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RECOVERY OF CARNOTITE FROM ITS ORES

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This invention relates to processes for the recovery of carnotite from its ores and more particularly to novel methods for the recovery of carnotite from siliceous ores thereof by flotation practices utilizing special combinations of reagents.

Large quantities of carnotite sandstone ores occur in western Colorado, southeastern Utah, and northern Arizona and New Mexico. These sandstone ores contain a relatively small amount of carnotite mineral associated with relatively important quantities of vanadium minerals of greatly varied compositions. The mineral values of the carnotite—which is practically the only uranium mineral of interest found in these ores—and vanadium are found as a cementing matrix for the rock forming material, which is mainly finely divided quartz grains. Calcareous or dolomitic material is often a constituent of the grain formation and/or the cementing matrix.

The ores employed in connection with the development of the present invention came from the vicinity of Uravan, Colorado, and they run from 0.23% to 0.26% in U_3O_8 content and from 1.45% to 1.75% in V_2O_5 content.

It is an object of the present invention to recover a concentrate of carnotite from siliceous ores of said mineral. A further object is to provide a flotation process for obtaining carnotite from its siliceous ores. A still further object is to use moderately priced flotation reagents for the separation of carnotite from its ores. Another object is to provide a special flotation practice which is highly effective in separating carnotite from its ores. Other objects will appear hereinafter.

These objects are accomplished in accordance with the present invention by subjecting siliceous ores of carnotite to flotation in the presence of a special combination of reagents comprising a long chain fatty acid and a high molecular weight aliphatic amine. As is usual in ore flotation processes, the ore is ground to the desired fineness, and the ground ore is made into an ore pulp with water of the desired softness and alkalinity. The aliphatic amine reagent is preferably used in an amount equal to from 3 to 8% by weight of the fatty acid reagent. If desired, the ore may be deslimed before flotation.

The following examples illustrate but do not limit the invention.

Example I

Carnotite ore which was found to contain 0.26% of U_3O_8 and 1.75% of V_2O_5 was wet ground

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for 15 minutes in a ball mill to a particle size of —100 mesh and mixed with water to form an ore pulp containing about 30% of solids. To said ore pulp there was added 3.5 pounds of emulsified oleic acid, 0.9 pound of raw oleic acid, 0.25 pound of "lorol" amine; 1 pound of 40% sodium silicate, and 5 pounds of soda ash for each 2000 pounds of ore in said ore pulp. The ore pulp with these added reagents was then agitated in a flotation machine for 8 minutes at a temperature of 32 to 35° C. The rougher concentrate obtained by flotation contained 78.5% of the uranium values and 37.9% of the vanadium values that were present in the ore being treated. The rougher concentrate analyzed 1.56% in U_3O_8 and 4.66% in V_2O_5. The rougher tailings analyzed 0.065% in U_3O_8 and 1.15% in V_2O_5. A cleaner concentrate obtained by treating the rougher concentrate contained 44.7% of the uranium values and 11.6% of the vanadium values that were present in the ore being treated. The cleaner concentrate analyzed 2.43% in U_3O_8 and 3.9% in V_2O_5.

In similar runs wherein the "lorol" amine was omitted it was visibly evident that the concentrate was so highly contaminated with gangue that it was not worth while to subject it to chemical analysis. It was also found that when oleic acid was replaced by fatty acids derived from the hydrolysis of palm oil, castor oil, peanut oil, or corn oil or the fatty and resin acid mixtures derived from tall oil, the concentrates obtained in the absence of "lorol" amine were so greatly contaminated with gangue that it was obviously not worth while to subject these concentrates to chemical analysis. Furthermore, it was found that when attempts were made to concentrate this carnotite ore by flotation in the presence of "lorol" amine or similar long chain aliphatic amines but in the absence of oleic acid or similar long chain fatty acids, the froth carried with it so much quartz gangue that chemical analysis of the concentrate was not worth undertaking. It was therefore a surprise to find that the use of a long chain fatty acid in conjunction with a long chain aliphatic amine was effective for concentrating carnotite in froth flotation processes.

Example II

Carnotite ore which analyzed 0.26% in U_3O_8 and 1.75% in V_2O_5 was wet ground for 10 minutes in a ball mill to a particle size of —65 mesh and mixed with water to form an ore pulp containing about 30% of solids. To said ore pulp there was added 8 pounds of emulsified oleic acid, 0.3

pound of "lorol" amine, 0.8 pound of 40% sodium silicate, and 5 pounds of soda ash for each ton of ore in said ore pulp. The ore pulp with these added reagents was then agitated in a flotation machine for 8 minutes at 33–35° C. The rougher concentrate obtained by flotation contained 82.3% of the uranium values and 38% of the vanadium values that were present in the ore being treated. The rougher concentrate analyzed 1.29% in U_3O_8 and 3.43% in V_2O_5 whereas the rougher tailings analyzed 0.06% in U_3O_8 and 1.2% in V_2O_5.

Example III

To the ore pulp described in the first sentence of Example II there was added 2.35 pounds of emulsified oleic acid, 4.6 pounds of emulsified acids made by hydrolysis of caster oil, 0.32 pound of "lorol amine, 1 pound of 40% sodium silicate, and 5 pounds of soda ash for each ton of ore in said ore pulp. The ore pulp with these added reagents was then agitated in a flotation machine for 4 minutes at 25–27° C. The rougher concentrate obtained by flotation contained 70.9% of the uranium values and 29.7% of the vanadium values that were present in the ore being treated. The rougher concentrate analyzed 1.86% in U_3O_8 and 4.43% in V_2O_5 whereas the rougher tailings analyzed 0.09% in U_3O_8 and 1.26% in V_2O_5.

Example IV

Carnotite ore which analyzed 0.23% in U_3O_8 and 1.45% in V_2O_5 was wet ground for 10 minutes in a ball mill to a particle size of −65 mesh and mixed with water to form an ore pulp containing about 30% of solids. To said ore pulp there was added 6.7 pounds of emulsified peanut oil acids, 0.28 pound of "lorol" amine, 0.7 pound of 40% sodium silicate, and 5 pounds of soda ash for each ton of ore in said ore pulp. The ore pulp with these added reagents was then agitated in a flotation machine for 10 minutes at 27–32° C. The rougher concentrate obtained by flotation contained 64.4% of the uranium values and 31% of the vanadium values that were present in the ore being treated. The rougher concentrate analyzed 1.19% in U_3O_8 and 3.6% in V_2O_5 whereas the rougher tailings analyzed 0.09% in U_3O_8 and 1.1% in V_2O_5.

Example V

When the procedure described in Example IV was repeated using the same amount of emulsified corn oil acids in place of emulsified peanut oil acids and increasing the amount of 40% sodium silicate to 0.8 pound per ton of ore, it was found that the rougher concentrate contained 64.4% of the uranium values and 31.6% of the vanadium values that were present in the ore being treated. The rougher concentrate analyzed 1.26% in U_3O_8 and 4.05% in V_2O_5 whereas the rougher tailings analyzed 0.09% in U_3O_8 and 1.1% in V_2O_5.

Example VI

Carnotite ore which had a U_3O_8 content of 0.23% and a V_2O_5 content of 1.45% was dry crushed to pass 10 mesh, after which the slimes inherent with the ore after dry crushing were removed by deflocculating the slimes followed by decantation. These slimes carried 18.9% of the uranium values and 22.9% of the vanadium values that were present in the ore being treated. These slimes analyzed 0.88% in U_3O_8 and 7.1% in V_2O_5. The removal of these slimes constituted a concentration step, and therefore these slimes were not subjected to flotation treatment.

The crushed ore from which the slimes had been removed was wet ground in a ball mill for 30 minutes to a particle size of −150 mesh and then mixed with water to form an ore pulp containing about 30% of solids. To said ore pulp there was added 0.25 pound of emulsified castor oil acids, 0.62 pound of an emulsified mixture of fatty and resin acids contained in a refined tall oil marketed as "Indusoil," 0.2 pound of sulfonated castor oil, 0.03 pound of "lorol" amine, 0.45 pound of fuel oil, 1.5 pounds of 40% sodium silicate, and 5 pounds of soda ash for each ton of ore in said ore pulp. With the added reagents the ore pulp had a pH of 8.7. This ore pulp was then agitated in a flotation machine for 20 minutes at a temperature slightly in excess of 25° C. The rougher concentrate obtained by flotation contained 64.4% of the uranium values and 44.9% of the vanadium values that were present in the ore being treated. The slimes plus the rougher concentrate together contained 83.3% of the uranium values and 67.8% of the vanadium values originally present in the ore being treated. The rougher concentrate analyzed 0.57% in U_3O_8 and 2.63% in V_2O_5 whereas the rougher tailings analyzed 0.057% in U_3O_8 and 0.73% in V_2O_5.

A comparison of the data given in Examples I to V with the data given in Example VI shows that inclusion of the slime removal step prior to flotation of the ore increases the overall recovery of U_3O_8 and V_2O_5 from the ore being treated. The procedure of Example VI which includes a slime removal step as well as a flotation step makes it possible to recover more than 80% of the uranium values and more than 65% of the vanadium values present in the original ore by combining the slimes removed with the rougher concentrate obtained by flotation after desliming. The increase in the overall recovery of U_3O_8 by reason of this separation of primary slimes was almost as large as the amount of U_3O_8 recovered in the slimes. This indicates that slimed carnotite is not readily recovered by flotation methods. The increase in the overall recovery of V_2O_5 by reason of this separation of primary slimes was considerably greater than the amount of V_2O_5 recovered from the slimes. This indicates that removal of the slime eliminates a factor which seriously interferes with the flotation of certain vanadium minerals in carnotite ore.

In following a procedure such as that described above in Example VI the combined primary slimes and recleaned concentrate from the flotation phase should ordinarily show a U_3O_8 content of at least 1.3% and a V_2O_5 content of at least 5% upon analysis. It is not necessary to grind the ore to a particle size of −150 mesh in the procedure of Example VI since grinding to a particle size of −65 mesh will not materially affect the results secured in the subsequent flotation procedure.

The fatty acid reagent employed in the flotation of carnotite in accordance with the present invention may be any one of a number of higher fatty acids and higher fatty acid mixtures such as oleic acid, lauric acid, palmitic acid, and the mixtures of fatty acids obtained by hydrolyzing such fatty oils as palm oil, castor oil, peanut oil, corn oil, coconut oil, cottonseed oil, cardine oil, linseed oil, etc. Other suitable fatty acid reagents include mixtures of fatty acids and resin

acids derived from tall oil such as the fatty and resin acid mixtures marketed under the trade names "Indusoil" and "Liqro" which are described in detail on pages 361 and 401 respectively of the 3rd edition of The Condensed Chemical Dictionary. As is obvious, all of the long chain fatty acid reagents mentioned above contain 10 or more carbon atoms. Oleic acid is the preferred fatty acid reagent for use in the flotation of carnotite because of its low fusion point.

The long chain aliphatic amine reagents used in the flotation of carnotite comprise primary aliphatic amines containing 8 or more carbon atoms and their water soluble salts such as the acetates, sulfates and hydrochlorides of said amines. Suitable amines include the primary octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and octadecenyl amines. Instead of using the individual amines mentioned in the preceding sentence it is cheaper to use mixtures of these amines such as the "lorol" amine mentioned in the examples above. "Lorol" amine is a mixture containing about 50% of dodecyl amine and 50% of still higher molecular weight aliphatic amines derived by converting coconut oil acids to amines and eliminating the amines having a lower molecular weight than dodecyl amine from the product. Another suitable amine mixture which was used contained about 93% of dodecyl amine and about 7% of octadecyl amine. Still another suitable amine mixture comprises the primary amines corresponding in alkyl chain length to the fatty acids normally obtainable from coconut oils. This latter mixture contains about 47% of dodecyl amine and the remaining 53% of the amines is a mixture of hexyl, octyl, decyl, tetradecyl, cetyl and octadecyl amines. All of these amine mixtures may be employed in the form of one of their water soluble salts, such as the hydrochloride.

The amount of the long chain aliphatic amine reagent used to best advantage lies in the range of 3 to 8 percent of the quantity by weight of the fatty acid reagent employed. A 1:20 or a 1:25 ratio of amine reagent to fatty acid reagent has been found to be optimum. The use of the amine reagent in a proportion as high as 1 part of amine to 10 parts of fatty acid was markedly detrimental to the flotation in respect to the selectivity for carnotite as well as by reason of the excessively low grade of the concentrate obtained.

It was found best to introduce both the fatty acid reagent and long chain aliphatic amine reagent together in an emulsified form. The emulsion so obtained was definitely stable, and the fatty acid dispersion appeared to be excellent. This may be the real reason for the successful flotation of carnotite in accordance with the present invention since the extreme dispersion of the fatty acid reagent resulting from the use of a small amount of a higher aliphatic amine may cause more extensive reactivity between the fatty acid reagent and the mineral surfaces. Flotation of carnotite was also satisfactorily accomplished when an aqueous solution of a hydrochloride of a higher aliphatic amine was added to the ore pulp after the fatty acid emulsion.

It has been found that the relative softness of the water and also the pH of the water used in the flotation of carnotite ore are important factors affecting the separation of carnotite from the quartz gangue of its ore. Different water supplies require different treatments to secure the proper softness for carnotite flotation. The water used in the procedure described in the above examples was such that it only needed the addition of ordinary soda ash in order to have adequate frothing possibilities. The optimum amount was found to be of the order of about 5 pounds of soda ash per ton of ore in a pulp of about 30% solids. This gave an alkalinity to the water equivalent to a pH of 8.4 to 9.0. In view of the buffering action of sodium carbonate the total alkalinity is greater than what might be suspected from a consideration of the pH findings taken by themselves. It has been found that caustic alkalinity is detrimental to the flotation requirements and that best results are obtained by the use of sodium carbonate—commercial soda ash.

The interference to flotation by the presence of gangue slimes was best controlled by the use of ordinary sodium silicate (waterglass) in which the ratio of SiO_2 to Na_2O is about 3.2. The optimum requirements for flotation of the integral or (without preliminary desliming) were found to be from 0.6 to 1.5 pounds of 40% sodium silicate per ton of ore.

The temperature of the flotation circuit is of importance in case fatty acids having fusion points much above the temperature of the water are used. Unless the temperature of the pulp is maintained within 3 to 5 degrees centigrade of the fusion point of the organic reagent with the highest melting point, poor efficiency of flotation and high consumption of reagents results. This influences the choice of fatty acid and amine to be used if the expense of pulp heating is to be kept at a minimum.

Effectiveness and economy in use of fatty acid reagents are increased by feeding them in an emulsified form to the ore pulp or by modifying the ore pulp with an effective emulsifying agent for the fatty acid being used. Best results in carnotite flotation were obtained by emulsifying the fatty acid reagents either by agitation in water made slightly alkaline with soda ash or by agitation in the dilute aqueous solution of the higher aliphatic amine being used. Most of the long chain aliphatic amines are excellent emulsifiers for the fatty acid reagents. Satisfactory flotation was secured with the fatty acid reagents emulsified alone in water or together with the higher aliphatic amine. The amine was added to the ore pulp as a dilute aqueous solution or it was mixed with the fatty acid reagent and the mixture of these two reagents added to the ore pulp and agitated to emulsify them therein.

In all carnotite ore flotation it is essential that the wet grinding in a ball mill prior to actual flotation be such as to free the mineral and gangue with the least possible production of slimed mineral. With carnotite ores coming from the vicinity of Uravan, Colorado, such separation was effected by grinding to −65 mesh, although at that grinding there were still grains of quartz carrying a very thin adhering film of carnotite on part of the grain surface. Such middling grains could be recovered by flotation with the proper pulp conditions, but recovery of such grains diminished the grade of the concentrate.

A study of the results recorded in Examples I to V shows that when an integral carnotite ore which has not been deslimed is concentrated in accordance with the present invention it is possible to recover at least 60% of the uranium

values and about 30% of the vanadium values that were present in the ore being floated with due allowance for all possible losses in a closed circuit operation that includes one or two steps of cleaning. Removal of the primary slimes from the ore prior to flotation, as shown in Example VI, makes it possible to recover more than 80% of the uranium values and about 65% of the vanadium values from the ore being treated. In recovery systems such as that described in Example VI the primary slimes may constitute only about 10% by weight of the ore being treated, but said slimes may contain nearly half of the uranium and vanadium values of said ore. The tailings left after the removal of the primary slimes and the flotation concentrate may amount to as much as 85% by weight of the ore being treated but should generally contain less than 20% of the uranium values of the ore being concentrated.

The novelty of the present invention is based upon the discovery that carnotite can be concentrated from its siliceous ores by a flotation process wherein a fatty acid flotation agent is supplemented by a small and critical amount of a high molecular weight aliphatic amine. Under proper conditions of alkalinity and dispersion of gangue slimes the flotation recovery can be confined to mineral values such as carnotite and similarly flotation-responsive mineral forms, such as carbonates (malachite, calcite, dolomite, etc.) and phosphates (torbernite, autunite, etc.) by the utilization of a higher fatty acid supplemented with a long chain aliphatic amine as the flotation reagent.

Resort may be had to such modification and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. A process of recovering carnotite from its siliceous ores which comprises subjecting said ores to flotation in the presence of a long chain fatty acid containing at least 10 carbon atoms and a high molecular weight primary aliphatic amine reagent containing at least 8 carbon atoms.

2. A process of separating carnotite from its siliceous ores which comprises subjecting said

ores to flotation in the presence of a special combination of reagents comprising a long chain fatty acid reagent containing at least 10 carbon atoms supplemented with from 3 to 8% of its weight of a long chain primary aliphatic amine reagent containing at least 8 carbon atoms.

3. A process of separating carnotite from a siliceous ore thereof which comprises grinding said ore, adding water to said ground ore to form an ore pulp, subjecting said ore pulp to flotation in the presence of a long chain fatty acid reagent containing at least 10 carbon atoms and a long chain primary aliphatic amine reagent containing at least 8 carbon atoms, said amine reagent being used in an amount equal to from 3 to 8% by weight of the fatty acid reagent.

4. A process of separating carnotite from a siliceous ore thereof which comprises dry crushing said ore, desliming said dry crushed ore, wet grinding the deslimed ore, adding water to said wet ground ore to form an ore pulp, subjecting said ore pulp to flotation in the presence of a long chain fatty acid reagent containing at least 10 carbon atoms and a long chain primary aliphatic amine reagent containing at least 8 carbon atoms, said amine reagent being used in an amount equal to from 3 to 8% by weight of the fatty acid reagent.

5. A process as recited in claim 2 in which the long chain fatty acid reagent is oleic acid.

6. A process as recited in claim 2 in which the long chain fatty acid reagent consists of peanut oil acids.

7. A process as recited in claim 2 in which the long chain fatty acid reagent consists of corn oil acids.

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