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PROGRESS REPORT ON RAW MATERIALS

FOR JANUARY, 1957

K. B. Brown
C. F. Coleman
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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS

FOR JANUARY, 1957

Chemical Development Section C
K. B. Brown, Section Chief

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D. J. Crouse
A. D. Ryon

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ABSTRACT

This initial report serves to identify and describe many of the various activities which will be covered in the monthly status report series. The necessary background information is summarized briefly, with references to the pertinent reports and publications.

1.0 INTRODUCTION

The work on uranium raw materials was started in the Oak Ridge National Laboratory approximately ten years ago with studies on methods for the extraction of uranium (and by-products) from domestic ores. The major portion of the Laboratory's effort on raw materials has continued to be concerned with these sources. Although recovery from low-grade oil shales, lignites, and phosphate rock has been investigated, current studies are being directed toward the commercial-grade domestic ores and ores of similar grade from other countries. A large part of the recent work has been on the origination and development of solvent extraction processes for recovering uranium, thorium, vanadium, and possibly other by-products from these ore leach liquors and slurries. Considerable interest in this work has been evidenced by the metallurgical industries, and, after further examination by the mill operators, processes developed at ORNL have been placed in commercial operation in some mills, and several others are in the design stage.

In view of the rapid expansion that is taking place in the milling industry, and the interest in ORNL developments as a possible guide to improved uranium metallurgy, monthly progress reports are planned to make experimental results available as rapidly as possible. This document contains information that is old to some readers, the subject having been reported at intervals during the past several years. However, in initiating a new series it was felt best to orient the reader by background information and descriptions of the various phases of the raw materials program at ORNL. A bibliography of previous ORNL reports in the raw materials field is included. When possible the source (e.g., Office of Technical Services, OTS) and price of these documents are

given. In some cases arrangements for public sale have not been completed, but it is hoped that this will be accomplished soon. This and subsequent progress reports will also be available for sale by OTS.

Material covered in the future will include all the direct raw materials studies carried out at the Laboratory, both fundamental and applied. As indicated above, solvent extraction studies comprise most of the current work. However, studies outside this field have been conducted in the past and will undoubtedly be included in the future.

2.0 ORGANONITROGEN EXTRACTION PROCESSES

Investigation and evaluation of organonitrogen compounds as solvent extraction reagents for uranium have been underway at this laboratory since early 1952. (2-6,8,10) The primary objective of this work has been the practical application to large-scale recovery of uranium from aqueous solutions, especially acidic sulfate solutions of the type encountered in ore leaching. Screening of some 200 organonitrogen compounds of a variety of types, followed by systematic testing of the extraction behavior of those which were able to extract uranium (see below), disclosed a number of long-chain amines suitable for such use.

The more favorable of those compounds were then studied in a laboratory-scale process development program, and amine extraction (Amex) processes were developed for recovery of uranium, thorium, and vanadium and for the separation and recovery of uranium-thorium and uranium-vanadium occurring together. Testing of these processes has been carried through the stage of continuous countercurrent operation in the chemical laboratory with respect to chemical and operating variables, and some of them have been studied in the engineering laboratory for process design and scale-up.

2.1 Amex Process for Uranium

In this process, selected long-chain amine reagents, dissolved in a hydrocarbon diluent, are used to extract uranium from the aqueous liquor. In most cases, kerosene, or kerosene modified with a small percentage of a long-chain alcohol, has proved to be a suitable diluent. Various methods have been developed for stripping uranium from the organic extract. For example, neutral or acidic salt solutions (chloride or nitrate) and solutions of sodium carbonate have proved to be useful stripping agents. In addition, uranium may be precipitated directly from the organic phase with solutions of sodium or ammonium hydroxide or with a magnesium oxide slurry, use of the latter being preferred because of superior physical performance. Chemical reagent costs for the process are attractively low.

With a variety of extractants and stripping methods to choose from, Amex offers an extremely versatile operation for application to a wide range of aqueous liquors. Studies have shown a strong correlation between the type and structure of the particular amine compound used and its ability to extract uranium selectively in preference to other metals in the liquor. With the more selective compounds, uranium can be effectively separated in the extraction cycle from all the common metal contaminants except molybdenum. Molybdenum can be separated in the stripping cycle or in subsequent precipitation operations. Under certain conditions molybdenum can cause precipitation of the amine reagent in the extraction or chloride stripping cycle. This effect can be alleviated by proper choice of the amine-diluent combination.

Descriptions of the laboratory-scale batch and countercurrent studies are presented in ORNL-1734, -1914(Del.), -1922, -1959, -1970(Del.), -2025, -2026, -2034, -2035, -2099, -2112. Engineering studies of scale-up factors for the Amex process have been made and extrapolated to the design of a full-scale plant (ORNL-1949). Eldorado Mining and Refining Ltd. of Canada has evaluated the process both in the laboratory and in a pilot plant at their Port Radium mill, and a full scale Amex installation at Port Radium is planned. Other studies on laboratory or pilot scale are being conducted at other installations, including Rohm and Haas Company, National Lead Company of Winchester, Mass., and Grand Junction, Colo., the Bureau of Mines at Salt Lake City, and Columbia University. At least one commercial domestic installation is planned.

2.2 Amex Process for Vanadium

Under the proper conditions the amines may also be used for the extraction and recovery of vanadium from sulfate liquors. Vanadium(IV) is not extracted to a useful extent but vanadium(V) is extracted efficiently at relatively high pH levels, i.e., 1.8-2.5. Stripping is readily accomplished with alkaline solutions, from which vanadium product is recovered by conventional precipitation methods.

When uranium is present in the liquor a number of process paths are possible to recover both elements separately. Both one- and two-cycle extraction processes have been developed, but present results favor the latter approach.

The vanadium Amex processes have been subjected to continuous countercurrent bench-scale testing. Engineering studies have not been conducted as yet.

Brief descriptions of the experimental studies have been included in ORNL-1734, -CF-54-12-6, -1959, -1970(Del.), -2002, -2099, and -2112. Topical reports giving a detailed account of the studies will be prepared.

2.3 Amex Process for Thorium

The extraction of thorium from sulfate solutions by amines has been shown to be strongly dependent on the amine type and structure. Owing to this wide diversity in the thorium extraction performance of the various amine types, all of which are favorable uranium extractants, Amex offers a versatile method for separating uranium from thorium and recovering these two elements separately from sulfate liquors in which they co-exist.

To date this separation has been of little concern in the Western milling industry, since the known occurrence of appreciable amounts of thorium in domestic uranium ores is relatively rare. In Canada, however, large bodies of uranium-thorium ores have been found, and are being processed, in the Blind River District. At present, no provision has been made for recovering thorium. Thorium extraction studies thus have been directed toward treatment of liquors similar in composition to those produced at Blind River. Depending on choice of amine, either the uranium or the thorium may be extracted first. For selective uranium extraction, the tertiary amines give best performance, although it can also be effectively separated from thorium with certain highly branched secondary amines. Following uranium removal, the thorium can be easily recovered with an amine of high thorium extraction power. Of the amines examined thus far, di(tridecyl P)amine appears to be the most suitable for the thorium recovery cycle. Removal of thorium from the liquor by selective thorium extraction prior to uranium removal has also been studied and found feasible. Primary amines are suitable for this purpose.

Most of the reagents that have proved useful for stripping uranium, e.g., chloride, nitrate, and carbonate, are also applicable for stripping thorium. Data on extraction of thorium and on the separation of uranium and thorium with various amines are given in ORNL-1734, -1922, and -2173. The use of the Amex process for separation and recovery of uranium and thorium from a liquor similar to those obtained at Blind River has been demonstrated in small-scale continuous countercurrent equipment. Data on this run and on batch thorium stripping tests are described in ORNL-2173. Larger-scale evaluations of the Amex process for thorium recovery will be made later.

Thorium and Uranium from Monazite Liquors. A process has been developed through bench scale for solvent-extraction recovery of thorium and uranium from sulfuric acid digests of monazite sands with amine extractants. Thorium is extracted from the liquor by a primary amine dissolved in kerosene diluent. Effective separation of thorium from uranium, rare earths, and phosphate has been demonstrated. Contamination is limited by loading the organic extract to near saturation with thorium. As explained in the previous section, chloride,

nitrate, and carbonate solutions effectively strip the extracted thorium. Following thorium removal from the liquor, the uranium is extracted with a tertiary or secondary amine. The rare earths can then be extracted with a primary amine, thereby separating them from phosphate and certain other contaminants in the liquor, or can be precipitated directly as phosphates by addition of a base.

Preliminary tests on the process were described in ORNL-1859. Batch tests which define the expected operation in the uranium and rare earth extraction cycles have since been completed, and the thorium recovery cycle has been studied on a continuous countercurrent basis. Further tests are in progress.

2.4 Scavenging of Iron from Beryllium Solutions

Results on extraction of iron(III) and beryllium from sulfate solutions with amines suggest that the Amex process might be a useful, inexpensive method for removing iron from beryl sulfuric acid digests prior to precipitation of beryllium (ORNL-1959). A primary amine or one of the less selective secondary amines, e.g., di(tridecyl P)amine, should be a suitable extractant. Process possibilities are being studied briefly.

2.5 Extractions from Alkaline Solutions

Besides the major interest in recovery of uranium and allied metals from acidic sulfate solutions, attention is also being given to other systems. Promising preliminary results have been obtained with certain quaternary ammonium compounds as extractants for uranium(VI) from carbonate solution (ORNL-1922, -2099). The same reagents are being explored for use in extracting and separating other values from alkaline solutions.

3.0 ORGANOPHOSPHORUS EXTRACTION PROCESSES

Since early 1951 there has been interest at Oak Ridge National Laboratory and at other AEC installations in the use of organophosphorus compounds in solvent extraction systems for recovering uranium and other metals from acid liquors, especially those encountered in ore processing. (1-3, 7, 9) This, of course, was in addition to the well established uses of tributyl phosphate (TBP) in other uranium processing operations. The particular organophosphorus reagents developed for process use at ORNL were selected from hundreds of reagents of many types tested in a program of systematic evaluation (Sec. 4.0).

3.1 Dapex Process for Uranium

The extractant in the Dapex process is a solution of a selected dialkylphosphoric acid in a suitable diluent, usually

the commercially available di(2-ethylhexyl)phosphoric acid in kerosene. Uranium is stripped from the pregnant extract with solutions of sodium carbonate or possibly ammonium carbonate. Concentrated mineral acids might also be used. With alkaline stripping it is advantageous to modify the kerosene diluent to prevent separation of the alkali dialkylphosphate. Several classes of effective modifiers have been found. Some of these depress the uranium extraction power of the extractant, but certain others (see below) produce a large and useful synergistic enhancement of uranium extraction power.

By appropriate adjustment of conditions, the Dapex process can be used to recover uranium from a wide range of aqueous compositions. Since iron(III) is extracted fairly strongly by these reagents, the process liquors are reduced before treatment. Process developments and the influence of significant process variables are discussed in ORNL-1903, -2172, -2213, -2214, and -2215. The work has included laboratory batch tests, laboratory continuous countercurrent tests, and larger scale engineering studies for estimation of equipment requirements, scale-up factors, and costs.

After further examination on the part of mill operators, the Dapex process for uranium is now used commercially in two uranium mills and others are in the design stages. In addition to its application to recovery of uranium from leach liquors, the Dapex method has been used successfully by the Winchester Laboratory for recovery of uranium from sulfuric acid ion exchange (Resin-in-Pulp process) eluates.

3.2 Dapex Process for Vanadium

In addition to uranium recovery, the Dapex process has also been developed for recovery of vanadium. By adjusting the vanadium in the liquor to the tetravalent state, and by using higher reagent concentrations than ordinarily employed in the uranium circuit, effective extractions of vanadium are obtained. Stripping is easily accomplished with dilute sulfuric acid or solutions of a base. Even with acid stripping, alkaline stripping of the solvent is employed as needed to remove other extracted contaminating metals.

The process can be adjusted to the recovery of vanadium from uranium-barren liquors or to the simultaneous recovery of both uranium and vanadium. In the latter case the two metals are co-extracted and are separated in the stripping step. Vanadium is first selectively stripped with dilute sulfuric acid and uranium is stripped subsequently with sodium carbonate.

The Dapex vanadium processes have been tested in continuous countercurrent bench-scale equipment. Engineering studies to establish equipment requirements and operational costs have not yet been conducted.

Brief descriptions of the experimental studies were included in ORNL-1903, -2002, and -2172. Topical reports giving a detailed account of the studies will be prepared.

Independent evaluations of these same reagents for vanadium recovery have been conducted by the Kerr-McGee Oil Industries, and by the Union Carbide Nuclear Company at Rifle, Colorado. Commercial installations are planned.

3.3 Synergistic Reagent Combinations

As indicated above, combinations of dialkylphosphoric acids with certain neutral organophosphorus compounds show much greater uranium extraction power than the acid reagents alone. Since the neutral reagents when used alone extract little uranium from the ordinary sulfate liquor, the extraction power shown by the combination is also much greater than can be accounted for as cumulative extraction power of the components acting separately; hence, the enhancement is ascribed to synergism. The magnitude of the enhancement varies with the neutral compound selected, increasing when combinations with dialkylphosphoric acids are made in this sequence: trialkylphosphates, dialkyl alkylphosphonates, alkyl dialkylphosphinates, and trialkylphosphine oxides. Tributylphosphate and dibutyl butylphosphonate are commercially available.

The high extraction power of synergistic reagent combinations at low uranium levels is useful in continuous countercurrent extraction since it provides more efficient reduction of raffinate uranium level per stage, i.e., lower uranium raffinates can be obtained in a set number of stages, or fewer stages are required to obtain a specified low uranium raffinate. Uranium loading from a low-grade aqueous liquor is higher, and the usefulness of the Dapex process is extended to liquors that otherwise might be extremely difficult to extract.

Descriptions of these synergistic systems are reported in ORNL-2002, -2172, and -2259 (in preparation). In view of the success with these particular reagent combinations, studies of other reagent systems are being continued.

3.4 Phosphonates, Phosphinates, and Phosphine Oxides

Apart from their use in synergistic combinations, the phosphonates, phosphinates, and phosphine oxides are useful extractants in their own right. They effectively remove uranium from nitrate and chloride systems of widely varying concentration levels and acidities, from sulfuric acid solutions, and (at least the phosphine oxides) even from sulfate and phosphate solutions if small amounts of chloride or nitrate can be added. In addition to uranium, these reagents have shown versatile extraction behavior with regard to many other elements. Although phosphine oxides are not yet available in commercial supply, applications have already been made with considerable success in the analytical laboratories of ORNL (ORNL-2161, -CF-56-9-18, -CF-57-1-5).

On the assumption that the reagents could be made commercially available in event of a demand, preliminary tests have been made of various process applications. Some of the applications considered have been uranium recovery from nitrate-phosphate fertilizer solutions, green-sludge liquors, high-chloride sulfate leach liquors, and sulfuric acid ion exchange eluates, in lyometallurgical treatment of uranium ores, and in scavenging and salvage operations (Y-B34-3, ORNL-1964, -CF-54-12-6).

The studies of phosphine oxides are described in ORNL-1964. Work is continuing on new reagents in this family and on additional process possibilities.

4.0 SYSTEMATIC STUDIES

The central part of the raw materials chemistry program consists of the systematic study of reactions and reagents which are potentially useful in separations processes. At present, as for the past several years, this part of the program includes principally the search for reagents applicable to liquid-liquid extraction and the determination of their properties and extraction behavior. The most thorough examination is, of course, given to the reagents that show the most promise, first in compiling the data needed as basis for process development and subsequently in continuing support of the development studies. Some of the reagents so selected and studied have already provided a basis for practicable processes, i.e., the Amex and Dapex processes. Attention is also given to reagent types that show unusually high extraction power, even though the particular compounds available may not meet all the other criteria for process use. Very high uranium extraction power has been shown by some N-benzyl branched alkyl amines, by a bis(α -hydroxyalkyl)phosphinic acid, and by the reaction products of P_2O_5 with dialkylphosphoric acids.

Initially, many types of acidic, basic, and neutral organic compounds were screened for their ability to extract uranium from solutions of interest, principally sulfate but with attention also to phosphate, chloride, and nitrate.^(1,2) The results soon led to concentration of attention on three classes of compounds — organophosphorus acids,⁽⁷⁾ neutral organophosphorus compounds,⁽¹¹⁾ and amines.⁽⁴⁾ Some of the compounds tested were standard commercial or specialty chemicals and some were experimental samples furnished by manufacturers, but many not otherwise available had to be synthesized in this laboratory. Intercomparisons of many closely related compounds provided considerable understanding of the dependences of extraction power, selectivity, and amenability to stripping on reagent structure. The important extraction variables were identified and were evaluated over sufficient ranges to permit prediction of process applications. Chemical and physical properties significant to process use

(e.g., stability, compatibility with diluents, distribution to aqueous solutions) were also identified and measured. Special analytical procedures were developed for some of these measurements, as also for assessment of reagent purity. (4,7,11) At present, all aspects of the systematic testing program, from screening of newly available compounds to detailed measurements, are active.

Extractions with the acidic reagents studied usually involve exchange of hydrogen ions for the extractable cations, and show analogies to resinous cation exchange. Extractions with amines show close analogies with (weak base) resinous anion exchange, and these analogies have been useful in describing and even in correlating amine extraction behavior. The increasing understanding of the dependences of extraction behavior on structure of extractant may lead to design of improved ion exchange resins (and perhaps also of some nonionic coordination resins). At the same time there are differences, not only the obvious physical differences inherent in liquid-liquid versus liquid-solid systems but also physicochemical differences (e.g., sharper selectivity for uranium over thorium), by virtue of which the technology of extraction may well prove even more far-reaching than that of resin sorption. While most of the work in this laboratory has been on uranium and associated metals, a small but increasing amount of attention is being given to other aspects of this new technology, e.g., separation of rare earths, hafnium-zirconium, niobium-tantalum, and cobalt-nickel.

5.0 FUNDAMENTAL CHEMISTRY

An important portion of the Raw Materials Laboratory activity is allocated to fundamental chemistry. Many of the systems selected for fundamental study have been selected because of their known or predicted application to problems in raw materials processing. At the same time, these studies are designed and prosecuted so that the information obtained shall constitute a significant contribution to chemical knowledge. The completed results are usually reported by means of articles in the appropriate journals, and also by means of ORNL reports when the more rapid distribution or the inclusion of more detailed data is desired.

Attention has been given to solid-liquid equilibria and to soluble species in aqueous solution in several uranium systems, and, increasingly, to liquid-liquid distributions and study of species in the organic solutions. Solubility and solid-liquid phase studies have included uranyl phosphates in phosphoric acid, (14) perchloric acid, (15) and trisodium phosphate solutions, uranous phosphates in phosphoric acid (16) and perchloric acid, (17) and considerable portions of the systems $UO_3-Na_2O-CO_2-H_2O$ (18) and $ThO_2-Na_2O-CO_2-H_2O$.

The solubility data have provided also some information about complex species in solution, which has been checked and extended by spectrophotometric measurements in carbonate(18) and fluoride(19) solutions and by spectrophotometric(20) and potentiometric measurements in phosphate solutions. Studies of liquid-liquid distribution are also providing some pertinent information about the aqueous uranium(VI) sulfate system. Other studies of soluble species include the redox equilibria of U(IV)/U(VI)-Fe(II)/Fe(III) in phosphoric acid solutions(21) and the sulfuric acid activity coefficients in sulfuric acid-sulfate solutions.

Solvent extraction equilibria are being studied in relatively simple, well-defined systems, including extraction by dialkylphosphoric acid of uranium(VI) from perchlorate(22) and sulfate solutions, and extraction by amines of sulfuric acid(23,24) and of uranium(VI) and iron(III)(23) from sulfate solutions. The equilibria found show association phenomena in the organic phases to be important and give some measure of their nature and extent; this is being studied further by direct physicochemical measurements.

Some of the foregoing studies have provided information of particular significance to analytical chemistry. In addition, in the course of these studies it has been expedient to devise some special analyses, a few of which have been developed to complete analytical methods.(25)

The information obtained from the fundamental chemistry studies has made important contributions to the understanding and optimizing of processing methods, and further need, especially in solvent extraction, is obvious. Of more ultimate importance, these studies of solution phases and interphase equilibria may be expected to combine with the extensive studies of liquid-solid ion-exchange equilibria in providing a better understanding, both theoretical and empirical, of all distribution processes.

6.0 ENGINEERING STUDIES

Geography has precluded pilot-scale activities with uranium ore liquors at ORNL. Consequently, engineering studies(8,9) have been limited to certain unit operations, principally organic-aqueous countercurrent contacting, in order to develop fundamental data for mixing and phase separation and to determine scale-up factors for extrapolation to large-scale operations.(10) Of the various types of extraction equipment that could be used, a simple mixer-settler was chosen for most studies. Some of the reasons for this choice are: (1) low-stage requirements for extraction and stripping in either the Amex or Dapex process; (2) inherent flexibility with wide range of control over mixing and phase separation; and (3) adaptability to very high flow rates as can be encountered in uranium milling.

Of the several types of mixers that have been successfully used in industry, a baffled-tank turbine-agitated mixer was selected because the fluid mechanics are well defined and the small models can be scaled up by direct dimensional and power relations. The dependence of uranium mass-transfer rates on agitator size, agitator speed, and liquid throughput were determined. From these data, mixing requirements (to give greater than 90% stage efficiency) for the Dapex and Amex uranium extraction and stripping systems have been evaluated.

Phase-separation rates were studied in a horizontal gravity-type settler. Two types of phase-separation problems are of concern: (1) achievement of a primary break of the phases, which is the main function of the settlers in the extraction system, and (2) reduction of organic entrainment in the aqueous discard stream, which might best be accomplished in an external settler. Settler capacity requirements for achieving the primary break have been evaluated for various operating conditions expected to be used in Amex or Dapex.

The magnitude of organic loss by entrainment in the aqueous discharge stream has been studied as a function of the type and degree of dispersion and the hold-up times before discard. The results indicate relatively low entrainment losses, contributing only a small increment to the process costs. This should be examined further on a larger scale, and it is desirable that phase separation rates should be evaluated for each installation with the actual liquors to be handled. However, it is encouraging to note that experience to date in large-scale installations corroborates the favorable indications from the small-scale tests.

In addition to the application of solvent extraction to clear liquors, extraction from leach slurries has been investigated. (8) Results with the Dapex process have shown some encouragement, although not enough to recommend its use; reagent losses were excessively high in the Amex process.

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