

UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING COMPLEX SULFID ORES.

No. 832,341.

Specification of Letters Patent.

Patented Oct. 2, 1906.

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To all whom it may concern:

Be it known that we, WILLIAM GEORGE RUMBOLD and GEORGE PATCHIN, subjects of the King of Great Britain, residing at London, England, have invented a certain new and useful Process for the Treatment of Complex Sulfid Ores After Oxidation and Naturally-Oxidized Ores Containing Zinc, of which the following is a specification.

10 This invention refers to an improved process for the extraction of zinc and other metals from complex oxidized ores containing zinc, resulting in the dissolving of the oxids, sulfates, and carbonates of zinc, nickel, cobalt, 15 manganese, copper, and cadmium from the complex ores containing these metals, an essential feature of the process being the treatment of the aforesaid oxidized ores, which have been crushed to a requisite degree of 20 fineness, with a solution consisting of ferric sulfate, sulfuric acid, and sodium chlorid in water in certain proportions and as hereinafter described and claimed. Heretofore various solvents have been employed for dissolving the metallic substances in such complex ores. Thus it has been proposed to 25 crush the ore to be treated, which ore may or may not be in an oxidized condition, and then to mix the powdered ore with ferric salts—generally acid ferric salts—and to 30 treat the mixture electrolytically to produce a solution of metals. It has further been proposed to subject copper sulfid and oxid to the action of a solvent containing ferric sulfate, produced electrolytically by the oxidation of ferrous sulfate, by which copper sulfate, ferrous sulfate, and free sulfur are obtained, and also to dissolve zinc sulfid in a 35 similar manner with an analogous production of zinc sulfate, ferrous sulfate, and free sulfur, the copper and zinc sulfates thus obtained being dissolved in the solution of ferrous sulfate produced by the reaction. It has also heretofore been proposed to leach 40 partially or completely oxidized zinc ores first with a solution of ferrous sulfate and afterward with a solution containing a mixture of ferric and ferrous sulfates and to remove the zinc from the solution obtained in this way by electrolysis and then to convert the ferrous sulfate into ferric sulfate, and, 45 further, to reduce a portion of this ferric sulfate thus produced to ferrous sulfate by

means of sulfurous anhydrid. It has further been proposed to leach roasted zinc ores with 55 a solution of zinc sulfate and ferric sulfate and from the solution thus obtained to recover zinc by electrolysis, producing ferrous sulfate, which by further electrolysis is converted into ferric sulfate. 60

Now according to the present invention it is essential that the ore must be in a completely-oxidized condition before treatment, and therefore where the ores are not naturally oxidized they are subjected to an oxidizing roasting until the sulfur is removed as far as possible. The ore is crushed (generally previous to roasting, where such is necessary) to the requisite degree of fineness to pass a screen having, say, forty meshes to the 65 inch. The crushed and oxidized product is then treated with a solution consisting of ferric sulfate, sulfuric acid, and sodium chlorid in water in the proportions hereinafter more particularly stated, whereby all the sulfuric-acid radicals in the solvent are used in dissolving zinc compounds or other metallic compounds from the ore without the production of ferrous compounds, and a neutral solution is obtained which is entirely free from 70 salts of iron, and this without the employment of electrolytic action. The results, therefore, attained by this invention are the production of a pure and white zinc oxid suitable for paint and other commercial and 75 metallurgical uses from complex sulfid and oxidized ores containing zinc and the recovery also as by-products of any copper, manganese, nickel, or cobalt there may be in such ores. Moreover, by the removal of the copper, manganese, nickel, cobalt, zinc, and other 80 refractory substances it is possible to recover any gold and silver there may be in the ores treated by this process, this recovery being effected from the ore residues by any of the 85 ordinary methods adopted for the recovery of these metals. 90 95

The approximate proportions composing the solution employed according to this invention, consisting, as aforesaid, of ferric sulfate, sulfuric acid, sodium chlorid, and water, consist of about one per cent. of ferric sulfate, ten parts, by volume, of commercial sulfuric acid, (or sufficient chamber acid to equal this strength,) and a small proportion of sodium 100 chlorid, the latter ingredient varying in quan- 105

tity according to the composition of the ore to be treated, but in no case being sufficient to dissolve the silver chlorid which may have been formed. These ingredients are dissolved in one hundred parts of water. These proportions are selected with a view to the employment of a relatively small proportion only of ferric sulfate, (which is the main object of the invention,) and this small proportion, when mixed, as stated, with a comparatively large proportion of sulfuric acid, as we do by our invention, is continuously decomposed and regenerated until all the free acid has become neutralized, so that a small portion of ferric sulfate is capable of reacting theoretically for an indefinite period, whereby the object of this invention is attained.

The solution, as before described, acts as a solvent upon the crushed oxidized ore, and by this solvent the oxids, sulfates, and carbonates of copper, manganese, nickel, cobalt, and zinc, with other substances, are dissolved and ferric sulfate decomposed. So long as free sulfuric acid remains in the solution the ferric sulfate thus decomposed is regenerated and again becomes available for solvent purposes; but when the solvent becomes saturated with dissolved matter from the ore and free from uncombined sulfuric acid the iron is precipitated from the solution chiefly in the form of ferric hydrate, and the solution is then ready to be filtered. The addition of sodium chlorid to the solvent has been found to have a beneficial effect in making the extraction of the metallic compounds from the ore more complete, especially when the compounds of copper are found in the ore. The sodium chlorid, in the presence of sulfuric acid, is converted into sodium sulfate (which is of no value in the process) and hydrochloric acid. The hydrochloric acid so formed acts upon such portions of the metallic compounds as are not readily dissolved by sulfuric acid and ferric-sulfate solution, resulting in the formation of metallic chlorids, which are decomposed by the free sulfuric acid to form soluble sulfates, thus regenerating the hydrochloric acid. It will thus be seen that the beneficial effect of hydrochloric acid is under these conditions obtained by the employment of a small proportion only of sodium chlorid, which is only a convenient and economical method of introducing the hydrochloric acid radical. The sodium chlorid also serves the further purpose of converting any silver sulfate which passes into solution into insoluble silver chlorid, which remains with the ore residues, from which it is subsequently recovered by any of the known methods. The solvent claimed, therefore, is not sulfuric acid, ferric sulfate, and sodium chlorid separately, but the combined and simultaneous action of the three.

The reactions which take place between the solvent and the metallic compounds in

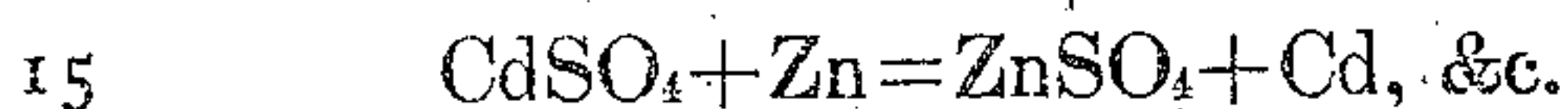
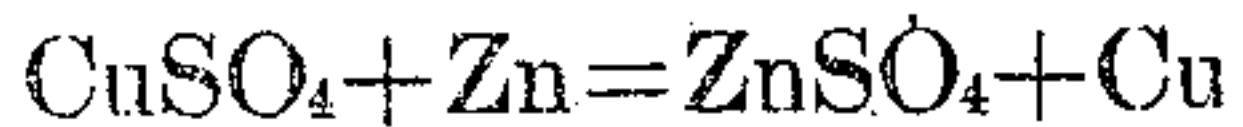
the ore are as follows, which also include some of the secondary reactions described above:

1. $3\text{ZnO} + \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} = 3\text{ZnSO}_4 + \text{Fe}_2(\text{OH})_6$ 70
2. $3\text{CuO} + \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} = 3\text{CuSO}_4 + \text{Fe}_2(\text{OH})_6$
3. $\text{Fe}_2(\text{OH})_6 + 3\text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$ 75
4. $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$
5. $\text{CuO} + 2\text{HCl} = \text{CuCl}_2 + \text{H}_2\text{O}$
6. $\text{CuCl}_2 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2\text{HCl}$
7. $3\text{ZnO} \cdot \text{ZnSO}_4 + 6\text{HCl} = \text{ZnSO}_4 + 3\text{ZnCl}_2 + 3\text{H}_2\text{O}$ 80

In carrying on the process the solution is passed over successive lots of ore until it becomes saturated with dissolved matter, the partially-saturated solution thus coming onto partly-spent ore, and having been so treated the saturated solution is then in the condition in which the extraction of the metal it contains is proceeded with, as will be hereinafter described. Before proceeding further in the description we would point out that some variation in the solution may be made in certain circumstances—that is, for instance, where sulfuric acid is not conveniently obtainable the oxidized or roasted ores may be treated with a solvent consisting of sulfurous acid, sodium chlorid, and water—and this solution is then passed over ore which contains ferric oxid, which it takes up, although it should be understood that with this alternative solution if the ore contains a little or no iron then ferric oxid should be added to the solution. The sulfurous acid contained in this what we have termed “alternative” solution may, as is well known, be obtained by absorbing in water the sulfur dioxide contained in the furnace-gases from the roasting of sulfid ores and which can be effected by allowing these gases to meet a stream of water flowing down an absorption-tower packed with coke or other suitable material, although this mode of obtaining sulfurous acid does not form part of this invention. To the solution thus obtained is added the requisite quantity of sodium chlorid, and it is then passed over the ore, as previously explained, until all free sulfurous acid has been removed to form metallic sulfites. The solution is then permitted to again absorb a further quantity of sulfur dioxide and again is passed over ore, and these operations are repeated until the solution is saturated with dissolved matter from the ore. This saturated solution is then oxidized by the action of the atmosphere, or steam or air, or both, are blown through it in order to oxidize the metallic sulfites to sulfates. Further, with our new solvent, whether prepared by the mixture of ferric sulfate, sulfuric acid, sodium

chlorid, and water, or whether it has been prepared with sulfurous acid and water, with an added quantity of sodium chlorid and the ferric oxid obtained from ore containing ferric oxid, or separately added, and then the resultant product oxidized, the subsequent treatment which we shall now describe is always the same.

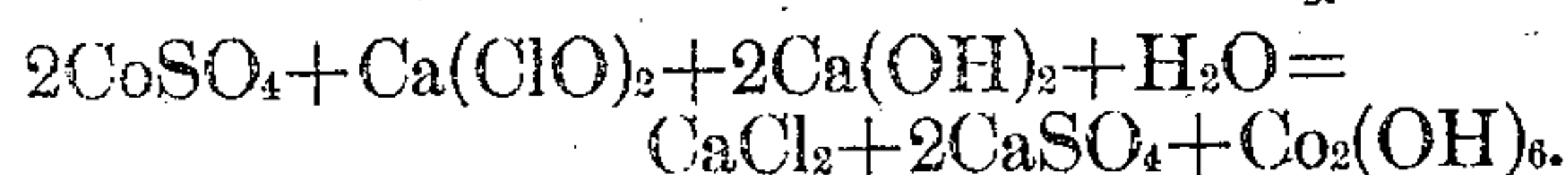
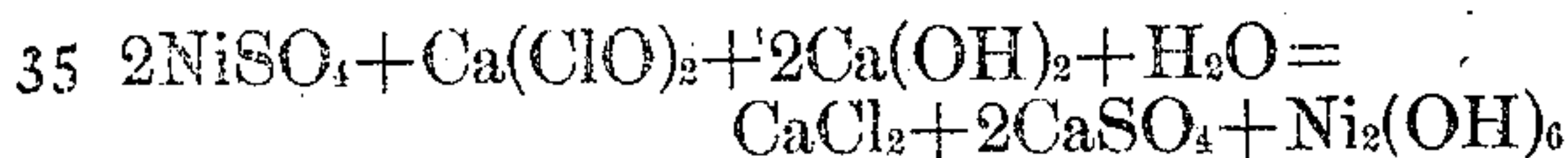
The saturated solution is first treated with zinc-dust or metallic zinc in some other form by which copper, arsenic, antimony, lead, bismuth, cadmium, and tin are precipitated.



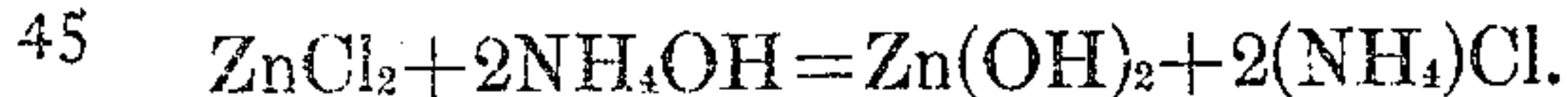
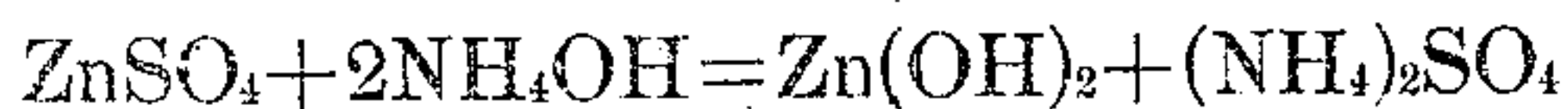
The solution is filtered from the above precipitated matters and treated with an oxidizing agent to oxidize and precipitate the manganese as hydrate. For this purpose we have found the alkaline permanganates, such as potassium and sodium permanganates, most suitable, and when these are employed the manganese in solution, together with that in the permanganate, is precipitated as manganese dioxid or in the form of a hydrate, as represented in the following equation:



The nickel and cobalt are precipitated as the hydrated oxids from the solution by the proper addition of bleaching-powder or some of the other recognized precipitants for these substances.

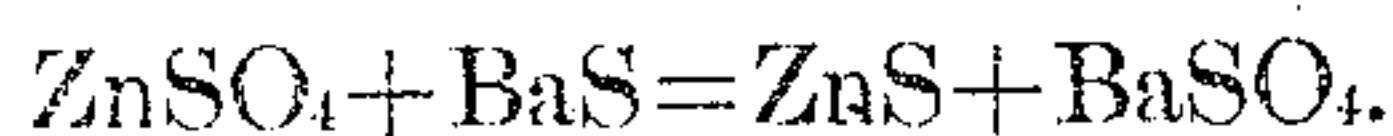
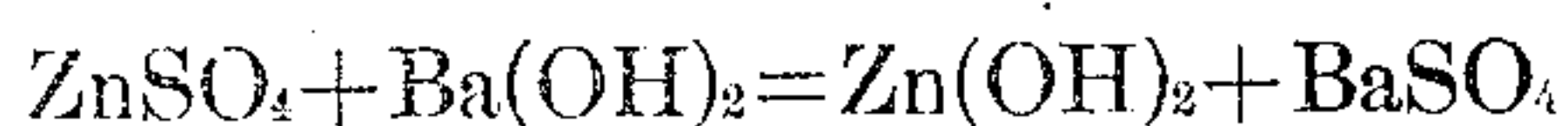


The solution is finally treated with just sufficient ammonium hydrate to decompose the zinc salts in solution and hydrate oxid of zinc is precipitated.



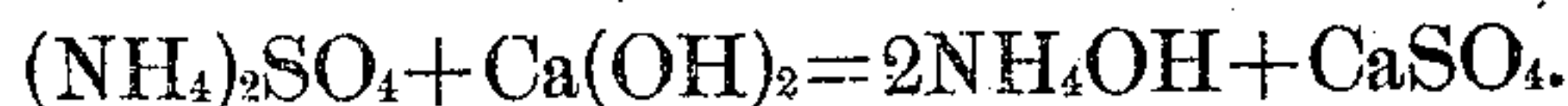
The hydrated oxid of zinc is separated by filtration, washed, dried, ground, and prepared for paint or other commercial and metallurgical uses.

Alternatively, the zinc may be precipitated from the solution of zinc salts obtained by this process by means of barium hydrate or barium sulfid to form a mixed product of either barium sulfate and hydrated oxid of zinc or barium sulfate and zinc sulfid.



When ammonia is used, this is recovered from the residual liquors after the precipitation of hydrated oxid of zinc by distilling

these liquors with lime or other oxids of alkaline earths.



The ferric sulfate which is used in the solvent is regenerated by passing sulfuric acid and sodium chlorid in the proportion of one part, by volume, of acid to ten parts, by volume, of water over the spent ores, and thus redissolving the precipitated ferric hydrate or other iron compounds precipitated therein, as before described, so that in the continuous use of this process only sufficient ferric sulfate to form the original solvent is required.



The ore residues from the above operation retain any gold and silver originally present in the ore and may be treated for the recovery of these metals by any of the existing methods.

What we claim as our invention, and desire to secure by Letters Patent, is—

1. The process for the extraction of zinc and other metals from complex oxidized ores containing zinc; consisting in passing over successive lots of crushed ore a solution consisting of ferric sulfate, sulfuric acid, sodium chlorid and water, until such solution becomes saturated with dissolved matter, such dissolved matter consisting of the zinc, and also the copper, cadmium, manganese, nickel, cobalt, antimony, lead, bismuth, and tin, or any or all of these metals when contained in said ores, a small proportion of ferric sulfate being employed in the solution in relation to a large amount of sulfuric acid whereby the ferric sulfate is continuously decomposed and regenerated until all the free acid has become neutralized substantially as set forth.

2. The process for the extraction of zinc and other metals from complex oxidized ores containing zinc; consisting in passing over successive lots of crushed ore a solution consisting of about one per cent. of ferric sulfate, ten parts by volume of commercial sulfuric acid, a small proportion of sodium chlorid—but not sufficient of the latter to dissolve any silver chlorid which may be formed—and one hundred parts of water, the ore being so treated until such solution becomes saturated with dissolved matter, such dissolved matter consisting of the zinc, and also the copper, cadmium, manganese, nickel, cobalt, antimony, lead, bismuth, and tin, or any or all of these metals when contained in said ores, substantially as set forth.

3. The process for the extraction of zinc and other metals from complex oxidized ores containing zinc; consisting in passing over successive lots of crushed ore a solution containing ferric sulfate, sulfuric acid, sodium chlorid and water, until such solution becomes saturated with dissolved matter, then

treating the saturated solution with metallic zinc to precipitate the copper, arsenic, antimony, lead, bismuth, cadmium, and tin, substantially as set forth.

5 4. The process for the extraction of zinc and other metals from complex oxidized ores containing zinc; consisting in passing over successive lots of crushed ore a solution containing ferric sulfate, sulfuric acid, sodium
10 chlorid and water, until such solution becomes saturated with dissolved matter, then treating the saturated solution with metallic zinc to precipitate the copper, arsenic, antimony, lead, bismuth, cadmium, and tin, then
15 filtering the solution from the above precipitated matters; and treating the filtered solution with an oxidizing agent, to oxidize and precipitate the manganese as hydrate, substantially as set forth.

20 5. The process for the extraction of zinc and other metals from complex oxidized ores containing zinc; consisting in passing over successive lots of crushed ore a solution containing ferric sulfate, sulfuric acid, sodium
25 chlorid and water, until such solution becomes saturated with dissolved matter, then treating the saturated solution with metallic zinc to precipitate the copper, arsenic, antimony, lead, bismuth, cadmium, and tin, then
30 filtering the solution from the above precipitated matters, and treating the filtered solution with an oxidizing agent, to oxidize and

precipitate the manganese as hydrate, then filtering out the manganese hydrate, and then adding bleaching-powder for precipitating from the solution the nickel and cobalt, substantially as set forth. 35

6. The process for the extraction of zinc and other metals from complex oxidized ores containing zinc; consisting in passing over
40 successive lots of crushed ore a solution containing ferric sulfate, sulfuric acid, sodium chlorid and water, until such solution becomes saturated with dissolved matter, then treating the saturated solution with metallic
45 zinc to precipitate the copper, arsenic, antimony, lead, bismuth, cadmium, and tin, then filtering the solution from the above precipitated matters, and treating the filtered solution with an oxidizing agent, to oxidize and
50 precipitate the manganese as hydrate, then filtering out the manganese hydrate, then adding bleaching-powder for precipitating from the solution the nickel and cobalt, then
55 filtering out the nickel and cobalt precipitates, then finally treating the solution with ammonium hydrate, to decompose the zinc salts in solution, and precipitate the zinc as hydrated oxid substantially as set forth.

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Witnesses:

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WILLIAM A. MARSHALL.