[redacted]

ORNL-1384

2a
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0353151 4

1952 OCT 24 AM 11 03
RECEIVED - ORNL
OFFICE OF DIRECTOR

MATERIALS CHEMISTRY DIVISION

PROGRESS REPORT

URANIUM CHEMISTRY OF RAW MATERIALS SECTION

April 1, 1952 to June 30, 1952

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE

[redacted]

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

[redacted]

[redacted]

Index No ORNL-1384
This document contains 156 pages
This is copy 2 of 77, Series A

Subject Category Metallurgy - Raw Materials

PROGRESS REPORT

URANIUM CHEMISTRY OF RAW MATERIALS SECTION

April 1, 1952 to June 30, 1952

K B Brown, Supervisor

DECLASSIFIED

CLASSIFICATION CHANGED TO
BY AUTHORITY OF TID-1148
BY R. Morrison 7/22/57

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

Contract No W-7405-eng-26

[redacted]

3 4456 0353151 4

[redacted]

Index No ORNL-1384
Metallurgy-Raw Materials

Distribution Series A

1	Carbide and Carbon Chemicals Company
26-27	American Cyanamid Company (Watertown)
28-29	Argonne National Laboratory
30-31	Atomic Energy Commission Washington
32	Battelle Memorial Institute
33	Brookhaven National Laboratory
34	Carbide and Carbon Chemicals Company (ORNL)
35	Catalytic Construction Company
36	Chicago Patent Group
37-40	Colorado Raw Materials Office
41-47	Division of Raw Materials Washington
48	Dow Chemical Company (Pittsburg)
49	General Electric Company Richland
50	Hanford Operations Office
51	International Minerals and Chemical Corporation
52	Iowa State College
53	Knolls Atomic Power Laboratory
54-55	Los Alamos
56	Mallinckrodt Chemical Works
57	Merrill Company
58	National Lead Company
59	New Brunswick Laboratory
60	New York Operations Office
61	Patent Branch Washington
62	Rohm and Haas Company Philadelphia
63	Tennessee Valley Authority
64	U S Geological Survey
65	University of California Radiation Laboratory
66-67	Vitro Corporation of America
68-77	Technical Information Service Oak Ridge

Carbide and Carbon Chemicals Company internal distribution as follows

1	C	E	Center	8	F	L	Steahly	15	W	R	Grimes
2	C	E	Larson	9	E	H	Taylor	16	[illegible]	H	Clewett
3	L	B	Emlet	10	G	E	Boyd	17	[illegible]	B	Brown
4	W	B	Humes	11	K	A	Kraus	18	C	[illegible]	Coleman
5	A	M	Weinberg	12	R	S	Livingston	19	C	[illegible]	Baes
6	E	D	Shipley	13	C	P	Keim	20	J	M	Schreyer
7	J	A	Swartout	14	C	D	Susano	21	C	A	Blake
								22-25	Reports Office TID		

Issuing Office
Technical Information Department Y-12 Plant
Date Issued OCT 23 1952

[redacted]

[redacted]

TABLE OF CONTENTS

		Page
I	INTRODUCTION AND SUMMARY	7
II	PROCESS DEVELOPMENT	11
	A Uranium from Lignite	11
	Introduction	11
	Composition and Properties of Lignite Sample	11
	Mineral Composition	11
	Uranium Content of Mineral Fractions	12
	Sink-Float Tests	12
	Heating Value	14
	Chemical Processing	14
	Leaching the Ash with H_2SO_4	15
	Leaching the Ash with Na_2CO_3	16
	Leaching the Ash from Beneficiated Lignite with Na_2CO_3	17
	The Ammonium Carbonate Process	17
	Comparison of Chemical Costs in the Foregoing Processes	18
	Controlled Roasting of Lignite Followed by Water Leaching	22
	Future Work	23
	B Recovery of Uranium from the Florida Leached Zone	26
	Acid Leaching	26
	Constant pH Leach with Resin	26
	Direct Leach	28
	Basic Leaching	41
	Leaching with Organic Reagents	41
	Uranium Recovery from Solutions	46
	Precipitation Tests	46
	Liquid-Liquid Extraction	51
	Ammonium Sulfate Fusion	52

[redacted]

[redacted]

		Page
C	Miscellaneous	65
	Pressure Leaching of Marysvale Ores	65
	Precipitation of Uranium from Sodium Carbonate Solutions with Sodium Hydrosulfite	65
	Nature of the Precipitate	68
	Precipitation of Uranium and Vanadium from Sodium Carbonate Solutions with Sodium Hydrosulfite	68
III	URANIUM CHEMISTRY	70
A	Organic Reagents for Solvent Extraction and Precipitation of Uranium (and Thorium)	70
	Screening of Possible Organic Complexing Agents	72
	Screening of Organophosphorus Compounds	72
	Detailed Study of Organophosphorus Acids in Pure Solutions	74
	Concentrations of Typical Organophosphorus Acids Required to Extract Uranium from Various Solutions	74
	Effect of Solvent on Extraction with Di(2-ethylhexyl)phosphinic Acid	78
	Extraction of Iron and Aluminum by Organophosphorus Acids	84
	Saturation Experiments to Determine Combining Ratio of Extractable Uranium Complex	84
	Determination of Formation Constant for the Uranium Complex with Di(2-ethylhexyl)phosphinic Acid	90
	Determination of the Combining Ratio of the Iron-Phosphinic Acid Complex and Its Formation Constant	93
	Stripping Uranium from the Organic Extract	95
	Extraction of Reduced Uranium (IV) by Organophosphorus Compounds	95

[redacted]

[redacted]

	Page
Extraction from Process Liquors by Means of Organophosphorus Acids	96
Competition Between Complexing Agent and Other Uranium Complexers	109
Selectivity of the Organic Complexing Agent for Uranium in the Presence of Other Metal Ions	109
Rate of Uranium Extraction	110
Physical Behavior of Reagent During Extraction	110
The Stripping Cycle	111
Loss of Reagent to Raffinate	111
Recycle of Reagent	114
Concentration Across System	114
Product Purity	115
Recovery of Thorium from Sulfuric Acid Solutions of Monazite Sand by Solvent Extraction	115
Experimental Solutions and Analyses	115
Extraction of Thorium and Separation from Rare Earths Using Mono(2-ethylhexyl)phosphoric Acid	115
Uranium Extractions from Monazite Sand Solutions with Mono(2-ethylhexyl)-phosphoric Acid	116
Extraction of Thorium with Other Reagents	117
Stripping of Thorium from the Organic Phase of Mono(2-ethylhexyl)phosphoric Acid in Petroleum Ether	117
Future Work	119
Anionic Solvent Extraction	121
Comparison of Uranium Extractions Using Various Amines	121
Stripping Uranium from the Organic Phase	123
Effect of Solvent	123
Recycle of Reagent and Solubility	123
Effect of Sulfate Concentration and pH	127
Influence of Fe, Al and NO_3	127
Extractions from Leached Zone Liquors	127

[redacted]

[redacted]

		Page
	Extraction of Titanium with Esters of Phosphoric Acid	131
	Preparation of Organic Compounds	132
	Nomenclature	132
	Phosphoric Esters	132
	Phosphonic Acids	132
	Phosphinic Acids	133
	Amines	134
	Miscellaneous Phosphorus Compounds	134
	New Compounds	138
	Old Compounds	139
	New Methods	140
B	Chemistry of Uranium Phosphate Solutions	142
	Analytical	142
	Stability of Uranium (IV) Phosphate Solutions	142
	Composition of Uranium (IV) Phosphate	143
	Polarographic Analysis	143
	Solubility Studies in Acid Solution	144
	Solubility Measurements of Uranium (VI) in Phosphoric Acid	144
	Acid Dependence of UO_2HPO_4 Solubility	145
	Discussion of Solubility Results	150
	Solubility of Uranium (VI) in Alkaline Phosphate Solutions	152
C	Reduction of Uranium in Sodium Carbonate Solutions	153
IV	REFERENCES	155

[redacted]

[redacted]

URANIUM CHEMISTRY OF RAW MATERIALS

K B Brown

INTRODUCTION AND SUMMARY

The Uranium Raw Materials program at Oak Ridge National Laboratory during the second quarter of 1952 has continued in the development of processes for recovering uranium (and by-products) from various types of ores and in the study of those phases of uranium chemistry which seem especially pertinent to the current raw materials situation

Process development work has been devoted primarily to two projects, (1) uranium recovery from lignite, and (2) recovery of uranium from the Florida Leached Zone A small amount of additional time was devoted to studies such as (a) pressure leaching of Marysvale ores and (b) precipitation of uranium and vanadium from sodium carbonate solutions with sodium hydrosulfite

The uranium chemistry program has included (1) investigation of the solvent extraction of uranium from aqueous nitrate, sulfate, phosphate, and fluoride solutions through use of organic complexing agents, especially organophosphorus compounds, (2) extraction of thorium from sulfuric acid solutions of monazite sand with organophosphorus acids, (3) extraction of uranium from sulfate and phosphate solutions with secondary amines tertiary amines and quaternary ammonium salts (4) studies of the behavior of hexavalent uranium in phosphate solutions and (5) reduction of uranium in sodium carbonate solutions

Sink-float tests and other mineral studies with raw crushed Dakota lignite have continued to show the possibility of discarding a large share of the inorganic material while retaining most of the uranium with the organic-rich fraction Other more practicable methods for achieving the physical separation are now being studied, e g , air classification of the dried lignite prior to burning as a pulverized fuel

Studies of methods for chemically processing lignite ash have been started during the quarter Two methods have shown promise The first of these employs an ammonium carbonate leach of the ash and gives promise of a low

[redacted]

consumption of chemicals since the ammonia may be recycled and carbon dioxide is available in copious quantities from the lignite burning By-product ammonium sulfate and molybdenum oxide may also be possible, in quantities large enough to offset the cost of chemicals consumed Uranium extractions are acceptable if the ash has not been formed at too high a temperature The second method studied utilizes a controlled burning of the lignite to obtain maximum conversion of the sulfide sulfur to sulfates With proper burning the resulting ash is acidic and about 75% of the uranium has been dissolved by a water leach

A total of seven samples of LZ (Florida Leached Zone) ores have been obtained, three of these being representative of special mineral types Comparative leaching tests have been completed except for a pseudowavellite sample The results show that the fraction of the uranium which is readily soluble, and the acid consumption to extract this fraction, both correlate with the calcium content of the ore Unless the response of pseudowavellite to leaching proves to be different from the other results, and unless there are important mineral types not represented in these samples, the response of an LZ ore to leaching with nitric or sulfuric acid can be predicted from the chemical analysis

Uranium has been recovered from the LZ acid leach liquors by solvent extraction, anion exchange and precipitation A topical report of the leaching studies (above) and the solution recovery studies is being prepared

Preliminary tests have been made in which the Leached Zone material has been opened up by baking with a small excess of ammonium sulfate at 400-430°C followed by dissolution of phosphate and alumina in a water leach These results suggest a process wherein uranium and by-products would be recovered from the sulfate liquor, and the sulfur recovered and recycled as ammonium sulfate

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 Further fundamental studies in pure solutions concerning the nature of the extractable complex and the relation of its stability to the structure of the complexing agent are reported For example, saturation experiments with di(2-ethylhexyl)phosphinic acid show that the extractable uranium (VI) complex has a combining ratio of two moles of phosphinic acid for each mole of uranium A preliminary estimate of the formation constant for this complex is $K_f=3x10^3$ The

extractable iron complex appears to have a combining ratio of one mole of phosphinic acid for each mole of iron and the formation constant is in the order of $K_f=10^{-1}$ Similar data are being obtained for other types of reagents

Very promising results have been obtained from the extraction of western sulfate leach liquors (U=2-3 gms/l) with di(2-ethylhexyl)phosphinic acid This reagent has shown the following advantages over other reagents tested with this liquor (1) excellent selectivity for uranium in the presence of iron and aluminum, (2) good physical performance, i e , complete lack of precipitation or emulsion, (3) ease of stripping with mineral acids and (4) reagent stability Though the price of phosphinic acids may be relatively high the loss of reagent was low enough (<0 05 lb/lb of recovered U) so that the reagent cost should be rather small Here, then, is another class of organophosphorus compounds to be considered when making a choice of the best reagent for any particular extraction problem

Phosphinic acids have also shown promise as extractants for low level uranium liquors Using di(2-ethylhexyl)-phosphinic acid the uranium (70ppm) was extracted from a nitric acid leach of Florida Leached Zone material and concentrated by a factor of 30 with only a small utilization of reagent per pound of uranium extracted

A portion of the effort on organic preparations is being placed on the development of new and less expensive methods for preparing some of the organophosphorus compounds A new method of preparing phosphinic acid has been devised Reaction of benzenephosphorus dichloride with 2-ethylhexyl chloride in the presence of aluminum chloride yielded phenyl-2-ethylhexyl phosphinyl chloride which was distilled and hydrolyzed to the acid This method has also been used in preparing butylphenyl-phosphinic acid in forty-five percent yield

Recent tests have confirmed previous work in showing that thorium can be readily extracted from a sulfuric acid solution of monazite sand using certain organophosphorus compounds in common organic solvents Separation of thorium from the rare earth constituents is very good Stripping of thorium from the organic phase has been accomplished by several methods, none of which are considered completely satisfactory at this time

The use of methyldioctylamine and di(2-ethylhexyl)amine in extracting uranium (VI) from sulfate and sulfate-phosphate liquors was mentioned previously Further studies with other

amines have shown acceptable uranium extractions and stripping of uranium from the organic phase is readily obtained with small volumes of dilute HNO_3, NaCl-HCl, or Na_2CO_3 Most of the compounds studied thus far have had one obvious drawback, i e , the solubility of the reagent in aqueous sulfate solutions At the present time a number of amines are being examined in search of a compound that will combine high uranium extraction with low reagent solubility

The screening program for new uranium complexing agents has shown that certain neutral bifunctional phosphorus compounds, notably, tetrabutyl ethylene diphosphonate, tetrabutyl m-phenylene diphosphate, tetrabutyl diethylene glycol diphosphate and tetraphenyl ethylene diphosphate demonstrate the ability to extract hexavalent uranium in the presence of phosphate in spite of their neutrality It is anticipated that some of the bifunctional acids will form even stronger complexes Compounds of this type are being prepared

The solubility behavior of uranyl phosphates in 0 001M to 15M phosphoric acid has been determined The data in the range 0 001M to 3M phosphoric acid have been interpreted semiquantitatively in the terms of the formation of three complex species between UO_2^{++} and H_3PO_4, i e , $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)_2$, $UO_2(H_2PO_4)_2(H_3PO_4)$ Measurements of pH during the dissolutions of UO_2HPO_4 $4H_2O$ are also in agreement with the formation of these complexes

As a part of the phosphate solubility work the following compounds have been identified as the stable solid phases in the concentration ranges indicated

0 001M - 0 014M	H_3PO_4	$(UO_2)_3(PO_4)_2$ $4H_2O$
0 014M - Ca7M	H_3PO_4	UO_2HPO_4 $4H_2O$
Ca7M - 15M	H_3PO_4	UO_2HPO_4 H_3PO_4 $3H_2O$ (tentative)

PROCESS DEVELOPMENT

Uranium from Lignites

F A Schimmel, R C Nelson, F J Hurst

Introduction

Sink-float tests and other mineral separation studies have continued to show the possibility of discarding a large share of the inorganic material while retaining most of the uranium with the organic-rich fraction Physical separations of the uranium-bearing material from the ashed lignite are now being attempted

Studies of methods for chemically processing the lignite ash have been started during the quarter Two methods have shown promise The first of these employs an ammonium carbonate leach of the ash and gives promise of a low consumption of chemicals since the ammonia may be recycled and carbon dioxide is available in copious quantities from the lignite burning By-product ammonium sulfate and molybdenum oxide may also be possible, in quantities large enough to more than offset the cost of chemicals consumed The second method utilizes a controlled burning of the lignite to obtain maximum conversion of the sulfide sulfur to sulfates With proper burning the resulting ash is acidic and about 75% of the uranium has been dissolved by a water leach

Additional samples of uraniferous coals have been received recently from the U S Geological Survey but have not been prepared for laboratory use All of the tests mentioned below were made using the sample from Dakota which was described previously[1]

Composition and Properties of Lignite Sample

Mineral Composition

Petrographic examination of the lignite sample was made by Dr T N McVay Dr McVay reported the presence of jarosite (to be confirmed by X-ray), considerable gypsum and minor amounts of clay and quartz In a different sample of Dakota lignite, Battelle Memorial Institute[2] has reported the presence of anhydrite, zircon and tourmaline These minerals were not noted in the sample here and all of them are comparatively easy to identify

Uranium Content of Mineral Fractions

During the petrographic work Dr McVay hand-picked small amounts of several minerals from a large batch of air-dried lignite and these samples were submitted for uranium analyses The results tabulated below show very clearly that the uranium is not associated with any of the major mineral constituents, but definitely concentrates with the organic-rich fraction Recently, fourteen samples of organic-rich material were hand-picked from a large batch of lignite Each sample is being analyzed for uranium as well as other metals to determine whether the uranium concentration can be correlated with any of the trace constituents

Constituent*	U Content ppm	U Content %
Jarosite	17	0 002
Coarse-grained clay	29	0 003
Fine-grained clay	33	0 003
Gypsum ("satin-spar")	22	0 002
Gypsum (dehydrated)	17	0 002
Lignite (carbonaceous)**	550	0 055
Head Sample (approximate)	440	0 044

* None of the samples were completely free from carbonaceous matter

** The ash content was not measured Other similar samples have shown about 15% ash whereas the head material is about 30%

Sink-Float Tests

Two sink-float tests were made previously using -8 to +20 mesh, and -20 to +60 mesh lignite[1] Another such test is now complete in which a finer sample, -100 to +325 mesh, has been used The experimental procedure was the same as previously described except that the zinc chloride solutions were replaced by solutions of barium perchlorate as the separation media

The test results as shown in Table 1 serve to confirm the earlier work in that over 50% of the total ash has been separated into a discard product containing 20% of the total uranium and 18% of the total carbon Separation by the methods used for these experiments would of course not be

Table 1

SINK-FLOAT TEST NO 3 (-100 +325)

Sample	Chem Analysis (as submitted) % Moist	% Tot C	% Ash	% U	Sink-Float Test Results (Dry) Wt % Ret	Cum Wt % Ret	% Distribution Tot C	Ash	U
Head Sample	7 9	33 8	30 3	0 0344	--	--	--	--	--
Sink 1 70	2 1	17 5	56 7	0 0210	32 31	31 75	18 35	50 60	20 75
Sink 1 50	4 7	35 1	29 8	0 0420	26 21	57 57	47 45	71 56	53 45
Sink 1 45	1 24	39 3	26 3	0 0360	15 80	73 04	67 83	83 11	70 99
Sink 1 40	5 4	40 7	17 3	0 0160	6 62	79 55	76 31	86 17	74 10
Sink 1 35	6 5	28 1	16 3	0 0440	5 61	85 06	81 20	88 58	81 29
Sink 1 30	2 5	32 1	24 5	0 0380	4 88	89 86	86 28	91 86	86 93
Sink 1 25	3 7	39 2	24 8	0 0420	2 89	92 70	89 90	93 80	90 57
Sink 1 20	1 22	39 7	29 4	0 0440	1 48	94 15	91 82	95 01	92 57
Sink 1 15	2 3	38 4	38 1	0 0220	0 98	95 11	93 04	96 03	93 23
Float 1 15	0 39	42 3	28 4	0 0440	4 98	100 00	100 00	100 00	100 03
					100 00				

feasible as an industrial practice The possibility of concentrating the uranium by physical methods prior to chemical processing is attractive enough, however, to encourage the consideration of other more practicable methods Air classification of the dried pulverized lignite has been suggested as a method which might be easily fitted into processes for handling pulverized fuel

Heating Value

Three grab samples from the original batch of untreated lignite were submitted for Parr bomb calorimetric determinations The results presented below are in good agreement Lignites currently utilized as fuels have somewhat greater heat values due to lower ash contents

Sample No	BTU's/lb (dry basis)
LR-1	5300
LR-2	5400
LR-3	5300

Chemical Processing

A limited amount of work on the recovery of uranium from lignite ash was conducted some time ago at the Battelle Memorial Institute[2] Three methods for processing the ash were studied (1) leaching with sulfuric acid, (2) leaching with sodium carbonate, and (3) beneficiation of the raw lignite, or the ash, prior to leaching with sodium carbonate All of these methods, especially the first two, required large quantities of chemicals In the current work it has been of interest to consider processes in which the consumption of chemicals is lower so that a wet extraction process might look more attractive from an economical point of view

Two methods for treating the lignite have been considered thus far (1) leaching the ash with $(NH_4)_2CO_3$, which would include the recycle of NH_3, the utilization of CO_2 from stack gases, and the production of $(NH_4)_2SO_4$, MoO_3, and uranium as products, (2) controlled burning of the lignite to form an acidic ash which will yield uranium to a water leach The first of these methods is discussed in some detail below and is compared in a very qualitative fashion to the H_2SO_4 and Na_2CO_3 leaching treatments as described by Battelle Only a small amount of experimental work has been accomplished at

this time but the process, on paper, looks good enough to justify a closer examination The second process mentioned above is also discussed below but since this approach would require the preparation of a special ash it has not been compared directly with the other methods

Of course, the ash to be processed can vary within rather wide limits, not only in its composition, but also in its chemical behavior depending on its history, the type of the raw lignite, roasting temperature, previous dressing operations, and so on Direct comparison of different approaches to the uranium recovery problem is allowable, therefore, only if the feed material has been the same for each For purposes of the subsequent discussions it has been assumed that a rather uniform material is available of the same composition as that used by Battelle in most of their studies

The analysis given by BMI on a calcined ash basis is as follows U = 0 051%, SiO_2 = 12 3%, Fe_2O_3 = 16 6%, Al_2O_3 = 7 5%, MoO_3 = 0 17%, CaO = 24 9%, MgO = 3 9%, Na_2O = 5 9%, K_2O = 0 3%, CO_2 = 1 4%, P_2O_5 = 0 2%, SO_3 = 20 8%, Total S as SO_3 = 24 9% The greatest part of the sulfur was present as sulfate, the remainder probably as sulfide As a simplification it is supposed that the atmosphere during the roast is sufficiently oxidizing to convert all the sulfide into sulfate Upon considering the possible form in which the constituents may be present in this ash, the following assumptions seem to be essentially correct (1) if sodium and potassium are not water soluble, they may have reacted to form an alkali alumina silicate, and (2) ferric sulfate has not been formed since the roasting temperature is too high The main constituents of the ash may then be postulated as follows

$CaSO_4$	42 35%
$CaCO_3$	3 2
CaO	5 65
MgO	3 4
Fe_2O_3	16 6
Al_2O_3	3 3
$Na_2O\ Al_2O_3\ 4SiO_2$	20 7
	95 20%

the remainder containing 2 7% Na_2O, 0 3% K_2O, 0 2% P_2O_5, 0 17% MoO_3 The reaction of the ash is basic

Leaching the Ash with H_2SO_4

If the ash described above is leached with 10-20% H_2SO_4, the $CaCO_3$ will be attacked along with the CaO and MgO since it

is assumed that the latter were originally present in the lignite as dolomite rather than silicates Iron oxide will also go into solution, at least in part On this basis a calculation of the consumption of acid during leaching may be made as follows

	Content in Ash	H_2SO_4 Consumed lbs/ton of Ash
$CaCO_3$	3 2 %	64
CaO	5 65%	196
MgO	3 4 %	166
Fe_2O_3 (Assume 80% soluble)	16 6 %	480
		906

For this ash the requirement would be about 890 lbs H_2SO_4/lb of uranium which is in good agreement with the experimental value of 840 lbs /lb as determined by Battelle Apparently the foregoing assumptions as to the composition of the ash are nearly correct This could have been easily checked by BMI by an analysis of the leach liquor, but, unfortunately, such an analysis was not made

It is true that the ash could be made less reactive by heating to temperatures high enough (1000-1200°C) to cause formation of calcium and magnesium silicates and refractory iron oxide Extraction of uranium would also be very difficult however unless steps are taken to prevent melting which would complicate the problem too much It is also true that the average lignite ash could be of lower basicity than the Battelle sample A consumption low enough to be unimportant from the standpoint of cost and sulfur availability would, however, be difficult to attain For these reasons the prospect of a sulfuric acid leach does not look particularly encouraging

Leaching the Ash with Na_2CO_3

Upon treating the ash with sodium carbonate solution the following reaction will take place

$$CaSO_4(s) + Na_2CO_3 = CaCO_3(s) + Na_2SO_4$$

Partial reaction might also be expected with the SiO_2 For the particular ash under consideration these reactions, especially the first, will be the major factors contributing to the soda ash consumption The amounts of P_2O_5 and MoO_3 in the ash are quite small and the alumina will not act as

a consumer unless it is present as calcium aluminate, the formation of which would require temperatures above 800°C

If one assumes, as did Battelle, that the sulfate reaction accounts for essentially all of the soda ash consumption, the calculated requirement would be about 660 lbs of Na_2CO_3/ton of ash With 75% extraction of uranium from the Battelle ash the requirement would be about 900 lbs /lb of uranium

The price of chemicals used is unusually high, e g , 6 to 8 dollars per ton of ash Molybdenum would be extracted by the sodium carbonate leach and may be considered as a potential by-product (see below) The sale of Na_2SO_4 in quantity, however, can be ruled out

Leaching the Ash from Beneficiated Lignite with Sodium Carbonate

Battelle has reported that a physical separation (sink-float) of about 50% of the inorganic minerals from the raw lignite will significantly reduce the consumption of Na_2CO_3/lb U during leaching of the subsequent ash Presumably this is due to the discard of much of the $CaSO_4$ with the inorganic fraction

Although the reagent consumption is still rather high, the possibilities of such a process may be worth further attention It would be of interest, for example, to determine (1) whether the molybdenum follows the uranium in the beneficiation step and hence remains a potential by-product and (2) whether the same reagent saving would be noted using fresh underground lignite which should contain much of its sulfur or sulfides and thus should form significant quantities of sulfates during the roast

The Ammonium Carbonate Process

Another method for treating the ash has been considered recently at this laboratory Experimental results are limited at this time but the few that are available, along with the "paper" chemistry present a picture encouraging enough to require further investigation This process produces a sulfate that can be sold in considerable quantities ($(NH_4)_2SO_4$) and uses an easily regenerated base ($(NH_4)_2CO_3$)

Upon treating the ash with ammonia and carbon dioxide, the calcium sulfate will be converted to calcium carbonate according to the equation

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3 + (NH_4)_2SO_4$$

Industrially, the reaction is usually carried out in closed containers at about 45 C using ground gypsum rock or anhydrite as raw material Since calcium carbonate is insoluble, the main constituent of the filtrate will be ammonium sulfate Other major constituents of the ash, SiO_2, Fe_2O_3, Al_2O_3, and CaO will not be dissolved

Most of the uranium and most of the molybdenum, if in the hexavalent state, should report to the carbonate solution along with perhaps small quantities of magnesium or phosphate Indeed, the extraction of uranium from several types of ash has been confirmed by the experiments described in Table 2 Considerable molybdenum has also been noted in the leach solutions but percentage extractions cannot be calculated due to the incomplete analytical data

Since the decomposition temperature of the ammonium carbonate is around 54°C, boiling of the pregnant liquor will effect the recycle of all surplus ammonia and carbon dioxide The heat required for distillation should be available from the lignite burning The fate of the uranium and molybdenum during this operation is not known but the recovery of these elements from such a pure solution should not be difficult

If it is assumed that the greatest part of the ammonium sulfate cannot be sold, the ammonia can easily be distilled with burned lime and thus recycled Carbon dioxide is available in practically unlimited quantities from the burning of the lignite Therefore, so far as the chemical processing of the ash goes, no chemicals should be needed other than limestone and such quantities of ammonia as to make up for losses (see below) and for the amount sold as ammonium sulfate A postulated flowsheet for a process using ammonium carbonate is shown in Figure 1

Comparison of Chemical Costs in the Foregoing Processes

In order to have an approximate idea as to the costs of chemicals involved in various treatments, it is assumed that one million tons of lignite of the same composition as the Battelle sample (1090-500) is being processed per year This will amount to 250,000 tons of ash per year, or 700 tons per day The cost comparison as shown in Table 3 was made on the following bases

Table 2

$(NH_4)_2CO_3$ LEACHING OF LIGNITE ASH

Test No	Roast Time hrs	Roast Temp °C	Leach Conditions Time hrs	Leach Conditions Temp °C	Leach Conditions Pressure PSI	Leach Conditions Sol'n * Type	pH (at Atm P)	U Extracted %	SO_4 Extracted %
33	16	500	4	110	100	A	8 0	61	97
34	16	500	2	110	160	B	8 0	75	97
36	16	500	2	80	80	B	8 3	84	98
37	16	500	2	110	80	C	8 8	75	98
35	2	800	2	110	130	B	8 4	79	96
38	2	800	2	110	100	C	9 2	74	91

Leach Conditions 100 ml of leach sol'n * per 50 g of ash (ground to -20M)

*Leach Solution
A-100 ml H_2O, 30 g $(NH_4)_2CO_3$
B-100 ml H_2O, 45 g $(NH_4)_2CO_3$
C- 80 ml H_2O, 45 g $(NH_4)_2CO_3$,
20 ml NH_4OH(28%NH_3)

Figure 1

TENTATIVE AMMONIUM CARBONATE

PROCESS FOR LIGNITE

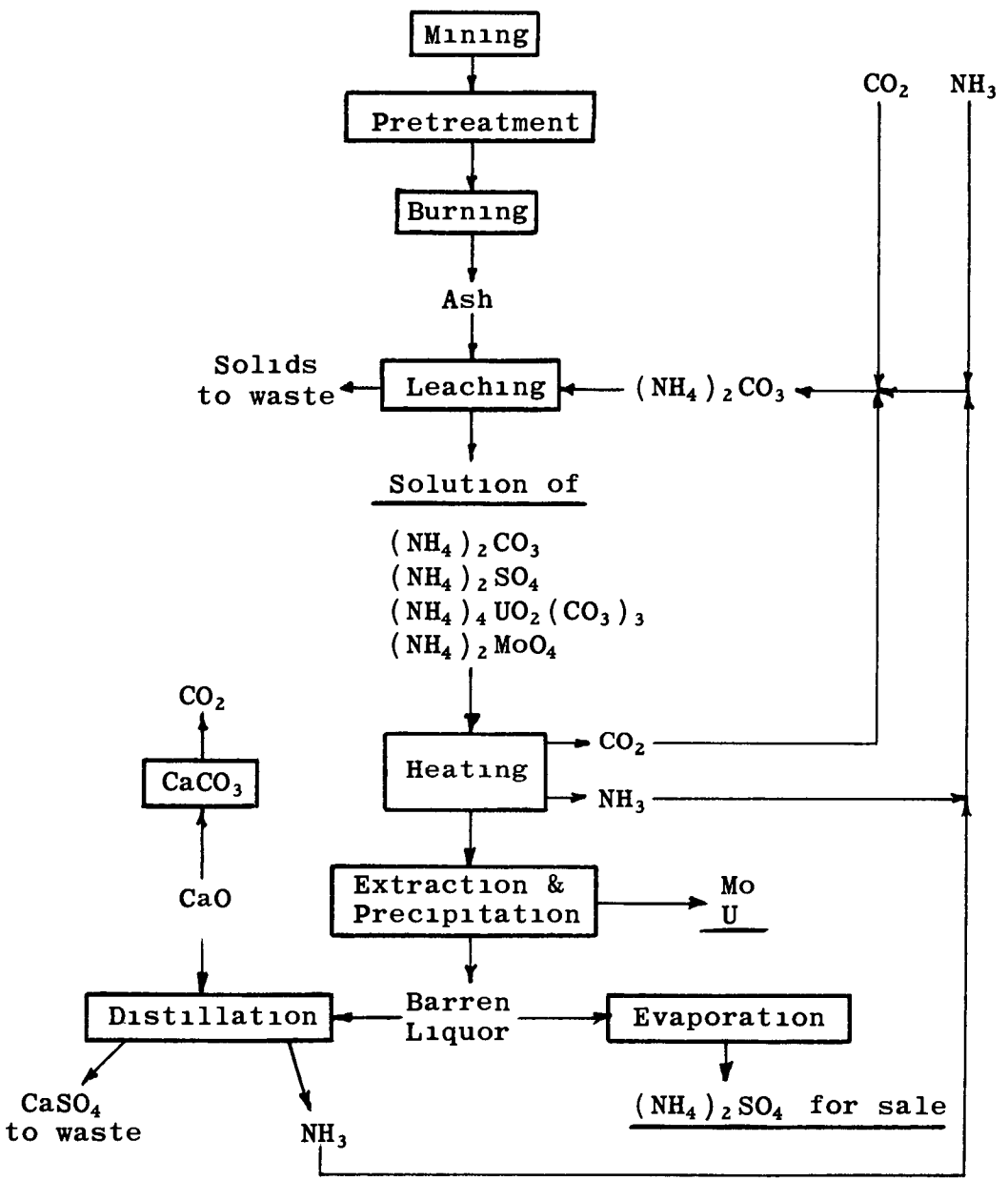


Table 3

A ROUGH COMPARISON OF PROCESS REAGENT COSTS

Material	Quantity Ton	Quantity Unit Price	H_2SO_4 Leach $ Input	Na_2CO_3 Leach Beneficiation Without	Na_2CO_3 Leach Beneficiation With	$(NH_4)_2CO_3$ Process
H_2SO_4 60°Bé	380	16 50/ton	6300	--	--	--
Soda ash	245	1 20/100 lb	--	5900	--	--
"	75	"	--	--	1800	--
Ammonia	3 75	04/lb				300
Limestone(1)	165	5 00/ton				825
		Expenditures $	6300	5900	1800	1125
		Possible Output of Byproducts		$	$	$
MoO_3	2000 lb	1 30/lb	--	2600	2600	2600
$(NH_4)_2SO_4$	75 ton	02/lb	--	--	--	3000
Byproducts sold minus chemicals bought		$	-6300	-3300	+800	+4475
Per ton of ash		$	-9	-4 7	+1 14	+6 4
Per lb of U for the(2) particular ash studied		$	-9	-6 3	+1 4	+8 5

(1) The cost of limestone weighs heavily in the last column Its price varies greatly with the location It is probably not necessary to use the highest grade of stone

(2) Chemical consumptions are better considered on the basis of a ton of ash rather than a lb of uranium Uranium content of the ash will vary considerably The ash described above has a greater uranium content than the expected average over large tonnages

(a) If these 700 tons were subjected to an acid leach and if a 98% recovery could be achieved, 700 pounds of uranium would be extracted with a consumption of 850 pounds of 100% H_2SO_4 per pound of uranium or approximately 380 tons of 60° Bé acid per day No useful by-product could be produced

(b) If the 700 tons were subjected to a soda ash leach with 78% efficiency, 545 pounds of uranium would be produced with an approximate use of 245 tons of soda ash per day It can be assumed that no sizeable quantities of salt cake can be sold, but molybdenum can be considered a by-product

(c) If the ash is beneficiated before the leach, 490 pounds of uranium would be produced with the aid of about 75 tons of soda ash Molybdenum could probably be extracted also

(d) In an ammonium carbonate process, the losses of ammonia would be approximately as follows distillation $<2\%$, loss in residue 1%, loss through leakage and handling $<2\%$ A total loss of 5% seems a conservative estimate The amount of NH_3 used per day would be about 75 tons (for an 85% conversion of the calcium sulfate plus a surplus of NH_3 in the leach required for the extraction of the uranium) Of this amount, 3 75 tons is a loss or about 10-1/2 pounds per pound uranium for the particular ash considered

Seven hundred tons of ash containing 25% SO_3 would require approximately 64 tons of NH_3 for an 85% conversion to ammonium sulfate To distill this amount of ammonia, about 220 tons of limestone in the form of slaked lime is required If one quarter of the ammonium sulfate is sold, only 165 tons of lime are needed The total production of products would be (assuming a 78% of uranium and an 85% Mo extraction) 545 pounds uranium and 1320 pounds molybdenum besides 230 tons of ammonium sulfate of which let it be assumed that 75 tons can be sold on the market

As stated previously, the outlook for an ammonium carbonate process on limited evidence is promising Further studies of the controlling points in the process are being made

Controlled Roasting of Lignite Followed by Water Leaching

Preliminary tests of the roasting and leaching of lignite batch No 1 (see ORNL-1308) has shown that the ash is acidic when formed at a low temperature ($\sim$500°C) and that most of the

uranium (70-80%) can be extracted by a water leach Experiments comparing water and acid leaching of ashes formed under various conditions of burning are described in Table 4

Increasing the roasting temperature (e g , 800°C) causes the formation of a basic ash and the uranium is available to a dilute (5%) sulfuric acid leach At temperatures near 1000°C, the ash becomes more basic and the percentages of the uranium readily available to an acid leach are smaller

The reactions taking place during the roasting of the lignite are similar to those which occur during the roasting of oil shale[3] Sulfur oxides are formed from the oxidation of sulfides in the raw lignite and these may react in turn to form sulfate salts such as ferric sulfate A water leach will dissolve these salts and become acidic due to hydrolysis of the metal ion Basic ash is produced at the higher temperatures because the acid forming sulfate salts are decomposed At very high temperatures the ash will sinter or melt and the uranium is refractorized, probably due to the formation of stable silicates

There is one important difference, however, between the roasting of shales and lignites To obtain reasonable extractions of uranium from shales by water leaching it was necessary to roast the material at low temperatures for a long period of time Low temperatures are also required in the lignite treatment but it has been possible to cut the roasting time to 2 hours while maintaining reasonable extractions of uranium into water This feature is encouraging from a process standpoint, and additional tests using samples from other lignite sources will be made

Future Work

The possibility of upgrading the raw lignite prior to burning, by air classification or other means, will be considered further Physical beneficiation of the lignite ash will also be studied

The important steps in the ammonium carbonate process will be examined in order to obtain a closer measure of the feasibility of the method Several of the variables in the low temperature roast, water leach method for extracting uranium from lignite will also be examined

Methods will be studied for treating raw lignite, prior to any operations other than perhaps physical concentration

Table 4

THE EFFECT OF ROASTING TIME AND TEMPERATURE ON THE EXTRACTION OF URANIUM FROM LIGNITE

Test No	Roast Conditions Time hrs	Roast Conditions Temp °C	Roast Conditions % Ash	Leach Conditions Agent	Leach Conditions Time hrs	Leach Conditions Temp °C	U Final pH	U Extractions % of Total	U Tails % of Total	U Tails % of wt
11	16	500	21	H_2O	2	25	2 7	76	24	027
12	"	"	"	"	2	80	2 9	75	25	027
13	"	"	"	1% H_2SO_4	2	25	1 3	78	22	027
14	"	"	"	"	2	80	1 8	82	18	020
24	5	"	"	H_2O	1	25	2 7	68	32	040
25	"	"	"	5% H_2SO_4	1	80	0 7	78	22	027
28	2	"	22	H_2O	1	25	3 0	68	32	040
29	"	"	"	5% H_2SO_4	1	80	0 5	78	22	027
30	3	400	21	H_2O	1	25	3 2	68	32	040
31	"	"	"	5% H_2SO_4	1	"	3 4	71	29	040
20	4	800	19	H_2O	1	25	7 8	0	100	133
21	"	"	"	5% H_2SO_4	1	80	0 5	82	18	027
22	6	800	19	H_2O	1	25	8 0	0	100	147
23	"	"	"	5% H_2SO_4	1	80	0 4	76	24	027
26	5	500	--	---	-	--	---	--	--	----
	2	800	19	H_2O	1	25	8 0	0	100	140
27	5	500	--	---	-	--	---	--	--	----
	2	800	19	5% H_2SO_4	1	80	0 4	62	38	053
16*	2	1000	19	H_2O	1	25	11 0	0	100	120
17*	"	"	"	5% H_2SO_4	1	80	1 4	45	55	073
19	4	1000	18	H_2O	1	25	12 0	0	100	140
20	"	"	"	5% H_2SO_4	1	80	0 4	55	45	600

Roast Conditions — The raw lignite was placed in a muffle furnace at 400°C and heated rapidly to the desired temperature The resulting ash was ground to -20M

Leach Conditions — 15 g samples of the ash were agitated with 150 ml of leach agent

* Sample placed directly in furnace at 1000°C

Other approaches to the lignite problem will be reserved until additional information has been obtained concerning the properties of the ash from a commercial lignite-fueled power plant If the successful production of power requires that the ash be formed at temperatures high enough to cause sintering and therefore excessive refractorization of the uranium, other methods for handling this type ash will be considered immediately

Recovery of Uranium from the Florida Leached Zone

D J Crouse F A Schimmel C F Coleman
L R Phillips F G Seeley

Work has continued on the extraction of uranium from the -200 mesh fraction of Florida Leached Zone material and on recovery of uranium from the resulting liquors A topical report is being prepared summarizing the results obtained to date in acid leaching and recovery of uranium from solution

Preliminary tests have also been made in which the Leached Zone material has been opened up by baking with ammonium sulfate followed by dissolution of phosphate and alumina in a water leach These results suggest a process in which the sulfur is recovered and recycled as ammonium sulfate rather than sulfuric acid

Three special samples have been obtained from the U S Geological Survey (through the courtesy of Mr Z S Altschuler and Mr J B Cathcart), representing fractions high in wavellite and in pseudowavellite A sample was also obtained from the TVA Laboratory of Wilson Dam (through the courtesy of Dr J H Walthall) of Florida material which appeared considerably different from previous LZ samples received here This latter sample is lower in uranium and in phosphate than the other LZ samples Partial analyses of these different samples are given in Table 5

Samples BC-1, -2, -3, and -7 were -200 mesh as received, except for a few percent of coarser sand in BC-2 The others were received as dug, and portions of each have been dispersed and wet-screened through 200 mesh to provide fines for comparative leaching tests Analyses of the fractions obtained are included in Table 5

Acid Leaching

Comparative leaching tests with relatively low quantities of sulfuric acid have been made under set conditions for each of the -200 mesh samples available The following procedures were used

Constant-pH Leach with Resin

Anion exchange resin (7 meq for 20g ore, dry basis) was added to the ore sample slurried at 10% pulp density Sulfuric

Table 5

LZ HEAD ANALYSES
per cent, dry basis

Sample Number	U_3O_8	CaO	Al_2O_3	Fe_2O_3	SiO_2	P_2O_5	F	LOI
BC-O	0 024	17 4	8 8	1 9	49 8	15 1	1 0	6 6
BC-OA**	0 018	16 9	3 9		60 5	13 3		3 8
BC-OB*	0 030	21 1	19 1	2 8	21 8	22 4	1 2	10 1
BC-1*	0 061	16 3	24 2	2 8	12 2	26 6	1 1	12 5
BC-2*	0 042	17 2	19 3	2 7	23 1	23 2	1 4	
BC-3*	0 040	7 1	28 7	1 7	32 1	15 2	1 3	13 6
BC-4	0 044	1 8	20 8	1 9	48 1	15 3	1 3	11 7
BC-4A**	0 027	1 0	14 4		59 9	11 3	1 0	
BC-4B*	0 062	3 4	34 5		12 7	24 2	2 2	
BC-5	0 031	4 9	18 0	2 6	51 8	12 2	0 8	9 4
BC-5A**	0 015	4 7	9 4	2 2	67 6	9 6	1 0	4 8
BC-5B*	0 048	5 9	30 9	2 2	25 6	16 1	1 0	15 4
BC-6	0 008	5 4	10 0	2 4	70 0	5 8	0 5	6 7
BC-6B*	0 014	3 5	20 9	6 8	46 3	8 0	0 6	10 3
BC-7*	0 053	6 6	29 0	5 1	19 1	23 2	0 9	14 7

* -200 mesh
** +200 mesh

acid was added to each sample in increments to keep the pH at 1 0, 1 5 or 2 0 for 24 hours The resin was removed by screening and followed by a second batch of resin The leached slurry was then filtered and washed The filtrate, the solid residue, and the loaded resin were each analyzed for uranium Nearly all the solubilized uranium was taken up by the resin

Direct Leach

The total quantity of sulfuric acid used in each constant-pH test was recorded, and a direct leach was made with the same quantity of acid added at one time to the 10% pulp-density slurry The acidified slurry was stirred for 24 hours at room temperature, then filtered and washed for solution and tailings analysis

On the basis of pounds of sulfuric acid per ton of dry ore, the acid consumptions varied from 30 to 535 at pH 2, and from 250 to 1137 at pH 1 When the acid consumption is referred to the amount of calcium present, there is much less variation With the exception of the atypical sample BC-6, the acid consumptions per unit of calcium are grouped together in a fairly narrow band, as shown in Figure 2, with the consumption at pH 1 5 being close to the amount of sulfuric acid equivalent to the calcium Figure 3 shows the pH's obtained in the corresponding direct leaches (Direct leaches were made corresponding to all the constant pH leaches, together with several interpolated tests) As expected, the final pH was generally higher when the acid had been added all at one time, but the differences were not great, and these curves also cross pH 1 5 at close to the amount of acid equivalent to the calcium

The amount of uranium dissolved in these leaches also correlates fairly well with the calcium content This is illustrated by the curves of Figures 4 and 5, which show the percent of the uranium content which was dissolved plotted against the acid consumption per unit of calcium in the ore head The resulting curves group more closely together in this plot than when plotted against acid consumption per total weight of ore head, and breaks in most of the curves fall fairly near the acid consumption equivalent to calcium content The percent of the uranium dissolved by this amount of acid varied from 35 to 85% for the various ore heads This variation also conformed to the correlation with calcium content, as shown in Figure 6 The ordinates in this figure are from the intersections of the various curves with the acid equivalent to calcium lines in Figures

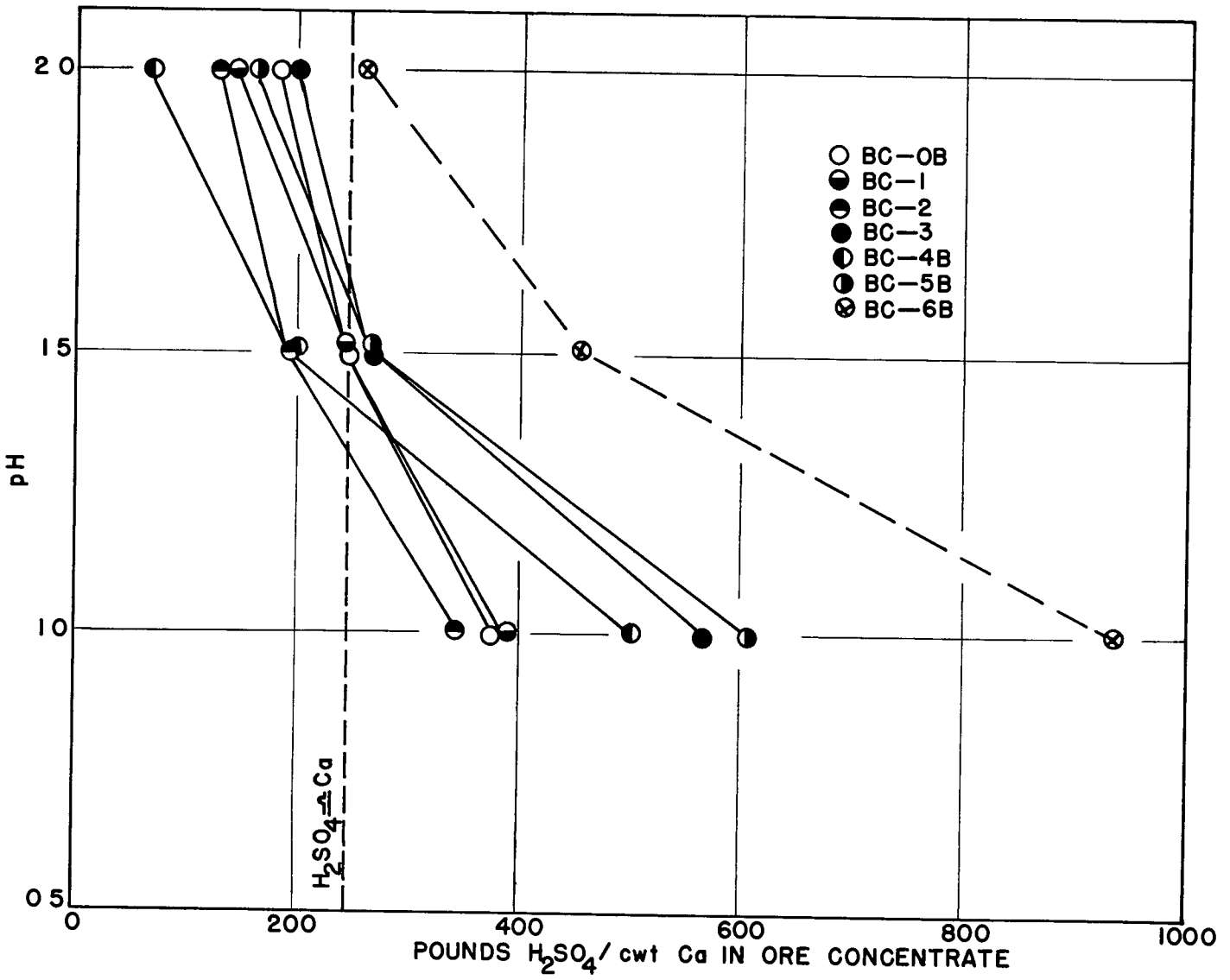


FIGURE 2 ACID CONSUMPTION IN CONSTANT pH LEACHES REFERRED TO CALCIUM CONTENT

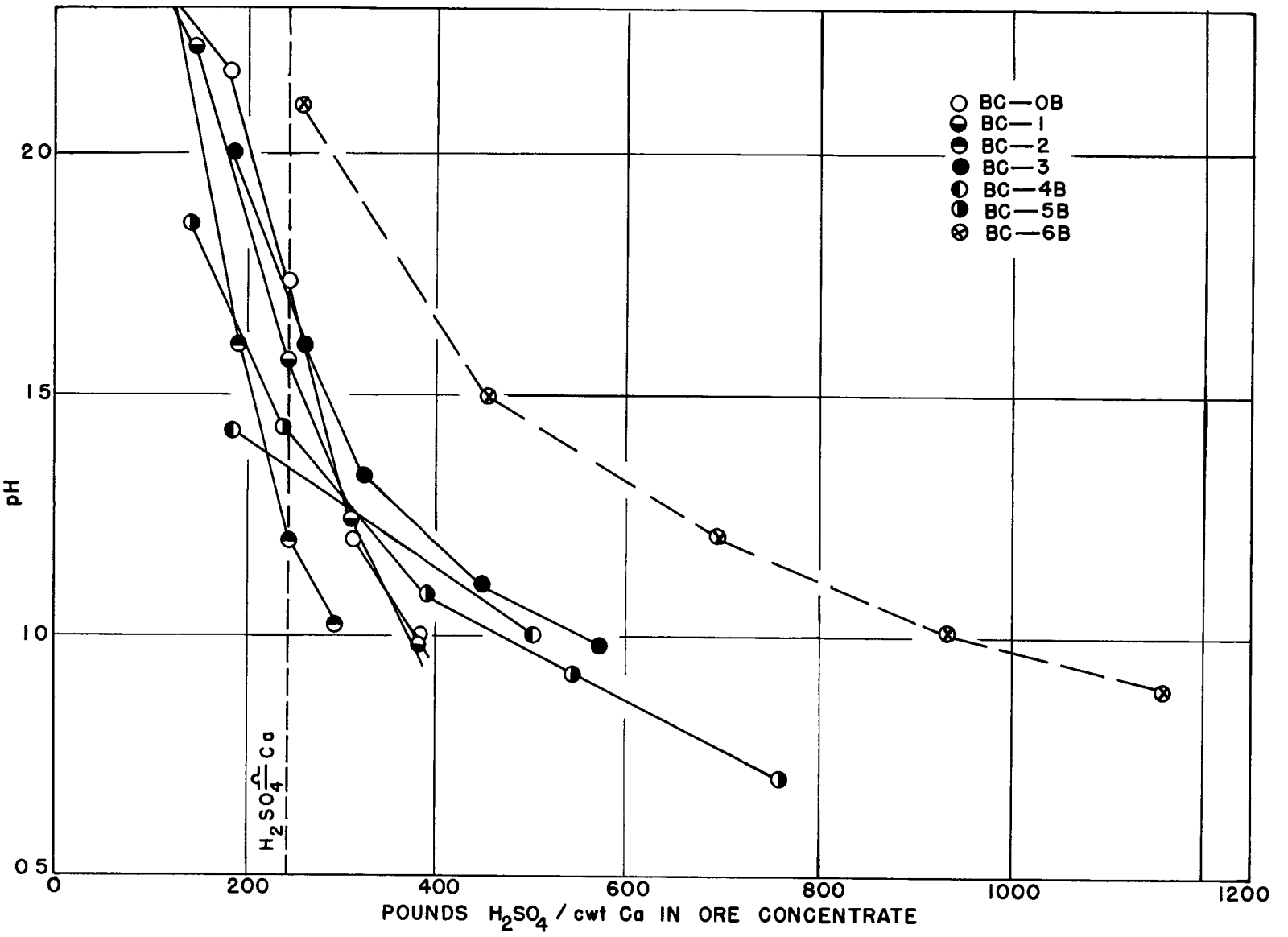


FIGURE 3 ACID CONSUMPTION IN DIRECT LEACHES, REFERRED TO CALCIUM CONTENT

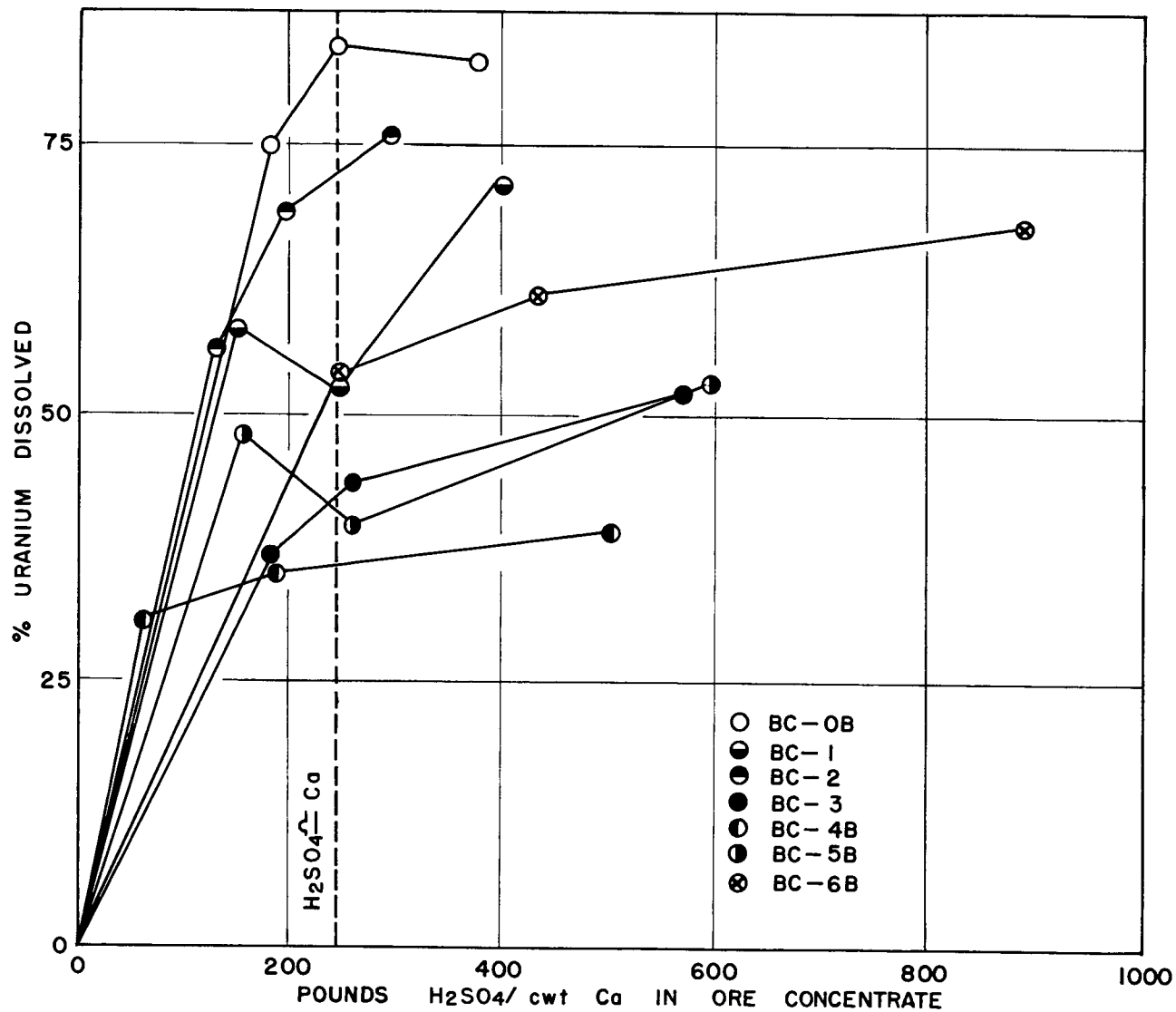


FIGURE 4 URANIUM DISSOLUTION IN CONSTANT pH LEACHES WITH ANION EXCHANGE RESIN

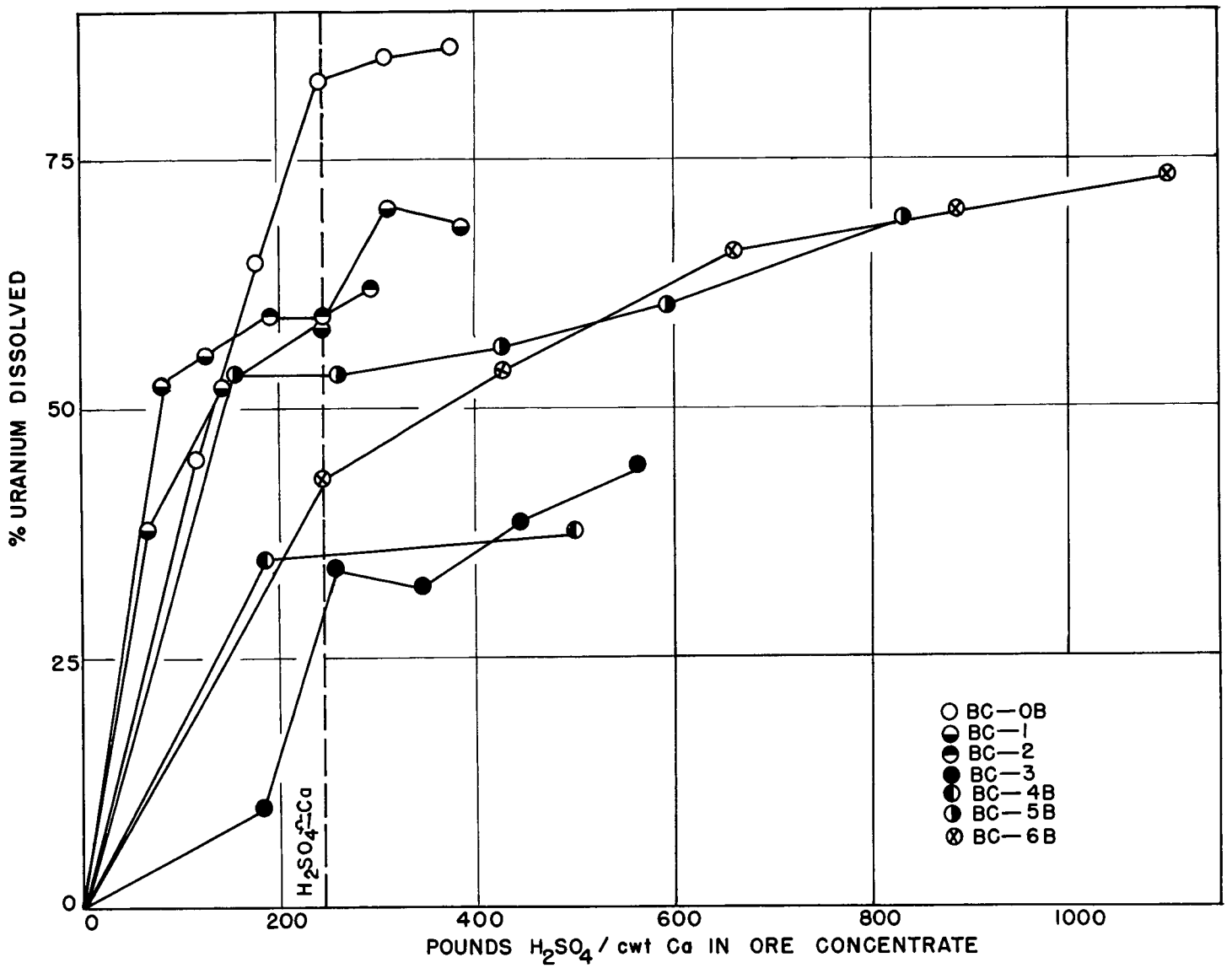


FIGURE 5 URANIUM DISSOLUTION IN DIRECT LEACHES

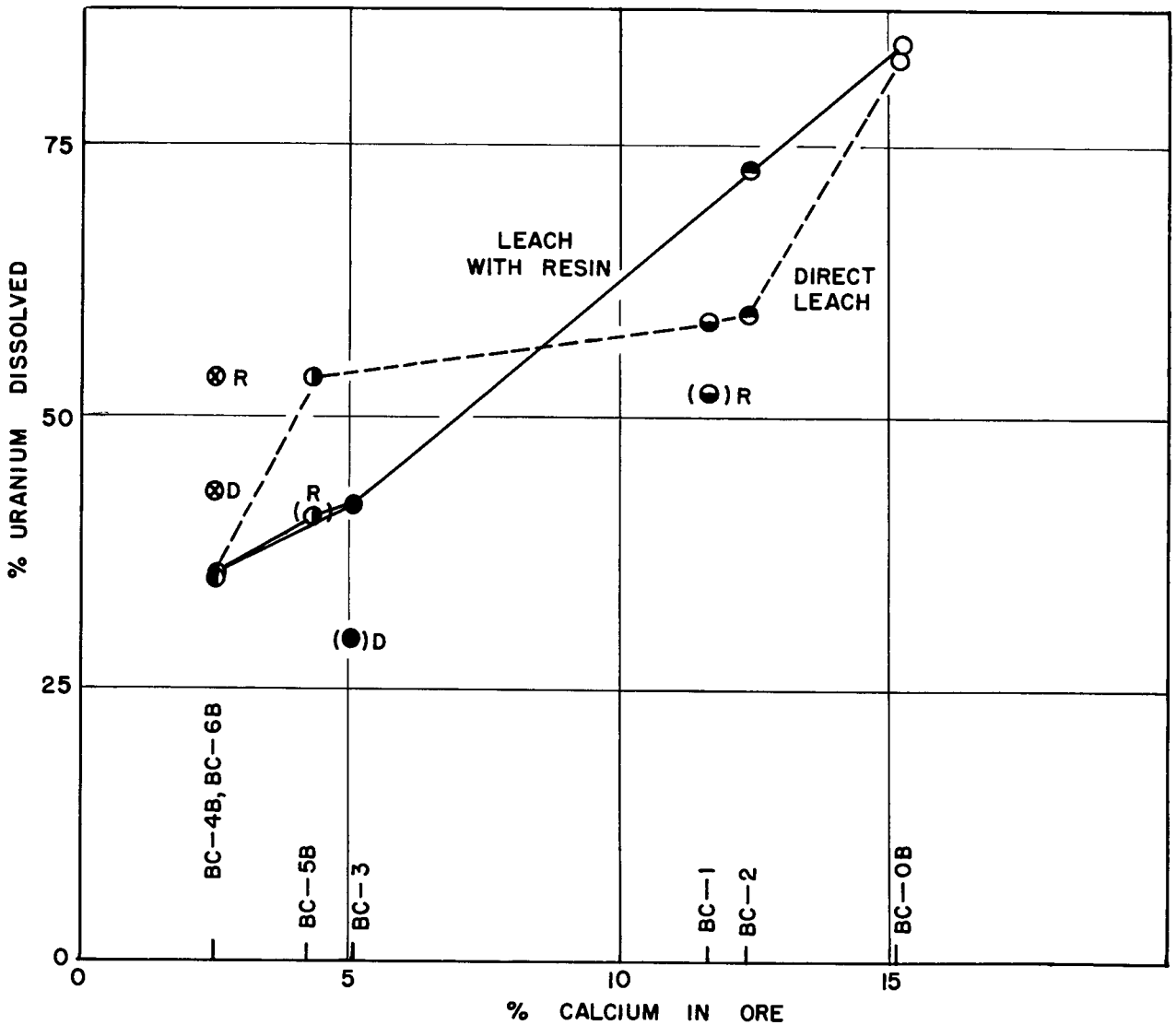


FIGURE 6 URANIUM DISSOLVED BY ACID EQUIVALENT TO CALCIUM

4 and 5, plotted against the head calcium contents The resulting curves are reasonably close to linear (The points set in parentheses are from leaches which showed large discrepancies both in shape of dissolution curves, and in material balances These tests are being repeated)

Analyses have not been reported for the comparative leaches with BC-7, the only sample known to contain pseudowavellite, hence, it is not yet established whether the calcium in pseudowavellite will or will not conform to the foregoing generalities Sample BC-7 was prepared by the U S Geological Survey to contain principally pseudowavellite, with very little wavellite or apatite

Results of leaching tests of ore head BC-3 at higher acid levels are shown in Figures 7 to 11 (cf Figures 5 to 9 of Y-823)[4] The lag in aluminum dissolution is less noticeable with this ore head than in the earlier tests with BC-1, in accordance with the relatively smaller calcium content of BC-3 The phosphate dissolution from BC-3 rose toward completion almost as rapidly as did the calcium dissolution, while with BC-1 the phosphate curve was more nearly parallel to the aluminum curve The indication is that a considerable fraction of the aluminum is present as silicate in BC-3 This is also indicated by the degree of dissolution of total solids (Figure 12), which was less with BC-3 than with BC-1, and also more variable with acid concentration, temperature, and time, reflecting the slow attack on clay minerals

The effect of time was checked by leaches for 1, 6, and 24 hours At 500 pounds nitric acid per ton, Figure 8, there was very little effect after one hour At 1000, 1500 (Figure 9), 2000, and 2500 pounds acid per ton, there were appreciable differences between one and six hours but not much change after six hours, except for the aluminum Aluminum curves for the other acid levels are included in Figure 9

Leaching results with sulfuric acid, shown in Figure 10, are similar to those with nitric acid in Figure 7 The results with phosphoric acid, however, show much lower dissolution The uranium curve is far below the calcium curve, in contrast to the nitric acid results Results were essentially similar for a 24 hour leach at room temperature, except that the aluminum dissolution appeared to level off at around 30% Results were not better in 24 hours at 80°C, in fact, the calcium dissolution was lower than in the 6 hour leach In comparison with BC-1 (Figure 9, Y-823)[4], BC-3 shows higher dissolution of calcium, somewhat higher dissolution of aluminum, and lower dissolution of uranium

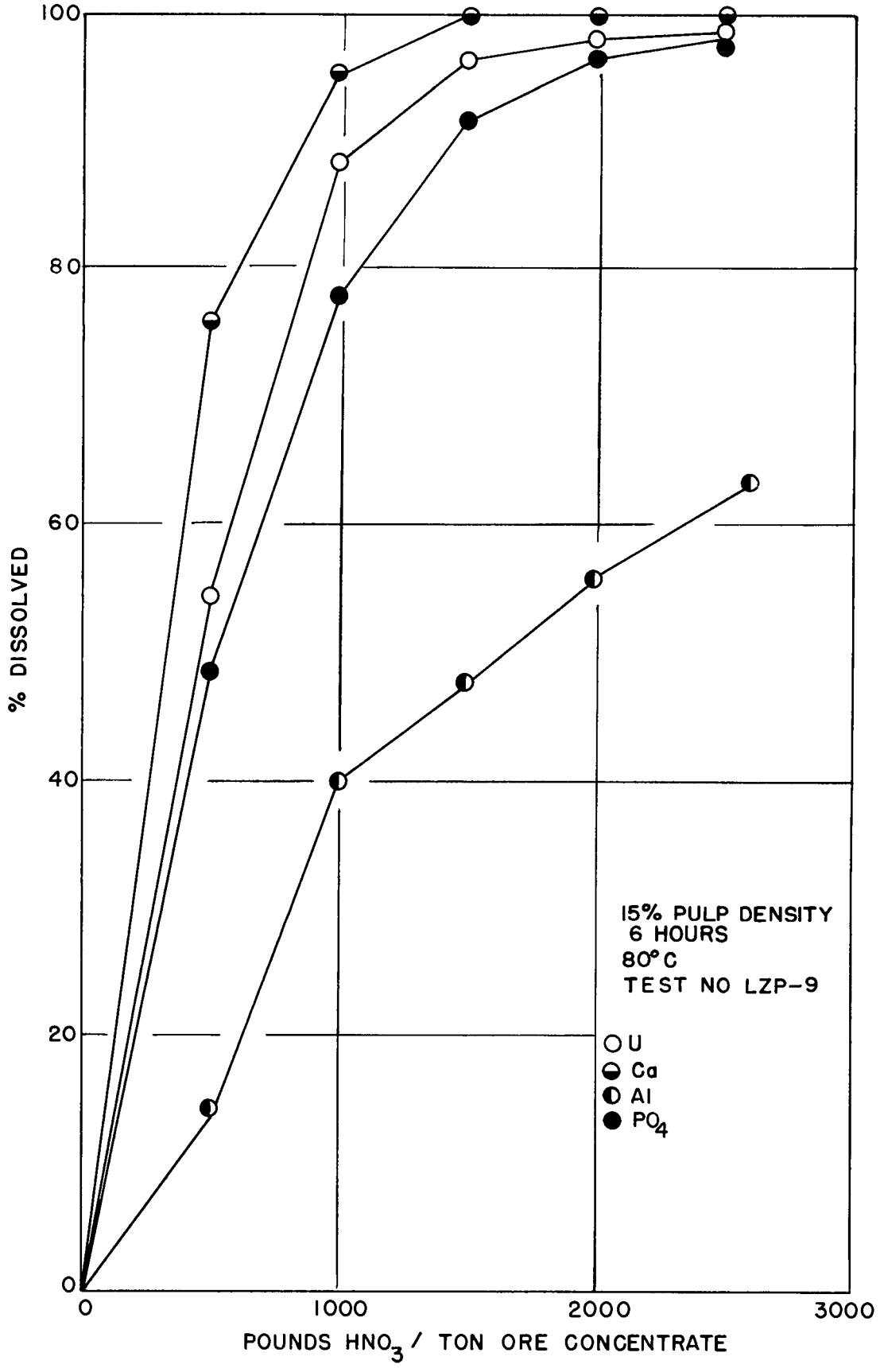


FIGURE 7 LEACHING OF BC-3 ORE WITH NITRIC ACID

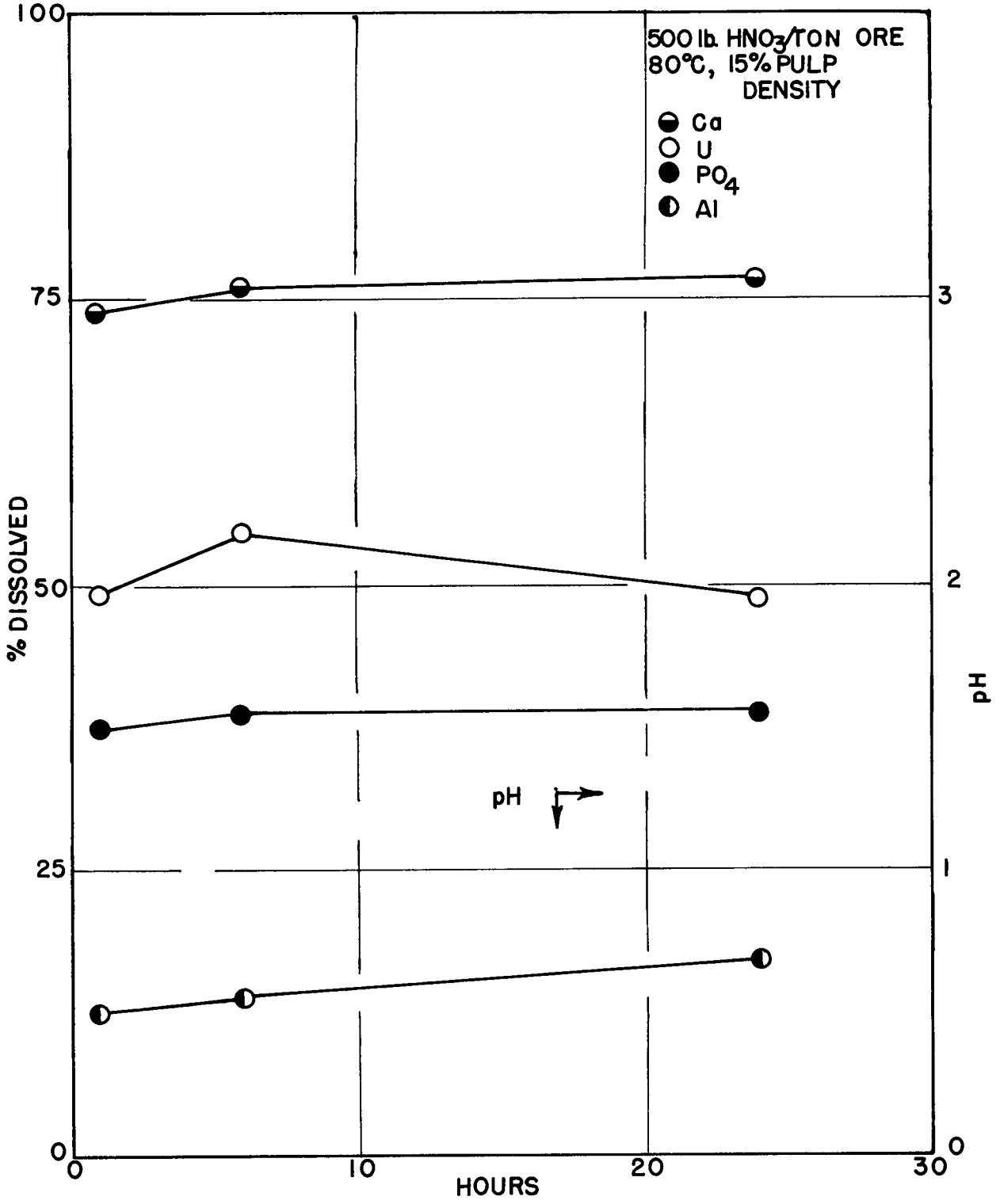


FIGURE 8 EFFECT OF TIME ON NITRIC ACID LEACHING OF BC—3 ORE

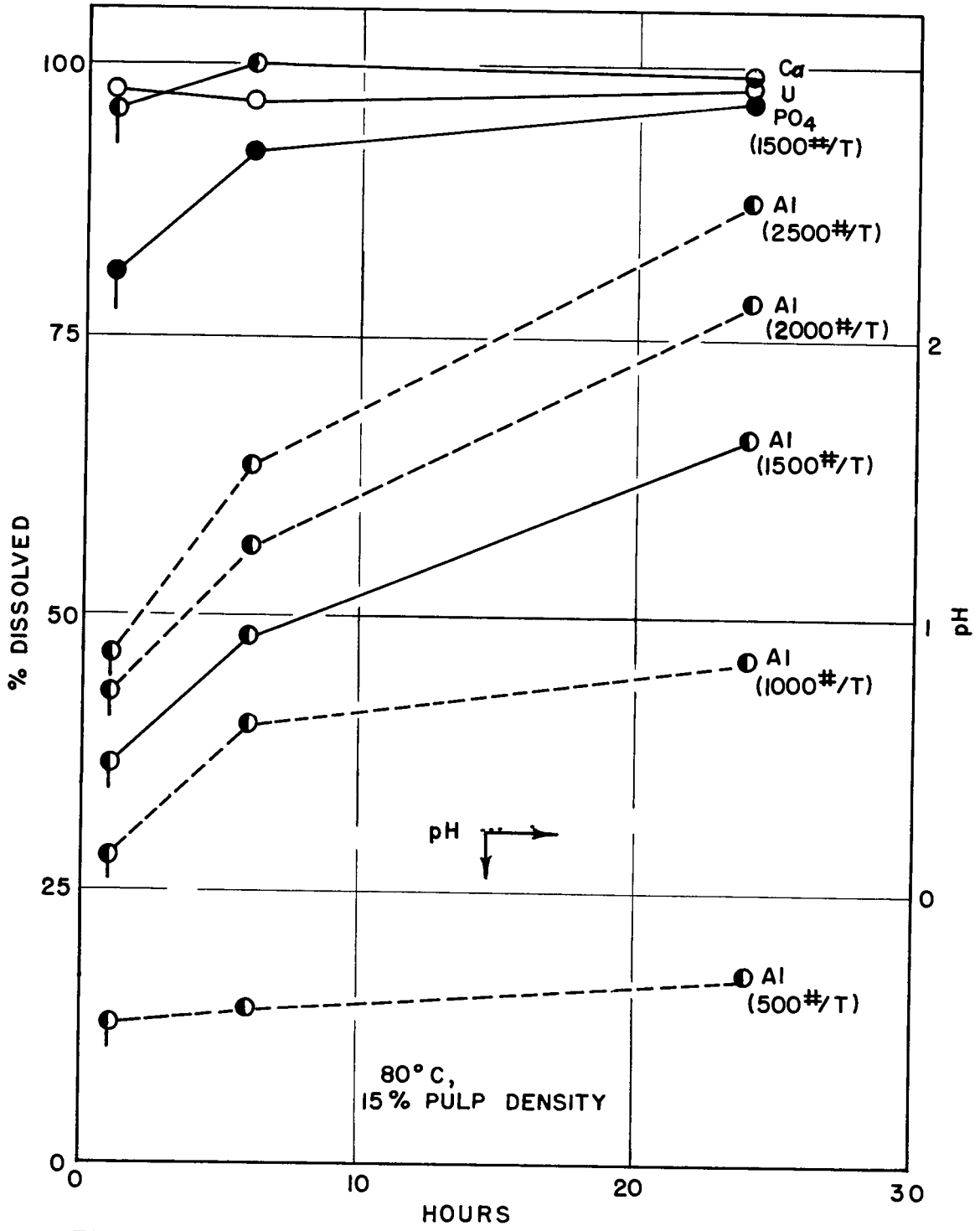


FIGURE 9 EFFECT OF TIME ON NITRIC ACID LEACHING OF BC-3 ORE

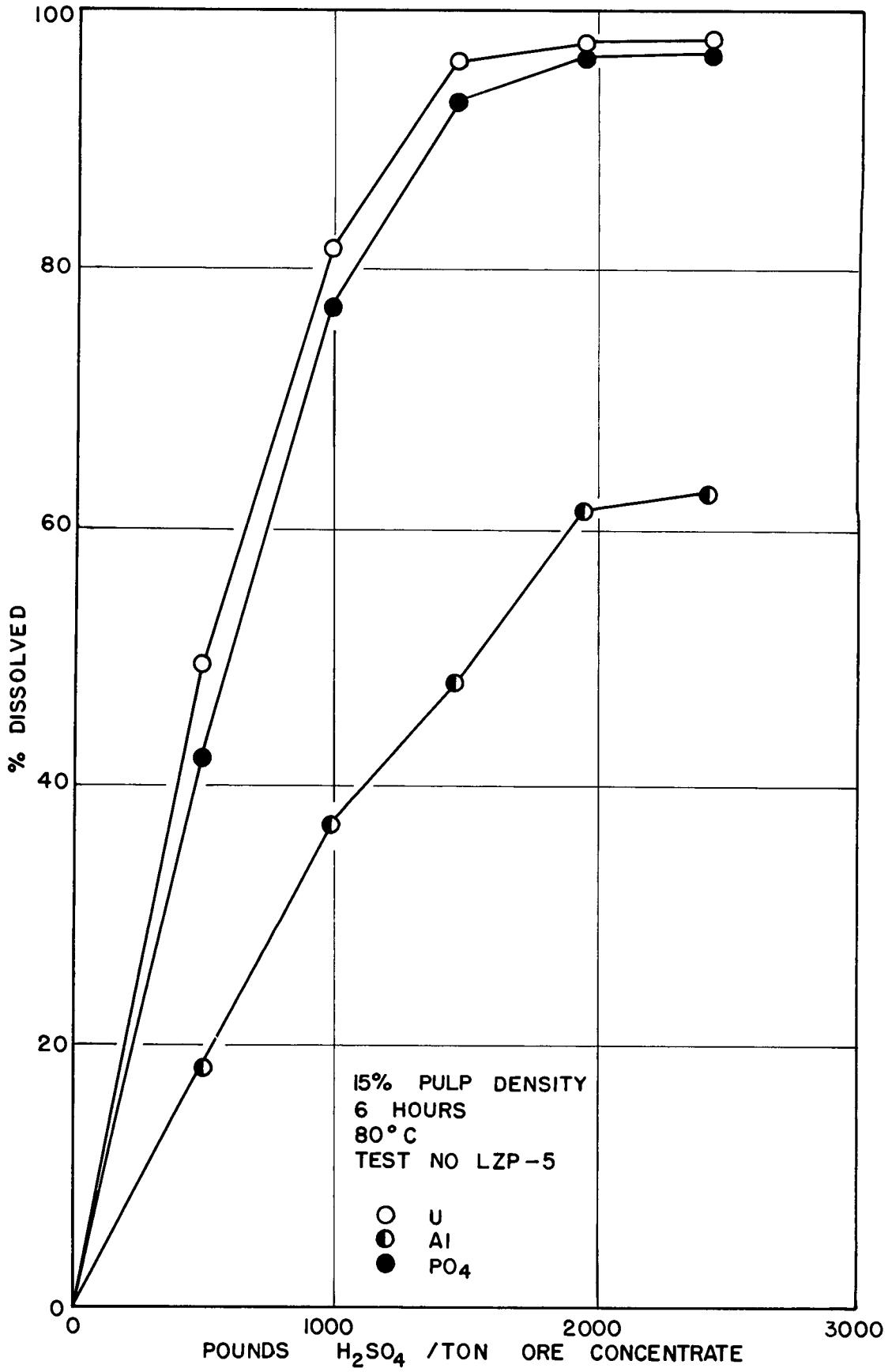


FIGURE 10 LEACHING OF BC-3 ORE WITH SULFURIC ACID

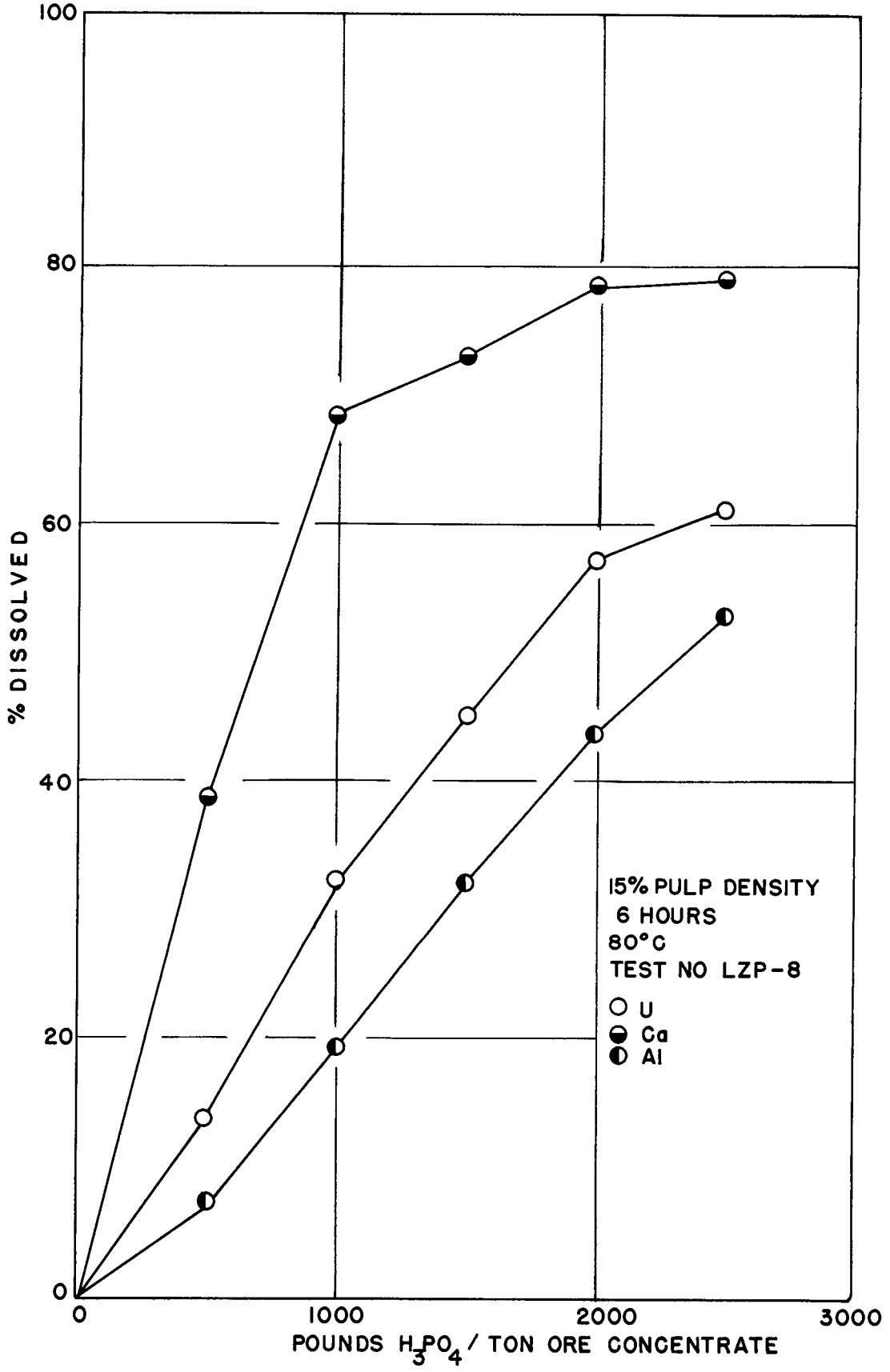


FIGURE 11 LEACHING OF BC—3 ORE WITH PHOSPHORIC ACID

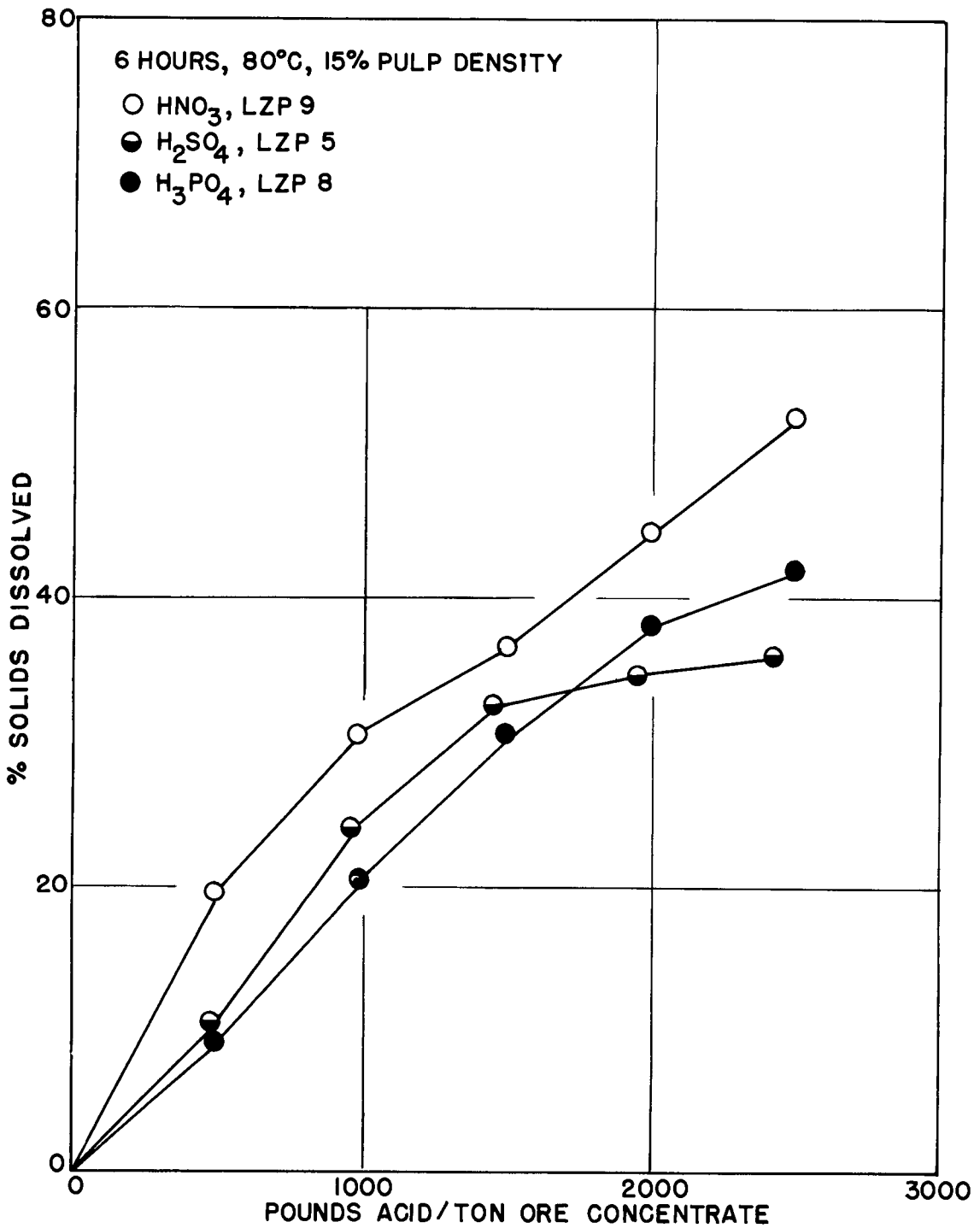


FIGURE 12 ACID LEACHING OF ORE BC—3, TOTAL SOLIDS DISSOLVED

Large bench scale leaches were prepared with nitric acid and sulfuric acid from ore head BC-3 The leaching conditions and results are shown in Tables 6, 7, and 8

Basic Leaching

No systematic study of basic leaching has been carried on during this quarter, but a few particular tests were made with sodium hydroxide and with trisodium phosphate, as shown in Figure 13 BC-3 was used in a slurry at 20% pulp density Samples were leached for 24 hours with each reagent at levels from 80 to 1600 lb /ton of ore (dry basis), corresponding to reagent concentrations of 1, 3, 8, 14, and 20% Filtration was extremely slow with the lowest concentration of either reagent, improving somewhat at higher concentrations The material balances were high for 640, 1120, and 1600 lb TSP per ton Except for the last point, the dissolution by TSP increased in proportion to the amount of reagent Dissolution by sodium hydroxide up to 640 lb /ton was much less This may have been due to insufficient attack on the minerals, but more likely was due to insufficient phosphate ion in solution to complex and solubilize the uranium The sodium hydroxide points of 640, 1120, and 1600 lb /ton parallel the TSP points of 640 and 1120

Leaching with Organic Reagents

Tests were previously reported of organic leaching of LZ from which all water had been removed Similar attempts to extract uranium directly from the acidified aqueous slurry at first gave emulsions which could not be handled By contact without violent mixing in later tests, extractions were obtained without serious emulsions, although at the cost of slow equilibration Further improvement was attained when a new supply of di(2-ethylhexyl)phosphinic acid, presumably purer than the previous batch, showed less tendency to form emulsions

In one slurry extraction with dibutyl phosphate in petroleum ether, 29% of the uranium was solubilized and 27% extracted, with material balance of 115% The ore was BC-3, treated with nitric acid (500 lb /ton) at 20% pulp density, and extracted with 13% DBP at a volume ratio of 0 75 organic/ aqueous The phases were contacted by rolling a cylindrical separatory funnel for one hour In a similar test continued for six hours, a stable emulsion was formed

Table 6

NITRATE LEACH LZP-3

Ore	2 0 kg (d b) batch BC-3
HNO_3	1 73 kg (1730 lb/ton)
Leach Conditions	6 hours at 80°C 15% pulp density
Volume	6 13 liters of filtrate recovered, before washing
Solids Dissolved	33%
Uranium Dissolved	98% (pregnant liquor and washings)
Uranium Balance	97%

Pregnant Liquor
(without washings)

U	0 007%
Al	2 0
Fe	0 12
Ca	0 96
PO_4	3 86
pH	0

Table 7

LOW SULFATE LEACHES

BC-59-1 and -2

Ore	Each 230 g (d b) batch BC-3
H_2SO_4	-1, 80 g (700 lb/ton) -2, 40 g (350 lb/ton)
Leach Conditions	16 hours at 80°C 20% pulp density
Volumes (including washings)	-1, 900 ml -2, 900 ml
Dissolution of Uranium	-1, 79% -2, 41%
Uranium Balances	-1, 104% -2, 110%

Pregnant Liquors
(including washings)

	BC-59-1	BC-59-2
U	0 006%	0 004%
Al	1 32	0 54
Fe	09	05
PO_4	2 96	1 48
pH	1 0	1 4

Table 8

LOW SULFATE LEACH BC-73

Ore	6 kg (d b) batch BC-3
H_2SO_4	1 8 kg (600 lb/ton)
Leach Conditions	20 hours at R T 20% pulp density
Volume	19 5 liters, filtrate plus washings
Uranium Dissolved	39%

Pregnant Liquor
(including washings)

U	0 004%
Al	64
Fe	06
Ca	07
PO_4	2 1
SO_4	4 75
F	0 12
pH	0 8

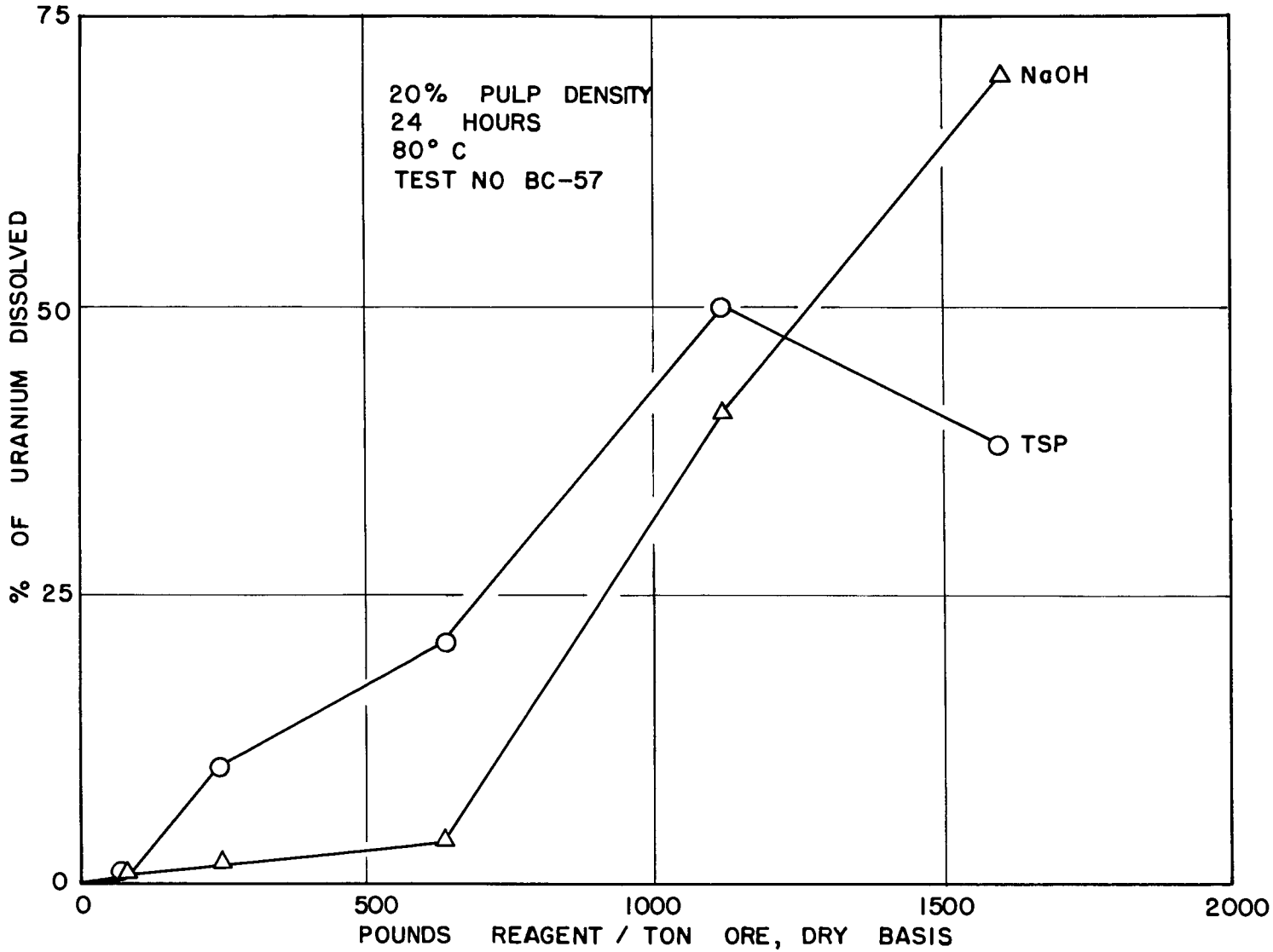


FIGURE 13 LEACHING OF BC-3 ORE WITH SODIUM HYDROXIDE AND TRISODIUM PHOSPHATE

In another extraction test, BC-3 ore was digested with nitric acid (1000 lb /ton) at 15% pulp density, then diluted to about 7% pulp density and extracted by four stages of 0 05M di(2-ethylhexyl)phosphinic acid in petroleum ether, at a volume ratio of about 0 012 organic/aqueous for each stage The phases were contacted by a very gentle shaking in a separatory funnel The total dissolution was 80% of the uranium The successive stages extracted 48%, 11%, 10%, and 1% of the uranium, totalling 70% The material balance was 92%

In further slurry extraction tests with di(2-ethylhexyl)-phosphinic acid, one phase was sampled at intervals to follow the rate of extraction In these tests contact was made either by slow stirring without mixing of two liquid layers, or by means of a small spray column giving large drop size The aqueous slurry was the dispersed phase in the spray column The overall results of these tests are shown in Table 9 The intermediate samples (not shown) indicated that the extraction was approaching equilibrium only in tests BC-74 and -76 The loss of organic phase from the spray column appeared to be excessive, further tests will be required to determine whether this apparent loss was real, or if it can be decreased

Uranium Recovery from Solution

Recovery studies have been continued on low-sulfate liquors BC-32[5], BC-41[1], BC-59-1, and BC-73 (this report, Table 8), and nitrate liquor LZP-3 (Table 6)

Precipitation Tests

Recovery of uranium from sulfate liquor by precipitation was previously reported[1] Tests have been continued of upgrading of the low grade cakes Two such cakes were prepared for analysis, with the compositions shown in Table 10 In the first cake, precipitation was less complete and cake grade was higher than had been usual, while the second precipitation was similar to previous results However, the gross composition of the two cakes was similar In another test, the precipitation was carried out in steps by addition of increments of ammonium hydroxide to the reduced liquor, and a sample of the slurry was removed at each step for filtrate analysis The compositions of the increments of precipitate and of the cumulative precipitate, calculated by differences, are shown in Table 11

Tests of upgrading of cakes are shown in Table 12 For the primary precipitations, the liquors were reduced with

Table 9

EXTRACTION OF URANIUM FROM ACIDIFIED LZ SLURRY

BY DI(2-ETHYLHEXYL)PHOSPHINIC ACID IN PETROLEUM ETHER

Ore BC-3 in 20% slurry

Extractant 0 05M

Test No	BC-63	BC-64	BC-66	BC-68[a]	BC-74	BC-75	BC-76
Method of Contact	Slow stirring in two layers					Spray column	
Acid Used	H_2SO_4	HNO_3					
Lb acid/ton ore	400	400	400	600	570	800	800
Digestion Time, hrs	0	0	16	16	22	24	24
Digestion Temp , °C			R T			70°	70°
Vol Ratio, org/aq	1 5	1 5	1 5	1 5	0 7	0 10	0 14
Extraction Time, hrs	5	5	4 5	5	25	3 5	8
U in Extract, mg/liter	25	60	33	50	110	230	295
% of U Dissolved [b]	34	37	48	47	59	(75)	(78)
% of U Extracted [b]	16	31	28	32	54	(42)	(71)
Uranium Balance, % [c]	118	119	79	99	73		

a) Kerosene used instead of petroleum ether

b) % Dissolved and % Extracted based on total uranium found in Tests BC-63 to 74, calculated by differences in Tests BC-75 and -76

c) Material balance based on head analysis

Table 10

COMPOSITION OF PHOSPHATE CAKES

PRECIPITATED FROM REDUCED SULFATE LIQUOR

BC-41

Test No	Per cent BC-47	Per cent BC-55
U_3O_8	3 6	2 2
CaO	72	0
Al_2O_3	39 7	31 8
Fe_2O_3	6 8	0 7
P_2O_5	44 4	48 3
SO_4		1 1
	95 2	84 1

Table 11

COMPOSITION OF PHOSPHATE CAKES

PRECIPITATED FROM REDUCED SULFATE LIQUOR

BC-41
Stepwise Precipitation

pH	Calculated Compositions[a], Cumulative Per cent U_3O_8	Al_2O_3	Fe_2O_3	P_2O_5	g dry ppt/liter[b]
2 2	0 66	34	1	64	2 0
2 3	52	35	2	63	8 7
2 6	33	33	2	65	16 4
3 4	33	35	2	64	21 9

pH	Calculated Compositions[a] of Increments Per cent U_3O_8	Al_2O_3	Fe_2O_3	P_2O_5	g dry ppt/liter[b]
1 4 - 2 2	0 66	34	1	64	2 0
2 2 - 2 3	41	36	2	62	6 7
2 3 - 2 6	11	30	2	68	7 7
2 6 - 3 4	33	54	0	49	5 5

a) Calculated by differences from filtrate analyses of slurry aliquots

b) Weights of dried cakes from slurry aliquots

Table 12

UPGRADING OF PHOSPHATE CAKES

PRECIPITATED FROM REDUCED SULFATE LIQUORS

Test No	Primary cake: Uranium Recovery %	Primary cake: Grade % U	Primary cake: Uranium Balance %	Upgrading Method	Secondary Cake: Uranium Recovery: % of Total U	Secondary Cake: Uranium Recovery: % of U in Primary Cake	Secondary Cake: Grade % U	Secondary Cake: Uranium Balance %
BC-49*	(62)	(0 6)		Double Pptn	57	92	7 8	134
BC-52	(76)	(1 5)		NaOH Leach**	41	54	22	83
					Secondary Leach			
BC-55-1	92	1 5	112	DEHP*** Extrn	2	2		67
-2				5% Na_2CO_3 Leach	65	71		76
BC-59-1a	(83)			5% Na_2CO_3 Leach	66	79		86
				10% Na_2CO_3	77	93		59
-2a	(97)			5% Na_2CO_3	83	86		85
				10% Na_2CO_3	91	94		64

* Primary precipitation with MgO, reprecipitation with NH_4OH
** Cake calcined before leaching
*** Di(2-ethylhexyl)phosphinic acid

metallic iron (plus zinc in BC-49) at 60-70°C, to final potentials of -0 26v* or below, and precipitated at pH 2 2 - 2 7 Aqueous ammonium hydroxide was used except in BC-49, where magnesium oxide was used The double precipitation in BC-49 consisted of complete dissolution of the primary cake with hydrochloric acid and hydrogen peroxide, reduction, and reprecipitation of uranous phosphate at pH 1 9 The lower pH and improved results in the second precipitation were possible because the contamination was less in the second solution than in the original liquor, and because hydrochloric acid is more favorable than sulfuric for uranous phosphate precipitation The sodium hydroxide leach in BC-52 effectively dissolved aluminum and phosphate, decreasing the dry weight of the cake from 2 9g to 0 11g However, nearly half of the uranium content was dissolved in the caustic, because of complexing by the high phosphate content

The other tests in Table 12 were attempts to redissolve the precipitated uranium without dissolution of a large fraction of the cake Extraction by di(2-ethylhexyl)phosphinic acid (0 1M, in carbon tetrachloride) was hoped to provide specific leaching, but the uranium extraction was nil No nitric acid was used in this test with the phosphinic acid, it is possible that under different conditions extraction with a complexing agent might provide satisfactory upgrading Most but not all of the precipitated uranium was recovered by sodium carbonate leaching High concentration of carbonate was required, so that its use would be feasible only if recycle or regeneration were possible

A series of precipitation tests were made using phenylphosphonic acid in mole ratios to uranium (in sulfate liquor BC-41) from 5 1 to 300 1, at pH's from 1 to 2 No precipitation was observed with mole ratios up to 20 1 At 150 1 and 300 1, slight precipitates were formed which were filtered off but not analyzed Filtrate analyses indicated 50 to 70% of the uranium removed Thus, relatively specific precipitation of uranium must have occurred, though only with large excess of the reagent

Liquid-Liquid Extraction

Extraction of uranium from LZ nitrate liquor with di(2-ethylhexyl)phosphinic acid in carbon tetrachloride was reported

---

*Solution potential measured by platinum electrode referred to saturated calomel electrode, the sign is that of platinum

in the preceding report[1] Similar extraction tests from LZ sulfate liquor are shown in Table 13 The effects of reagent concentration and pH are similar to the effects found for nitrate liquor, but the percent extractions are lower throughout the range The contaminant ratios found in the extracts from sulfate liquor are somewhat greater than from the nitrate liquor, but they still represent a considerable purification of the uranium

The uranium extraction was considerably improved, especially at the higher phosphinic acid concentrations, by reduction of the sulfate liquor, as shown in Table 14 The reason for this increased extraction is not clearly understood Subsequent tests in "pure" solutions show no improvement in uranium extractions with di(2-ethylhexyl)phosphinic acid during reduction Metallic iron was used for the reduction, and the iron content was not determined again before the extraction, hence, the iron extraction in the two tables cannot be exactly compared

Further tests were made of loading of the organic phase by multi-pass extractions Three of the four tests shown in Table 15 show almost unimpaired extraction in the last passes, hence did not bring the organic phase close to saturation With a much smaller quantity of organic solution (of the same order of concentration in phosphinic acid), the fall-off of extraction efficiency from nitrate liquor was still slight in five successive passes The loading obtained was 2 9g uranium per liter from nitrate liquor, 1 3 from sulfate liquor In these tests (Table 16) a second stage extraction was made on the raffinates from the first stage The two extractions for each pass totalled 96 to 99% from the sulfate liquor, 99 to 100% from the nitrate

Ammonium Sulfate Fusion

Preliminary tests have shown that LZ ore can be decomposed by baking with a small excess of ammonium sulfate (or bisulfate) followed by dissolution of phosphate and alumina in a water leach This attack suggests a process in which sulfur could be recovered and recycled as ammonium sulfate avoiding the additional step of preparing sulfuric acid A schematic flow-sheet for such a process is shown in Figure 14

Section I of this flowsheet consists of the ammonium sulfate fusion Chemically, there is no difference in fusion in the normal sulfate (with evolution of ammonia) or in prior calcination of the normal sulfate to bisulfate Physically, the latter appears to give better mixing of reagent and ore,

Table 13

EXTRACTION OF URANIUM FROM SULFATE LIQUOR WITH

DI(2-ETHYLHEXYL)PHOSPHINIC ACID IN CARBON TETRACHLORIDE

Head Liquor BC-41, Volume ratio 1 1

Test No	Molarity of Reagent	pH of Pregnant Liquor[b]	Raffinate Uranium mg/liter	Organic Extract, mg/liter			Contaminant Ratio[c] In Extract	Uranium Extracted %[d]	Uranium Balance %[e]
				Uranium	Iron	Aluminum			
BC-54-1	0 002	0 8	60	0 2	5	1	26	<1	86
-2	002	1 8	60	1 3	7	<0 1	5 5	2	88
-3	01	8	46	1 7	10	1	6 5	4	68
-4	01	1 8	49	9	28	6	3 8	16	83
-5	03	8	60	13	45	8	4 1	18	104
-6	03	1 8	24	24	189	6	8 1	50	69
BC-58-1	002	8	70	4	2	2	10 5	<1	101
-2	002	1 9	60	1 2	2	1	2 7	2	87
-3	01	8	70	2 5	8	2	4 1	3	103
-4	01	1 9	50	11	12	3	1 3	18	87
-5	03	8	60	15	24	9	2 2	20	107
-6	03	1 9	23	43	53	26	1 8	65	94
-7	08	8	29	50	75	28	2 1	63	113
-8	08	1 9	9[f]	29	74	32	3 6	24[f]	54[f]

Notes for Table 13

b) pH adjusted with sodium hydroxide

c) "Contaminant ratio" is weight ratio of Fe+Al to U In the head liquor the ratio was 50

d) "% Uranium extracted" based on uranium found in each test

e) "% Uranium balance" based on head analysis

f) Precipitate formed in the raffinate of BC-58-8 Cloudiness to slight precipitates in the other raffinates

Table 14

EXTRACTION OF URANIUM FROM REDUCED SULFATE LIQUOR

BY DI(2-ETHYLHEXYL)PHOSPHINIC ACID IN CARBON TETRACHLORIDE

Head Liquor BC-41, reduced over iron metal
pH ~1
Volume ratio 1 1

Test No	Molarity of Reagent	Raffinate Uranium mg/liter	Organic Extract, mg/liter			Contaminant Ratio in Extract[a]	Uranium Extracted %[b]	Uranium Balance %[c]
			Uranium	Iron	Aluminum			
BC-56-1	0 002	80	1 0	10	<1	11	1	114
-2	01	47	20	10	<1	0 5	30	96
-3	03	16	60	19	<1	0 3	79	108

a) "Contaminant ratio" is weight ratio of Fe+Al to U In the head liquor, before reduction, the ratio was 50

b) "% Uranium extracted" based on uranium found in each test

c) "% Uranium balance" based on head analysis

Table 15

MULTI-PASS EXTRACTION OF URANIUM BY DI(2-ETHYLHEXYL)-PHOSPHINIC ACID IN PETROLEUM ETHER

Volume Ratio 75 75 for each pass
pH adjusted with sodium hydroxide

Test No	Head Liquor	Molarity of Reagent	Pass No	Raffinate Uranium mg/liter	Extraction per Pass %[a]	Organic Volume Recovered ml	Uranium in Extract mg/liter	Contaminant Ratio in Extract[b]	Uranium Balance %[c]
BC-65 -1	LZP-3 (Nitrate) pH 1 4	0 05	1	8	86				
			2	11	81				
			3	3 7	94				
			4	4 0	93				
			5	1 5	97				
			6	1 4	98	71	340	0 6	84
-3	LZP-3 (Nitrate) pH 1 4	0 2	1	0 7	99				
			2	1 9	97				
			3	1 6	98				
			4	2 3	97				
			5	2 6	97				
			6	2 0	97				
			7	1 4	98				
			8	2 4	97	69	640	1 6	108
-2	BC-41 (Sulfate) pH 2 0	0 05	1	3 9	95				
			2	10	86				
			3	15	80				
			4	18	76				
			5	22	70				
			6	25	66	69	380	0 13	106
-4	BC-41 (Sulfate) pH 2 0	0 2	1	0 5	99				
			2	1 0	99				
			3	1 7	98				
			4	1 8	97				
			5	2 1	97				
			6	2 6	96				
			7	3 8	95				
			8	3 5	95	69	590	0 27	100

Notes for Table 15

a) "% Uranium extracted per pass" by difference from each raffinate, based on the total uranium found in each test

b) "Contaminant ratio" is weight ratio of Fe+Al to U In the head liquors, the ratio was 300 for LZP-3 and 50 for BC-41

c) "% Uranium balance" based on head analyses

Table 16

MULTI-PASS EXTRACTION OF URANIUM BY DI(2-ETHYLHEXYL)-PHOSPHINIC ACID IN PETROLEUM ETHER

Volume ratios 10 organic 100 aqueous, first stage
10 organic 80 aqueous, second stage
pH adjusted with sodium hydroxide
Molarity of reagent = 0 1

Test No	Head Liquor	Stage No	Pass No	Raffinate Uranium mg/liter	Extraction per Pass %[a]	Organic Volume Recovered ml	Uranium in Extract mg/liter	Contaminant Ratio in Extract[b]	Uranium Balance %[c]
BC-67	BC-59-1	1	1	3 2	94				
	(Sulfate)		2	11	80				
	pH 1 9		3	17	68	10	1300		90
		2	1	0 5	5				
			2	1 4	17				
			3	2 4	28	10	350		94
BC-69	LZP-3	1	1	1 1	98				
	(Nitrate)		2	1 0	98				
	pH 1 2		3	1 7	97				
			4	3 7	93				
			5	5	91	9 0	2900	0 08	78
		2	1	0 08	2				
			2	5	1				
			3	5	2				
			4	7	6				
			5	5	8	9 7	250	1 3	82

Notes for Table 16

a) "% Uranium extracted per pass" based on the total uranium found in the first stage, so that percent extractions for corresponding passes in the two stages are additive

b) "Contaminant ratio" is the weight ratio of Fe+Al to U In the head liquor the ratio was 300 for LZP-3

c) "% Uranium balance" for the first stage is calculated as first stage raffinate plus extract over head analysis, for the second stage it is calculated as second stage raffinate plus both extracts over head analysis

Test Procedure

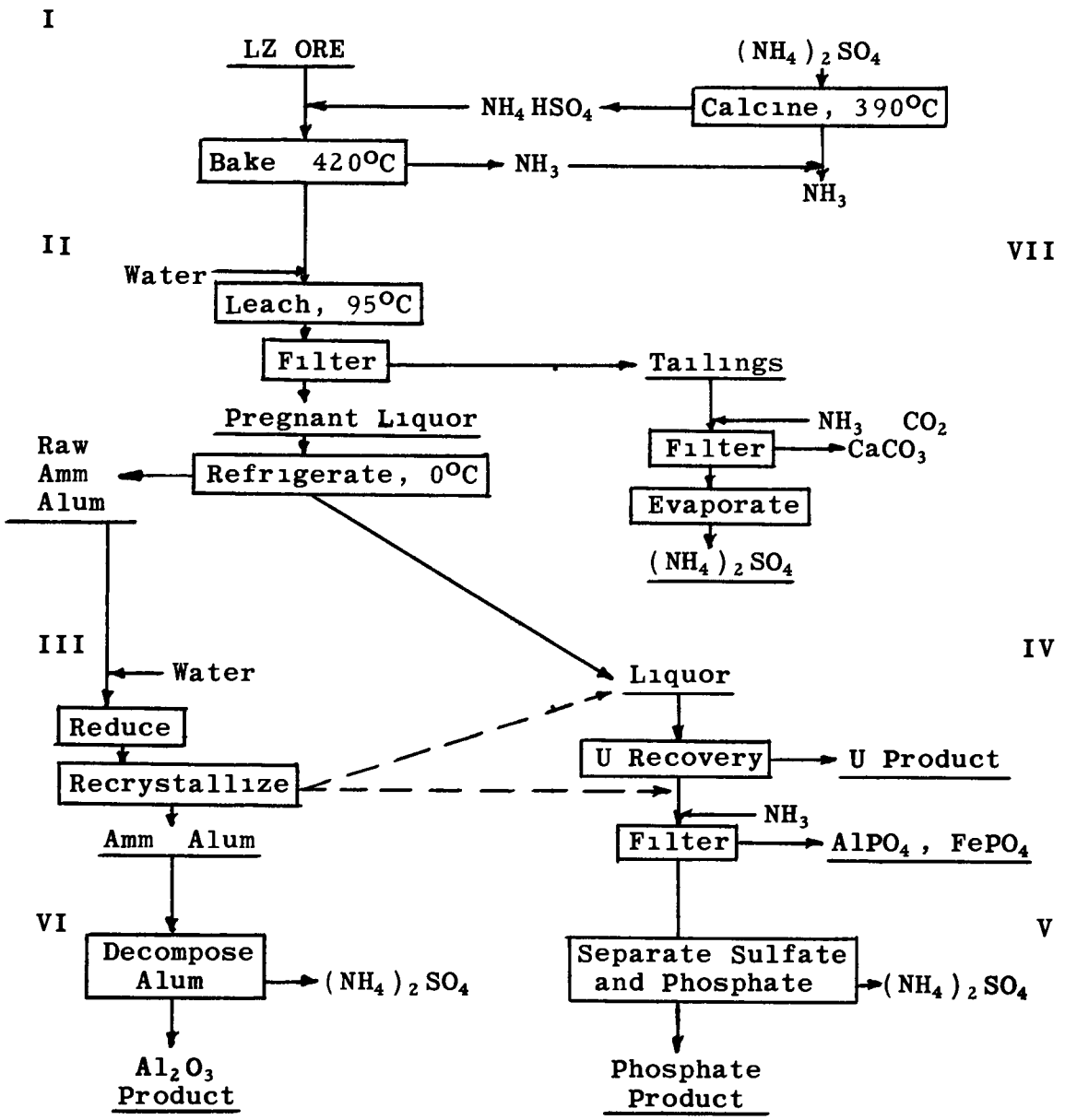
First stage 10 ml organic contacted successively with 100 ml batches of head liquor

Second stage 10 ml organic contacted successively with 80 ml portions of the corresponding first-stage raffinates

Figure 14

SCHEMATIC FLOWSHEET

FOR AMMONIUM SULFATE FUSION PROCESS



and would probably also be better for recovery of the ammonia, which is to be used in Sections IV and VII The additional ammonia evolved during the fusion will also contain fluorides, separation of these has not yet been examined

Table 17 shows the results of tests made with ore BC-1 Nearly complete dissolution of phosphate and of R_2O_3 was obtained with 25 to 50% excess (mole basis) of sulfate over the total bases present With smaller excess of sulfate, phosphate dissolution remained high but alumina dissolution began to drop, this probably represents differential attack on aluminum phosphate and clay It is not expected that any effort would be made to recover the clay alumina, unless other benefits (e g , improved filtration) would justify the increased reagent consumption Table 18 shows the quantities of ammonium sulfate calculated for stoichiometric equivalence and for 25% (molar) excess for several of the ores being examined Uranium analyses have not yet been made for the tests shown in Table 17 It is assumed, on basis of the sulfuric acid leaching tests of the LZ ores, that nearly all the uranium will be dissolved by an acid attack which dissolves most of the phosphate

The water leach of the fused material (Section II of the flowsheet) is acidic because of the excess bisulfate, and is expected to be a suitable liquor for crystallization of ammonium alum, preferably by refrigeration If the leaching can be accomplished satisfactorily with a minimum amount of water, no evaporation would be needed before the alum crystallization

The raw alum would be contaminated with ferric ion, which could be eliminated by recrystallization from reduced solution (Section III) The mother liquor from the recrystallization would contain both iron and alum (solubility of about 2% at $0^{o}C$), and perhaps uranium and phosphate The latter, if in significant quantity, might be recovered by combining this liquor with the primary liquor in Section IV of the flowsheet, either before or after the uranium recovery step

Liquors have not been available in sufficient quantity to test methods of uranium recovery, but comparison with tests on other liquors suggests that anion exchange, and/or liquid-liquid extraction, should be possible Estimates based on the fusion tests made with ore BC-1 indicate that the weight ratio of sulfate to uranium after alum removal would be between 200 and 600, and of phosphate to uranium, about 700 If the leaching were accomplished with one ton of water per ton of original ore, the corresponding concentrations would be 10 to 30% sulfate and 35% phosphate

Table 17

AMMONIUM SULFATE FUSIONS OF LZ ORE

BC-1

Test No	Reagent	Temp °C	Time hrs	Mole Ratio[a] Sulfate/Clay	Extraction into Subsequent Water Leach % P	R_2O_3[b]
1-202	NH_4HSO_4	300	4	4	54	
1-205[c]	NH_4HSO_4	350	6	5	20	20
1-204	$NH_4HSO_4 + H_2SO_4$	350	4	5	94	100
1-206[c]	" "	350	6	5	80	75
1-211	" "	350	6	5	87	50
1-213	NH_4HSO_4	430	6	2 5	98	90
1-215	"	430	6	1 5	99	80
1-216	"	430	6	1 22	93	65
1-219	$(NH_4)_2SO_4$	425	6	1 75	92	83
1-217	"	425	6	1 5	90	90
1-218	"	425	6	1 25	89	65

a) Mole ratio of sulfate to sum of bases found by head analysis (see Table 5)

b) The R_2O_3 is an approximate measure of the Al_2O_3 extraction

c) Test made after previous chloridization with 10% NaCl at 850°C for 1 5 hour

Table 18

ESTIMATE OF AMMONIUM SULFATE

REQUIRED FOR FUSION

Ore	Size	lb $(NH_4)_2SO_4$ required		
		Stoichiometric*		25% Mole Excess
		per ton ore	per lb U	per ton ore
BC-O	all	1680	4200	2100
BC-OB1	-200	2760	5440	3450
BC-1	-200	2940	2820	3680
BC-3	-200	2760	4190	3450

* Including the bases in silicate minerals

After the uranium recovery, the residual aluminum and the iron would be separated as phosphate, together with any remaining gypsum There may prove to be other impurities, e g , fluosilicate, requiring elimination at this point

Section V consists of separation of a phosphate product, probably either a calcium or an ammonium salt, or possibly a double salt with ammonium sulfate, and evaporation for recovery and recycle of the remaining ammonium sulfate

Section VI consists of decomposition of the alum to alumina and ammonium sulfate One of the following procedures may be suitable (1) thermal decomposition, (2) dissolution, and precipitation of alumina with ammonia, (3) autoclaving at 200°C to form basic aluminum sulfate, (4) autoclaving at 200°C with ammonia to form alumina Ammonium sulfate would be recycled

The tailings from the leach of Section II will consist mainly of silica, gypsum, and varying amounts of clay This slurry can be treated with ammonia and carbon dioxide for metathesis of gypsum to the carbonate, producing a solution of ammonium sulfate for recovery and recycle

It is understood, although no official report has been received of the investigation or its results, that a process can be used for LZ ore which consists of high pressure leaching with sulfuric acid, with recovery of uranium, alumina, and phosphate from the liquor It is probable that some or all of the recovery steps of such a process would be similar to those shown in Figure 14 Specific comparisons cannot be made of the two methods of opening the ore, but the ammonium sulfate fusion appears to offer the following advantages (1) The fusion is carried out at atmospheric pressure, avoiding the handling of ore in autoclaves (2) The sulfur is recovered for recycle in the form in which it is to be used, ammonium sulfate (3) Ammonium sulfate can be recovered from the gypsum, so that the net sulfur consumption would consist only of handling losses plus whatever quantity is desirable to include with the phosphate product

A comparison of the pros and cons of an ammonium sulfate attack versus a sulfuric acid attack of the Leached Zone would be in order

Miscellaneous

Pressure Leaching of Marysvale Ores

Several pressure leaching tests have been made in which samples of a Marysvale ore were treated with solutions of sodium carbonate at 150°C In some cases potassium permanganate was added in an attempt to increase uranium extractions by encouraging so far as possible the complete oxidation of any reduced uranium minerals With the particular ore studied, however, neither the increased pressure, the increased temperature, nor the presence of an oxidant were of any particular advantage As shown on Table 19, the tailings from treatments at atmosphere pressure and 95°C had essentially the same uranium content as those from the pressure tests at 150°C The ore sample (M-4) used for these tests has the following chemical composition

Constituent	% by Weight
U_3O_8	0 27
SiO_2	56 3
Fe_2O_3	5 5
Al_2O_3	14 4
CaO	4 9
MgO	2 1
Na_2O	2 1

Precipitation of Uranium from Sodium Carbonate Solutions Using Sodium Hydrosulfite

Previous data have shown that essentially complete precipitation of uranium can be obtained from 0 5M sodium carbonate solutions at 60°C using stoichiometric quantities of sodium hydrosulfite according to equation 1 Recent tests, described in Table 20, have shown a much more rapid precipitation at higher temperatures (95°C) Recoveries from 1M Na_2CO_3 solution (pH=9 65) In tests at 60°C a precipitate was not obtained in this solution after standing for as long as 10 days with 9 times the stoichiometric $Na_2S_2O_4$

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

Table 19

PRESSURE LEACHING OF MARYSVALE ORES

Test No	Leach Conditions Time Hrs	Temp (°C)	Pressure	Mesh Size	$KMnO_4$ Added (gms)	Na_2CO_3 %	% U Extd	Tails % U
H-846	3	95	Atm	-20	0	5	82	026
847	3	95	"	-20	1	5	91	012
848	3	95	"	-20	3	5	87	017
850	3	105	25 psi	-80	1	5	87	019
834	6	95	Atm	-20	0	5	90	016
835	6	95	"	-20	0	10	89	015
840	6	95	"	-20	1	3	85	019
841	6	95	"	-20	1	5	86	018
836	3	150	58 psi	-20	0	5	80	027
839	3	150	"	-20	1	3	85	019
831	3	150	"	-20	1	5	84	021
832	3	150	"	-20	5	5	91	013
837	3	150	"	-80	0	5	88	016
838	3	150	"	-80	1	5	90	013
844	3	95	Atm	-80	5	5	92	010

Ore Type Marysvale (M-4)
Leach Conditions 200 ml of Na_2CO_3 solution per 100 g of ore

Table 20

PRECIPITATION OF URANIUM FROM SODIUM CARBONATE SOLUTIONS WITH SODIUM HYDROSULFITE

Test No	$CO_3^{=}$ M	$S_2O_4^{=}$ *	Time	Temp (°C)	pH	% U Precipitated
HS-125	0 5	5x	4 hrs	95	11 5	63
122	0 5	5x	1 day	95	"	60
129	0 5	1x	4 hrs	95	"	98
62	0 5	86x	1 day	60	"	83
107	0 5	1x	3 days	60	"	99
109	1 0	1x	3 days	60	"	61
100	1 0	1x	10 days	60	"	62
135	1 0	1x	4 hrs	95	"	78
112	1 0	1x	1 day	95	"	96
110	1 0	1x	3 days	60	9 7	0
103	1 0	8 7x	10 days	60	9 7	0
130	1 0	2x	1 day	95	9 7	19

Note
1. Uranium concentrations of original Na_2CO_3 solutions were 2 g U/liter
2. All tests were made under an inert (argon) atmosphere
3. Solutions of pH 9 7 were made by mixing equal portions of Na_2CO_3 and $NaHCO_3$

* x = Stoichiometric quantity according to eq 1

Nature of the Precipitate

In a simple test designed to study the extent of reduction of the precipitated uranium, 100 ml of 5% Na_2CO_3 solution was treated under an argon atmosphere with a stoichiometric amount of $Na_2S_2O_4$ for three days at 60°C The resulting precipitate, containing 99% of the total uranium, was washed thoroughly with 1% Na_2CO_3 solution, twice with water and then was dissolved into 5% H_2SO_4 (all under an argon atmosphere) A cupferron separation on this solution showed 92% of the uranium to be tetravalent Oxidation of the other 8% could have occurred during handling

Precipitation of Uranium and Vanadium from Sodium Carbonate Solutions with Sodium Hydrosulfite

Since many of the western leach liquors contain small amounts of vanadium as well as uranium several tests have been made with Na_2CO_3 solutions containing both of these elements The results from these experiments, described in Table 21, show that both the uranium and vanadium can be precipitated with $Na_2S_2O_4$ using quantities which are not much greater than stoichiometric On a weight basis, however, even the stoichiometric requirements for the vanadium reduction are large in view of the reagent price If, for example, the vanadium is reduced to the tetravalent state (eq 2) 1 7 lbs of $Na_2S_2O_4$ would be required for each lb of vanadium If the vanadium is further reduced to the trivalent form, the quantity would of course be twice as great (eq 3)

$$VO_2^+ + 1/2\ S_2O_4^= = VO^{++} + SO_3^= \qquad (2)$$

$$VO_2^+ + S_2O_4^= = V^{+++} + 2SO_3^= \qquad (3)$$

Table 21

PRECIPITATION OF U AND V FROM Na_2CO_3 SOLUTIONS WITH $Na_2S_2O_4$

Test No	$Na_2S_2O_4$ mg	% pptn U	% pptn V
HS-126	73	0	0
127	146	4	0
128	192	70	12
131	212	87	22
132	251	97	36
133	312	99	52

Note All tests were made at 60°C for 3 days using 50 ml of 0 5M Na_2CO_3 solution containing 1 98 g U/l and 1 39 g V/l Reduction of the U(VI) to U(IV), according to eq 1, would require 73 mg of $Na_2S_2O_4$, V(V) to V(IV), according to eq 2, 119 mg, V(V) to V(III), according to eq 3, 238 mg

URANIUM CHEMISTRY

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

D E Horner
J M Lesser
R S Lowrie
J G Moore
J M Schmitt
W M Whaley
C A Blake

The investigation and evaluation of solvent extraction as a method for removing uranium and other metal ions from various types of aqueous solutions as described in previous reports [1,5,4] have been concerned, for the most part, with extractions from pure solutions and with fundamental studies relating the composition and stability of the extractable complex to the structure of the organic complexing agent These studies have been continued, but emphasis during the last quarter has been placed upon use of the results obtained in pure solutions to determine the general applicability of a solvent extraction process to liquors which vary widely in anion, cation, and uranium composition

The problem of removing uranium from aqueous solutions containing small amounts of uranium and relatively large amounts of other material involves (1) the ability of the extracting reagent to compete for the uranium with the other uranium complexers present, e g , $SO_4^{=}$, $CO_3^{=}$, $PO_4^{\equiv}$, (2) the relative strengths of the complexes formed by the reagent with uranium and other metal ions such as Fe^{+++}, Al^{+++}, Ca^{++}, (3) the rate of uranium extraction, (4) the physical behavior of the reagent (emulsification, precipitation, etc), (5) the stripping cycle, (6) the loss of reagent to the raffinate (7) the recycle of reagent, (8) the factor by which the uranium may be concentrated across the system, and (9) the product purity

The type of liquor treated and the cost of the reagent used decide the relative importance of the above factors in determining the economic feasibility of any process Thus, it is apparent that if the losses of a certain reagent due to solubility and entrainment amount to as many as 100 parts of reagent per million parts of liquor treated during the extraction of a liquor containing but 100 ppm uranium, then the price of one pound of uranium extracted must, at the onset, be augmented by the cost of one pound of reagent However, the same losses during the extraction of a liquor containing 1000 ppm uranium entail the addition of only one-

tenth the cost of a pound of reagent to the price of each pound of uranium recovered When using an expensive reagent an efficient recycle of reagent is especially important Concentration across the system, critical in the case of low level uranium liquors, is somewhat less important in higher level liquors, whereas the importance of selective extraction is increased

It is therefore possible that a certain process, after combination of the best answers to these problems, will not be able to compete economically with other recovery schemes in solutions where the metal values lie in a certain concentration range, and yet, this same process may still play a very important role in extraction from solutions having an entirely different concentration range Experiments, of the cascade-batch type, have been devised to demonstrate the behavior of certain promising reagents in (a) liquors having moderate uranium concentrations such as those obtained from plant operations in the western U S A and (b) liquors having low uranium concentrations such as leach solutions of the Florida Leached Zone and industrial phosphoric acid Recognizing the differences that exist within these broad categories as a result of wide variations in compositions of process liquors, continued studies are being made of the possible applications and comparisons of extracting agents representative of all the various classes of organophosphorus acids, i e , phosphinic acids, phosphonic acids and the inexpensive esters of phosphoric acid

Very favorable results have been obtained by extraction with di(2-ethylhexyl)phosphinic acid of liquors (2 5g U/l) prepared from a sulfuric acid leach of ores from Marysvale, Utah Some other reagents have a higher extraction coefficient for uranium from this liquor, but the excellent extraction properties demonstrated by this reagent appear, at present, to be the best combination of answers to the extraction problems involved Di(2-ethylhexyl)phosphinic acid demonstrates excellent selectivity for uranium in the presence of iron and aluminum (not shown by di(2-ethylhexyl)-phosphoric acid) and causes no precipitations or emulsions (as does mono(2-ethylhexyl)phosphoric acid or "octylpyro-phosphoric" acids) With mineral acids it is easier to strip the uranium from di(2-ethylhexyl)phosphinic acid than it is from mono(2-ethylhexyl)phosphoric acid Loss of the phosphinic acid to the aqueous raffinate is low in comparison with the uranium content (70ppm vs 2500ppm) and the reagent may be recycled many times without loss in extraction efficiency The uranium may be concentrated across the system by a factor of 10 or greater and a sodium uranate precipitate containing 64% uranium with 3% iron and only 0 3% aluminum has been obtained

This same reagent has concentrated by a factor of 30 the uranium contained in a nitric acid leach of Florida Leached Zone material

As previously reported, a very important part of the solvent extraction research program at this laboratory involves the screening of possible organic complexing agents and the synthesis and testing of additional promising reagents This work has been continued and is described in this report Screening results have shown that certain neutral bifunctional phosphorus compounds, i e , tetrabutyl ethylenediphosphonate, tetrabutyl m-phenylene diphosphate and tetrabutyl diethylene glycol diphosphate exhibit ability to extract uranium from phosphate solutions In view of the success in treating certain leach liquors with di(2-ethylhexyl)phosphinic acid emphasis is now being placed on development of new and less expensive methods of preparing phosphinic acids

Recent tests have confirmed previous work in showing that thorium can be readily extracted from a sulfuric acid solution of monazite sand using certain organophosphorus compounds in common organic solvents Separation of thorium from the rare earth constituents of the sand is very good A number of methods for removing the thorium from the organic phase have also been examined

The use of methyldioctylamine and di(2-ethylhexyl)-amine in extracting uranium (VI) from sulfate and sulfate-phosphate liquors was mentioned previously Further studies have been made since that time and a recent shipment of other primary, secondary and tertiary amines as well as quaternary ammonium salts has received attention

Screening of Possible Organic Complexing Agents Other Than Amines and Organophosphorus Compounds

Additional organic compounds have been selected, fitted into the classification scheme proposed in a previous report[4] and tested for their ability to extract uranium from dilute uranyl nitrate solutions having a pH of 2 2 The method of testing and the results are presented in Table 22 None of the compounds appears promising as a solvent extraction agent

Screening of Organophosphorus Compounds

Several samples of organophosphorus compounds have been obtained from Westvaco Chemical Division of the Food Machinery and Chemical Company of New York and Virginia-Carolina Chemical Corporation of Richmond, Virginia These reagents consisting

Table 22

SCREENING OF POSSIBLE ORGANIC COMPLEXING AGENTS

Screening Procedure

Equal volumes of organic and aqueous phases (50 ml)
Concentration of organic compound in organic solvent, unless otherwise indicated = 0 1M
Solvent as indicated
Concentration of uranium (VI) in aqueous phase = 0 004M
Uranium present as $UO_2(NO_3)_2$
Initial pH = 2 2
Contact time one hour, mechanical agitation
Analyses of uranium in aqueous phase made by fluorimetric methods Extractions of less than 15% have doubtful significance

Complexing Agent	Percent Extraction From $UO_2(NO_3)_2$, pH=2 2	
	BuOAc	Hexone
Sulfosalicylic acid	5	6
4,4'-Dihydroxydiphenyl sulfone	1	2
Thiosalicylic acid	0 4	0
p-Benzylaminophenol	44*	71
Sodium isoamylsulfonate	6	2
Acetonylacetone	5	9
p-Phenolsulfonic acid	0	0
Thioacetanilide	0	2
α-Mercapto-N-(2-naphthyl)-acetamide	6	1
N N'-Dibutylurea	0	22
α-Benzil monoxime	0	4
2,5-Dimethylpiperazine	97*	--
2-Naphthol-3,6-disulfonic acid sodium salt	47	17
3-Hydroxy-2-naphthoic acid	10	0
Acetanilide	0	4
Sodium dl-camphorsulfonate	10	--
p-Amoxybenzoic acid	8	0
Sodium m-benzenedisulfonate	1	24
2-Mercaptobenzothiazole	--	11
Butyraldoxime	0	21
Benzyl thiocyanate	6	13
Cetylpyridinium chloride	--	21
Laurylpyridinium chloride	--	17
Cetyltrimethylammonium bromide	--	28

*Large rise in pH during extraction leading to hydrolytic precipitation

of alkyl phosphites, neutral esters of phosphoric and phosphonic acids, neutral esters of diphosphonic acids and one diphosphonic acid, have been screened according to the procedure given in Table 23, which also presents the results obtained It is surprising that several of the neutral compounds demonstrate fair ability to extract uranium from phosphate solutions These reagents will receive further testing It is disappointing, though, that the reagent (tetrabutyl ethylenediphosphonate) showing best extraction from phosphate solution has the unfortunate property of causing emulsification during extraction Further purification of this compound may alleviate some of this difficulty

Extractions with bidentate compounds are of interest because it is entirely possible that one such molecule can provide, within itself, the necessary functional groups to complex completely a uranyl ion in accord with the results presented in a later discussion concerning identification of the complex Moreover, because of steric effects, the extraction of iron and aluminum by these compounds, that is, their selectivity for uranium in the presence of other metal ions, may vary considerably from those obtained when the monofunctional compounds are used

It has been learned recently that several batches of di(2-ethylhexyl)phosphinic acid, apparently over 90% pure by titration, have had rather low extraction coefficients Different methods have been used to prepare and purify this reagent and it appears that the resulting products are not chemically identical The reasons for these deviations are now being investigated

Detailed Study of the Organophosphorus Acids in Pure Solutions

In order to characterize the behavior of the organophosphorus compounds the detailed study of certain reagents thought to be representative of classes of these compounds has been continued

Concentrations of Typical Organophosphorus Acids Required To Extract Uranium from Various Solutions

Extractions in nitrate, phosphate, sulfate and fluoride solutions with dioctylphosphinic acid, di(2-ethylhexyl)-phosphinic and mono(2-ethylhexyl)phosphoric acid* were

---

* Listed in previous reports as monooctyl and dioctyl phosphates Communication with the Victor Chemical Company has ascertained that all "octyl" phosphorus compounds marketed by that company are, in reality, derivatives of 2-ethylhexanol

Table 23

SCREENING OF ORGANOPHOSPHORUS COMPOUNDS

Screening Procedure

Equal volumes of organic and aqueous phases (50 ml)
Concentration of organic compound in organic solvent, unless otherwise indicated = 0 1M
Solvent as indicated
Concentration of uranium (VI) in aqueous phase = 0 004M
Uranium present as $UO_2(NO_3)_2$
Initial pH as indicated
Contact time one hour, mechanical agitation
Analyses of uranium in aqueous phase made by fluorimetric methods Extractions of less than 15% have doubtful significance
Source of reagent V-C - Virginia-Carolina Chemical Corp
W - Westvaco Chemical Co

Complexing Agent Name	Source	Solvent	% Extraction From Solutions Containing 0 008M NO_3^- pH=2 2	0 5M $PO_4^{\equiv}$ pH=1 1
Triethyl phosphite	V-C	CCl_4	9	--
		Bu_2O	13	--
Triisoprypyl phosphite	V-C	CCl_4	5	--
		Bu_2O	7	--
Tributyl phosphite	V-C	hexone	2	--
		BuOAc	6	--
Tri(2-ethylhexyl) phosphite	V-C	CCl_4	24	12
		Bu_2O	36	--
Tri-"isooctyl" phosphite	V-C	CCl_4	27	16
		Bu_2O	27	--
Dimethyl hydrogen phosphite	V-C	CCl_4	0	--
		Bu_2O	10	--
Diethyl hydrogen phosphite	V-C	CCl_4	1	--
		Bu_2O	13	--
Dibutyl hydrogen phosphite	V-C	CCl_4	31	--
		Bu_2O	24	--

Table 23 (Cont'd)

Complexing Agent Name	Source	Solvent	% Extraction From Solutions Containing 0 008M NO_3^- pH=2 2	0 5M $PO_4^{\equiv}$ pH=1 1
Di(2-ethylhexyl) hydrogen phosphite	V-C	CCl_4	39	31
		Bu_2O	80	--
Triethyl phosphate	W	CCl_4	3	8
		Bu_2O	0	--
Tributyl phosphate	V-C	CCl_4	0	--
		Bu_2O	14	--
Triamyl phosphate	W	CCl_4	6	6
		Bu_2O	3	--
Triheptyl phosphate	W	CCl_4	13	2
		Bu_2O	0	--
Tri(2-ethylbutyl) phosphate	W	CCl_4	40	8
		Bu_2O	50*	--
Trioctyl phosphate	W	CCl_4	5	3
		Bu_2O	9	--
Tribenzyl phosphate	W	CCl_4	18	8
		Bu_2O	12	--
Triphenyl phosphate	W	CCl_4	4	14
		Bu_2O	6	--
Diethyl 2,4-dichlorophenyl phosphate	V-C	CCl_4	5	--
		Bu_2O	15	--
Dibutyl octylphenyl phosphate	W	CCl_4	0	--
		Bu_2O	12	--
Triethyl thionophosphate	V-C	CCl_4	10	--
		Bu_2O	13	--
Tetraphenyl ethylene diphosphate	W	CCl_4	99	54
		Bu_2O	56	--
Tetrabutyl diethylene glycol diphosphate	W	CCl_4	97	55
Tetra(2-butoxyethyl) diethylene glycol diphosphate	W	CCl_4	33	24
		Bu_2O	31*	--

Table 23 (Cont'd)

Complexing Agent Name	Source	Solvent	% Extraction From Solutions Containing 0 008M NO_3^- pH=2 2	0 5M $PO_4^{\equiv}$ pH=1 1
Di(2-butoxyethyl) diphenyl diethylene glycol diphosphate	W	CCl_4	14	--
Tetrabutyl p-phenylene diphosphate	W	CCl_4	7	--
		Bu_2O	24	--
Tetrabutyl m-phenylene diphosphate	W	CCl_4	96	59
		Bu_2O	98	--
Diethyl trichloromethylphosphonate	V-C	CCl_4	11	--
		Bu_2O	0	--
Diethyl ethylphosphonate	V-C	CCl_4	0	--
		Bu_2O	21	--
Diisoöctyl heptylphosphonate	W	CCl_4	88	6
		Bu_2O	--	--
Isoöctyl phenyl heptylphosphonate	W	CCl_4	99	56
		Bu_2O	100*	--
Diphenyl heptylphosphonate	W	CCl_4	83	15
		Bu_2O	68	--
Diethyl phenylmethylphosphonate	V-C	CCl_4	0	--
		Bu_2O	20	--
Tetraethyl ethylenediphosphonate	V-C	CCl_4	12	--
		Bu_2O	23	--
Tetrabutyl ethylenediphosphonate	V-C	CCl_4	98[e]	90[e]
		Bu_2O	99	--
Tetrabutyl trimethylenediphosphonate	V-C	CCl_4	38	10
		Bu_2O	58	--
Trimethylene diphosphonic acid	V-C	CCl_4	83	10
		Bu_2O	83	--
3,4-Dichlorobenzylphosphonic acid	V-C	Bu_2O	4 5	--
		Isoamyl alc	99	21

*0 08M reagent

e - Emulsion

reported last quarter[1] Similar studies with two additional reagents, dibutylphosphoric acid and di(2-ethylhexyl)phosphoric acid* have been made and the results are presented in Figures 15 and 16 The relative importance of sulfate and phosphate ions in decreasing uranium extractions are the same as reported previously

Comparisons of the extracting ability of all reagents tested in this manner are made in Tables 24, 25 and 26 On the basis of extraction alone and neglecting selectivity properties, mono(2-ethylhexyl)phosphoric acid is the most effective reagent Tests with phosphonic acids are now being completed

The tremendous ability of some of these reagents to extract uranium from aqueous solution is demonstrated by a few incidental tests made with di(2-ethylhexyl)phosphinic acid In one case an acid (pH=0 3) solution of uranyl nitrate containing 6g uranium/liter was extracted twice with one-fifth its volume of 10% reagent in kerosene with a subsequent reduction of uranium concentration to 400ppm in the first stage and 50ppm in the second In another test, 100 ml of solution containing a large amount of ammonium nitrate at pH=2 but with only 1 5-2ppm uranium was extracted with 20 ml of 10% reagent in kerosene, with a final raffinate analysis of less than 0 1ppm

Effect of Solvent on Extraction with Di(2-ethylhexyl)-phosphinic Acid

Extractions have been made with di(2-ethylhexyl)-phosphinic acid in sixteen common solvents The resulting extraction coefficients are listed in Table 27 A reagent concentration of 0 06M was used since it was known that this amount when dissolved in carbon tetrachloride was insufficient to extract completely the uranium from a 0 5M phosphate solution It is fortunate that the best coefficients are obtained in the least expensive solvent, kerosene Hydrocarbons with eight and twelve carbon atoms performed well, and carbon tetrachloride, which has been used for all the detailed studies is also a very good solvent Bad emulsions were usually obtained when "pentaether" or isoamyl alcohol was used

*See note, page 74

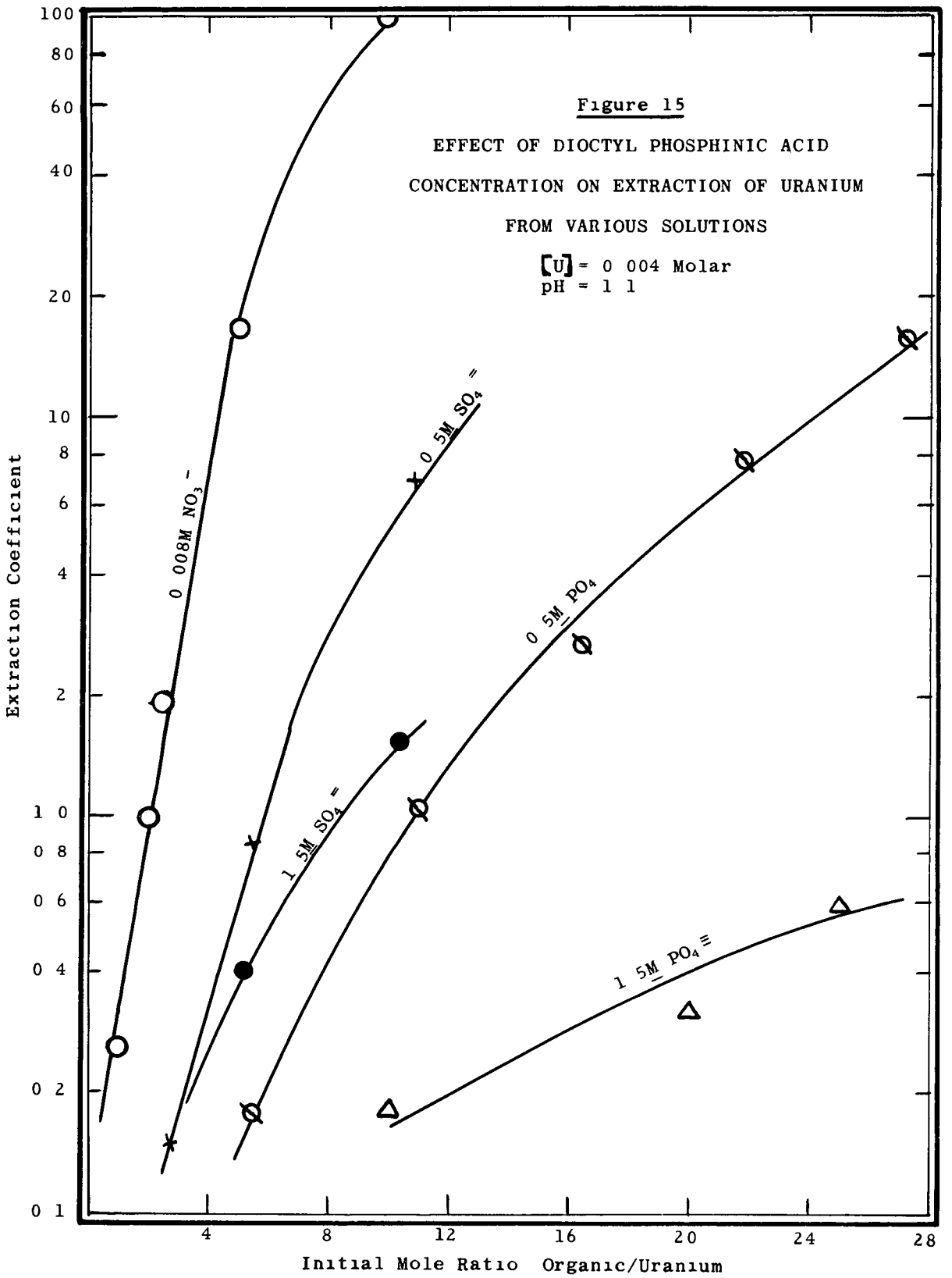


Figure 15
EFFECT OF DIOCTYL PHOSPHINIC ACID
CONCENTRATION ON EXTRACTION OF URANIUM
FROM VARIOUS SOLUTIONS
[U] = 0 004 Molar
pH = 1 1
0 008M NO3 -
0 5M SO4 =
0 5M PO4
1 5M SO4 =
1 5M PO4 ≡
Extraction Coefficient
100
80
60
40
20
10
8
6
4
2
1 0
0 8
0 6
0 4
0 2
0 1
4
8
12
16
20
24
28
Initial Mole Ratio Organic/Uranium

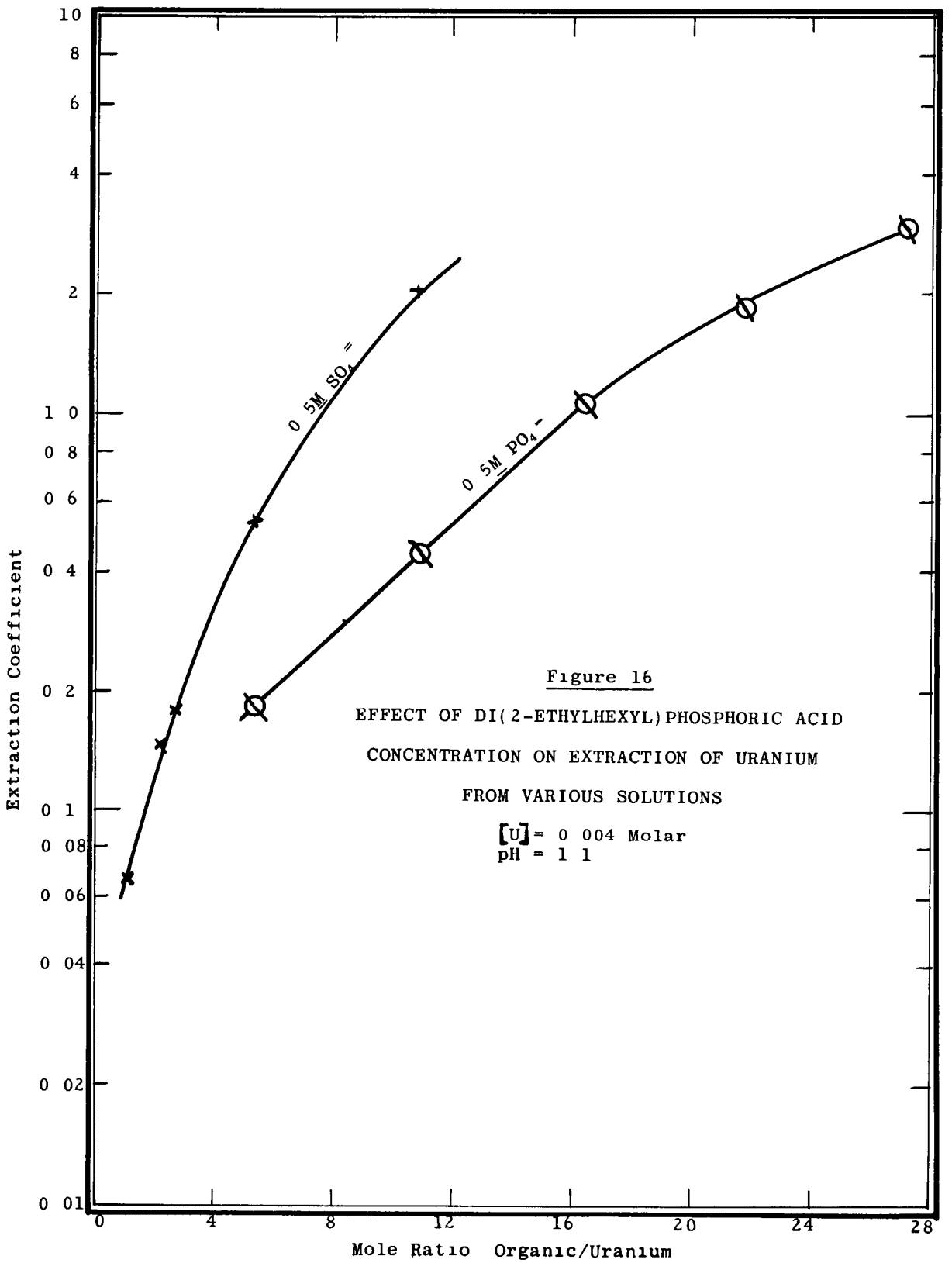


Figure 16

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

[U] = 0 004 Molar
pH = 1 1

Table 24

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN NITRATE SOLUTIONS WITH ORGANOPHOSPHORUS ACIDS

[U] = 0 004 molar
pH = 1 1
$[NO_3^-]$ = 0 008 molar

Phosphorus Acid	Mole ratio Organic/uranium 1	2	4	6	8
Mono(2-ethylhexyl)phosphoric	0 7	11	280	540	---
Di(2-ethylhexyl)phosphinic	0 2	0 8	9 2	17	26
Dibutylphosphoric	0 3	0 9	7 1	31	66
Dioctylphosphinic	0 3	1 3	11 0	---	---
Di(2-ethylhexyl)phosphoric	---	---	---	---	---

Table 25

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN PHOSPHATE SOLUTIONS WITH ORGANOPHOSPHORUS ACIDS

[U] = 0 004 molar
pH = 1 1

A In 0 5M $PO_4^{\equiv}$

Phosphorus Acid	Mole ratio Organic/uranium 8	12	16	20	24
Mono(2-ethylhexyl)phosphoric	10	26	50	86	110*
Di(2-ethylhexyl)phosphinic	0 6	1 3	2 3	3 6	5 4
Dibutylphosphoric	0 4	1 3	3 0	5 6	10 0
Dioctylphosphinic	1 4	2 5	4 0	5 8	8 0
Di(2-ethylhexyl)phosphoric	0 3	0 5	1 0	1 7	2 4

*This figure, erroneously listed in ORNL-1308 as "7100", should have read ">100"

B In 1 5M $PO_4^{\equiv}$

Phosphorus Acid	Mole ratio Organic/uranium 8	12	16	20	24
Mono(2-ethylhexyl)phosphoric	3 6	8	15	20	24
Di(2-ethylhexyl)phosphinic	0 3	0 5	0 8	1 1	1 6
Dibutylphosphoric	0 1	0 2	0 3	0 4	0 5
Dioctylphosphinic	0 05	0 1	0 1	0 2	0 3
Di(2-ethylhexyl)phosphoric	---	---	---	---	---

Table 26

COMPARISON OF EXTRACTION COEFFICIENTS OBTAINED IN SULFATE SOLUTIONS WITH ORGANOPHOSPHORUS ACIDS

[U] = 0 004 molar
pH = 1 1

A In 0 5M $SO_4^{=}$

Phosphorus Acid	Mole ratio Organic/uranium 1	2	4	6	8
Mono(2-ethylhexyl)phosphoric	1 0	2 5	26	80	140
Di(2-ethylhexyl)phosphinic	0 1	0 2	0 5	1 5	4 0
Dibutylphosphoric	---	---	0 3	1 1	3 0
Dioctylphosphinic	0 1	0 2	0 9	3 2	6 2
Di(2-ethylhexyl)phosphoric	0 07	0 1	0 3	0 7	1 1

B In 1 5M $SO_4^{=}$

Phosphorus Acid	Mole ratio Organic/uranium 1	2	4	6	8
Mono(2-ethylhexyl)phosphoric	1 0	2 0	12	36	74
Di(2-ethylhexyl)phosphinic	0 1	0 2	0 5	1 5	3 0
Dibutylphosphoric	---	---	0 2	0 5	0 9
Dioctylphosphinic	0 04	0 07	0 3	0 7	1 1
Di(2-ethylhexyl)phosphoric	---	---	---	---	---

Table 27

EFFECT OF SOLVENT ON EXTRACTION WITH DI(2-ETHYL-HEXYL)PHOSPHINIC ACID

0 06M Di(2-ethylhexyl)phosphinic acid
0 004M Uranium in 0 5M phosphate
pH=1 I

Solvent	Extraction Coefficient
Kerosene	4 5
n-Dodecane	4 1
n-Butyl ether	3 7
n-Octane	3 6
Triglycol dichloride	2 4
Carbon tetrachloride	1 7
Benzene	1 7
Dichlorobenzene	1 6
Hexone	1 5
Chlorobenzene	1 3
Trichloroethylene	0 8
Pentaether *	0 7
Butylacetate	0 5
Chloroform	0 3
Isoamyl alcohol*	0 1
Cyclohexanol	0 02

*Emulsion

Extraction of Iron and Aluminum by Organophosphorus Acids

The ability of an organic complexing agent to extract uranium selectively from solutions containing other metal ions such as iron and aluminum is important if it is to be used in any solvent extraction uranium recovery process Accordingly, concentration studies similar to those just described are being conducted for iron and aluminum solutions Figures 17 and 18 show that the extraction of iron with di(2-ethylhexyl)-phosphinic acid is lower than when mono(2-ethylhexyl)phosphoric acid is used

Coefficients for uranium, iron and aluminum are compared for the two reagents in Table 28 It is significant that when the phosphinic acid is used the extraction coefficients are higher for uranium than for iron and aluminum, while in the case of the phosphoric acid the extraction coefficients are higher for iron and aluminum than they are for uranium Thus, though the phosphinic acid extracts less uranium than will the same amount of phosphoric acid, the selectivity for uranium of the first reagent is the better of the two reagents

Saturation Experiments to Determine Combining Ratio of Extractable Uranium Complex

In an attempt to determine the actual combining ratio of the extractable uranium complexes, saturation experiments have been run in which the organic phase has been contacted with a series of solutions having uranium concentrations increasing to relatively high levels Table 29 presents the results when di(2-ethylhexyl)phosphinic acid was used to extract concentrated uranyl nitrate solutions A plot of the mole ratio of complexing agent to uranium in the organic phase versus the concentration of uranium in the aqueous phase is shown in Figure 19 The steepness of the initial portion of the curve followed by the sharp break and rapid approach to an asymptote of 2 indicates the formation of a strong complex whose lowest combining ratio is two moles of di(2-ethylhexyl)phosphinic acid to one uranyl ion The formation of this neutral complex may be described by the following equation,

$$UO_2^{++} + 2HPh \longrightarrow UO_2(Ph)_2 + 2H^+ \qquad (4)$$

where Ph = $(C_8H_{17})_2P(=O)(-O-)$

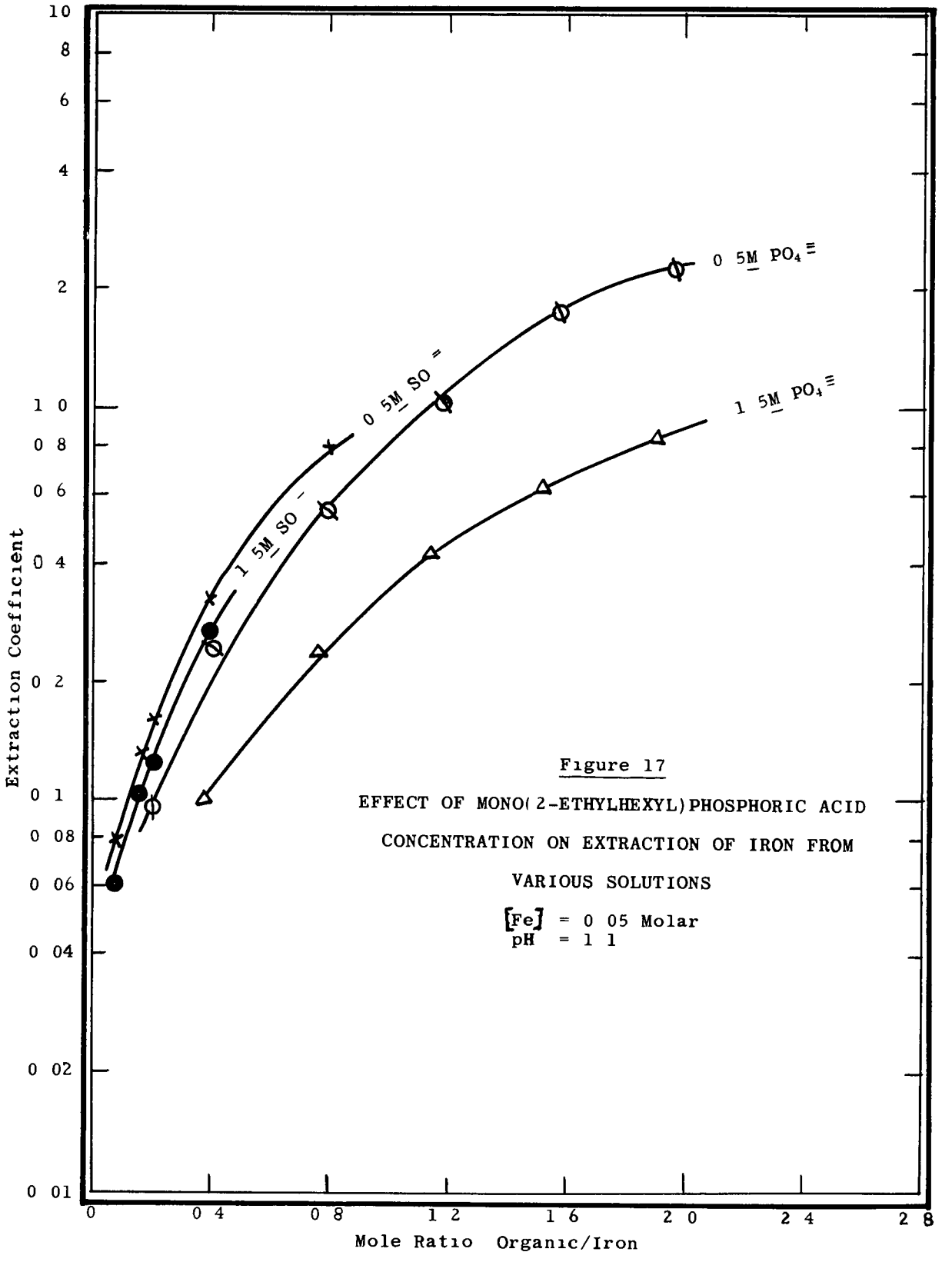


Figure 17

EFFECT OF MONO(2-ETHYLHEXYL)PHOSPHORIC ACID CONCENTRATION ON EXTRACTION OF IRON FROM VARIOUS SOLUTIONS

[Fe] = 0 05 Molar
pH = 1 1

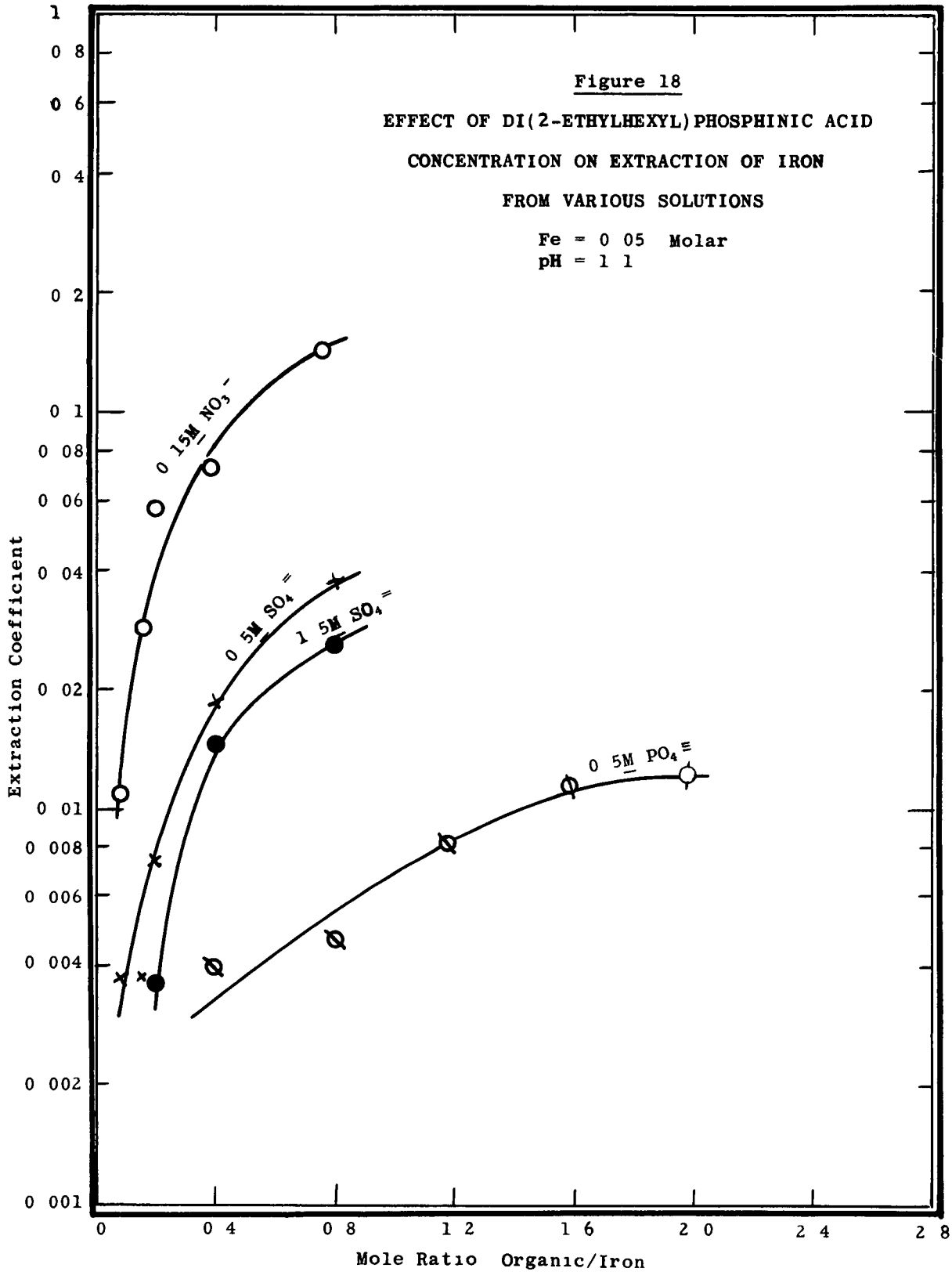


Figure 18
EFFECT OF DI(2-ETHYLHEXYL)PHOSPHINIC ACID
CONCENTRATION ON EXTRACTION OF IRON
FROM VARIOUS SOLUTIONS
Fe = 0 05 Molar
pH = 1 1
0 15M NO3-
0 5M SO4=
1 5M SO4=
0 5M PO4≡
Extraction Coefficient
1
0 8
0 6
0 4
0 2
0 1
0 08
0 06
0 04
0 02
0 01
0 008
0 006
0 004
0 002
0 001
0
0 4
0 8
1 2
1 6
2 0
2 4
2 8
Mole Ratio Organic/Iron

Table 28

COMPARISON OF URANIUM, IRON AND ALUMINUM EXTRACTION COEFFICIENTS OBTAINED WITH ORGANOPHOSPHORUS ACIDS IN 0 5M $PO_4^{\equiv}$

pH=1 1

A Di(2-ethylhexyl)phosphinic Acid

Mole ratio Organic/metal ion	Extraction Coefficient For Uranium	Iron	Aluminum
1	0 05	0 007	0
2	0 10	014	0

B Mono(2-ethylhexyl)phosphoric Acid

Mole ratio Organic/metal ion	Extraction Coefficient For Uranium	Iron	Aluminum
1	0 19	0 86	~0 3
2	0 43	2 30	---

Table 29

SATURATION EXPERIMENTS TO DETERMINE THE COMBINING RATIO OF THE EXTRACTABLE URANIUM COMPLEX

Di(2-ethylhexyl)phosphinic Acid, 0 02M
pH=1 1

Molar Uranium Concentration		Mole ratio
Aqueous	Organic	Organic/uranium
1 053	0 01050	1 91
1 053	00849	2 32
0 584	00987	2 02
279	00958	2 09
166	00941	2 12
088	00907	2 20
031	00832	2 40
028	00655	3 05
003	00382	5 25

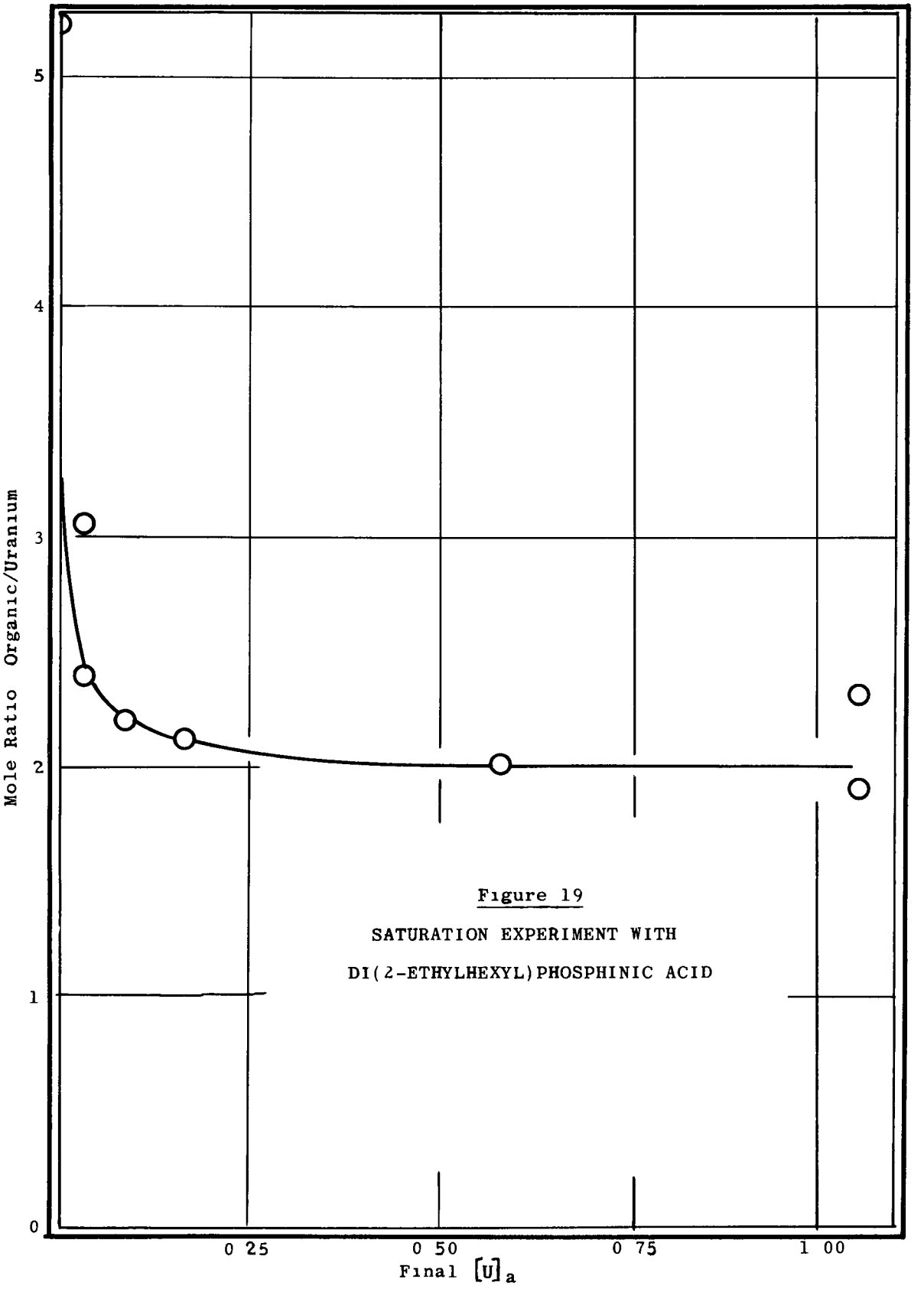


Figure 19

SATURATION EXPERIMENT WITH

DI(2-ETHYLHEXYL)PHOSPHINIC ACID

Determination of the Formation Constant for the Uranium Complex with Di(2-ethylhexyl)phosphinic Acid

The formation constant for the complex described by equation (4) of the previous section is

$$K_f = \frac{[UO_2Ph_2]_o}{[UO_2^{++}]_a} \frac{[H^+]^2}{[HPh]^2_{final}} \qquad (5)$$

In order to estimate a value for K_f in the formation of the uranium complex with di(2-ethylhexyl)phosphinic acid a series of extractions have been made with this reagent in very dilute uranyl nitrate solutions The experimental results are listed in Table 30, where the extraction coefficient, E_a^o, is defined as being the ratio $[UO_2Ph_2]_o / [UO_2^{++}]_a$ and is approximated by the expression,

$$E_a^o = \frac{\text{final conc of uranium in organic phase}}{\text{final conc of uranium in aqueous phase}} = \frac{[U]_o}{[U]_a} \qquad (6)$$

Table 30

EXTRACTION OF URANIUM BY DI(2-ETHYLHEXYL)PHOSPHINIC ACID FROM VERY DILUTE URANYL NITRATE SOLUTIONS

pH=1 1

$[HPh]$ (final)	$[U]_o$	$[U]_a$	E_a^o
3 95x10^{-4}	25 97x10^{-7}	3 79x10^{-5}	68 59x10^{-3}
1 99 "	6 72 "	3 98 "	16 90 "
1 80 "	1 72 "	4 03 "	4 28 "
0 80 "	1 13 "	4 03 "	2 81 "

The determination of K_f involves the substitution of equation (6) into equation (5),

$$E_a^o = \frac{K_f}{[H^+]^2} [HPh]^2_{final} \quad (7)$$

whence,

$$\log E_a^o = \log \frac{K_f}{[H^+]^2} + 2 \log [HPh]_{final} \quad (8)$$

under the condition of constant hydrogen ion concentration, it is seen that equation (8) is that of a straight line and when log E_a^o is plotted versus log [HPh] the slope of the resulting line should be 2, the combining ratio of the complex When [HPh] = 1, then E_a^o assumes the value

$$E_a^o = \frac{K_f}{[H^+]^2}, \quad [HPh] = 1 \quad (9)$$

The data of Table 30 have been plotted in this manner and Figure 20 shows the resulting straight line The slope of this line is 2, verifying the saturation experiments previously described Extrapolating, the value of E_a^o when [HPh] = 1 is

$$E_a^o = 4\ 3 \times 10^{-}$$

Since the pH level is 1 1 then according to equation (9)

$$K_f = 2\ 7 \times 10^3$$

This value of K_f was used to calculate values of E_a^o for the extraction experiments with di(2-ethylhexyl)phosphinic acid in more concentrated uranyl nitrate described previously[1] Where the experimental error is small, agreement within a factor of 3 was achieved between the experimental and calculated extraction coefficients C Baes and J Schreyer of this laboratory have determined formation constants for the complexes of uranium in acidic phosphate solutions Their results are presented in a later section of this report The expressions for the constants of three of these complexes are as follows

$$k_1 = \frac{C_1\ (H^+)}{(UO_2^{++})\ (H_3PO_4)} = 30 \quad (10)$$

$$k_2 = \frac{C_2\ (H^+)^2}{(UO_2^{++})\ (H_3PO_4)^2} = 20 \quad (11)$$

$$k_3 = \frac{C_3\ (H^+)^2}{(UO_2^{++})\ (H_3PO_4)^3} = 280 \quad (12)$$

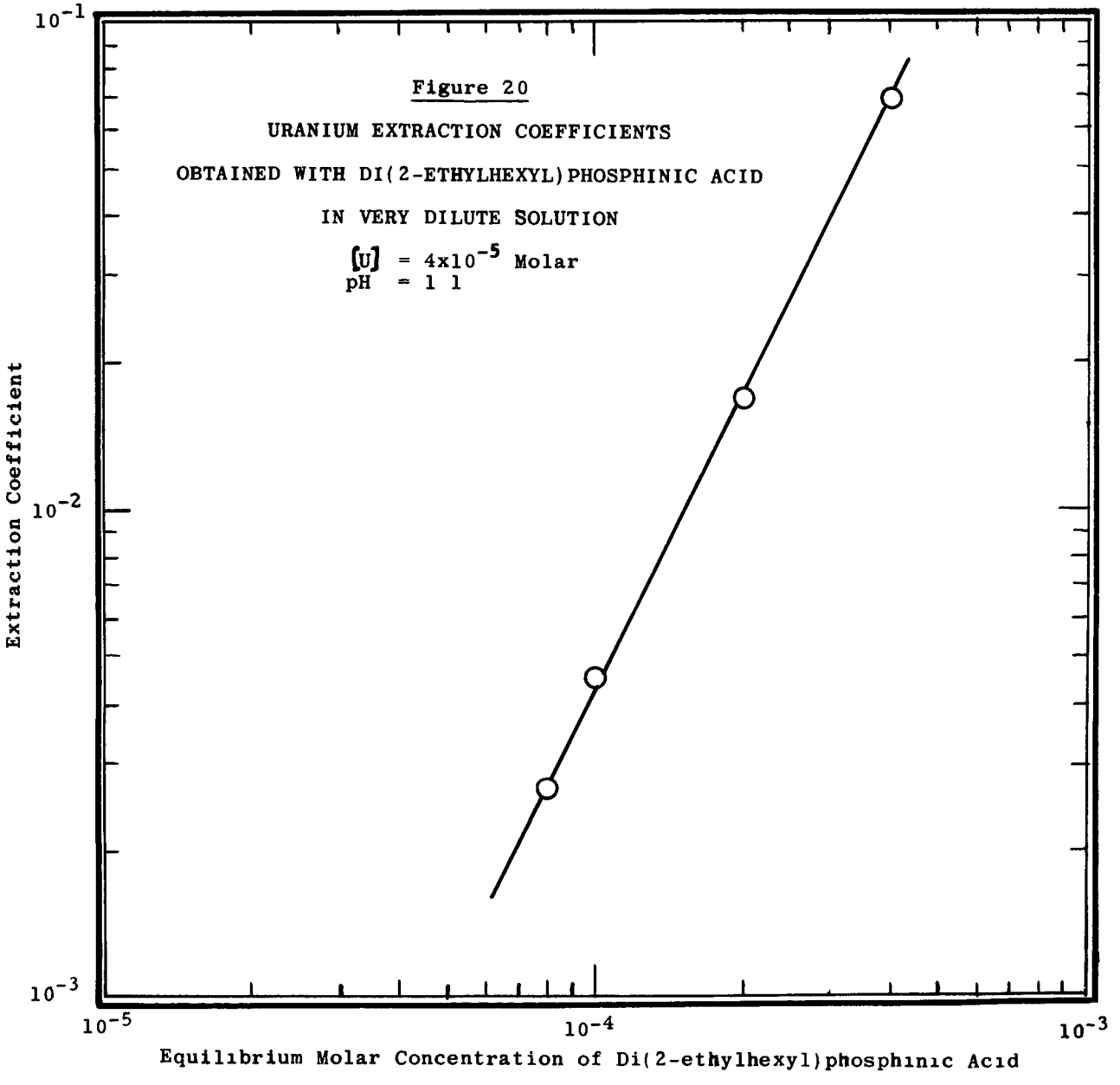


Figure 20
URANIUM EXTRACTION COEFFICIENTS
OBTAINED WITH DI(2-ETHYLHEXYL)PHOSPHINIC ACID
IN VERY DILUTE SOLUTION
[U] = 4x10^-5 Molar
pH = 1 1
Extraction Coefficient
10^-1
10^-2
10^-3
10^-5
10^-4
10^-3
Equilibrium Molar Concentration of Di(2-ethylhexyl)phosphinic Acid

Simultaneous solution of equations (5), (10), (11) and (12) leads to an expression for $[UO_2^{++}]$ in terms of the total uranium and allows calculation of uranium extraction coefficients in the presence of phosphate This has been done for the extractions in 0 5M $PO_4^{\equiv}$ by di(2-ethylhexyl)-phosphinic acid and it is found that the actual extraction coefficient is about 6 times larger than the theoretical one These calculations may only be regarded as approximations because the exact nature of the solutions and the equilibria within them are not yet known Moreover, activity coefficients in some of the moderately concentrated solutions will play a part in reducing effective concentrations Some effort has been made to minimize this latter effect by conducting the original equilibrium studies in solutions of very low concentrations From these results empirical expressions are being developed for determination of the predicted uranium extraction coefficient in phosphate solutions

Determination of the Combining Ratio of the Iron-Phosphinic Acid Complex and Its Formation Constant

The formation of a complex between iron and a phosphorus acid may be expressed by the following equation

$$nHPh + Fe^{+++} \longrightarrow FePh_n^{3-n} + nH^+ \qquad (13)$$

for which the expression for the formation constant becomes

$$K_f = \frac{[FePh_n^{\ 3-n}][H^+]^n}{[HPh]^n\ [Fe^{+++}]} \qquad (14)$$

Treatment of the di(2-ethylhexyl)phosphinic acid-iron extraction data according to this equation in a manner identical with that used in the uranium calculation yields the information appearing on Figure 21 The slope of the line is 1, indicating that the complex extracted has a combining ratio of one molecule of phosphinic acid to one molecule of iron Since the iron-phosphinic complex must be neutral this combining ratio indicates extraction of iron as some singly positive charged ion with possibilities being FeO^+, $Fe(OH)_2^+$, $Fe(NO_3)_2^+$, etc There is no experimental evidence as yet to justify a choice of any of these as being correct

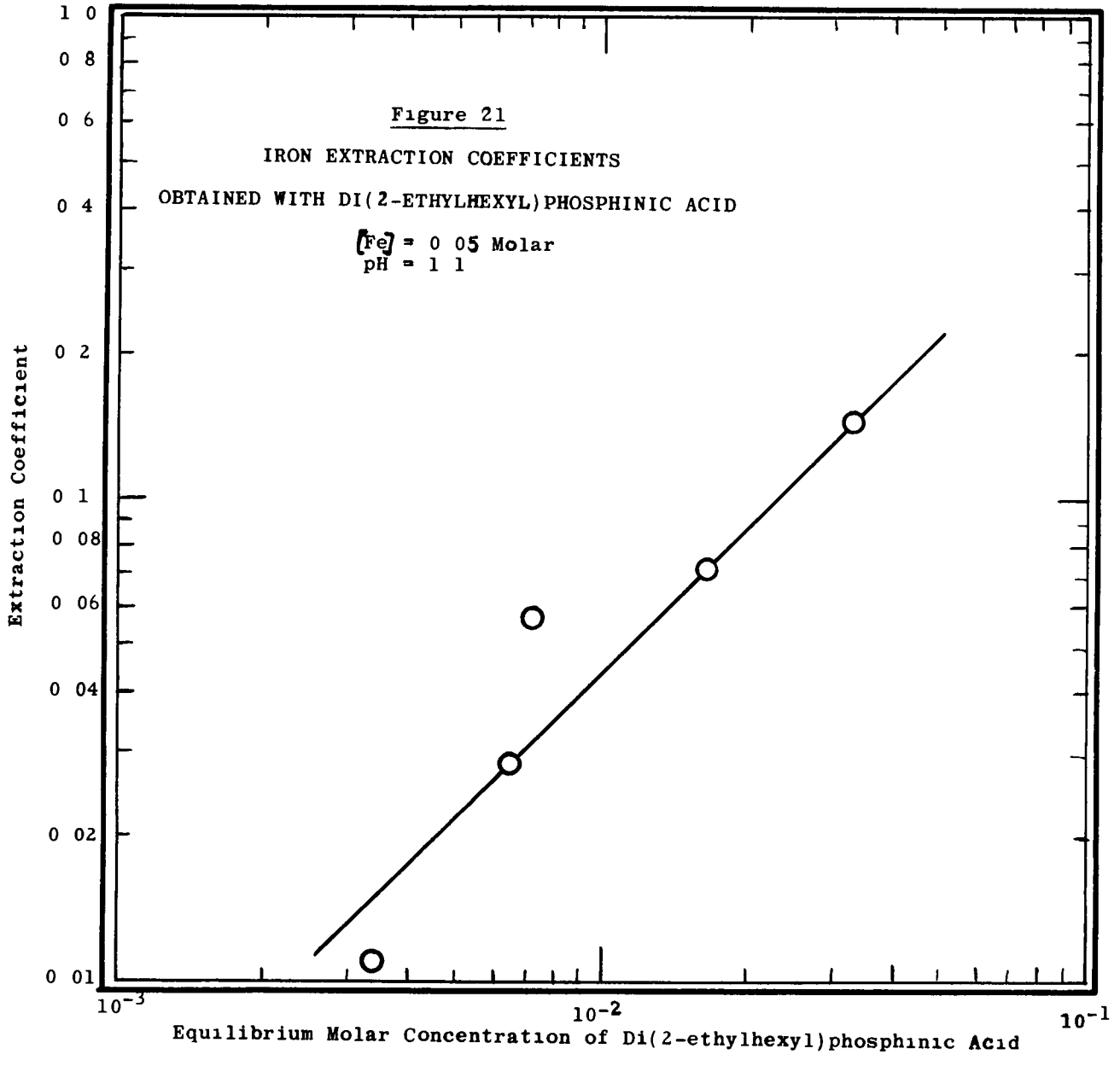


Figure 21
IRON EXTRACTION COEFFICIENTS
OBTAINED WITH DI(2-ETHYLHEXYL)PHOSPHINIC ACID
[Fe] = 0 05 Molar
pH = 1 1
Extraction Coefficient
1 0
0 8
0 6
0 4
0 2
0 1
0 08
0 06
0 04
0 02
0 01
10^{-3}
10^{-2}
10^{-1}
Equilibrium Molar Concentration of Di(2-ethylhexyl)phosphinic Acid

An estimate of the formation constant for the complex has been made by extrapolating the curve of Figure 21 to find the value of E_a^o when $[HPh] = 1$ This, when divided by $[H^+]$ becomes the formation constant for equation 13,

$$K_f \approx 3\ 5 \times 10^{-1}$$

This value, when compared with the constant for uranium complex formation, $K_f = 2\ 7 \times 10^3$, agrees with the observed preferential extraction of uranium by di(2-ethylhexyl)-phosphinic acid

A few results obtained by extraction of iron with mono(2-ethylhexyl)phosphoric acid indicate that this reagent also combines with iron in equal mole quantities

Stripping Uranium from the Organic Extract

Efficient and inexpensive removal of the uranium from the organic extract is essential to a successful solvent extraction process A series of experiments are now being made to study (1) relative effectiveness of various stripping reagents, e g , H_2SO_4, $H_2SO_4+Na_2SO_4$, HCl, HCl+NaCl, HF, etc , (2) effect of the concentration of reagent in the organic phase upon the ease of stripping, (3) effect of the volume ratio of stripping phase to organic phase and (4) the purity of the product obtained from precipitation of the stripping solutions

Preliminary results indicate that the effectiveness of acids as stripping agents decreases in the order HF, H_2SO_4, HCl, providing the normalities of the acids are equal and other variables are held constant Addition of NaCl does not improve the extractability over that possessed by the acid alone Stripping coefficients appear to increase nearly linearly with the concentration of the stripping agent and decrease appreciably with an increase in concentration of the organic reagent

Extraction of Reduced Uranium (IV) by Organophosphorus Compounds

All of the work reported thus far on the solvent extraction of uranium from aqueous solutions has dealt with uranium in its highest valence state U (VI) Preliminary experiments have now been made to compare the extraction of U (VI) and reduced uranium (IV) The data show that in

uranium perchlorate solutions (pH~0 4), where little inorganic complexing of the uranium takes place, extractions with equimolar quantities of the same reagent are nearly identical for U (IV) and U (VI) Addition of some inorganic uranium-complexing ion such as $PO_4^{\equiv}$ produces a marked change in the comparative extractability of the two valence states The results for U (IV) are very similar to those for Th (IV) reported previously and indicate that competition between inorganic and organic complexing agents is not as great for reduced uranium (IV) as it is for U (VI), resulting in higher extractions of the former with equalmolar quantities of the same reagent

The nature of the extractable complex with U (IV) has not yet been determined

Extraction From Process Liquors by Means of Organophosphorus Acids

The problem of removing uranium from aqueous solutions containing small concentrations of uranium and relatively large amounts of other material is receiving considerable attention in the Raw Materials program, and solvent extraction may provide a suitable means of recovering uranium from several of these solutions Emphasis during the last quarter has been placed upon the use of extraction results obtained in pure solutions to determine the general applicability of a solvent extraction process to liquors having (a) moderate uranium concentrations such as those obtained from plant operations in the western U S A or (b) low uranium concentrations such as leach solutions of the Florida Leached Zone material

Experiments of the cascade batch type have been devised to demonstrate the behavior of certain promising reagents in these liquors and to study the problems associated with any solvent extraction process A summary of the data for such extractions with di(2-ethylhexyl)phosphinic acid and di(2-ethylhexyl)phosphoric acid made on a sulfuric acid leach of a Marysvale ore, a hydrochloric acid leach of a carnotite ore from the Rifle plant and a nitric acid leach of Florida Leached Zone material appears on Tables 31, 32, 33, 34, 35 and 36 A description of the procedure for each test is included in these tables

Of the reagents tested these two gave good physical performance (quick separation, no emulsions) in all liquors used and are the only ones which gave no difficulty in the Marysvale liquor Mono(2-ethylhexyl)phosphoric acid (94%)

Table 31

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Marysvale Liquor

REAGENT TESTED Di(2-ethylhexyl)phosphinic acid - 5 8% (0 199M) solution in kerosene (weight-volume)

LEACH LIQUOR EXTRACTED Marysvale Process Liquor, (M-3L)

U= 2 80 g/l	Ca= 0 73 g/l	
Fe=12 6 "	PO_4= 2 54 "	pH=1 3
Al= 5 5 "	SO_4=64 8 "	

DESCRIPTION OF TEST

Extraction
- Number of cycles 5
- Number of stages/cycle 3
- Agitation (separatory funnel) 3 min
- Mole ratio/stage 10 moles complexing agent/mole uranium
- Phase ratio/stage 100 ml liquor/50 ml organic phase

Stripping
- Number of cycles 5 (one following 3rd stage of each extraction cycle)
- Number of cycles before using fresh stripping solution 1
- Number of stages/cycle 2
- Reagent 6% HF
- Phase ratio/stage 50 ml organic phase/25 ml stripping solution

Physical behavior Rapid separation, no emulsions

Raffinate analyses (In parts uranium/million parts aqueous)

Cascade Stage	Cycle 1	2	3	4	5
1	9	15	22	18	22
2	70	80	110	130	80
3	350	420	440	460	510

Table 31 (cont'd)

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Marysvale Liquor

RESULTS

Cumulative percent uranium extraction

Stage	Cycle 1	Cycle 5
1	99 7	99 3
2	98 7	98 2
3	94 8	92 8

Stripping analyses

Concentration of uranium in 1st stripping solution		25 g/l
Total uranium extracted	3 94g,	93 8%
Total iron extracted	0 16g,	0 9%
Total aluminum extracted	0 05g,	0 6%

Concentration across system in first strip without recycle 9

Table 32

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Marysvale Liquor

REAGENT TESTED Di(2-ethylhexyl)phosphinic acid - 6 0% (0 208M) solution in kerosene (weight-volume)

LEACH LIQUOR EXTRACTED Marysvale Process Liquor (M-3L)

U= 2 80 g/l	Ca= 0 73 g/l	
Fe=12 6 "	PO_4= 2 54 "	pH=1 3
Al= 5 5 "	SO_4=64 8 "	

DESCRIPTION OF TEST

Extraction
- Number of cycles 12
- Number of stages/cycle 4
- Agitation (separatory funnel) 2 min
- Mole ratio/stage 10 moles organic complexing agent/mole uranium
- Phase ratio/stage 100 ml liquor/50 ml organic phase

Stripping
- Number of cycles 12 (one following 4th stage of each extraction cycle)
- Number of cycles before using fresh stripping solution 1
- Number of stages/cycle 3
- Reagent 12N H_2SO_4
- Phase ratio/stage 50 ml organic phase/25 ml stripping solution

Physical behavior Rapid separation, no emulsion

Raffinate analyses (In parts uranium/million parts aqueous)

Cascade Stage	Cycle 1	3	5	7	9	11	12
1	13	60	50	50	190	230	193
2	80	140	156	250	240	260	540
3	700	750	730	860	1110	1110	1170
4	1500	1820	1870	1460	1620	1500	1780

Table 32 (cont'd)

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Marysvale Liquor

RESULTS

Cumulative percent uranium extraction

Stage	Cycle 1	Cycle 12
1	99 5	93 2
2	98 3	86 9
3	90 5	77 3
4	79 5	67 1

Stripping analyses
Concentration of uranium in stripping solution 23 g/l
Total uranium extracted 7 8 g

Concentration across system in first strip without recycle 8 2

Uranium recovery/pound of reagent (according to the measured loss of reagent to the extent of 70 parts reagent/million parts aqueous contacted) 23 lbs

Table 33

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphoric Acid - Marysvale Liquor

REAGENT TESTED Di(2-ethylhexyl)phosphoric acid - 6 4% (0 200M) solution in kerosene (weight-volume)

LEACH LIQUOR EXTRACTED Marysvale Process Liquor (M-3L)

U= 2 8 g/l	Ca= 0 73 g/l	
Fe=12 6 "	PO_4= 2 54 "	pH=1 3
Al= 5 5 "	SO_4=64 8 "	

DESCRIPTION OF TEST

Extraction
- Number of cycles 5
- Number of stages/cycle 3
- Agitation (separatory funnel) 3 min
- Mole ratio/stage 10 moles organic complexing agent/mole uranium
- Phase ratio/stage 100 ml liquor/50 ml organic phase

Stripping
- Number of cycles 5 (one following 3rd stage of each extraction cycle)
- Number of cycles before using fresh stripping solution 1
- Number of stages/cycle 2
- Reagent 12N H_2SO_4
- Phase ratio/stage 50 ml organic phase/25 ml stripping solution

Physical behavior Rapid separation, no emulsions

Raffinate analyses (In parts uranium/million parts aqueous)

Cascade Stage	Cycle 1	2	3	4	5
1	580	830	1090	890	1000
2	2140	2150	2510	2720	2220
3	2700	2720	2720	2920	2830

Table 33 (cont'd)

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphoric Acid - Marysvale Liquor

RESULTS

Cumulative percent extraction

Stage	Cycle 1	Cycle 5
1	79 2	64 2
2	51 4	42 5
3	35 4	27 9

Stripping analyses

Concentration of uranium in stripping solution		8 g/l
Total uranium extracted	0 900g,	21 4%
Total iron extracted	0 736g,	3 9%
Total aluminum extracted	0 066g,	0 8%

Concentration across system in first strip without recycle 2 9

Table 34

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Rifle Liquor

REAGENT TESTED Di(2-ethylhexyl)phosphinic acid - 6 8% (0 234M) solution in kerosene (weight-volume)

LEACH LIQUOR EXTRACTED Rifle Process Liquor

U=2 80 g/l	Ca=2 0 g/l	
V=2 27 "	PO_4=0 8 "	pH=1 2
Fe=0 97 "	SO_4=8 8 "	
Al=1 65 "		

DESCRIPTION OF TEST

Extraction
- Number of cycles 5
- Number of stages/cycle 3
- Agitation (separatory funnel) per stage 3 min
- Mole ratio/stage 10 moles organic complexing agent/mole of uranium
- Phase ratio/stage 100 ml liquor/50 ml organic phase

Stripping
- Number of cycles 5 (one following 3rd stage of each extraction cycle)
- Number of cycles before using fresh stripping solution 1
- Number of stages/cycle 2
- Reagent 6% HF
- Phase ratio/stage 50 ml organic phase/25 ml stripping solution

Physical behavior Rapid separation, no emulsions

Raffinate analyses (In parts uranium/million parts aqueous)

Cascade Stage	Cycle 1	2	3	4	5
1	5	5	9	10	6
2	19	15	17	20	22
3	68	96	70	85	73

Table 34 (cont'd)

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Rifle Liquor

RESULTS

Cumulative percent extraction

Stage	Cycle 1	Cycle 5
1	99 8	99 7
2	99 7	99 5
3	99 0	98 8

Stripping analyses

Concentration of uranium in first stripping solution		28 4 g/l
Total uranium extracted	4 16g,	99 1%
Total vanadium extracted	0 26g,	7 6%
Total iron extracted	0 07g,	4 8%
Total aluminum extracted	0 03g,	1 2%

Concentration across system in first strip without recycle 10 1

Table 35

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphoric Acid - Rifle Liquor

REAGENT TESTED Di(2-ethylhexyl)phosphoric acid - 7 6% (0 236M) solution in kerosene (weight-volume)

LEACH LIQUOR EXTRACTED Rifle Process Liquor

U=2 80 g/l	Ca=2 0 g/l	
V=2 27 "	PO_4=0 80 "	pH=1 2
Fe=0 97 "	SO_4=8 8 "	
Al=1 65 "		

DESCRIPTION OF TEST

Extraction
- Number of cycles 5
- Number of stages/cycle 3
- Agitation (separatory funnel) 3 min
- Mole ratio/stage 10 moles organic complexing agent/mole uranium
- Phase ratio/stage 100 ml liquor/50 ml organic phase

Stripping
- Number of cycles 5 (one following 3rd stage of each extraction cycle)
- Number of cycles before using fresh stripping solution 1
- Number of stages/cycle 2
- Reagent 12N H_2SO_4
- Phase ratio/stage 50 ml organic phase/25 ml stripping solution

Physical behavior Rapid separation, no emulsion

Raffinate analyses (In parts uranium/million parts aqueous)

Cascade Stage	Cycle 1	2	3	4	5
1	43	117	138	88	160
2	320	360	429	514	506
3	1310	870	1420	1420	1370

Table 35 (cont'd)

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphoric Acid - Rifle Liquor

RESULTS

Cumulative percent extraction

Stage	Cycle 1	Cycle 5
1	98 4	94 2
2	93 5	88 1
3	80 0	75 7

Stripping analyses

Concentration of uranium in 1st stripping solution 22 4 g/l

Total uranium extracted	3 3g, 78 5%
Total vanadium extracted	0 02g, 0 7%
Total iron extracted	0 62g*,43 0%
Total aluminum extracted	0 02g, 0 9%

Concentration across system in first strip without recycle 8

* Including a build-up of iron in the organic of 0 227 grams representing 16% of total iron

Table 36

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Leached Zone Nitrate Liquor

REAGENT TESTED Di(2-ethylhexyl)phosphinic acid - 0 16% (0 0055M) solution in kerosene (weight-volume)

LEACH LIQUOR EXTRACTED Leached Zone Process Liquor, LZ P-3

U= 0 07 g/l	NO_3^- 250 g/l	
Al=18 8 "	PO_4= 38 6 "	pH=1 1
Fe= 1 2 "	Ca= 9 57 "	

DESCRIPTION OF TEST

Extraction
- Number of cycles 5
- Number of stages/cycle 3
- Agitation (separatory funnel) per stage 3 min
- Mole ratio/stage 10 moles organic complexing agent/ mole uranium
- Phase ratio/stage 100 ml liquor/50 ml organic phase

Stripping
- Number of cycles 5 (one following 3rd stage of each extraction cycle)
- Number of cycles before using fresh stripping solution 5
- Number of stages/cycle 1
- Reagent 6% HF
- Phase ratio/stage 50 ml organic phase/25 ml stripping solution

Physical behavior Rapid separation, no emulsions
Slight precipitation of 1st stage of 2, 3, 4 and 5th cycles Precipitate analyzes to be mixture of Al, Ca and Na fluorides

Raffinate analyses (in parts uranium/million parts aqueous)

Cascade Stage	Cycle 1	2	3	4	5
1	10	16	15	19	16
2	21	25	29	22	36
3	40	46	46	55	49

Table 36 (cont'd)

PROCESS LIQUOR EXTRACTION

Di(2-ethylhexyl)phosphinic Acid - Leached Zone Nitrate Liquor

RESULTS

Cumulative percent extraction

Stage	Cycle 1	Cycle 5
1	85 7	77 2
2	77 8	62 8
3	66 3	51 9

Stripping analyses

Concentration of uranium in stripping solution 2 25 g/l
Total uranium extracted 0 057g, 54 3%
Total iron extracted 005g, 0 3%
Total aluminum extracted 028g, 0 1%

Concentration across system in strip 32

and a commercial product of the same name (52%) caused some trouble in the Marysvale liquor where a slight emulsion was formed Other reagents all forming unmanageable emulsions with Rifle and Marysvale liquors are dibutylphosphoric acid, octylphosphonic acid, dicyclohexylphosphinic acid, di(3,5,5-trimethylhexyl)phosphinic acid, tetrabutyl 1,2-ethylene-diphosphonic acid and a mixture of 2-octyl phosphoric and pyrophosphoric acids Most of these reagents behave well in the highly acid, high-phosphate Leached Zone liquors

The results obtained with the di(2-ethylhexyl)phosphoric and phosphinic acids are compared in the following discussion and are classified according to an outline of the problem involved in a solvent extraction process

Competition between Complexing Agent and Other Uranium Complexers ($SO_4^{=}$, $CO_3^{=}$, $PO_4^{\equiv}$)

Experiments conducted in pure solutions indicate that certain anions inhibit the extraction of uranium by organo-phosphorus acids In the order of increasing effect they are NO_3^-, F^-, $SO_4^{=}$ and $PO_4^{\equiv}$ Less extensive tests show that Cl^- resembles NO_3^- in its inhibitive effect This relationship is substantiated by results obtained with di(2-ethylhexyl)phosphinic acid, where extractions from the Rifle liquor, essentially a hydrochloric acid solution containing small amounts of $SO_4^{=}$ and $PO_4^{\equiv}$, are better than those obtained in the Marysvale sulfate liquor These, in turn, are better than extractions obtained in the Leached Zone nitrate liquor which has a high phosphate content The behavior of di(2-ethylhexyl)phosphoric acid in the Rifle and Marysvale liquors is about the same, but it is obvious from the raffinate analyses that the latter reagent cannot compete with other uranium complexing anions nearly as well as does the phosphinic acid The uranium analyses of less than 10 ppm obtained with di(2-ethylhexyl)phosphinic acid on the first aqueous raffinates would be acceptable in a commercial operation designed to process these liquors

Selectivity of the Organic Complexing Agent for Uranium in the Presence of Other Metal Ions (Iron and Aluminum)

In removing uranium from aqueous solution it is naturally undesirable to extract simultaneously any appreciable quantity of other metals such as iron and aluminum Aside from contamination of the resulting product with unwanted ions,

any reagent forming complexes with these extraneous ions is necessarily unavailable for the extraction of uranium This selectivity is especially important in liquors of the Leached Zone type where the quantity of iron and aluminum is far in excess of the uranium present Di(2-ethylhexyl)phosphinic exhibits remarkable selectivity in all liquors treated, extracting less than 1% of the iron and aluminum in the Marysvale and Leached Zone liquors and less than 5% in the Rifle Di(2-ethylhexyl)phosphoric acid shows very low extractions of aluminum, but high extractions of iron reaching 40% in the Rifle liquor Moreover, in the Rifle extractions with the latter reagent, the iron is not completely removed from the organic phase by stripping and the quantity of uranium remaining in the raffinate gradually increases due to the adverse effect upon the extraction coefficient

Rate of Uranium Extraction

Precise measurements of the rate of uranium extraction are not available, but measurements in pure solution indicate that extraction is rapid The agitation period of 2-3 minutes given in these tests is certainly more than ample

Physical Behavior of the Reagent During Extraction

It is difficult to describe adequately the physical behavior of these organic reagents when in contact with aqueous phases which vary widely in composition The degree of any resulting emulsification or precipitation depends upon the reagent concentration, the method and time of agitation, the purity of reagent, the hydrogen ion concentration, and the composition of the aqueous phase In many cases the formation of emulsions is unpredictable, and results obtained with a reagent in supposedly identical tests may be inconsistent These discussions of physical behavior, therefore, are qualitative only The term "slight" emulsions refers to those which separate in 5-15 minutes while "bad" emulsions are those stable for hours, sometimes so persistent that no clear sample of either phase may be taken

Both di(2-ethylhexyl)phosphinic acid and di(2-ethylhexyl)-phosphoric acid have behaved ideally during extractions After agitation there is an immediate separation of the phases with no emulsions and but a slight cloudiness of the layers Behavior of other reagents tested is poor Mono(2-ethylhexyl)-phosphoric acid forms slight emulsions in the Marysvale liquor while several additional phosphinic acids, and two phosphonic

acids cause bad emulsions The mixture of 2-octylphosphoric acids and pyrophosphoric acids, reported[6] to give excellent results in commercial phosphoric acid, separates fairly well in the acid Leached Zone liquors, but causes unmanageable emulsions with the Rifle and Marysvale liquors

The Stripping Cycle

The stripping reagents used in these cascade extractions have been 3N HF and 12N H_2SO_4 Preliminary results had shown these concentrations to be effective in removal of uranium from the organic phase and the results of a 2-3 stage cycle show that nearly complete stripping is obtained with both the di(2-ethylhexyl)phosphoric and phosphinic acids

Stripping solutions containing 20-30 grams of uranium per liter have been obtained in extractions of Rifle liquor with both reagents and of Marysvale liquor with the phosphinic acid The concentrations are somewhat lower (8g/l) when di(2-ethylhexyl)phosphoric acid is used to extract Marysvale liquor Recycle of the stripping reagent in extractions of the nitric acid leach of Leached Zone material results in a solution containing 2 25 g U/l

Use of acids of such high concentration was made to insure complete stripping so that the uranium extraction cycle could operate at its highest efficiency Economic operation of a continuous extraction process demands a higher uranium build-up and/or use of lower reagent concentrations Multistage contacts of uranium-bearing di(2-ethylhexyl)-phosphinic acid (2g U/l of 0 04M reagent) have resulted in loadings of greater than 60g U/l with 12N H_2SO_4 and 40g U/l with 8N H_2SO_4

The ease of stripping uranium from various organic complexes depends upon the stability of those complexes In agreement with previous data from tests in pure solutions results obtained with di(2-ethylhexyl)phosphoric acid, di(2-ethylhexyl)phosphinic acid and mono(2-ethylhexyl)-phosphoric acid show that the difficulty of stripping these reagents increases in that order

Loss of Reagent to Raffinate

Critical to the success of a solvent extraction process is the loss of reagent to the aqueous raffinate If the complexing agent can be recycled without lowering its extraction efficiency, it is this loss which ultimately

determines the maximum uranium recoverable with a given amount of reagent An estimate of this loss has been made for the test described in Table 32, in which di(2-ethylhexyl)-phosphinic acid was used to extract Marysvale liquor

The losses in such experiments might stem from four sources (1) solubility of reagent in aqueous raffinate, (2) solubility of reagent in aqueous stripper, (3) mechanical losses, and (4) loss to the aqueous phase because of formation of water soluble complexes

An estimate of the extent of the combined losses by solubility, (1) and (2), may be made by determination of the decrease in concentration of the organic reagent during extraction The mechanical losses (3) are indicated by a lowering in volume of the organic phase Determination of the extent of aqueous complexing is difficult by ordinary methods Scrubbing of both aqueous raffinates and aqueous stripping solutions with a pure organic solvent should recover a large portion of the reagent lost by mechanical means and dissolution This has been done for the test described in Table 32 and the results appear in Table 37 The indicated unrecoverable reagent amounts to 74 parts reagent per million parts of aqueous treated

This loss, although small, is a determining factor in the price which can be paid for the extracting reagent Extraction of a Leached Zone liquor where the uranium concentration is as low as 70 ppm with a reagent having losses as large will recover, at the maximum, only one pound of uranium for each pound of reagent consumed For this reason a program has been initiated to develop new and less expensive methods of synthesis of promising organic reagents The situation is not as critical when liquors having a higher uranium concentration are extracted for, in the case of Marysvale and Rifle liquors, extractions of 20-30 pounds of uranium per pound of reagent consumed are possible The data of Table 36 indicate that losses during extraction of the Leached Zone liquor cannot be as high as 70 ppm as such a loss would represent 105 mg of reagent when only 80 were originally present Moreover, extraction in the first stage of the fifth cycle is as high as that of the second stage first cycle, indicating that the loss of reagent over four cycles is equivalent to the amount effectively removed from solution during complexing in the first stage of the first cycle Using this assumption, the amount of unrecoverable reagent is nearer 30 ppm, and would represent an extraction of at least 5 pounds of uranium per pound of reagent consumed

Table 37

ESTIMATED REAGENT LOSSES DURING EXTRACTION OF MARYSVALE LIQUOR WITH DI(2-ETHYLHEXYL)PHOSPHINIC ACID

(1) Solubility in aqueous raffinate, and

(2) Solubility in aqueous stripping solutions

Original concentration of organic phase = 60 2 mg/ml
Final concentration of organic phase = 53 8 mg/ml

Solubility Loss = 6 4 mg/ml

Since the original volume was 50 ml this represents a total loss due to solubility of 320 mg

(3) Mechanical losses

Original volume = 50 ml
Final volume = 43 ml

Mechanical loss = 7 ml

This represents a total mechanical loss of 377 mg

Recovery by scrubbing = 342 mg

Unrecoverable loss = 355 mg

Since the total volume of aqueous liquor contacted was 4800 ml this amounts to a

Total estimated unrecoverable loss = 74 ppm

The reagent losses with mono- and di(2-ethylhexyl) phosphoric acid have not yet been measured

The Recycle of Reagent

Both di(2-ethylhexyl)phosphinic and phosphoric acids show nearly ideal performance (no emulsion, clean separation) in recycles amounting to as many as 50 separate contacts Except for the small reagent loss, di(2-ethylhexyl)phosphinic acid, after treatment with the stripping solution, is as efficient in uranium complexing as fresh reagent Unfortunately, the stripping of pregnant di(2-ethylhexyl)phosphoric acid does not completely remove the iron and this build-up causes decreased extractions during recycling through Rifle liquor No recycle data have been obtained for other uranium extracting reagents Many of these, as mentioned in the section describing physical behavior, cause serious emulsions in Rifle and Marysvale liquors, and in their present form are unsuitable for recycle It is possible that further purification of some of these reagents will make them useful

Concentration Across System

The preceding data show that when acid liquors having 1-3 g/l uranium are extracted with di(2-ethylhexyl)phosphinic acid it is possible to concentrate the uranium by a factor of 10 These figures were obtained without recycle of the stripping acid It is known that the loading of 8N or 12N H_2SO_4 is higher than 20-30 g/l, therefore, countercurrent stripping and use of an increased organic phase/aqueous phase ratio, should be able to increase the concentration across these systems by a much greater factor The concentrations obtained with di(2-ethylhexyl)phosphoric acid are lower than 10 because of its lower extraction of uranium To obtain an appreciable concentration factor in the nitrate Leached Zone experiments the stripping reagent was recycled 5 times with a resulting concentration across the system of 32 This figure, also, may be improved by better extraction of uranium and continued recycle of the stripping reagent

The ability of di(2-ethylhexyl)phosphinic and its stripping cycle to concentrate the uranium coupled with a high selectivity for uranium in the presence of other metal ions make this a very promising reagent

Product Purity

Sulfuric acid strip solutions from di(2-ethylhexyl)-phosphinic acid extractions of Marysvale liquor have been precipitated with sodium hydroxide and the purity of the precipitate has been determined A typical result is shown below

Element	%
Uranium	64
Iron	3
Aluminum	0 3

The remainder of the precipitate is mainly sodium and oxygen Since the calculated percentage of uranium in sodium diuranate is 75 the figure of 64 represents a nearly 85% pure product

Recovery of Thorium from Sulfuric Acid Solutions of Monazite Sand by Solvent Extraction

Recent tests have confirmed previous work in showing that thorium can be readily extracted from a sulfuric acid solution of monazite sand using certain organophosphorus compounds in common organic solvents Separation of thorium from the rare earth constituents of the sand is very good

A number of methods for removing the thorium from the organic phase have also been examined Acceptable extractions have been obtained in a number of cases but further tests must be made before the most desirable stripping cycle can be established

Experimental Solutions and Analyses

The solution of monazite sand as well as the other solutions used in the experimental studies were described last quarter (p45, ORNL-1308)[1] The analytical methods were also discussed

Extraction of Thorium and Separation from Rare Earths Using Mono(2-ethylhexyl)phosphoric Acid

Two additional experiments have been made to determine the purity of the extracted thorium In the first of these,

20 ml of the monazite solution[1] was contacted with 20 ml of 0 1M mono(2-ethylhexyl)phosphoric acid in petroleum ether After separation, the organic fraction was washed with 10 ml of 10% H_2SO_4 and the thorium was precipitated from the organic layer with 25 ml of 0 5 N NaOH Some titanium and uranium were found in the ignited precipitate but, according to spectrographic analyses, none of the rare earths were present within the limits of detection In the second experiment 20 ml of rare earth solution[1] was contacted with 25 ml of 0 1M mono(2-ethylhexyl)phosphoric acid and carried through the same procedure described above In this case uranium and a possible faint trace of La and Pr were noted Cerium and the other rare earths could not be detected Titanium was not found but probably was not present in the head solution

Uranium Extractions from Monazite Sand Solutions with Mono(2-ethylhexyl)phosphoric Acid

As shown by the data tabulated below, reasonable extractions of uranium can be obtained from the monazite solutions if the concentration of complexing agent in the organic phase is sufficiently great The extractions are not as complete however as might be predicted from tests on pure solutions

Solution*	% U Ext'd (Approximate)	Mono(2-ethylhexyl)-phosphoric Acid Conc (M)
Monazite Solution (U=110 ppm)	20 to 32	0 1
10% H_2SO_4 (U=102 ppm)	99	0 1
10% H_2SO_4 containing H_3PO_4 in amount equivalent to Monazite solution (U=89 ppm)	97	0 1
Monazite Solution (U=110 ppm)	>75**	0 15
Monazite Solution (U=110 ppm)	>75**	0 2

* All tests were made using equal volumes of organic and aqueous

**Analytical balances on these tests were not good

Extraction of Thorium with Other Reagents

Three new reagents were tested during the quarter di(2-ethylhexyl)phosphoric acid, a mixture of 2-octylphosphoric acids and pyrophosphates, and a mixture of di(2-ethylhexyl)-phosphoric acids and pyrophosphoric acids The last two of these, as shown below are quite effective in extracting thorium from solutions of thorium sulfate (3 9 grams Th/l) in 10% sulfuric acid Equal volumes of organic and aqueous were used in all of the tests

Extractant	Concentration	Th Ext'd %
Di(2-ethylhexyl)phosphoric acid in CCl_4	0 1 M	<5
2-Octylphosphoric Acid, pyrophosphoric acid* mixture in kerosene	0 1 M (in phosphorus)	>99
Di(2-ethylhexyl)phosphoric acid**, pyrophosphoric acid mixture in kerosene	0 1 M (in phosphorus)	>99

* Prepared according to the procedure described by Dow in DOW-76[7]

**Obtained from Victor Chemical Co

Kerosene solutions of the 2-octylphosphate mixtures have also given good extractions of thorium from monazite solutions According to Table 38, however, the purification from rare earths is not as acceptable as obtained with the mono(2-ethylhexyl)phosphoric acid This may be partly due to incomplete separation of aqueous from organic Further tests will be made of this possibility

Stripping of Thorium from the Organic Phase of Mono(2-ethylhexyl)phosphoric Acid in Petroleum Ether

As described last quarter, thorium may be removed from the organic phase by treating with NaOH in sufficient quantity for conversion of thorium to the hydroxide and conversion of the organic acid to the sodium salt About 80% of the organophosphate has been recovered by acidifying the caustic solutions and extracting the petroleum ether Recently

Table 38

EXTRACTION OF THORIUM FROM SULFURIC ACID SOLUTIONS

OF MONAZITE SAND

Solution Ext'd	Th Ext'd %	R E Content of Organic ppm (Spectrographic)					Remarks
		Ce	La	Nd	Pr	Sm	
Monazite	>97	800	200	500	ND	ND	Slight turbility in organic
Rare Earth	>97	700	Trace	500	ND	ND	

Note 1 Analyses of solutions see ORNL-1308, p46

2 20 ml of aqueous and 20 ml of organic were used for all tests

3 The organic phase is composed of mixtures of 2-octylphosphoric acids and pyrophosphates dissolved in kerosene (0 1M in phosphorus)

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

other methods for removing thorium from the organic extract have been studied and the results from these experiments are presented in Table 39

Partial precipitation of the thorium was obtained with HF and also with sodium citrate, tartrate, and acetate In the latter cases the solutions are alkaline It is possible, therefore, that the thorium was precipitated as a hydroxide and that the organic reagent was extracted into the aqueous solution as a soluble sodium salt

Extractions of thorium were obtained by treating the organic phase with solutions of either ammonium oxalate, strong phosphoric acid, or strong sulfuric acid Unfortunately, in the case of sulfuric acid, the organic complexing agent was also extracted into the aqueous The same was not true of phosphoric acid, however, and further tests with this reagent showed that an appreciable concentration of thorium could be obtained in the aqueous strip solution (see Table 40)

Table 40

H_3PO_4 AS A STRIPPING AGENT

Cycle No	Th in Raffinate g/l	Ext'n /Cycle %	Th in H_3PO_4 g/l
1	0 020	99 5	8
2	0 025	99 4	16
3	0 020	99 5	24
4	0 085	97 9	32
5	0 125	97 0	40

Note 10 ml of 85% H_3PO_4 used to contact 20 ml of 0 1M mono(2-ethylhexyl)phosphoric acid in petroleum ether containing 4 11 g Th/l

Future Work

As time permits further studies will be made of the following

(1) Extractions of thorium with other reagents such as phosphinic acids (p28, ORNL-1220)[5] which might be easier to handle in the stripping cycle

(2) Precipitation of thorium fluoride in as pure a state as possible by contacting the organic phase with acid fluoride solutions

Table 39

THORIUM STRIPPING FROM SOLUTIONS OF

MONO(2-ETHYLHEXYL)PHOSPHORIC ACID IN PETROLEUM ETHER

Stripping Reagent	% Th Ext'd
5% H_2O_2	<1
5% Oxalic Acid	<1
Sat'd $(NH_4)_2\overline{Ox}$	50-80
Sat'd $Na_2\overline{Ox}$	35
30% Citric Acid	<1
30% Sodium Citrate	73 (precipitate)
30% Tartaric Acid	<1
30% Sodium-potassium Tartrate	73 (precipitate)
30% Sodium Acetate	68 (precipitate)
30% Ammonium Acetate	<1
20% HNO_3	<1
20% $NaNO_3$	<1
20% HCl	<1
20% NaCl	<1
6% HF	64 (precipitate)
30% H_2SO_4	<1
70% H_2SO_4	<5
85% H_2SO_4	>75
95% H_2SO_4	~100
49% H_3PO_4	6
60% H_3PO_4	65
85% H_3PO_4	~100
10% HIO_3 in 10% H_2SO_4	>90 (precipitate)

Note 10 ml of 0 1M mono(2-ethylhexyl)phosphoric acid in petroleum ether containing 3 2 mg Th/ml extracted with 10 ml of the solutions listed

(3) Stripping of thorium with the reagents mentioned above and with new reagents or techniques, e g , ion exchange

Anionic Solvent Extraction

The use of methyl dioctylamine (MDOA) and di(2-ethylhexyl)-amine (D2EHA) in extracting uranium (VI) from sulfate and sulfate-phosphate liquors was mentioned previously Further studies have been made since that time and a recent shipment of other primary, secondary and tertiary amines as well as quaternary ammonium salts has received attention

Many of the compounds studied have given acceptable uranium extractions, and stripping of the uranium from the organic phase has been readily obtained with small volumes of dilute HNO_3, NaCl-HCl, or Na_2CO_3 These properties along with a possible low reagent price, suggest a potential application of these reagents to certain raw materials as well as other separation problems The compounds studied thus far however (with the possible exception of Di-"coco"-dimethylammonium chloride) have had one obvious drawback, i e , the solubility of the reagent in aqueous sulfate solutions Recovery of this reagent by a separate scrubbing stage might be possible but the elimination of such a problem would be highly desirable At the present time a large number of amines are being examined in the search for a compound that will combine high uranium extraction with low reagent solubility There is every reason to believe that such reagents can be prepared if they are not already available commercially

Comparison of Uranium Extractions Using Various Amines

The uranium extraction properties of several amines have been examined by contacting a 0 1M solution of the amine in chloroform with a uranyl sulfate solution similar to one which might be obtained from a sulfuric acid leaching process, U=1 g/l, SO_4=1M and pH=0 98 The results of these tests are to be found in Table 41 Although only a small number of amines have been studied, the results so far indicate that the aliphatics are superior to the aromatics for extracting uranium from a sulfate solution Further tests are being conducted using those amines which show reasonable extraction and other new reagents are being screened

A quaternary ammonium salt has also given extractions which are high enough to encourage further examination of this and other quaternary salts

Table 41

COMPARISON OF URANIUM EXTRACTION USING VARIOUS AMINES

Type Amine	Compound	% U Ext'd
Secondary	s-Diphenylethylenediamine	Emulsion
	Decahydroquinoline	12
	Dicyclohexylamine	38
	Di-n-heptylamine	99
	Di(2-ethylhexyl)amine	95
	Di(2-ethylhexyl)amine salt of di(2-ethylhexyl)phosphinic acid	97
Tertiary	Octadecyldimethylamine	Emulsion
	Di-n-butylaniline	0
	Tribenzylamine	0
	4-n-amylpyridine	0
	Dimethylbenzylamine	0
	Trihexylamine	75
	Methyldioctylamine	97
Quaternary ammonium	Di-"coco"-dimethylammonium chloride	49

Note
Reagent concentration 0 01M in chloroform
Uranium concentration 0 004M in 1M H_2SO_4, pH=0 98

Stripping Uranium from the Organic Phase

Qualitative tests have shown that uranium may be stripped from the organic phase with dilute nitric acid, carbonate (Na_2CO_3 or $(NH_4)_2CO_3$) or chloride solutions (0 1N HCl in 0 9N NaCl) In several single stage experiments where uranium sulfate solutions have been extracted with MDOA in benzene and the organic stripped with chloride solution, it has been possible to concentrate the uranium by a factor of 20 (i e , 0 2 g/l to 4 g/l) In a counter-current system a much greater increase in concentration should be achieved

Effect of Solvent

Almost all of the preliminary tests have been made using chloroform as the solvent Since this reagent is not particularly attractive from an economic point of view, a number of other solvents have also been tried The results from these experiments listed in Table 42 and Figure 22, show several solvents to be acceptable It is also demonstrated (1) that the nature of the solvent can have an important effect on the extraction process, especially in instances where the amine concentration is low, and (2) that the effect is not necessarily of the same magnitude or in the same direction with different amines In process development work it will be necessary, therefore, to evaluate rather closely the properties of various solvents from the standpoint of reagent cost, uranium extraction, reagent solubility, density, volatility, loss of amine to aqueous, etc

Reagent Recycle and Solubility

Recycle tests have been made with both MDOA and D2EHA In these experiments extractions were made of uranium sulfate solutions and 0 1N HCl, 0 9N NaCl solutions were used as the stripping medium, the extraction and stripping cycle was repeated several times The results which may be found in Figure 23, show that the extraction decreases as the amine is recycled, and that this decrease is greater in cases where the organic extractant had been washed with H_2SO_4 prior to extractions It may also be noted that the extractions with MDOA did not fall off as rapidly as with D2EHA

Apparently the solubility losses with the particular amines tested are important ones and further experiments were made to study the magnitude of the solubility in

Table 42

EFFECT OF SOLVENT ON EXTRACTION OF URANIUM

WITH VARIOUS AMINES

Amine	Solvent	% U Ext'd
0 1 gm MDOA/100 mls	Kerosene	1
	Toluene	75
	Xylene	41
	Benzene	71
	Petroleum ether (BP 30-60°C)	0
	Petroleum ether (BP 90-120°C)	0
	Chloroform	31
1 gm MDOA/100 mls	Benzene	99
	Toluene	99
	Xylene	98
	Ethylbenzene	99
	Nitrobenzene	100
	Petroleum ether (BP 90-120°C)	3 phases formed
	Diethyl ether	97
	Methyl n-hexyl ketone	98
	Methyl Isobutyl ketone	98
0 1 gm D2EHA/100 mls	Kerosene	0
	Toluene	0
	Xylene	<1
	Benzene	15
	Petroleum ether (BP 30-60°C)	0
	Petroleum ether (BP 90-120°C)	0
	Chloroform	34
1 gm D2EHA/100 mls	Benzene	100
	Toluene	100
	Xylene	100
	Ethylbenzene	99
	Nitrobenzene	99
	Petroleum ether (BP 90-120°C)	99
	Diethyl ether	99
	Methyl n-hexyl ketone	97
	Methyl Isobutyl ketone	96

Note Uranium solution = 225 ppm U, 0 048M SO_4 and pH=1 12

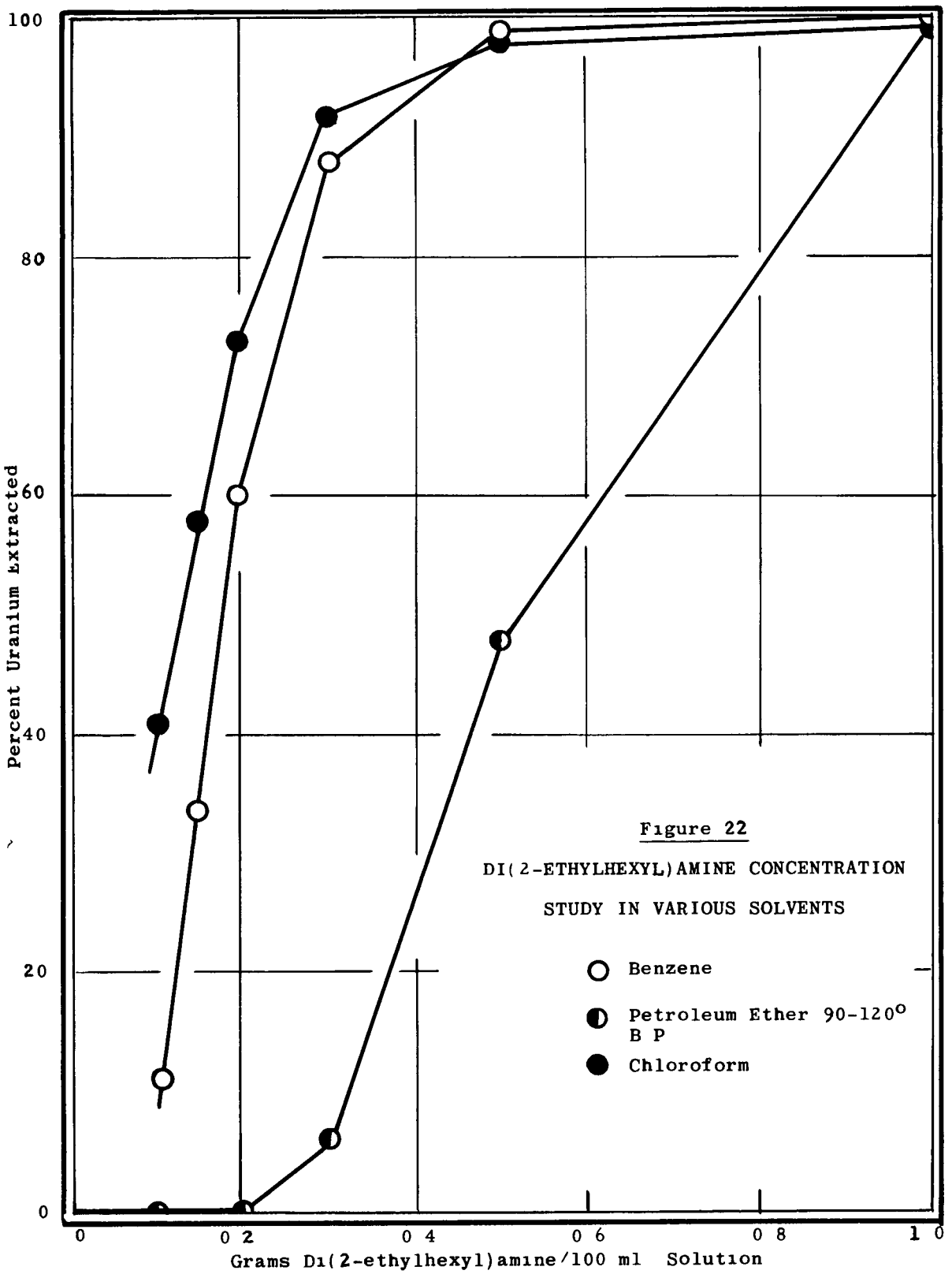


Figure 22

DI(2-ETHYLHEXYL)AMINE CONCENTRATION STUDY IN VARIOUS SOLVENTS

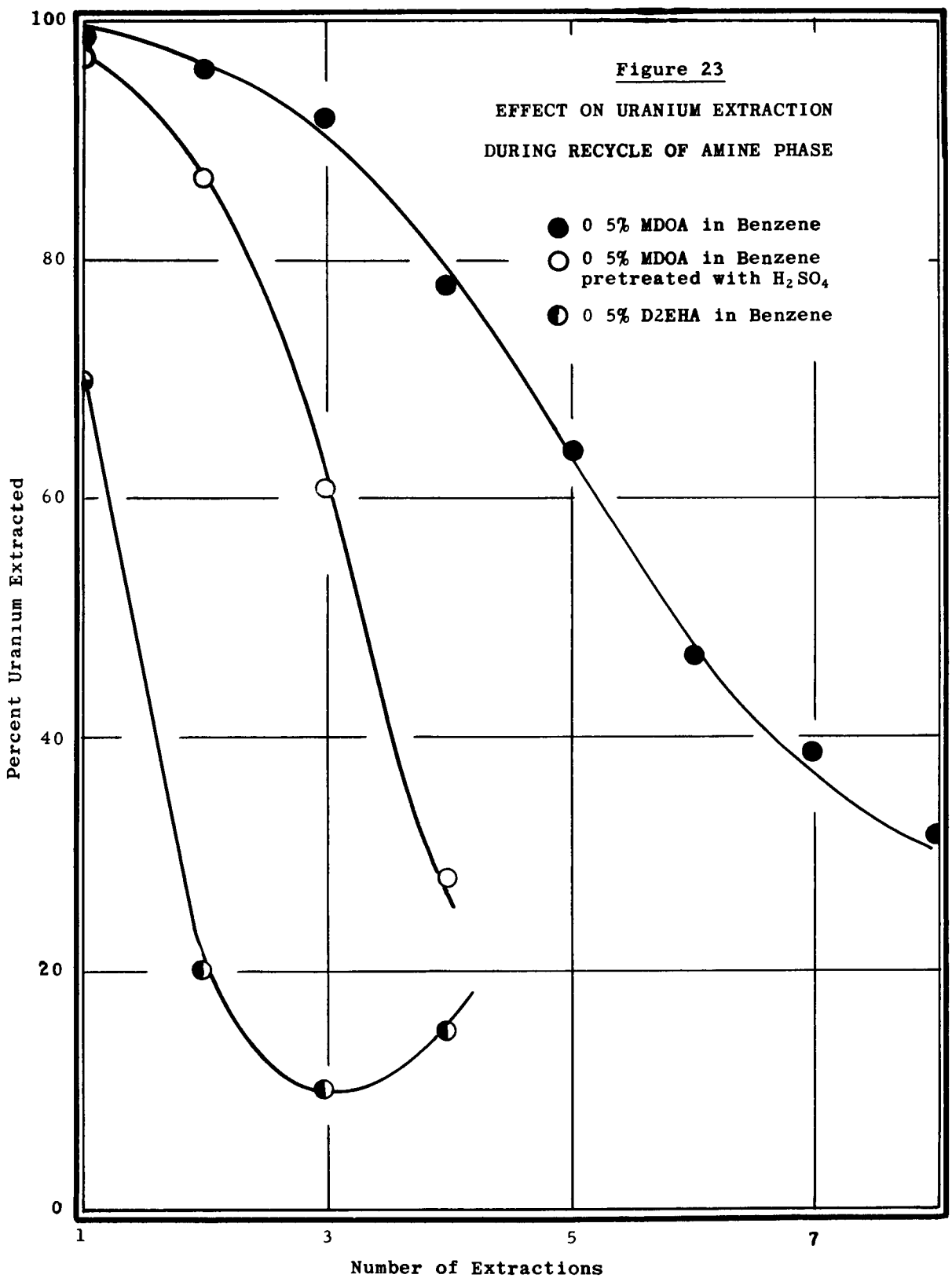


Figure 23
EFFECT ON URANIUM EXTRACTION
DURING RECYCLE OF AMINE PHASE
0 5% MDOA in Benzene
0 5% MDOA in Benzene pretreated with H_2SO_4
0 5% D2EHA in Benzene
Percent Uranium Extracted
100
80
60
40
20
0
1
3
5
7
Number of Extractions

several aqueous systems Estimates of the solubilities were obtained by contacting the systems to be studied with a 10% solution of D2EHA in benzene The aqueous solutions were contacted in turn with fresh benzene to remove any amine that may have dissolved into the aqueous phase If the fresh benzene contained amine it should now be able to extract uranium from sulfate liquors and, using this as a test, it was found that the solubility of D2EHA was (1) inappreciable in 1M HNO_3, 0 5M $NaHCO_3$, and 0 1N HCl + 0 9N NaCl, (2) slight in water and (3) appreciable in 1M H_2SO_4

Effect of Sulfate Concentration and pH

The extractions of uranium from sulfuric acid systems are dependent upon the sulfate concentration and the pH As depicted by the curves in Figures 24 and 25, a pH of 2 and a sulfate concentration of 1M are about optimum for extraction with D2EHA under the particular conditions tested A change in the sulfate concentration in either direction caused a decrease in extraction

Influence of Fe, Al, and NO_3

Tables 43, 44 and 45 show the influence of Fe^{+++}, Al^{+++}, and NO_3^- respectively on the extraction of uranium from a sulfate solution Of the three ions, only NO_3^- shows any influence by severely inhibiting the extraction of uranium This effect is to be expected in view of the results from stripping studies (above) and is qualitatively similar to the effect shown in anion resin separations

Extractions from Leached Zone Liquors

Cyclic contacts of dilute H_2SO_4 LZ leach liquors with MDOA in benzene have given good single-stage extractions through six cycles with perhaps a small drop off due to solubility loss The experiments shown in Table 46 were made with 25 mls of 1% MDOA in benzene contacted first with 25 mls of leach solution and then with 2 mls of stripping solution (0 1N HCl + 0 9N NaCl) Similar tests with D2EHA gave a much more rapid decrease in extraction due to the greater solubility of this reagent

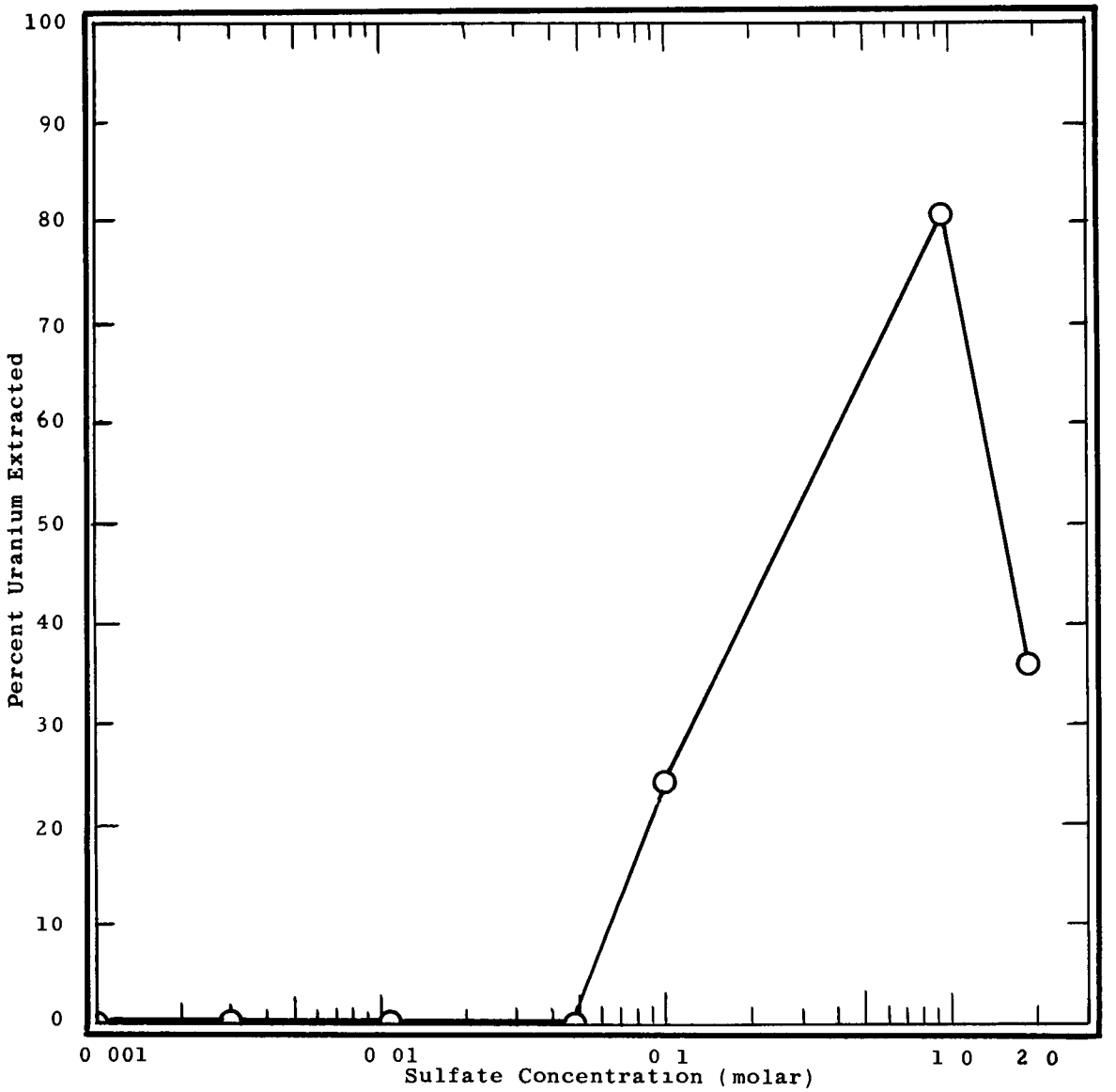


Figure 24

EFFECT OF SO_4 ON URANIUM EXTRACTION

WITH DI(2-ETHYLHEXYL)AMINE

[U] = 10^{-3}M D2EHA=0 2% wt/vol in Benzene
pH= 3 (range = 2 65 to 3 70)

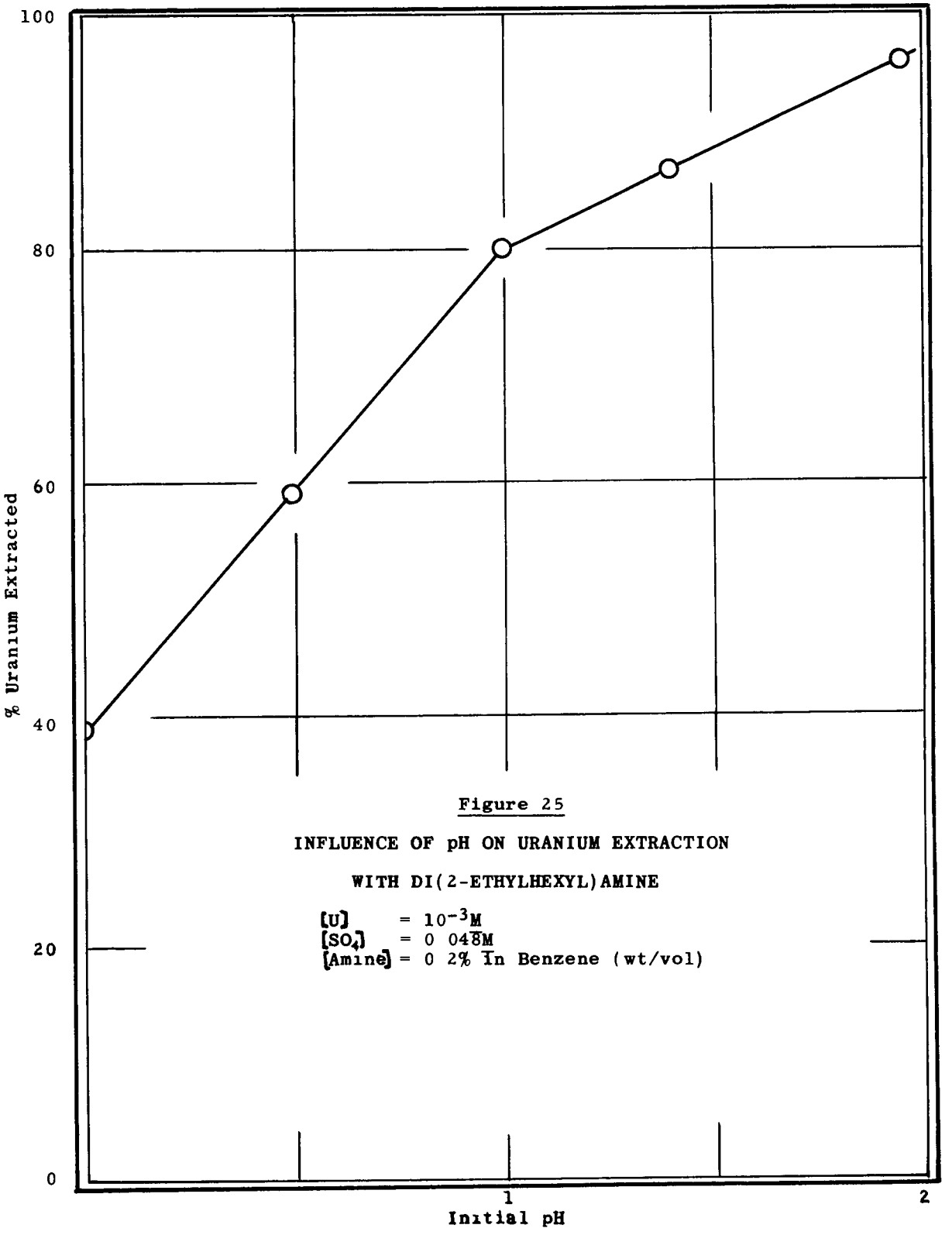


Figure 25

INFLUENCE OF pH ON URANIUM EXTRACTION

WITH DI(2-ETHYLHEXYL)AMINE

[U] = 10^{-3}M
[SO_4] = 0 048M
[Amine] = 0 2% In Benzene (wt/vol)

Table 43

EFFECT OF IRON ON URANIUM EXTRACTION

WITH AMINES

Fe Conc mg/ml	0	0 1	0 5	1	5
Initial pH aqueous	1 17	1 12	1 15	1 19	1 31
Final pH aqueous	1 24	1 21	1 21	1 32	1 36
% U Ext'd	96	96	93	97	93

Table 44

EFFECT OF ALUMINUM ON URANIUM EXTRACTION

WITH AMINES

Al Conc mg/ml	0	0 11	0 53	1 06	5 3
Initial pH aqueous	1 17	1 19	1 12	1 22	1 45
Final pH aqueous	1 24	1 29	1 32	1 37	1 45
% U Ext'd	96	93	95	92	91

Table 45

EFFECT OF NITRATE ON URANIUM EXTRACTION

WITH AMINES

NO_3 Conc mg/ml	0	3	15	30
Final pH aqueous	1 24	1 31	1 23	1 19
% U Ext'd	96	0	0	0

Table 46

EXTRACTION OF URANIUM FROM LZ LIQUORS WITH MDOA

Cycle	I	II	III	IV	V	*
% U Ext'd	86%	66%	62%	65%	62%	78%
Total mg U Ext'd	1 29	1 02	93	98	93	1 18

*Extraction made after treatment of the organic phase with 0 5M $(NH_4)_2CO_3$

After several cycles with the LZ leach liquor the MDOA benzene solution had become a dark brown Upon changing the strip solution from chloride to carbonate the brown color was removed and the uranium extraction in the next cycle was increased It is believed, therefore, that the color was due to humic acids which were extracted into the organic and reacted to same extent with the amine

Extraction of Titanium with Esters of Phosphoric Acid

The strong complexing action of some of the organo-phosphorus compounds with thorium suggests further applications for these reagents, e g , the extraction of other tetravalent metal ions such as titanium, zirconium and hafnium Preliminary experiments show that titanium may be extracted from acid solution by complexing with esters of phosphoric acid A solution of the following composition

Ti(as $TiCl_4$)	= 7 6	gm/l
H_2SO_4	= 196	gm/l
HCl	= 24	gm/l

was extracted with an equal volume of a 20% solution of Victor "mono octyl acid orthophosphate"* in kerosene, (weight-volume) The organic phase became red in color Subsequent extraction of the aqueous phase with two additional organic solutions produced an aqueous raffinate containing less than 10-20 ppm of titanium, the limit of analysis by the colorimetric method

No coloration of the organic phase was noted in the second and third extractions so it is assumed that the major portion of the titanium was extracted during the first contact

---

*Containing 50% mono(2-ethylhexyl)phosphoric acid

Preparation of Organic Compounds

In the screening of organic compounds there are numerous substances which require synthesis either to fill gaps in our knowledge of the correlation of structure with extraction behavior or to determine the utility of those compounds which can be prepared from cheap intermediates The list which follows indicates the compounds and types of compounds which are currently desired, though the list is considered tentative and flexible

Nomenclature

A recent report[8] issued jointly by the American Chemical Society and the Chemical Society of London has fixed upon what is hoped to be a final system of nomenclature for organophosphorus compounds The types of compounds falling in the scope of this report are to be named as follows

$R\text{-}PO(OH)_2$	alkylphosphonic acid (not alkanephosphoric)
$R_2\text{-}PO(OH)$	dialkylphosphinic acid
$POCl_3$	phosphoric trichloride
$R\text{-}P(OH)_2$	alkylphosphonous acid

Phosphoric Esters

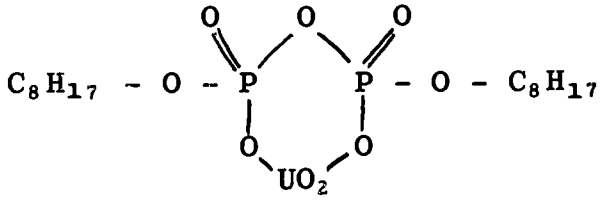
Although the monalkyl and dialkyl esters examined so far have had disadvantages, there is no reason to suppose that they all will have the same faults Derivatives should be made of various inexpensive alcohols such as octyl alcohol, capryl alcohol, 2-ethylbutanol, methylisobutylcarbinol 3 5 5-trimethylhexanol 3 5 5-trimethylcyclohexanol, diisobutylcarbinol, "butyl cellosolve", and "butyl carbitol"

Phosphonic Acids

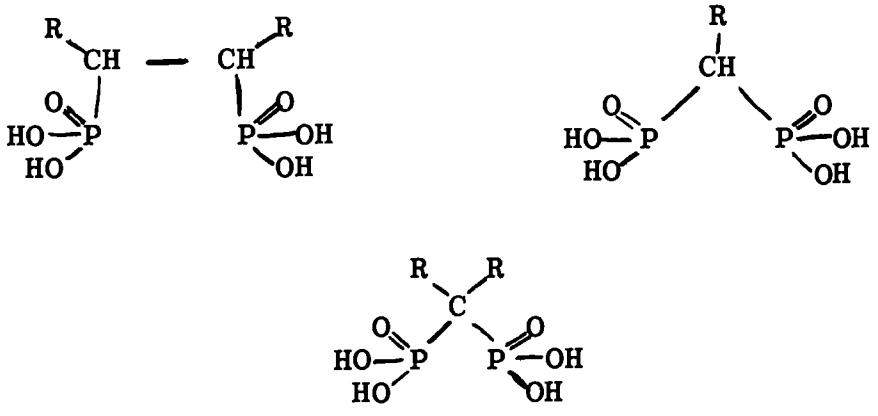
The phosphonic acids examined have had the drawbacks of poor selectivity and a tendency toward emulsification with most leach liquors Relatively few phosphonic acids have been prepared, however, and it is quite possible that some of them will be more desirable They do possess a relatively great extracting power for uranium Compounds should be prepared having such groups as cyclohexyl, methylcyclohexyl, butoxyethyl, butoxyethoxyethyl, phenylethyl, trimethylhexyl, 2,6-dimethyl-4-heptyl, 4-nonylphenoxyethyl,

dodecylphenyl, biphenyl, and diphenyl ether, the latter two as possible precipitants

The strong extracting power of dicapryl pyrophosphate can probably be attributed to the formation of a six-membered cyclic salt



Since the pyrophosphate linkage is quite labile, it would be desirable to replace it with a carbon linkage, and compounds of the following types are contemplated or in preparation

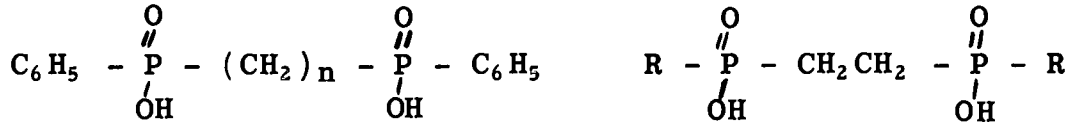


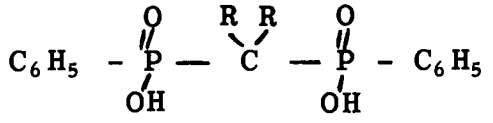
Phosphinic Acids

Di(2-ethylhexyl)phosphinic acid has shown considerable promise as an extractant and it certainly would be desirable to determine whether another phosphinic acid derivable from accessible starting materials might be superior Compounds which may be explored would have such groups as 3-heptyl, 2-octyl, butoxyethyl, butoxyethoxyethyl, 2,4-dimethyl-3-pentyl, 2,6-dimethyl-4-heptyl, alkylphenyl, methylcyclohexyl, naphthyl, xenyl, and dibenzophosphazinic acid, the last three being intended as precipitants

Bifunctional compounds capable of forming cyclic salts are desirable, since there is evidence that ring formation

increases the stability of the extractable entity Contemplated types are





Amines

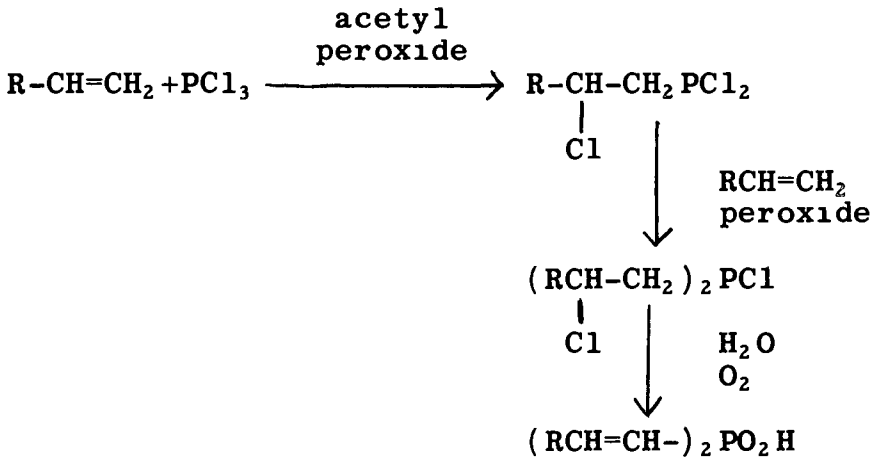
An attempt will be made to prepare amines and ammonium salts which will be good extractants and also be proof against loss by forming soluble salts with the acidic leach liquors Some of the amines which seem desirable at present are di(2,6-dimethyl-4-heptyl)amine, di(2-ethylhexyl)methylamine, didecylmethylamine, 1,6-bis(di-2-ethylhexylamino)-hexane, 1,x-bis(di-2-ethylhexylamino)alkanes, didecyldimethyl ammonium chloride, dimethyldi(2-ethylhexyl)ammonium chloride

Miscellaneous Phosphorus Compounds

When time permits, it is hoped that some of the following types of compounds will be prepared amidophosphonic acids, long-chain trialkylphosphines, phosphonium salts, phosphine oxides

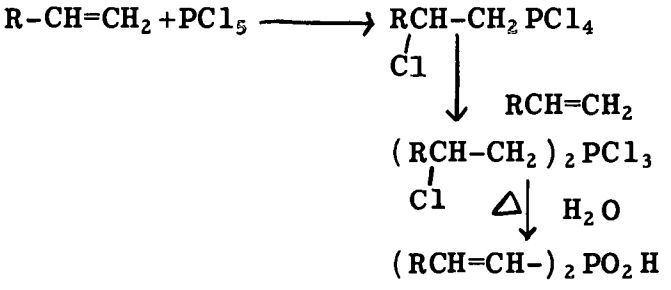
The phosphinic acids having proved so able as extractants, it has become necessary to consider the cost of their production The only suitable method now available for preparing the aliphatic derivatives is the Grignard method The yields are erratic and the method is not a desirable industrial process for large-scale synthesis For these reasons, research is now in progress on ideas for new methods of synthesizing phosphinic acids The ideas which are currently under consideration are

Method A Synthesis from Olefins and PCl_3 -



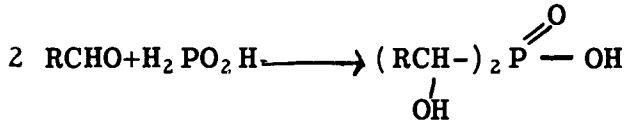
This sequence may not be useful One example of the first step is known[9], the yield of the dichlorophosphine being 16% If the dichlorophosphine could be prepared in greater yield it could be used for other reactions than those shown The olefin must have a terminal double bond

Method B Synthesis from Olefins and PCl_5 -



If necessary the double bonds would be reduced The first step of this reaction has been effected many times but the second step is unknown

Method C Synthesis from Aldehydes -



This reaction is known to give good yields but pure hypophosphorous acid is expensive, and also it may be necessary to remove the hydroxyl groups from the reagent as they would contribute to the water-solubility and the instability of the product

Method D Synthesis from Alkyl Halides and PCl_3 -

$$2\ RCl + PCl_3 + 4Na \xrightarrow[\Delta]{} R_2PCl + 4NaCl$$

$$R_2PCl \xrightarrow[O_2]{H_2O} R_2PO_2H$$

If this reaction (or a similar one with PCl_5) could be stopped at the stage shown it should be cheap However, a mixture of products would be expected

Method E Synthesis from Phenylphosphorus Dichloride -

$$C_6H_5PCl_2 + RCHO \longrightarrow C_6H_5\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}\text{-CHOH-R}$$

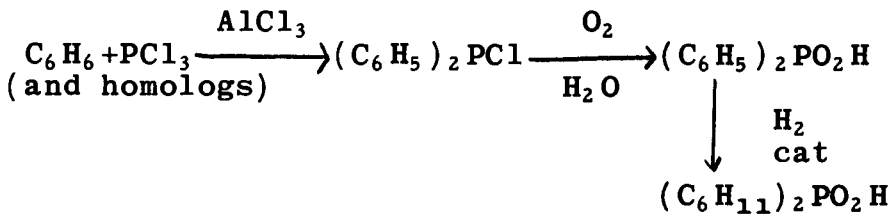
It may be necessary to remove the hydroxyl group in this compound

$$C_6H_5PCl_2 + RCl \xrightarrow{AlCl_3} C_6H_5\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}} - R$$

$$2C_6H_5PCl_2 + BrCH_2CH_2Br \xrightarrow{AlCl_3} C_6H_5\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}} - CH_2CH_2 - \overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}} - C_6H_5$$

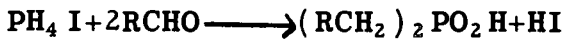
This is an adaptation of the method of Clay[10] for preparing phosphonic acids from PCl_3 and RCl Preliminary experiments indicate that this reaction has some potential value

Method F Synthesis from Aromatics by Friedel-Crafts Reaction and Reduction -



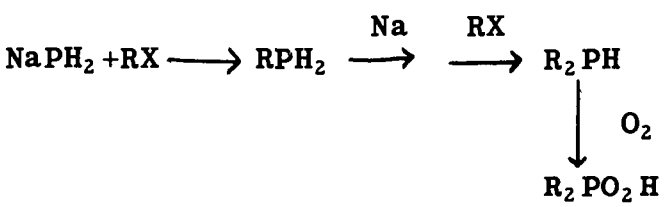
The preparation of aromatic phosphinic acids by this method is well known, but their reduction to cyclohexyl derivatives appears to be untried

Method G Synthesis from PH_4I -



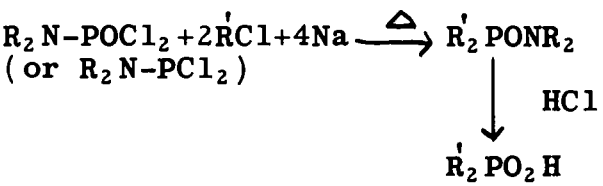
This reaction with benzaldehyde is the only example known and there are apparently several side reactions Phosphonium iodide may be difficult to obtain

Method H Synthesis from Phosphine -



Phosphines can be prepared in this way, but the utility of the reaction for large-scale synthesis is doubtful

Method I Variation of Method D -



Attempts to effect this reaction with sodium or magnesium have been unsuccessful

New Compounds

The preparation of new phosphinic acids has continued in the study of the effect of structure upon the extracting power and selectivity of the reagents The Grignard reaction has been used in all cases, usually as described in the preceding quarterly report[1], i e , treating the phosphoric trichloridepyridine complex with two moles of Grignard reagent In preparing the new compounds the reaction has been run only once (in most cases) and no attempt has been made to attain maximum yield The following compounds were prepared

1) Di(3,5,5-trimethylhexyl)phosphinic acid - a dark, viscous liquid, not pure enough for an acceptable analysis

Anal	Theoretical	67 8%C, 11 9%H, 9 75%P
	Found	62 2%C, 11 5%H, 11 8 %P

2) Di(3,3,5-trimethylcyclohexyl)phosphinic acid - a white, crystalline solid, m p 168-170°

Anal	Theoretical	68 8%C, 11 1%H, 9 9%P
	Found	68 9%C, 12 0%H, 10 0%P

3) Di(2-amyl)phosphinic acid - a dark, liquid, not pure enough for acceptable analysis

Anal	Theoretical	59 9%C, 10 9%H, 15 9%P
	Found	53 8%C, 10 8%H, 16 3%P

4) Phenyl-2-ethylhexylphosphinic acid - described under New Methods

5) Phenylbutylphosphinic acid - described under New Methods

Some new phosphonic acids have been prepared The triethyl phosphite method previously described is still the favored method, though the sodium salt of dibutyl phosphite

has been used a number of times with success Triphenyl phosphite was tried in place of triethyl phosphite, but without success The following new compounds were investigated

1) 3-Heptylphosphonic acid - prepared from dibutyl phosphite Titration of the product indicated only one acidic hydrogen atom as though one butyl group was not removed by the vigorous hydrolysis employed A new preparation using triethyl phosphite will be attempted

2) 2-Ethylhexylphosphonic acid - could not be obtained by the triphenyl phosphite method Using the triethyl phosphite procedure, 37% of the diethyl ester was obtained The ester was difficult to hydrolyze, conc hydrobromic acid being more efficient than conc hydrochloric acid The compound was a yellow liquid and was found by titration to be 92% pure

Old Compounds

It has been necessary to prepare larger quantities of several reagents for more extensive examination as extractants Dicyclohexylphosphinic acid was easily prepared (300 g) by the usual method Octylphosphonic acid was prepared from dibutyl phosphite, but several attempts were necessary before the product was obtained Di(2-ethylhexyl)-phosphinic acid has been prepared ten times The yields have varied greatly, ranging from 20% to 70% The reason for the variation is not known In several cases the method was modified to the extent that the phosphoric trichloride-pyridine complex was replaced by diethylamidophosphoric dichloride The latter was used in several large runs (4 moles and 10 moles) because it permits normal addition rather than inverse addition The 4-mole preparation resulted in 20% yield, whereas the 10-mole preparation resulted in 48% yield Some difficulty with emulsions had been encountered in using the di(2-ethylhexyl)phosphinic acid with leach liquors and it was found that purification of the acid by conversion to the acid chloride with thionyl chloride or phosphorus pentachloride, distillation of the acid chloride at 155-165°/1mm , and hydrolysis with boiling sodium hydroxide yielded a superior product with no tendency to induce emulsification The product was shown by titration to be 96% pure and was analyzed

Anal	Theoretical	66 3%C, 12 1%H, 10 4%P
	Found	66 2%C, 12 4%H, 9 8%P

Di(2-ethylhexyl)phosphinic acid was the first compound to reveal the interesting property of forming an ether-soluble sodium salt If the phosphinic acid is added to aqueous sodium hydroxide it forms an immiscible layer of the sodium salt, which can be extracted with ether Apparently, it is forced into the ether by the excess alkali present, because it can be re-extracted from the ether by pure water Lithium and ammonium salts behave similarly A quantitative study of this phenomenon is contemplated

New Methods

Some of the proposed new methods for preparing phosphinic acid have been tried The experiments will be described under the number of the method given in the Introduction

Method E The reaction between phenylphosphorus dichloride, aluminum chloride and 2-ethylhexyl chloride (ratio 1 1 3) yielded an acid chloride which was distilled up to 230°/1mm It was hydrolyzed with boiling sodium hydroxide and the yellow product was found to be 97% pure by titration Analysis of the phenyl-2-ethylhexylphosphinic acid was not corroborative

Anal	Theoretical	66 1%C, 9 1%H
	Found	64 9%C,10 1%H

The product was obtained in very small amount and could not be thoroughly examined Another reaction was carried out using one mole each of phenylphosphorus dichloride and aluminum chloride, and 2 moles of butyl chloride, ligroin being used as a solvent In order to ensure isolation of all the product complete hydrolysis was effected and there was obtained 89g (45%) of phenylbutylphosphinic acid which titrated for 99% purity It was later purified by conversion to the acid chloride with PCl_5 and distillation at 125-135°/1mm The acid chloride was hydrolyzed by refluxing with aqueous sodium hydroxide The product was a yellow, very viscous liquid

Method I Diethylamidophosphoric dichloride was prepared in ether from phosphoric trichloride and diethylamine The ethereal solution was mixed with four moles of sodium shot and one mole of 2-ethylhexyl bromide and kept at room temperature for three days It was then refluxed for one hour, but there was little evidence of reaction so the ether was replaced by toluene and the mixture refluxed for three hours There was a voluminous black precipitate The excess sodium was destroyed and ethanol and the mixture worked up in the usual way, but there was so little product that purification was not attempted

The reaction was repeated in refluxing benzene with disappointing results A variation using magnesium in dibutyl ether instead of sodium in benzene was also unsuccessful

Chemistry of Uranium Phosphate Solutions

J M Schreyer, C F Baes, Jr

The investigation of uranyl phosphate solutions described in the last report[1] has been continued

Analytical

A topical report "The Volumetric Determination of Uranium (VI) in Phosphate Solutions", ORNL-1292[11], has been issued

Further work seemed desirable to determine the stability of uranium (IV) phosphate solutions and to attempt to characterize the precipitate of uranium (IV) phosphate

Stability of Uranium (IV) Phosphate Solutions

A uranium (VI) phosphate solution (500 ml) which was approximately 0 04M UO_2^{++}, 3M H_3PO_4, and 3 6M H_2SO_4 was reduced in the Jones Reductor The final uranium (IV) solution was diluted to 1000 ml after the addition of enough H_2SO_4 to make the final solution 3M in H_2SO_4 This uranium (IV) phosphate solution was aerated for 843 hours in a covered beaker containing a capillary side arm for final adjustment of the volume The air was bubbled through a solution of the same acid concentration before passing into the uranium (IV) solution in order to minimize evaporation Aliquots were removed for analysis and treated directly with ferric chloride as outlined in the analytical procedure (ORNL-1292)[11] This made possible the determination of only the uranium (IV) in the solution The data are shown in Table 47 Considering the error inherent in the adjustment to volume each time a sample was removed these data indicate that if oxidation does occur in this solution it was within the experimental error

Table 47

STABILITY OF URANIUM (IV) PHOSPHATE SOLUTIONS

Aliquot No	Hours Aerated	Uranium (IV) Concentrations
1	0	0 02050
2	19 1/2	0 02044
3	44 1/2	0 02034
4	164 1/2	0 02044
5	214	0 02041
6	843	0 02029

Composition of Uranium (IV) Phosphate

A solution of uranium (VI) phosphate of equal molar ratio of uranyl and phosphate whose initial acidity was 5M in H_2SO_4 was reduced in the Jones Reductor The final uranium (IV) phosphate solution was diluted with water to 500 ml, allowed to stand for 24 hours, and filtered The precipitate was agitated in 1 liter of 1M $HClO_4$ in a closed container for 9 days The solution was then filtered, the precipitate washed with water and acetone The final gelatinous solid was dried in a vacuum desiccator and ground to a fine powder Chemical analysis of the sample gave a ratio of uranium/phosphate/water of 1/2 025/3 83 From these data, it may be concluded that the formula for this uranium (IV) phosphate precipitate is $U(HPO_4)_2\ 4H_2O$

A 100g sample of this compound was prepared in a similar manner which gave, when analyzed, a ratio of uranium/phosphate of 1/1 9

Polarographic Analysis

To facilitate the measurement of low uranium solubilities in dilute phosphoric acid solution, a procedure for polarographic analysis of the mother liquors has been developed

Orthophosphate is known to interfere with the polarographic determination of uranium[12,13], presumably because of the precipitation of uranium (IV) phosphate at the dropping mercury electrode However, it has been found in the present work that by the addition of oxalic acid to the supporting electrolyte, well formed waves are produced

($E_{1/2}$=ca 0 08v vs S C E), the heights of which are independent of the phosphate concentration, at least in phosphoric acid solutions up to 0 01M The maximum permissible phosphate concentration has not yet been determined

The polarograph which was used is an automatic recording instrument constructed by the Y-12 instrument shop according to the specifications of John Horton of ORNL The instrument sensitivity ranges from 0 05 to 20 microamps per full scale division

The procedure of analysis consisted in adding 20 ml of a stock solution, 0 6M in oxalic acid, 0 1M in sulfuric acid, and containing 015% gelatin, to 20 ml of the unknown solution in the dropping electrode cell Purified hydrogen was then bubbled through the solution for at least twenty minutes to remove dissolved oxygen A saturated calomel electrode was connected to the cell by means of an agar-sat'd KCl salt bridge, and a polarogram was recorded from +0 15 to -0 35 volts The diffusion current was measured from the polarogram as follows The current was read at -0 10v and +0 30v and from the difference was subtracted the residual current correction determined from a solution of the supporting electrolyte which contained no uranium

The diffusion current was found to be proportional to the uranyl concentration The method was applicable to uranyl concentrations as low as $5x10^{-5}$ molar, though normal accuracy (ca 5%) was limited to concentrations above about $5x10^{-5}$molar, where the residual current correction is not large compared to the diffusion current

Solubility Studies in Acid Solution

Solubility Measurements of Uranium (VI) in Phosphoric Acid

In the study of the solubility of UO_2HPO_4 $4H_2O$ in 0 001 to 6 03M phosphoric acid solutions at 25°C, it was found that a solid phase change occurred at low phosphate concentrations An extensive survey of the solid phases in equilibrium with the mother liquors was made over the entire range of phosphate molarities

Microscopic examination proved very useful in detecting the tetragonal crystals characteristic of UO_2HPO_4 $4H_2O$ and the needle-like crystals characteristic of $(UO_2)_3(PO_4)_2$ $4H_2O$ In all cases, the stable solid phases above 0 014M H_3PO_4 were observed to be tetragonal crystals while below were needle-like crystals Observation of the solid phase in equilibrium

with the 0 014M H_3PO_4 showed both crystals

A few identifications of solid phases were made by X-ray diffraction analysis which verified the existence of UO_2HPO_4 $4H_2O$ above and $(UO_2)_3(PO_4)_2$ $4H_2O$ below the transition point

Solubilities above 0 014M H_3PO_4 were determined by using UO_2HPO_4 $4H_2O$ as the added solid phase and those below by adding $(UO_2)_3(PO_4)_2$ $4H_2O$ The latter compound was prepared according to the procedure proposed by Ryon and Kuhn[14] and gave upon analysis a ratio of uranyl/phosphate/water of 3/2 026/4 10 The uranium concentrations below 0 017M H_3PO_4 were determined polarographically as described in the analytical section The solubility curves for this system are shown in Figure 26 It is pointed out that although experiments have been run to validate the solubility data for the UO_2HPO_4 $4H_2O$, similar experiments are not complete to determine whether the reported solubilities for $(UO_2)_3(PO_4)_2$ $4H_2O$ are at equilibrium

Spot checks of solubilities in the high phosphate range were made using $(UO_2)_3(PO_4)_2$ $4H_2O$ and at equilibrium the final solid phases were identified as UO_2HPO_4 $4H_2O$ Additional solubilities were determined in the low phosphate range using UO_2HPO_4 $4H_2O$ and a transformation to $(UO_2)_3(PO_4)_2$ $4H_2O$ was shown to occur

The assembled data are shown in Table 48

Acid Dependence of UO_2HPO_4 Solubility

An investigation of the acid dependence of the solubility of UO_2HPO_4 $4H_2O$ in perchlorate media has been carried out in the range 0 1M to 1M $HClO_4$ at an approximately uniform ionic strength of 1 15M, maintained by the addition of sodium perchlorate The solid phase resulting from the run at the lowest acidity was subjected to chemical analysis and found to be the unchanged UO_2HPO_4 $4H_2O$ Each sample was shaken in a 25°C water bath for a period of one to two days before the mother liquor was analyzed The results of the present measurements, as well as those of G R Leader[4], who performed similar measurements in nitric acid, are listed in Table 49 and plotted in Figure 27

The final acidities indicated in Table 49 and plotted in Figure 27, were calculated as follows

$$[H^+]_{final} = [H^+]_{initial} - 2(\Sigma UO_2)_{final},$$

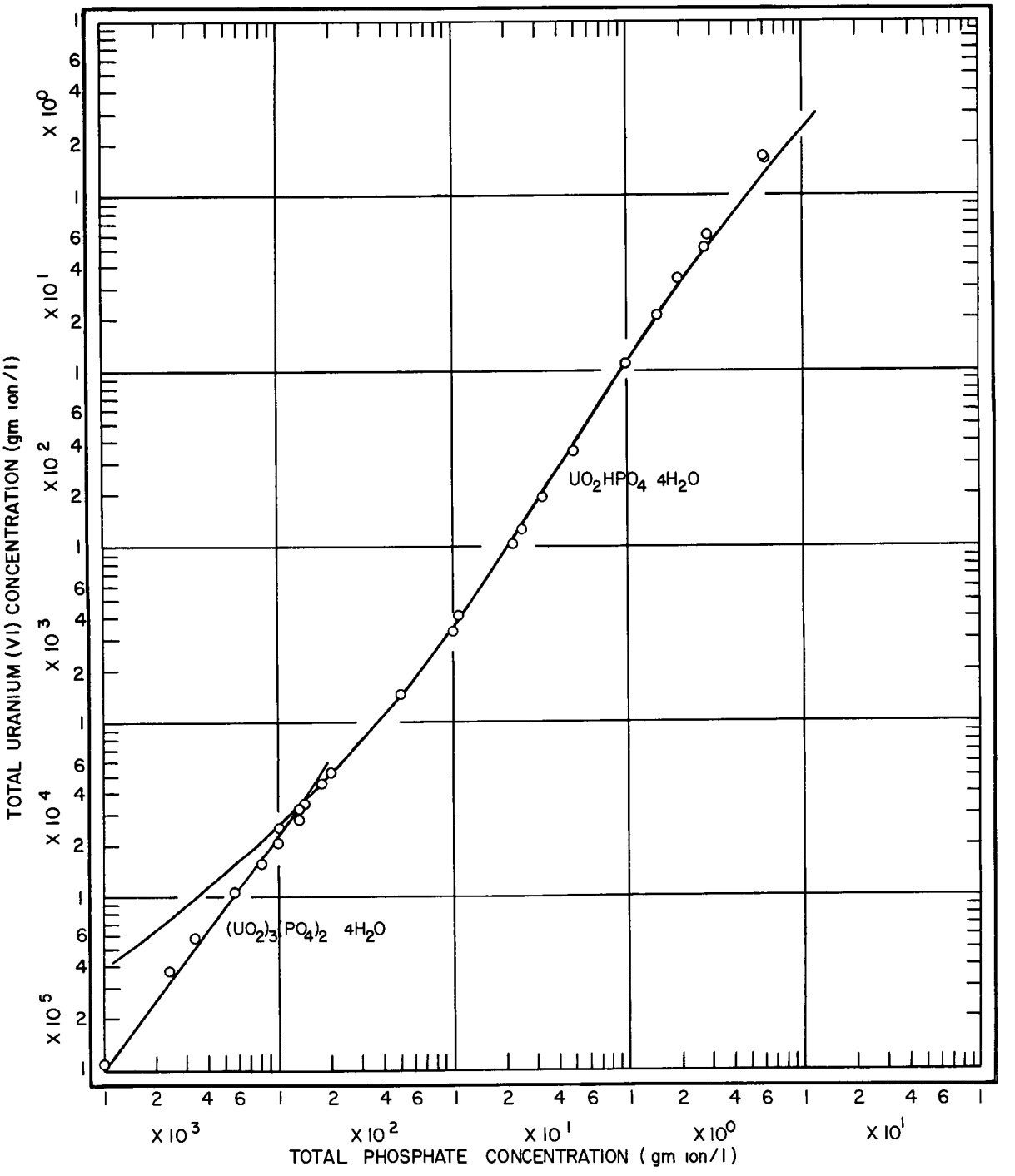


FIGURE 26

SOLUBILITY OF $UO_2HPO_4\ 4H_2O$ AND $(UO_2)_3(PO_4)_2\ 4H_2O$

IN PHOSPHORIC ACID SOLUTIONS

Table 48

SOLUBILITY OF UO_2HPO_4 $4H_2O$ AND $(UO_2)_3(PO_4)_2$ $4H_2O$ IN PHOSPHORIC ACID SOLUTIONS

Solid Added	Mother Liquor		Final Solid Identification	
	$[PO_4^{\equiv}]$	$[UO_2^{++}]$	Microscopic Appearance	X-ray Diffraction Analysis
$(UO_2)_3(PO_4)_2$ $4H_2O$	0 001	0 000011	Needles	---
UO_2HPO_4 $4H_2O$	0 00235	0 0000376	"	---
"	0 0033	0 000058	---	---
$(UO_2)_3(PO_4)_2$ $4H_2O$	0 0056	0 000108	Needles	$(UO_2)_3(PO_4)_2$ $4H_2O$ >90%
"	0 0081	0 000156	"	---
"	0 0101	0 000206	"	---
UO_2HPO_4 $4H_2O$	0 0105	0 000252	---	---
$(UO_2)_3(PO_4)_2$ $4H_2O$	0 0132	0 000282	Needles	---
UO_2HPO_4 $4H_2O$	0 0133	0 000324	Tetragonal	---
$(UO_2)_3(PO_4)_2$ $4H_2O$	0 014	0 000345	Mixture	---
"	0 0179	0 00045	Tetragonal	---
UO_2HPO_4 $4H_2O$	0 020	0 000528	"	---
"	0 050	0 00144	"	---
"	0 10	0 0033	"	UO_2HPO_4 $4H_2O$ >95%
"	0 108	0 00407	"	---
"	0 22	0 0103	"	---
"	0 249	0 0124	"	---
"	0 328	0 0186	"	---
"	0 494	0 036	"	---
"	0 987	0 11	"	---
"	1 48	0 207	"	---
"	1 97	0 339	"	---
$(UO_2)_3(PO_4)_2$ $4H_2O$	2 74	0 505	"	UO_2HPO_4 $4H_2O$ >90%
UO_2HPO_4 $4H_2O$	2 899	0 6008	"	---
"	6 035	1 69	"	---
$(UO_2)_3(PO_4)_2$ $4H_2O$	6 09	1 583	"	---

Table 49

ACID DEPENDENCE OF UO_2HPO_4 SOLUBILITY

$[H^+]_{initial}$ moles/l	$[UO_2^{++}]$ moles/l	$[H^+]_{final}$ moles/l	$[NaClO_4]$ moles/l	Ionic Strength moles/l
		Part I, $HClO_4$ - $NaClO_4$		
0 1116	0 00414	0 1033	1 034	1 150
0 1674	0 00667	0 1541	0 977	1 151
0 2232	0 00955	0 2041	0 919	1 152
0 3340	0 01553	0 3029	0 804	1 154
0 5580	0 30150	0 4950	0 575	1 165
0 7812	0 0495	0 6822	0 345	1 176
1 1227	0 0837	0 9553	---	1 206
		Part II, HNO_3 *		
0 1	0 0078	0 0844		
0 2	0 0166	0 1668		
0 4	0 0358	0 3284		
0 8	0 0796	0 6408		
1 0	0 104	0 792		
1 6	0 180	1 240		
2 0	0 222	1 556		

* G R Leader, Ref 15

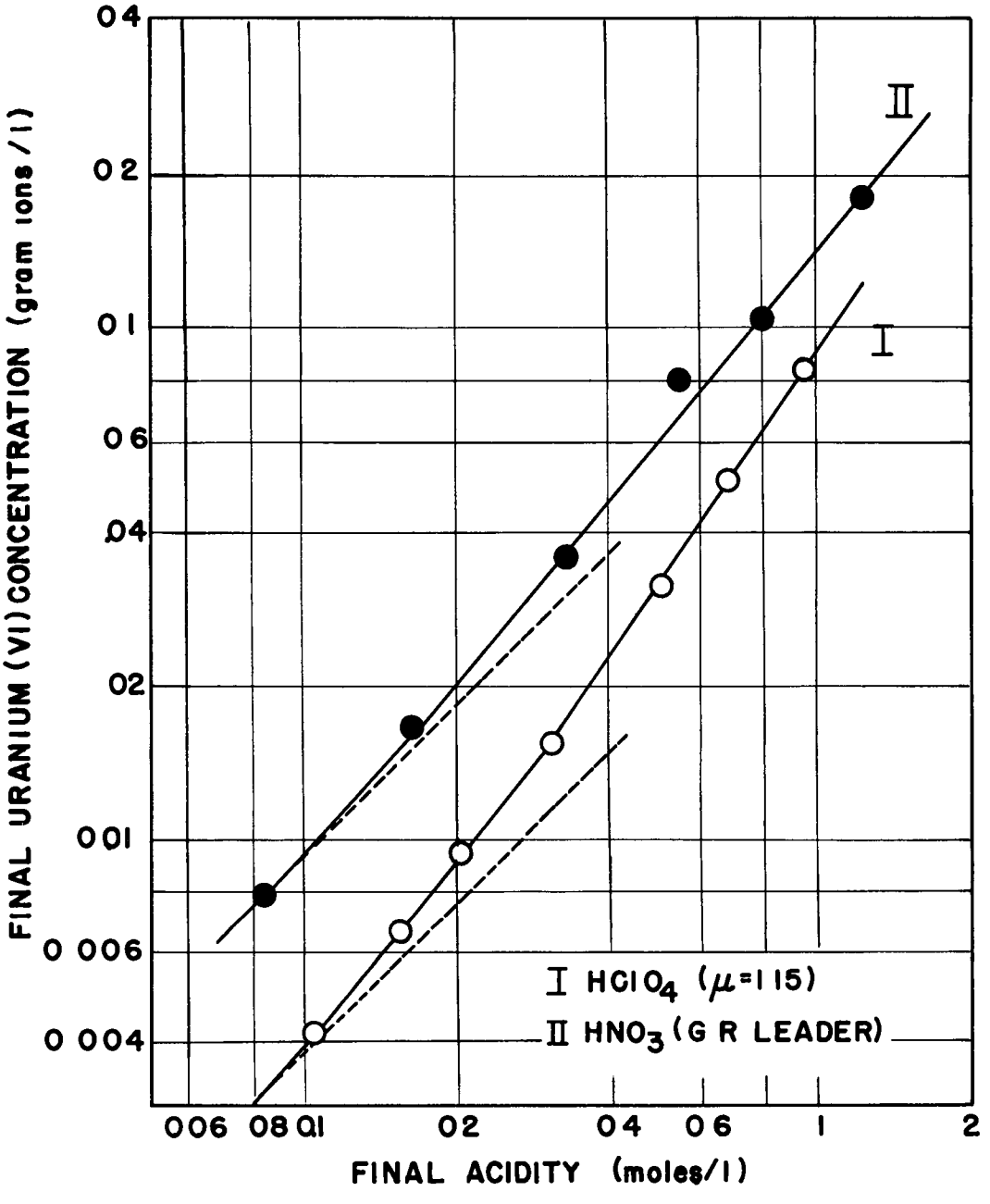


FIGURE 27

ACID DEPENDENCE OF $UO_2HPO_4\ 4H_2O$ SOLUBILITY

since, in all but the most acid runs, the primary dissolution reaction is probably,

$$UO_2HPO_4 + 2H^+ = UO_2^{++} + H_3PO_4 \qquad (15)$$

Discussion of Solubility Results

As mentioned in the previous report (ORNL-1308)[1], it has been found possible to construct a calculated solubility curve, based on the following equilibria, which agrees well with the observed solubility data in 0 2 - 1 5M phosphoric acid

$$UO_2HPO_4 + 2H^+ = UO_2^{++} + H_3PO_4, \qquad K_S = \frac{[UO_2^{++}]\,[H_3PO_4]}{[H^+]^2} = 0\ 0017 \qquad (16)$$

$$UO_2HPO_4 + H^+ = UO_2H_3PO_4^+, \qquad K_1 = \frac{[UO_2H_2PO_4^+]}{[H^+]} = 0\ 03 \qquad (17)$$

$$UO_2HPO_4 + H_3PO_4 = UO_2(H_2PO_4)_2, \qquad K_2 = \frac{[UO_2(H_2PO_4)_2]}{[H_3PO_4]} = 0\ 02 \qquad (18)$$

$$UO_2HPO_4 + 2H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4), \qquad K_3 = \frac{[UO_2(H_2PO_4)_2(H_3PO_4)]}{[H_3PO_4]^2} = 0\ 28 \qquad (19)$$

The K_1 and K_2 values indicated above differ from those previously proposed (K_1=0 05, K_2=0 01) These revised values yield the best fit to the data in the lower concentration region presently under investigation, without materially affecting the calculated solubility curve above 0 2M H_3PO_4 The solubility curves which were calculated from the above equilibria are represented by the solid lines in Figure 26

Below the solid phase transition point at 0 014M total phosphate, the following equilibria were employed in the calculation of the theoretical curve

$$(UO_2)_3(PO_4)_2 + 6H^+ = 3UO_2^{++} + 2H_3PO_4, \qquad K_S' = \frac{[UO_2^{++}]^3\,[H_3PO_4]^2}{[H^+]^6} = 7\ 66\times10^{-7} \qquad (20)$$

$$(UO_2)_3(PO_4)_2 + H_3PO_4 + 3H^+ = 3UO_2H_2PO_4^+, \qquad K_1' = \frac{[UO_2H_2PO_4^+]^3}{[H_3PO_4]\,[H^+]^3} = 0\ 004212 \qquad (21)$$

$$(UO_2)_3(PO_4)_2 + 4H_3PO_4 = 3UO_2(H_2PO_4)_2, \qquad K_2' = \frac{[UO_2(H_2PO_4)_2]^3}{[H_3PO_4]^4} = 0\ 001246 \qquad (22)$$

$$(UO_2)_3(PO_4)_2 + 7H_4PO_4 = 3UO_2(H_2PO_4)_2(H_3PO_4),$$

$$K_3' = \frac{[UO_2(H_2PO_4)_2(H_3PO_4)]^3}{[H_3PO_4]^7} = 3\ 422 \qquad (23)$$

These equilibria represent the dissolution of the solid phase, $(UO_2)_3(PO_4)_2\ 4H_2O$, to form the same complex ions as in the case of $UO_2HPO_4\ 4H_2O$ The K' values were determined in each case by the concentrations of the various ionic and molecular species which were calculated from (16) - (19) for the transition point Thus the calculation of the $(UO_2)_3(PO_4)_2$ branch of the curve involves no new assumptions and only one additional parameter, i e , the total phosphate concentration at the transition point, which has been evaluated experimentally

The agreement between the calculated and observed solubilities, as shown in Figure 26, is satisfactory over a 1500 fold change in the total phosphate concentration, and over a 30,000 fold change in the total uranyl concentration

G R Leader's results[15] on the solubility of UO_2HPO_4 as a function of nitric acid concentration (Figure 27), indicating an approximate proportionality between the solubility and the acidity, are consistent with equilibria (16) to (19) Thus, in 0 1M - 1M acid solution, in which the total uranyl and phosphate concentrations are equal, (16) and (19) may be shown to be the only important dissolution reactions of the four listed, with the result that

$$\Sigma UO_2^{++} = UO_2H_2PO_4^{+} + UO_2^{++} \qquad (24)$$

$$\Sigma UO_2^{++} = K_1(H^+) + \sqrt{K_0}(H^+) = (K_1 + \sqrt{K_0})(H^+) \qquad (25)$$

The present data in perchlorate solution as well as those of Leader exhibit considerable deviation from a true proportionality as indicated by the deviation of the two log-log plots from a slope of unity At present it is not possible to decide whether this deviation is simply an activity effect or a real effect in the sense that other

equilibria than (15) and 16) are involved Certainly, at an ionic strength as high as 1 15M, it is entirely possible that the activity coefficients of the ions involved in the dissolution equilibria could change sufficiently with the composition of the solutions to account for the observed deviations

In considering alternative equilibria, the most likely possibility appears to be

$$UO_2HPO_4 + 2H^+ = UO_2H_3PO_4^{++} \qquad (26)$$

Unless the bonding of the $H_2PO_4^-$ ion to UO_2^{++} involves both the unoccupied phosphate oxygen atoms, such a complex is certainly to be expected in acid solution The results of accurate pH measurements now underway should settle this question more definitely Further discussion will await the presentation of these results

Solubility of Uranium (VI) in Alkaline Phosphate Solutions

Preliminary studies of the solubility of uranium in trisodium phosphate solutions have indicated that there are regions of appreciable solubility in this system At pH-12 in 0 5148M PO_4, the solid, $NaUO_2PO_4$, has been identified by X-ray diffraction analysis and has a solubility of 7 03x10^{-3}M UO_2^{++} at 25°C At higher pH values (13 3) greater solubilities (1 2x10^{-2}M UO_2^{++}) have been obtained, but identification of the solid phase has not been made as yet It is not possible at present to say whether these solubilities represent equilibrium values

Reduction of Uranium in Sodium Carbonate Solutions without Precipitation

In the report for last quarter[1] it was pointed out that uranium could be reduced but not necessarily precipitated from Na_2CO_3 - $NaHCO_3$ solutions with $Na_2S_2O_4$ if the pH was about 9 6 or below Evidence for reduction of the uranium to the tetravalent state was obtained from spectrophotometric measurements

Recent experiments have given support to the colorimetric evidence In these tests various quantities of $Na_2S_2O_4$ were added to uranium-bearing Na_2CO_3-$NaHCO_3$ solutions at a pH of 9 65 After a reduction period of several days, the solutions were acidified with H_2SO_4 (under argon), heated for several minutes to drive off excess CO_2 and SO_2, and filtered to remove sulfur The tetravalent uranium in the acidified solution was then determined by cupferron precipitation

As shown by Table 50, all of the uranium in the acidified solution was in the tetravalent form when sufficient $Na_2S_2O_4$ had been added to the carbonate liquor When 0 5 or 1 0 times the stoichiometric (Eq 1) $Na_2S_2O_4$ had been added, 44 and 85% respectively of the total uranium was in the tetravalent state Though the possibility of some reduction during the acidification cannot be discounted, these data add to the evidence that most, if not all, of the uranium in the carbonate solution is in the tetravalent condition

Table 50

EXTENT OF REDUCTION BY $Na_2S_2O_4$

Test No	$S_2O_4^{=}$ Conc (X = theoretical)	Time (days)	U (IV) % of Total
HS-119	2x	2	100
120	6x	2	100
123	0 5x	5	44
124	1x	5	85

Note All tests were made at room temperature using a 0 5M Na_2CO_3, 0 5M $NaHCO_3$ solution (pH = 9 65) containing 2 g U/l

[redacted]

REFERENCES

1 "Progress Report Uranium Chemistry of Raw Materials Section, January 1, 1952 to March 31, 1952"; ORNL - Y-12, ORNL-1308, May 23, 1952

2 R A Ewing, H W Adam, F W Miles, A E Bearse and A C Richardson, "Final Report on Recovery of Uranium from North Dakota Lignites", Battelle Memorial Institute, BMI-237, July 31, 1950

3 K B Brown, J M Schmitt, F J Hurst and D J Crouse, "Recovery of Uranium from Oil Shales, Part I - Extraction of Uranium from the Shale Gangue", ORNL - Y-12, Y-564, February 10, 1950

4 "Progress Report Uranium Chemistry of Raw Materials Section, July 1 1951 to September 30, 1951", ORNL - Y-12, Y-823, October 30, 1951

5 "Progress Report Uranium Chemistry of Raw Materials Section, October 1, 1951 to December 31, 1951", ORNL - Y-12, ORNL-1220, February 28, 1952

6 D A Ellis, "Recovery of Uranium from Industrial Phosphoric Acids by Solvent Extraction, Part I - Summary Status Report, Part II - Index of Monthly Progress Reports", Dow Chemical Company, DOW-81, July 14, 1952

7 R H Bailes "April Progress Report" Dow Chemical Company, DOW-76, May 12, 1952

8 "Staff Report", Chemical & Engineering News, 30, 2336 (1952)

9 Kharasch, Jensen, and Urry, J Am Chem Soc , 67, 1864 (1945)

10 Clay, J Org Chem , 16, 892 (1951)

11 J M Schreyer and C F Baes, Jr , "The Volumetric Determination of Uranium (VI) in Phosphate Solutions", ORNL - Y-12, ORNL-1292, May 7, 1952

12 W E Harris and I M Kolthoff, J Am Chem Soc , 67, 1484 (1945)

[redacted]

[redacted]

13 E D Marshall, F S Voss, and E M Baer, "Polarographic Determination of Uranium in Solutions Containing Orthophosphate", C&CCC - K-25 Plant, K-585, March 31, 1950

14 A D Ryon and D W Kuhn, "Solubility of Uranyl Ammonium Phosphate in Nitric Acid and Ammonium Nitrate Solutions as a Function of Temperature", C&CCC - Y-12 Plant, Y-315, January 10, 1949

15 G R Leader, "Solubility of Uranyl Phosphate in UNH Solutions, Progress Report, August 15, 1944 to October 1, 1944", Chemistry Division, Clinton Laboratories, CN-2195, 1944

[redacted]