but which contained 53 of the total ash with only 3% of the total carbon and 21% of the total uranium.

With -20 to +60 mesh material in Test No. 2 (Table 40), separations at 1.7 gave a sink product that was 25% of the total and contained 56% of the total ash with only 8% of the total carbon and 12% of the total uranium. A gradual increase in uranium content of the sink products with decreasing specific gravity seemed apparent between 1.7 - 1.55 though such a limited amount of data is not conclusive. The same effect was noted to a much lesser extent in Test No. 1.

Though the reported uranium values were obtained from an average of two or more analyses it would not be advisable to accept them as absolute quantities at this time. Significant variations have appeared occasionally in analyses of samples, indicating a measurable degree of non-uniformity in mineral distribution and uranium dispersion. This observation, in itself, is interesting and is receiving further attention.

Future Work

The emphasis on the lignite problem will be increased somewhat. Chemical beneficiation studies will be started.

Table 39

SINK-FLOAT TEST NO. 1 (-8 +20 MESH)

Sample	Chem. Analysis (As Submitted)				Sink-Float Test Results (Dry)		% Distribution		
	% Moist.	% Tot. C	% Ash	% U	Wt. % Ret.	Cum. Wt. % Ret.	Tot. C	Ash	U
Head Sample	8.12	39.5	29.7	0.046	--	--	--	--	--
Sink 1.70	4.70	5.60	74.6	0.057	20.84	20.84	2.96	52.94	20.88
Sink 1.65	7.40	35.5	27.9	0.059	2.02	22.86	1.87	1.98	2.16
Sink 1.60	10.2	44.2	20.7	0.062	3.93	26.79	4.67	2.94	4.54
Sink 1.55	8.98	45.7	18.2	0.084	5.97	32.76	7.24	3.87	9.23
Sink 1.50	8.48	46.1	17.6	0.056	6.00	38.76	7.30	3.74	6.15
Sink 1.45	7.70	46.3	17.4	0.053	4.04	42.80	4.90	2.47	3.88
Sink 1.40	7.02	47.8	15.9	0.057	6.10	48.90	7.58	3.39	6.26
Sink 1.35	8.14	46.1	15.9	0.053	8.04	56.94	9.75	4.52	7.77
Sink 1.30	9.06	46.9	16.6	0.050	8.95	65.89	11.15	5.30	8.25
Sink 1.25	7.86	47.3	16.2	0.051	10.58	76.47	13.12	6.04	9.82
Sink 1.20	5.84	48.3	16.5	0.050	8.23	84.70	10.20	4.68	7.32
Sink 1.15	6.72	48.4	15.5	0.050	12.24	96.94	15.34	6.60	10.99
Float 1.15	6.52	49.7	14.4	0.050	3.06	100.00	3.93	1.53	2.74
					100.00				

Table 40

SINK-FLOAT TEST NO. 2 (-20 +60 MESH)

Sample	Chem. Analysis (As Submitted)				Sink-Float Test Results (Dry)		% Distribution		
	% Moist.	% Tot. C	% Ash	% U	Wt. % Ret.	Cum. Wt. % Ret.	Tot. C.	Ash	U
Head Sample	0.77	37.9	31.0	0.049	--	--	--	--	--
Sink 1.70	1.66	12.6	68.3	0.020	25.37	25.37	8.29	56.12	11.63
Sink 1.65	0.62	43.5	23.4	0.049	4.11	29.48	4.59	3.08	4.57
Sink 1.60	1.18	46.8	20.5	0.055	5.10	34.58	6.16	3.37	6.41
Sink 1.55	1.64	47.3	18.8	0.058	6.09	40.67	7.47	4.20	8.11
Sink 1.50	1.17	48.0	18.8	0.060	7.14	47.81	8.85	4.33	9.78
Sink 1.45	0.37	48.5	18.4	0.049	5.14	52.95	6.38	3.02	5.71
Sink 1.40	0.29	49.8	17.6	0.058	7.20	60.15	9.17	4.05	9.46
Sink 1.35	0.67	47.2	17.6	0.045	9.22	69.37	11.18	5.20	9.43
Sink 1.30	0.72	47.2	17.5	0.052	12.29	81.66	14.91	6.90	14.54
Sink 1.25	1.37	48.3	17.2	0.050	7.12	88.78	8.90	3.96	8.15
Sink 1.20	1.76	48.6	16.4	0.053	5.57	94.35	7.03	2.96	6.78
Sink 1.15	0.88	49.6	15.9	0.042	3.58	97.93	4.57	1.83	3.43
Float 1.15	<0.20	47.3	14.9	0.043	2.06	99.99	2.49	0.98	2.00

Precipitation of Uranium from Sodium Carbonate Solutions with Sodium Hydrosulfite

F. J. Hurst

Previously reported data have shown that with sufficient excess hydrosulfite ($Na_2S_2O_4$), precipitations of uranium from Na_2CO_3 solutions are quantitative and the recoveries are favored by low concentrations of total carbonate.[2] Recent tests have shown that much less hydrosulfite, in fact near stoichiometric quantities according to reaction (1), will give complete precipitation from carbonate solutions of reasonable strength if the reaction is carried out in an inert atmosphere.

$$S_2O_4^{=} + UO_2^{++} = U^{+4} + 2SO_3^{=} \qquad (1)$$

It was also found that by extending the reaction time, the effect of the higher carbonate concentrations could be overcome to a great extent.

Experimental Data and Discussion

A number of precipitation tests have been made at 60°C for various lengths of time in which the uranium ($Na_4UO_2(CO_3)_3$ concentration has been held constant at 2g U/l and the amounts of carbonate and hydrosulfite varied. The effect of pH was also studied by adding the excess carbonate as Na_2CO_3, $NaHCO_3$, or mixtures of the two. All of the tests were made in an inert (argon) atmosphere. The resulting data are plotted in Figures 15, 16, 17 and 18.

Figure 15 shows the effect of $CO_3^{=}$ concentration using slightly less than stoichiometric quantities of $S_2O_4^{=}$, according to reaction (1), for one day and at two pH levels. It is readily seen that pH as well as carbonate concentration is a critical factor in the precipitation step. For high pH solutions (pH~11.5, curve 1) the precipitation was almost complete at the low carbonate levels (.3M or less) after one day at 60°C but dropped off rapidly as the $CO_3^{=}$ concentration increased. For instance, in a 0.5M $CO_3^{=}$ solution, only 83% of the uranium was precipitated and in a 1.0M $CO_3^{=}$ solution, precipitation had dropped to 32%.

Curves 2 and 3 of Figure 15 show that equilibrium had not been reached in one day and that precipitation increased with a longer reaction period. If the reaction time was increased to

FIGURE 15

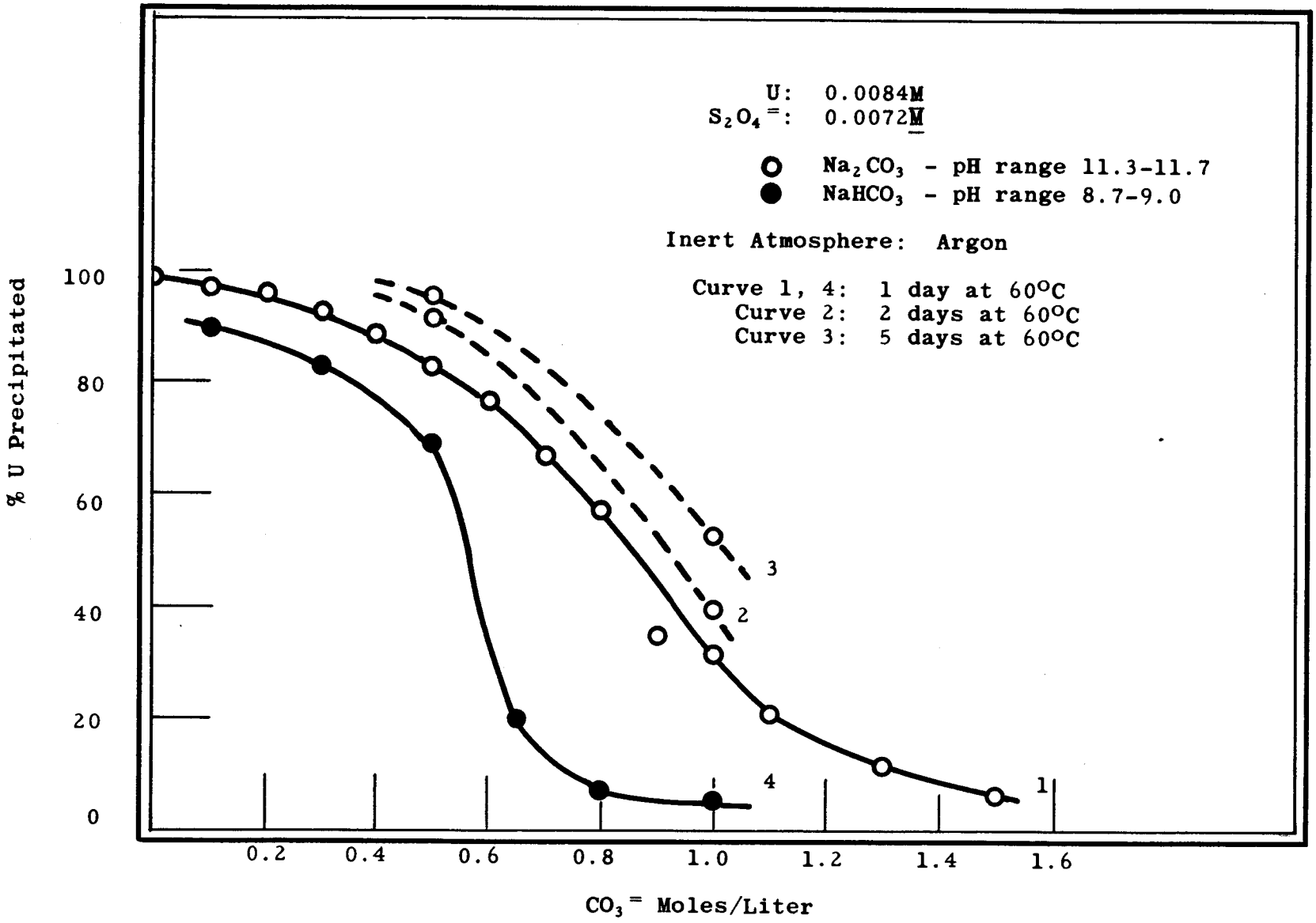

U: 0.0084M
$S_2O_4^{=}$: 0.0072M
Na_2CO_3 - pH range 11.3-11.7
$NaHCO_3$ - pH range 8.7-9.0
Inert Atmosphere: Argon
Curve 1, 4: 1 day at 60°C
Curve 2: 2 days at 60°C
Curve 3: 5 days at 60°C
% U Precipitated
100
80
60
40
20
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
$CO_3^{=}$ Moles/Liter
1
2
3
4

FIGURE 16

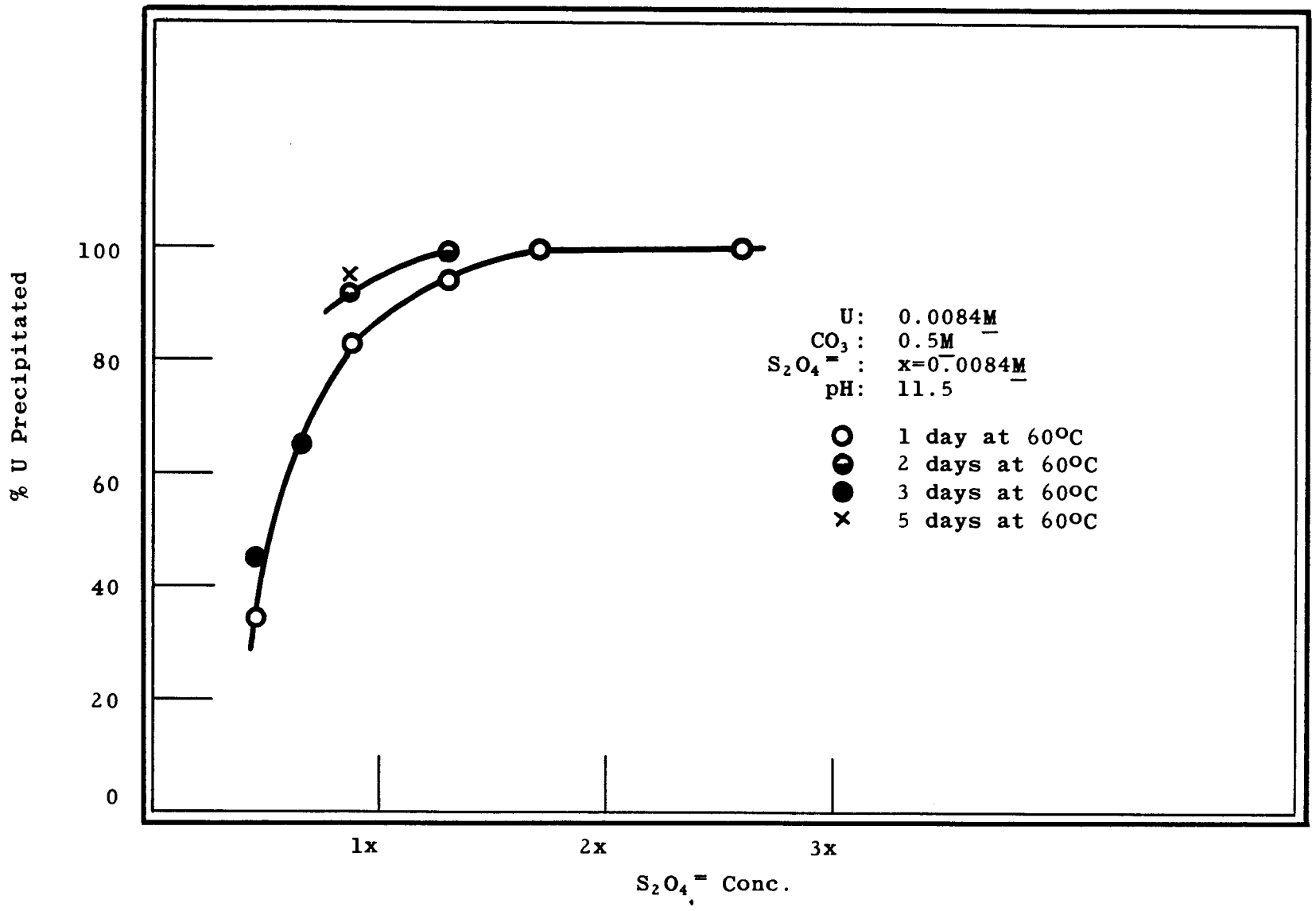

% U Precipitated
100
80
60
40
20
0
1x
2x
3x
$S_2O_4^{=}$ Conc.
U: 0.0084M
CO_3: 0.5M
$S_2O_4^{=}$: x=0.0084M
pH: 11.5
1 day at 60°C
2 days at 60°C
3 days at 60°C
5 days at 60°C

FIGURE 17

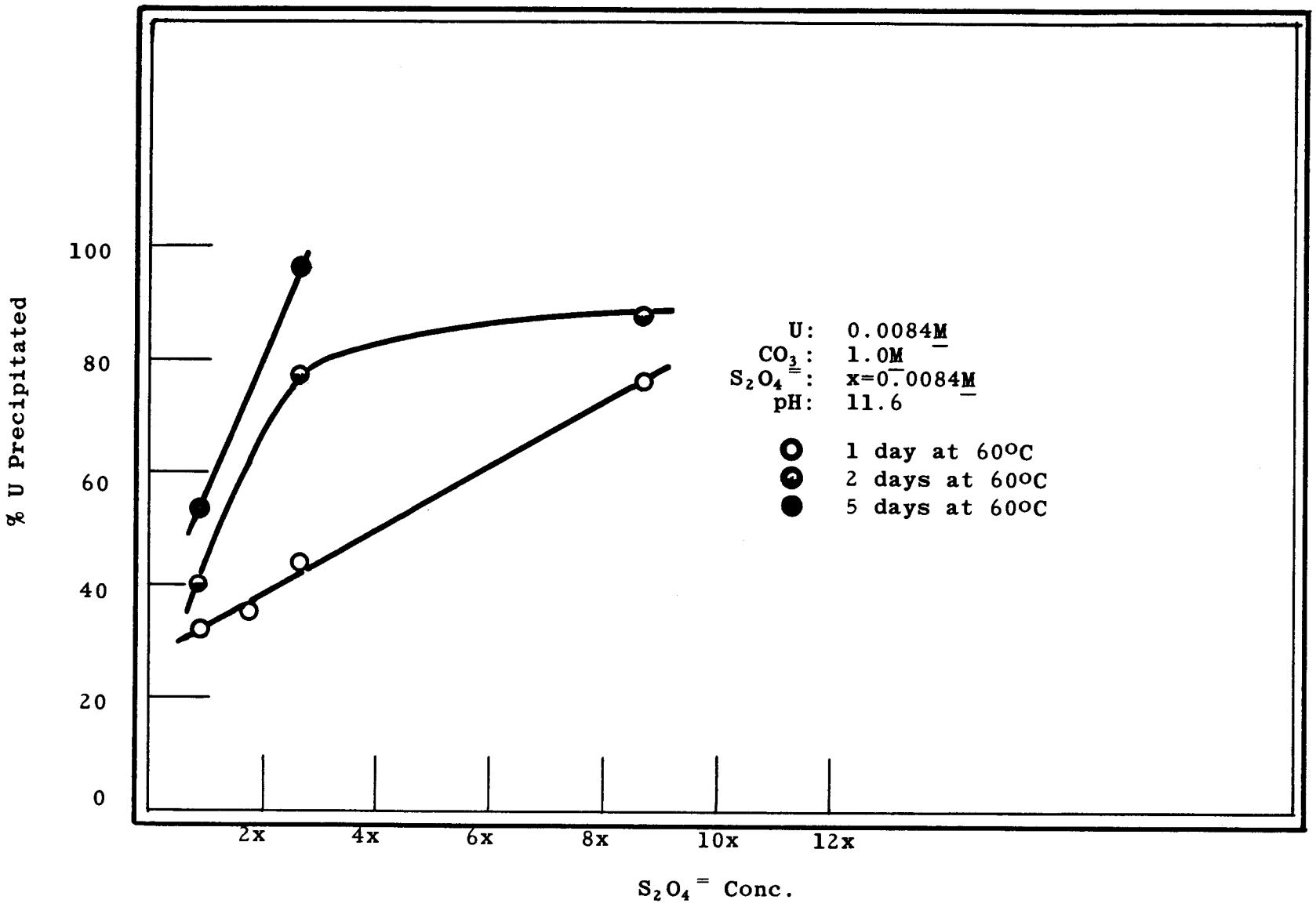
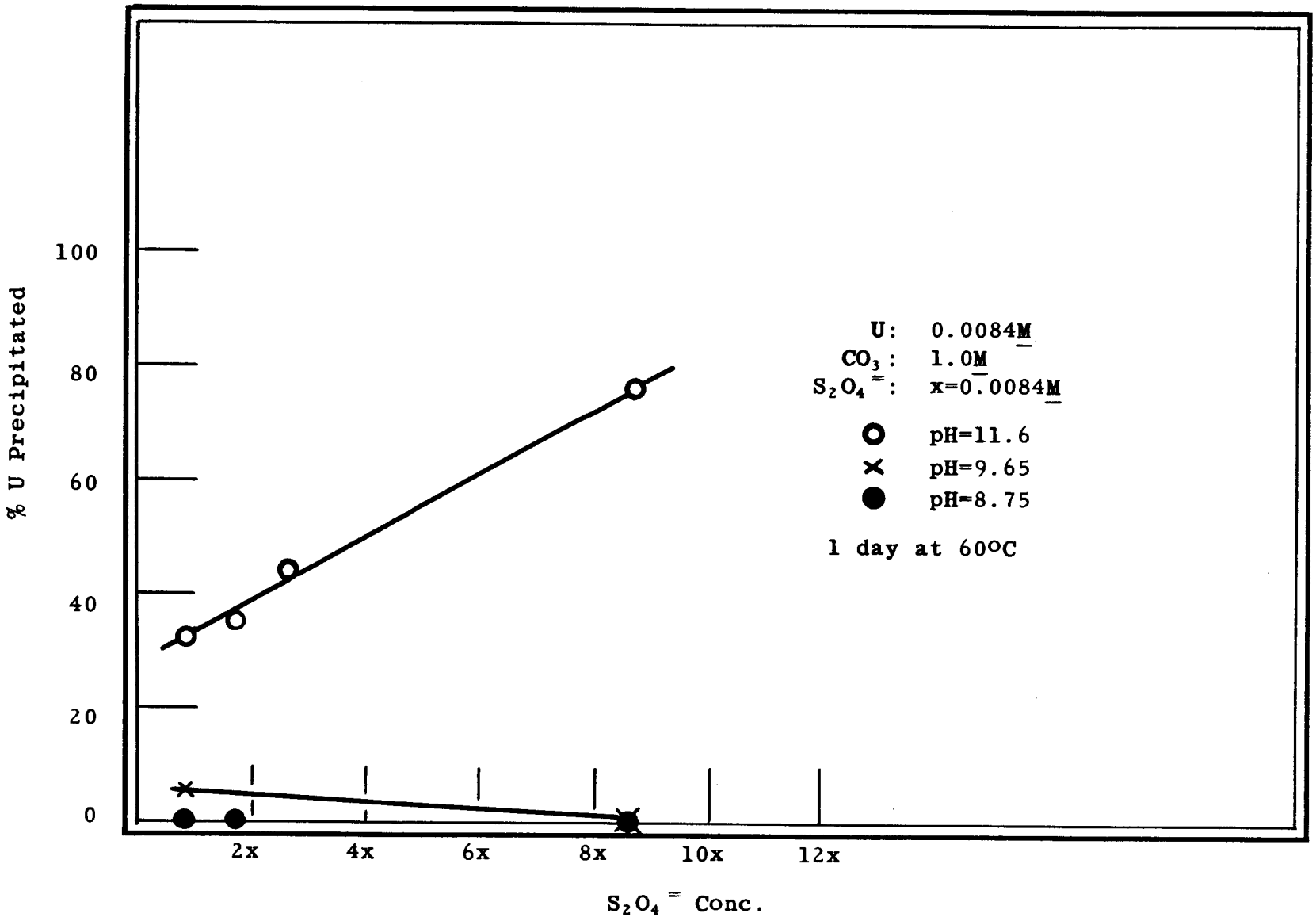

% U Precipitated
100
80
60
40
20
0
2x
4x
6x
8x
10x
12x
$S_2O_4^{=}$ Conc.
U: 0.0084M
$CO_3^{=}$: 1.0M
$S_2O_4^{=}$: x=0.0084M
pH: 11.6
1 day at 60°C
2 days at 60°C
5 days at 60°C

FIGURE 18


% U Precipitated
100
80
60
40
20
0
2x
4x
6x
8x
10x
12x
$S_2O_4^{=}$ Conc.
U: 0.0084M
CO_3: 1.0M
$S_2O_4^{=}$: x=0.0084M
pH=11.6
pH=9.65
pH=8.75
1 day at 60°C

five days, 95% and 53% recoveries were obtained in 0.5M and 1.0M $CO_3^=$ solutions, respectively. In a 0.5M solution, 92% was precipitated in only two days.

Figure 16 shows the effect of $S_2O_4^=$ concentration at different times for 0.5M $CO_3^=$ solutions. By increasing the $Na_2S_2O_4$ concentration to 1.7 times theoretical (reaction 1), 100% recoveries were obtained after a one-day reaction period. For 1.3 times theoretical $Na_2S_2O_4$, a 94% recovery was obtained and this was raised to 99% by increasing the time to two days. In tests with lesser amounts of $Na_2S_2O_4$, stoichiometric recoveries for the hypothetical reaction (reaction 1) were obtained; that is, 45% and 65% with 0.44 and 0.64 moles of $S_2O_4^=$ per mole of uranium.

Data are reported in Figure 17 for 1.0M $CO_3^=$ solutions. At this high carbonate concentration a precipitate is more difficult to obtain. However, by using 2.6 times the theoretical $S_2O_4^=$, precipitations of 96% of the uranium were obtained after an aging period of 5 days.

The effect of pH is shown in Figures 15 and 18. Figure 15 shows that the effect of $CO_3^=$ concentration is much more severe at lower pH (8.5-9.0) values. The sharp break in the low pH curve at 0.5 to 0.6M $CO_3^=$ may indicate the point at which the formation of some new complex becomes stable enough to resist precipitation.

The effect of $Na_2S_2O_4$ concentration is shown in Figure 18 for three pH levels. Even with a $Na_2S_2O_4$ concentration as high as 8.7 times theoretical, no precipitation occurred at the low pH range ($\gtrsim$9.65). However, these tests are for only one day and the results of an increase in reaction time are not known at present.

More tests are planned to complete the data described above. Future experimentation will also include liquors containing a small amount of vanadium.

Uranium and Vanadium from Carnotite Ores

F. J. Hurst

Several leaching tests have been made on Lukachukai ore with solutions containing sodium carbonate and an oxidant under pressures of 60-240 psi and at temperatures of 150 to 200°C. Extraction results are shown in Table 41.

Table 41

PRESSURE LEACHING OF LUKACHUKAI ORE WITH Na_2CO_3 SOLUTION

Exp. No.	Oxidant	Time (Hrs)	Leach Conditions Temp. (°C)	Leach Conditions Pressure (psi)	% of Total U	% of Total V	Tails % U	Tails % V
H-829	6% $Na_2S_2O_8$	3	150	58	98	25	.011	.520
H-830	3% $KMnO_4$	3	150	58	96	36	.022	.450
H-833	2% $KMnO_4$	3.5	150-195	180	93	49	.037	.370
H-842	2% $KMnO_4$	3 2	150-200 200	200-240	15	60	.464	.290

Leach Conditions: 100g ore (-80 mesh) per 300 ml 10% Na_2CO_3.

With $Na_2S_2O_8$ as the oxidant, the extraction of vanadium at 150°C was only 25%. This is little, if any, better than the results from leaching at atmospheric pressure and 95°C (~22% recovery).[2] Using $KMnO_4$ as the oxidant under the same conditions (150°C) the extraction of vanadium was increased to 36%. As the leach temperature was raised to 200°C, the extraction increased to 49% with perhaps small decrease in uranium recovery. With prolonged heating at 200°, the vanadium extraction increased to 60%, whereas the uranium dissolution was reduced to only 15%.

The low solubility of uranium may be due to the instability of uranium-bearing carbonate solutions at high temperatures (see ORNL-1220). Further treatment at room temperature may improve these recoveries.

Uranium from Marysvale Type Ores

D. J. Crouse

Work with Marysvale ore during the past quarter has been confined to a few tests of methods for refining the cake from the uranous phosphate precipitation process. In current practice the cake is fused with a Na_2CO_3-NaCl mixture at 1000°C. Some trouble has been experienced in the plant due in part to the corrosive action of this mixture at high temperatures.

Fusion of Uranous Phosphate Cake

The results from fusion in which two low melting eutectics were used as flux materials are presented in Table 42. Ni and Fe crucibles were used to contain the melts and neither appeared to corrode appreciably. The best product contained 78% U_3O_8 which was somewhat lower in grade than those obtained by the simple caustic leach described below.

Caustic Leach of Uranous Phosphate Cake

As shown in Table 43, the cake was upgraded to over 80% U_3O_8 by a 10% caustic leach using a 25:1 weight ratio of solution to dry cake. Leaching at room temperature seemed to be as effective as leaching at 80°C. In some instances, an attempt was made to further upgrade the product by following the basic leach with a dilute acid wash. The acid wash, however, dissolved enough uranium, even at a pH of approximately 4.0, to make this treatment impractical. All of the products showed a fairly high percentage of phosphate which could probably be decreased by increasing the leaching time or the temperature.

Table 42

FUSION OF URANOUS PHOSPHATE*

Fusion: 1/2-Hr. at indicated temperature. Product washed in hot water (total wash volume = 1000 ml)

Grams of Cake	Flux	Melt. Temp.	Crucible	Fusion Temp.	Wt. (g) of Prod.	Analyses: Wash Soln. mg U/l	Analyses: Product - % U_3O_8	Analyses: Product - % Na	Analyses: Product - % PO_4	Grams U_3O_8: Wash Soln.	Grams U_3O_8: Prod.	Grams U_3O_8: Total
11.5	12g NaOH 11g KOH	190°C	Ni	600°C	7.00	42	78.1	2.11	1.62	.04	5.47	5.51
6.5	20g NaOH 6g Na_2CO_3	290°C	Ni	500°C	3.71	70	74.8	7.90	1.77	.07	2.78	2.85
17	18g NaOH	190°C	Fe	500°C	11.87	60	68.8	--	1.73	.06	8.17	8.23

*Cake Analysis: U_3O_8, 50.1%; Fe, 1.63%; Al, 0.63 ; PO_4, 32.1%; SO_4, 13.1%
Cake prepared from synthetic leach liquor
Approximating normal plant liquors.

Table 43

UPGRADING OF URANOUS PHOSPHATE CAKE*

NaOH Leach		Constant pH-HCl Leach		Wt. of Prod.	Product - %				Grams U_3O_8				% of U in Acid Leach
									Leach				
NaOH Conc.	Time-Temp.	pH	Time Temp.		U_3O_8	Fe	Al	PO_4	NaOH	HCl	Prod.	Total	
5%	2Hrs-80°C	--	--	3.631	78.5	3.15	<.3	4.94	.02	--	2.85	2.87	--
10%	"	--	--	3.592	80.6	3.25	<.3	2.91	.01	--	2.90	2.91	--
10%	3Hrs-RT	--	--	3.552	80.4	3.23	<.3	3.61	.02	--	2.86	2.88	--
10%	2Hrs-RT	2.3-2.7	1Hr-RT	2.075	81.5	4.02	<.3	2.86	.02	.99	1.69	2.70	37
10%	2Hrs-80°C	3.2-3.4	"	1.380	77.5	5.89	.48	5.47	.01	.62	1.07	1.70?	36
10%	"	4.1-4.3	"	2.565	82.2	3.58	.42	3.36	.004	1.55	2.11	3.66?	42
10%	2Hrs-RT	3.5-3.7	1/2Hr-RT	2.575	82.1	3.63	<.3	3.93	.01	.60	2.11	2.72	22
20%	2Hrs-RT	--	--	3.383	81.4	3.39	<.3	2.05	.01	--	2.75	2.76	--

Leaches: 6g Phosphate Cake
150 ml Solution

*Cake Analysis: U_3O_8=50.1%, Fe=1.63%, Al=.63%, PO_4=32.1%, SO_4=13.1%

Uranium Recovery from Metal Production Salvage

F. J. Hurst

Kilogram samples of both slag and liner were screened and each fraction was analyzed for uranium. The results from these screening tests are presented in Table 44.

The plus 200 mesh fraction was given four one-hour ball mill treatments. Each treatment was followed by a 30-minute screening through a 200 mesh screen. The results from these tests are presented in Table 45.

Similar to the results reported last quarter,[2] the data in Table 45 show that over one half of the uranium in both the slag and liner can be concentrated into a small coarse fraction; that is, 58% of the uranium into a material that was only 5% of the total weight of the liner (assaying 3.2% U), and 58% of the uranium into 3.5% of the total slag (assaying 41% U).

Preliminary leaching tests on the minus 200 mesh material (both slag and liner) have not been encouraging. Only a few other tests are planned.

Table 44

SCREEN ANALYSIS*

	Liner				Slag			
Mesh Size	Wt. (gms)	U (gms)	Distrib. U %	Cumulative Distrib. U %	Wt. (gms)	U (gms)	Distrib. U %	Cumulative Distrib. U %
+14	12	.389	18.1	18.1	232	6.055	34.8	34.8
-14+20	31	.174	8.1	26.2	106	1.611	9.3	44.1
-20+35	97	.035	1.6	27.8	94	1.936	11.1	55.2
-35+60	104	.385	17.9	45.7	108	1.814	10.4	65.6
-60+100	377	.792	36.8	82.5	73	2.307	13.3	78.9
-100+200	102	.107	5.0	87.5	124	1.575	9.0	87.9
-200	270	.270	12.5	100.0	269	2.098	12.1	100.0
TOTAL	993	2.152	100.0		1006	17.396	100.0	

*Due to the heterogeneous nature of this material and since only one-fourth of each fraction was used for uranium analysis, the chance for error in the coarse fractions was great. This danger was eliminated in the small, coarse, heterogeneous residue resulting from the grinding tests and described in Table 45 by dissolving the whole sample in HNO_3.

Table 45

Mesh Size	Liner Wt. (gms)	Liner U (gms)	Liner Distrib. U (%)	Liner Cumulative Distrib. U (%)	Slag Wt. (gms)	Slag U (gms)	Slag Distrib. U (%)	Slag Cumulative Distrib. U (%)
+200	40	1.260	58	58	26	10.624	58	58
-200	704	.915	42	100	718	7.539	42	100
TOTAL	744	2.175	100		744	18.163	100	

[redacted]

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