Circular 53

Froth Flotation of Ion-Exchange Resins and its Application

by Roshan B. Bhappu

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ABSTRACT

Efforts to froth-float ion-exchange resins from unclarified liquors and pulps containing a high percentage of solids have resulted in the development of effective procedures for floating such resins. Cation-exchange resins are collected and floated with cationic amine-type collectors, whereas anion-exchange resins are amenable to flotation with collectors of the anionic sulfonate and thiophosphate types. The results of preliminary tests of the resin-flotation technique in the hydrometallurgical treatment of natural ores of copper, uranium, and gold have demonstrated the technical and economic feasibility of such a process.

INTRODUCTION

With the ever-increasing demand for today's metals and for others whose uses are only now being explored, it is inevitable that wet-process metallurgy will be increasingly employed in metals production. Even in the case of metals that have been in use for hundreds of years, the increased recoveries now required, which spell the margin between profit and loss, and the more complex and poorer grades of ore that must be worked, can only mean that new hydrometallurgical processes must be developed and existing processes improved.

One newly developed technique, whose potentialities in hydrometallurgy have only recently been recognized, is ion exchange. This age-old process is finding new uses in many fields of endeavor because it is often uniquely suited where conventional techniques fail. Ion-exchange processes are flexible, and the necessary equipment can be designed for a minimum of operating attention. Generally speaking, there are three areas in which ion exchange can be profitably employed in hydrometallurgical practice: (1) where metals are being recovered by less economical methods; (2) where metals are being lost; and (3) where recovery of metals is otherwise economically impractical. These areas immediately suggest several applications of ion-exchange techniques in the mining and metallurgical industry. Some of these have been successfully used in practice for years, whereas others are in the development or pilot-plant stage.

In most of the ion-exchange applications using clear solutions, the equipment and design characteristics are generally similar to those encountered in water treatment. This technique, however, is unsuitable for extracting metals from difficult-to-treat solutions and from pulps containing a high percentage of solids. Necessary modifications have to be made in order to employ ion exchange in such processes. This disadvantage, moreover, discourages the widespread use of ion-exchange techniques in many prospective applications.
In some recent applications of ion exchange in hydrometallurgical processes (for example, in the extraction of uranium), efforts have been made to extract the soluble values directly from the pulp by the so-called resin-in-pulp techniques (R-I-P and the Continuous Countercurrent process using the CST exchangers manufactured by Infilco, Inc.). However, even the best resin-in-pulp procedure will not tolerate more than 10 percent solids, which is attained by elaborate physical plant facilities and complicated flowsheet design, accompanied by close supervision and high production cost.

An ion-exchange process is therefore desirable in which the metal-bearing ions can be recovered directly from the leached pulp by adding ion-exchange resin and separating the loaded resins from the unclassified or unclarified pulps by a relatively cheap and simple procedure. Since the well-established froth-flotation process has been found very effective in separating one, two, or more minerals from the pulp, it is felt that such a process could be applied to the separation of resins from the pulp.

In the current investigation, efforts were made to determine the flotation characteristics of the ion-exchange resins with the hope of utilizing the well-established froth-flotation technique for collecting and transporting the resins in the various stages of the ion-exchange process in unfiltered or unclassified pulps and difficult-to-treat liquors. Such a procedure would render the process more effective, less complicated, and economically more attractive.

This paper presents the results of the initial test work carried out on the resin-flotation technique and on its practical application. Research on the process is continuing, and the data developed will be presented in subsequent publications.

FLOTATION OF ION-EXCHANGE RESINS

Advantages of Resin-Flotation Process

The flotation of ion-exchange resins from unfiltered or unclassified pulps would be an attractive feature in the application of ion exchange to hydrometallurgical problems. Considerable economic advantage would be gained by adapting the ion-exchange operation to a resin-flotation procedure. Such a process would eliminate the expensive filtration, clarification, and classification steps, and by avoiding the excessive dilution of the pregnant solution associated with conventional filtration, countercurrent decantation, or classification, enable adsorption to take place from more concentrated solutions than usually occur in the typical ion-exchange procedures. Moreover, in the resin-flotation process it would be possible to use more stable, finer sizes of resins, which would give increased efficiency per unit volume of resin owing to the shorter time required for the resins to reach equilibrium in the loading and elution phases. Additional advantages would be the saving in plant space, equipment, labor, supervision, and overall cost.
Theoretical Considerations

In regard to the flotation characteristics of ion-exchange resins, it was thought that the resins, manufactured from organic materials, such as polymerized styrene and divinylbenzene, would exhibit a nonpolar water-repellent surface and would be readily floatable with the aid of frother alone or in combination with neutral hydrocarbon collectors. The initial test work indicated, however, that although some floatability of resin occurs, it is not possible to float resins with these reagents alone.

A further study of the chemical composition of the resins indicates that they contain active charged groups bound to a cross-linked matrix. The cation-exchange resins contain negatively charged sulfonic, carboxylic, or phosphonic groups. On the other hand, the anion-exchange resins contain positively charged amine or quaternary ammonium groups. Because of the presence of these active groups on the resins, there appeared to be a good possibility of floating the resins with suitable, cationic or anionic collectors.

There seemed yet another possible answer to the problem of resin flotation, especially in regard to the cation-exchange resins. In the case of specific cationic-exchange application, such as in the recovery of copper, lead, zinc, nickel, cobalt, and the like, it was considered possible to sulfidize the metal ions on the resins and float them with suitable anionic sulphydryl collectors.

In general, theoretical considerations indicate that it would be possible to float the resins, and efforts should be made to explore all possible means of accomplishing this.

Plan of Investigation

In order to carry out a systematic study on the problem under investigation, the test work was conducted in four phases. In phase 1, efforts were made to determine the suitable collectors and optimum flotation conditions for the two types of resins; namely, the cation exchangers and the anion exchangers. The flotation conditions investigated included the type of collectors, frothers, and conditioning agents; the amounts of these reagents; the time of conditioning and flotation; and the optimum pH for the resin flotation. Efforts were also made to determine the possibility of floating cation-exchange resin after sulfidization.

Once the optimum flotation conditions for each class of resins were established, further flotation tests were carried out in phase 2 of the investigation to determine the effect of the common variables encountered in practice. These variables include the size of the resins, the temperature of the pulp, the type of gangue minerals and the tolerance to their slimes, and the percentage.
of solids in the pulp. Tests were also run to determine changes in the loading and elution characteristics of the resins after they are collector coated, floated, regenerated, and recycled to the process.

On the basis of the results obtained from the first two phases of the investigation, in phase 3 a standard flotation test procedure for the two types of resins was developed, and the floatability of the commercially available ion-exchange resins evaluated.

In the final phase (phase 4) of the investigation, the results of the three preliminary tests were applied to natural ores, through batch and locked flotation tests, in order to determine the effectiveness of the resin-flotation procedure on such ores. To obtain a broad coverage of the field of application, three different metal-bearing ores were investigated: (1) a base-metal ore, such as an oxide-copper ore containing quartz-sericite schist and granite as primary gangue constituents; (2) an exotic-metal ore, such as a uranium-bearing sandstone, and (3) a precious-metal ore, such as a gold ore having a tendency to slime badly.

Ion-Exchange Resins Tested

The ion-exchange resins tested in this investigation included both the commercially available cation and anion exchangers manufactured by the Permutit Co., Rohm & Haas Co., Chemical Process Co., and Dow Chemical Co. A list of the commercially available ion exchangers is given in Table 1.

In general, these resins are hard, insoluble, spherical solids containing active chemical groups bound to a cross-linked matrix of polymerized styrene and divinylbenzene. In most cation exchangers, the active groups are of the sulfonic type, although cation exchangers containing carboxylic and phosphonic groups are also available. In anion exchangers, the active groups are amine groups in weakly basic resins, quaternary amine groups in strongly basic resins, and mixtures of these groups in resins of intermediate basicity.
### TABLE 1. COMMERCIALY AVAILABLE ION EXCHANGE RESINS

#### CATION EXCHANGERS

<table>
<thead>
<tr>
<th>Sulfonated Coals</th>
<th>Sulfonated Resins</th>
<th>Carboxylic Acid Resins</th>
<th>Phosphonic Acid Resins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2. Amberlite IRC-50</td>
<td>2. Amberlite IR-120</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. Nalcite HCR (Dowex 50)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4. Duolite CS-101</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4. Duolite C-61</td>
</tr>
<tr>
<td>Phenol Formaldehyde</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Zeo-Rex</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Duolite C-3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross-linked Polystyrene Copolymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Permutit Q</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Amberlite IR-120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Amberlite IR-112</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Nalcite HCR (Dowex 50)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Duolite C-20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Dowex 30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### ANION EXCHANGERS

<table>
<thead>
<tr>
<th>Weakly Basic</th>
<th>Intermediate Basicity</th>
<th>Strongly Basic or Quaternary Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. De-Acidite</td>
<td>1. Permutit A</td>
<td>Type I (Alkyl Amine)</td>
</tr>
<tr>
<td>1. Permutit W</td>
<td>1. Ionac A-300</td>
<td>1. Permutit S-1</td>
</tr>
<tr>
<td>2. Amberlite IR-45</td>
<td></td>
<td>3. Nalcite SBR</td>
</tr>
<tr>
<td>4. Duolite A-4</td>
<td></td>
<td>5. Dowex 1 &amp; 2</td>
</tr>
<tr>
<td>4. Duolite A-6</td>
<td></td>
<td>5. Dowex 21K</td>
</tr>
<tr>
<td>5. Dowex 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. = The Permutit Co.
2. = Rohm & Haas Co.
3. = National Aluminate Corp.
5. = Dow Chemical Co.
In order to reduce the number of variables in flotation testing, synthetic samples consisting of 580 grams of either Ottawa sand, sandstone, or quartz monzonite, and 20 grams of resins, were subjected to flotation under predetermined conditions. The above-mentioned gangue minerals were selected because they represent typical gangue material found in natural ores. The gangue minerals used were minus-65, plus-325-mesh fractions except for tests in which slimes of the above gangue minerals were investigated. The size of the resins used was minus-16, plus-48-mesh except for tests in which finer sizes of resins were investigated. The resins used in tests under phases 1-3 were loaded and regenerated outside with appropriate loading and elution solutions.

All the flotation tests were run with Socorro tapwater, having a pH of 7.2, in a 600-gram Fagergren laboratory flotation machine. Since the mechanical agitation in such a machine showed a tendency to break up the resin beads at higher speeds, the machine was operated at 1,200 rpm, at which the breakage of the beads was negligible and favorable flotation conditions were possible. It would appear that a pneumatic flotation machine would be ideally suitable for resin flotation. The use of such a machine in the future testing program is contemplated.

All the tests in a series were run under identical conditions except for the variable under investigation. Throughout the entire investigation the aim was to conduct the tests so that they would simulate the actual conditions met in practice. The attempt was made to use resins and reagents of a purity commonly found in practice and to adopt procedures that might easily be duplicated in practice.

Phase 1

Aim. To determine suitable flotation collectors and some optimum flotation conditions for the cation- and anion-exchange resins.

Procedure. Permutit Q and Amberlite IRA-400 were selected to represent cation and anion exchangers respectively. The collectors selected for the test program included those commercially available belonging to the anionic oxhydryl, anionic sulfhydryl, and cationic classes. For each type of collector 12 tests were run, 6 for cation-exchange resins and 6 for anion-exchange resins. Under the six tests for each resin, three tests each were run for the loaded and the regenerated resins, using the three types of gangue minerals; namely, the Ottawa sand, the sandstone, and the quartz monzonite. The amount of collectors used varied from 0.015 to 0.10 pound per ton of resin content in the pulp, depending upon the effectiveness of the collector. The collectors were prepared fresh daily in the form of very dilute solutions or...
emulsions with water and kerosene. The reagent addition was made through a calibrated syringe or medicine dropper. Of the commercially available frothers investigated, Dow Froth 250 was found to be the most effective; this frother, in small amounts (0.05 to 0.1 lb per ton of solution), was used in all the tests. A conditioning time of 3 minutes and a flotation time of 3 minutes were found adequate and were used in all the tests. The pH of the pulps was adjusted to the level at which the particular ion-exchange reactions would take place in practical applications. Thus, in the case of cation exchanger Permutit Q, which was loaded with copper cations, the pH of the pulp was adjusted to 2.0. On the other hand, for the anion exchanger Amberlite IRA-400, which was loaded with [UO2(CO3)3]−4 anions, the pH was adjusted to 9.5.

In the case the collectors did show some selectivity for the resins, the pH of the pulp was varied from highly acidic to strongly basic side in order to determine the optimum pH range for the particular collector.

Since by this time it was evident that the degree of ionization of the collectors at particular pH values had substantial bearing on their effectiveness as resin floaters, the approximate pK values (numerically equal to pH at which 50 percent ionization occurs) for the various collectors were either experimentally determined by obtaining acid-base titration curves or were established through literature searches and efforts made to correlate the effectiveness of the collectors through their degree of ionization or pK values.

Results. The results of the tests under phase 1 are given in Table 2, which shows the effectiveness of various collectors for floating cation- and anion-exchange resins. Listed in the table are the active groups of both the resins and the collectors, the pK values, as well as the optimum pH range for effective collection, since all these characteristics play an important part in the reaction between the collectors and the resins. The results indicate that cation-exchange resin Permutite Q was amenable to flotation only with a cationic amine type of collector. On the other hand, the anion-exchange resin Amberlite IRA-400 was collected and floated more or less by all types of anionic collectors. Of the anionic oxhydryl group, the acid alkyl sulfates and sulfonates were found to be excellent collectors with respect to both collection and selectivity for all pH values. The anionic carboxylate collector, on the other hand, indicated good collection for the anion-exchange resins only above pH 7.0. In this case, however, the selectivity for the resins was very poor, as indicated by flotation of considerable amounts of gangue minerals along with the resins. Of the anionic sulfhydryl collectors, the thiophosphates proved to be excellent promoters for all pH values, whereas all the other collectors of this class exhibited fair to poor collection of the resins only at some specified basic pH values. It should be noted that the pK values for the effective cationic and anionic collectors are comparatively low, indicating a high degree of ionization over a wide pH range.

Tests were also run in this phase of the investigation to explore the possibility of floating sulfidized cation-exchange resins with anionic sulfhydryl collectors, such as xanthates, mercaptans, thiophosphates, and the like.
<table>
<thead>
<tr>
<th>Class of collectors</th>
<th>Chemical structure</th>
<th>Approx. pK values</th>
<th>Optimum pH range</th>
<th>Collection for cation-exchange resins</th>
<th>Collection for anion-exchange resins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic - Oxohydroxyl Carboxylates</td>
<td>R-COOH</td>
<td>5.0 (pKa)</td>
<td>7 - 14</td>
<td>Negative</td>
<td>Fair*</td>
</tr>
<tr>
<td>Acid alkyl sulfates and sulfonates</td>
<td>R-O-SO$_3^-$</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Negative</td>
<td>Good</td>
</tr>
<tr>
<td>Anionic - Sulphydryl Mercaptans</td>
<td>R-SH</td>
<td>9.7</td>
<td>11 - 14</td>
<td>Negative</td>
<td>Poor</td>
</tr>
<tr>
<td>Thiocarbonates (xanthates)</td>
<td>RO-$\ce{C-S}^-$</td>
<td>4.8</td>
<td>6 - 14</td>
<td>Negative</td>
<td>Fair</td>
</tr>
<tr>
<td>Thiocarbamates</td>
<td>RR$^1$N-$\ce{C-S}^-$</td>
<td>10.4</td>
<td>11 - 14</td>
<td>Negative</td>
<td>Poor</td>
</tr>
<tr>
<td>Thioureas</td>
<td>RR$^1$N-$\ce{C-S}^-\ce{HN}$</td>
<td>10.7</td>
<td>11 - 14</td>
<td>Negative</td>
<td>Poor</td>
</tr>
<tr>
<td>Organic sulfides (mercaptans)</td>
<td>RO-$\ce{C-S-S-C-OR}^-$</td>
<td>no acid function</td>
<td>-</td>
<td>Negative</td>
<td>Negative</td>
</tr>
<tr>
<td>Thiophosphates</td>
<td>ROR$^1$OP-$\ce{S}^-$</td>
<td>3.8</td>
<td>0 - 14</td>
<td>Negative</td>
<td>Good</td>
</tr>
<tr>
<td>Cationic collectors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amines (bases)</td>
<td>NR$_3$</td>
<td>3-4 (pKb)</td>
<td>0 - 9</td>
<td>Good</td>
<td>Negative</td>
</tr>
<tr>
<td>Amine salts (primary to quaternary)</td>
<td>RNR$_3^+$-X</td>
<td>100% ionized</td>
<td>0 - 14</td>
<td>Good</td>
<td>Negative</td>
</tr>
</tbody>
</table>

*Fair collection of resins, but without selectivity.
Sulfidization was accomplished by adding sodium sulfide to the pulp after loading the cation-exchange resin Permutit Q with suitable cations, such as copper, lead, zinc, nickel, and cobalt. The results of these tests indicate that it is possible to float sulfidized cation-exchange resins with anionic sulfhydryl collectors. Of these collectors, the highly stable mercaptans are effective under all pH conditions, whereas the xanthates are effective only in pulps containing a pH above 5.5, since they hydrolyze readily at lower pH values.

Phase 2

Aim. In phase 2 of the investigation, efforts were made to determine the effect of different variables encountered in practice, on the flotation of resins with appropriate collectors.

Variables. The variables examined, together with the procedures applied and the results obtained in this phase of the study, are listed below:

1. Temperature. In the leaching stages of most of the hydrometallurgical processes, the temperature of the pulp invariably rises. For this reason, tests were run to observe the effect of pulp temperature on resin flotation, the temperature being varied from 35°F to as high as 200°F in the case of the cation-exchange resin and to 150°F in the case of the anion-exchange resin (the maximum operating temperatures specified by the manufacturer). No difficulty was observed in resin flotation up to the prescribed temperature limits.

2. Percentage Solids in the Pulp. In typical ion-exchange applications either clear solutions or slimy liquors are encountered. In hydrometallurgical applications, however, it would often be desirable to apply ion-exchange procedures to pulps containing as high as 66 percent solids. A series of flotation tests were run in order to investigate the possibility of floating resins from pulps containing a high percentage of plus-325-mesh solids. The results of these tests indicate that it is possible to float resins both from clear solutions and pulps containing as high a percent solids as it would be convenient to handle in the flotation machine (about 55 percent solids in the case of the laboratory Fagergren machine). The flotation of resins, like any other typical flotation process, would be affected adversely by the presence of excessive slimes of both the resins and the gangue in the pulps. These factors will be considered next.

3. Effect of Fine Sizes of Resins. In order to study the effect of fine sizes of a resin on its flotation, series of flotation tests were run on closely sized fractions of an anion-exchange resin (Amberlite IRA-400). The fraction sizes included were: minus-10, plus-28-mesh; minus-28, plus-48; minus-48, plus-100; minus-100, plus-150; minus-150, plus-200; minus-200, plus-270; minus-270, plus-325; minus-325, plus-400; and minus-400-mesh. In the first series of tests, the amount of the anionic sulfonate type of collector, such as American Cyanamid Co.’s Aero Promoter 801, at 0.015 pound pet
ton of resin contained in the pulp, was held constant, and the resins floated as long as they were brought up in the froth. The results of the tests indicate that there is a decrease in the recovery of resins with the finer sizes below 100-mesh, even with prolonged flotation time. This is probably due to a deficiency in the amount of the collector required for the larger surface areas presented by the finer sizes of resin. The hypothesis was confirmed in the second series of tests by increasing the amount of the collector for the finer sizes of resins below 100-mesh. The results of this test series show that it is possible to recover nearly 100 percent of the finer sizes of resins by increasing the amount of the collector down to 400-mesh. The ultimate collector consumption for the finest sizes of resins amounted to 0.05 pound per ton of resin contained in the pulp. Below 400-mesh, because of the presence of near-colloidal sizes of resins, which commonly are poor floaters, the recovery is somewhat lower in spite of the increase in the amounts of the collector.

It was also observed that the flotation time for the nearly complete removal of resins increases with the increase in the amount of the collector for resins below 100-mesh, thereby indicating the slower flotation characteristic of fine sizes of resins. For example, the flotation time of 3 minutes was sufficient to float resin sizes up to 100-mesh with 0.015 pound of the sulfonate collector per ton of resins. For sizes below 100-mesh, however, it was necessary to lengthen the flotation time; for the ultimate removal of resins below 400-mesh, for instance, a flotation time of 6 minutes was required in addition to increasing the amount of the collector to 0.050 pound per ton of resins.

The results of the above series of tests are given in Figure 1.

4. Effect of Fine Sizes of Gangue. In the flotation testing up to this point, only the coarse (minus-65, plus-325-mesh) gangue minerals were employed to make up the pulp, and no difficulty in the flotation of resins was encountered with pulps containing such coarse gangue minerals. In practical applications, however, pulps would be encountered that might contain substantial amounts of gangue slimes. This is especially true in the case of some uranium and gold ores. Since these gangue slimes invariably exercise an adverse effect on flotation, efforts were made to determine the effect of such gangue slimes on the flotation of resins.

In order to achieve the desired information, flotation tests were run on samples containing a coarse gangue, the anion-exchange resin Amberlite IRA-400, and varying amounts of the slimes of the gangue mineral under investigation. The gangue minerals included the Ottawa sand, sandstone, and quartz monzonite, and the slimes were made up of minus-325-mesh fractions of these gangue minerals. In three series of tests, experimentation was done on 5, 10, 15, 20, 25, 30, and 35 percent by weight of the slime fractions of the gangue minerals under investigation. Except for the slime fraction investigated, all the tests in each series were run under identical conditions, use being made of a sulfonate collector, American Cyanamid Co.'s Aero Promoter 801, in the amount of 0.02 pound per ton of resin content of the pulp.
Figure 1. Effect of fine sizes of a typical resin on collector consumption as indicated by flotation of fine sizes of anion-exchange resin Amberlite IRA-400 with American Cyanamid Co.'s Aero Promoter 801.
The results of these tests, as shown in Figure 2, indicate that gangue slimes in larger quantities yield lower flotation recoveries of the resins. Probable causes for such lower flotation recoveries are consumption of the collector by the gangue slimes and slime coating on the surface of the resin beads, both of which prevent some of the resins from floating. Further examination of the resin particles under a microscope at high magnifications revealed that the surfaces of the resin beads were free from slime coating, thereby eliminating the second of the two suggested causes of lower recoveries. The consumption of the collector by the gangue slimes was then confirmed by running a series of tests on the various slime fractions with increasing amounts of the collector. The results of these tests indicate that by increasing the amount of the collector it is possible to float nearly 100 percent of the resins.

The use of additional amounts of the collector resulted, however, in a somewhat dirty resin concentrate, owing to the inclusion of some gangue slimes. This difficulty was overcome by flotation cleaning of the rougher resin concentrates whereby the gangue slimes were rejected and a clean resin concentrate obtained.

It was also possible to overcome the detrimental effect of slimes by adding small amounts of slime depressants to the flotation pulp. Organic slime depressants, such as gum, starch, and cellulose, were found to be quite effective. On the other hand, the use of sodium silicate, the most common inorganic slime depressant, was found to be undesirable because it destroyed the flotation of resins completely.

5. Effect of Flotation on the Resin Properties. In order to make the resin flotation process economically feasible, it would be necessary to recirculate the loaded resins after their flotation and regeneration; this could be accomplished in a separate flotation circuit. Under these conditions, it would be desirable to know if the resins' properties, especially their loading capacities, are impaired by successive flotation, regeneration, and recirculation. In order to obtain this information, locked tests were run on both types of resins, involving the following steps: loading the resins outside with the appropriate ions, measuring the capacities of the resins, adding the loaded resins to the flotation cells containing the suitable pulp, floating the resin after proper addition of the collector, regenerating the floated resin with an appropriate eluting solution, reloading the regenerated resins with the desirable ions, measuring again the capacities of the resins, and repeating the entire procedure 10 times.

The cation and anion loading and elution characteristics of the resins were evaluated by the procedure described by Mindler and Termini, of The Permutit Co. (Ind. Eng. Chem., v. 50, p. 166, February 1958).

The results of the above locked tests on the cation- and anion-exchange resins indicate that their loading and elution characteristics are not affected adversely by collector coating on their surfaces and their repeated recirculation in the ion exchange-flotation-regeneration circuit. In the case of
Figure 2. Effect of gangue slimes on the flotation of a typical resin as indicated by flotation of anion-exchange resin Amberlite IRA-400 in the presence of varying amounts of different gangue slimes.
the cation-exchange resin Permutit Q, with the use of copper cations, the loading capacities determined after each recirculation were within ± 0.2 pound of the normal capacity of 3.3 pounds of copper per cubic foot of resin. In the case, moreover, of the anion-exchange resin Amberlite IRA-400, with the use of uranyl sulfate anions, the loading capacities determined after each recirculation were within ± 0.2 pound of the normal capacity of 5.0 pounds of uranium oxide per cubic foot of resin.

Phase 3

Aim. The primary aim of phase 3 of the investigation was to evaluate the flotation characteristics of the commercially available ion-exchange resins in order to determine their suitability for metallurgical applications in which the resin-flotation technique might be employed.

Procedure. To obtain the desired information on the floatability of commercial resins, standard flotation tests were run under identical conditions on various classes of commercially available cation- and anion-exchange resins.

The standard flotation test consisted of floating the resin under investigation from the synthetic pulp consisting of 20 grams of resin and 580 grams of minus-65, plus-325-mesh Ottawa sand gangue and Socorro tapwater at room temperature. The cation-exchange resins were loaded outside with copper cations, and their flotation pulps adjusted to pH 2.0. The anion-exchange resins, on the other hand, were loaded outside with uranyl carbonate anions, and their pulps adjusted to pH 9.5. For cation-exchange resins, the collector employed was Alamac 26 (primary tallow amine acetate) in the amount of 0.015 pound per ton of resin contained in the pulp. For the anion-exchange resins, the sulfonate collector employed was the American Cyanamid Co.'s Aero Promoter 825, amounting to 0.015 pound per ton of resin contained in the pulp. The conditioning time of 3 minutes and the flotation time of 3 minutes were kept constant for all the tests. Dow Froth 250 was used as a frother in all the tests. In cases where the minimum amount of the collector (0.015 pound per ton of resin) was not sufficient to float all the resin, the amount of the collector was increased until complete flotation was achieved or it was ascertained that the resin either was a poor floater or could not be floated at all. Similarly, in the case of certain classes of resins, the pH of the flotation pulp was adjusted to the minimum concentration of the collector to achieve the flotation of the resins if they were reluctant to float at the prescribed pH. As pointed out earlier, the primary aim in this phase of the investigation was to determine the floatability of the resins, and every effort was made to facilitate their flotation, even if it was necessary to adapt the prescribed flotation conditions to the particular resin.

In order to compare the floatability of the resins, they were classified under the following floatability index:
The results of the tests under phase 3 are given in Tables 4 and 5. The results indicate that of the cation-exchange resins investigated, those containing active sulfonic groups are better floaters than those containing carboxylic or phosphonic groups; of the anion-exchange resins, those possessing strongly basic quaternary amine groups are readily floatable under all pH conditions, while those containing intermediate basic or weakly basic amine groups are floatable only under specified pH conditions.

Phase 4

Aim. Sufficient information on the resin-flotation technique having been obtained through preliminary test work in the first three phases of the investigation, efforts were directed in the final phase of the study toward applying the resin-flotation procedure to natural ores in order to determine its effectiveness on such ores.

Procedure. The experimental test work consisted of applying batch and locked resin-flotation procedure to selected natural ores. These ores included an oxide-copper ore from Inspiration, Arizona, containing quartz-sericite schist and granite as the gangue constituents; a uranium-bearing sandstone ore from Grants, New Mexico; and a gold ore from the workings of the Golden Cycle Corp., in Colorado.

The batch and locked tests on the above natural ores consisted of leaching 1,200 grams of minus-35 mesh fractions of these ores with suitable lixivients for a predetermined time, adding a precalculated amount of appropriate resins for ion exchange, conditioning the loaded resins with appropriate collectors (Alamac 26 for cation-exchange resins and the American Cyanamid Co.'s Aero Promoter 825 for anion-exchange resins) in amounts varying from 0:02 to 0.1 pound per ton of resin contained in the pulp, floating the collector-coated resins with Dow Froth 250, eluting the loaded resins outside by means

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### TABLE 3. FLOATABILITY INDEX FOR COMMERCIAL AVAILABLE RESINS

<table>
<thead>
<tr>
<th>Class</th>
<th>Amount of collector</th>
<th>Flotation characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>0.015 lb per ton resin</td>
<td>Very easy and selective</td>
</tr>
<tr>
<td>Good</td>
<td>Up to 0.025 per ton resin</td>
<td>Easy and selective</td>
</tr>
<tr>
<td>Fair</td>
<td>0.025 to 0.05 per ton resin</td>
<td>Selective</td>
</tr>
<tr>
<td>Poor</td>
<td>0.05 to 0.10 per ton resin</td>
<td>Some selectivity</td>
</tr>
<tr>
<td>Negative</td>
<td>Above 0.10 per ton resin</td>
<td>No selectivity</td>
</tr>
</tbody>
</table>
TABLE 4. FLOATABILITY OF COMMERCIALLY AVAILABLE CATION-EXCHANGE RESINS USING A COLLECTOR OF THE CATIONIC AMINE TYPE

<table>
<thead>
<tr>
<th>Name</th>
<th>Manufacturer</th>
<th>Active group</th>
<th>Approx. pKa values</th>
<th>Optimum pH range</th>
<th>Floatability index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ducalso</td>
<td>Permutit</td>
<td>Aluminum silicate</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Zeo-Dur</td>
<td>Permutit</td>
<td>Aluminum silicate</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Zeo-Karb</td>
<td>Permutit</td>
<td>Sulfonated coal</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Good</td>
</tr>
<tr>
<td>Amberlite IR-120</td>
<td>Rohm and Haas</td>
<td>Sulfonated styrene</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Good</td>
</tr>
<tr>
<td>Duolite C-20</td>
<td>Chemical Process</td>
<td>Sulfonated styrene</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Fair</td>
</tr>
<tr>
<td>Permutit Q</td>
<td>Permutit</td>
<td>Sulfonated styrene</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nelcine HCR</td>
<td>National Aluminate</td>
<td>Sulfonated styrene</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Good</td>
</tr>
<tr>
<td>Dowex 50</td>
<td>Dow Chemical</td>
<td>Sulfonated styrene</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Good</td>
</tr>
<tr>
<td>Dowex 30</td>
<td>Dow Chemical</td>
<td>Methyl lead sulfonate</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Fair</td>
</tr>
<tr>
<td>Amberlite IR-100</td>
<td>Rohm and Haas</td>
<td>Methyl lead sulfonate</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Fair</td>
</tr>
<tr>
<td>Duolite C-3</td>
<td>Chemical Process</td>
<td>Sulfonated phenolic</td>
<td>&lt;1</td>
<td>0-14</td>
<td>Fair</td>
</tr>
<tr>
<td>Amberlite IRC-50</td>
<td>Rohm and Haas</td>
<td>Carboxylic</td>
<td>5</td>
<td>7-14</td>
<td>Poor</td>
</tr>
<tr>
<td>Permutit H-70</td>
<td>Permutit</td>
<td>Carboxylic</td>
<td>5</td>
<td>7-14</td>
<td>Poor</td>
</tr>
<tr>
<td>Duolite C-61</td>
<td>Chemical Process</td>
<td>Phosphonic</td>
<td>5</td>
<td>7-14</td>
<td>Poor</td>
</tr>
</tbody>
</table>

* Not investigated.
<table>
<thead>
<tr>
<th>Name</th>
<th>Manufacturer</th>
<th>Active group</th>
<th>Approx. pKb values</th>
<th>Optimum pH range</th>
<th>Floatability index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IR-4B</td>
<td>Rohm &amp; Haas</td>
<td>Weak-base amine</td>
<td>7-9</td>
<td>0 - 5</td>
<td>Fair</td>
</tr>
<tr>
<td>Amberlite IR-45</td>
<td>Rohm &amp; Haas</td>
<td>Weak-base amine</td>
<td>7-9</td>
<td>0 - 5</td>
<td>Fair</td>
</tr>
<tr>
<td>Deacidite</td>
<td>Permutit</td>
<td>Weak-base polyamine</td>
<td>7-9</td>
<td>0 - 5</td>
<td>Good</td>
</tr>
<tr>
<td>Dowex 3</td>
<td>Dow Chemical</td>
<td>Weak-base polyamine</td>
<td>7-9</td>
<td>0 - 5</td>
<td>Good</td>
</tr>
<tr>
<td>Amberlite IRA-400</td>
<td>Rohm &amp; Haas</td>
<td>Strong-base quaternary amine</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Excellent</td>
</tr>
<tr>
<td>Amberlite IRA-425</td>
<td>Rohm &amp; Haas</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Amberlite XE-123</td>
<td>Rohm &amp; Haas</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Permutit SKB</td>
<td>Permutit</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Nalcite SBR</td>
<td>National Aluminate</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Duolite A-40</td>
<td>Chemical Process</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Dowex 1 &amp; 2</td>
<td>Dow Chemical</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Dowex 11 &amp; 12K</td>
<td>Dow Chemical</td>
<td>do.</td>
<td>&lt;1</td>
<td>0 - 14</td>
<td>Good</td>
</tr>
<tr>
<td>Permutit A</td>
<td>Permutit</td>
<td>Intermediate-base quaternary amine</td>
<td>5-5</td>
<td>0 - 9</td>
<td>Fair</td>
</tr>
<tr>
<td>Duolite A-70</td>
<td>Chemical Process</td>
<td>do.</td>
<td>5-5</td>
<td>0 - 9</td>
<td>Fair</td>
</tr>
</tbody>
</table>
of a columnar technique, recirculating the regenerated resins to the second batch of freshly leached ore, and repeating the procedure five times.

In the case of the uranium and the gold ores it was necessary, owing to the presence of excessive detrimental gangue slimes, to use an organic slime depressant, such as Jaguar 507 (0.2 lb per ton of solids), and larger amounts of the collector.

Although the test work in this phase of the investigation was at its best on a batch or semicontinuous basis, it was accompanied by the inherent shortcomings associated with such testing. For this reason, the results of the tests on the three ores investigated were more or less qualitative rather than quantitative, and no attempts were made to obtain optimum final tailings, concentrates, and recoveries. Nevertheless, the results of the tests clearly indicate the feasibility of the resin-flotation procedure for the treatment of the natural ores investigated. The resin flotation from the natural pulps was positive, and it was possible to recirculate the resins repeatedly without losing their loading capacities.

DISCUSSION OF RESULTS

Suitable Collectors for Cation- and Anion-Exchange Resins

The results of the test work have shown that the cation-exchange resins containing active sulfonate, carboxylate, and phosphonic groups are collected and floated from the pulp by cationic collectors of the amine type with the use of normal flotation procedures. On the other hand, the anion-exchange resins containing active ammonium or amine groups are more or less collected and floated from the pulp by all types of anionic collectors, the oxhydrolyl sulfonate and the sulfhydryl thiophosphate collectors being effective over a wide pH range.

The explanation of this behavior of the resins for the particular collectors is evident on examination of the presence of appropriate charges on the active groups of both the resins and the collectors. Thus, cation-exchange resins containing negatively charged sulfonate (-SO\textsubscript{3})\textsuperscript{−}, carboxylate, or phosphonic groups attract the positively charged ammonium (NR\textsubscript{3}\textsuperscript{+}) groups of cationic collectors of the amine type. This results in the concentration of the positively charged (NR\textsubscript{3}\textsuperscript{+}) groups on the surface of the cation-exchange resins. Since the active (NR\textsubscript{3}\textsuperscript{+}) groups of the cationic amine-type collectors are always accompanied by a nonpolar hydrocarbon tail that exhibits strong water repellency or air avidity, such collector-coated resins are readily floated when the air bubbles are introduced in the pulp. The force responsible for this concentration of the oppositely charged active groups is electrostatic, accounting for the presence of relatively strong bonds at the surface of the resins.
On the other hand, the anion-exchange resins containing positively charged ammonium (NR₃⁺) groups more or less attract the negatively charged active groups possessed by all types of anionic collectors, including even those belonging to the sulfhydryl class, such as xanthates, mercaptans, and thiophosphates. This results in the concentration of the negatively charged groups on the surface of the resins. Here again, the nonpolar hydrocarbon tail, attached to the active polar groups, is available for ready pickup by the air bubbles.

It is easy to realize that the degree of ionization of the collectors and the resins in donating the required active groups, and the relative magnitude of the charges on such active groups, play an important part in the mechanism responsible for the flotation of resins with the appropriate collectors. In addition, there are probably other factors, such as the steric configuration and size of the hydrocarbon radicals in the collectors, the hydrocarbon chain length, and the like, which may also influence the above mechanism.

The degree of ionization of the active groups of the collectors and the resins is indicated by their pK values; the lower the pK value, the higher the ionization, and the more effective the collector and the resin over a wide pH range. Thus, in Table 2 we find that the cationic amine and the anionic sulfonate, as well as the thiophosphate, types of collectors show relatively low pK values and are found to be excellent collectors for cation- and anion-exchange resins respectively over a wide pH range.

Of special significance is the effectiveness of thiophosphates, which were found to be as effective collectors as sulfonates over a wide pH range in spite of their higher pKa values (3.8) as compared with those of sulfonates (1.0). This behavior of thiophosphates may be attributed to the presence of highly polar negative groups in such compounds. The high polarity compensates for the lack of ionization at lower pH values.

On the other hand, the anionic oxhydryl carboxylates (fatty acids) and sulfhydryl thiocarbonates (xanthates), whose pKa values are about 5, show fair collection for anion-exchange resins only above pH 6.0. The anionic sulfhydryl mercaptans, ionizing only in alkaline pulps and having a high pKa value of about 9.7, exhibit mediocre collection for the anion-exchange resins and only above the same pH, whereas the anionic sulfhydryl collectors of the thiocarbonates and thiourea classes, having weak acid functions, both show very poor collection for the anion-exchange resins and only at very high pH values. Finally, the organic sulfides, having no acid function at all, show very poor or no collection for the anion-exchange resins regardless of the pH.

Difference in the Floatability of Commercially Available Resins

The difference in the floatability of the commercially available cation- and anion-exchange resins maybe attributed to the degree of ionization.
and the magnitude of the charges or polarity possessed by the active groups of the resins. The strongly polar sulfonate and amine groups show greater surface activity than the weakly polar carboxylic and phosphonic groups. Thus, in Table 4 we find that the cation-exchange resins containing active sulfonate groups exhibit excellent floatability under a wide pH range, not only because of their higher degree of ionization due to their low pKa values (about 1.0), but also because of the stronger polarity of the negatively charged sulfonate groups. On the other hand, the cation-exchange resins of the weakly polar carboxylic and phosphonic types, which ionize only at a higher pH, owing to their pKa value of about 5.0, show fair to poor floatability and only above pH 7.0.

In the case of the floatability of the commercially available anion-exchange resins, however, the differences in their floatability should be attributed only to their degree of ionization or pKb values, since all such resins contain equally strong, positively charged amine (NR₃⁺) groups. Thus, in Table 5 we find that the strongly basic quaternary amines exhibit good floatability over a wide pH range because of the higher degree of ionization due to their low pKb values, whereas the weakly basic polyamine type of resins, owing to their high pKb value of about 9.0, show good floatability only below pH 5.0. The intermediate base quaternary amines, on the other hand, resembling more the strongly basic type of resins, and having a pKb value of about 5, show good floatability only below pH 9.0.

The above mechanism, in which only organic ions charged oppositely to the resin surfaces function as collectors, implies that some of the ions present on the loaded resins are replaced by similarly charged active groups of the collectors. In this exchange, however, the number of ions involved must be comparatively small, as indicated by the very low collector consumption by the resins (.015 pound per ton of resins) and hardly any change in the loading capacity of the recirculated resins. The above contention was confirmed by further experimentation, the results of which revealed only trace amounts of adsorbed ions in the pulp solution after collection of the loaded resins with the appropriate collectors. It is postulated that in the above mechanism only 5 to 10 percent of the resin surface needs to be collector coated in order for the resins to show good floatability.

Surface-Active Agents as Collectors for the Resins

The above discussion indicates that the phenomenon displayed by the flotation collectors is best characterized by surface-active agents, and that all one has to do in order to float ion-exchange resins is to select an appropriate cationic or anionic surface-active agent. This theory was confirmed by running flotation tests with the series of reagents belonging to the following groups of commercially available surface-active agents:
- Cationic: Armac, Alamac, Arquads, Alkaterge, Aciterge, etc.
- Anionic: Emulsol, Avivol, Dupnol, Ultratwet, Daxad, Aerosol, etc.
In all the tests the cationic surface-active agents were more or less able to float the cation-exchange resins, whereas the anionic surface-active agents showed more or less selectivity toward the anion-exchange resins.

Cation-Exchange Resin Flotation After Sulfidization

It is also possible to float cation-exchange resins after sulfidization with anionic sulfhydryl collectors. Of such collectors mercaptans were found to be the most effective, since they are stable in the acid circuits that are usually encountered in the leaching of metallic ores, such as copper, lead, zinc, cobalt, and nickel. Of the cations loaded and sulfidized, the copper- and lead-loaded resins floated the best, because of the relative ease of sulfidizing such cations. Such a sulfidization-flotation technique would be very handy in the case of certain difficult-to-treat ores containing excessive amounts of gangue slimes that would be activated with increasing amounts of amine-type cationic collectors specified for cation-exchange resin flotation.

General Discussion of Resin Flotation

The results of the investigation have shown that the flotation of resins under optimum conditions is very rapid, clean, and nearly complete, under conditions of both loading and regeneration.

The test work, moreover, has shown that the loading capacities and the elution characteristics of the resins are not adversely affected by their flotation and recirculation.

The size of the resin particles is not critical in the resin-flotation process as it is in the typical resin-in-pulp procedures, which require a closely sized range, such as minus-16-mesh, plus-28-mesh. It is possible to float unsized resin particles effectively from about 16-mesh down to a size at which the resin beads lose their normal physical characteristics (below 400-mesh in most cases). The finer the size, the greater is the physical stability of the resins and the greater the efficiency of a given volume of resin, owing to decrease in the time required for the resin to reach equilibrium in the loading and elution phases.

The amounts of collectors required for the flotation of resins vary from 0.015 to 0.1 pound per ton of resins contained in the pulp, depending upon the amount of detrimental gangue slimes present in the pulp. The finer sizes of resins, below 100-mesh, require correspondingly larger amounts of collectors and a longer time of flotation. A frother, such as pine oil or Dow Froth 250, in small amounts is necessary to create desirable froth conditions. A little neutral oil, such as kerosene, is sometimes desirable to stabilize the froth conditions.
Test work has also indicated that the presence of excessive amounts of gangue slimes may have a detrimental effect on the flotation of resins, owing to the consumption of collectors by such slimes. This difficulty, however, is overcome by increasing the amounts of the collectors. In some cases the increase of the collector results in slightly dirty resin concentrates, but it is possible to clean such concentrates by subjecting the rougher concentrate to refloating in the cleaner flotation circuit. The addition of organic slime depressants has been found effective for controlling the gangue slimes; however, sodium silicate (a general inorganic slime depressant) is harmful to the flotation of resins. This is possibly due to interaction between silicic acid or silicate ion and the active amine groups on the anion-exchange resins during their flotation, or to the interaction between silicic acid or silicate ion and active amine groups in the cationic collector used in cation-exchange resin flotation. In both cases the presence of sodium silicate prevents flotation of resins.

Practical Application of Resin-Flotation Procedure

Tests of the resin-flotation procedure on the natural ores of copper, uranium, and gold have indicated that the process is technically and economically feasible and that a continuous process using this new procedure can be developed. Such a process would be applicable to all metals that are capable of recovery from a leached pulp, or from difficult-to-treat waste liquors, in cationic or anionic form by means of ion-exchange resins. Applications that are of particular economic interest at present include uranium and gold extractions, using anion-exchange resins; and copper, zinc, nickel, and cobalt extractions, using cation-exchange resins. Further test work with natural ores, especially uranium and gold ores, is being undertaken in order to determine the optimum flotation conditions and to develop a workable flowsheet for this process.

Inasmuch as the newly developed procedure involves the leaching of ores followed by ion exchange and the flotation of resins, it may be designated as the Leach-Ion Exchange-Flotation (L-I-F) process. It is hoped that such a process will fill the need for a versatile procedure incorporating the best techniques available in hydrometallurgical processing for the recovery of metals from low-grade and complex ores.

CONCLUSIONS

The following conclusions may be drawn from the results of the above investigation:

1. It is possible to float the majority of the commercially available cation- and anion-exchange resins from unclarified solutions, as well as pulps containing a high percentage of solids.
2. The cation-exchange resins containing negatively charged active sulfonic, carboxylic, and phosphonic groups are amenable to flotation with positively charged amine-type cationic collectors and cationic surface-active agents.

3. Anion-exchange resins containing positively charged active amine groups are more or less collected and floated from the pulp by all types of negatively charged anionic collectors and anionic surface-active agents, the oxhydrly sulfonate and the sulfhydryl thiophosphate collectors being the most effective over a wide pH range.

4. It is postulated that the mechanism involved in the selective flotation of resins with appropriate collectors is the electrostatic attraction of both the oppositely charged active groups of the resins and the collectors, the predominant factors governing the mechanism being the degree of ionization (depending upon the pK value) and the magnitude of the charges on the active groups involved.

5. Under optimum conditions the flotation of resins is very selective, rapid, and nearly complete. Moreover, the flotation of resins is not affected adversely by fine sizes of resins or the presence of coarse and fine typical gangue minerals, if the usual precautions prescribed for such flotation are observed.

6. The results of the preliminary tests using the Leach-Ion Exchange-Flotation (L-I-F) technique on natural ores of copper, uranium, and gold indicate that the process is technically and economically feasible.

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