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RMO-2679

Metallurgy--Raw Materials

UN-TR-4

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TOPICAL REPORT

DEVELOPMENT OF ORGANIC COLLECTORS
for the
FLOTATION OF URANIUM MINERALS

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December 10, 1954

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ABSTRACT

A series of organic reagents for the collection and flotation of several secondary uranium minerals has been developed, this being the mono-alkyl nitrogen substitutions of the dithiocarbamate grouping with a chain length of at least eight carbon atoms. In flotation tests, using the potassium salt of n-decyl dithiocarbamate as collector, high recoveries of autunite have been obtained from mixtures of finely-ground synthetic autunite and silica sand.

Certain base-metal salts added as conditioning agents have increased the collecting properties and selectivity of the dithiocarbamates in the flotation of both autunite and carnotite. In single batch and locked tests, using lead as the base metal ion, recoveries of over 95 percent of the uranium have been obtained, with ratios of concentration as high as 13:1. Preliminary tests on natural ores show encouraging results; the problems of liberation and conditioning must be solved for each ore.

ACKNOWLEDGMENTS

While the investigations on the collecting properties of the dithiocarbamates were made by the authors, most of the staff members (both full-time and part-time) on this project contributed materially to various parts of the work. Particularly the authors wish to acknowledge the help given by Dr. Lon S. McGirk on mineralogical studies, Dr. H. J. Seim on preparation and alteration of synthetic minerals, Mr. J. S. Winston for X-ray studies on synthetic minerals, and Mr. D. W. Frew, Jr. for synthesis of the collectors.

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DEVELOPMENT OF ORGANIC COLLECTORS FOR THE
FLOTATION OF URANIUM MINERALS

By

R. J. Morris, H. P. Ehrlinger III, and J. N. Butler

INTRODUCTION

From earlier surveys of a large number of organic compounds which showed some promise as collectors for uranium minerals, a series of reagents has now been developed which appears to have a high selectivity in the flotation of autunite; these may also be satisfactory collectors for carnotite and torbernite. The first investigations, covering tests on approximately twenty reagents, all proved negative. These were reported in UN Topical Report No. 3, July 1, 1954, as a first progress report. This report covered work on oxygen-containing uranyl-chelates only.

A continuation of the study of collector properties of nitrogen- and sulfur-containing organic compounds with synthetic minerals is in progress. Results of this investigation that have so far been completed are summarized in the following section.

In order to eliminate the many variables inherent in ore samples, synthetic minerals were prepared and these were then mixed with several gangue minerals. This procedure makes possible an evaluation of the collecting properties of the dithiocarbamates in comparison with other reagents.

SUMMARY AND CONCLUSIONS

Flotation tests on the separation of synthetic autunite from various gangue minerals have shown recoveries of as high as 98 percent of the autunite with ratios of concentration up to 13:1. Under the conditions of these tests, however, complete liberation and non-interference by slimes, etc., was assured. Continuation of these investigations will now be on natural minerals and ores. Results as indicated above have been obtained under fairly variant test conditions, both on single batch and locked tests.

From results of tests completed to this time, the following conclusions can be drawn:

1. Several of the dithiocarbamates are good collectors for autunite. These include the ammonium salt of n-octyl and potassium salts of n-octyl up to n-tetradecyl dithiocarbamate.
2. Additions of certain base metal ions to the flotation materially increase the selectivity of these collectors and enhance their collecting properties. The most effective base metal ion is lead.
3. These collectors are not sensitive to extremely close pH control and satisfactory recoveries have been obtained in the pH range from 4 up to 10.
4. These reagents are also collectors for carnotite and torbernite, although their collecting properties and selectivity do not appear to be quite as good as for autunite.
5. The present work shows that the potassium n-decyl dithiocarbamate, in combination with lead nitrate, gives the best flotation. With this reagent, recovery of 98 percent of contained autunite has been obtained, with a ratio of concentration of 13:1.

The above conclusions are based primarily on flotation of synthetic minerals. Thus the work represents recovery under conditions of complete liberation and clean mineral surfaces. Application of these reagents to recovery of uranium from natural ores is dependent upon determinations of proper grinding and conditioning.

DEVELOPMENT OF COLLECTOR STUDIES

General Consideration of Uranium Ores

Examination of specific ores, and consideration of the mineral species content of uranium-bearing ores in general, led to the conclusion that a logical attack on the general problem of the beneficiation of uranium ores should be two-fold: one phase should deal with the concentration of uranium-bearing material from primary, predominantly uraninite-pitchblende-gummite type ores, and the other with the dominantly supergene ores of which autunite is an example. Ores containing mixtures of these types might then be successfully tested.

Each of the above types of ore presents a different problem. The primary ores contain uranium minerals of the oxide type, with subordinate lead compounds and others. Basic research on the structures of the primary minerals, while productive, is not yet definitive. Also, the primary minerals in the past have been of less common occurrence in domestic uranium deposits than the ores containing secondary minerals. Therefore, first attention has been given in this project to the ores containing secondary (or supergene) minerals.

Secondary Uranium Minerals

The important secondary (or supergene) minerals of uranium include autunite, torbernite (and meta-torbernite), carnotite, tyuyamunite, etc. The usual problem in a study of beneficiation by flotation contemplates the determination of the most economic means of extraction of a single mineral species, as for example sphalerite, or galena. The zinc and lead deposits have few supergene mineral species. Secondary, or supergene species bearing uranium are many. In the process of flotation alone, it could be reasonably expected that any one reagent and conditions could only deal effectively with a very few mineral species.

The groupings adopted by mineralogists (to include the calcium and copper uranyl phosphates) are as follows:

Torbernite Group

Torbernite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-12 \text{H}_2\text{O}$
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10-12 \text{H}_2\text{O}$
Uranocircite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$
Saleite	$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10 \text{H}_2\text{O}$
Zeunerite	$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10-16 \text{H}_2\text{O}$
Uranospinite	$\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8 \text{H}_2\text{O}$

Meta-torbernite Group

Meta-torbernite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$
Meta-autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6 \text{H}_2\text{O}$
Meta-zeunerite	$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8 \text{H}_2\text{O}$

The two groups above include species which may exist in one or the other group, depending on their exposure to conditions of temperature and chemical environment which can exist in Colorado Plateau deposits. It is of interest to note that in several of the above species the water content is variable. This water is presumed to be "zeolitic water".

Any actual specimen obtained from the Plateau cannot be immediately placed in either of the above groups without careful x-ray analysis. One can therefore place all of the above species within the mineralogist's "uranite group", recognizing the great similarity between the (PO_4) and the (AsO_4) molecular groupings.

When starting with a "uranyl phosphate or arsenate of (a cation), with variable zeolitic water", an examination of x-ray data shows a very close structural similarity. The cation, whether it be Ca, Cu, Mg, or Ba, is in the interstices between molecular layers, more or less as if it were glue between sheets. The sheets are made up of (UO_2) , and (PO_4) or (AsO_4) groups in intimate relation. This structure gives these minerals their perfect basal cleavages.

As the mineral species of the "uranite group" seem to be isostructural, it was decided that work upon the most conveniently-utilized member of the group should be reasonably valid for all members of the group. The species of the group which is most convenient to work upon is autunite, not only because the synthetic autunite mineral can be quite easily prepared, but also because its fluorescence affords a ready means of checking upon its concentration in laboratory tests. The major success to date has been realized with autunite, as detailed later in the data on metallurgical tests.

Another group which is isostructural within its members, is the carnotite group. This includes:

Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3 \text{H}_2\text{O}$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot n \text{H}_2\text{O}$

Carnotite and tyuyamunite have often been mistaken for each other. It is a fair probability that much of the Plateau material labelled "carnotite" is actually tyuyamunite, or a mixture of the two minerals. On a mineralogical basis the two species appear to be of distinct structural types. However, because of the ease of conversion of one to the other by admixture of the proper ions, it can be considered that the two species

are of identical mineralogical nature, if not in fact isostructural. It may be pertinent to note here that previous mineralogical investigations of the structure of carnotite have been confined to work on anhydrous $K(UO_2)(VO_4)$, a fused material. In the present work it has been possible to produce material which appears to be identical with the natural product, and in which the K/Ca ratio can be varied at will.

The carnotite-tyuyamunite group also has cation bonded sheets, and here the sheets are of $(UO_2VO_4)_n^-$. The known similarity between phosphorous, arsenic and vanadium may indicate that the uranite group and the carnotite group should present similar metallurgical problems. The two groups have been treated as separate problems, but results indicate that their similarities are important.

The two major groups of the various species of secondary uranium minerals have been considered, but several groups of some importance remain. These are the uranium (or uraniferous) carbonates, oxides, sulfates, and silicates, plus other minor species. In view of their estimated relative scarcity, as yet none of these have been studied.

Therefore, work has been done on this basis: there are two groups of supergene minerals; of the species within these groups all have uranyl bonded to either phosphates, arsenates, or vanadates, in a sheet, and the sheets are held together with Ca, Cu, Mg, K, or Ba as cations. Therefore, it may be possible to develop a flotation reagent which will hook on to the cation of any of the species, the uranyl "ion", the phosphate-arsenate-vanadate "ion", or any combination of these active centers.

Flotation Collector Studies

In previous research under this project a number of studies were initiated on oxygen-, nitrogen-, and sulfur-containing organic compounds in an attempt to develop a suitable series of flotation reagents for uranium minerals. Of the compounds considered to date the greatest success has been found with nitrogen- and sulfur-substituted organic systems, particularly where both of these elements are found in the functional group. This promising behavior supported earlier reasoning that such systems might be expected to be suitable collectors because of the bond angles, atomic size and negativity exhibited by such nitrogen and sulfur functions. It now appears that more satisfactory bonding is developed between the collector and mineral surfaces, for either chelation or salt formation by the use of these functional groups than by any other elemental substitution so far studied.

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1. Sundberg and Sillen - Arkiv fur Kemi, 1:42, pp. 337-351 (1949)

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A number of organo-sulfur and organo-nitrogen compounds, with a variety of functional groupings, were first studied. Later, attention shifted to a careful consideration of organic compounds in which the active grouping was composed of both nitrogen and sulfur substitutions. In all about forty-five compounds--representing mainly the acid, amide, ester, aldehyde, ketone, and other functions and their nitrogen and sulfur counterparts, representing both the aliphatic and aromatic organic series--were considered for their collector properties. A study of these compounds led to a focusing of attention on a few organic compounds with a nitrogen-sulfur functional group belonging to the dithiocarbamate series. As it was learned that some of these compounds had been previously considered for flotation and extraction work with other minerals,² a decision was made to thoroughly investigate some aliphatic and aromatic compounds containing this functional group.

Encouragement in the continuation of this research came through the collector activity shown by some of the low molecular weight compounds. Further interest in examining this functional grouping for collector possibilities was engendered when it was learned that the abstract literature,³ as near as determinable from available library facilities, carried no co-ordinated study of such compounds. Indeed, little published data was found on the mono alkylated dithiocarbamate function for any specific use and such data as was reported sparingly mentioned the use of these compounds for collector purposes.⁴ It was found, however, that some data was available on the dialkyl dithiocarbamate series outlining their use as extracting agents for uranium.⁵

Having decided to make a thorough study of the dithiocarbamate series, a general plan was laid out for the necessary developmental studies. Essentially this consisted of the following parts:

1. A comparison of the collector characteristics between aliphatic and aromatic substituted dithiocarbamates.
2. U. S. Patent Nos. 1,497,699 (1924), 1,879,871 (1932), 1,922,247 (1934).
3. J. Chem. Soc. Abstracts, p. 55 (1892), Losanitsch, Ber., 24, p. 3021 (1892); J. Chem. Soc., 118-1, p. 536 (1920); Compin, Bul. Soc. Chem., 27, p. 464 (1920); Delépine, *ibid* 3, p. 643 (1908); Bedford & Gray, Ind. Eng. Chem., 15, p. 720 (1923); Doria et al., J. Org. Chem., 14, p. 952 (1949).
4. A. F. Taggart, "Handbook of Mineral Dressing", John Wiley & Sons (1948).
5. U. S. Atomic Energy Commission Reports: C-4.360.9, C-4.100.23, H-4.100.38, R/GC/1073, MX-182.

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2. A comparison of the collector properties for the mono- and disubstituted nitrogen in the functional group, as for example the case of the mono- and diethyl dithiocarbamates.
3. A study of how the length of carbon chain may alter the collector properties of the functional grouping.
4. A comparison of the flotation characteristics of the even and odd carbon chain systems, particularly for the saturated aliphatic substitutions from four to eighteen carbon atoms.
5. A survey of the salt modifications, solubility, stability and purity of each of the compounds prepared and the effect of each factor in turn upon the utility of the compound as a collector.
6. A study of the pH range in which collector action appears most successful with an ultimate goal of obtaining the optimum pH range for each collector on each uranium mineral investigated.

The work to date on this extended study is by no means complete. However, a number of the objectives have been sufficiently investigated to suggest some conclusions. The general conclusions are briefly reported here.

1. In a study of some twenty aromatic and aliphatic compounds containing the dithiocarbamate grouping the aliphatic compounds showed consistently better collector properties for autunite and carnotite minerals than did the aromatic compounds.
2. A comparison of results obtained with the saturated aliphatic mono- and disubstituted nitrogen loadings on the dithiocarbamate function left little doubt of the proper choice. In all cases studied the mono-substituted nitrogen compounds were more effective as collectors.
3. So far the most satisfactory flotation results have been obtained with mono-alkyl nitrogen substitutions with a chain length of at least eight carbon atoms. Incomplete studies on this series up to eighteen carbon atoms indicates an optimum in collector activity at ten carbon atoms for autunite and carnotite minerals.
4. As yet no conclusive data can be reported from comparison studies of the even and odd saturated alkyl dithiocarbamates. It appears from the data now available that there is little choice between the even and odd carbon chain series for collector purposes for autunite and carnotite minerals. The alteration of any single collector from an even to an odd carbon series of one more or one less carbon atom does not seem to materially change the flotation characteristics for that collector.

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5. A study of salt modifications of these compounds has resulted in narrowing the choice of metal ions to the alkaline or alkaline earth members. A further restriction to be placed on the dithiocarbamate salts, although it does not appear to limit the use of the above cationic centers, is that chelation between the dithiocarbamate grouping and the metal cation must be avoided as this usually impairs its solubility, its stability, and its chelating ability, and hence destroys its value as a collector.

Results obtained to the present time indicate that good salt preparations for these compounds up to eight carbon atoms in size would be the strontium salts, and beyond eight carbon atoms up to eighteen the potassium salts show better solubilities and can be sufficiently purified for isolation and flotation studies.

In any case, it has been found that if the salt modification is pure and dry no deterioration in the usual handling and storage will result. These salts in turn are sufficiently soluble to act as suitable collectors for autunite and carnotite minerals.

6. A detailed study of the effect of pH on collector activity was made on each promising collector prepared. The most successful pH range for optimum collector action of these dithiocarbamate compounds, when tested with autunite and carnotite minerals, appears to lie between 6 and 8. It is possible however, that these pH values may need to be altered in use either because of altered efficiency of the collector with different mineral surfaces or because of gangue conditions encountered in the ore.

Preparation of Collectors

Care has been exercised in preparing pure amines by fractionation of the organic compounds after the crude was obtained either from commercial sources or by synthesis here. It was then possible to prepare the dithiocarbamate series by gently refluxing the desired pure amine with carbon disulfide and the proper base to prepare the crude salt. The pure salt product was then isolated by repeated recrystallization from suitable solvents. The need for pure preparations became evident when it was found that on handling and storage, the impure dithiocarbamates were not stable. It might also be noted here that no lack in collector efficiency was found by the use of relatively pure single dithiocarbamate salts. On the contrary, they appear at least as successful as any mixed salt combination for collector purposes and obviously are much more suitable for a flotation study of this kind.

Further investigations of the collector possibilities for the complete series of mono-alkyl dithiocarbamate compounds from four to eighteen carbon atoms are being continued. Developmental studies of these collectors

are still being conducted along the pattern discussed above and further data on their usefulness as collectors are being assembled. However, in addition to the above consideration of these compounds, it is obvious that the development of successful flotation procedures also demands careful studies of proper mineral liberation and surface conditioning. Hence, these phases of flotation techniques, along with the proper adaptation of the more mechanical techniques of flotation to meet the specific needs of this project, are also being given careful consideration. The progress in these studies may be found in this report under another section.

USE OF SYNTHETIC ORES

In order to evaluate the collecting properties of the dithiocarbamates for uranium minerals, or the properties of any collector for uranium or other minerals, it is desirable to eliminate the many variables encountered in floating a natural ore. For this reason the decision was made to use synthetic ores, these being prepared by adding pure synthesized uranium minerals to gangues of ground silica sand or other gangue minerals, such as calcite, iron oxide, etc.

Relatively pure autunite and carnotite have been prepared in the laboratory and these in turn have been altered to torbernite and tyuyamunite, respectively. In the alteration, it is probable that only surface alteration took place--not complete alteration.

A study of the surface alteration of various uranium minerals is of importance in order to determine the possibility of enhancing the floatability when other metal ions are substituted or exchanged on the surface.

Preparation of Synthetic Autunite

After a few preliminary tests, a standard procedure for making synthetic autunite was adopted as follows:

Dissolve 12.5 gr. of mono-calcium phosphate in one liter of cold distilled water and 25 gr. of uranyl nitrate in 100 ml. of water. The uranyl nitrate solution is then added slowly to the calcium phosphate solution, with constant stirring. The precipitate is allowed to settle and clear solution is decanted off. Precipitate is then washed with water until a test with citro-molybdate reagent indicates that excess PO_4 has been removed. A solution of 10 gr. of calcium acetate in 500 ml. of water is then added and the precipitate agitated for two days in order to produce relatively coarse autunite crystals. The precipitate is then filtered and air-dried. This procedure produces autunite crystals of a maximum size of 325-mesh.

X-ray patterns of this synthetic autunite and of synthetic carnotite are identical with patterns for pure natural minerals.

Preparation of Synthetic Carnotite

The method of Sundberg and Sillen⁶ was investigated but was found unsuitable for preparing relatively large amounts of carnotite. The product appears to be quite impure and is anhydrous; therefore, it does not have properties the same as a natural mineral. A method that suggested

6. Sundberg and Sillen--op. cit. p. 10

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itself was precipitation from a potassium carbonate solution with sulfuric acid, which is similar in principle to the precipitation of yellow cake in the carbonate leach process. Early attempts at this method gave a nice crystalline product that had all the physical characteristics of carnotite and gave excellent X-ray diffraction patterns.

Procedure: A typical run for preparing about 12-13 grams of synthetic carnotite is made in the following manner: 3.2 grams of C. P. vanadium pentoxide is dissolved in 700 ml. of solution containing 50 grams of potassium carbonate, by boiling gently until a clear solution is obtained. The solution is then cooled and 14 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in it using rapid stirring. Tests showed the uranyl nitrate to be difficultly soluble at higher temperatures but quite soluble at room temperature. After complete solution is effected the solution is heated to boiling, and with rapid stirring and continued boiling 6 N sulfuric acid is added until precipitation starts. This takes about 40-50 ml. of the 6 N acid. Further addition of the acid is continued dropwise from a burette, until the pH is in the range of 5-7. This takes about 40-50 ml. additional acid. A good drop rate has been found to be a drop every 3-5 seconds, the process taking about 60 to 90 minutes. Replenish with water if necessary. The preparation is then allowed to digest on the low-temperature hotplate for 8 or more hours, after which it is cooled, filtered, washed, and air dried. The amount of reagents specified above provides a slight excess of vanadium, which gives the filtrate a slight orange color but quantitatively precipitates all the uranium.

Surface Alteration Studies

Another important phase of this work is a systematic study of the possibility of altering the surface of uranium minerals in order to make them more amenable to flotation. The polarographic method appeared to be a suitable means of checking results of studies involving treatment with many of the common metal ions. It offers not only a qualitative but also a quantitative method of determining the extent of ion exchange or adsorption on the mineral surface. The importance of having pure minerals for these investigations is obvious and most of the flotation tests thus far have been conducted using synthetic minerals of known purity.

Because of its ease in preparation and its fluorescent properties the first synthetic uranium mineral considered was autunite and studies thus far have been largely limited to this mineral. The fact that autunite does undergo ion exchange with a number of metal ions has been known for many years. However, the conditions under which these exchanges were effected involved the using of concentrated solutions of the metal ion. Therefore, it was considered desirable to learn more about the extent of

7. Am. Mineralogist 14, p. 265 (1929)

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this ion exchange using relatively dilute solutions having a concentration more feasible economically for standard flotation procedures.

The exchange studies were therefore made using 0.01 M solutions of the metal ions and so far tests have been made with chloride solutions of copper, zinc, lead, cadmium and manganese. Four solutions of each metal ion were prepared, varying the pH of each series from approximately 5 to 2 with dilute hydrochloric acid. Polarograms were run for each solution as a standard and to determine if pH had any effect on the wave heights. The same solutions were then used in the treatment of the mineral in which 0.25 gram samples of the synthetic autunite were treated with 20 ml. of the metal ion solutions for 10 minutes. The solutions were mechanically stirred during the treatments. The solutions were then filtered through a dry filter and polarograms run on each filtrate. The number of millimoles of the metal ion exchanged was then determined by the decrease in wave heights and the percent of exchange calculated from the volume and strength of the metal ion solution and the weight and percentage composition of the synthetic autunite. Results of this investigation are given in Table 1. Even though the copper exchange was low, the treated mineral after washing had a slight bluish green color. Whether the treatment with lead is all ion exchange or partly adsorption is debatable since early workers in the field reported an exchange considerably higher than theoretical when synthetic autunite is treated with lead solutions.⁸ However, this does not detract in any way from the possible usefulness of this relatively high exchange for surface treatment in flotation. The relatively high exchanges may also be partly attributed to the fact that the synthetic autunite has an extremely small particle size.

Expansion of this study to other metal ions and also to carnotite and uraninite is contemplated.

Exchange of Autunite to Torbernite: Following the procedure of Fairchild,⁹ samples of synthetic torbernite were prepared from autunite as follows: 2.0 grams of synthetic autunite were treated with 200 ml. of solution containing 40 grams NaCl (half saturated) on a low temperature hotplate (70-80° C) for 48 hours. This prepared sodium autunite, after filtering and washing, was treated similarly with 200 ml. of solution containing 80 grams of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ for 48 hours or longer. Synthetic torbernite prepared in this manner showed excellent X-ray diffraction patterns and was submitted for flotation tests. Chemical analysis of the air-dried

8. Am. Mineralogist, 14, pp. 265-275 (1929)

9. *ibid.*

Table 1 - Exchange Studies on Synthetic Autunite with 0.01 M Solution of Various Metal Chlorides for 10 minutes.

Metal Salt	pH		Percentage of Exchange
	Before Treatment	After Treatment	
CuCl ₂	4.62	4.44	10.3%
	3.85	4.13	9.5%
	3.06	3.27	6.5%
	2.02	2.07	8.0%
ZnCl ₂	5.84	4.80	26.5%
	4.06	4.54	27. %
	3.05	3.52	29. %
	2.02	2.16	26. %
PbCl ₂	4.80	4.01	42. %
	4.07	3.83	40.5%
	3.02	3.09	39. %
	2.03	2.06	44.5%
CdCl ₂	5.88	4.65	23. %
	4.12	4.60	23. %
	3.07	3.40	23. %
	2.04	2.20	23. %
MnCl ₂	6.25	4.78	20. %
	4.00	4.47	20. %
	3.00	3.40	23. %
	2.0	H ⁺ ion interference in polarogram	

The results indicate a very high percentage of exchange with lead and a rather low exchange with copper. The other metals tested showed a lower percentage of exchange than lead, with very little variation between them.

mineral showed a water content equivalent to 7.7 H₂O per molecule. Analysis for copper on the anhydrous mineral gave 8.02% CuO as compared to a theoretical 10.03%. Analysis for uranium gave results slightly higher and P₂O₅ slightly lower than theoretical.

The possibility of preparing torbernite by a one-step exchange by treating the autunite directly with CuCl₂ was also investigated. For this treatment, a copper solution similar to that described above was used, and was run for 48 hours. Analysis for copper gave 3.12% CuO indicating an exchange of only a third. A dehydration study was also made on this synthetic mineral and the water mol content of the air-dried mineral was found to be approximately equal to 7.4 H₂O.

The treatment of synthetic autunite with a solution of CaCl₂ (80 gr. in 200 ml.) at 70° to 80°C. to improve crystal size was also investigated. Crystal size improved only slightly by this one step exchange, but when the product was treated with NaCl solution and then followed by a CaCl₂ treatment, crystal size improved considerably. Analysis of this air-dried product gave a water content equivalent to 6.6 H₂O and a P₂O₅ content equal to theoretical. The uranium content was slightly higher than theoretical.

Alteration of Synthetic Carnotite: Hillebrand¹⁰ has reported that he had some success in the exchange of calcium and potassium on natural samples of carnotite and tyuyamunite. The best reagent for altering the carnotite was Ca(HCO₃)₂ saturated with CO₂. Two grams of synthetic carnotite were therefore treated with 750 ml. of saturated Ca(HCO₃)₂ with CO₂ bubbling through the solution for two days from a dry ice generator. The solution was then filtered and washed and a small sample retained for X-ray studies. The treatment was repeated a second time in exactly the same manner with new Ca(HCO₃)₂ solution. Similarly, a third treatment was started and allowed to run for 43 days. Qualitative analysis on the filtrates indicated appreciable potassium in the first filtrate with decreasing amounts thereafter. X-ray diffraction patterns on the altered carnotite after each of three stages of treatment gave the pattern of carnotite indicating that the exchange was by no means complete even after a total of 43 days treatment. Chemical analysis on the final product has not as yet been completed. Since the X-ray diffraction pattern is derived from the crystal structure rather deep in the individual crystals, analysis of the product by electron diffraction methods is contemplated.

10. Am. J. Sci. 205:201 (1942)

TEST PROCEDURES

Contact Angle Studies

In the early phases of the study of organic collectors for uranium minerals, attempts were made to determine contact angles for the several minerals being studied with various possible collectors. The procedure for determining contact angles was modified from the work of Taggart, Taylor and Ince¹¹ and Wark and Cox¹². Because of the small contact angles obtainable in most cases, procedure was modified by mounting the mineral specimen and suspending it in the solution with the polished face above the bubble holder. The bubble was then forced from the inverted holder and in rising through the solution, adhered to the mineral surface if any contact occurred. In order to obtain comparative results, the bubble size, depth of solution, and distance of bubble travel had to be held constant.

The technique of contact angle determinations on uranium minerals failed to give the required information, primarily because of difficulty in obtaining uranium samples having large single crystal faces. A few satisfactory specimens of autunite and uraninite were obtained, but not in sufficient quantity for the large number of contact angle determinations to be made.

Finely divided relatively pure minerals were then mounted on faced nail heads, but difficulty was again encountered because many of the organic reagents gave excellent contact angles with the cements used for mounting the fine-sized minerals. Some valuable preliminary information was obtained, but because of the difficulties encountered it was decided to use a beaker flotation test procedure.

Beaker Flotation Tests

A procedure for beaker floatability tests is described by Lublowitz¹³. This procedure proved to be unsatisfactory on uranium work, and a technique was therefore developed for making relatively rapid beaker flotation tests. The beaker flotation test procedure adopted on this work includes aeration in place of the rotation of the beaker, and it has been possible to use these relatively rapid beaker tests for both qualitative and semi-quantitative flotation testing. The procedure can be applied equally well to comparative tests on a series of collectors, a series of frothers, or for the comparison of effects of various conditioning agents on the mineral particles.

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11. Trans. A. I. M. E. - Milling Methods, 285 (1930)
 12. Trans. A. I. M. E. - 112:189 (1934)
 13. Mining Engineering, 3:522 (1951)

From 0.1 to 0.5 grams of ore (or mineral) is added to 100 ml. of water in a 250 ml. beaker. The reagents are added and the ore-water-reagent pulp is then aerated by a low-pressure air jet for five to ten minutes. If conditioning is required before floating, the pulp in the beaker may be agitated either by hand rotation or shaking for the required conditioning time. The concentrate obtained after aerating can be skimmed off and studied for desired characteristics, and preliminary evaluations made.

It must be pointed out that, with this rather crude type of flotation test, considerably more reagent is required than in standard batch laboratory tests. Thus types of reagents can be evaluated, but not the required quantities.

The beaker tests are now used in place of contact angle determinations, and have proved quite satisfactory in the rapid evaluation of a large number of possible organic reagents as collectors or as froth producing reagents.

Advantages of the beaker tests over running batch flotation tests are: (1) Small amounts of pure minerals can be tested under more ideal conditions; (2) Much time is saved in the preparation of samples; (3) An entire series of tests (such as a pH range) can be run simultaneously in a number of beakers.

Single Cycle Batch Tests

The single-cycle batch test is the one most generally used in this ore testing program for the comparison of different reagents and conditions. Ore is prepared by adding five grams of synthetic autunite to 500 grams of silica sand, previously ground to 100% -100 mesh. This synthetic ore is then ground 15 minutes in an Abbe mill with 400 ml. of water, and when required, an aqueous solution of conditioning agent.

The ground pulp is then placed in a Fagergren 600 gram laboratory flotation machine, and diluted to flotation volume; the pH is adjusted to the desired value by the addition of H_2SO_4 or NaOH and the pulp is agitated until it has stabilized at that value. Collector is then added and the pulp conditioned for five minutes, pH again adjusted and frother added. In floating, a first concentrate is floated for five minutes with slow froth withdrawal. The pH is then readjusted, additional conditioning agent added as required, the pulp conditioned, collector added and conditioned for five minutes, and frother added. A second concentrate is then floated for five minutes similarly to the first concentrate. The identical procedure is again repeated but with vigorous flotation for 10 minutes to produce a third or scavenger concentrate. Material remaining unfloated is the tailing.

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Multiple Cycle Batch Tests

This is a repetition of the single cycle tests outlined above, with the following exceptions: Rougher concentrates (equivalent to Conc. Nos. 1 and 2 from single tests) are combined and floated in a smaller machine to produce a cleaner concentrate, with collector and frother as required.

The cleaner tailing and scavenger concentrate from the first cycle are combined and added to the feed of the next cycle. In the practice used, the combined cleaner concentrates from five cycles are floated again in order to observe what grade of concentrate can be expected by recleaning. Tests are carried to five cycles as this appears to be sufficient to have stabilized the flotation circuits. A schematic flowsheet of the five-cycle tests is shown in Figure 1, page 39.

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FLOTATION OF SYNTHETIC AUTUNITE

In the flotation tests on synthetic autunite ores which follow, certain standard conditions were set up and these were adhered to as closely as possible. Synthetic ore, grind, and pulp density during conditioning and floating were held constant throughout. Time of conditioning and floating were constant, except as noted under the tables. Types and quantities of reagents, pH, etc., were varied to determine optimum conditions for flotation of synthetic autunite. Standard conditions were as follows:

1. Synthetic Ore: 500 gr. minus 100-M silica sand plus 5 gr. synthetic autunite.
2. Grind: 15 min. in Abbe mill, giving following screen analysis:

plus 150-M	7.7%
plus 200-M	27.3%
minus 200-M	65.0%

The synthetic autunite before grinding had a maximum size of 325-M. Therefore, autunite after grinding can be presumed to be considerably finer in size.

3. Pulp Density: 17% solids.
4. Conditioning Time: each stage, 5 min.
5. Floating Time: 1st stage, 5 min.
2nd stage, 5 min.
3rd stage, 10 min.

pH of Pulp

Early work on contact angle studies of the dithiocarbamate series of collectors indicated that flotation would have to be run at a fairly high acid condition. This presented a problem, not only in corrosion of equipment, but also in high acid consumption in the beneficiation of high-line ores. Subsequent beaker flotation tests, however, indicated good flotation in the pH range of 5.0 to 8.0. A series of single-cycle tests was therefore run in a 600 gr. Fagergren flotation machine in order to determine optimum pH for the ammonium n-octyl dithiocarbamate. Results of these tests are given in Table 2 and 3.

Data in Table 2, with pH variable from 3.0 to 6.0, indicate the highest grade of concentrate, best recovery and a high ratio of concentration is obtained at a pH of 5.0, when using ammonium n-octyl dithiocarbamate as collector for autunite. A further test (not tabulated) was

Table 2 - Flotation of Synthetic Autunite. pH Studies (Acidic)
(Ammonium n-octyl Dithiocarbamate as Collector)

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-5: pH 3.0</u>			
Feed	100.0	0.545	100.0
Conc. No. 1	5.1	4.225	39.5
Conc. No. 2	5.3	4.307	41.9
Conc. No. 3	2.5	1.772	8.2
Tailing	87.1	.065	10.4
Ratio of Concentration: Conc. No. 1, 19.6; all conc., 7.7			
<u>Test No. SA-3: pH 4.0</u>			
Feed	100.0	0.577	100.0
Conc. No. 1	4.1	7.190	50.7
Conc. No. 2	3.7	5.296	33.7
Conc. No. 3	2.0	2.132	7.6
Tailing	90.2	.051	8.0
Ratio of Concentration: Conc. No. 1, 24.6; all conc., 10.2			
<u>Test No. SA-4: pH 5.0</u>			
Feed	100.0	0.596	100.0
Conc. No. 1	4.3	8.917	64.7
Conc. No. 2	3.4	4.309	24.3
Conc. No. 3	2.9	1.359	6.8
Tailing	89.4	.029	4.2
Ratio of Concentration: Conc. No. 1, 23.1; all conc., 9.4			
<u>Test No. SA-8: pH 6.0</u>			
Feed	100.0	0.603	100.0
Conc. No. 1	12.5	2.800	58.0
Conc. No. 2	4.1	2.625	17.9
Conc. No. 3	11.9	1.039	20.5
Tailing	71.5	.030	3.6
Ratio of Concentration: Conc. No. 1, 8.0; all conc., 3.4			

Standard Conditions

Collector: NH₄-A-8, 1.8 lb/ton, added in 3 stages.

Frother: B-70, 1.2 lb/ton, added in 3 stages.

In Tests SA-5, SA-3, and SA-4, 0.8 lb of oleic acid was added before floating Conc. No. 3. Test SA-8, 0.2 lb of oleic acid was added before each stage of flotation, which accounts for the lower ratio of concentration.

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Table 3 - Flotation of Synthetic Autumite. pH Studies (Basic).
(Ammonium n-octyl Dithiocarbamate as Collector)

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-9: pH 8.0</u>			
Feed	100.0	0.609	100.0
Conc. No. 1	14.5	3.308	78.7
Conc. No. 2	7.8	1.308	16.7
Conc. No. 3	3.4	.246	1.4
Tailing	74.3	.026	3.2
Ratio of Concentration: Conc. No. 1, 6.9; all conc., 3.9			
<u>Test No. SA-10: pH 9.0</u>			
Feed	100.0	0.614	100.0
Conc. No. 1	12.6	3.668	75.2
Conc. No. 2	8.3	1.478	19.9
Conc. No. 3	2.7	.284	1.3
Tailing	76.4	.029	3.6
Ratio of Concentration: Conc. No. 1, 7.9; all conc., 4.2			
<u>Test No. SA-11: pH 10.0</u>			
Feed	100.0	0.597	100.0
Conc. No. 1	10.3	3.657	63.3
Conc. No. 2	16.6	1.146	31.9
Conc. No. 3	5.0	.337	2.8
Tailing	68.1	.018	2.0
Ratio of Concentration: Conc. No. 1, 9.7; all conc., 3.4			
<u>Test No. SA-12: pH 10.8</u>			
Feed	100.0	0.572	100.0
Conc. No. 1	44.2	.983	76.0
Conc. No. 2	8.5	1.168	17.3
Conc. No. 3	3.7	.395	2.6
Tailing	43.6	.054	4.1
Ratio of Concentration: Conc. No. 1, 2.3; all conc., 1.8			

Standard Conditions

Collector: NH₄-A-8, 1.8 lb/ton, added in 3 stages.

Oleic acid 6.6 lb/ton, added in 3 stages.

Frother: B-70, 1.2 lb/ton, added in 3 stages.

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run at as close to a pH of 7.0 as possible, but at or close to neutrality it is difficult to maintain a constant pH and the results of this test were not reliable.

Test No. SA-8 is not directly comparable to the previous three tests, because of a difference in the addition of oleic acid, which caused more gangue to be floated with the autunite, with consequent low grade concentrate and low ratio of concentration. Later tests show that equally good results are obtained at either a pH of 5.0 or pH of 6.0.

Table 3 gives results of separating synthetic autunite from finely ground silica sand in the pH range of 8.0 to 10.8. These tests were all run under the same conditions as Test SA-8 (Table 2) and are comparable to this test. While a high recovery is obtained up to pH of 10.8, ratios of concentration are consistently low. This in part is due to the staged additions of oleic acid, although at pH of 10.8, ratio of concentration is considerably less than in the other tests.

From results shown in Tables 2 and 3, it was decided to standardize on a pH of 6.0 ± 0.5 for further testing, with oleic acid addition only before floating Concentrate No. 3. The general conclusion drawn from the data in Tables 2 and 3 is the pH control is not critical when using the ammonium salt of n-octyl dithiocarbamate to float autunite.

Collector Studies

In order to definitely establish the effectiveness of the dithiocarbamates as collectors for autunite, and to determine which salt modification and what length of carbon chain would give best recoveries, two series of tests were run, using several reagents of the series as collectors. The two series were run, first at a pH of 6.0 and then at a pH of 8.0. Results of these tests are given in Table 4 and 5. Recovery of only 44.2 percent of the autunite was obtained in a control test (Test No. SA-7) using oleic acid and B-70 only, without any dithiocarbamate additions.

Comparisons of results shown in Tables 4 and 5 indicate that at a pH of 6.0 the ammonium salt is not quite as effective a collector as the potassium n-octyl or n-decyl dithiocarbamates, while at a pH of 8.0, the ammonium salt appears to be the most effective collector.

A number of further tests have been completed, using the potassium salts of the mono alkyl n-substituted dithiocarbamates with 9, 13 and 14 carbon chains, respectively. Results of these tests vary only slightly from the results given in Tables 4 and 5; such variations as do occur are within the limits of variations in test procedures. Therefore, there

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Table 4 - Flotation of Synthetic Autunite. Collector Studies.
pH = 6.0

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-8a:</u> Collector: Ammonium n-octyl dithiocarbamate			
Feed	100.0	0.639	100.0
Conc. No. 1	11.4	3.017	54.0
Conc. No. 2	5.7	2.936	26.1
Conc. No. 3	6.5	.913	9.4
Tailing	76.4	.088	10.5
Ratio of Concentration: Conc. No. 1, 8.8; all conc., 4.2			
<u>Test No. SA-16a:</u> Collector: Potassium n-octyl dithiocarbamate			
Feed	100.0	0.598	100.0
Conc. No. 1	5.5	4.333	39.9
Conc. No. 2	5.1	2.490	21.1
Conc. No. 3	12.8	1.496	32.1
Tailing	76.6	.054	6.9
Ratio of Concentration: Conc. No. 1, 18.2; all conc., 4.3			
<u>Test No. SA-18a:</u> Collector: Potassium n-decyl dithiocarbamate			
Feed	100.0	0.521	100.0
Conc. No. 1	7.6	3.567	51.9
Conc. No. 2	5.0	2.638	25.6
Conc. No. 3	7.7	1.196	17.6
Tailing	79.7	.032	4.9
Ratio of Concentration: Conc. No. 1, 13.2; all conc., 4.9			
<u>Test No. SA-20:</u> Collector: Potassium n-dodecyl dithiocarbamate			
Feed	100.0	0.627	100.0
Conc. No. 1	4.0	4.589	29.6
Conc. No. 2	2.2	4.804	16.9
Conc. No. 3	6.3	4.302	43.1
Tailing	87.5	.075	10.4
Ratio of Concentration: Conc. No. 1, 25.0; all conc., 8.0			

Standard Conditions

Collector: Variable, 1.8 lb/ton, added in 3 stages.

Frother: B-70, 1.2 lb/ton, added in 3 stages.

pH = 6.0

Table 5 - Flotation of Synthetic Autumite, Collector Studies.
pH = 8.0

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-9:</u> Collector: Ammonium n-octyl dithiocarbamate			
Feed	100.0	0.609	100.0
Conc. No. 1	14.5	3.308	78.7
Conc. No. 2	7.8	1.308	16.7
Conc. No. 3	3.4	.246	1.4
Tailing	74.3	.026	3.2
Ratio of Concentration: Conc. No. 1, 6.9; all conc., 3.9			
<u>Test No. SA-17a:</u> Collector: Potassium n-octyl dithiocarbamate			
Feed	100.0	0.579	100.0
Conc. No. 1	6.1	3.445	36.3
Conc. No. 2	8.5	2.419	35.3
Conc. No. 3	10.7	1.161	21.4
Tailing	74.7	.054	7.0
Ratio of Concentration: Conc. No. 1, 16.4; all conc., 4.0			
<u>Test No. SA-19:</u> Collector: Potassium n-decyl dithiocarbamate			
Feed	100.0	0.738	100.0
Conc. No. 1	7.1	4.408	42.2
Conc. No. 2	5.3	2.224	16.0
Conc. No. 3	12.4	1.236	20.8
Tailing	75.2	.206	21.0
Ratio of Concentration: Conc. No. 1, 14.1; all conc., 4.0			
<u>Test No. SA-21:</u> Collector: Potassium n-dodecyl dithiocarbamate			
Feed	100.0	0.576	100.0
Conc. No. 1	3.3	4.625	26.2
Conc. No. 2	3.4	4.483	26.6
Conc. No. 3	4.4	4.182	32.2
Tailing	88.9	.097	15.0
Ratio of Concentration: Conc. No. 1, 30.3; all conc., 9.0			

Standard Conditions

Collector: Variable, 1.8 lb/ton, added in 3 stages.

Frother: B-70, 1.2 lb/ton, added in 3 stages.

pH = 8.0

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appears at this time to be no definite improvement in collecting properties when using carbon chains above 10, or when using the odd-numbered carbon chains.

Surface Alteration for Improved Bonding

In the surface alteration studies reported on pages 16 and 17, small amounts of autunite altered by various base metal salts were produced. These small quantities of altered autunite were used in flotation tests to determine whether the floatability of autunite could be improved by such alteration. Results of these tests are presented in Table 6. Autunite which had been altered by exchange with lead chloride showed much better floatability than either the unaltered autunite or autunite altered by exchange with cadmium, manganese, copper, or zinc chlorides.

A series of tests was therefore run to determine the effect of adding the same base metal salts (with the exception of manganese) to pulps before flotation. Because of greater ease of ionization and improved solubility, lead nitrate was used in the place of chloride. Results of these tests, presented in Table 7, show a marked improvement in flotation by the addition of any of the base metal salts as compared to the control test (SA-22) without any conditioning agent. The addition of 3.0 lbs. of lead nitrate to the pulp in stages of 1.0 lb. to each conditioning cycle before floating brought the recovery to 99.7 percent of the autunite in the three concentrates and 98.1 percent in the first two concentrates. Additions of the same amounts of zinc chloride gave equally good recovery of the autunite, but the ratios of concentration and grade of the first two concentrates were considerably lower as compared to tests where lead nitrate was added.

Additional tests using lead nitrate in varying amounts as a conditioning agent show that with 0.5 lb. per ton added in three stages (total of 1.5 lb), the recovery of autunite is only slightly lower than with 3.0 lbs. per ton. The grade and recovery in the first concentrate, however, are lower with the lesser amount of lead nitrate. This indicates more rapid flotation of autunite with 1.0 lb. of lead nitrate added before floating the first concentrate than with 0.5 lb. Increasing the lead nitrate above 3.0 lb. per ton had no beneficial effect.

In the tests shown in Table 7, the addition of small amounts of oleic acid to the third stage of flotation was discontinued. In earlier tests a small amount of oleic acid appeared to be necessary in order to produce a low tailing with consequent high recovery of uranium. The oleic acid tended to float silica as well as autunite, thus lowering the grade of concentrate. In plant practice, where some oleic acid would be returned to the head of the flotation circuit through the cleaning and recleaning circuits, this could considerably lower the grade of final concentrate and ratio of concentrate. As a result of these and other tests, it now appears that

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Table 6 - Flotation of Synthetic Autunite. Surface Alterations.

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-15: Unaltered (control)</u>			
Feed	100.0	0.102	100.0
Conc. No. 1	5.8	.558	31.7
Conc. No. 2	10.0	.320	32.1
Tailing	84.2	.044	36.2
<u>Test No. SA-13: Autunite altered with lead</u>			
Feed	100.0	0.049	100.0
Conc. No. 1	9.6	.426	83.8
Conc. No. 2	8.6	.073	12.9
Tailing	81.8	.002	3.3
<u>Test No. SA-14: Autunite altered with cadmium</u>			
Feed	100.0	0.076	100.0
Conc. No. 1	5.9	.957	74.4
Conc. No. 2	8.6	.136	15.5
Tailing	85.5	.009	10.1
<u>Test No. SA-16: Autunite altered with manganese</u>			
Feed	100.0	0.059	100.0
Conc. No. 1	6.9	.383	45.0
Conc. No. 2	3.8	.389	24.7
Tailing	89.3	.020	30.3
<u>Test No. SA-17: Autunite altered with copper</u>			
Feed	100.0	0.081	100.0
Conc. No. 1	7.6	.514	48.4
Conc. No. 2	6.8	.392	32.6
Tailing	85.6	.018	19.0
<u>Test No. SA-18: Autunite altered with zinc</u>			
Feed	100.0	0.091	100.0
Conc. No. 1	6.1	.729	49.2
Conc. No. 2	3.8	.591	25.0
Tailing	90.1	.026	25.8

Standard ConditionsCollector: NH₄-A-8, 1.2 lb/ton, added in 2 stages.

Frother: B-70, 0.8 lb/ton, added in 2 stages.

Conditioning Time: 5 min. each period.

Floating Time: 5 and 10 min.

pH: Natural (7.4 approx.)

Table 7 - Flotation of Synthetic Autunite.
Metal Ion Conditioning Studies.

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-22: No metal ion addition (control)</u>			
Feed	100.0	0.630	100.0
Conc. No. 1	4.4	5.715	39.8
Conc. No. 2	3.1	5.715	28.0
Conc. No. 3	5.3	3.305	27.8
Tailing	87.2	.032	4.4
Ratio of Concentration: Conc. No. 1, 22.7; all conc., 7.8			
<u>Test No. SA-23: Conditioned with 3 lb lead nitrate per ton</u>			
Feed	100.0	0.677	100.0
Conc. No. 1	4.7	10.970	76.5
Conc. No. 2	3.3	4.519	21.6
Conc. No. 3	16.1	.067	1.6
Tailing	75.9	.002	.3
Ratio of Concentration: Conc. No. 1, 21.2; all conc., 4.1			
<u>Test No. SA-25: Conditioned with 3 lb cadmium chloride per ton</u>			
Feed	100.0	0.601	100.0
Conc. No. 1	7.4	6.140	75.6
Conc. No. 2	3.0	4.129	20.9
Conc. No. 3	24.4	.060	2.4
Tailing	65.2	.010	1.1
Ratio of Concentration: Conc. No. 1, 13.5; all conc., 2.9			
<u>Test No. SA-27: Conditioned with 3 lb cupric chloride per ton</u>			
Feed	100.0	0.637	100.0
Conc. No. 1	8.4	5.068	66.7
Conc. No. 2	10.9	1.852	31.6
Conc. No. 3	19.3	.031	.9
Tailing	61.4	.008	.8
Ratio of Concentration: Conc. No. 1, 11.9; all conc., 2.6			
<u>Test No. SA-26: Conditioned with 3 lb zinc chloride per ton</u>			
Feed	100.0	0.652	100.0
Conc. No. 1	8.3	6.069	77.1
Conc. No. 2	7.0	2.047	22.0
Conc. No. 3	5.6	.080	.7
Tailing	79.1	.002	.2
Ratio of Concentration: Conc. No. 1, 12.0; all conc., 4.9			

Standard Conditions

Collector: NH₄-A-8, 1.8 lb/ton, added in 3 stages.

Frother: B-70, 1.2 lb/ton, added in 3 stages.

Conditioning Agent: Variable, 3 lb/ton, added in 3 stages.

pH = 6.0

additions of oleic acid are not necessary, in order to float essentially all of the autunite, when using dithiocarbamates as collectors.

Frother Selection

In using organic collectors such as the dithiocarbamates, selection of a frother which is compatible with the collector is of importance, because of the possibility of direct reaction of frother with the collector; also it is desirable to have a frother with a minimum of collecting properties. In previous tests, American Cyanamid Co. Frother B-70 (methyl isobutyl carbinol) had been used exclusively.

In order to determine the most desirable frother to use with the dithiocarbamates, beaker tests were run on a total of fifteen different frothers. These preliminary tests limited the suitable frothers to three, namely: B-70, B-77, and Dowfroth. Two series of single-cycle flotation tests were then run on these frothers, using potassium n-octyl (K-A-8) and potassium n-tetradecyl (K-A-14) dithiocarbamates as collectors. Data on these tests are given in Tables 8 and 9, respectively. In Test SA-31 (Table 8), 1.0 lb. of lead nitrate was added to the synthetic ore in the grinding operation to give additional contact time.

From the data Frother B-70 appears to be the most desirable in combination with the dithiocarbamate collectors. While the first concentrate is not quite as high in grade as given by Frother B-77, using K-A-8 as collector, total recovery is slightly better with B-70. The Dowfroth is less efficient as a frothing agent. Addition of lead nitrate to the grinding circuit gives improved recovery with Dowfroth but ratio of concentration is considerably lower than when lead nitrate is added to the conditioner. Since there was a considerable excess of lead nitrate present in all these tests, this may indicate possible complexing or adsorption of lead ion on the silica.

Effect of Various Gangues

Tests to determine the effects of various gangue minerals have not progressed too far at this time, but preliminary flotation tests have been run with additions of calcite and limonite to silica-autunite synthetic ore. Results of these tests are given in Table 10. Potassium n-octyl dithiocarbamate with quartz has been shown to give practically no flotation of the quartz. Calcite and limonite, however, are collected and floated to a much higher degree than quartz, and limonite is floated more readily than calcite. The presence of calcite does not appear to have any adverse effect on the recovery of autunite, while limonite does. When both calcite and limonite are present (Test SA-34), recovery of autunite is considerably lower.

Table 8 - Flotation of Synthetic Autunite. Frother Studies.
(Potassium n-octyl dithiocarbamate as Collector)

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-30: Frother B-70, 1.2 lb/ton</u>			
Feed	100.0	0.534	100.0
Conc. No. 1	9.1	4.931	83.6
Conc. No. 2	8.1	.904	13.8
Conc. No. 3	6.0	.217	2.4
Tailing	76.8	.001	.1
Ratio of Concentration: Conc. No. 1, 11.0; all conc., 4.3			
<u>Test No. SA-29: Frother B-77, 1.2 lb/ton</u>			
Feed	100.0	0.454	100.0
Conc. No. 1	8.9	4.510	88.7
Conc. No. 2	7.2	.514	8.2
Conc. No. 3	9.0	.040	.8
Tailing	74.9	.014	2.3
Ratio of Concentration: Conc. No. 1, 11.2; all conc., 4.0			
<u>Test No. SA-28: Frother Dowfroth, 1.2 lb/ton</u>			
Feed	100.0	0.697	100.0
Conc. No. 1	6.0	5.267	45.3
Conc. No. 2	6.9	4.107	40.9
Conc. No. 3	5.8	.988	8.2
Tailing	81.3	.048	5.6
Ratio of Concentration: Conc. No. 1, 16.7; all conc., 5.3			
<u>Test No. SA-31: $\sqrt{\text{Pb}(\text{NO}_3)_2}$ added to grinding⁷ Dowfroth, 1.2 lb/ton</u>			
Feed	100.0	0.481	100.0
Conc. No. 1	10.3	3.367	72.1
Conc. No. 2	7.8	.829	13.4
Conc. No. 3	12.7	.523	13.8
Tailing	69.2	.005	.7
Ratio of Concentration: Conc. No. 1, 9.7; all conc., 3.2			

Standard Conditions

Collector: K-A-8, 1.8 lb/ton, added in 3 stages.

Conditioning Agent: Lead nitrate, 3.0 lb/ton, added in 3 stages.

Frother: Variable, 1.2 lb/ton, added in 3 stages.

pH = 6.0

Table 9 - Flotation of Synthetic Autunite. Frother Studies.
(Potassium n-tetradecyl dithiocarbamate as Collector)

Product	Weight %	Assay % U ₃ O ₈	Distribution % of U ₃ O ₈
<u>Test No. SA-41: Frother B-70, 1.2 lb/ton</u>			
Feed	100.0	0.499	100.0
Conc. No. 1	7.5	5.214	78.1
Conc. No. 2	4.4	1.657	14.4
Conc. No. 3	3.5	.740	5.3
Tailing	84.6	.013	2.2
Ratio of Concentration: Conc. No. 1, 13.3; all conc., 6.5			
<u>Test No. SA-40: Frother B-77, 1.2 lb/ton</u>			
Feed	100.0	0.512	100.0
Conc. No. 1	8.0	4.784	75.1
Conc. No. 2	2.8	3.021	16.7
Conc. No. 3	4.0	.780	6.0
Tailing	85.2	.013	2.2
Ratio of Concentration: Conc. No. 1, 12.5; all conc., 6.8			
<u>Test No. SA-39: Frother Dowfroth, 1.2 lb/ton</u>			
Feed	100.0	0.554	100.0
Conc. No. 1	8.5	4.209	64.9
Conc. No. 2	4.9	2.751	24.2
Conc. No. 3	6.2	.740	8.3
Tailing	80.4	.018	2.6
Ratio of Concentration: Conc. No. 1, 11.8; all conc., 5.1			

Standard Conditions

Collector: K-A-14, 1.8 lb/ton, added in 3 stages.

Conditioning Agent: Lead nitrate, 3.0 lb/ton, added in 3 stages.

Frother: Variable, 1.2 lb/ton, added in 3 stages.

pH = 6.0

Table 10 - Flotation of Synthetic Autunite.
Floatability of Various Gangue Minerals.

Product	Weight %	Assay %			Distribution		% of
		U ₃ O ₈	CaO	Fe ₂ O ₃	U ₃ O ₈	CaO	
<u>Test No. SA-32:</u> Gangue, 9.5% CaCO ₃ with Silica Sand							
Feed	100.0	0.584	5.3	--	100.0	100.0	--
Conc. No. 1	18.1	2.530	5.9	--	78.3	20.0	--
Conc. No. 2	27.7	.416	11.7	--	19.7	60.7	--
Tailing	54.2	.021	1.9	--	2.0	19.3	--
Ratio of Concentration: Conc. No. 1, 5.5; both conc., 2.2							
<u>Test No. SA-33:</u> Gangue, 8.9% Fe ₂ O ₃ with Silica Sand							
Feed	100.0	0.615	--	8.9	100.0	--	100.0
Conc. No. 1	16.9	2.725	--	15.0	75.1	--	28.5
Conc. No. 2	6.2	1.688	--	16.0	17.0	--	11.1
Tailing	76.9	.063	--	7.0	7.9	--	60.3
Ratio of Concentration: Conc. No. 1, 5.9; both conc., 4.3							
<u>Test No. SA-34:</u> Gangue, 9.8% CaCO ₃ , 7.6% Fe ₂ O ₃ with Silica Sand							
Feed	100.0	0.598	5.5	7.6	100.0	100.0	100.0
Conc. No. 1	12.7	1.998	5.7	11.4	42.4	13.0	19.0
Conc. No. 2	11.1	2.056	8.3	11.4	38.3	16.7	16.7
Tailing	76.2	.152	5.1	6.4	19.4	70.3	64.3
Ratio of Concentration: Conc. No. 1, 7.9; both conc., 4.2							

Standard Conditions

Collector: K-A-8, 1.8 lb/ton, added in 3 stages.

Conditioning Agent: Lead nitrate, 3.0 lb/ton, first addition to grind,
2nd and 3rd additions to conditioner.

Frother: Dowfroth, 1.2 lb/ton, added in 3 stages.

pH = 6.0

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These tests are of a preliminary nature only and results are not conclusive. Further tests, including cleaning and recleaning tests are necessary in order to properly evaluate the effects of the above gangue minerals on autunite recovery.

Summarizing the results shown in Tables 2 to 9, inclusive, optimum conditions for floating synthetic autunite from a silica gangue have been determined as follows:

1. pH	6.0 $\pm$ 0.5
2. Collector	Potassium n-decyl dithiocarbamate, 0.6 lb/ton, added to each of three stages of conditioning.
3. Conditioning Agent	Lead nitrate, 0.5 to 1.0 lb/ton, added to each of three stages of conditioning.
4. Frother	B-70 (methyl isobutyl carbinol), 0.4 lb/ton, added to each of three stages of floating.

The conditioning and floating time given on page 23 has been entirely satisfactory and any further work to determine optimum time factors becomes an individual problem for each ore studied.

Floating autunite under the above conditions should give better than 95 percent recovery, with ratio of concentration dependent upon the stages of cleaning and recleaning of the rougher concentrate. These conclusions are premised on complete liberation and a clean, slime-free surface on the autunite. In the flotation of ores containing autunite, this is a problem of grinding and conditioning prior to flotation.

Dithiocarbamates vs. Other Collectors

A limited number of tests have been completed to definitely establish whether other widely accepted collectors in the flotation industry might have collecting properties for autunite equal to those of the dithiocarbamates. Such tests show that none of those so far tested even approached the dithiocarbamates in collecting power or selectivity.

Oleic acid has good collecting properties toward autunite, but it also collects and floats silica, as well as other gangue minerals. Therefore, although a high recovery of uranium may be possible, ratios of concentration in the order of 2 or 3 are the best that can be obtained.

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Tests using sodium ethyl xanthate (Z-4), potassium amyl xanthate (Z-5), and Minerec B as collectors showed no more collection of the autunite than a control test with no collector, B-70 being used as frother.

Multiple-Cycle Tests

The general procedure for the multiple-cycle tests is outlined on page 22 and further detailed in Figure 1. The procedure adopted does not completely close all circuits, with finished concentrates and tailings being the only two end products, but this procedure gives all the information required at this time.

Results obtained in the cyclic tests are highly gratifying and establish the dithiocarbamates as excellent collectors for autunite, provided that it is liberated and has a clean surface. Fine size of the autunite does not appear to inhibit its flotation. In the two cyclic tests run, recoveries of 98.0 percent were obtained at an average ratio of concentration of 9.4, in a rougher concentrate. These tests produced rougher concentrates of 6.1 percent U_3O_8 from flotation feed assaying 0.62 percent. The rougher concentrates can be readily up-graded to 10 to 12 percent U_3O_8 with two-stage cleaning, without returning large amounts or very high grade materials to the head of the rougher circuit.

Rejection of gangue into the tailings is 88 percent, with 1.1 to 1.4 percent loss of uranium. In a continuous, closed circuit, there will be a slight increase in the tailing loss because of the return of intermediate products to the rougher circuit, but this increase in loss should be under two percent. Results obtained in these cyclic tests are given in Table 11.

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Table 11 - Five-Cycle Flotation Tests on Synthetic Autunite.

Product	Weight %	Assays % U ₃ O ₈	Distribution % of U ₃ O ₈	Ratio of Conc'n.
<u>Test No. SA-43:</u>				
1. Feed	100.00	(0.618)	100.0	
2. Recleaner Conc.	3.74	13.325	80.6	26.7
3. Recleaner Tailing	3.87	1.989	12.5	
4. Cleaner Conc. (2 + 3)	(7.61)	(7.561)	93.1	13.1
5. Cleaner Tailing	2.24	1.338	4.8	
6. Rougher Conc. (2 + 3 + 5)	(9.85)	(6.146)	97.9	10.2
7. Scavenger Conc.	2.83	.203	.9	
8. Scavenger Tailing	87.32	.008	1.2	
<u>Test No. SA-44:</u>				
1. Feed	100.00	(0.629)	100.0	
2. Recleaner Conc.	6.18	8.838	86.8	16.2
3. Recleaner Tailing	2.14	2.788	9.5	
4. Cleaner Conc. (2 + 3)	(8.32)	(7.283)	96.3	12.0
5. Cleaner Tailing	1.80	.609	1.7	
6. Rougher Conc. (2 + 3 + 5)	(10.12)	(6.096)	98.0	9.9
7. Scavenger Conc.	1.72	.213	.6	
8. Scavenger Tailing	88.16	.010	1.4	

NOTE: Weights and assays in parentheses are calculated figures.

Flotation Conditions

See Figure 1 for flotation stages.

Collector: K-A-10, 1.2 lb/ton to rougher
 .6 lb/ton to scavenger
 .3 lb/ton to cleaner
 .3 lb/ton to recleaner

Frother: B-70, 0.8 lb/ton to rougher
 .4 lb/ton to scavenger
 .1 lb/ton to cleaner

Conditioning Agent: Pb(NO₃)₂, 2.0 lb/ton to rougher
 1.0 lb/ton to scavenger
 .2 lb/ton to cleaner

pH = 6.0

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FIG 1.— FLOWSHEET FOR CYCLIC TESTS

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FLOTATION TESTS ON SYNTHETIC CARNOTITE AND TORBERNITE

Since synthetic autunite was readily produced in the laboratory and as it was fluorescent under ultraviolet light, its recovery during the flotation tests could be easily observed. Because of these advantages, much of the work on evaluation of collectors and determinations of other conditions of flotation has been done on autunite.

Small amounts of synthetic carnotite and torbernite, however, have been floated and the results of these tests are encouraging. Two single-cycle tests show that addition of lead salt is necessary to collect and float the carnotite. Without the lead salt, 38.6 percent of the uranium was recovered, while with lead salt added, 77.2 percent was recovered. In a five-cycle test on synthetic carnotite, a 61.1 percent recovery was made in the recleaned concentrate, with ratio of concentration of 34.8. The cleaner concentrate gave a recovery of 80.9 percent with ratio of concentration of 14.4, and rougher flotation recovered 91.1 percent with an 8.4 ratio of concentration. Data on this cyclic test is given in Table 12.

Testing of synthetic torbernite includes several beaker tests and one single-cycle flotation test. Results of this test gave a recovery of 71 percent of the torbernite with a 5.6 ratio of concentration. This test was run before the advantage of lead salt addition had been established—therefore no lead salt was added. Potassium n-decyl dithiocarbamate, however, appears to have definite collecting properties for torbernite.

Table 12 - Five-Cycle Flotation Test on Synthetic Carnotite.

Product	Weight %	Assays % U ₃ O ₈	Distribution % of U ₃ O ₈	Ratio of Conc'tn.
<u>Test No. SC-5:</u>				
1. Feed	100.00	0.448	100.0	
2. Recleaner Conc.	2.87	9.547	61.1	34.8
3. Recleaner Tailing	3.99	2.221	19.8	
4. Cleaner Conc. (2 + 3)	(6.86)	(5.286)	80.9	14.4
5. Cleaner Tailing	4.96	.928	10.2	
6. Rougher Conc. (2 + 3 + 5)	(11.82)	(3.457)	91.1	8.4
7. Scavenger Conc.	3.98	.540	5.7	
8. Scavenger Tailing	84.20	.017	3.2	

NOTE: Weights and assays in parentheses are calculated figures.

Flotation Conditions

See Figure 1 for flotation stages.

Standard Conditions: See Table 11.

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FLOTATION OF NATURAL ORES

Work to date on flotation of natural ores is of a preliminary nature only, but these results are encouraging. Recovery of 92.3 percent with ratio of concentration of 2.9 has been obtained from a highly micaceous ore sample containing autunite. The head sample assayed 0.17 percent U_3O_8 . A rougher concentrate only was produced, and cleaning of the rougher concentrate should give a considerably higher ratio of concentration.

On a small sample of relatively clean carnotite, 94.6 percent of the uranium was recovered with ratio of concentration of 2.4, without cleaning the concentrate. Work on marginal grade ores is now in progress.

On the basis of the above tests, a projected flowsheet is shown in Figure 2. Quantities of reagents are not specified because such quantities will be determined by the requirements of the individual ore.

REAGENTS: $Pb(NO_3)_2$ STAGE FED TO CELLS
R1, R2, R3

K-A-10 STAGE FED TO CELLS
R1, R2, R3, C1, RC, S1

B-70 STAGE FED TO ALL CIRCUITS
TO KEEP GOOD FROTH
CONDITION.

FIG 2.— PROJECTED FLOWSHEET

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