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A SUMMARY REPORT ON THE ION EXCHANGE
PROCESS FOR THE RECOVERY OF URANIUM

By
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1954

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TOPICAL REPORT ACCO 68

A SUMMARY REPORT ON THE ION EXCHANGE PROCESS FOR THE RECOVERY OF
URANIUM

by

David Kaufman

and

George W. Lower

A B S T R A C T

This report summarizes the development of the ion exchange process for the recovery of uranium from acid and carbonate leach liquors. The historical background of the use of ion exchange for uranium recovery as well as theoretical and practical considerations are covered. Complex ion formation and the adsorption and elution processes are detailed. Factors effecting uranium adsorption and elution as well as a discussion of the effect of extraneous ions are discussed in detail.

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I. Introduction and Historical Background

Existing processes for uranium may be divided into two major groups: (1) acid leaching processes, (2) alkaline leaching processes. As far as the essential elements of these processes are concerned, the alkaline leach processes are simpler. They depend on the fact that uranium forms a strong complex with carbonate which is water soluble. Most of the other elements present in ores will not dissolve in carbonate and the carbonate process, therefore, is quite selective. The uranium can be recovered from the carbonate liquor either by acidification and reneutralization or by the addition of excess caustic which destroys the carbonate complex. However, in a number of ores, particularly those containing primary uranium minerals, the uranium is difficultly soluble in carbonate solution and acid leaching processes were developed for ores of this type.

Acid leaching is relatively unselective, and although uranium extraction into the liquor is generally high, the liquors are highly contaminated with such elements as iron and aluminum. In the past the separation of uranium from other elements in the leach liquor has created certain difficulty. One approach was to pour the acid liquors into carbonate solution to precipitate most of the other metallic constituents as insoluble hydroxides and keep the uranium in solution as the tricarbonat complex. However, the bulky alkaline precipitates tended to carry uranium with them and the uranium in these so-called impurity sludges

represented a serious loss. More recently, selective precipitation processes for uranium from acid solutions were developed. These depended on the fact that uranous phosphate or arsenate is insoluble in liquors which are sufficiently acidic to keep most of the other elements in solution. The main difficulty with the uranous phosphate process was that precipitation of uranium was not complete. If the barren liquors were discarded the uranium contained in them represented a loss which could run as high as 5% or more of the uranium present in the ore. This loss could be avoided by recycle of barren liquors to the leaching circuit but the accumulation of unprecipitated elements caused difficulties.

The use of ion exchange to recover uranium from acid leach liquors provided a selective method which provided almost complete recovery, and, therefore, represented a considerable advance over the chemical precipitation process then in existence. Laboratory studies indicated that the ion exchange process would also have an economic advantage over existing chemical precipitation processes. As a result, ion exchange is now the most popular process under consideration for new uranium recovery plants. At the present time full-scale plants for the recovery of uranium by ion exchange are in existence in the South African Witwatersrand and in the Belgian Congo. Other plants are under construction for the recovery of uranium from Athabaska ore in Canada, Radium Hill and Rum Jungle ores in Australia, and Lukachukai ore in Shiprock, N.M. Other ion exchange plants are being considered for the recovery of uranium from Ute ores at Moab and Monticello, Utah, and sandstone ores from the Grants area in Grants, New Mexico.

The investigation of ion exchange for the recovery of uranium from acid leach liquors was undertaken as early as March, 1945 at the M.I.T. Mineral Engineering Laboratory where the use of cation type resins was investigated. This investigation was undertaken because of the successful application of ion exchange to the separation of rare earths and some fission products under the Manhattan Project. The cation investigations at M.I.T. were stopped in 1946 before a useful process was developed and no reports were published on this early investigation which was undertaken under the direction of Professor R. Schuhmann, Jr. Tests with cation resin were started again in 1948. Work covering the period from September of 1948 to April of 1949 is reported in MITG-A64. It was found that uranium could be adsorbed from acid leach liquors on cation resins, and under the proper conditions, the recovery of uranium could be made quantitative. However, cation adsorption was non-selective. There proved to be relatively little difference in the affinities of the major cation constituents in the solutions for the resin. As a result, in order to obtain complete adsorption of uranium, almost all the cations in solution

had to be adsorbed. The effluent from the cation columns was an acid liquor that could be recycled if the resin was in the hydrogen form initially. The uranium could be eluted either with acid or salt and the eluates could be precipitated with alkali. However, these alkali precipitates had about the same composition as precipitates made directly from the liquor and resulted in no purification of uranium. Further processing of these precipitates was required and thus the process had little advantage over alkaline precipitation processes then in existence. Attempts to obtain selective elution of uranium from cation resin were made but these proved relatively unsuccessful. Ultimately the use of cation resin to adsorb uranium was considered to be impractical economically and experimentation with this process was abandoned.

Other laboratories working under contract with the Raw Materials Division of the Atomic Energy Commission were also testing cation resins with relatively little success. However, in December of 1948 the Battelle Group reported in BMI-JDS 158 that uranium could be adsorbed from artificial sulfate and phosphate solutions on a strong base anion exchange resin, in this case Amberlite IRA-400. This report gave the first indication that uranium could be adsorbed on anion exchange resins from sulfate solutions but the importance of this observation was for a time overlooked. The fact that uranium could be adsorbed from phosphate solutions came as no surprise because the existence of uranium phosphate complexes was well known and they were presumed to be anionic in nature. On January 26, 1949, Mr. John O. Dasher and Mr. N. N. Schiff of the M.I.T. Mineral Engineering Laboratory met with Drs. F. J. Meyers, R. J. Meyers and Robert Kunin of the Rohm and Haas Company in Philadelphia. At this meeting the possibilities of recovering uranium from leach liquors by an ion exchange process were discussed. The main consideration was given to methods of converting uranium into an anionic complex which could be selectively adsorbed. The tricarbonat complex of uranium was known to be anionic and in addition it was thought that complexes with organic acids such as glycolic acid would also be negatively charged. The proceedings of this meeting were reported in a memorandum from Dasher and Schiff to Professor A. M. Gaudin, the M.I.T. Project Director, on February 7, 1949. As a result of this meeting Dr. Kunin and Dr. Paul Klass of Rohm and Haas carried out some work in their laboratories which de-

monstrated that a uranium glycolic acid complex was formed in sulfuric acid solution and could be adsorbed selectively on a strong base anion resin. This work, which was done in February and March of 1949, is described in Rohm and Haas Laboratory Report No. 36-94.

At approximately the same time that Rohm and Haas was carrying out their investigation with complexing agents, the Dow A.E.C. Laboratory in Pittsburgh, California began to work on the adsorption of uranium from wet process phosphoric acid on anion exchange resins. The first developments were reported in Dow-12. In March of 1949 the M.I.T. Mineral Engineering Laboratory also began using anion exchange resins on phosphoric acid solutions. The work at M.I.T. was completed in June of 1949 and reported in MITG-226. Dow continued with their work on the ion exchange process and carried the development to the pilot plant stage. Unfortunately the high acidity and the competition from the high concentration of phosphate in phosphoric acid resulted in the resin having very low capacity for the adsorption of uranium from these liquors. Partly as a result of this fact and partly as a result of the use of very fine resin which presented certain problems in chemical engineering, the pilot plant work indicated that the ion exchange process could recover uranium from phosphoric acid only at high cost, and this process was abandoned in favor of the solvent extraction process now in commercial use.

In spite of the fact that the Battelle report on the adsorption of uranium from sulfate solutions had been issued in December 1948 and the work had presumably been done in November of that year, no other work on the adsorption from sulfate solutions was done for some time. Apparently, the fact that uranium in sulfuric acid liquors could be adsorbed on cationic resin had led to the belief that it was predominantly present in cationic form in these leach liquors and an intensive investigation into the possibility of the existence of anionic sulfate complexes was not undertaken for a number of months following the first report of adsorption of uranium from sulfate solution. Finally, the Battelle Group verified the fact that uranium could be adsorbed from acid sulfate solutions on anion resin and attempted to apply this phenomenon to the adsorption of uranium from liquors produced by acid leaching of shale. The work of the Battelle Group during this period culminate in three reports: BMI-JDS-210, and 210-A on shales, and BMI-JDS-211 on fundamental studies. These reports were issued on September 30, 1949.

The application of ion exchange to the recovery of uranium from shale liquors showed little promise. Shale ores were low in grade - less than .01 % U_3O_8 - and the liquors produced from them usually contained less than 100 milligrams of U_3O_8 per liter. On the other hand, the iron and aluminum content of these leach liquors was relatively high - of the order of 10 grams per liter. The high ratio of other elements to uranium in the leach solution meant that there would be an adverse ratio of competitive anions to uranium and as a result the capacities of resin for uranium adsorbed from shale liquors was relatively low. However, the shale program was abandoned before a true evaluation of the applicability of the ion exchange process could be made.

In December of 1949 work was started on the application of ion exchange resins to the recovery of uranium from Rand liquors. The first stage of this work covering the period from January 10, 1950 to January, 1952, is reported in MITG A-93. This work represents the first promising application of ion exchange to the recovery of uranium from acid leach solutions. The outcome of this work was so successful that it was carried through the pilot plant into the full-scale plant stage and has resulted in the application of ion exchange to acid leach liquors from other ores.

II. THE ADSORPTION OF URANIUM

A. Theoretical Considerations

The first work that was done in connection with the adsorption of uranium on ion exchange resins involved the use of cation exchangers. The fact that uranium could be adsorbed on a cation resin led to the belief that the predominant form of uranium in acid leach liquors was the UO_2^{++} cation. Even the fact that uranium could be adsorbed from shale liquors was not conclusive evidence of the existence of a uranyl sulfate anion complex because the shale liquors were also high in phosphate and it was thought that it was the phosphate complex rather than a sulfate complex that was being adsorbed on the anion resin. It was not until the M.I.T. Laboratory demonstrated that uranium could be adsorbed from Rand liquors which were low in phosphate that the definite existence of a sulfate anion complex could be postulated.

Early attempts made to identify the uranium sulfate complex adsorbed by an anion exchange resin were unsuccessful insofar as they did not identify a definite ionic species. Information reported in Y-721, Dow-57, MITG-428, MITG-108, Y-816, ACCO-1, and CRL-AE-80 describes attempts to determine the charge on the complex by comparing the milliequivalents of uranium adsorbed with the milliequivalents of sulfate adsorbed and, from the equivalent capacity of the resin, establishing the complex charge. From this work it was impossible to do more than reach a general conclusion that probably more than one species of uranium was involved and that the complexes were of the type $[\text{UO}_2(\text{SO}_4)_x]^{2x-2}$ where x is probably either 2 or 3. In 1951 Ahrland reported the existence of neutral, divalent and tetravalent sulfate complexes of uranium in solution. This work was based on both potentiometric and spectrophotometric studies. Ahrland also made some calculations of the equilibrium constants for the reactions involved in the formation of these complexes. Dr. T. L. O'Connor of the Raw Materials Development Laboratory in Winchester, in work reported recently in ACCO-61, definitely established the existence of two uranium complexes on the resin. O'Connor showed that both a divalent and tetravalent complex could be adsorbed in varying ratios, the ratio depending upon the uranium concentration, sulfate concentration and the ratio of sulfate to bisulfate in the solutions. This work which was done in artificial systems showed that the principal uranium species which would be adsorbed from a typical sulfuric acid leach liquor is a tetravalent sulfate complex, $[\text{UO}_2(\text{SO}_4)_3]^{-4}$. From

these adsorption studies, O'Connor was able to determine the relative amounts of the anionic complexes that were present in the solutions from which the uranium was adsorbed, and the equilibrium constants that he was able to calculate were in good agreement with those of Ahrlund.

The fact that uranium can be adsorbed on both anion and cation ion exchange resins can be explained by the existence in solution of at least four forms of uranium all in equilibrium with each other. These forms are: uranyl cation, UO_2^{++} , un-ionized uranium sulfate, UO_2SO_4 , a divalent uranium sulfate complex $[\text{UO}_2(\text{SO}_4)_2]^{-2}$, and a tetravalent uranium sulfate complex $[\text{UO}_2(\text{SO}_4)_3]^{-4}$. The equations for the formation of the complex ions can be written as follows:

It is apparent from the mass action law that the removal of any one species of uranium from the solution would drive the reactions in the direction of forming more of the removed species so that ultimately all of the uranium in the solution would be converted over to the species which was being removed; this accounts for the quantitative removal of uranium by both anion and cation resins. Although no definite rate data for the rate of equilibrium shift have been obtained, it is apparent that this rate is very fast, and other factors, principally the rate of diffusion of uranium through surface films surrounding the resin and the rate of diffusion through the resin itself, rather than the rate of equilibrium shift, are the controlling factors in the rate of adsorption of uranium on ion exchange materials.

B. Factors Influencing the Adsorption of Uranium on Anion Exchange Resins

1. Equivalent Capacity of the Resin

The anion exchange materials used for the adsorption of uranium are stoichiometric. In other words, a fixed weight of resin has a fixed number of exchange positions or sites and for any given exchange material an equivalent weight could be calculated. This means that the maximum amount of uranium that could be adsorbed would be that amount of uranium equivalent to the equivalent weight of the ion exchange material. If the uranium species that is adsorbed is the tetravalent one, then $1/4$ of a mole of uranium could be adsorbed per equivalent of resin. If the species adsorbed were divalent, then the theoretical maximum capacity would be $1/2$ mole of uranium per equivalent of resin. The ion exchange materials which to date have been found most satisfactory for the adsorption of uranium have a theoretical capacity of about 3 milliequivalents per gram. If the adsorption of a tetravalent complex is assumed, then the theoretical maximum capacity for a resin with an equivalent capacity of 3 milliequivalents per gram would be of the order of 180 milligrams of uranium metal per gram of resin. If we assume the adsorption of a divalent complex, then the theoretical capacity of a typical resin would be 360 milligrams of uranium metal per gram of resin. In actual practice both species of uranium are adsorbed so that the theoretical limits would be somewhere between 360 and 180 milligrams of uranium metal per gram of resin. However, from a consideration of other factors which will be described in more detail below, the theoretical capacity limits are never achieved; although in some leach liquors with high uranium concentrations, capacities as high as 300 milligrams of U_3O_8 per gram of resin have been reported.

2. Uranium Concentration

The amount of uranium adsorbed under equilibrium conditions increases rather sharply with increasing solution concentration up to a concentration of about 2 grams of U_3O_8 per liter. Above this concentration the amount of uranium adsorbed increases much less rapidly. In general a plot of the amount of uranium adsorbed as a function of the amount of uranium in solution gives a typical adsorption isotherm. The effect of uranium concentration with other factors constant on the adsorption of uranium on anion resins has been reported in Dow 57 and MITG-108. From an artificial solution containing 1 gram of U_3O_8 and 30 grams of sulfate as magnesium sulfate per liter at pH 1.5, equilibrium capacities for a resin such

as IRA 400 are of the order of 70 grams of U_3O_8 per liter of resin or 210 grams of U_3O_8 per kilo of dry resin are obtained. By increasing the concentration of uranium from 1 gram per liter to 2 grams per liter, with other factors constant, equilibrium loading is increased by approximately 20%.

3. Sulfate Concentration

Uranium adsorption is a function of sulfate concentration. This is to be expected because of the dependence of the type of uranium anion formed in solution on the amount of sulfate that is present and on the uranium to sulfate ratio.

When the resin is in the chloride form and the concentration of sulfate in solution is equivalent to that of uranium, assuming a formula of UO_2SO_4 for uranyl sulfate, then an increase in sulfate concentration results in an increase in the amount of uranium adsorbed at equilibrium. However, when the sulfate concentration is sufficiently high with respect to the uranium concentration so that the equivalent ratio of sulfate to uranium is greater than 2 to 1, an increase in sulfate concentration decreases the amount of uranium adsorbed at equilibrium. As the ratio of sulfate to uranium increases above 2 to 1, initially there is a sharp decrease in uranium capacity with increasing sulfate. With a solution containing about 1 gram U_3O_8 per liter this sharp decrease continues until the sulfate concentration has reached about 30 grams per liter. Above this concentration of sulfate the decrease in uranium loading is more gradual. The effect of sulfate on uranium loading is reported in MITG A-97 and MITG A-108. It is shown in these reports that the effect of other cations will influence the effect of sulfate. For example, when sulfate is added as magnesium sulfate with no cations other than uranium and hydrogen present in the solution, the decrease in loading of uranium with sulfate concentrations above 30 grams per liter is gradual. However, when sodium sulfate is added in place of magnesium sulfate the decrease in uranium loading with increase in sulfate continues sharply above 30 grams of sulfate per liter. It is probable that as the sulfate concentration of the solution is increased up to a ratio of 2 equivalents of sulfate for 1 of uranium the first reaction is to increase the concentration of uranium complex anion, thus increasing the amount of uranium that can be adsorbed. Above this ratio, however, the increase in sulfate results in the presence of excess sulfate ions which can compete with the uranium sulfate complex for resin sites. The differences observed when sulfate is added with different cations probably is a result of the effect of the cation on the activity of the disulfate ion.

Sulfate also influences the rate of elution of uranium from ion exchange resins. There, also, the nature of the cation added with the sulfate is of importance. This work, reported in ACCO 59, is recent. It will be discussed in more detail in the section on elution.

4. The Effect of pH

The pH of a leach liquor is an important variable in the adsorption of uranium by anion exchange resins. In general, uranium adsorption increases with increase in pH. This fact is confirmed by data in the following reports: BMI-JDS-211, Dow 57, Dow 42, Dow 73, ACCO 15 and MITG A-96. Most of this work was done with liquors which were varied over the normal pH range that is encountered in solutions of this type. In ACCO 1 and MITG-108 however, studies made with synthetic uranium solutions are reported and with solutions of this type it was possible to study the pH range from zero to the point of precipitation of the uranium at approximately pH 6.5. These studies with synthetic solutions showed that uranium adsorption increases sharply with increasing pH up to a pH of approximately 3.5. Above this pH value, adsorption increased very slowly and finally reached a plateau which continued until the pH of uranium precipitated.

It would appear from the synthetic solution studies that a pH of 3.5 would be optimum for uranium adsorption. However, with actual leach liquors the optimum pH for uranium adsorption depends upon a number of factors. These solutions normally contain some arsenate or phosphate which cause the precipitation of certain heavy metals at relatively low pH values. When the pH of a solution is raised to a point where a precipitate forms, it has been found by experience that some uranium may be carried down by this precipitate. As a rule, therefore, it is necessary to keep pH values sufficiently low to prevent precipitation of hydrolyzable salts.

The ferric iron concentration in the leach liquor also influences the optimum pH for uranium adsorption. Ferric sulfate, like uranium, can be adsorbed as an anion complex. The equilibrium adsorption of ferric iron complex also increases with increase in pH. However, its rate of increase is greater than that of the uranium. Therefore, in some solutions high in ferric iron, increase

in the pH of the solution may give little or no increase in uranium loading because the competition from iron will be increased. Because of the adsorption of iron, the grade of the final precipitate obtained after the iron and uranium are removed from the resin and precipitated will be low in grade. In general, pH values between 1.3 and 1.5 have been found to be satisfactory on a large number of different acid leach liquors. However, it is desirable to make an evaluation of the effect of pH on any particular liquor because in exceptional cases the ion exchange process can be operated at higher pH values with profit.

The effect of pH on uranium adsorption can be correlated with the effect of pH on the shift in the sulfate-bisulfate equilibrium. In solutions of low pH most of the sulfate in the solution is present in the form of bisulfate. An increase in the bisulfate concentration has two effects as far as the adsorption of uranium is concerned. First, as described above under the effect of sulfate concentration, in the concentration ranges that normally exist in leach liquors bisulfate has a greater affinity for the resin than does sulfate and provides greater competition for the uranium. Secondly, a shift in the sulfate-bisulfate equilibrium toward the formation of bisulfate results in a decrease in the amount of sulfate available to form the uranium sulfate complex. In solutions of high pH value the reverse situation is true and most of the sulfur present in the solution is present as sulfate. The sulfate ion causes less competition with uranium than the bisulfate and the presence of a sufficient quantity of free sulfate to form the uranium complex assists in its formation. Both factors lead to an increased adsorption of uranium.

5. The Effect of Oxidation State

The oxidation state of a solution is usually determined by a measurement of what is called the oxidation reduction potential. Such measurements are easily made by using a Calomel electrode as one-half of a cell, with the solution acting as the other half. Under these conditions a voltage difference is obtained which can be measured on a potentiometer or millivoltmeter. Oxidation reduction potential measurements are commonly made with ordinary pH meters in which the glass electrode has been substituted by a metallic

electrode, usually of platinum. It has been established (ACCO-60) that from the oxidation reduction potential of the solution in a wide range of types of leach liquors it is possible to predict the valence states of iron, uranium and vanadium, the three most commonly found elements that can be reversibly oxidized and reduced. Fe^{2+} , U^{4+} and V^{4+} are not adsorbed on anion exchange resins from ordinary leach liquors. However, Fe^{3+} , U^{6+} and V^{5+} are strongly adsorbed. When iron and vanadium are present in solution in their higher valence states, they can compete with uranium for the available resin sites and cause a decrease in the uranium capacity of the resin. Pentavalent vanadium represents a special problem in that it is not readily removed by the ordinary eluting solutions used for the removal of uranium, and its presence on the resin interferes with the elution of uranium. As a result, it is almost a necessity for an efficient ion exchange process for uranium recovery for the vanadium to be present in one of its lower valence states. The main effect of ferric iron is that of competition and a considerable amount of ferric iron can be tolerated. However, the less ferric iron present in the solution the higher the uranium loading on the resin, other factors being equal. Fortunately, the potentials of the V^{4+} - V^{5+} , Fe^{2+} - Fe^{3+} and U^{4+} - U^{6+} couples are such that vanadium can be reduced to V^{4+} before any of the uranium is converted to U^{4+} . In fact, V^{5+} can be reduced by Fe^{2+} which in turn goes to Fe^{3+} . Theoretically, all of the Fe^{3+} can be reduced to Fe^{2+} without reducing any U^{6+} to U^{4+} . However, for the reduction of Fe^{3+} more powerful reducing agents such as SO_2 , H_2S or metals such as iron, zinc or aluminum are required. SO_2 has not been found to be a satisfactory reductant because of the tendency to form sulfite complexes which are strongly adsorbed by anion exchange resins and interfere with the adsorption of uranium. The use of H_2S results in the formation of precipitates which would interfere with column operation and are undesirable if columns are used for ion exchange. When sulfur-containing reductants are used there is also some risk of the formation of polythionates which, as will be described later, have been found to be strongly adsorbed anions which compete with uranium for resin positions and may cause other difficulties. Therefore, the most commonly used reductants are metallic and these metals are such powerful reducing agents that if reduction is carried too far, plus four uranium will be produced. Generally it has been found that if the EMF of a liquor is reduced to a potential between -350 and -400 millivolts (the more negative the value the more oxidizing the solution) the bulk of the iron will be in the ferrous state and all of the uranium will still be present

as U^{6+} . Obviously, since ferrous iron will reduce pentavalent vanadium, no V^{5+} can be present in such a solution.

6. The Presence of Other Metallic Anions

a. Iron

It has been stated in many reports, MITG-529, ACCO-3, ACCO-4, MITG A-97 and CRL-AE-101, for example, that while ferrous iron is not adsorbed on strong base anion exchange resins, ferric iron can be adsorbed to an appreciable extent. Data reported in MITG A-97 and ACCO-4 indicate that ferric iron is less strongly adsorbed than uranium and can be displaced by the uranium complex when the resin is loaded to saturation with respect to uranium. Investigators at the Chemical Research Laboratories in Britain report in CRL-AE-101 that the amount of ferric iron that will be adsorbed by the strong base resin such as Amberlite IRA 400 from sulfate solutions at pH 1.8 will be dependent on the magnitude of the ferric iron concentration and on the ratio of the iron and uranium concentrations in the solutions. They suggest that with solutions containing small amounts of uranium and large quantities of ferric iron that the resin initially becomes saturated with the ferric iron complex. The adsorption of uranium then involves the displacement of some of the ferric iron until the equilibrium loading with respect to both iron and uranium from that particular liquor on that particular resin is reached. Because of the necessity of displacing the ferric sulfate complex (which is more tightly held than sulfate) in order to adsorb uranium, the rate of attainment of equilibrium with respect to uranium and iron on the resin from solutions high in iron is slow. In a conventional multicolumn ion exchange system a decrease in rate of adsorption is equivalent to a drop in resin capacity. Consequently, from solutions that are high in iron, the uranium loading that can be obtained in multicolumn operation will be lower. In addition, if the adsorption cycle is stopped before true equilibrium is attained, in other words before the resin is saturated with respect to uranium, the resin will contain more iron and less uranium. It is believed that iron is adsorbed as a ferric sulfate anion complex. Presumably, as with uranium, more than one ferric sulfate complex may be involved. As explained above under "the Effect of Oxidation State", the competition from iron can be removed by reducing it to the ferrous state. Such reduction is usually accomplished by the addition of metallic iron or metallic aluminum to the leach liquor.

b. Vanadium

It has been reported in Dow 34 and Y-816 that pentavalent vanadium can be adsorbed strongly on ion exchange resins. It was also established that V^{+4} was not adsorbed. As described under "The Effect of Oxidation State", vanadium present in large concentrations in the pentavalent state constitutes an interference in the adsorption of uranium from solution. Present in only small amounts, pentavalent vanadium causes relatively little difficulty, because small amounts of vanadium can be removed from the resin by the normal eluting solution and the only effect of the adsorbed vanadium is to contaminate the final product. When large amounts of vanadium are adsorbed, the capacity of the resin for the uranium is lowered and the uranium is difficult to remove from the resin during elution. It is possible to remove adsorbed vanadium by passing an SO_2 solution over the resin. Most of the uranium will remain behind on the resin during this treatment. A process for the recovery of vanadium itself by means of ion exchange has been applied to uranium barren solutions. The liquor which is in the reduced state is oxidized with sodium chlorate, and the oxidized vanadium is then adsorbed preferably at elevated temperatures. The recovery of vanadium by an ion exchange process is described in ACCO 7, ACCO 53 and ACCO 63.

c. Miscellaneous Metallic Ions

1. Thorium is reported to be adsorbed along with uranium (BMI 242). In this connection it has been observed in the Winchester Laboratory that there is an increase in the beta count of barren effluents up until the point where uranium starts to break through. It is possible that this increase in beta count is the result of the displacement of UX_1 and UX_2 , isotopes of protoactinium and thorium, which were originally adsorbed on the resin and then displaced by the uranium.

2. Antimony

It is reported in MITG-525 that antimony is adsorbed on ion exchange resins. It is quite possible that antimony is precipitated rather than adsorbed as antimony tends to hydrolyze readily from acid solution.

3. Aluminum

It is reported in ACCO 1 and MITG A-97 that aluminum is adsorbed in small amounts by anion exchange resins. However, it has also been found that aluminum is always present as a constituent in new resin. It appears likely that the aluminum found on the resin was either already present or resulted from improper washing of aluminum bearing solutions from the resin. No evidence for the existence of aluminum sulfate anionic complexes in solution exists.

4. Manganese

It is reported in MITG A-97, ACCO 3 and ACCO 12 that manganese in the divalent form is not adsorbed. Permanganate is adsorbed on anion exchange resins but is immediately reduced to MnO_2 by the organic matter of the resin and is precipitated within the resin structure. The resin turns brown and shows little capacity for other ions until the brown color is removed by passing a reducing solution such as SO_2 through the resin bed.

5. Chromium

Chromium in the trivalent form is not adsorbed as reported in ACCO-3 and ACCO-12. However, chromium can be adsorbed as chromate in significant amounts as reported in ACCO-1.

6. Cobalt

Cobalt $^{+2}$, as reported in ACCO 3 and 12, is not adsorbed on the resin and does not interfere with uranium adsorption.

7. Molybdenum

That molybdenum is strongly adsorbed on anion exchange resins was reported in BMI-JDS-211, ACCO-3 and in unpublished reports of the Vitro Uranium Company in Salt Lake City. Molybdenum is probably adsorbed as the molybdate anion but at least a partial reduction to molybdenum blue, a mixed oxide, occurs when the molybdenum on the resin is exposed to light. This is evidenced by the formation of a blue color which is not found if the resin columns are covered with paper or foil. Molybdenum is quantitatively adsorbed and will displace uranium initially adsorbed on the resin. Molybdenum is not removed in the normal elution procedure for uranium and, therefore, progressively accumulates on the resin, leading to an ultimate decrease in total capacity. The adsorption of molybdenum also appears to have an effect on the rate of adsorption of uranium as well as on the total capacity of the resin for uranium. Molybdenum can be removed from the resin by periodic treatment with 1 Normal sodium hydroxide solution. Information on how to deal with the molybdenum problem is presented in ACCO 35 and ACCO 46.

Up to this time molybdenum has represented a problem only in connection with the recovery of uranium from Marysvale ores. Molybdenum has also been found in leach liquors obtained in the Belgian Congo and in liquors from Utex ore, but the concentrations that appear in these liquors are too small to be of importance.

d. Metal Cyanide Complexes

1. Cobaltous Cyanide

It is reported in CRL-AE-80 that cobaltous cyanide is adsorbed somewhat more strongly than uranium and would represent a competing ion for the available sites on the resin. As such, the presence of cobaltous cyanide at high concentration should decrease the uranium loading on the resin.

2. Cobalticyanide

Cobalticyanide is very strongly adsorbed and can displace uranium from an anion exchange resin as reported in ACCO-3 and -12. Cobalticyanide, once adsorbed, is very difficult to remove and represents a serious problem. This problem will be discussed in more detail later.

3. Zinc Cyanide

The divalent zinc cyanide complex is only weakly adsorbed by anion exchange resins as reported in CRL-AE-80.

4. Copper Cyanide

It is reported in CRL-AE-80 and CRL-21A that divalent copper cyanide anion is strongly adsorbed by the resin. However, this anion is not so strongly adsorbed that it cannot be removed and can be eluted with a solution 1 normal in sodium cyanide.

5. Ferricyanide

It is reported in ACCO 3 and 12 that ferricyanide anion is strongly adsorbed and can displace uranium already adsorbed on the resin.

6. Nickel Cyanide

Nickel cyanide is very strongly adsorbed by IRA 400

resin but unlike cobalticyanide can be partially eluted by 1 normal sulfuric acid solution as reported in GML L-144. Most of the cyanides are decomposed in strong acid and with the exception of cobalticyanide have not represented problems in the ion exchange process for the recovery of uranium.

7. The Presence of Non-Metallic Ions

a. Arsenate

It has been reported in MITG-525 and Dow-38 that arsenic is adsorbed on anion resins. Additional work described in Dow-73 and ACCO-3 showed that arsenic is adsorbed only as the arsenate and that it is not adsorbed if reduced to the arsenite form. Arsenic can combine with certain metallic elements such as iron and uranium to form anionic complexes which, like arsenate itself, can also be adsorbed on the resin.

b. Phosphate

It is reported in ACCO-73 and Dow-15 that phosphate is adsorbed by anion exchange resins. As with arsenate, phosphate may form complex ions with iron and uranium and these complexes may be adsorbed. Data on the adsorption of arsenate and phosphate complexes is meager.

c. Fluorine

Little information is available on the adsorption of fluorine by resin, but data reported in ACCO-4 and Y-816 show that the presence of fluoride ion, or possibly fluosilicate, decreases the adsorption of uranium on resin. It has been demonstrated in Winchester that the addition of sodium fluosilicate to artificial solutions containing uranium will decrease the amount of uranium adsorbed on resin at equilibrium.

d. Silicon

Silicon is usually present in the form of silicate or as colloidal silicic acid in leach liquors, and silicate can be adsorbed by anion exchange resins. The silicate anion is not very strongly held and usually is displaced by other anions in the solution. However, from Rand liquors there is a tendency for the adsorption of silicates in a non-elutable form. This represents a special problem which will be discussed in detail later.

e. Thiocyanate

Thiocyanate ion is strongly adsorbed, perhaps more strongly than uranium, as reported in CRL-AE-80. There is some evidence for the formation of a uranyl thiocyanate complex which is adsorbed with about the same affinity for resin as the uranium sulfate complex, but is more difficult to elute. Evidence for the existence of a uranyl thiocyanate complex is presented in ACCO-12. Also reported in ACCO-12 are tests in which attempts were made to adsorb cobaltous and ferric thiocyanate on resin. Under the conditions used, very little adsorption occurred and the presence of these complex thiocyanates in solution did not interfere with adsorption of uranium.

f. Chloride

Chloride is not normally present in the majority of acid leach liquors. The adsorption of chloride on the resin follows the mass action law; it shows no unusual affinity for the resin and will be adsorbed if in high concentration in solution and will be displaced by sulfate if sulfate is present in high concentration. The main effect of chloride is on the formation of the uranyl sulfate anion complex. Data reported in ACCO-15, ACCO-3, Y-816 and Dow-57 all confirm the fact that the presence of chloride ion in the leach liquor lowers the uranium adsorption on the resin. If the chloride concentration is of the order of 1 or 2 grams per liter the interference on uranium adsorption is not serious. However, at chloride concentrations above this level, the uranium loading decreases rapidly with increase in chloride concentration. The reason for the marked effect of chloride on the adsorption of uranium is not known. All that can be said is that chloride, when present, provides an unfavorable environment for the formation of the uranyl sulfate complex. If the chloride concentrations become quite high, of the order of 2 molar, then there is a reversal of the effect of chloride on uranium adsorption and the amount of uranium that can be adsorbed begins to increase. In the presence of high concentrations of chloride, uranium is known to form an anion chloride complex. From 6 molar chloride solutions, uranium can be strongly adsorbed on anion exchange resins.

g. Nitrate

Nitrate is similar to chloride in that it shows no unusual affinity for resin, but in relatively low concentrations interferes seriously with the adsorption of uranium from sulfate liquors. If anything, the presence of nitrate is more effective than chloride in decreasing uranium capacity. For example, the presence of 1/10 mole of chloride per liter decreased the saturation loading for uranium by 32% in comparison with a solution of similar composition but containing no chloride. However, the addition of the same concentration of nitrate to this liquor decreased the uranium saturation loading 68%. Unlike chloride, nitrate forms no anionic complex with uranium and there is no adsorption of uranium from solutions of high nitrate concentration.

8. Special Problems in Connection with the Recovery of Uranium From Rand Ores.

The Rand ores are unusual in that they contain gold in addition to uranium. The customary procedure that is followed on the Rand involves removal of the gold first by cyanidation, after which the cyanide residue is leached with acid for the recovery of uranium. The cyanidation process, which is done in dilute alkali, creates certain problems with respect to the recovery of uranium from the acid leach liquors which, to date, have been found to be peculiar to the Rand. During the cyanidation leaching step there is some tendency for pyrite, present to the extent of one to several percent in these ores, to become oxidized probably to thiosulfate or to other partially oxidized sulfur compounds. Also, as a result of the cyanidation step, some of the heavy metals such as iron, cobalt, nickel and copper, etc., may form complex cyanides. Probably the major portion of the oxidized sulfur compounds and the complex cyanides go into solution in the alkaline cyanide liquor and remain with the liquor when the residue is filtered off. However, of necessity, some of the liquor and the constituents in the liquor must accompany the filter cake. When the cyanide residue is subsequently leached with acid and an oxidant, thiosulfates or other partially oxidized sulfur compounds are converted to polythionates. In contact with the acid liquors, most of the metallic cyanide complexes are decomposed, but cobaltcyanide is so stable that it continues to exist even in strong acid

solutions. The presence of these two materials, polythionates and cobalticyanide, in Rand liquors is responsible for most of the difficulties that have been encountered in the recovery of uranium from these liquors by ion exchange. The polythionate compounds, of which tetrathionate is probably the most stable, are strongly adsorbed by the conventional anion exchange resins of the type used for the adsorption of uranium and will displace uranium from the resin. Polythionates are partially removed during the elution process for the recovery of uranium from the resin and the amount of polythionate removed is dependent upon the amount of polythionate present on the resin. Ultimately, an equilibrium point is reached at which the amount of polythionate being removed each cycle is equal to that being adsorbed each cycle and beyond this point there should be no decrease in uranium capacity. However, polythionate represents another ion in competition with uranium for the resin, with the polythionate, for all practical purposes, fixing a certain percentage of the sites on the resin. In the presence of polythionate the resin capacity for uranium is lower. If the only effect of polythionate was a drop in uranium loading on the resin, this would represent only a minor difficulty. However, on the Rand, elution is done with nitrate. Nitrate tends to oxidize polythionate and one of the oxidation products is sulfur. If the nitrate is in prolonged contact with the resin, sulfur deposition occurs and some of this deposition may take place within the resin pores, blocking them and preventing the uranium from having access to adsorption sites. There appears to be an accumulation of sulfur from partial oxidation each cycle until eventually the resin may contain as much as 5% sulfur by weight. Resin blocked with sulfur shows low uranium capacity and slow adsorption rates which, in multiple column operation, cause, in effect, an even greater reduction in capacity. Polythionates can be removed from the resin by prolonged elution with the ordinary nitrate eluting solution, or more readily by elution with 1 Normal nitric acid. Sulfur if deposited can be removed by a treatment with sodium sulfide and sodium hydroxide. Thiocyanate treatment is also effective in removing sulfur. The use of thiocyanate will be discussed in connection with the removal of cobalticyanide.

The polythionate concentration in the leach liquors is of the order of 1/100 molar and polythionate can be destroyed by the use of strong oxidants such as hydrogen peroxide, potassium

permanganate or chlorine. It was found that chlorine gas was particularly effective and quite selective in the removal of polythionate. On certain samples of Western Reef leach liquor which contained polythionate, the addition of 1/2 gram of chlorine gas per liter of solution was sufficient to destroy all polythionate.

There is some accumulation of polythionate in the eluting solution as a result of partial removal from the resin during uranium elution. When the eluting solution is recycled, there is a tendency for some of this polythionate to be readsorbed on the resin. This results in a higher equilibrium concentration of polythionate on the resin than would be present if there was no readsorption from the eluting liquor. It was found that if the eluting solution was acidified and heated to 90°C., the polythionate in the solution could be destroyed in approximately one hour.

Chlorine treatment not only destroys polythionate but also eliminates thiocyanate from the Rand liquor. The presence of thiocyanate does not represent a serious problem. Thiocyanate like polythionate is created as a result of the oxidation of sulfur compounds during the cyanide leach. The main effect of thiocyanate is that it forms a complex with uranium which is more slowly eluted than the uranium sulfate complex. So far, thiocyanate doesn't seem to be a serious problem on the Rand.

Cobalticyanide adsorption represents a problem because the cobalticyanide is so strongly held that the presence of very small quantities of cobalticyanide in the leach liquor eventually results in the accumulation of quite large concentrations on the resin. The amount of cobalticyanide in the liquors from the various Rand uranium plants differs. Samples that have been received at the Winchester Laboratories have varied from a tenth of a milligram to 2 milligrams of cobalt as cobalticyanide per liter. This would appear to be a very small concentration of material to be causing difficulty, but tremendous volumes of liquor pass through the ion exchange columns daily; all of the cobalticyanide present in these liquors is adsorbed and scarcely any of it is removed during the normal elution process. Even with an ion as strongly adsorbed as cobalticyanide, ultimately an equilibrium is reached where the amount removed during ordinary elution is equal to that put on each cycle, but by the time this condition is achieved the uranium capacity of the resin has dropped by 50 %.

Attempts were made to remove the cobalticyanide from solution by precipitation as a copper salt or by adsorption on basic ferric sulfate. To date, no process for the precipitation

of cobalticyanide from solution has been successful. The most effective method to minimize the amount of cobalticyanide adsorbed on the resin has been to improve the washing of cyanide residue as it comes from the gold circuit to remove as much cyanide as possible. The washing step may also be removing some cobalticyanide that may already have been formed during the alkaline leach. On West Rand cyanide residues, additional washing has been successful in reducing the cobalticyanide concentration in the leach liquor from 2 parts per million to approximately 1/10 of a part per million. While cobalticyanide is not removed to any large extent during the normal elution procedure and is scarcely touched by treatments with sodium hydroxide or sodium sulfide, the following fairly drastic treatment has been found to be effective in removing cobalticyanide.

The resin is heated at 80°- 90°C. for several hours in contact with a 1/2 % solution of ammonium thiocyanate. The thiocyanate solution is then removed and the resin is given two successive contacts with 5 % sulfuric acid at 80°C. for 16 to 24 hours per contact. Details of the procedure for the removal of cobalticyanide are described in ACCO 62. The test work indicates that in spite of the high temperature treatment the resin will stand at least one such cobalticyanide removal step without an appreciable loss of resin capacity or uranium adsorption rate.

9. The Effect of Temperature

An increase in temperature increases the rate of adsorption of uranium on an ion exchange resin. In other words, the time required to reach equilibrium between the resin and the uranium sulfate solution is decreased with increase in temperature. However, temperature has no effect on the equilibrium loading. It has been reported in Dow-35, 57, 59 and 73, MITG-429 and MITG A-107 that the operational loadings on ion exchange resin can be increased to some extent by an increase in temperature. The effect of temperature on the operational loading can be explained by the fact that under plant conditions it is rarely possible to allow sufficient time for time equilibrium to be reached. An increase

in the rate of adsorption results in the attainment of equilibrium in a shorter time so that at higher temperatures in a commercial operation, resins would be loaded more nearly to saturation. In general, it appears to be unwise to operate with ion exchange resins of the polystyrene-divinylbenzene type continuously at temperatures above 70°C. At this temperature and above there is some tendency for the resin to soften, become sticky and adhere in clumps. In general, the increase in operational loading that can be achieved by increasing the temperature has not been considered sufficiently large to warrant the expenditure of heating the liquor prior to passage through the ion exchange system. Another factor against the use of temperatures higher than ambient is the potential increase in rate of resin degradation.

10. The Effect of Resin Size

It has been reported in Dow 57, Dow 73, MITG A-96 and ACCO 20 that more rapid exchange rates and higher saturation loading can be obtained with the finer sized fractions of a given resin sample than with the coarser sized fractions. The degree of difference between fine and coarse resin will vary with different resin batches and with different resin types. The increase in rate of adsorption with decrease in resin particle size is easily explained by the greater resin surface that is offered to the solution with the finer resin. The increase in capacity that has been reported may in part be due to rate effects because inadequate time of contact was allowed for equilibrium to be reached with the coarser sized fractions. On the other hand there may actually be a true increase in capacity with finer resin because of the method of resin manufacture. As reported in U.S. 2,591,573 and 2,591,574, ion exchange resins with a polystyrene-divinylbenzene base are made by first forming beads of polystyrene and divinylbenzene by polymerization. These beads are activated by treatment with a chloromethylating reagent and then given exchange properties by reaction with primary or secondary amines, in the case of the weak and intermediate base resins, or with tertiary amines to form the strong base anion exchange resins. The degree of activation, among other factors, will determine the number of exchange sites on a given weight of polymer. With small polystyrene beads it is easier to get complete activation of all of the resin than it is with large sizes which may not be completely activated at the center. However, an attempt to correlate the difference in uranium capacity between large resin beads and small resin beads of the

same type on the basis of the number of exchange groups on the resin showed that the decrease in uranium capacity could not be entirely attributed to the difference in number of exchange groups per unit weight of resin. What factors other than degree of activation that might account for the observed differences in capacity of large size and small size resin beads have not been established.

C. The Adsorption of Uranium From Carbonate Solution

The existence of carbonate complexes of uranium is well known. A rather complete description of these complexes and the conditions under which they exist in solution is presented in reports issued by K. B. Brown and his group at Y-12 in Oak Ridge. The predominant form of uranium in carbonate solution is presumed to be the tricarbonat ion with a -4 charge. Investigators at Battelle reported in BMI-242 that ion exchange resins of the quaternary amine type were effective in adsorbing uranium from sodium carbonate solutions. That the adsorbed species is $(\text{UO}_2(\text{CO}_3)_3)^{-4}$ was indicated in BMI-JDS-209. The British report in CRL-AE-86 that as the free carbonate ion in the solution decreases in concentration, the molar ratio of carbonate ion concentration to uranium concentration in the resin phase approaches 3. This is additional evidence for the existence on the resin of a complex ion of the structure $(\text{UO}_2(\text{CO}_3)_3)^{-4}$. Investigators at Oak Ridge reported in Y-816 that both the tetravalent and divalent carbonate complexes of uranium are adsorbed by anion exchange resins.

In comparison with the amount of information available on the adsorption of uranium on resins from acid systems, the knowledge concerning the effect of variables on the adsorption of uranium from carbonate solutions is meager. Much of the work that is published was done during the early stages of ion exchange development and, therefore, is not too reliable. A reinvestigation of the adsorption of uranium from carbonate solutions in light of present knowledge of the ion exchange process is indicated. What information is available on such factors as the effect of uranium concentration and the presence or absence of other anions, will be reported below.

British investigators reported in CRL-AE-86 that the more dilute the solution the higher the ratio of carbonate to uranium could be without impairing the uranium adsorption. They found that there is a decrease in the equilibrium loading on the resin as the free sodium carbonate in the solution increases, but the effect of increasing carbonate concentration is relatively small. This observation was confirmed by investigators in this country as reported in Y-816. In BMI-242 it is reported that nitrate, chloride, sulfate and phosphate will decrease the amount of uranium that can be adsorbed at equilibrium on the resin, in the order named. It is reported in Y-816 that sulfate, sulfite, fluoride and acetate ions all decrease the adsorption of uranium on ion exchange resins from carbonate solutions. The interference caused by these common mineral acid anions represents one of the major difficulties encountered in attempting to recover uranium from carbonate solutions by ion exchange. Any process for recovering uranium from carbonate solutions must have some provision for recirculating the barren carbonate liquor after the uranium has been removed. Because of this necessity for recycle, constituents that might normally be present in the carbonate liquor in small concentration initially, may ultimately reach high concentrations, if there is no provision for a bleed. Such constituents as nitrate, chloride and sulfate, which may be added to the carbonate liquor during the leaching operation or as a result of contamination of the carbonate solution with the eluting liquors, may build up to sufficiently high concentrations to cause difficulty. That chloride ion seriously interferes with the adsorption of uranium from carbonate solution is reported in ACCO-3, ACCO-8, BMI-JDS-213 and Y-816. Chloride ion may be present in the carbonate leach if the ore has been given a preliminary salt roast for recovery of uranium prior to carbonate leaching. Alternately, if a chloride solution is used to remove uranium from the resin, on subsequent adsorption of uranium from carbonate solution, the chloride on the resin will enter the barren solution. In ACCO-3 nitrate is reported to be a serious interference and in confirmation of the results presented in BMI-242 nitrate is shown to be a more serious contaminant than chloride. ACCO-3 also reports an interference from the presence of sulfate but indicates also that the amount of sulfate that would be added to the carbonate system by the use of sulfate elution can be tolerated. In BMI-JDS 208, 213, 211 and 217 it is reported that the addition of ammonium hydroxide up to concentrations of 1% in carbonate solution decreases the capacity of the resin for uranium. These reports assume that the effect is the

result of an increase in the hydroxyl ion concentration. However, a more complex phenomenon may be involved because an increase in pH of the carbonate liquor increases rather than decreases the adsorption of uranium. According to BMI-JDS 211, phosphate does not inhibit the adsorption of uranium. However, it is stated in BMI-JDS 217 that in the presence of trisodium phosphate in concentrations up to about 1%, there is a decrease in the capacity of the resin for uranium. Above concentrations of 1% the addition of trisodium phosphate appears to have little effect.

The effect of pH is very important in that it effects the ratio of bicarbonate to carbonate in the liquor. The presence of high concentrations of bicarbonate ion seriously lowers the capacity of resin for uranium as reported in BMI-JDS 213, 208 and ACCO 3. In CRLAE-86 it is reported that uranium adsorption dropped sharply when a concentration of sodium bicarbonate greater than .2 moles/L. was present in solution. Up until this concentration of sodium bicarbonate was reached, changes in the bicarbonate concentration had only a negligible effect on uranium loading. It is reported in ACCO 3 that at a pH of 10.5 good adsorption of uranium will occur. However, as the pH decreases there is a decrease in the amount of uranium adsorbed until at pH values in the vicinity of 9 the equilibrium loadings for uranium are less than 10 grams per liter of resin. The adverse effect of bicarbonate can be eliminated by the addition of caustic. The amount of caustic that should be added is a question of economics and requires an evaluation of the economic advantage of a higher uranium resin loading as compared with the cost of the caustic that has to be added to the solution to obtain this higher loading.

It is probable that the bicarbonate ion behaves in a uranium carbonate system in a manner similar to the behavior of the bisulfate ion in the uranium sulfuric acid system. In order to form the uranyl tricarbonat complex, carbonate anion must be present in the solution. In the presence of bicarbonate alone an adsorbable uranium complex anion cannot be obtained. The higher the bicarbonate to carbonate ratio and the lower the concentration of carbonate ion in solution, the smaller the tendency to form the uranyl tricarbonat anion. In addition, the bicarbonate ion like the bisulfate ion represents a competing ion for resin adsorption sites, and if the bicarbonate to carbonate ratio is high, the competition from bicarbonate will be a second factor in decreasing the uranium loading on the resin. In Y-816 it is reported that pH variation from 8.2 to 11.2 at a constant total carbonate concentration has a negligible effect on uranium adsorption. This is contradictory to other reports, particularly the work reported in ACCO-3.

Vanadium, like uranium, can be adsorbed from carbonate leach liquors. Reports Dow 28 and Dow 55 indicate that not only is vanadium adsorbed but that it has a greater affinity for the resin than uranium. If a carbonate solution containing both uranium and vanadium is passed over an ion exchange resin until uranium breakthrough is achieved, passage of additional liquor will result in the displacement of the adsorbed uranium by the vanadium until ultimately very little uranium will remain on the resin.

III THE ELUTION OF ADSORBED URANIUM

The adsorption of uranium on anion exchange resins is relatively selective and effects a separation of uranium from the bulk of the other metallic constituents present in sulfuric acid leach liquors. (In carbonate systems selectivity is provided by the leaching agent itself which does not dissolve much other than uranium and, possibly, vanadium from the ore.) The ion exchange process, as far as the acid systems are concerned, therefore, constitutes a purification process. However, the uranium now must be removed from the resin so that the resin can be recycled and the uranium recovered in a form in which it can be given additional treatment.

It has been demonstrated that when resin is in contact with a dilute sulfuric acid solution containing uranium and other ions, an equilibrium will be reached in which a certain amount of uranium will be adsorbed on the resin, and the amount adsorbed will depend on a number of factors including the relative concentrations of the various ions that are present. It has been shown that if water alone is passed over the resin that ultimately all of the uranium can be removed but the volumes of solution required are so large as to make this method of elution impractical. Advantage can be taken of the mass action law by passing over the resin a solution containing another anion which will displace the uranium sulfate complex and be adsorbed in turn. The addition of another anion such as sulfate to water will increase the rate of removal of uranium, and the higher the sulfate concentration, the more rapidly will uranium be removed. However, it has been found that elution systems which involve only displacement of uranium by another anion require long contact times or large solution volumes or both to obtain complete removal.

The adsorption studies revealed a number of conditions under which uranium could not be adsorbed on the resin. In other words, the environment in which the uranium was present was not conducive to the formation of a uranyl anion complex which could be adsorbed. Advantage can be taken of this principle of creating an unfavorable environment to remove uranium from the resin. Common systems which are known to create unfavorable environments are those containing strong acid, chloride solutions between .5 and 3 molar,

and nitrate solutions containing concentrations higher than .5 molar.

In general, it is desirable to maintain sufficient acidity in any eluting solution to prevent precipitation of uranium. But, as will be discussed later, the amount of acid used should be kept to a minimum. When elution of uranium is dependent on the presence of a competing ion, then the required time of contact between the resin and the eluting solution will be governed by the rate at which equilibrium between the eluting anion and the uranium on the resin is reached. In systems where elution is dependent upon the presence of an unfavorable environment the establishment of such an environment is almost instantaneous, and the problem then becomes one of washing the uranium, no longer present as uranyl sulfate anion, from the beads. The rate of this washing operation is dependent upon the rate of diffusion of uranium in its non-adsorbable form from the intermolecular spaces of the resin beads. Actually, in systems depending upon an unfavorable environment, the mass action effect of a displacing anion is also present so that a combination of the two effects is achieved.

It is important that a good eluting anion is not too strongly adsorbed since it itself must be displaced during the succeeding adsorption cycle in order to allow uranium to be adsorbed on the resin. The eluting anion should also be low in cost, because, although a large percentage of the eluting solution can be recycled, there is always a certain loss which, in certain systems, may represent a high percentage of the total cost of the ion exchange process. A great deal of work on a number of eluting agents investigated in various concentrations has been reported in BMI-JDS-211; Dow 40, 42, 44, 57 and 73; MITG A-96, A-97 and A-108, and ACCO 6, 15, 17 and 20.

A. Factors Influencing Elution

1. The Effect of Retention Time

The comparative efficiency of elution with different solutions can be measured in several ways. For any given system the volume of eluting solution required to remove all of the uranium when the liquor is passed through the resin bed at a given retention time, can be determined. The smaller the volume required, the more efficient is the eluting solution. On the other hand, the volume of

eluting solution can be maintained constant and the percentage of removal of uranium determined after this volume of liquor is passed over a resin bed at a given retention time. A third possible alternate would be to determine the retention time necessary to remove all of the uranium with a given volume of a given liquor; this third alternative is rarely used. The most common approach is to fix the retention time for a given system and then determine the volume of liquor required to remove the uranium. Since it is difficult to establish when all of the uranium has been removed, as a matter of laboratory convenience in the MIT and Cyanamid laboratories, it was arbitrarily established that when the instantaneous concentration of the effluent from the ion exchange column during elution reached a uranium concentration of 0.1 grams of U_3O_8 per liter elution should be considered as complete. Because of the high specificity of the resin for uranium, it is possible to determine the elution end point by means of a simple spot test. In general, this is done on filter paper by taking a drop or two of eluate and adding to it a drop of potassium ferrocyanide solution. In the presence of uranium a brown coloration is obtained; the limit of detection of this color is approximately 0.1 grams of U_3O_8 per liter.

In order to determine the effect of retention time (the time that any one particle of solution remains in a column of resin), the composition of the solution is fixed and the volume required to remove the uranium from the resin at the different retention times is measured. Some idea of the practical limits for retention time was obtained by rate studies in which a batch of resin was contacted with a given volume of a given liquor and the time required to reach equilibrium established. Data presented in ACCO 26 show that the rate of reaction between a uranium bearing resin of the IRA 400 type and an eluting solution of the unfavorable environment type is quite rapid. In the batch tests, equilibrium was reached in somewhere between 30 and 45 minutes, although the reaction was essentially complete at the end of 30 minutes. For eluting solutions that operate solely by displacement the equilibrium times would be about the same as those for adsorption, which for IRA 400 may be of the order of 1 hour. The fact that there is little difference between the time required to reach equilibrium for a displacing anion system and an unfavorable environment system, indicates

that the rate of diffusion of uranium, whether as an anion complex or in an undissociated or cationic form, is the most important factor.

Inasmuch as equilibrium is essentially complete with unfavorable environment systems at the end of 30 minutes, retention times of greater than 30 minutes would have no advantage for elution. Studies on the effect of retention time have demonstrated this to be true. With retention times shorter than 30 minutes a decrease in retention time results in an increase in the volume of eluent required for complete elution. Verification is provided in Dow 57, Dow 73 and ACCO 11. It is reported in MITG 258 that an increase in elution retention time from 10 minutes to 15 minutes materially reduces the amount of solution required for complete elution. However, the reduction in volume obtained by increasing the retention time beyond 15 minutes is relatively small. It has also been established, as reported in ACCO 39, that, although the volume of eluting solution required increases with the decrease in retention time, the total time required for elution may decrease with decrease in retention time. This means that the increase in volume is not directly proportional to the decrease in retention time and in certain installations where the time required for elution is critical, the use of additional eluting solution to obtain elution in a shorter time may be justified.

2. The Effect of Cross Linkage and Mesh Size

Since the primary factor determining rate of elution is the diffusion rate of uranium through the resin, it would be anticipated that resins of lower cross linkage, which are more porous and permit more rapid movement of solution through the resin structure, would elute more rapidly than resins of high cross linkage. Studies reported in Dow 57 compared samples of Dowex 2 resin cross linked with divinylbenzene to the extent of 1, 4, 6, 8 and 16%. The resins with only 1 and 4% cross linkage were by far the easiest to elute. These results have been confirmed in a number of tests on a wide variety of resin materials. With resins of small particle size there is a decrease in the length of the diffusion path and, as would be expected, fine mesh resins show more rapid elution than those of coarser mesh.

3. Effect of Temperature

Data reported in Dow 57 and ACCO 6 indicate that, as expected, an increase in temperature results in an increase in the rate of elution. However, an increase in temperature from 25°C. to 60°C. gave only approximately a 20% increase in elution rate and, in general, this small amount of increase does not warrant the cost of heat and special equipment and possible loss of resin life that might result from the use of liquors at elevated temperatures.

4. The Effect of Uranium Loading

It is shown in ACCO 11 and ACCO 17 that the volume of solution required to elute a given resin bed with a fixed retention time is relatively independent of the uranium concentration of the resin. However, this is true only if the volumes required to obtain a given percentage of elution are used as the basis for comparison. If the end point of elution is considered to be the 0.1 grams of U_3O_8 per liter mentioned previously then the higher the loading on the resin the higher the percentage of uranium that will be eluted when this concentration is reached, and, consequently, the more eluting solution required to obtain this concentration.

5. Effect of Resin Type

With respect to the strong base resins the main difference between the different types of commercially available resin appears to be differences in cross linkage, and the effect of cross linkage has been discussed above. It has been mentioned in the adsorption section that uranium can also be adsorbed on weak base or intermediate base resins. The rate of adsorption on these resins is somewhat slower than that for resins of the strong base type. Similarly, the rate of elution with ordinary solutions from these resins is also much slower than from strong base resins. A detailed study of the effect of various factors on the rate of elution from weak base resins has not been made, but, in general, because of their slow adsorption rates and even slower elution rates, weak base resins have not found application as yet for the adsorption of uranium.

B. Types of Eluents

The eluting solutions most commonly used for the removal of uranium are the acids, and sodium and ammonium salts of chlorides, nitrates and sulfates. A wide variety of concentrations and combinations of salts and acids have been studied. From a practical point of view solutions containing high concentrations of acid generally have been avoided because the uranium must be recovered from the eluting liquors and this is usually done by precipitation with an alkali such as ammonia or MgO . Consequently, the use of high acid concentrations requires a high consumption of precipitating agent which represents an important factor in cost. The use of very large volumes of eluting liquor, even though they may be of low acid concentration, is also to be avoided because of the cost of the alkali and the cost of the acid to reconstitute the initial acid strength of the barren eluting solution. A discussion of cost factors in the ion exchange process will be presented in more detail in a later section.

1. Sulfate Elution

Because uranium can be adsorbed from dilute sulfuric acid solutions containing quite high concentrations of sulfate, elution with neutral or slightly acid sulfate solutions is relatively inefficient. Such sulfate solutions depend on mass action displacement for the removal of uranium, and, although elution can be achieved with such solutions, the volumes required are large and the times involved are long. Studies of sulfate eluting solutions have been reported in Dow 40, 59; ACCO 15, ACCO 59 MITG A-96. If sulfate solutions are acidified by the addition of sulfuric acid, elution efficiency improves but concentrations of the order of 1 molar sulfuric acid are required to provide eluting efficiencies that are comparable with chloride or nitrate elution systems. In the early phase of the development of the ion exchange process, a common eluting solution was one containing 1 mole of sulfuric acid and 2 moles of sodium or ammonium sulfate per liter. This solution was satisfactory until consideration was given to the precipitation of uranium from it. Sulfuric acid was a relatively cheap acid and roughly ten times as much sulfuric acid could be used as hydrochloric or

nitric acid for the same reagent cost. However, much more alkali was required to neutralize the higher acid concentrations and the cost of the alkali was the factor that makes the use of sulfate elution with strong sulfuric acid uneconomical.

The addition of sulfuric acid provides the environment which prevents the formation of the uranyl sulfate complex. This is accomplished, probably, by shifting the sulfate-bisulfate equilibrium far to the bisulfate side. The resulting high concentration of bisulfate and the decrease in the concentration of sulfate required to form the complex makes it impossible to adsorb uranium from such a solution, and, therefore, the solution constitutes a fairly good eluting liquor. If an effective system of sulfate elution could be devised, it would have certain advantages, primarily because the resin would be left in the sulfate form at the end of the elution cycle. This will be discussed later.

2. Chloride Eluting Systems

As described previously under "Adsorption", the presence of chloride in concentrations above 0.1 normal in the leach liquor is undesirable and interferes with the adsorption of uranium. Therefore, a solution high in chloride, of the order of 1 normal, for example, would provide an environment from which uranium could not be adsorbed on the resin and which must, therefore, prevent the formation of a uranyl sulfate anion complex. A solution of this type should be a good eluting solution and experimental data have confirmed that this is so. However, as described under "Adsorption", in solutions that have high concentrations of chloride, of the order of 5 to 6 normal, a uranium chloride anion complex is formed which can be adsorbed on the resin. Therefore, only chloride solutions in the intermediate concentration range should be useful for the removal of uranium from anion resins. Data reported in Dow 40, Dow 73, ACCO 20 and ACCO 17 show that the efficiency of elution of a chloride eluting solution increases as the concentration of a chloride increases up to 1.5 molar. In concentrations above 1.5 molar, chloride solutions do not give as good results as those of lower concentration.

Hydrochloric acid, sodium chloride and ammonium chloride have all been used as sources of chloride ion. Hydrochloric acid

alone in 1 molar concentration appears to be somewhat superior than such solutions as 0.9 normal ammonium chloride, 0.1 normal HCl or 0.9 normal sodium chloride- 0.1 normal HCl. In the absence of any other ions in the solution there does not seem to be any difference in elution efficiency whether the cation is sodium or ammonium. Neutral ammonium chloride or sodium chloride solutions are quite efficient for the removal of uranium from resin when the uranium has been adsorbed from artificial solutions which contain no constituents such as arsenates or phosphates and there is no problem with the adsorption of other metallic anions such as ferric sulfate complex or vanadium. With uranium adsorbed on resin from actual leach liquors, however, it has been found necessary to maintain enough acidity to prevent the formation of hydrolytic precipitates in the eluting liquor. In general, the presence of 0.1 normality of acid in the eluting solution is sufficient, although with liquors from some ores, for example those of the Belgian Congo, less acid can be used, whereas on liquors from other ores, such as those obtained from Temple Mountain, higher concentrations of acid are required. The problem of high acidity for eluting liquors is discussed more in detail later under "Special Problems in Elution". As discussed previously, from an economic point of view it is desirable to keep the acidity of the eluting solution as low as possible. For general use a solution 0.9 normal in ammonium chloride and 0.1 normal in hydrochloric acid has been found to be effective.

3. Nitrate Eluting Systems

Again, because of the interference of nitrate in the adsorption of uranium from sulfuric acid solutions it could be anticipated that nitrate would represent a good anion for the removal of uranium from resin. It is reported in Dow 44 and ACCO 17 that nitric acid and the sodium and ammonium salts may be used as eluting solutions for uranium. In general, the behavior of nitrate eluents is similar to that of chloride eluents, with the exception that since nitrate does not form an anionic complex with uranium at high nitrate concentrations, there is no limit to the concentration of nitrate that could be used for elution other than that dictated by economic factors. It has been demonstrated that nitrate solutions do not exhibit any decrease in efficiency of elution in concentrations as high as 6 molar. However, there is relatively little improvement

in elution efficiency at nitrate concentrations above 1.5 molar. Within the range from .1 molar to 1.5 molar elution efficiency increases with increase in concentration. As with chloride, there is some increase in the efficiency of elution as the ratio of acid to salt increases for a given nitrate concentration. However, with acid concentrations above 0.1 molar little improvement is observed with increase in acidity.

As a general rule, nitrates are more expensive than chlorides, and therefore, chlorides are being considered for elution in most of the ion exchange plants now under construction. However, on the Rand, chlorides in any form are almost unavailable, whereas nitrates, although not cheap or abundant, are being produced in nitrogen fixation plants, and at the present time all of the Rand ion exchange plants are using nitrate elution. Because of certain difficulties with respect to polythionates, the Rand eluting solution is approximately 1 molar in nitrate but is three tenths molar in acid.

Chloride has one difficulty in that it provides a corrosion problem, if stainless steel equipment is used. Where plants have been designed to handle chloride, there is no difficulty but in those plants which were designed initially for nitrate or where stainless steel equipment is required and rubber-covered equipment cannot be substituted, chloride cannot be used and the higher cost of nitrate elution must be borne. For example, because of the need for stainless steel screen for the fabrication of baskets, nitrate elution is being proposed for the resin-in-pulp process where the use of basket machines is contemplated.

4. Mixed Elution Solutions

All of the elution solutions that have been considered up to this point initially have had only one anion or in the case of sulfate solutions two anions (sulfate and bisulfate) present; however, these solutions are of academic interest because as soon as the eluting solution has passed over the resin, sulfate originally present on the resin is displaced into the elution solution and normally is not removed during the precipitation process. For all practical purposes, therefore, whether one starts off with an all chloride or an all nitrate eluting system, after this

eluting system has passed over the resin once, it becomes a chloride-sulfate or nitrate-sulfate eluting solution. Inasmuch as a system originally all nitrate or all chloride quickly becomes a mixed system in which sulfate is present, investigators at the Winchester Laboratory conceived the idea of starting off with a solution that had the proper chloride or nitrate concentration but, instead of acidifying with either hydrochloric acid or nitric acid, which are relatively expensive forms of acid, they acidified these solutions to the desired pH with sulfuric acid. It was found, in general, that sulfuric acid could be substituted for hydrochloric or nitrate acid for the acidification of eluting solutions with little loss in eluting efficiency. Since the acid that is added is neutralized in order to precipitate the uranium this acid must be replaced to reconstitute the eluting solution and by using sulfuric acid in place of the more expensive acids, some economies resulted. Sodium chloride is usually the cheapest form of chloride and an elution solution that is one normal in sodium chloride and adjusted to pH 1 with sulfuric acid has been recommended as the most economical combination of reagents for elution of uranium. This salt-sulfuric acid system is now in use on a large scale in the Belgian Congo. Laboratory tests with this eluting liquor are described in ACCO-59.

5. Decrease in Eluting Efficiency with Recycling

In almost every instance, whether on laboratory or plant scale, where the eluting solutions after the precipitation of uranium with alkali has been reconstituted and recycled, there has been observed a decrease in the efficiency of the elution until a certain number of elution cycles, usually of the order of 20, have been run. After this point, the efficiency of the eluting solution remains constant with continued recycle but is only about 75% as efficient as the eluting solution when first used. This phenomenon has been reported in ACCO-11 and 43. A careful investigation of this phenomenon was made in the Winchester Laboratories and reported in ACCO-59. In this investigation, Amberlite IRA-400 resin was loaded from a synthetic uranium solution and the uranium then eluted under very carefully controlled conditions. In one series of tests, the resin was eluted with a standard eluting solution, initially nine-tenths normal in ammonium chloride and one-tenth normal in hydrochloric acid. After the precipitation of uranium, the chloride concentration of the eluting solution and its acidity were adjusted

to the original chloride and acid concentration by the addition of HCl, and ammonium chloride if necessary. The reconstituted eluting solution was then used for elution on the next cycle. At the end of each cycle, portions of the eluting solution were submitted for chemical analysis to determine what changes had occurred as a result of recycle. It was found under the conditions used in this test work that there was a steady rise in the concentration of sulfate and a corresponding increase in the concentration of ammonium ion until the sulfate concentration in the eluting solution reached 35 grams of SO_4 per liter. During this test the number of column volumes (a column volume is the volume of resin in the column) required for a complete elution increased from an initial figure of 10, to 14.6. However, when the volumes required for elution reached its maximum, the sulfate concentration was only 10 grams per liter. Thus the plateau with respect to volume was reached before the plateau with respect to sulfate concentration. The indications were that the increase in sulfate concentration was the factor responsible for the increase in the number of column volumes required for elution. To confirm this fact, elution studies were made with solutions which were nine-tenths normal in ammonium chloride and one-tenth normal in hydrochloric acid but which contained, in addition, different concentrations of sulfate added as ammonium sulfate. The same phenomenon that had been observed with recycling of the eluting solution was not observed with eluting solutions that were used only once but which had different concentrations of sulfate present originally. The assumption that the increase in column volumes required for elution with recycle was caused by the increase in sulfur concentration was thereby confirmed.

In the test with recycle, the maximum sulfate concentration reached was only 35 grams of sulfate per liter. In the tests with eluting solution with added sulfate, a much wider range of concentration was studied. It was found in both recycle and non recycle tests that the volume of eluting solution required increased with increasing sulfate concentration until the sulfate concentration was of the order of 10 grams per liter. From 10 to 60 grams of sulfate per liter the number of column volumes required remained constant. However, when the sulfate concentration was increased beyond this point, a new phenomenon was observed and it was found that the number of column volumes required now showed a decrease with increasing sulfate concentration, until a new plateau was

reached starting at about 100 grams of sulfate per liter. The volume of eluting solution required in the ammonium chloride-HCl system when the sulfate concentration was above 100 grams per liter, was only slightly higher than that required by nine-tenths normal ammonium chloride and one-tenth normal HCl in the absence of sulfate. This phenomenon was also observed in pilot plant studies conducted at Monticello on Utex ores. Normally the effect of very high sulfate concentrations would never have been observed because in the bulk of the recycle eluting solutions that have been analyzed, no sulfate concentrations higher than about 60 grams per liter have been encountered. However, in the Monticello tests, the eluting solution was being reconstituted with respect to chloride by the addition of ammonium chloride rather than HCl, and reconstituted with respect to acid by the addition of sulfuric acid. The additional sulfate thus added, in addition to that removed from the resin during elution, caused the sulfate concentration of the eluting solution to increase to approximately 200 grams of sulfate per liter before the concentration leveled off.

Tests in which sodium chloride was substituted for ammonium chloride failed to show this same phenomenon of increase in elution efficiency at very high sulfate concentrations. With the sodium chloride elution system, the volume of eluting solution required reached a maximum at about 10-15 grams of sulfate per liter and remained at that same level over the entire range from 10 to 200 grams of sulfate per liter. When magnesium chloride was substituted for sodium chloride, again no increase in elution efficiency occurred at very high sulfate concentrations. However, unlike the sodium chloride system, in the presence of magnesium chloride, there was a continued gradual decrease in the elution efficiency as the sulfate concentration increased. Although with the sodium chloride system, a maximum elution volume was reached quite rapidly, this solution volume was higher than the first level achieved with ammonium chloride elution system and much higher than the second plateau found with the ammonium chloride system at very high sulfate concentrations. It appears that the cation, or rather, the type of cation, represents an important factor in the efficiency of elution. The reason for this is not well understood but probably has something to do with the difference in activities of the bisulfate ion in solutions made from different sulfate salts. Elution solutions with mixed cations showed efficiencies that were intermediate between the eluting efficiencies of the two ions concerned, depending upon the ratio of the ions present. Magnesium and sodium were the only

cations other than ammonium that were tested because it was thought unlikely that anything other than MgO or sodium hydroxide or carbonate would be used as a substitute for ammonium hydroxide for the precipitation of uranium from eluates. No investigation was made to determine whether or not the phenomenon observed with the ammonium chloride system would also be observed with the ammonium nitrate system. However, the increase in elution efficiency at very high sulfate concentrations appeared to be a function of the cation rather than the other anion present so that presumably in a nitrate system as well as in chloride system, in the presence of ammonium ion as the only cation other than hydrogen, an increase in elution efficiency should occur.

C. Miscellaneous Elution Systems

A variety of other elution systems have been tried, without too much success. For example, in ORNL 1418, it is reported that 97% of the uranium can be eluted from Dowex-1 type resin by passing one column volume of 10 normal hydrochloric acid through the bed and following it with 4 column volumes of water. The high chloride concentration converts the uranium originally adsorbed as sulfate complex into the chloride anion complex which then can be removed simply by decreasing the chloride concentration. A similar elution scheme using 3-5 molar sodium chloride solution followed by water, is reported in Dow-57 and Dow-59. The same type of system was also tried as reported in MITG A-97. The use of high chloride followed by water would appear theoretically to have certain advantages. The chloride systems used could be strongly acid because, in theory, this solution should only convert the uranium into the chloride anion form, and after it had passed through the resin bed it should contain no uranium. The bulk of the acid thus would be available for re-use. All the uranium would be in the water solution that would follow the strong chloride solution and only a small amount of alkali would be required for precipitation. The only reagents required for an eluting system of this type would be the chloride adsorbed on the resin and required to convert the uranium into the anionic complex, and a very small amount of alkali required to precipitate the uranium from an almost neutral solution. In practice, however, it was found that as much as one-third of the uranium was removed from the resin with the chloride solution which was used for the conversion of the uranium to the chloride complex. This meant that both the chloride solution plus the water solution would have to be neutralized to precipitate the uranium and, there-

fore, the advantages anticipated for this elution scheme could not be realized in practice.

An attempt was made to use certain ions which are known to have high affinity for the resin as eluting solutions for uranium, the theory being that these strongly held anions would displace uranium readily and only a small number of volumes of eluting liquor would be required for complete removal. Perchloric acid was one of those tried, as reported in MITGA-97. Polythionates were also tested. Both of these reagents proved to be very good eluting agents for uranium, but the problem in both instances was how to remove the perchlorate or the polythionate from the resin. With respect to perchlorate, the situation was almost hopeless. It was possible to remove polythionate from the resin but the reagent cost for so doing was greater than the reagent cost for the use of a one normal chloride at pH 1. It was thought that certain complexing agents such as versene and dithiophosphates, which form stable complexes with uranium, might be useful for elution.

These complexes are presumed to be un-ionized, and therefore, once the complexes are formed, the uranium should be readily removed from the resin. However, it was found, as reported in ACCO-6, that neither versene or the ammonium salts of disecundary butyl-dithiophosphoric acid were of any use for elution by themselves and when used in conjunction with a one molar sodium chloride solution, actually decreased the amount of uranium eluted.

As described above, with chloride elution, the presence of acid in the eluting solution is not absolutely essential and merely serves to keep the uranium and other ions adsorbed on the resin from forming hydrolytic precipitates. It was found that as a result of the adsorption of bisulfate on the resin because of the presence of bisulfate in the leach liquors which contained the uranium, the pH of the eluate is of the order of 2.5 to 3 as a result of the elution of bisulfate. However, after the bisulfate is all removed from the resin, the pH of the solution starts to rise and any uranium that has not been removed or any ion left on the resin may precipitate in the resin bed. Therefore, a one molar sodium chloride neutral solution followed by a column volume of 1 molar sulfuric acid has been used for elution, and has been reasonably successful. The bulk of the uranium is removed with the neutral salt and the small amount of uranium that is eluted with the sulfuric acid could be recycled to the leaching circuit; as a result there would only be a small consumption of alkali for the precipitation

of uranium from the unacidified sodium chloride. This scheme to date has not been applied to any large scale operation but appears to be theoretically sound and might find some application in the future.

D. Special Problems in Elution

The presence of certain ions in the leach liquor may result in difficulties when the so-called standard elution solution, that is, a liquor that is 1 normal in chloride or nitrate and approximately 1/10 normal in acid, is used. Special provision must be made for the removal of uranium adsorbed on resin from solutions containing these particular ions. Phosphate and arsenate when present in high concentrations in the leach solutions have been known to cause difficulty in the removal of uranium from resin loaded from such a liquor. It is difficult to say just what concentration of phosphate will cause trouble, because the presence of other ions such as iron and aluminum which can form un-ionized or cationic complexes with phosphate influence the effect of phosphate on the elution of uranium. Phosphate ion can be adsorbed by the resin as such. In addition, phosphate forms an anionic complex with uranium and this can be adsorbed on the resin. The adsorption of such a complex was the basis of the Dow ion exchange proposal for the recovery of uranium from phosphoric acid solutions. Arsenate behaves in a manner very similar to phosphate.

In addition to the formation of complexes with uranium, both phosphate and arsenate form compounds with uranium, both hexavalent and tetravalent, which are insoluble in dilute acids. A study of the formation of such precipitates and the effect of concentration of uranium and phosphate or arsenate is reported in MITG A44. Both the CRL Laboratory in Teddington, England and the Y-12 group at Oak Ridge have suggested the use of uranyl arsenate or phosphate precipitation for the recovery of uranium from certain types of liquors. If the concentration of uranium and phosphate is of the order of that normally encountered in acid leach liquors, the solubility product of the uranium phosphate or arsenic compounds is generally not exceeded and they remain in solution. However, as the concentration of uranium and/or phosphate and arsenate or both is increased, there is a decrease in the pH at which precipitation will take place. When resin containing uranium and phosphate or arsenate or both is eluted with a solution such as 1 normal ammonium chloride:1/10 normal HCL, in

the immediate vicinity of the resin a condition is created which provides for a very high concentration of both uranium and phosphate or arsenate. As a result, precipitations of uranium with phosphate and arsenate can take place inside the resin bed, even though the eluting solutions have a pH of 1. If the quantity of precipitate that is formed is small, it cannot be observed even in transparent columns, and, of course, would not be noticed in an opaque column. The elution curve that is obtained appears to be normal although the elution peak might not be as high as anticipated. If there is no visible precipitate, the only indications of such precipitation would be a difference between the amount of uranium adsorbed and the amount of uranium eluted as determined by material balance calculation, or the observation of high barrens in first fractions of effluent on the next adsorption cycle. The reason for this will be discussed in more detail below. The use of a more strongly acid solution for example 1 normal hydrochloric or nitric acid, will dissolve any uranyl phosphate or arsenate that is precipitated in the column and uranium would be found in such an acid eluate if precipitation has taken place. Therefore, it is common practice, on solutions in which the presence of phosphate or arsenate has been established, to determine in the course of the preliminary investigations on the adsorption of uranium from such liquors, whether or not treatment of the resin with 1 normal HCl after the normal elution has been completed will remove additional uranium. If additional uranium is found, then it is known that a condition exists where the ordinary eluting solution is not adequate for uranium removal.

There are several solutions to the phosphate problem: one is to use an eluting solution which is higher in acidity than 1/10 normal. In some instances, eluting liquors that contain as much as 1/2 normal acid have been used. However, the use of higher acidities requires increased amounts of alkali for precipitation of uranium and as a result, the elution costs are increased. It has been found that if a small amount, 1 column volume of a 1 normal HCl solution for example, is used in place of the 1/10 normal acid eluting solution at a point somewhere in the middle of the normal elution cycle, a complete removal of uranium can be obtained with only a relatively small increase in the total amount of acid required. However, the use of two solutions for elution rather than one complicates the elution scheme and makes automatic operation of columns difficult.

It has been observed as previously mentioned that if solutions high in phosphate are also high in ferric iron, that little difficulty with phosphate or arsenate may result presumably because of the formation of non-adsorbable ferric phosphate or arsenate complexes. Therefore, solutions that are deficient in iron may have iron added to them to eliminate the phosphate difficulty. Aluminum may also function in the same manner. As an alternate ferric iron can be added to the eluting solution to complex the phosphate which would prefer to combine with the iron than with the uranium. From such a solution which is 1 normal in chloride at pH 1, complete elution can be obtained in the usual number of column volumes even though phosphate is present on the resin. However, the presence of iron in the eluting solution will cause dilution of the uranium precipitate unless the iron is removed first by a 2 stage precipitation process such as that which is being used now as standard practice in the Rand plants in South Africa. None of the solutions to the phosphate problem are particularly attractive, but fortunately most leach liquors have sufficient iron and aluminum to compete with uranium for the phosphate so that only small amounts of phosphate are adsorbed on the resin and normally these cause little difficulty. In liquor from only one ore, Temple Mountain, as reported in ACCO-33, has phosphate presented a serious problem.

Vanadate ion in acid solution behaves very much like phosphate and arsenate. The problem of vanadate was discussed in some detail under Adsorption. It was also mentioned there that vanadate may cause difficulty in the elution of uranium from the resin by normal eluting solutions. The cause of this probably is the formation of a uranyl vanadate precipitate which is insoluble in dilute acid just as are the uranyl arsenates and phosphates. The problem of vanadium can be eliminated by reducing the vanadium to the plus 4 state in the liquor before the adsorption of uranium; under these conditions vanadium is not adsorbed. Small amounts of vanadium as vanadate can be tolerated because some vanadium is eluted with ordinary chloride or nitrate eluting solutions. In theory, the vanadium could be left as vanadate in the leach liquor and both uranium and vanadium adsorbed on the resin. The vanadium could be removed prior to the removal of uranium by passing SO_2 over the resin. However, the SO_2 solution always carries a small amount of

uranium with it and then the uranium must be recovered from both the SO_2 -vanadium solution and from the normal eluting solution. It is generally much simpler to avoid the vanadium problem entirely by reduction of the leach solution. As described under the Special Problems with respect to adsorption of uranium from Rand liquors, thiocyanate ion if present in solution can cause some difficulty in elution of uranium. It appears that a uranium thiocyanate complex can be adsorbed on the resin. This is evidenced by a bright red color which can be observed in the resin bed during elution. That this red color is the result of a combination between uranium and thiocyanate can be shown by tests with pure solutions. However, chloride or nitrate ion may also be involved because this color appears only during the elution cycle. It is not evident during adsorption. The course of the uranium elution can actually be followed by observing the passage of this band of red color down the column. When all of the red color has disappeared from the resin bed, there is no uranium to be found in the eluate. The normal uranium thiocyanate complex has a yellow color. Therefore, the solutions, which are produced on elution of uranium and thiocyanate, do not show this red. Small amounts of thiocyanate cause no difficulty. However, the uranium thiocyanate complex, whatever it may be, is more slowly removed from the resin than the normal uranium sulfate complex and, as a result, in the presence of high concentrations of thiocyanate, the elution rate of uranium is greatly decreased. This could be caused either by the formation of such a stable complex between uranium and thiocyanate that it can be formed even in the presence of chloride, which normally provides an environment in which the sulfate complex cannot be formed, or else the uranyl thiocyanate complex has such a large molecular size that its diffusion rate is slow.

In connection with the absorption of uranium from Rand liquors on ion exchange material, it was found that three components, silica, polythionate, and cobalticyanate interfered with the adsorption of uranium. Silica and polythionate (through the decomposition of sulfur) caused a decrease in the rate of diffusion. Both polythionate and cobalticyanide occupied resin sites and interfered with the capacity of the resin for uranium. To the extent that they influenced rate of diffusion, silica and polythionate also influenced elution by slowing down rate of elution. Both of these elements act to decrease rate by blocking pores within the bead structure through which liquor must diffuse in order to reach the adsorption sites. As explained previously, the silica problem can be eliminated by caustic treatment, and polythionate can be eliminated partially by caustic and more

completely by sodium sulfide plus caustic, or by ammonium thiocyanate.

IV ECONOMIC CONSIDERATION

The elements of cost that go into an ion exchange plant are as follows: 1. Capital equipment such as columns and auxiliary tanks, or cells and tanks if the resin-in-pulp process is to be used. It is rather difficult to separate the capital expenditures for the ion exchange portion of the plant particularly if a comparison is to be made between two different types of ion exchange operations. For example, a resin-in-pulp operation vs. a column operation or in comparing an ion exchange process with a chemical precipitation process; for example, the uranic phosphate process for the recovery of uranium. If columns are to be used, then a clear liquor is needed which means that either a CCD system or a filter plant plus clarifiers will be required ahead of the ion exchange system. If

resin-in-pulp is selected, then equipment is required for sand-slime separation. In both types of processes, of course, equipment for elution and precipitation of the final uranium product will be needed. However, in comparing the cost of an ion exchange plant with that of a chemical precipitation plant, a chemical precipitation plant will have no columns but may have other items of equipment that the ion exchange plant eliminates. In order to get a true picture of the capital costs for an ion exchange process for recovering uranium as compared to a non-ion exchange plant, the costs figures for the entire plant should be compared or at least complete flow sheets should be drawn up and those items that are common to both plants removed and the cost calculations made on the difference between the items of capital equipment that are dissimilar. However, it is a safe statement to make that the larger the ion exchange plant the more costly will be the capital equipment for uranium recovery.

2. The volume and type of resin.

3. Installation

4. Chemical reagent costs for adjustment of liquor before ion exchange, elution of the adsorbed uranium, precipitation of uranium from the eluate, and special chemical treatments required to restore capacity to the resin.

5. Labor

For the purposes of this report, such items as maintenance overhead, and factory expense can be neglected.

The total amount of uranium to be adsorbed in a given period of time, the capacity of the resin for uranium, and the rate at which uranium can be adsorbed and eluted from the resin will determine the size of the ion exchange plant and the volume of resin that is necessary. Provision must be made for the replacement of this resin as ultimately its capacity will drop to a point where it will no longer be capable of adsorbing all of the uranium which must be adsorbed in a given period of time. The cost of resin replacement can be considered as a reagent charge. Unfortunately, until full scale plants are in operation it is impossible to get a good estimate of resin life. The only plants that have been operating for a sufficient period of time to obtain some information on life of resin are those in the Rand and the Belgian Congo in Africa. The Rand problem is an unusual one in that poisoning agents such as cobalticyanide have been encountered there and have not been encountered elsewhere and are unlikely to be encountered in any other ion exchange installation, except one which involves the previous cyanidation treatment of the ore for the recovery of gold. On the Rand at the present time resin life is estimated as somewhere between 6 months and 1 year although recent developments in the removal of cobalticyanide from resin may permit regeneration at lower cost than replacement and resin life may be extended. It has been common practice in the Winchester Laboratory to assume a 1 year life for resin with the understanding that this figure is probably a minimum one and that for most installations resin life may be of the order of 3 or 4 years. The capacity of the resin for uranium has been given as one of the factors involved in determining the volume of resin required. One might assume from this that if one had a type of resin that had higher capacity than another that the one with the higher capacity would be preferred. However, as a general rule, the higher the resin capacity for the adsorption of uranium from a given liquor, the slower the rate of both adsorption and elution. A better factor to use for determining which resin is most desirable would be the amount of uranium that could be adsorbed per unit weight or volume of resin in a unit period of time. Normally a resin that shows a high adsorption rate can be expected to also show a high elution rate. Most resins produced by the different manufacturers have approximately the same cost per unit volume. The special resins that have been designed for resin-in-pulp operations at the present time are more costly than the others and this is an important factor that must be considered in determining whether or not one should select conventional column type operation or a resin-in-pulp operation. Normally, in column operation, losses from abrasion are negligible and the physical

structure of the resin is not too important. Mechanical losses by overflowing resin during backwashing are possible but can be made negligible by proper plant design. With resin-in-pulp processes where the resin is in more or less free contact with a pulp containing abrasive particles, the loss from abrasion may be an important factor and may actually produce more loss than chemical degradation. For resin-in-pulp processes, it may be necessary to revise resin life figures downward. It has been stated under the Adsorption section that a pH somewhere between 1.3 and 1.5 has been considered as optimum for ion exchange; however, it has also been shown that the higher the pH at which the liquor can be used, the higher the loadings on the resin.

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