UNITED STATES PATENT OFFICE.

MAY KRUMP CODDING, OF SAN FRANCISCO, CALIFORNIA.

PROCESS OF TREATING ORE.

1,402,740. Specification of Letters Patent. Patented Jan. 10, 1922.

No Drawing. Application filed December 1, 1919. Serial No. 341,586.

To all whom it may concern:

Be it known that I, MAY KRUMP CODDING, a citizen of the United States, residing at San Francisco, in the county of San Francisco and State of California, have invented certain new and useful Improvements in Processes of Treating Ore, of which the following is a specification.

This invention relates to processes of treating ore; and it comprises a method of assisting in recovering the values of various metalliferous ores wherein such ores in a raw finely divided or powdered condition are vigorously agitated for a time with water containing small amounts of a dissolved neutral salt, such salt being advantageously sodium nitrate, and also containing an alkali or an alkaline reacting body, the agitation being continued sufficiently long to permit thorough action by the solutes of said solution upon the fine particles of ore causing various changes in said particles, and the values are then recovered by a process involving gravital separation of said particles; and it comprises a method of making gold ores amenable to amalgamation wherein such a gold ore in a finely divided state is vigorougly agitated at the ordinary temperature for a time with a dilute solution containing an oxidizing salt, such salt being advantageously sodium nitrate, and a basic salt, such salt being advantageously sodium or potassium carbonate and is treated to amalgamate the contained gold, the amalgamation treatment being simultaneous or subsequent to said agitating; all as more fully hereinafter set forth and as claimed.

Metallic ores may contain any one of very many substances; and as a rule they are rather complicated, being composed of many minerals in greater or less amount. In addition to the ore minerals themselves, all ores contain more or less gangue mineral. Most ores contain silica or silicates; many contain sulfids; and some contain free metals. In ordinary methods of concentration it is usual preliminarily to grind the ore and associated gangue to a finely powdered condition; to grind to convert the ore into the so called "pulp." With many ores the fineness of grinding may be as great as 800 to 100 mesh; that is the ore is so finely ground that all of it will go through an 80 mesh screen or 100 mesh screen as the case may be. But in such fine grinding of course very many of the particles are much finer than the dimensions indicated; an 80 mesh ore, for example, is an ore of which the coarsest particles will go through an 80 mesh sieve. Even with much coarser grinding, as to 20, 40 and 60 mesh, a very large proportion of the particles are impalpably fine; of a fineness approaching that of the particles of ordinary clay. The ore minerals, as a rule, are more frangible and brittle than the gangue particles or silicates and they crush finer. In concentration the pulped ore is mixed with water and subjected to a gravital separation of one kind or another. Whether this separation be on tables or any of the very many other types of apparatus in use the principle is the same as settling in a vat; the particles of greater specific gravity go to the bottom first while those of less specific gravity or density reach the bottom afterwards. In amalgamating gold ores the principle is much the same but the heavier gold particles are caught by mercury. In practically all methods of concentration, including amalgamation as a concentration method for the present purposes, the effort is to separate heavy fine particles from light fine particles by taking advantage of their differential settling in water.

In this separation however the difficulty is experienced that the relation of the various particles to water is not the same. Irrespective of specific gravity or density, some particles have a greater tendency to stay in suspension in water than have others. Ordinary clay, which is a component of very many ores, for example, in its ordinary natural or raw state, has a greater tendency to stay in suspension in pure water than have other minerals; even than some which are lighter in density; but this tendency is profoundly influenced by even traces of substances dissolved in the water. The influence of a dissolved electrolyte upon particles of clay and the like is profound; neutral electrolytes, as a general rule, tending to flocculate and precipitat suspensions of clay while alkaline electrolytes, or those alkaline to indicators and containing the 'OH ion tend to keep it in suspension. Most finely ground silicates, as well as silica itself, tend to act more or less like clay; the tendency being the greater the finer the subdivision and the nearer the particles approach clay particles in size. On the other hand, the characteristic ore minerals, sulfids, free metals,

etc., in the presence of water all behave quite differently from clay even when in a state of extreme subdivision. But with all finely divided materials, the presence or absence of electrolytes in water in which they are suspended, and the character of the electrolytes, make differences in the way the particles settle out of a suspension. Most earthy materials and many ores contain enough soluble matter to affect gravital separation methods more or less; and sometimes this influence is in the direction of promoting a clean separation and sometimes not.

In the present invention I utilize these facts. I have discovered that in recovering the values of nearly all metalliferous ores in practically any gravital separation it is of advantage to effect preliminary physical (or physical and chemical) changes in the ore particles by electrolytes in order to affect their relation to water; that is the relations by which they tend to stay suspended or not to stay suspended as the case may be. In so doing it is commonly advantageous to employ both classes of electrolytes, the neutral and the alkaline, in order to effect differential changes in the various classes of particles. As the neutral electrolyte I may use sodium nitrate, sodium chlorid, sodium sulfate or any other soluble neutral salt. As the alkaline electrolyte while I may employ caustic alkalies yet since these quickly become carbonated, it is generally better to use sodium carbonate (sal soda, soda ash, etc.) or potassium carbonate directly.

As stated, in a measure, as regards at least some of the fine-particled component of an ore, such as clay, these two materials have opposite effects. Taking salt and sodium carbonate, for example, in solution in water containing clay, the salt will tend to precipitate the clay while the sodium carbonate tends to keep it in suspension. Both effect changes in the physical structure of the clay particles corresponding to these alterations in the behavior the particles exhibit towards water. Whether it be for the reason that the suspension-favoring tendency of the alkaline electrolyte is predominantly exhibited on the gangue or silicate particles while the suspension-breaking effect of the neutral electrolyte is predominantly exhibited towards ore minerals, sulfids, native metals, etc. or for some other reason I find that the conjoint influence of these two materials on ore mixtures favors carrying down heavy metals and heavy metal compounds to the bottom while keeping light metal compounds (silicates and the like) in suspension. The net effect favors separation. Any solubles which may be in the ore become immaterial in their effect. The effect of these electrolytes on the physical consistency of the ore particles is not instantaneous; it takes time to develop even with fine particled ore and thorough admixture. I find that as a rule vigorous agitation of the ore and the solution should occur for at least 40 minutes, and in the case of some refractory ores 4 or 5 hours are requisite prior to attempting any gravital separation. No high temperature is necessary or desirable—I find it better to work at the ordinary temperature.

Many of the saline solutions which I employ may have chemical activity upon the ore as hereinafter set forth, but they have the physical activity just described. Insofar as the physical activity alone is concerned the solutions suffer no substantial change and they may be repeatedly used on successive batches of ore being merely replenished sufficiently to make up for losses. Taking for example scheelite, or calcium tungstate in its usual gangues, I find that about 40 minutes agitation of the ore, ground to the usual mesh with a 6 per cent solution of common salt containing, say, 0.25 per cent carbonate of soda, suffices to produce such a change in the scheelite itself and in the accompanying clay-like minerals as to give a quick, clean and complete separation of the so-treated suspension on the tables in the case of ores which would otherwise not separate well. The same is true of wolframite and other tungsten minerals.

The higher in sulfids the ore is, as a rule the longer the agitation should be continued in order to be certain of effecting the physical changes in the particles which I desire. With such sulfid ores however the physical action may be, and often is, attended by favoring chemical changes in the valuable minerals themselves. With long agitation in an electrolyte, electrolytic actions set up between the more electro-positive and the more electro-negative materials present, which may, and often do, set free or clean particles of the noble metals, gold, silver, mercury, platinum, etc. In the case of ores rich in pyrites and containing gold, chemical action often goes so far that after the agitation not only are the auriferous particles gravitally separable, but they are susceptible of free amalgamation. The same is true of many silver ores. In many embodiments of my invention treating ores of the precious or noble metals I therefore contemplate amalgamating as a part of my gravital treatment.

As is well known, free milling gold ores are those in which on treatment with water and mercury the gold is wetted by the mercury and can be collected with the mercury. With such an ore, for example, on stamping it in the ordinary stamp mill together with mercury and passing the pulp over amalgamated tables, much or most of the gold is

collected by the mercury. There are many ores which are known as refractory, being ores which do not yield their contained gold to mercury. The state in which the gold exists in these ores is not definitely known and it probably varies with the ore; but in at least most cases the ore contains sulfids, tellurids, arsenids, and is of unoxidized nature. These ores not being amenable to the ordinary amalgamation processes and apparatus they must be treated by various methods of more or less complicated nature in order to regain the gold.

In another application, Serial No. 141.298, filed January 8, 1917, whereof the present case is a continuation, I have described a method of rendering such refractory ores amenable to amalgamation which in substance consists in agitating the ore, during or prior to amalgamation, with a solution containing sodium nitrate and potassium carbonate.

As to why agitation with materials such as these should facilitate amalgamation in the case of refractory ores, I am unable to say and can only give the result. It is perhaps due to electrolytic action with perhaps oxidation by the nitrate. Refractory ores always contain in addition to the gold which is strongly electro-negative the stated sulfids, etc., which are electro-positive and readily undergo oxidation. The solution of nitrate and carbonate conducts electricity freely and is adapted for forming couples between the particles of the metal and particles of the sulfids, etc. A solution of alkaline reaction, which is imparted by the potassium carbonate, is capable of wetting sulfids, etc., better than a neutral solution or one of acid reaction. However, the matters mentioned are theoretical. The actual result is that with the solution mentioned amalgamation becomes ready.

I have found that various other oxidizing salts than the sodium nitrate may be employed, as for instance potassium nitrate, sodium or potassium chlorate, hypochlorite solutions, chromates, etc.; but I have found that the sodium nitrate in addition to its cheapness seems to exercise a much better action than the other salts mentioned. Similarly I have found that sodium carbonate may be substituted for the potassium carbonate. But I find potassium carbonate to work the better.

It is possible and indeed probable from certain observations which I have made that the beneficial action of the electrolytic bath is not only exerted upon the gold of the mineral but that part of the benefit resides in keeping the mercury clean-surfaced. In operating with the described bath in the presence of mercury which I regard as the best way of operating, the mercury does not tend to flour and remains clean-surfaced. With most of these refractory ores the mercury dirties and flours.

The action of the described solution upon refractory gold ores is so far reaching that it may be used in assaying, a weighed amount of ore being agitated at the ordinary temperature with mercury and the solution for one to three hours, the mercury separated from the amalgam and the residue taken as representing the gold in the ore. No heating being required, agitation may be effected in any ordinary glass beaker. Heating disturbs the actions which I wish to secure.

In making the bath the best proportions I have found are about one part of commercial sodium nitrate or "caliche," one-sixth part of commercial carbonate of potassium of pearlash and thirty-two parts of water.

In using such a solution or bath, it may be employed in various ways in performing the present process. In one way of operating, the ore reduced to a fineness of 80 mesh or finer is agitated with the solution at the ordinary temperature for one to ten hours; the exact length of time depending upon the character of the ore. The ore so treated is readily amalgamated by mercury. Any type of stirring or agitating apparatus which is capable of producing thorough agitation with positive contact between all parts of the ore and the solution may be employed. The type of agitation I desire is really a sort of churning action. After the agitation the solution may be removed from the ore pulp and reused. Sometimes I find it necessary to treat it with a little quicklime or slaked lime to regenerate it more or less. It may be strengthened by addition of fresh chemicals. The ore pulp may be washed and the washings used in preparing fresh solutions. After the treatment the ore pulp may be amalgamated in any of the usual ways, as for instance by flowing over the ordinary amalgamate plates.

A better method of operation is afforded by having more or less mercury present during the agitation or churning. Ordinarily no flouring of the mercury is to be feared.

The mercury cleaning action of the composition described may be used in treating amalgam plates and the like or in preparing such plates. For example, a plate of pure soft copper rubbed with mercury in the presence of the stated bath, the operation being repeated at intervals, say 5 times with intervals of 10 hours, gives a collecting plate of better character than a silver plate.

The solution is not deteriorated by its contact with the ore constituents save insofar as sodium nitrate is reduced. This gives sodium carbonate. In such cases fresh sodium nitrate may be added from time to time.

The other chemicals mentioned may be used in the same manner as the described mixture of potassium carbonate and sodium nitrate.

I find that sodium nitrate or Chili saltpeter is an exceptionally good neutral electrolyte for the present purposes; and it also furnishes loosely-bound oxygen which much accelerates many of the electro-chemical actions heretofore mentioned. Chili saltpeter, as a result of reduction, itself develops more or less alkalinity so that with some ores using Chili saltpeter it is unnecessary to add an alkaline electrolyte.

So far as the physical results are concerned however, I find that common salt with a little sodium carbonate or potassium carbonate answers very well. Common sea salt usually contains enough alkaline material, or is susceptible of furnishing such alkaline material under the influence of ores, to serve well for the present purposes.

In a specific embodiment of the present invention treating a refractory gold ore containing pyrities, I may grind the ore to 80 or 100 mesh and stir violently from 3 to 4 hours with a solution of Chili saltpeter containing say 6 per cent of sodium nitrate. About 0.25 to 0.50 per cent of potassium carbonate is ordinarily a useful addition. Sometimes it is advantageous to use a little sodium carbonate as well although sodium carbonate is furnished by the sodium nitrate itself under the influence of reduction by the sulfids and the action of atmospheric carbon dioxid. The stirring should be effective, thoroughgoing and drastic agitation; not merely a shaking together. After the stirring is complete the mixture may be run through or over any ordinary amalgamating device in the usual way. The gold settles well and, because of the action of the sodium nitrate, and the electrolytic actions which go on between the particles of ore, it is made clean surfaced and readily amalgamable.

For many purposes a solution of about 1 part of commercial sodium nitrate or Chili saltpeter and one-sixth part of commercial potassium carbonate or pearlash dissolved in about 32 parts of water make a very good solution or bath, and especially for refractory gold ores containing sulfids. Sometimes it is desirable to add a little acid, or acid reacting salt, such as alum, to the mixture. One very good composition may be made by dissolving 100 parts of commercial Chili saltpeter, 37.5 parts of commercial sal soda, 2 parts of commercial potassium carbonate and one-eighth part of ordinary alum in water sufficient to give a 5 or 6 percent solution. This composition is particularly good in treating mercury ores containing mercury in a sulfid form. The electrolyte has an action tending toward the separation of metallic mercury from the sulfid. For some reason, and because of some reaction not understood, I have found that vigorous agitation of sulfid ores of mercury with a dilute solution of sodium nitrate, and especially in the presence of a little carbonate, causes a separation of globules of metallic mercury.

This application is a continuation and consolidation of my application Serial No. 287,577, filed April 4, 1919 and my application Serial No. 281,057, filed March 6, 1919.

What I claim is:

1. In the recovery of values from metallic ores by differential gravity separation, the process which includes preliminarily violently agitating such an ore in a finely powdered state at the ordinary temperature with a solution containing a neutral electrolyte and an alkaline electrolyte for a time sufficient to effect physical changes in the granules and thereafter gravitally separating.

2. In the recovery of values from metallic ores by differential gravity separation, the process which includes preliminarily violently agitating such an ore in a finely powdered state at the ordinary temperature with a solution containing sodium nitrate and an alkaline electrolyte for a time sufficient to effect physical changes in the granules and thereafter gravitally separating.

3. In the recovery of values from metallic ores by differential gravity separation, the process which includes preliminarily violently agitating such an ore in a finely powdered state at the ordinary temperature with a solution containing sodium nitrate and potassium carbonate for a time sufficient to effect physical changes in the granules and thereafter gravitally separating.

4. The process of amalgamating metals which comprises agitating mercury and such metal in contact at the ordinary temperature in the presence of a bath containing sodium nitrate and potassium carbonate.

5. The process of recovering metals from ores by amalgamation which comprises agitating an ore at the ordinary temperature with mercury in the presence of a bath containing sodium nitrate and potassium carbonate.

6. In the treatment of refractory gold ores the process which comprises agitating such a gold ore at the ordinary temperature with a dilute solution containing an oxidizing electrolyte and an alkaline reacting salt.

7. In the treatment of refractory gold ores the process which comprises agitating such an ore at the ordinary temperature with a dilute solution containing sodium nitrate and potassium carbonate.

In testimony whereof, I affix my signature hereto.

MAY KRUMP CODDING.