

March 8, 1955

E. A. SCHOELD

2,703,646

BENEFICATION OF POTASH ORES AND THE LIKE

Filed Jan. 11, 1951

3 Sheets-Sheet 1

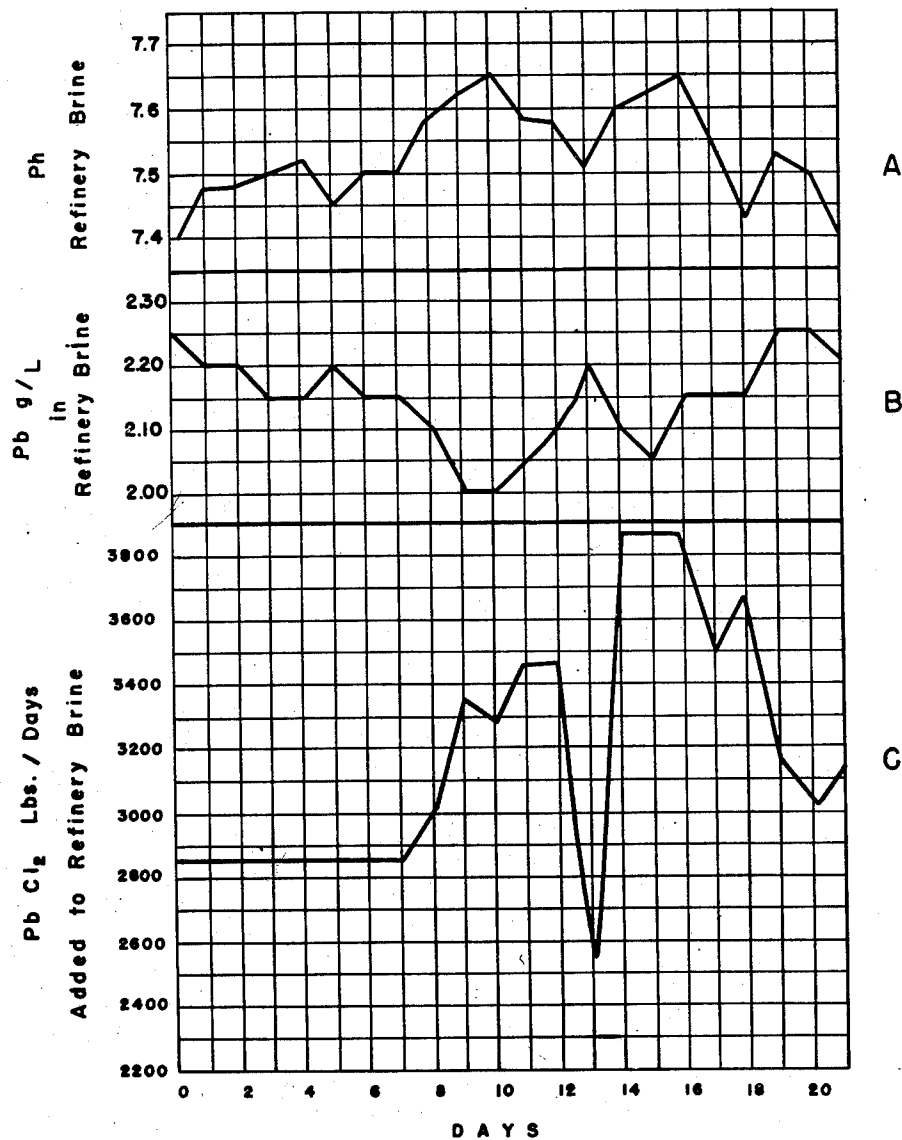


FIG. - 1

INVENTOR.
Edmund A. Schoeld

BY

H. A. Schoeld

ATTORNEY

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3 Sheets-Sheet 2

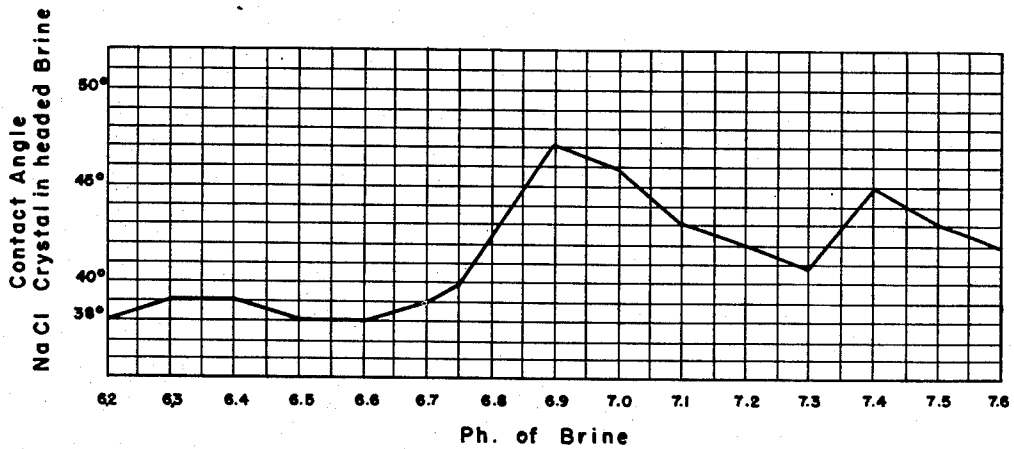


FIG. - 2

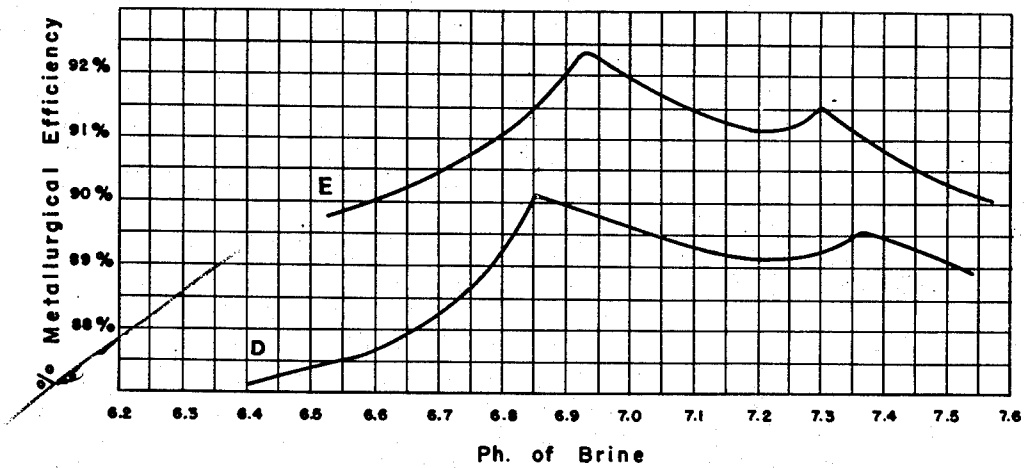


FIG. - 3

INVENTOR.

Edmund A. Schoeld

BY

H. A. McGraw

ATTORNEY

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E. A. SCHOELD

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3 Sheets-Sheet 3

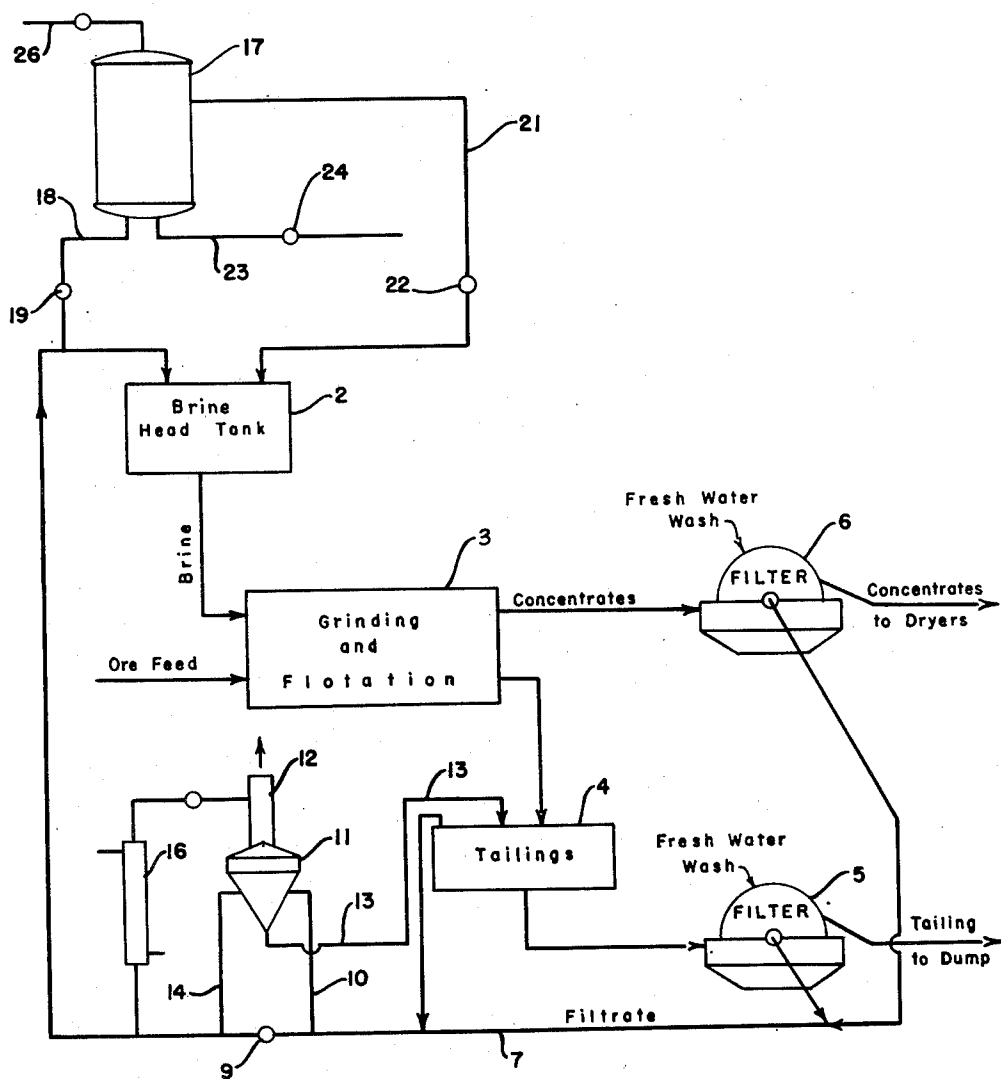


FIG. - 4

INVENTOR.
Edmund A. Schoeld
BY
H. A. Green
ATTORNEY

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2,703,646

BENEFICIATION OF POTASH ORES AND THE LIKE

Edmund A. Schoeld, Carlsbad, N. Mex., assignor to
Potash Company of America, Carlsbad, N. Mex., a cor-
poration of Colorado

Application January 11, 1951, Serial No. 205,500

6 Claims. (Cl. 209—166)

My invention is directed to an improvement in a process for the beneficiation of potash ores by froth flotation.

Various potash ores, such as sylvinites, which contains KCl, NaCl, and gangue, may be concentrated by froth flotation processes in which the ground ore is carried in a brine saturated with respect to the water-soluble ore constituents. These processes divide themselves logically into a first type in which KCl is collected in the froth of the flotation apparatus and a second type in which the NaCl and gangue are collected in the froth. The latter type, described by Weinig in his Patent No. 2,105,295, is operable only when the brine contains lead or bismuth ions and is the process to which my invention is directed.

One of the most satisfactory compounds available for maintaining the necessary lead ion concentration in the brine is PbCl₂, which is frequently added to the brine prior to the addition of the collector reagent, the latter preferably, but not necessarily, being one of the fatty acid compounds conventionally employed for such purpose, such as the alkali metal soaps of caprylic or pelargonic and/or mixtures containing these compounds. Causticized starch is also conventionally added to the brine prior to flotation and serves as a froth conditioner.

In the above-defined process, the NaCl and gangue collected in the froth are washed with clear water on a filter to remove occluded solution containing lead ions and KCl. The concentrated potash salts are also washed on a filter for similar reasons, the filtrates from the two filtering operations being subsequently combined and recycled through the process. In some instances where it is desirable to obtain substantially pure KCl, the concentrated KCl is further treated, by solution process, the brine from this treatment being later returned to the primary process or circuit mentioned above.

Although either lead or bismuth salts may be employed, practical considerations based on experience dictates the use of lead, rather than bismuth, salts. Hence the following disclosure and the various limitations stated therein refer to lead, rather than to either lead or bismuth, since the specific values assignable to bismuth differ substantially from corresponding values assignable to lead. The necessary minimum concentration of lead ions is maintained by daily addition of soluble lead salts and constitutes an important item in the cost of operation.

One of the principal objects of my invention is the provision of a process of the type described, in which the consumption of lead or bismuth salts is reduced.

Another primary object of my invention is to maintain the efficiency of such process at a maximum, particularly by holding the quantity of potash salts included in the tailings to a minimum and by maintaining at a maximum the purity of the concentrated potash salts.

Other important objects of my invention include the provision of a process of the type described, in which the contact angle between the brine and the principal material to be floated is maintained at or near a maximum and in which improved reagents prepared by novel methods are provided.

Further objects of my invention will be disclosed in the following description and in the appended drawings, in which:

Fig. 1 is a graph indicating the relationship between the pH value of the brine, the lead content of the brine, and the quantity of lead salts required to maintain a predetermined minimum lead content;

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Fig. 2 is a graph indicating the variation of the contact angle between the material to be floated and the brine, with the pH value of the brine;

Fig. 3 is a graph indicating the relationship between the pH value of the brine and the percentage metallurgical efficiency; and

Fig. 4 is a schematic diagram of the process.

In brief, I have found that the pH value of the brine markedly influences both the efficiency of the process and the lead consumption, the optimum pH value being approximately 6.9. If the pH value of the brine drops below 6.5 or exceeds 7.5, the loss in efficiency is quite marked and in the latter instance the increase in alkalinity drastically increases the consumption of lead.

Sylvinites dissolved in water yields a substantially neutral solution, which is satisfactory for use in the subject process. However, the fatty acid soaps and many other similar collector reagents are alkaline, as is the starch compound, which is usually prepared by heating the starch in an alkaline solution. As a result, the pH value of the brine gradually increases as the brine is recycled through the process until it exceeds a pH value of 7.5. If a portion of the potassium chloride is diverted for further purification treatment involving the addition of alkali directly or indirectly and the resulting carrier brine is returned to the main brine system, the rate of increase in the pH value of the brine will be more rapid.

The pH value of the brine may be maintained between 6.5 and 7.5 by preparing the additive reagents in the process in such manner as to yield substantially neutral or slightly acid compounds, or by treating the recycled brine with an acid or acid anhydride, or by a combination of both procedures. In many instances, utilization of an acid compound is necessary, particularly if the addition of alkaline compositions to the brine can not be avoided.

The relationship between the pH value of the brine, its lead content, and the quantity of lead required per day of operation is illustrated in Fig. 1, wherein the line A represents the pH value of the brine, the line B, the lead content of the brine in grams per liter, and the line C, the quantity of PbCl₂ added to the brine. This figure depicts graphically the results of a series of tests conducted at a large commercial potash refinery in the plant circuit at room temperature over a ten day period. It will be noted that an increase in the pH value of the brine is followed by a reduction in the lead content, thus requiring the addition of increased quantities of PbCl₂ to maintain the desired minimum lead concentration, which is approximately 2.0 grams of lead per liter of brine. The slight lag in response noted in the above curves is occasioned by the very large volume of brine circulated in the process, and by the slowness of the reaction precipitating the lead.

Laboratory experiments indicate that the increase in lead consumption corresponding to the increase of pH value of the brine is due to the precipitation of the dissolved lead as an insoluble compound. For example, on titration of the refinery brine with caustic, the pH value of the brine increases, as would be expected, and then slowly precipitates lead from the brine as basic lead chloride. If the titrated solution is allowed to stand, the pH value falls until equilibrium is attained. This usually requires about twenty-four hours. On addition of caustic equivalent to the lead, the basic lead chloride is converted at a very slow rate into lead hydroxide.

The lead precipitate formed at pH values above 7.5 clings tenaciously to the solids collected on the filters and can be washed therefrom only with the greatest difficulty. As a result, at pH values in excess of 7.5, a substantial quantity of lead is removed from the system with the solids and the concentrated potash salts contain lead compounds which reduce the purity of the salts. If, however, the pH value of the brine is maintained between 6.5 and 7.5, and preferably at about 6.9, very little if any precipitate of lead is formed, and the quantity lost is markedly reduced.

By maintaining the pH value of the brine between 6.5 and about 7.5, an increase in metallurgical efficiency is also noted. Fig. 2 demonstrates graphically the change in contact angle at room temperature between the brine

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containing lead ions and a pelargonic acid soap and a crystal of sodium chloride as the pH value of the brine varies. It will be noted that the maximum contact angle, which indicates maximum floatability, occurs near a pH value of 6.9.

To confirm the above, a series of flotation tests were performed at room temperature, using sylvinitic ore disposed in a leaded brine circuit. In series I, indicated graphically by line D in Fig. 3, 0.4 pound of fatty acid soap of the type previously mentioned were added for each ton of dry ore, while in series II, indicated by the line E in Fig. 3, the amount of soap reagent was increased to 0.58 pound per ton of ore. Other conditions were held substantially constant between the two series of tests. The results of these tests were as follows:

Series I		Series II	
pH	Met. Eff.	pH	Met. Eff.
6.34	89.1	6.54	89.9
6.40	87.2	6.68	90.5
6.48	87.4	6.74	89.9
6.53	87.6	6.87	91.8
6.75	88.7	6.98	92.2
6.85	90.3	7.12	91.5
6.95	88.3	7.15	90.9
7.05	89.5	7.23	91.2
7.12	89.3	7.30	91.5
7.24	89.2	7.41	89.8
7.35	89.6	7.52	90.3
7.43	89.4		
7.44	88.8		
7.53	89.0		

¹ Maximum.

Per cent metallurgical efficiency, utilized above, is calculated as follows:

Metallurgical efficiency=

$$\frac{\text{Recovery of concentrate} + \text{recovery of tailings}}{2}$$

Recovery of concentrate=

$$\frac{\text{Tons of concentrate} \times \text{percent value}}{\text{Tons of feed} \times \text{percent value}} \times 100$$

Recovery of tailings=

$$\frac{\text{Tons of tailings} \times \text{percent gangue}}{\text{Tons of feed} \times \text{percent gangue}} \times 100$$

In Fig. 3 it will be noted that the metallurgical efficiency drops off rapidly as the pH value of the brine exceeds about 7.4. Similar tests indicate that the consumption of lead becomes critical if the brine exceeds a pH value of slightly less than 7.6. Thus, the maximum efficiency will be obtained by holding the pH value of the brine between about 6.8 and 7.4 and at the same time, minimum lead consumption will be obtained.

To maintain the brine within the desired pH range, ordinary mineral acids such as sulfuric or hydrochloric acid may be added directly to the circuit in such quantities as may be necessary. This, however, is a relatively expensive procedure and is therefore considered less desirable than other processes, which accomplish the same result.

Similar results and a higher order of control may be obtained by treating the brine with a gaseous acid anhydride, particularly carbon dioxide, such as may be obtained in a conventional submerged combustion unit, or from internal engine exhausts, and other similar sources. Carbon dioxide brought into contact with an alkaline brine will be absorbed rapidly and thus reduce the pH value of the brine, the rate of absorption gradually being reduced as the brine becomes more acidic, and eventually reaching equilibrium at a pH value of about 6.75. Various methods may be employed for carbonating the brine and are indicated diagrammatically in Fig. 4, in which the numeral 2 designates a brine head tank from which brine is supplied to the grinding and flotation units 3 of the process. Ore is preferably introduced for admixture with the brine at the grinding stage, after which the flotation and conditioning reagents are added and the pulp fed to the flotation apparatus. In the flotation operation, the material collected in the froth is discharged to a tail-

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ings thickener 4, which in turn discharges to a suitable filter 5, where the solids are separated from the liquid, washed with water, and discharged. The concentrated potash salts from the flotation operation are discharged to a similar filter 6, where they are also washed while on the filter with water and discharged for subsequent drying and storage. The filtrates from the filtering operation and the liquid discharged from the thickener 4 are combined and recycled to the brine head tank 2. Lead chloride or other soluble lead salt may be added at any point in the process to maintain the desired minimum lead concentration.

It is at times necessary to utilize as a wash on the filter a quantity of water which exceeds in volume the quantity of water removed from the system by the discharged solids. In such instances it is necessary to eliminate this excess water from the system if a proper balance is to be maintained. To accomplish this purpose, it has been proposed that a portion of the circulating brine be cycled through a submerged combustion unit or other suitable evaporator where the excess water is removed by evaporation. Precipitated solids formed in this operation are returned to the system for further treatment. Under such system of operation, only a small quantity of brine is subjected to the action of carbon dioxide formed by the combustion of fuel in the burners which are submerged beneath the liquid in the submerged combustion unit, with the result that return of the carbonated brine to the system may not yield the desired reduction in the alkalinity.

As illustrated in Fig. 4, however, a valve 9 may be provided in the circulating brine conduit 7, which by adjustment permits passage of substantially all of the brine flowing in the circuit through a conduit into a submerged combustion unit 11 having an exhaust 12 communicating with the atmosphere and a solid discharge conduit 13 for passing precipitated solids from the unit 11. The carbonated brine from the unit 11 may be returned to the system through a suitable conduit 14 and if treated for a sufficient period of time in the unit 11 will have a pH value of about 6.75. The quantity of water evaporated in the unit 11 may be controlled by passing the desired quantity of exhaust through a conventional condenser 16, which discharges into the brine circuit.

The above-described arrangement is usually satisfactory in plants where the quantity of wash water required exceeds the quantity of liquid necessarily removed from the system with the solids. If, however, excess water is not introduced into the system during processing, the submerged combustion unit 11 and the accessories thereto may be eliminated from the circuit, substituting therefor a reactor vessel 17 having a brine inlet 18 controlled by a valve 19 and a brine outlet 21 communicating with the brine head tank 2 through a valve 22. Carbon dioxide from a suitable source, such as the exhaust from diesel engines, may be introduced into the vessel 17 through a conduit 23 having a valve 24 and subsequently discharged from the vessel 17 through an exhaust 26. Pure carbon dioxide may be of course substituted for exhaust gases from internal combustion engines, but the cost of such a procedure is usually excessive. It will be understood, however, that the exhaust may be treated in any desired manner prior to introduction into the reactor vessel, provided the treatment does not reduce materially the carbon dioxide content of the gases. Regardless of whether the reactor vessel 17 or the submerged combustion unit 11 employed in the process, it may be desirable to cycle a major portion of the circulating brine through one of the devices in order to reduce the pH value of the brine to the desired point. However, if the reagents added during the process are not alkaline in nature, or if reagents are mildly acid, the quantity of brine circulated through the unit 11 or the vessel 17 may be reduced, and in certain instances, it is possible to eliminate completely treatment of the brine with carbon dioxide by proper control of the pH value of the additives.

Starch added to the brine preferably should not be prepared by heating the dry material in contact with an alkaline solution, but on the contrary, should be prepared by cooking the starch in water under superatmospheric pressure. The resultant compound is substantially neutral and will not materially affect the pH value of the brine.

The fatty acid soap preferably employed as a col-

lector reagent is ordinarily fully saponified with lye or a similar alkali metal caustic; and as a result, is highly alkaline. Preferably, in preparing such a reagent for use in my process, the addition of alkali to the fatty acid is stopped when only about 50% of the fatty acid is neutralized. At this point the pH value of the soap composition will be about 7.0 and an increase in viscosity of the mixture will be noted, as will the formation of a homogeneous composition of uniform appearance. This phenomenon is apparently due to the formation of a distinct compound, referred to as the alkali metal salt of the fatty acid involved. Best results will be obtained by adding the caustic to the fatty acid, rather than the fatty acid to the caustic. The resulting alkali metal salt of the fatty acid can be diluted and added directly to the flotation circuit in the manner described without materially increasing the pH value of the brine. The fatty acids employed in forming the collector reagents should preferably be saturated aliphatic compounds containing from 5 to 12 carbon atoms per molecule.

For descriptive purposes I have in the foregoing specification referred to the use of substantially pure fatty acid soaps as collector agents. However, in many instances, cost considerations may dictate the use of soaps of relatively impure fatty acid compounds, such as those derived from petroleum, as described by Anderson in his patent application Serial No. 672,719, now abandoned, filed May 27, 1946. These petroleum acid compositions may in many instances be profitably reinforced by the addition thereto of relatively pure fatty acid soaps, such as those derived from pelargonic or caprylic acid. The addition of fully saponified soaps of these and related acids to the saponified acid petroleum compositions causes the precipitation of a tarry material, which accumulates in the pipes, orifices, and pumps of the reagent system and eventually interrupt the flow of solution. However, when the alkali metal acid salts of the fatty acids prepared as described above are added to the petroleum compound no precipitate is formed and the resulting mixture shows no tendency to clog the pipes, orifices, or pumps.

In compliance with R. S. 4888, I have described in detail a preferred embodiment of my invention, as well as a preferred method of application. It should not be understood, however that it is my intention to thereby limit my invention specifically to the details therein set forth, except insofar as defined in the appended claims.

I claim:

1. In a process for extracting impurities from potash ores such as sylvinites in which the ground ore is suspended in a circulating brine saturated with respect to the soluble ore components and subjected to froth flotation in the presence of a collector reagent adapted for collecting the impurities in the froth, said brine containing lead ions, the improvement which comprises adding acidic material to the brine in quantities sufficient to maintain the pH value of said brine at approximately 6.9 during flotation, whereby to reduce the tendency of lead in solution to precipitate.

2. In a process for extracting impurities from potash ores such as sylvinites in which the ground ore is suspended in a circulating brine saturated with respect to the soluble ore components and subjected to froth flotation in the presence of a collector reagent adapted for collecting the impurities in the froth, said brine containing lead ions, the improvement which comprises adding acidic material

to the brine in quantities sufficient to maintain the pH value of the brine between 6.5 and 7.5 during flotation, whereby to reduce the tendency of lead in solution to precipitate.

3. In a process for extracting impurities from potash ores such as sylvinites in which the ground ore is suspended in a circulating brine saturated with respect to the soluble ore components and subjected to froth flotation in the presence of a collector reagent adapted for collecting the impurities in the froth, said brine containing lead ions, the improvement which comprises reacting the brine with carbon dioxide in quantities sufficient to maintain a brine pH value of between 6.5 and 7.5 during flotation, whereby to reduce the tendency of lead in solution to precipitate.

4. In a process for extracting impurities from potash ores such as sylvinites in which the ground ore is suspended in a circulating brine saturated with respect to the soluble ore components and subjected to froth flotation in the presence of a collector reagent adapted for collecting the impurities in the froth, said brine containing lead ions, the improvement which comprises substantially saturating the circulating brine at at least one position in the brine circuit with carbon dioxide.

5. In a process for extracting impurities from potash ores in which the ground ore is suspended in a circulating brine saturated with respect to the soluble ore components and subjected to froth flotation in the presence of a fatty acid collector reagent adapted for collecting the impurities in the froth, said brine containing lead ions, the improvement which comprises adding to the brine a brine-soluble, acid-reacting compound incapable of forming an insoluble precipitate with lead and in quantities sufficient to maintain the pH value of the brine to between 6.5 and 7.5, whereby precipitation of lead in the brine is substantially eliminated, and the efficiency of the froth flotation step is maintained at a maximum.

6. In a process for extracting impurities from potash ores such as sylvinites in which the ground ore is suspended in a circulating brine saturated with respect to the soluble ore components and subjected to froth flotation in the presence of a collector reagent adapted for collecting the impurities in the froth, said brine containing lead ions, the improvement which comprises adding sufficient acidic material to the circulating brine to maintain the pH of such a pulp throughout the flotation treatment between 6.5 and 7.5, whereby to reduce the tendency of the said lead in solution to precipitate.

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