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# NARRATIVE STATUS REPORT

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# NARRATIVE STATUS REPORT

## Raw Materials Chemistry Section

November 11, 1955

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Raw Materials Chemistry Section
K. B. Brown, Supervisor

MATERIALS CHEMISTRY DIVISION
G. H. Clewett, Division Head

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## ABSTRACT

Brief narrative descriptions are given of studies being made by the Raw Materials Chemistry Section, Oak Ridge National Laboratory. Detailed descriptions of the work and the experimental data will be presented in subsequent progress and topical reports.

# INTRODUCTION

In reporting on the studies conducted by the Raw Materials Chemistry Section, the recent practice has been to issue summary-type reports on the various projects only at such time as the experimental studies are nearly complete. This method of reporting has several advantages for both the author and the reader, but also has the disadvantage of delaying publication of data which, even though incomplete, could be of use to other investigators in the field. Of late, this disadvantage has become more important due to increased interest and work by others on reagents and processes which have been developed or are under study here. In view of this, progress type reports covering newly acquired data are now planned in addition to the usual publications.

This report gives a brief narrative account of the status and progress on several of the current projects which may be of particular interest to other workers in the field. (Projects under study by the Engineering Group of this division are not included and will be reported separately.) A fuller account of these and other studies, including experimental data, will be given later in a more detailed progress report which is now being prepared. Additional progress reports will also be issued from time to time, the frequency of reporting to be governed by the progress of the work rather than by an established reporting period.

In some of the discussions below, reference is made to Memorandum CF-54-12-6 entitled "Status of the Research Program for Uranium Chemistry of Raw Materials."[1] It should be mentioned that this memorandum (December 2, 1954) received only limited distribution. We understand, however, that it was distributed to most of the major centers of raw materials research and for this reason it has been considered a suitable reference for this report.

## SYNERGISTIC EXTRACTANTS FOR URANIUM

It was mentioned in CF-54-12-6 that certain combinations of organophosphorus reagents, e.g., a "neutral" reagent plus an acidic reagent, might be expected to show a greater uranium extraction ability than the cumulative ability of each component operating separately or, in other words, a synergistic effect. Since that time it has been found experimentally that combinations of this type do indeed exhibit such an effect. For example, when di(2-ethylhexyl)phosphoric acid is used in combination with certain neutral compounds, the uranium extraction power, in some cases, has been increased by 1 to 2 orders of magnitude.

Reagents which have been tested in combination with di(2-ethylhexyl)phosphoric acid are trialkylphosphates and -phosphites, $(RO)_3PO$ and $(RO)_3P$; dialkyl alkylphosphonates, $RP(O)(OR)_2$; alkyl dialkylphosphinates, $R_2P(O)OR$; and trialkylphosphine oxides, $R_3PO$. Each of the reagents demonstrated a synergistic effect, the magnitude of which depended upon type and structure of the compound. The enhancement of extraction coefficients at equivalent concentrations increased generally in the order listed, that is, with increasing number of carbon-phosphorus bonds. Extractions from 0.5 M sulfate, pH 1, solution with neutral reagents from the n-butyl series, alone and in combination with 0.1 M di(2-ethylhexyl)phosphoric acid, are shown in the following table. Extraction coefficients obtained with other

| U(VI) Extrn. Coeff., $E_a^o$, with: | | Reagent Alone | Synergistic Combination |
|---|---|---|---|
| Di(2-ethylhexyl)phosphoric Acid, | 0.1 M | 135 | |
| Tri-n-butylphosphate, | 0.08 M | 0.0002 | 800 |
| Tri-n-butylphosphite, | .07 | .0001 | 700 |
| Di-n-butyl n-Butylphosphonate, | .08 | .0002 | 3000 |
| n-Butyl Di-n-butylphosphinate, | .10 | .0015 | 2500 |
| Tri-n-butylphosphine Oxide, | .05 | .0025 | 7000 |

n-alkyl compounds were similar to those with the corresponding n-butyl compounds. Compounds with three 2-ethylhexyl radicals gave extraction coefficients which were much lower

than with the corresponding n-alkyl compounds (consistent with previous experience), but still considerably higher than with the acidic reagent alone.

The tests shown in the foregoing table were made at low levels of uranium, so that only a small fraction of the reagent was tied up (on the basis of two moles of di(2-ethylhexyl)phosphoric acid per mole of uranium) and "loading effects" on the extraction coefficients were not encountered. It should be pointed out that the synergistic advantage (as evaluated on basis of the estimated free reagent concentration) has not been obtained under conditions of high uranium loading. Thus the extraction isotherms given by the synergistic reagents are generally similar in the high uranium region to that obtained with the same concentration of di(2-ethylhexyl)phosphoric acid alone, and about the same uranium loading may be expected in practice. However, in the low uranium region, the extraction isotherms with the combined reagents are much steeper than with the di(2-ethylhexyl)phosphoric acid alone, corresponding to the higher extraction coefficients. This steepness will permit a much more rapid reduction of the aqueous uranium level per stage, and in some applications will considerably decrease the number of stages required for a specified performance.

A considerable amount of data past that described here has been obtained with respect to optimum concentrations of the reagents for most effective utility, performance of synergistic systems other than those listed, etc. These data will be presented in later reports. Since TBP is commercially available at a reasonable price, most attention thus far has been directed at the TBP - di(2-ethylhexyl)phosphoric acid system. Process tests have been made on a bench scale, and larger scale work has been initiated by the Engineering Group. The reagent has been described to representatives of the Kerr-McGee Oil Industries and is being used on a production basis in their plant at Shiprock, New Mexico.[2]

Dibutyl butylphosphonate is also commercially available (at a higher price than TBP) and is also being subjected to process testing. Others of the potentially useful synergistic systems are being studied.

In addition to the increased extraction power for uranium, other useful properties are shown by these synergistic extractants, i.e.,

1) While the extraction power for uranium is much greater than that of the acidic constituent alone, the

extraction power for common contaminating metal ions (including iron, aluminum, vanadium, titanium, molybdenum) is not. Hence, the selectivity of the synergistic reagents for uranium over these metal ions is better than that of the acidic constituent alone.

2) Uranium may be stripped from the reagent combinations by solutions of sodium carbonate without formation of a third phase containing the sodium salt of the acidic component. In other words, in addition to providing synergistic extraction properties, the neutral reagent components serve the same function as alcohols (see previous reports) in preventing immiscibility.

3) The losses of each reagent component to the aqueous phase during extraction are sufficiently small as to permit their use on liquors fairly dilute in uranium.

# FURTHER STUDIES OF THE DIALKYLPHOSPHORIC ACID EXTRACTION (DAPEX) PROCESS FOR URANIUM

Studies concerning the Dapex process for uranium recovery from acid liquors have been presented in a topical report, ORNL-1903,[3] and in previous progress reports.[4] Batch and continuous countercurrent experiments on process modifications and on applications of this process to various clear liquors and slurries have been continued as outlined in ORNL-1903. Process test studies have been made on both liquors and slurries by the Engineering Group and preliminary cost estimates have been obtained. The process has been described to some of the Western mill operators and it is being used by Kerr-McGee on a production scale in their plant at Shiprock, New Mexico.[5]

Some results from recent studies on the Dapex process are listed below.

## Alcohol Losses from Kerosene into Acidic Sulfate Solutions

The use of long chain alcohols, added to the organic phase to prevent third phase formation during alkaline stripping of alkylphosphoric acid extractants, has been described in ORNL-1903. Further studies of the amount of alcohol that would be distributed to acidic liquors during extractions with di(2-ethylhexyl)phosphoric acid-kerosene-alcohol solvent have been made to supplement previous data.

It was found that the losses of 2-ethylhexanol from kerosene alone into 0.5 M sulfate solution, pH 1, were apparently controlled by an aqueous solubility limitation rather than a distribution coefficient. Thus, when kerosene at different initial alcohol concentrations was contacted with the liquor at various phase ratios the alcohol reporting to the aqueous remained constant at about 120 mg per liter of aqueous solution. Similar measurements with 0.2 M sulfate, pH 1, solutions (at a constant phase ratio) gave values at some conditions which were more nearly representative of those expected from proportional distribution. In this case the alcohol concentration in the aqueous phase increased with increasing concentrations in the kerosene but appeared to approach a limiting value of ~300 ppm when the alcohol in the kerosene was greater than 30 w/v %. At alcohol levels used for many process applications, i.e., ~ 2 w/v % 2-ethylhexanol, the loss to a 0.2 M $SO_4$, pH 1, aqueous phase would correspond to 145 ppm,

and to 0.5 M $SO_4$, pH 1, 120 ppm. These compare with the previously determined values of 120 and 100 ppm, respectively, when di(2-ethylhexyl)phosphoric acid was also present in the organic diluent.[3]

As mentioned in ORNL-1903, longer chain primary decyl and tridecyl alcohols are now available in commercial quantities at fairly low prices. The concentration requirements to prevent third phase formation during alkaline stripping have been determined for these alcohols according to the method previously described. From the results below it is apparent that the requirements are similar to those found earlier for other primary alcohols.

Requirements for mixed primary decyl alcohols (Carbide & Carbon), w/v % primary decyl alcohols = 0.38 + 4.6 M, at 30°C.

Requirements for primary tridecyl alcohols (Carbide & Carbon), w/v % primary tridecyl alcohols = 0.58 + 4.6 M at 30°C.

where M = molarity of di(2-ethylhexyl)phosphoric acid in kerosene.

Because of the structure and molecular weight of these alcohols it was anticipated that losses to the aqueous phases would be lower than with 2-ethylhexanol (see previous data including results for 4-ethyloctanol in ORNL-1903). This was confirmed in measurement of the distribution to 0.5 M $SO_4$, pH 1, solution from a 0.1 M solution of di(2-ethylhexyl)phosphoric acid in kerosene containing 2 w/v % mixed primary tridecyl alcohols. The distribution was less than 5 mg/l of aqueous phase contacted, as compared to a loss of 100 mg/l previously described in similar tests with 2-ethylhexanol.

## Other Alkaline Stripping Reagents

It has been mentioned in previous reports (ORNL-1480) that ammonium carbonate solutions might be used to strip uranium from the di(2-ethylhexyl)phosphoric acid - kerosene solvent without formation of a third liquid phase. Other tests have also shown that calcium oxide slurries can remove uranium from this solvent without third phase formation. The usability and economics of these stripping methods, and also magnesium oxide slurries, are being evaluated.

## Continuous Countercurrent Extraction and Stripping Tests

Studies of applications of the Dapex process to uranium recovery from various liquors under conditions of continuous countercurrent operation have been continued. Mixer-settler units have been used both in the extraction and stripping cycles. Sodium carbonate was the stripping agent in all tests and both alcohols and tributylphosphate (see above) have been used as solvent additives. Some of the results from these tests may be itemized as follows:

1) Further measurements of organic reagent requirements for the Dapex process were made by processing of a synthetic Western ore leach liquor (1 g U/l) with 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene (1.5 w/v % capryl alcohol) through 95 complete extraction-stripping cycles. Good recoveries and good operation were maintained throughout the run. The total organic losses (comprising entrainment, evaporation, spillage and distribution loss of extractant and alcohol to the aqueous phase) were in nearly exact agreement with those estimated in ORNL-1903, Table 28.

2) Other runs of shorter duration have been made on a number of Western type liquors of variant composition. It has been shown that moderate amounts of Fe(III) can be tolerated in the liquor (at least up to 0.6 g/l) without encountering physical difficulties in the stripping cycle from precipitation of ferric hydroxide and without important impairment of uranium extraction efficiency due to iron competition. Appreciable extractions were obtained of any titanium or molybdenum in the liquor but these metals were removed from the organic phase in the stripping cycle and could be separated from the uranium in subsequent operations.

3) Comparative cyclic tests have demonstrated the greater extraction efficiency of di(2-ethylhexyl)phosphoric acid-tributylphosphate-kerosene solvent as compared to di(2-ethylhexyl)phosphoric acid-kerosene-alcohol. For example, with a synthetic liquor (U = 1.2 g/l, Fe(II) = 2.7 g/l, Fe(III) = 0.3 g/l, Al = 3.0 g/l, $SO_4$ = 0.5 M, pH = 1.3), 99.8% extraction of uranium was obtained in three stages with 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene + 3 w/v % TBP at a phase ratio of $4^a/1^o$. Under the same conditions but using 1.5 w/v % capryl alcohol instead of the TBP and four extraction stages instead of three, 99.3% recovery of uranium was obtained.

4) A single cyclic extraction run was made on a sample of liquor from the Kerr-McGee plant. The liquor pH was adjusted to 1.2 with lime and most of the Fe(III) present was reduced with powdered iron prior to extraction. Using 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene plus 3 w/v% TBP and a phase ratio of $4^a/1^o$, 99.4% of the uranium was recovered in 5 mixer-settler units. From the number of extraction stages required, it is apparent that the Kerr-McGee liquor is more difficult to extract than are a number of other liquors tested. This is due to the use of the "acid-cure" process at the Shiprock plant which gives rise to liquors unusually high in unfavorable contaminants. For example, vanadium(IV), at 3.5 g/l, was a significant competitor of uranium for the extractant. High concentrations of titanium, 0.24 g/l and $SO_4$ 110 g/l also contributed in decreasing the uranium extraction efficiency.

## Uranium Extraction from RIP Sulfuric Acid Eluates

Because of the interest shown by people at the Winchester Raw Materials Laboratory[6] and by people in the West[7] in extracting uranium from sulfuric acid RIP eluates, a brief paper study was made of this possibility with di(2-ethylhexyl)phosphoric acid as the extracting agent. Assuming a 1 M sulfuric acid eluate containing 6 g U/l and using experimental data already available on extraction and stripping efficiencies, the process criteria were estimated and the reagent and operating costs were calculated (the latter by the Engineering Group). Confirmatory to the promising experimental results being obtained at Winchester,[8] the reagent costs estimated in this manner were found to be encouragingly low, considerably lower than for the nitrate elution process now employed. When other operating costs, estimated by the Engineering Group, were included in the comparison, the favorability of the sulfuric acid process was apparently dependent upon the availability of existing plant labor and the manner of handling the amortization of the equipment and buildings.

Limited tests have shown that the amines might also be considered as extractants for the sulfuric acid eluates. Several amine-diluent combinations have given effective extractions from such solutions with reasonably rapid separation of phases. Uranium extraction coefficients obtained from 1 M sulfuric acid solution at amine concentrations of 0.2 M and at low uranium loading (2 g U/l in organic) are shown below.

| Amine | Diluent | Uranium Extraction Coefficient, $E_a^o$ |
|---|---|---|
| Tri-n-octyl | Kerosene + 5% tridecyl alcohol | 23 |
| " | Amsco G | 34 |
| Tri(iso-octyl) | Amsco G | 17 |
| R&H 9D-178 | Amsco G | 13 |
| N-benzyl-1-(3-ethyl-pentyl)-4-ethyloctyl | Kerosene | 400 |

No further experimental studies on eluate extraction are planned here as an active process development program is underway at the Winchester Laboratory.[8]

## FURTHER STUDIES OF THE AMINE EXTRACTION (AMEX) PROCESS FOR URANIUM

Systematic studies of amine extractants and laboratory development work on the Amex process for uranium have been summarized in ORNL-1734, ORNL-1922, and ORNL-1959. Reports covering the "Design of An Amine Extraction Demonstration Plant" and the "Cost of Uranium Recovery by the Amine Extraction Process" have been issued as ORNL-1963 and ORNL-1949 by the Engineering Group of the Materials Chemistry Division. Additional reports covering some of the experimental work in greater detail are being prepared.

Since the Amex process has been developed to a point where scale-up factors are known and the performance and costs on a wide range of Western ore process liquors can be predicted, most of the current work is concerned with studies of more or less secondary importance such as the relative advantages and disadvantages of different promising amine extractants, modifications of the extraction and stripping chemistry, etc. Also, attention is being given to those facets of the process which are of importance in extending its application to uranium recovery from liquors other than those encountered in the West and to the recovery and separation of metals other than uranium.

A brief summary of some of the recent studies on uranium stripping of the amine extractants is given below. More detailed results from these and other of the current studies will be given in subsequent progress and summary reports.

Magnesium Oxide Stripping: The use of chlorides, nitrates and alkali hydroxides for stripping uranium from the amine extracts has been described in previous reports. Recently, tests have been made with magnesium oxide slurries as the stripping agent. It has been shown that essentially complete precipitation of uranium from the organic phase can be obtained with only a small excess of magnesium oxide above stoichiometric requirements for neutralizing the amine salts and precipitating the uranium. If a high organic to slurry ratio is maintained in the mixer, emulsion formation is avoided. Although the rapidity and cleanness of phase separation has varied with the particular amine-diluent combination used, the performances in these respects have been exceptionally good for several of the combinations tested. With the better extractants, the magnesium uranate product formed

during the operation is easily settled and filtered and the amount of organic phase held by the precipitate is small. Larger scale studies of this stripping method are planned to better define the operational feasibility and the comparative economies.

## VANADIUM RECOVERY PROCESSES

Brief summaries of studies on the recovery of vanadium from sulfate solutions using both dialkylphosphoric acids and amines as extracting agents have been reported previously.[3,9] At this time batch test work is essentially complete and processes are being evaluated in small-scale continuous countercurrent equipment. Sufficient information has been obtained to permit a reasonably good evaluation of process flowsheets from the standpoint of reagent usage, operational characteristics, etc. Preliminary cost analyses of the processes have been started by the Engineering Group.

### Vanadium (and Uranium) Recovery with Di(2-ethylhexyl)-phosphoric Acid

In one of the process possibilities considered, the uranium and vanadium are co-extracted from a liquor in a multi-stage operation with approximately 0.3 M di(2-ethylhexyl)phosphoric acid in kerosene containing either about 4 w/v % TBP or about 3% w/v alcohol and are later separated by selective stripping. The function of either TBP or alcohol is to render the sodium salt of the extractant compatible with kerosene during the sodium carbonate stripping for uranium (see below). TBP also serves an additional function in that uranium distribution to the organic phase is increased in both the extraction and vanadium stripping cycle. Most of the ferric iron in the liquor is reduced and the pH of the liquor is adjusted to approximately 2 prior to extraction.

Vanadium is stripped effectively from the extract (3-4 stages) with approximately 0.7 M $H_2SO_4$ with only a minor transfer of uranium to the aqueous phase. This small amount of uranium can be recovered by re-extraction (single stage) of the pregnant vanadium strip solution with a small volume of the organic recycle stream. Vanadium can be precipitated by addition of ammonia and the precipitate calcined to give a very high grade vanadium product.

Uranium stripping is accomplished with sodium carbonate solution. This operation also serves another important purpose in removing other metals complexed with the reagent and thus permitting recycle of the solvent at full strength to the extraction system. In order to decrease sodium carbonate consumption, only about one third of the total organic volume is stripped of its uranium content in each cycle.

Other process variations in the use of di(2-ethylhexyl)phosphoric acid for vanadium recovery, too numerous for discussion here, have been considered and will be described in later reports. It is of course apparent that, by modification of conditions, vanadium could be recovered as a single product from uranium barren liquor if a separate recovery of the metals proved more desirable. Process conditions for such application with or without the use of diluent additives (depending upon the stripping procedure) have been examined. The work has been discussed with representatives from Kerr-McGee and studies by that organization on the Shiprock liquors have confirmed the results obtained here.

## Vanadium (and Uranium) Recovery with Amines

The amines are excellent extractants for uranium and will also extract vanadium under certain conditions so that consideration can be given to the recovery of both metals either separately or simultaneously. Thus far most attention has been given to processes wherein the uranium and vanadium are co-extracted and separated by selective stripping. In this case, the vanadium is oxidized to the +5 valence state and the pH of the liquor adjusted to approximately 1.8 prior to extraction. Manganese dioxide appears to be a favorable oxidant. Extractions of vanadium have shown little dependence upon the type or structure of amine used. However, since ferric iron can compete for the extractant at high pH levels, more effective results are obtained with reagents of high selectivity, e.g., secondary amines of appropriate branching or tertiary amines. Most of the test work to date has been with 0.1 M R&H Amine 9D-178 in kerosene.

Apparently due to polymerization of vanadium after extraction into the organic phase, the vanadium extraction isotherms do not follow a normal pattern. As the vanadium loading in the organic phase increases (within certain limits) the measured vanadium coefficients also increase rather than decrease.

Two methods of separating uranium from vanadium in the stripping cycle have been investigated. The first (previously reported) uses a solution of sodium chloride to strip the uranium, after which the vanadium is stripped with an alkaline solution such as sodium carbonate. In this procedure, difficulties have sometimes been encountered in affecting a sufficiently clean separation of the metals in the chloride stripping cycle. The second method, which

appears promising, utilizes sulfurous acid to reduce and strip the vanadium. Complete removal of vanadium from the organic phase has been accomplished with only a slight excess of sulfurous acid. The uranium is then removed by one of several methods described in previous reports.

As mentioned with regard to the work with di(2-ethylhexyl)phosphate described above, a more complete account of the vanadium recovery studies will be given later in reports now being prepared.

## SOLUBILITY AND PHASE EQUILIBRIA

### Solubility of Uranium(VI) in Trisodium Phosphate Solutions

A study of the chemistry of uranium in alkaline phosphate systems was undertaken in view of the interest in recovery of uranium from the phosphatic ores of the Florida Leached Zone by means of an alkaline attack. The solubility of uranium(VI) in trisodium phosphate solutions has been measured at 25°C. The solubility increased from about 0.001 to 0.006 M $UO_2^{++}$ as the phosphate concentration was increased from 0.3 to 0.6 M, in equilibrium with the metastable solid phase $Na_4UO_2(PO_4)_2 \cdot 6H_2O$. This solid changed slowly to $Na_4U_3O_8(PO_4)_2$ (perhaps hydrated). Uranium solubility in equilibrium with the latter increased from about 0.0001 to 0.002 M $UO_2^{++}$ as the phosphate concentration was increased from 0.1 to 1.2 M. X-Ray diffraction patterns were recorded, and dry samples of $Na_4UO_2(PO_4)_2 \cdot 6H_2O$ and of $NaUO_2PO_4 \cdot 4H_2O$ were prepared and identified.

### Solubility of Uranium(IV) in Phosphoric Acid Solutions Containing Other Ions

The solubility studies of uranium(VI) and (IV) orthophosphates in phosphoric acid solutions[11,12] have been extended to include solutions containing fluoride in concentration ranges comparable with those encountered in industrial phosphoric acids. These measurements were undertaken to obtain information which might be basically useful in explaining low uranium extractions during acid leaching of phosphatic ores and in obtaining a better understanding of the possibilities for precipitating uranium from phosphatic leach liquors.

A new solid with the approximate empirical formula $UFPO_4 \cdot H_2O$ was obtained as the stable equilibrium solid in contact with solutions up to about 0.5 M in HF over a range of at least 4 to 6 M in $H_3PO_4$. Chemical and physical studies of this compound have suggested that it may be best represented by the formula $(UO)HPO_4 \cdot HF$. The solubility of this compound at 25°C in 4, 5, and 6 M phosphoric acid solutions was measured as a function of fluoride concentration, both by dissolution and by precipitation. At each phosphoric acid concentration the uranium solubility went through a broad minimum (respectively, 0.0006, 0.0009, and 0.0017 M $U^{+4}$) at a fluoride concentration near 0.05 M.

A few measurements have been made of uranium solubility in phosphoric acid containing calcium at concentrations up to 0.6 M. The uranium solubility was slightly lower in the presence of the calcium, e.g., about 0.025 M $U^{+4}$ in the presence of 0.1 M $Ca^{++}$ as compared with 0.035 M $U^{+4}$ without calcium,[12] both in 5 M phosphoric acid.

## Equilibria in the $ThO_2$-$Na_2O$-$CO_2$-$H_2O$ System

The solubility of thorium has been measured in various sodium carbonate-sodium bicarbonate solutions at 25°C. Throughout the concentration ranges examined, the only thorium-containing equilibrium solids found were $Na_6Th(CO_3)_5 \cdot 12H_2O$[13] and $ThOCO_3 \cdot 8H_2O$,[14] except that a thorium hydroxide may have been present at the lowest carbonate level tested. The double salt is incongruently soluble in water, to the extent of 3.0 wt % Th. The solubility is lower in solutions containing additional sodium carbonate; tests are in progress with solutions containing small amounts of sodium bicarbonate and carbonate-bicarbonate mixtures. Solution compositions were measured at two invariant points (saturated with respect to the double salt-sodium bicarbonate-trona and with respect to the double salt-trona-sodium carbonate decahydrate) and along the bicarbonate univariant line (saturated with respect to the double salt and sodium bicarbonate). The thorium solubility was highest in the least basic solution, 1.2% Th with 10.9% $NaHCO_3$ and 1.25% $Na_2CO_3$, dropping to 0.54 and 0.42% Th at the two invariant points.

# COMPLEX IONS IN SOLUTION

## Further Spectrophotometric Study of Uranium(VI) Phosphate Complex Formation

Previously reported solubility measurements of uranium(VI) orthophosphate in perchloric acid-phosphoric acid solutions[15] suggested the formation of $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{++}$, and $UO_2(H_2PO_4)_2$, with some indication of 3P:U complexing at higher phosphoric acid concentrations. A spectrophotometric study of these solutions using the method of continuous variations established the existence of 1:1 complexes,[16] but did not give any evidence concerning species containing a higher ratio of phosphate. Another method has been developed for correlating absorption measurements in which the phosphoric acid concentration was varied while (in each series) the uranium and perchloric acid concentrations were held constant. The results of such measurements at 0.04 M U in 1 M $HClO_4$ and 0.001 M U in 1 M $HClO_4$ and 0.1 M $HClO_4$ - 0.9 M $NaClO_4$ solutions are consistent with the formation of 1:1 and 2P:U (mononuclear uranium) complexes, and permit estimation of the total formation constants as follows:

| | 1 M $HClO_4$ | 0.1 M $HClO_4$ - 0.9 M $NaClO_4$ |
|---|---|---|
| $K_1$ | 11 ± 2 | 58 ± 4 |
| $K_2$ | 24 ± 5 | 470 ± 50 |

where $K_n = Cn/[UO_2^{++}][H_3PO_4]^n$, Cn being the total molarity of all complexes having the ratio nP:U. The indicated uncertainties were estimated on the assumption that no complexes of ratio 3P:U or higher were present in appreciable amount. The acidity dependence can be accounted for in terms of the species $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{++}$, $UO_2(H_2PO_4)_2$, and $UO_2(H_2PO_4)(H_3PO_4)^+$. There is some quantitative inconsistency between these and the earlier results, which remains to be resolved. Appreciable formation of polynuclear uranium complexes at the highest uranium concentrations might be involved.

## Potentiometric Study of Uranium(VI) Phosphate Complex Formation

Solubility and spectrophotometric measurements are referred to above which gave evidence of formation of the

complex species $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{++}$, $UO_2(H_2PO_4)_2$, and $UO_2(H_2PO_4)(H_3PO_4)^+$ in perchloric acid-phosphoric acid solutions of uranium(VI) orthophosphate. A further investigation of this system has been made using potentiometric measurement of the hydrogen ion release accompanying complex formation according to reactions of the type

$$UO_2^{++} + nH_3PO_4 \rightleftharpoons UO_2H_x(PO_4)_n^{+(x+2-3n)} + (3n-x)H^+.$$

The measurements made thus far have employed the quinhydrone electrode in connection with concentration cells of the type

$$\text{Pt-Qh} \left| \begin{array}{ll} UO_2(ClO_4)_2, & C_1 \\ HClO_4, & C_2 \\ NaClO_4, & C_3 \end{array} \right\| \left. \begin{array}{ll} UO_2(ClO_4)_2, & C_1 \\ HClO_4, & C_2 \\ NaClO_4, & C_3 \\ H_3PO_4, & 0\text{-}C_4 \end{array} \right| \text{Qh-Pt}$$

Interpretation of the measurements in terms of $K_1$ and $K_2$ as evaluated from spectrophotometric measurements (above) gives the following approximate results -

| | x for n=1 | x for n=2 |
|---|---|---|
| 1 M $HClO_4$: | 2.1 - 2.2 | ~5 |
| 0.1 M $HClO_4$ - 0.9 M $NaClO_4$: | 1.6 - 1.8 | |

Thus it appears that in both media, $UO_2H_2PO_4^+$ is the principal 1:1 complex, along with relatively small amounts of $UO_2H_3PO_4^{++}$ in 1 M acid and $UO_2HPO_4$ in 0.1 M acid. The identification of $UO_2(H_2PO_4)(H_3PO_4)^+$ as the principal 2P:U species is supported, but this evaluation is less certain, the measurements at the higher phosphoric acid concentrations being complicated by an apparent interaction of both uranyl ion and phosphoric acid with the quinhydrone electrode. Accordingly, these measurements are to be rechecked and extended with the use of a sensitive glass-electrode assembly.

## Spectrophotometric Study of Uranium(IV) Phosphate Complex Formation

The increase in solubility of uranium(IV) orthophosphates in phosphoric acid solutions as the phosphoric acid concentration is increased[12] indicates formation of phosphate complexes in solution. Addition of phosphoric acid to a perchloric acid solution of uranium(IV) changes the color from a light yellow-green to a blue-green resembling acidic uranous sulfate solutions. Absorption spectra were measured for 0.0025 and 0.005 M U(IV) solutions in 5 M $HClO_4$ containing phosphoric acid at P:U mole ratios varying from zero to 20. The results indicate the existence of more than one uranium(IV) phosphate complex species in these solutions. Neither the continuous variations method nor the molar ratio method has proved sufficient for analysis of these data, and no more suitable treatment has as yet been found.

In the course of these measurements it was established that the uranium(IV) perchlorate spectrum was independent of perchloric acid concentration (1.2 to 5 M) and followed Beer's law with respect to uranium concentration. Uranium(IV) perchlorate absorption maxima were found at 430, 495, 548, 648, and 671 m$\mu$, in good agreement with the results of Kraus and Nelson.[17] This spectrum shifted to one with maxima at 428, 450, 480, 538, 642, and 658 m$\mu$ as the phosphoric acid was added up to a P:U mole ratio of 8, and was not further changed by additions up to P:U = 20.

## STUDIES OF SOLVENT EXTRACTION EQUILIBRIA

### Extraction of Uranium(VI) by Di(2-ethylhexyl)phosphoric Acid

Results of Stewart and Hicks[18] on the extraction of uranium(VI) from nitric acid solutions by dibutylphosphoric acid in n-hexane and in dibutyl ether showed the uranium extraction coefficient proportional to the square of the reagent concentration under some conditions and to a power greater than the square under others. Proportionality to a power greater than the square has also been found in this laboratory in uranium extraction with di(2-ethylhexyl)phosphoric acid/kerosene from various acidic solutions. Hence, the extraction equilibrium has been examined with simpler solutions, i.e., acidic perchlorate solutions at constant ionic strength (2 M). The organic diluent used was n-hexane. The results obtained over the range $10^{-5}$ - 0.2 M initial uranium, 0.001 - 2 M reagent, and 0.1 - 2 M perchloric acid conform to the reaction

$$UO_2^{++}{}_{aq} + 2HOPO(OR)_{2\,org} \rightleftharpoons UO_2\left[OPO(OR)_2\right]_{2\,org} + 2H^+{}_{aq}$$

$$K_c = \frac{\left[UX_2\right]\left[H^+\right]^2}{\left[UO_2^{++}\right]\left[HX\right]^2} \approx 7000$$

$$E_a^o = K_c\left[HX\right]^2 / \left[H^+\right]^2$$

where X represents the di(2-ethylhexyl)phosphate ion. However, the variations in $K_c$ were greater than expected to arise from the experimental uncertainties, with some suggestion of a systematic variation as a function of the reagent concentration or of the uranium:reagent ratio in the organic phase. There was also a suggestion that under some of the test conditions an appreciable amount of sodium ion might have been extracted. These points are being examined further.

### Extraction of Sulfuric Acid by Didecylamine

As a part of the fundamental study of amines as liquid-liquid extraction reagents, and also to help clarify some reactions encountered in applied work, the

equilibria between aqueous sulfuric acid and organic solutions of amines are being examined in detail. Preliminary equilibrations consisting of two-phase titrations of 0.01 to 0.1 M di-n-decylamine/benzene with aqueous sulfuric acid indicated that the resulting amine sulfate exists at approximately constant activity over a wide range of apparent concentrations in the benzene phase. More extensive examination of these equilibria by means of batch equilibrations corroborated the earlier conclusions and permitted more precise quantitative correlation. Sulfuric acid extraction below the equivalence point (i.e., in the presence of an appreciable concentration of the basic form of the amine) by 0.05 to 0.5 M di-n-decylamine/benzene is fitted by the empirical equation

$$K_1 = a_{H_2SO_4}[R]^3 \approx 6\times10^{-18}$$

where [R] represents molarity of amine remaining in the basic form. Sulfate-bisulfate exchange at 0.05 to 0.1 M total amine and at equilibrium bisulfate equivalent fractions up to around 0.3 is well fitted by an equation in the expected form,

$$K_2 = \frac{X^2_{RH_2SO_4}}{a_{H_2SO_4}X_{R_2H_2SO_4}} = \frac{C^2_{RH_2SO_4}}{2a_{H_2SO_4}C_{R_2H_2SO_4}C_R} = 2600$$

where X represents equivalent fraction in the amine sulfate-bisulfate mixture considered as a separate (colloidal) phase.

Other equilibrium measurements have been reported for extraction of sulfuric acid from sodium sulfate-sulfuric acid solutions by di-n-decylamine/benzene[19] and from sulfuric acid solutions by tri-n-octylamine/benzene.[20]

Brief tests have been made of sulfuric acid extraction by solutions of di-n-decylamine in other diluents. The results of two-phase titrations of the amine in petroleum ether, n-octane, n-octyl alcohol, methylisobutyl ketone, nitrobenzene, bromobenzene, and trichlorethylene suggested that, as in benzene, the resulting amine sulfate exists at approximately constant activity. Titrations of the amine in chloroform and in carbon tetrachloride were inconclusive, but batch equilibrations at constant aqueous acidity showed the bisulfate-sulfate ratio to be independent of the total amine concentration, again suggesting constant activity.

## Extraction of Uranium(VI) by Didecylamine Sulfate

Detailed study is being made of the extraction of uranium(VI) from acidic solutions by amines. So far this has been limited to equilibrium measurements, principally directed toward determination of the stoichiometry of the extracted species and the factors controlling the magnitude of the extraction coefficient. Sulfate systems were chosen for first study because of the preponderant importance of sulfate in extraction applications. Most of the tests have been made with di-n-decylamine, which is typical of one important class of the reagents and which has been available in satisfactory quantity and purity. Tri-n-octylamine is also being examined, and the studies will progress to include other compounds.

The molar ratio of amine to uranium in the equilibrium organic (benzene) phase was measured as a function of either varying amine concentration or varying uranium concentration. In extractions from sulfate solutions, pH in the range 1 to 2, a plateau or an inflection was found at amine:uranium mole ratio close to 6. Under some test conditions, lower ratios (higher uranium loadings) were found after an inflection at 6, reaching amine: uranium as low as 3.5. Thus, an association of 6 amines with each uranium is indicated as an important, but not limiting, "species." (Observations in process testing have been generally similar to these.[21,9]) One of the questions remaining to be answered is how the amines are associated with the uranium, and whether all six are equivalent.

The dependence of the extraction coefficient on reagent concentration was examined on basis of the assumption that exactly six moles of amine were tied up by each mole of uranium at all amine:uranium ratios greater than the 6:1 (the inflection point). The remaining uncomplexed amine sulfate was calculated for each equilibration test. The measured uranium extraction coefficient $E_a^o$ (for extraction by di-n-decylamine sulfate in benzene from 1 M sulfate solution at pH 1) was found to be directly proportional to the uncomplexed amine sulfate concentration as so calculated. If the extraction reagent were in true solution in the benzene phase, the extraction coefficient would be expected to vary with a power of the uncomplexed reagent concentration corresponding to the stoichiometry of the extracted species. The results found support the belief that the amine sulfate exists as aggregates dispersed in the organic phase, rather than in true solution.

Such results as the foregoing suggested that the uranium distribution might be completely independent of the amount of diluent in the organic phase. However, direct tests showed some dependence. When the di-n-decylamine sulfate concentration was varied by dilution with additional benzene while its ratio to uranium was held constant, the extraction coefficient $E_a^o$ was directly proportional to the calculated uncomplexed amine sulfate concentration only up to about 0.03 N (0.03 M amine). At higher concentrations, up to 0.25 N, it was proportional to a power between 2/3 and 1/2, suggesting that the nature of the amine sulfate aggregates may change to some extent with the overall "concentration" in the benzene phase.

Decrease of uranium extraction with increasing acidity has been noted in both screening and process testing, and has been measured as a function of pH in various solutions of interest. Measurements are in progress of the dependence of the uranium extraction coefficient on sulfuric acid activity in pure sulfate solutions.

The diluent used in all the foregoing tests was benzene. Similar tests were made using di-n-decylamine in chloroform or carbon tetrachloride. With both diluents, the loading ratio reached a plateau at about 6 amines: uranium. However, the "loaded" organic phase contained more sulfate than expected on basis of the amine and uranyl contents. This has not yet been accounted for; explanation in terms of bisulfate replacing sulfate appears difficult since the "excess" remained about the same over a wide range of aqueous pH. The power dependence of uranium extraction coefficient on uncomplexed reagent with both these diluents was unity or less. The differences found among the diluents may yield useful information about the nature of the organic phases.

## Extraction of Uranium(VI) by Trioctylamine Sulfate

Study of extraction by tri-n-octylamine sulfate, of generally similar scope to the studies described above, has been started. It has been observed in process testing[21,9] that the symmetrical tertiary amines load more uranium than do the secondary amines (i.e., reach amine:uranium ratios significantly below 6 under conditions where the other are close to 6). This was confirmed by tests with 0.05 and 0.5 M tri-n-octylamine in kerosene, which loaded to amine:uranium = 4.6 and 5.0, respectively, from a 0.004 M uranium - 0.5 M sulfate

solution at pH 1. These results indicate some decrease in relative uranium loading as the reagent concentration was increased. However, sulfate analysis showed that the amount of bisulfate in the equilibrium organic phases increased in the same direction, and if it be assumed that only the normal sulfate was associated with the uranium the resulting estimated amine:uranium mole ratio is close to 4 for each solution.

## Extraction of Hydrolyzed Uranium(VI) by Didecylamine

Solutions of di-n-decylamine (basic form) in benzene were observed to extract uranium from solutions of uranyl sulfate which contained no additional sulfate or acid. The extraction was accompanied by hydrolysis of the uranium remaining in the aqueous phase. Similarly, uranium was extracted from a solution prepared by dissolving uranium trioxide in uranyl sulfate solution to reach a ratio of $2U:SO_4$, the extraction being accompanied by precipitation of uranium trioxide. In the extractions from uranyl sulfate solutions ($U:SO_4 = 1$), the amount of uranium extracted by 0.1 M di-n-decylamine/benzene increased with increase of initial uranium concentration up to a maximum at around 0.07 M. At this point the uranium loading corresponded to amine:uranium = 1.8, and the extraction coefficient $E_a^o$ was 5. It is suggested that the extracted species may involve one mole of amine per mole of uranium, as perhaps $(R_2NH_2)_2U_2O_5(SO_4)_2$, the amine molecules having acquired protons at the expense of hydrolysis in the aqueous phase. Spectrophotometric measurements of the organic phase support the conclusion that the uranium was extracted in a hydrolyzed form.

## Examinations of the Organic Phase in Amine Extraction

Spectrophotometric Measurements. Absorption spectra in the range 365-426 mμ were measured for di-n-decylamine sulfate/benzene solutions containing uranium(VI) at amine: uranium mole ratios varying from 4 to 8. At each wavelength recorded, optical density plots showed a break at amine:uranium = 6. The absorption of solutions containing less than one uranium per six amines (0.1 M amine) obeyed Beer's law with respect to uranium concentration. At amine: uranium = 6, the spectrum showed a broad maximum at 426 mμ, molar extinction coefficient 23. At amine:uranium = 2 (extracted from hydrolyzed uranium solution) the maximum was shifted to 445 mμ and increased to a molar extinction coefficient of 96. These measurements will be continued as time permits. In addition, preliminary tests indicate that IR and UV spectrophotometry may be useful.

Colligative Properties. Di-n-decylamine (basic form) depressed the freezing point of benzene to the extent expected for monomeric molecules in true solution. The amine sulfate did not measurably affect the freezing point, indicating polymerization although the solubility of the amine sulfate in benzene at low temperature is so low as to impair the sensitivity of the test. Differential vapor pressure measurements (25°C) were not reproducible under the test conditions used but appeared to suggest that polymerization occurred only in the presence of water. Isopiestic vapor pressure determinations are in progress; equilibrations of di-n-decylamine sulfate/benzene with amine (basic form)/benzene at 25°C showed molality ratios (amine sulfate):amine = 5-6. Assuming ideal behavior, this suggests amine sulfate aggregates averaging 5-6 sulfate molecules.

Solids Prepared from the Organic Phase. Benzene solutions of di-n-decylamine and amine sulfate were submitted for electron microscopy.* It was reported that dried films of the amine sulfate solutions gave definite indication of 300-600 Å colloidal particles, and shadowing showed spheroid particles in the film. Dried films of the (basic form) amine solutions did not indicate colloidal particles.

X-Ray diffraction patterns were measured of solids obtained by slow evaporation of diluent (benzene, chloroform, carbon tetrachloride) from solutions of di-n-decylamine, amine sulfate, amine bisulfate, and amine sulfate-uranium at or near amine:uranium = 6. Reproducible characteristic patterns were given by the solids from the amine, sulfate, and bisulfate solutions. Solids from the uranium-bearing solutions did not give reproducible patterns; the cause of the variations has not been determined. In spite of the variations, these patterns did show some general conformity, and they can be differentiated from the amine and amine salt patterns.

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*Examined by T. E. Wilmarth, Analytical Division.

## PUBLICATIONS IN OPEN LITERATURE

Efforts on the open publication of information previously restricted to AEC standard distribution have progressed fairly well during the last year. A list of recent papers either (1) already published in the open literature, (2) accepted for publication, or (3) about to be submitted is given below. Numerous potentially publishable articles are still to be prepared and it is intended that the effort spent on this type of reporting will be increased during the next year. In addition to the fundamental studies, papers on process and systematic studies will be prepared as permitted by the recent change in classification policy.

### A. Papers Published

1. J. M. Schreyer and C. F. Baes, Jr., "Volumetric Determination of U(VI) in Phosphate Solutions," Anal. Chem. 25, 644 (1953). (Based on ORNL-1292)

2. J. M. Schreyer and C. F. Baes, Jr., "The Solubility of Uranium(VI) Orthophosphates in Phosphoric Acid Solutions," J.A.C.S. 76, 354 (1954). (Based on ORNL-1578)

   a. Also presented at the Southeastern Regional Meeting, ACS, Birmingham, Alabama, October 1954.

3. J. M. Schreyer, "The Solubility of Uranium(IV) Orthophosphates in Phosphoric Acid Solutions," J.A.C.S. 77, 2972 (1955). (Based on ORNL-1747)

   a. Also presented at the Southeastern Regional Meeting, ACS, Birmingham, Alabama, October 1954.

### B. Papers Accepted for Publication

1. J. M. Schreyer and L. R. Phillips, "The Solubility of Uranium(IV) Orthophosphates in Perchloric Acid Solutions," (Paper No. 218 at the Nuclear Engineering and Science Congress, Cleveland, Ohio, December 1955). (Based on ORNL-1898)

2. C. F. Baes, Jr., "A Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solution," (Paper No. 219 at the Nuclear Engineering and Science Congress, Cleveland, Ohio,

December 1955). (Based on ORNL-1577 plus another report not yet issued)

3. C. F. Baes, Jr., "The Extraction of Iron(III) from Acidic Sulfate Solutions by Di-n-decylamine Sulfate in Benzene," (Paper No. 220 at the Nuclear Engineering and Science Congress, Cleveland, Ohio, December 1955). (Based on ORNL-1930)

4. C. A. Blake, K. B. Brown, D. G. Hill, R. S. Lowrie, J. M. Schmitt, "Studies in the Carbonate-Uranium System," (Paper No. 221 at the Nuclear Engineering and Science Congress, Cleveland, Ohio, December 1955). (Based on Y-673, -678 and -794)

5. C. F. Baes, Jr., "The Reduction of Uranium(VI) by Iron(II) in Phosphoric Acid Solutions," (Paper No. 224 at the Nuclear Engineering and Science Congress, Cleveland, Ohio, December 1955). (Based on ORNL-1581)

6. J. M. Schreyer and C. F. Baes, Jr., "The Solubility of U(VI) Phosphates in Perchloric Acid Solutions," J. Phys. Chem. (Based on ORNL-1579)

7. K. A. Allen, "The Equilibrium Between Tri-n-octylamine and Sulfuric Acid," J. Phys. Chem. (Based on ORNL-1977)

8. K. A. Allen, "An Inexpensive Microtitrator," Anal. Chem.

## C. Papers About to be Submitted

1. R. A. Zingaro, "The Reaction of Uranyl Ion with Xanthates and Diethyldithiocarbamate," (to J.A.C.S.). (Joint contribution from Texas A&M and ORNL)

2. K. A. Allen, "An Automatic Micro-Oxidimetric Analytical Method for Uranium," (to Anal. Chem.).

## PUBLICATIONS IN PROJECT LITERATURE

Project publications by the Raw Materials Chemistry Section at the Oak Ridge National Laboratory since 1951 are listed below. Previous publications have been listed and described in ORNL-1203.


1. "Progress Report - Materials Chemistry Division, April 1, 1951 to June 30, 1951," Oak Ridge National Laboratory - Y-12, Y-796, August 10, 1951.

2. "Progress Report - Materials Chemistry Division, July 1, 1951 to September 30, 1951," Oak Ridge National Laboratory - Y-12, Y-827, November 16, 1951.

3. K. B. Brown, "A Bibliography of Reports Issued by the Uranium Raw Materials Group at Oak Ridge National Laboratory," Oak Ridge National Laboratory, ORNL-1203, January 14, 1952.

4. "Progress Report - Uranium Chemistry of Raw Materials Section, October 1, 1951 to December 31, 1951," Oak Ridge National Laboratory, ORNL-1220, January 25, 1952.

5. Spivey, E. Virginia, J. G. Moore and C. F. Coleman, "Anion Exchange Sorption of Uranium from Acid Solutions: Phosphate-Sulfate and Phosphate-Nitrate," Oak Ridge National Laboratory, ORNL-1264, April 9, 1952.

6. Schreyer, J. M. and C. F. Baes, Jr., "The Volumetric Determination of Uranium(VI) in Phosphate Solutions," Oak Ridge National Laboratory, ORNL-1292, May 7, 1952.

7. "Progress Report - Uranium Chemistry of Raw Materials Section, January 1, 1952 to March 31, 1952," Oak Ridge National Laboratory, ORNL-1308, May 23, 1952.

8. "Progress Report - Uranium Chemistry of Raw Materials Section, April 1, 1952 to June 30, 1952," Oak Ridge National Laboratory, ORNL-1384, October 23, 1952.

9. "Progress Report - Uranium Chemistry of Raw Materials Section, Part I. Uranium from Lignites, July 1, 1952 to September 30, 1952," Oak Ridge National Laboratory, ORNL-1446, November 13, 1952.

10. "Progress Report - Uranium Chemistry of Raw Materials Section, Part II. Studies in Uranium Chemistry: Solvent Extraction, July 1, 1952 to September 30, 1952," Oak Ridge National Laboratory, ORNL-1480, December 6, 1952.

11. C. F. Coleman, "Memo to G. H. Clewett, subject: Extraction of Uranium from LZ Nitric Acid Leach Liquor," Oak Ridge National Laboratory, Y-B34-3, January 12, 1953.

12. C. F. Coleman, "Recovery of Uranium as a Single Product from the Florida Leached Zone," Oak Ridge National Laboratory, ORNL-1500, March 31, 1953.

13. "Progress Report - Uranium Chemistry of Raw Materials Section, Recovery of Uranium from Lignites, October 1, 1952 to March 31, 1953," Oak Ridge National Laboratory, ORNL-1569, June 1, 1953.

14. C. F. Baes, Jr., "The Reduction of Uranium(VI) by Ferrous Iron in Phosphoric Acid Solution: The Formal Electrode Potential of the U(IV)/(VI) Couple," Oak Ridge National Laboratory, ORNL-1581, June 19, 1953.

15. Baes, C. F., Jr., J. M. Schreyer and J. M. Lesser, "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part I, A Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solution," Oak Ridge National Laboratory, ORNL-1577, June 22, 1953.

16. Schreyer, J. M. and C. F. Baes, Jr., "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part II, The Solubility of Uranium(VI) Orthophosphates in Phosphoric Acid Solutions," Oak Ridge National Laboratory, ORNL-1578, June 30, 1953.

17. Coleman, C. F., F. A. Schimmel and K. B. Brown, "Memo to G. H. Clewett, subject: A Process for Uranium as a Single Product from LZ Ore Using Minimum Sulfuric Acid: A Preliminary Cost Estimate," Oak Ridge National Laboratory, CF-53-6-176, June 30, 1953.

18. Baes, C. F., Jr., and J. M. Schreyer, "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part III, The Solubility Behavior of $UO_2HPO_4 \cdot 4H_2O$ in Perchloric Acid Solutions," Oak Ridge National Laboratory, ORNL-1579, July 1, 1953.

19. K. B. Brown, paper on "Solvent Extraction Reagents," Feed Materials Process Development Meeting, Cincinnati, Ohio, December 9-10, 1954.

20. Brown, K. B., C. F. Coleman, D. J. Crouse, J. O. Denis and J. G. Moore, "The Use of Amines as Extractants for Uranium from Acidic Sulfate Liquors: A Preliminary Report," Oak Ridge National Laboratory, ORNL-1734, May 27, 1954.

21. J. M. Schreyer, "The Chemistry of Uranium(IV) Orthophosphate Solutions: Part I, The Solubility of Uranium(IV) Orthophosphates in Phosphoric Acid Solutions," Oak Ridge National Laboratory, ORNL-1747, June 17, 1954.

22. K. B. Brown, "Memo to G. H. Clewett, subject: Status of the Research Program for Uranium Chemistry of Raw Materials," Oak Ridge National Laboratory, CF-54-12-6, December 2, 1954.

23. K. B. Brown, paper on "Uranium Raw Materials," Laboratory Directors Meeting, Oak Ridge National Laboratory, April 26-27, 1954.

24. Crouse, D. J. and J. O. Denis, "The Use of Amines as Extractants for Thorium (and Uranium) from Sulfuric Acid Digests of Monazite Sands," Oak Ridge National Laboratory, ORNL-1859, February 1, 1955.

25. Schreyer, J. M. and L. R. Phillips, "The Chemistry of Uranium(IV) Orthophosphate Solutions: Part II, Investigations of Solubility Equilibria of Uranium(IV) Orthophosphates in Perchloric Acid Solutions at 25°C," Oak Ridge National Laboratory, ORNL-1898, April 28, 1955.

26. Blake, C. A., K. B. Brown and C. F. Coleman, "The Extraction and Recovery of Uranium (and Vanadium) from Acid Liquors with Di(2-ethylhexyl)phosphoric Acid and Some Other Organophosphorus Acids," Oak Ridge National Laboratory, ORNL-1903, May 13, 1955.

27. Moore, J. G., K. B. Brown and C. F. Coleman, "Further Studies of Amines as Extractants for Uranium from Acid Sulfate Solutions," Oak Ridge National Laboratory, ORNL-1922, June 24, 1955.

28. C. F. Baes, Jr., "The Extraction of Iron(III) from Acidic Sulfate Solutions by Di-n-decylamine Sulfate in Benzene," Oak Ridge National Laboratory, ORNL-1930, July 25, 1955.

29. Blake, C. A., K. B. Brown and C. F. Coleman, "Solvent Extraction of Uranium (and Vanadium) from Acid Liquors with Trialkylphosphine Oxides," Oak Ridge National Laboratory, ORNL-1964, August 26, 1955.

30. Crouse, D. J. and K. B. Brown, "Amine Extraction Processes for Uranium Recovery from Sulfate Liquors," Oak Ridge National Laboratory, ORNL-1959, September 30, 1955.

31. K. A. Allen, "The Equilibria Between Tri-n-octylamine and Sulfuric Acid," Oak Ridge National Laboratory, ORNL-1977, September 30, 1955.

## REPORTS IN PREPARATION

In Memorandum CF-54-12-6,[1] descriptions and abstracts were given for a number of reports which were being prepared and had not been issued. Most of these, as well as some others, have now been published and are included in the listings above. The status of those reports which were listed in CF-54-12-6 but which are not yet published is described briefly below. (In addition to these, reports in preparation on other projects are mentioned in the narrative section of this report.)

A) The status of each of the following reports is essentially the same as outlined previously in Memorandum CF-54-12-6.

   1) Slurry Extraction of Leached Zone Ore (CF-54-12-6, No. 4, p. 4).

   2) Sulfuric Acid Leaching of Leached Zone Ore Types (ibid., No. 9, p. 8).

   3) Alkaline Leaching of Leached Zone Ore Types (ibid., No. 10, p. 9).

B) Preparations of the following reports are in progress. The first report listed will probably be issued in several separate volumes covering different classes of compounds studied.

   1) Survey of Organophosphorus Compounds (and Other Compounds) as Extractants (CF-54-12-6, No. 1, p. 2).

   2) Uranium from Lignites (ibid., No. 11, p. 9).

   3) Potentiometric Studies of Uranyl Phosphate Complex Formation in Perchloric Acid Solutions (ibid., No. 13, p. 11).

C) The following projects are briefly described in narrative fashion in this report and are to be described in greater detail in subsequent progress reports. Also, summary reports on some of the topics (3, 4, and 5) are in draft form and will be issued soon.

   1) Vanadium Extraction with Amines (CF-54-12-6, No. 7, p. 6).

2) Fundamentals of Uranium Extraction by Secondary Amines (ibid., No. 19, p. 14).

3) Fundamentals of Acid Extraction by Secondary Amines (ibid., No. 20, p. 15).

4) Uranium(VI) Solubilities in Alkaline Orthophosphate Systems (ibid, No. 16, p. 13).

5) Further Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solution (ibid., No. 12, p. 10).

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