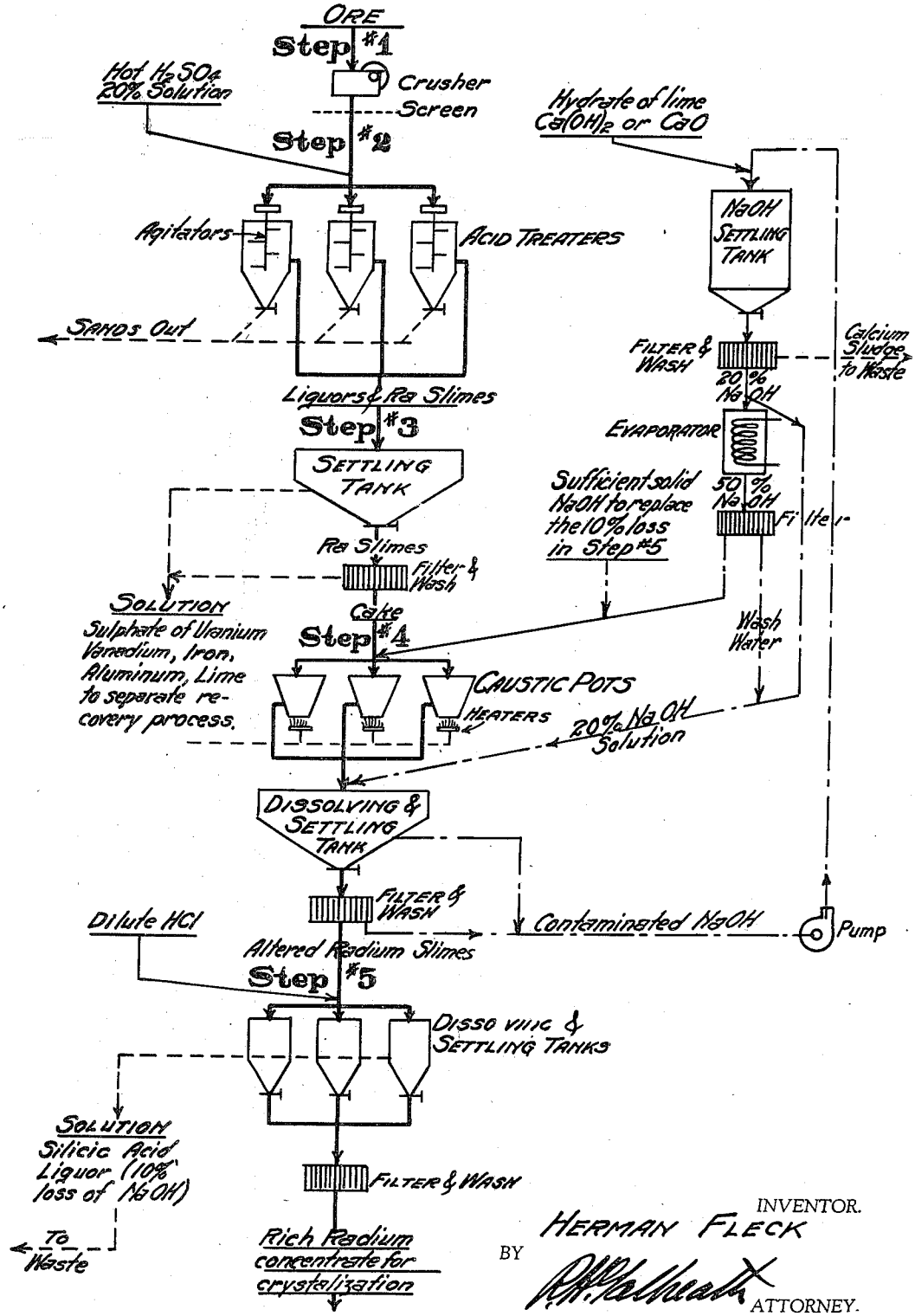
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METHOD OF CONCENTRATING RADIUM BEARING ORES

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INVENTOR.
HERMAN FLECK
BY
ATTORNEY.

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METHOD OF CONCENTRATING RADIUM BEARING ORES

Herman Fleck, Santa Monica, Calif.; Herman S. Fleck, administrator of said Herman Fleck, deceased

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1 Claim. (Cl. 23—22)

This invention relates to a process for concentrating radium bearing ores, more particularly to a method for freeing radium from the refractory, siliceous and aluminous gangue and impurities contained in low grade radium ores and concentrates.

Heretofore, the treatment of the low grade radium ores, which are relatively abundant in nature, has been an exceedingly costly and wasteful proceeding due to the sulphate radical, gypsum and other difficult impurities. Most prior methods have endeavored to avoid the detrimental constituents by a careful selection of the ore by cobbing or other means so as to retain for treatment only the ores or portions of the ores which have a minimum of the interfering constituents. This careful selection necessitates the discarding of the major portions of the radium bearing ores and the loss of large amounts of valuable radium carried therein.

Other processes endeavor to avoid the above selection losses by refining out the objectionable sulphate radical and the gypsum by long, tedious, costly and wasteful multi-step processes which are often highly destructive of apparatus and productive of noxious gases, and which are in most cases a menace to the health of the workers.

The principal object of this invention is to provide a simple and efficient process which will overcome the above objections to present processes and which will enable comparatively low grade ore or concentrates to be treated at a profit.

One of the difficulties encountered in the concentration of radium arises from the fact that the radium and radium bearing materials react similarly to the useless sand and gangue when subjected to acid treatment, that is, they all go down together with the tailings. Another object of this invention is to provide a method whereby the undesirable portions of the tailings or gangue will become acid soluble while the radium materials will remain insoluble so that the two can be quickly and easily separated by a simple acid bath.

Other objects and advantages reside in the improved process and in the means for carrying out the process. These will become more apparent from the following detailed description thereof in which reference is had to the accompanying drawing which illustrates a typical flow chart of the process.

While the process is particularly designed for the treatment of carnotite ore, it is of course not limited thereto as it will be found valuable for the recovery of radium, or the salts or compounds of radium, from pitchblende and other minerals carrying radium values and from radium slimes or other silicious, aluminous admixtures containing radium or radium compounds.

Carnotite is a mineral containing uranium, vanadium, radium and a well defined amount of barium. The mineral is usually found impregnating or encrusting sandstone and argillaceous shales, with lime as a binder between the sand grains. All combine to produce a very low grade original ore.

Briefly the method comprises (1) mechanically concentrating the ore to eliminate a major portion of the sandstone and shale; (2) dissolving off the vanadium, uranium and other metals with acid and settling out the sands while holding the insoluble radium bearing slimes in suspension; (3) filtering out the slimes; (4) digesting the slimes with heat in a water solution of caustic to change the worthless silicious portion of the slimes from an acid insoluble state to a water insoluble and acid soluble state while retaining the radium-barium salts acid insoluble; (5) thence dissolving out the worthless material from the slimes with acid to leave a rich radium-barium concentrate.

As an auxiliary to the main method a simple and efficient method (4*a*) is provided for removing the silica and recovering and purifying the used caustic for reuse in the alteration step of the main process.

The principal contribution of this invention is step (4) wherein the silicious matter in the slime which heretofore has been so difficult to handle is easily and rapidly changed to a state which allows it to be dissolved from the valuable radium bearing concentrate in a single, simple operation.

The process can best be understood by following through a typical batch of ore, reference being had to the flow diagram on the accompanying drawing.

Step #1

The ore is first prepared by a roughing treatment to obtain a rough concentrate richer in radium than the original ore. This may be done by crushing and grinding to a fineness not less than the size of the sand grain of the ore or more precisely to a state of comminution as exactly as possible to expose the radium bearing mineral particles, (usually 20 to 30 mesh).

Step #2

The above comminuted ore is now fed to acid

treaters, preferably conical bottomed discharge tanks provided with suitable agitators to which a hot aqueous solution of sulphuric acid (approx. 20% solution) is fed. In the acid treatment the uranium, vanadium, iron, and a portion of the aluminum and lime present go into sulphate solution.

The heavy barren sands gravitate to the bottom and are drawn off to waste, the lighter sand particles remain in suspension as a fine silicious slime.

The radium remains with the finer particles of the ore in the form of the insoluble sulphate. The latter particles are kept in suspension in the solution by the agitators and are drawn off with the sulphate solution to a suitable settling tank.

Step #3

The clear liquor from the settling tank is now drawn off for the recovery of the valuable constituents in the solution.

A method of treating the latter solution is outlined in applicant's copending application Serial No. 180,403 and forms no part of the present invention.

It is to the settled slimes that this invention is particularly directed. These slimes consist of a soft mud or slime of clay, shale, and gypsum in more or less colloidal state, containing radium, the amount depending upon the percentage of uranium in the ore and the nature and amount of slime forming ingredients. An ore containing one-half of one percent of uranium oxide (equivalent to one and three-tenths milligrams of radium metal per ton of ore) will yield a slime which may contain nearly all of the original radium varying from six to twelve milligrams per ton.

The slimes will be hereinafter referred to as "radium slimes." It is desired to be understood however that the following steps are applicable to the treatment of any radium bearing material and are not limited to the treatment of the specific acid radium slimes above described.

Step #4

The radium slimes are now placed in suitable caustic pots with an aqueous solution of caustic soda and heated sufficiently to cause active ebulition or digestion (below 200° C.). It has been found that other caustic hydroxides may be used in place of caustic soda. The latter, however, is the preferred caustic, and the preferred proportion is one part dry slime to two parts 80% aqueous caustic soda solution. A lower strength may be used if desired the only effect being upon the time element. The 80% caustic soda solution possesses the quality of low temperature liquidizing (below 200° C.). At this temperature the solution can be pumped or diluted and pumped or otherwise conveniently handled. These low temperatures are economical from the standpoint of fuel consumption, furnace upkeep and will permit the reuse of the caustic pots indefinitely. These advantages are lacking in higher concentrations whereas lower concentrations than 80% have volume and time elements to contend with. The manner of bringing the caustic solution and the slimes into contact with one another is immaterial. The solution may be poured on the slimes or the slimes added to the solution, etc.

Reaction begins immediately below 200° C. in the caustic pots and is completed in a few hours. The slimes will be disintegrated—a portion of the silica will go into solution as sodium silicate and a portion of the acidic alumina will be dissolved. Sodium as well as water leaves the solution and enters into composition with the now altered slimes. The valueless portion of the latter, while still insoluble in caustic and, or subsequently when leached, in water, has now become easily soluble in dilute acid. (It will be noted that they were insoluble in acid before this step.) Due to the sulphate radical present, however, the valuable radium-barium residue remain insoluble in acid.

These new properties of the radium slimes which were attained by a single, simple, economical step make it possible to now readily separate the worthless material from the valuable radium-barium residue.

The digested mass, while still hot, is now brought to a dilution of approximately twenty per cent of the original caustic (dry weight) and allowed to settle. The NaOH liquor with sodium silicate is decanted and refined for the removal of the latter as described in step 4*a*, below. The residue may be further washed or filter pressed to produce a highly concentrated, chemically altered slime cake.

Step #5

The concentrated slime cake is now admixed with dilute acid preferably, but not necessarily, hydrochloric acid. The solution is kept cold and the, now very small volume of, radium-barium sulphate residue, containing substantially all of the radium, will settle rapidly. The acidified supernatant liquor is quickly run off to waste before there is an appreciable formation of insoluble silicic acid.

The radium-barium sulphate residue (a concentration of from 75 to 100 times that of the original ore) is now ready for the crystallizing stage to produce salts of radium of high purity. The final crystallizing can be accomplished by the methods known to those skilled in the art and forms no part of the present invention.

Step 4a

The caustic liquor from step 4 containing sodium silicate, sodium aluminate and other impurities is now treated to recover the caustic for reuse in step 4. This is very economically and efficiently done by adding hydrate of lime in a suitable settling tank or cone. This lime reacts quantitatively to precipitate calcium silicate and calcium aluminate which are settled and or filtered off to waste. The remaining solution (approx. 20% NaOH) is evaporated back to a concentration of 70–80% for reuse in the caustic pots. A recovery of 90% of caustic can be made if all caustic wash waters and solutions are returned to step 4*a*.

While hydrate of lime is the most economical and convenient reagent for use in purifying the caustic solution of silica and aluminum, common burned lime or caustic lime may be used with equal results.

While the process has been described as using sodium hydroxide or soda lye as a caustic, it could be carried out equally well with potash lye at somewhat greater expense. The aqueous caustic solution liquefies at a much lower temperature than the pure undiluted caustic, and is much less destructive to equipment and personnel. It is also more easily manipulated as a fluid solution and more economical in cost.

If desired, the ground ore of step #1 may be

treated by any of the well known mechanical concentration methods to obtain a richer concentrate before the acid step #2. The preferred procedure, however, is to feed the natural ore direct to the acid treatment to immediately free and place the radium slimes in suspension so that they may be removed from the barren sand by elutriation in a single simple step.

Eighty per cent caustic solution is the most favorable caustic concentration in the caustic pots. However, the process is by no means limited to an 80% solution since even a 50% concentration will give perfect results over a longer time interval.

A higher concentration than an 80% solution is neither necessary nor desirable to accomplish the alteration to the acid soluble form. Extremely high concentrations would entirely destroy the composition of, and dissolve, the slimes which of course is not the purpose of the caustic step.

While the improved process has been described in some detail in order that those skilled in the art will be enabled to place it in practise after the expiration of any patent or patents which may be issued thereon, it is desired to be understood that the invention is not limited to the precise procedure described nor is it dependent upon the accuracy of any theories which may have been advanced herein. On the contrary, the invention is not to be regarded as limited in any way except in so far as such limitations are contained within the scope of the accompanying claims in which it is intended to claim the invention as broadly as possible in view of the prior art.

Having thus described the invention, what is claimed and desired secured by Letters Patent is:

A method of separating siliceous matter from radium-barium sulfate slimes, comprising: heating said slimes in a concentrated aqueous caustic soda solution consisting of not over 80% caustic soda to a temperature of not over 200° C. which will effect the solution of at least a portion of the silica in the siliceous material present, diluting said solution and separating the same from the residue, treating said residue while maintaining it cold with dilute acid to dissolve impurities in the residue while retaining the radium in said residues and separating said acid from the residue so rapidly that no siliceous precipitate separates.

HERMAN FLECK.