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METHOD OF CONCENTRATING FLUORSPAR ORES

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Our invention relates to improvements in the concentrattion of ores by flotation and is especially directed to the recovery of fluorspar of a high degree of purity from ores in which it is accompanied by calcareous substances, such as calcite and other forms of calcium carbonate, and/or various mineral sulfides such as galena (PbS) and sphalerite (ZnS).

We are aware it has heretofore been suggested that fluorspar of "acid grade", that is, containing 98% or more CaF_2, might be obtained by flotation from certain ores, for example after elaborate slime removal treatments, but so far as we are aware no methods heretofore known are economically suitable for this purpose when the ores contain the substances mentioned, being inadequate to effect sufficiently complete separation of the calcite and/or metallic sulfides from the fluorspar to attain this high degree of purity of the latter.

Practical difficulties encountered in efforts to recover acid grade fluorspar from calcite-bearing fluorspar ores containing metallic sulfides have thus heretofore inhibited commercial exploitation of these ores, and as our invention readily accomplishes such recovery it is consequently of particular utility in relation to such ores, although it may also advantageously be employed for recovery of acid grade fluorspar from fluorspar ores containing calcite and little or no metallic sulfides or metallic sulfides and little or no calcite.

By extended research and experimentation we have discovered that when such ores, after reduction by grinding or in any other suitable manner to sufficiently finely divided condition, for example about −100 mesh, are subjected to flotation by the ordinary mechanical operations but with certain novel reagents as hereinafter more specifically described, fluorspar of acid grade can be recovered without difficulty either directly from the ore pulp or from the tailings remaining after preliminary flotation recovery therefrom of galena and/or sphalerite, and a principal object of our invention is therefore the utilization of this discovery to provide a novel method of recovering acid grade fluorspar from fluorspar-bearing ores containing calcareous minerals and/or metallic sulfides, from which the fluorspar must be substantially freed to attain the requisite degree of purity.

A further object is the provision of a novel and economical flotation method for concentrating to a high degree of purity the fluorspar content of a flotation pulp derived from a natural fluorspar bearing ore.

Other objects, purposes and advantages of the invention will hereinafter more fully appear or will be understood from the following description of its practice in the production of acid grade fluorspar from flotation pulps of various specific kinds.

One example of this practice is the production of acid grade fluorspar from the tailings resulting from flotation recovery of galena and sphalerite by separate operations from an Illinois ore originally containing, in addition to galena, sphalerite and fluorspar, material quantities of calcite and siliceous gangue, as well as other minor impurities. These tailings, the ore having been initially ground to −100 mesh, analyzed as follows,

	Per cent
Pb	0.13
Zn	0.45
CaF_2	26.92
$CaCO_3$	42.96

and were pulped with water, introduced to the fluorspar flotation circuit with about 1.0 lb. of oleic acid and 0.92 lb. of quebracho extract per ton of the original dry ore, and agitated in the usual manner with resultant production of a froth from which we secured a fluorspar concentrate containing 97.0% CaF_2 and only 2.12% $CaCO_3$. The tailings from this operation contained 6.52% CaF_2 and 54.24% $CaCO_3$ showing a recovery in the concentrate of 81.2% of the fluorspar content of the feed and rejection from the concentrate of 98.7% of the $CaCO_3$ content of the feed. Thus while the ratio of fluorspar to $CaCO_3$ in the feed was 1:1.6, we were able to produce a concentrate in which this ratio became 97:2.12, showing the high degree of selectivity of our method.

In another case, using as a feed for the fluorspar flotation circuit the finely divided tailings after galena and sphalerite recovery from an ore having an appreciably higher fluorspar content and a lower calcite content, we were able to produce substantially equally good results. Thus a feed assaying 66.24% CaF_2 and 7.78% $CaCO_3$ was subjected to roughing and moderate cleaning in the fluorspar flotation circuit in the presence of 1.0 lb. of oleic acid and about 0.25 to 0.5 lb. of quebracho extract per ton of the original dry ore and produced a concentrate which assayed 94.12% CaF_2 and 2.85% $CaCO_3$, with a fluorspar recovery of 91.2% and rejection of 86.2% of the calcite in the feed. The concentrate was next cleaned in the presence of about 1.0 lb. of quebracho extract per ton but no additional oleic acid and the final concentrate then assayed 99.0% CaF_2 and 0.60% $CaCO_3$. This showed a total extraction of only 75% of the original fluorspar content of the feed but accomplished rejection of more than 95% of its original calcite content, producing fluorspar of an unusually high degree of purity.

The foregoing examples demonstrate that our method is effective to recover economically acid grade fluorspar from calcite bearing ore tailings which are relatively rich in fluorspar and contain only a small proportion of calcite as well as from those which are considerably richer in calcite with a correspondingly smaller proportion of flourspar from which it follows acid grade fluorspar can readily be produced in the same way from ore talings in which these substances are present in other proportions than those mentioned.

Our method is also effective for recovering acid grade fluorspar directly from ore pulp before removal of the metallic sulfides and containing considerably greater quantities of the latter than the said tailings. Thus an ore containing 1.75% Zn, 0.81% Pb, 84.0% CaF_2 and 5.0% $CaCO_3$ after grinding to −100 mesh was pulped, treated with 1.0 lb. of oleic acid and 0.25 lb. quebracho extract per ton of dry feed and agitated to produce a froth. The flotation concentrate obtained therefrom assayed 99% CaF_2, 0.03% Pb and 0.05% Zn, and the tailings contained 3.6% Pb and 5.98% Zn; that is, 96.8% of the lead and 97.9% of the zinc present in the original ore were excluded from the fluorspar concentrate recovered.

Iron sulfide is similarly rejected from fluorspar concentrates when produced in accordance with our method from pyrite-bearing ores, such concentrates containing not more than about 0.05% Fe and sometimes materially less than that amount.

Recovery of acid grade fluorspar by flotation can thus be effected in acordance with our method not only when the pulp treated is substantially free from metallic sulfides but also when the latter substances are present in material amounts and it is also substantially immaterial whether a large or a small amount of calcite is present. Our method is consequently particularly advantageous in connection with ores of the type found in the important Illinois-Kentucky fluorspar area, many of which contain galena, sphalerite and fluorspar in such quantities that their commercial exploitation is now warranted, although they have heretofore not been considered commercially important because of the unavailability of economic methods of separation and purification.

In United States Letters Patent 2,137,600, issued November 22, 1938, to Frederick C. Abbott, Strathmore R. B. Cooke, and Carl O. Anderson, there is described and claimed a method for removal of residual fluorine from zinc concentrates obtained by flotation from ores of this character, to permit production of commercially useful zinc concentrates, and the said method may be employed in conjunction with our method as herein described to greatly enhance economic exploitation of such ore deposits through permitting recovery therefrom of galena and of sphalerite and flourspar of the high degrees of purity required for industrial uses.

Oleic acid, to which we have herein referred, acts as a collector for the fluorspar in the practice of our method and as we have found it satisfactory in treating the ore pulps which we have described, and it is relatively inexpensive, we now prefer its use for this purpose. However, our invention contemplates it may be possible to substitute other reagents therefor, perhaps more particularly in the treatment of other ore pulps and/or tailings, but many reagents adapted for use as collectors in some non-metallic flotation methods heretofore practised cannot be so substituted for the reason, among others, they do not possess the requisite selectivity in view of the common calcium cation contained in both fluorspar and calcite.

We consider the ability of oleic acid to promote recovery of fluorspar in the manner described partly due to the greater solubility of fluorspar as compared with that of calcium oleate produced by reaction between fluorspar and the oleic acid. However, if an attempt were made to use, instead of oleic acid, a fatty acid, the hydro-carbon radical of which is of smaller size than that of oleic acid, the ester resulting from its reaction with fluorspar migh be of sufficiently great solubility as compared with that of fluorspar to impair the selectivity of the acid as a collector and it therefore cannot be said that fatty acids generally possess the desired qualities. Thus the reaction,

$$CaF_2+2RCOOH \rightleftharpoons Ca(RCOO)_2+2HF$$

in which R represent a hydro-carbon radical, proceeds to the right when oleic acid ($C_{17}H_{33}COOH$) is used as a collector to a greater degree than when a fatty acid having a smaller hydro-carbon radical is used.

We have also referred to the use of quebracho extract, a well known article of commerce derived from trees of the genus quebracho indigenous to the central part of the continent of South America, especially in the watersheds of the Parana and Uraguay Rivers, and a brand of this extract we have found satisfactory for the purpose named is that now marketed as "Powdered Purex Sm. Brand Quebracho Extract" by the Tannin Corporation of New York City. This brand of the extract contains about 71% tannin, but our invention is not limited to the use of any particular brand or to any specific tannin concentration, and while tannin is a major constituent of substantially all quebracho extracts we consider reasonably suitable, tests we have made demonstrate the results we obtain are not due solely to the tannin. Thus in an effort to duplicate by use of tannin alone a fluorspar recovery comparable to that we have obtained as heretofore described, we substituted tanning for the quebracho extract and ascertained analogous results could be obtained only by using about 5 to 10 times as much tannin alone as was contained in the necessary quantity of the quebracho extract. Thus the extremely high cost of tannin per pound as compared with quebracho extract militates against the use of tannin alone as a collector for the fluorspar, while the greater amount of it required renders it certain the results obtained by using quebracho extract cannot be attributed but in small part to the action of its tannin content and are obviously due in large measure to other constituents.

The extract is extremely effective as a depressant for the calcareous and metallic sulfide constituents of the ore, and is substantially equally effective in eliminating siliceous materials from the fluorspar concentrate, so that the latter when recovered in accordance with our invention usually contains appreciably less than 1% SiO_2 even when the feed is high in siliceous materials, but as various depressants for siliceous materials in flotation processes have heretofore been known, we do stress this property of the quebracho extract.

While we have thus far made no reference to the character of the water we employ, we have found it preferable to use soft water, or if only hard water is available, to soften it by means of a lime soda or a zeolite treatment, as the effectiveness of our method is most pronounced and its performance most easily carried out when water of approximately zero hardness is used in the flotation circuit. When hard water is employed without preliminary softening, the dissolved calcium and magnesium salts react with the oleic acid or other collector to form an undesirable precipitate and the practice of the method then requires a larger amount of the collector than would otherwise be necessary, while the product may be contaminated by the precipitate and separation of fluorspar from the calcite impaired.

We also prefer to maintain the pH in the flotation circuit between 8.0 and 8.6, but it is to be understood that this range is stated merely to facilitate explanation of the best way we have found for performing our method, and not as constituting a limitation upon it.

We have herein described our invention with considerable particularity, especially with reference to certain examples of our practice of it in the recovery of acid grade fluorspar from certain specific substances, but it will of course be understood that this is for purposes of illustration only and is not to be considered as limiting or confining our invention thereto, as the materials we employ therein and those we operate upon, and the manner of carrying out the method are all subject to variation and modification, as will readily occur to those skilled in the art, without departing from the spirit and scope of the invention as defined in the appended claims.

Having thus described our invention, we claim and desire to protect by Letters Patent of the United States:

1. The method of concentrating fluorspar ores which comprises mixing the ground ore with water to form a pulp, adding to the pulp a fatty acid fluorspar flotation reagent and quebracho extract, agitating the mixture to produce a froth and removing the froth.

2. The method of concentrating fluorspar ores which comprises mixing the ground ore with water to form a pulp, adding to the pulp a collector having a fatty acid radical and capable of forming a froth adapted to support fluorspar particles and a depressing agent including quebracho extract, agitating the mixture to produce a froth and removing the froth.

3. The method of concentrating fluorspar ores which comprises mixing the ground ore with water to form a pulp, adding to the pulp oleic acid and a depressing agent including quebracho extract, agitating the mixture to produce a froth and removing the froth.

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