

UNITED STATES PATENT OFFICE

1,926,045

FLOTATION PROCESS

Omer W. Greeman, Rosiclare, Ill., and Henry A. Lilly, Avondale Estates, Ga., assignors to Aluminum Company of America, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application August 7, 1931
Serial No. 555,856

19 Claims. (Cl. 209-166)

This invention relates to a method of treatment of waters which are to be used in froth flotation processes designed for the concentration of fluorspar values from fluorspar ores and similar fluorspar-bearing material.

The ores of fluorspar usually contain, in addition to variable amounts of other impurities, substantial quantities of siliceous and/or calciferous impurities, such as silica and calcite. Depending upon the location of the ore and the methods by which it is mined, the silica or the calcite is ordinarily the predominating impurity and both are often present in substantial amounts. The recognized undesirability of either or both of these impurities as a substantial constituent of the final fluorspar concentrate has led to extensive experimentation intended to devise a suitable process or combination of processes for the obtainment of a high purity concentrate from ordinary run-of-the-mine ore.

In United States Letters Patent No. 1,785,992, a froth flotation process for effecting the above results is described, which comprises the use of oleic acid and another reagent, usually cresylic acid, as flotation reagents, and in conjunction with and preliminary to this treatment, a preliminary operation designed to deslime the original ore. This process, while primarily designed for fluorspar ores containing calcite in substantial amounts, has been found to be very effective in the recovery of values from other fluorspar-bearing material. In experimenting with this and other fluorspar flotation processes, we have discovered that such processes can be substantially increased in recovery efficiency if the water in which the ore is floated is preliminarily treated in a certain way prior to the frothing operation.

It is the principal object of our invention to provide a water treatment which, when used in conjunction with and as a step of a froth flotation treatment, will materially increase the amount of fluorspar which may be recovered from the ore by the froth flotation. Other similar and varied objects of our invention will be apparent from the following description of our invention or will be hereinafter mentioned.

We have discovered that if water, heretofore considered as satisfactory for use in connection with the froth flotation of fluorspar, is treated prior to the froth flotation with an oxidizing agent, the efficiency of the froth flotation process is substantially increased. We have further discovered that if, in addition to the

pretreatment of the water with an oxidizing agent, the water is also treated with commercial cresylic acid, a further increase in flotation efficiency is obtained. Commercial cresylic acid is chiefly a mixture of the cresols with smaller amounts of xylenols. We have found that the constituents of commercial cresylic acid as well as the acid itself have the beneficial effect above noted.

For the purpose of suitably explaining the unexpected and remarkable results of our invention, it will be necessary to set forth in some detail a treatment of fluorspar ore in what we have found and taken to be the preferred manner. However, the application of our invention is not limited to the particular flotation treatments hereinafter described which are given only by way of convenient examples of the beneficial effects of the invention as applied to the froth flotation of fluorspar by any process of similar nature. This is also true as regards the particular flotation reagents used, it being understood that these reagents are but illustrative of those reagents found suitable for the frothing and floating of fluorspar or some water-ore pulp. When practiced in the preferred manner, the process with reference to which we will describe our invention consists in first suitably reducing the fluorspar ore in size, grinding it in a pebble mill to pass a 65 mesh screen, mixing the ground ore with suitable amounts of water, and desliming it by repeated settling operations of approximately five minutes each, the water and suspended material contained therein being siphoned off to within an inch of the ore after each period, and the deslimed ore being placed in a laboratory flotation machine. To it are then added substantially equal quantities of oleic and cresylic acid, the amount of reagent added to each ton of ore varying from about 0.2 to 0.5 pound. The mixture of pulp and reagents thus formed is frothed for a suitable period and the froth, together with the material carried by it, collected as it comes over the lip of the cell. The collected froth is then placed in another cell, diluted with water, and, with or without addition of further reagents, depending upon the particular operation involved, again floated. These "cleaning" operations are repeated from two to three times per charge of ore, depending upon the conditions, and the material carried by the froth of the final operation is accepted and designated as the final concentrate.

The water which is used in the practice of our invention should come from an original source

which is satisfactory. Generally speaking, any flotation process demands the use of certain types of water since, depending upon the type of flotation reagents used and the ore to be frothed, the water may contain such ingredients which would interfere with the selectivity of the process unless removed. These ingredients may in various cases, as is well known, consist of acids or soluble salts or organic impurities and other dissolved or undissolved and colloidal substances. In the practical application of the method of froth flotation above described, it has been found desirable to obtain an original water which is naturally soft or can be softened by suitable treatment and which contains a comparatively small amount of soluble salts. Under some conditions, the water may contain deleterious substances even in minute amounts which will hinder the subsequent flotation, and these, of course, must be removed, if possible, by other methods. Usually, however, good results are obtained by the use of a naturally soft water having a pH value lying between about 6.8 to 7.7. Preferably the pH value is adjusted, if necessary, to a somewhat narrower range and the best results are obtained in the above process by the use of a water having a pH of about 7.

Our invention broadly contemplates the addition to the water or to the pulp, prior to the frothing operation, of an oxidizing substance such as an alkali permanganate, an alkali dichromate, chlorine or the like. Of these substances we prefer to use potassium permanganate or a similar alkali permanganate since, with the use of this compound, we are able to produce consistently a fluorspar concentrate of very high purity and superior yield. With the use of chlorine the results obtained are satisfactory both as to purity of final concentrate and the amount of fluorspar recovered. Also, while chlorine gas is preferable, there may be used as a source of chlorine, a chlorine-producing substance such as an alkali hypochlorite. If high purity of the final concentrate is not a desideratum and a slightly lower purity is satisfactory, an alkali dichromate may be used as the oxidizing agent.

By our treatment, the amount of fluorspar recovered from the original ore is materially increased. The increase is, generally, on the order of about 4 per cent of the fluorspar of the original ore, and under some conditions exceeds this amount. While this increase is small as regards the total fluorspar in the ore, it represents a considerable economy when large amounts of fluorspar concentrates are daily produced.

The amount of oxidizing agent which should be added to the water in the practice of our invention is not critical and will vary considerably with the type of ore to be treated and the water available for treatment. Generally it is preferable to use a small amount not only for economic reasons, but also because the addition of unduly large amounts may unbalance other factors in a complex and delicately balanced flotation process. Using Illinois ores and under the particular conditions hereinabove set forth, we have observed that 0.5 grain or potassium permanganate per gallon of water need rarely be exceeded to produce desirable results. In the use of chlorine as the oxidizing agent and under similar conditions, an amount of about 0.5 grain per gallon of water has proven satisfactory.

From an operating standpoint it is usually desirable to add the oxidizing agent to the water before the pulp is made up, but addition at the time of forming the pulp or after forming the pulp will obtain good results. Therefore, it will be understood that the language of the appended claims does not limit the addition of the oxidizing agent to any particular step of the operations preliminary to the actual frothing. The pre-treated water is preferably used wherever water is introduced into the flotation process.

The beneficial results obtained by the addition of an oxidizing agent to the water prior to flotation can, as we have discovered, be increased if the water is also treated with a small amount of cresylic acid or a constituent of cresylic acid being, according to our experiment, the most advantageous. Consequently, we prefer to use this reagent. The reason for the fact that the addition of one of these reagents, in conjunction with an oxidizing agent, to the water prior to flotation produces an increased yield of fluorspar in the final concentrate is not by us known with any certainty, but by the use of a combined water treatment utilizing both an oxidizing substance and one of the reagents above named, the amount of fluorspar recovered from the ore is in the range of about 10 per cent more than when no treatment is used and generally about 6 per cent more than when the oxidizing agent is alone added to the water.

The amount of the reagent cresylic acid or one of its constituents which, when added to the water in conjunction with an oxidizing agent, will produce the effects above noted will vary with the type of ore being processed and the water being used but in any case should be small. We prefer to add about 0.2 to 0.4 grain per gallon of water of any of these reagents when practicing our invention in connection with the process above mentioned, but smaller or larger amounts may be used with effective results. Care should, however, be taken to keep the amount of reagent added as low as is consistent with good results.

It is an important advantage of our invention that its use not only increases the amount of fluorspar recovered without appreciably lowering the purity of the concentrate, but that by its use water may be re-used in the flotation process. Where a large supply of water is available, re-use of the water is seldom necessary but where, as in many cases, the body of ore is not located near large amounts of water, the use of my invention in treating water which has been used in the flotation process is an undoubted advantage. We have found that if a water which, when once used in the froth flotation process of concentrating fluorspar values from fluorspar ores, could not be satisfactorily re-used without a considerable decrease in the efficiency of the process be submitted to a treatment with suitable amounts of an oxidizing agent, or an oxidizing agent and a reagent of the type above mentioned, it will be rendered capable of satisfactory re-use. We have further found that a continuation of this treatment after each use of the water will allow re-use of the water in the process for a number of times before it must be finally discarded.

We claim:

1. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing an oxidizing agent into the water used in the pulp before frothing.

2. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing an alkali permanganate into the water used in the pulp before frothing.
- 5 3. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing an alkali dichromate into the water used in the pulp before frothing.
- 10 4. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing chlorine into the water used in the pulp before frothing.
- 15 5. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing potassium permanganate into the water used in the pulp before frothing.
- 20 6. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an oxidizing agent and cresylic acid or a constituent of cresylic acid.
- 25 7. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing potassium permanganate and cresylic acid.
- 30 8. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing, potassium permanganate and a cresol.
- 35 9. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing potassium permanganate and a xlenol.
- 40 10. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an alkali permanganate and cresylic acid.
- 45 11. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an alkali permanganate and a cresol.
12. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an alkali permanganate and a xlenol.
13. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an alkali dichromate and cresylic acid.
14. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an alkali dichromate and a cresol.
15. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing an alkali dichromate and a xlenol.
16. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing chlorine and cresylic acid.
17. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing chlorine and a cresol.
18. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp, before frothing chlorine and a xlenol.
19. In the froth flotation of fluorspar concentrates from fluorspar ore, the step comprising introducing into the water used in the pulp prior to the frothing operation, an oxidizing agent selected from the class composed of alkali permanganate, alkali dichromate, and elemental chlorine.

OMER W. GREEMAN.
HENRY A. LILLY.

120

CERTIFICATE OF CORRECTION.

Patent No. 1,926,045.

September 12, 1933.

OMER W. GREEMAN, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 69, for "or" read of; and line 92, after "acid" insert , cresylic acid; page 3, lines 20, 25, 35, 40, 76, 81, 86, 91, 96, 101, 105, and 109, claims 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18, inclusive, after "frothing" insert a comma; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of November, A. D. 1933.

(Seal)

F. M. Hopkins
Acting Commissioner of Patents.