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SULPHATING PROCESS FOR ORES AND CONCENTRATES.

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To all whom it may concern:

Be it known that we, JOHN BURNS READ and MELVILLE F. COOLBAUGH, citizens of the United States, residing at St. Louis, Missouri, and Golden, Jefferson County, Colorado, respectively, have invented certain new and useful Improvements in Sulphating Processes for Ores and Concentrates; and we do declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawings, which form a part of this specification.

This invention relates to a one-step process for treating ores and concentrates to convert them into sulphates, and while it applies particularly to sulphides, and more especially to complex sulphides of lead and zinc, it also applies to oxidized minerals and to mixtures of sulphides and oxidized minerals.

Throughout the present case; the term "ores" is intended to cover not only raw ores but also concentrates, matte, tailings and by-products containing metal or metal compounds in commercial quantities.

The object of this invention is to recover metals from ores. This is accomplished by forming sulphates and separating the soluble sulphates from the insoluble sulphates and other insoluble material by leaching methods.

Heretofore, in attempting to obtain sulphates from sulphides, the efforts have been largely unsuccessful for two reasons; first, because the temperatures could not be properly controlled, since the temperature attained by the combustion of the sulphides, and required for a rapid and complete decomposition of the sulphides, was above the temperature best adapted for the formation of many of the sulphates; and second, because the sulphurous gases and metallic oxide formed by the roast, and the excess of oxygen introduced with the air during roasting were not brought in contact with each other at the proper temperatures to form the desired sulphates, since the gas and ore were traveling in opposite directions.

The present one-step process has four important features: First, the temperature is

controlled by causing the ore or concentrate, and the gaseous products of the roast, to 55 together with the air required for roasting travel in the same direction, that is, "concurrently". By this means the larger portion of the desulphidizing action takes place nearer the feed end of the furnace, and the 60 larger portion of the sulphating action nearer the discharge end of the furnace. The reactions of desulphidizing and sulphating, however, are overlapping. The high temperatures developed by the combustion of the 65 sulphides and required for a rapid and efficient decomposition of the same are maintained in the desulphidizing zone. In this zone only those sulphates will form which have decomposition temperatures higher 70 than the temperature of this zone. The temperature is reduced in the sulphating zone by allowing radiation through the walls of the furnace, or by introducing cold 75 gases directly into the gases of the furnace which are too hot, or by cooling the walls or rabbles of the furnace with cold gases or liquids. In this zone those sulphates continue to form which have decomposition 80 temperatures higher than the temperature of this part of the furnace, and also some unchanged sulphides may be decomposed since the temperature may be sufficiently high for that purpose. Second, much sulphurous gas (SO_2) is converted to sulphuric 85 gas (SO_3) under the catalytic influence of oxids, chiefly ferric oxid— Fe_2O_3 . This action takes place most effectively at temperatures between 550° to 750° C. Third, these 90 gases and metallic oxids formed by the roast and the oxygen from the excess of air introduced for the roasting are caused by the "concurrent" movement of materials to come into contact with each other at the most efficient temperature for the formation 95 of the desired sulphates. Fourth, a basic ferric sulphate of the type $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$ is formed from the excess sulphur and iron, which, while insoluble in water, has a positive solvent action in the presence of water 100 on sulphides which have escaped desulphidization and on oxids which have escaped sulphating.

The formation of this basic sulphate takes place between 425° and 650° C., and is 105 especially effective between 475° and 550° C.

For the most successful operation of this process, it is necessary to understand the thermal effects which influence the temperatures in each zone of the furnace. In the desulphidizing zone, oxygen unites with the sulphur of the sulphide minerals and forms gases which are principally SO_2 , and metallic oxids, and liberates a large amount of heat. Oxygen unites also with sulphurous gas (SO_2), forming sulphuric gas (SO_3) under the influence of contact with already oxidized material, notably ferric oxid (Fe_2O_3). This reaction also liberates heat. The temperature of the mineral particles is considerably higher than the temperature of the gases in this zone, due to the fact that the chemical reaction which liberates the heat takes place in the particles themselves, and also that there is a decided resistance to heat flow from a solid to a gas. In the sulphating zone some heat is evolved by the union of the sulphurous gas and oxygen, and by the union of the sulphuric gas with the metallic oxids. Also in this zone the temperature of the particles is slightly higher than the temperature of the gases. Here, however, the total heat liberated is much less than in the desulphidizing zone not only because the heats of formation of the compounds from their respective constituents are less, but also because not all of the oxids (especially iron) formed in the desulphidizing zone are completely converted to sulphates in the sulphating zone.

So long as the materials are properly moved and the temperatures controlled, it is immaterial what the direction of movement is, or what kind of furnace is used. For instance, the furnace may be horizontal, or one slightly inclined from the horizontal either up or down, or a vertical furnace in which ore and gases move down, or a vertical furnace in which the ore, if very fine, is blown up with the gases. In the accompanying drawing, a horizontal furnace of the rotary type, having a slight downward inclination is shown by way of example.

In applying this invention to a complex lead and zinc sulphide, the ore or concentrate, or both, together with air (and fuel if there is not enough sulphide sulphur to give the heat required, and gases containing sulphur if not enough of these would be formed to sulphate the metals desired) are introduced into the head of the furnace. The fuel gases can be separated from the mineral charge by the use of a muffle furnace if desirable, although this is not generally necessary. Here most of the desulphidizing is accomplished, and a temperature between 600°C . and 1000°C . is generally maintained. The best temperature will depend somewhat upon the particular ore or concentrate treated. In this zone the lead, zinc, iron and copper sulphides are changed prin-

cipally to oxids. Some zinc ferrite may form. Any gold present is changed to or remains as metal, depending upon its original condition, and any silver present is changed to metal or remains as chloride, depending upon its original condition. The sulphur of the sulphides is liberated principally as SO_2 . But, as stated above, SO_2 is changed by the catalytic influence of ferric oxid and to a lesser extent by other oxids, into SO_3 . This gas in turn will act as an oxidizing agent upon undecomposed sulphides with the formation of oxids and SO_2 again. Since sulphides of iron are readily oxidized by the oxygen of the air forming ferric oxid and sulphurous gas, the ferric oxid becomes quickly available as a catalyzer for the formation of sulphuric gas (SO_3). Basic lead sulphate and silver sulphate may form here if the temperatures are not too high.

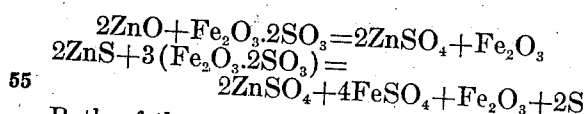
The converted minerals and gases are gradually moved along together into a cooler intermediate zone, the rate of travel depending upon the time required to decompose the sulphides. In this intermediate zone, sulphides are still decomposing and more sulphates and SO_3 forming.

After further travel, the converted minerals come to a third zone, wherein the temperature is maintained within limits for the formation of the sulphates desired. Here final traces of sulphides may be decomposed and more SO_3 formed. For an efficient separation of lead and zinc, a temperature of not less than 380°C . nor more than 850°C . is maintained. In the final discharge from the furnace, the lead will be found as sulphate or basic sulphate; the zinc (including that which in the first zone was converted into zinc ferrite), copper, metallic silver, and silver-chlorids, will be found as sulphates. If the temperature conditions have been properly maintained, the iron will be found as oxid and also as basic ferric sulphate of the type $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$, as described below. The metallic gold will be unaffected. But, if the temperature is allowed to drop too low, much normal ferric sulphate will form and interfere with the later recovery of metallic zinc. If the temperature runs too high, zinc sulphate will not form and the zinc and lead compounds can not then be separated. Under no circumstance will any silicic acid form at this place, or in the solution in the subsequent treatment of roasted material with water.

The hot gases in this zone may contain any amount of sulphur gases that will effect sulphating. For instance, the process may be carried on with great efficiency using roaster or other gases containing less than three percent by volume of such sulphur gases, which small amount is that found in many metallurgical gases. When ferric oxid is present in amounts of 2% or greater,

when the gases are not passed in excess of the usual roasting rate, and when temperatures are controlled as above stated, almost one hundred percent of the sulphurous and sulphuric gases will be absorbed when they are present in the gas being handled in an amount as low as one percent. When the gases leaving the furnace are high in sulphurous and sulphuric content, portions of these may be returned to the head of the furnace or to the sulphating zone as desired. As indicated above, and as disclosed in the drawings, all the products of combustion, including those from fuel when used, may be carried along through the various zones. These products of combustion from fuels used do not materially affect the process of sulphation, but, as above indicated, a muffle furnace may be employed if advantageous. The products from the third zone are treated with water to dissolve the sulphates of zinc, copper and silver. The solution is filtered from the insoluble residue and the above metals separated from the solution by any suitable method, for instance, electrolysis. The insoluble residue containing the normal or basic lead sulphate or both, the ferric oxid or basic ferric sulphate or both, the metallic gold and any gangue material, can be smelted to recover the values. Any arsenic or antimony impurities in the original ore or concentrate would be either driven off as gas, or left with the residue.

We have made the valuable discovery that, during the process of sulphating, if the temperature is controlled within proper limits—380° C. to 600° C. (or even up to 650° C.)—basic ferric sulphate, above mentioned, is formed from the excess of sulphur and iron which are usually present in complex ores. This basic ferric sulphate is not soluble in water, but in the presence of water it has a very decided solvent action upon sulphides which may have escaped desulphidization and upon oxids which may have escaped sulphating. This action causes a change of all convertible oxids and sulphides to sulphates. It is best expressed by the following chemical equations, which probably represent the reactions as related to zinc:



Both of these equations show the formation of soluble zinc sulphate which is a desirable product in the separation of lead from zinc in that it insures increased extraction. The basic ferric sulphate here formed is of the type in which the metallic element predominates.

In other words, the basic ferric sulphate, altho insoluble in water, enters into the re-

action and is responsible for practically 100% conversion of all convertible oxids and sulphides to sulphates, whereby it is possible to obtain nearly complete separation of metals whose sulphates are soluble from those whose sulphates are insoluble.

From the foregoing it is seen that the presence of ferric oxid increases the rate and extent of sulphating in two ways: First, by causing the sulphurous gas to become sulphuric gas which is more effective in sulphating and at the same time may act as an oxidizing agent in desulphidizing. Such sulphuric gas is forming in all zones of the furnace though the temperature for the most efficient production of this gas lies between 600° C. and 750° C. Second, by forming basic ferric sulphate from the excess of sulphurous and sulphuric gases, this basic compound in the presence of water still further increasing sulphating.

In treating different sulphides from those given in the above illustration, slightly different temperatures may be needed to effect the differential sulphating desired.

Naturally occurring oxids, carbonates and like compounds may be mixed with sulphides or sulphur and treated in a similar manner. Also, ferric oxid may be added to oxidized minerals, and sulphurous or sulphuric gases or both added from an independent source. Sulphurous gas may first be passed through or over ferric oxid at a temperature to form sulphuric gas and this passed over the oxidized mineral. In all cases the "concurrent" movement during sulphating is as essential as where desulphidizing precedes sulphating, because of the importance of keeping the mineral particles in contact with the gases for an appreciable length of time, so that chemical reaction can be effected.

We claim:

1. A process of sulphating the non-ferrous metal content of sulphide ores, which comprises treating the ores continuously, by continuously advancing the ores, roasting the ores while carrying the temperature of the ores at least as high as the decomposition temperature of copper sulphate to convert the sulphides of the ores principally into oxids, moving the liberated gases in contact with the ores, in the same direction as the ores being treated throughout the process, and subjecting the oxidized material during movement and in the presence of the gases produced in the roasting to a temperature sufficient to form sulphates from the non-ferrous metal content of the ore.

2. A process of sulphating sulphide ores which comprises treating the ore in one step, advancing the ore, roasting the ore in the presence of oxygen at temperatures high enough for the formation of oxid of copper, advancing the liberated gases and the ores

under treatment in the same direction while in contact with each other, then treating the roasted materials, during agitation and in the presence of said gases at a substantially lower temperature than that used in the roasting operation, to convert the oxides of non-ferrous metals formed in the roasting operation, into sulphates.

3. A process of sulphating ores which comprises roasting sulphide ores containing iron and at least one of the metals copper, lead and zinc, at a temperature of about 600° C. to 1000 C°, lowering the temperature of the roasted ore to a temperature at which CuSO_4 is stable, and subjecting the roasted product to the action of oxides of sulphur, and passing the ore and the oxides of sulphur in the same direction through the furnace throughout the entire process.

4. A process of sulphating ores containing iron and sulphatizable metal which comprises feeding such ores to and through a furnace, feeding air to and through such furnace, in the same direction therethrough as the ore, maintaining in the desulphidizing zone a temperature substantially above the temperature of decomposition of at least some of the sulphates of the sulphatizable metals in the ore, whereby the ore is roasted and the metals converted largely into oxides, then lowering the temperature of the roasted material and subjecting the cooled material to the action of gases containing oxides of sulphur, the gases and solids moving in the same direction throughout.

5. A process which comprises first submitting ores containing sulphides in the presence of air, to a relatively high temperature favorable to rapid and efficient desulphidization, carrying the sulphur oxides and the roasted ores together in the same direction into a cooler zone maintained at a temperature favorable to efficient sulphatization of the sulphatizable minerals the movement being concurrent throughout the entire process.

6. A process which consists in submitting ores containing sulphides, including iron sulphide, to a temperature favorable to rapid and efficient roasting and to the conversion of the liberated SO_2 to SO_3 , carrying the liberated sulphur oxides together with the roasted ore in the same direction while in the desulphidizing zone and thence into and through a cooler zone in which the temperature is maintained favorable to the efficient sulphatization of the sulphatizable minerals.

7. The herein described process which comprises subjecting an ore containing sulphides and containing commercial quantities of both zinc and lead, to a desulphidizing roast at a temperature at least as high as the decomposition temperature of zinc sulphate, conveying the roasting ore and the gases liberated in the roasting operation to a

cooler zone in which a temperature is maintained below the decomposing temperature of zinc sulphate and subsequently leaching the product, whereby substantially all of the zinc is dissolved and substantially all of the lead is left undissolved.

8. A process of sulphating the non-ferrous metals present in ores containing iron sulphide and zinc or copper compounds, which comprises dead-roasting the iron and copper or zinc content of the ore, cooling the roasted product somewhat, maintaining the roasted ore at a temperature favorable for the formation of SO_3 from SO_2 and O, maintaining the roasted product at a temperature favorable for the formation of anhydrous basic ferric sulphate and maintaining the roasted product at a temperature favorable for the sulphating of the non-ferrous metals, all while passing the ore and the gases in contact with each other in the same direction throughout the entire process.

9. A process of sulphating the non-ferrous metals present in ores containing iron sulphide and zinc or copper compounds, which comprises dead-roasting the iron and copper or zinc content of the ore, cooling the roasted product somewhat, maintaining the roasted ore at a temperature favorable for the formation of SO_3 from SO_2 and O, maintaining the roasted product at a temperature favorable for the formation of anhydrous basic ferric sulphate and maintaining the roasted product at a temperature favorable for the sulphating of the non-ferrous metals, all while passing the ore and the gases in contact with each other in the same direction throughout the entire process, and subsequently treating the resulting product with water whereby the basic ferric sulphate aids in dissolving any unsulphated copper or zinc.

10. A process which comprises first submitting ores containing sulphur mineral in the presence of air to a relatively high temperature favorable to rapid and efficient liberation of sulphur oxides, carrying the sulphur oxides and the ores along together in the same direction while in the desulphidizing zone, and passing said sulphur oxides and ores into a cooler zone maintained at a temperature favorable to efficient sulphatization of the sulphatizable minerals by said liberated sulphur oxides.

11. A process which comprises submitting ores containing sulphur mineral in the presence of air to a temperature which is at least as high as the decomposition temperature of the sulphates of certain of the non-ferrous sulphatizable metals to produce rapid and efficient liberation of sulphur oxides, carrying the sulphur oxides and the treated ores along together in the same direction while in the desulphidizing zone and passing the same thence into a cooler zone

and maintaining said cooler zone at a temperature below said decomposition temperature for the formation of said sulphates of said certain metals.

12. A process which comprises submitting ores containing sulphur mineral in the presence of air to a temperature to roast considerably the greater portion of the sulphides of the ores to oxides and produce rapid and efficient liberation of sulphur trioxide, advancing said sulphur oxides including the sulphur trioxide and the roasted ores together into a cooler zone, and maintaining said cooler zone at a temperature favorable to the formation of sulphates of the metals of said ores.

13. A process which comprises submitting ores containing zinc sulphide and iron to a relatively high temperature to produce zinc ferrite and liberate sulphur oxides with the simultaneous formation of sulphur trioxide, continuously moving the minerals and the liberated sulphur oxides including the sulphur trioxide along together into a cooler zone, and maintaining said cooler zone at a temperature favorable to the formation of zinc sulphate from said zinc ferrite and said sulphur oxides.

14. A process which comprises first submitting ores containing sulphur mineral and silver in at least one of the forms of metallic silver, silver chloride and silver sulphide, to a relatively high temperature favorable to rapid and efficient liberation of sulphur oxides and whereby any silver sulphide present is roasted and metallic silver formed, carrying the sulphur oxides and the ores along together and maintaining a temperature favorable to the formation of silver sulphate direct from said metallic silver and silver chloride.

15. The process which comprises submitting ores containing zinc sulphides and iron to a relatively high temperature in the presence of air, to produce zinc oxide and iron oxide and sulphur oxides, allowing the temperature to rise sufficiently to produce substantial amounts of zinc ferrite from said zinc oxide and iron oxide, continuously moving the solid material and the gases along together into a cooler zone and maintaining such cooler zone at a temperature favorable to the formation of zinc sulphate from the zinc ferrite and sulphur oxides.

16. A process of sulphating ores containing sulphides of iron and of non-ferrous sulphatizable metal capable of forming ferrite, such process comprising roasting said ores while allowing the temperature in the roasting operation to rise high enough to decompose large amounts of the sulphate of said non-ferrous metal if formed, allowing the formation of ferrite during such operation, progressively moving the ore to

lower temperature zones of the furnace, causing the gases in the furnace to travel through the furnace in the same direction as the ore material, and maintaining in some zone of the furnace a temperature low enough for reaction of the ferrite with the oxides of sulphur.

17. The process of sulphating zinc sulphide or blende which consists in roasting the material at a temperature of about 900° C., and then subjecting the material to the action of the roast gases at a temperature decreasing from 800° C. to 400° C. and in the presence of iron oxide, while moving said gases in parallel current with the material, all the while passing ore and gases in contact with each other and concurrently throughout the entire process substantially as described.

18. A continuous process of sulphatizing sulphide ore and minerals which comprises roasting the ore in the presence of oxygen at a temperature at least as high as the decomposition temperature of copper sulphate, whereby the minerals are desulphidized efficiently with the formation of oxides, ferrites, sulphates and sulphurous oxide, and with the simultaneous formation of catalyzers for the efficient conversion of sulphurous oxide to sulphuric oxide, all while advancing the ores and gases in the same direction.

19. A one-step continuous process of sulphatizing sulphide ores and minerals which comprises roasting the ore in the presence of oxygen at a temperature at least as high as the decomposition temperature of copper sulphate, whereby the minerals are desulphidized efficiently with the formation of oxides, ferrites, sulphates and sulphurous oxide, and with the simultaneous formation of catalyzers for the efficient conversion of sulphurous oxide to sulphuric oxide, then advancing and gradually cooling the sulphur oxides and roasted ore together and maintaining a temperature favorable to the further formation of sulphates and basic sulphates, all while agitating and advancing the ores and gases in the same direction throughout the entire process, and subsequently leaching the product to separate the soluble sulphates from the insoluble minerals.

20. A process for sulphatizing sulphur bearing minerals containing iron, comprising roasting the minerals at a high temperature in the presence of oxygen while agitating the minerals for the rapid and efficient desulphidization of the minerals with the simultaneous formation of metallic oxides and efficient formation of sulphur trioxide for relatively high concentration of said sulphur trioxide, all while advancing the minerals and liberated gases concurrently, whereby sulphates will form readily at said high temperature.

21. A process for sulphatizing sulphur bearing minerals containing iron, comprising roasting the minerals at a high temperature in the presence of oxygen while
 5 agitating the minerals for the rapid and efficient desulphidization of the minerals with the simultaneous formation of metallic oxides and efficient formation of sulphur trioxide for relatively high concentration of
 10 said sulphur trioxide, all while advancing the minerals and liberated gases concurrently, whereby sulphates will form readily at said high temperature, and carrying the
 15 treated minerals and the gases into a cooler zone maintained at a temperature favorable to the efficient further formation of sulphates of the sulphatizable metals.

22. A method of treating sulphide ores, the step comprising roasting the sulphides
 20 at a temperature in excess of 600° C., causing the said ores together with the air required for roasting and the gaseous products of the roast to travel in the same direction through the furnace.

23. In a method of treating sulphide ores, the step comprising causing the said sulphides together with the air required for
 25 roasting and the gaseous products of the

roast to travel in the same direction through the furnace and at such a temperature as
 30 will cause substantial desulphidization of the ore.

24. The method of roasting sulphides to produce sulphate which comprises causing
 35 the said sulphides together with the air required for roasting and the gaseous products of the roast to travel in the same direction through the furnace, effecting the
 40 desulphidizing action largely near the feed end of the furnace and the sulphating action largely near the discharge end of the furnace.

25. The method of desulphidizing ore containing at least one of the metals, copper and zinc, which comprises roasting the
 45 same at a temperature above the decomposition point of the sulphates of at least one of the said metals, causing the said ores together with the air required for roasting
 50 and the gaseous products of the roast to travel in the same direction through the furnace.

In testimony whereof we affix our signatures.

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