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PROCESS FOR OBTAINING METALS FROM ORES

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The present invention has for its object to provide an improved process for obtaining metals in a substantially pure state from ores which are not in general suitable for direct metallurgical treatment or which have hitherto had to be subjected to expensive and complicated processes in order to disengage the pure metals. Another object is to provide a new and improved method for the treatment of bituminous ores enabling the pure metals to be obtained directly therefrom with very little trouble or expense, while in part utilizing on the spot the valuable decomposition products of the bitumen. Yet another object is to provide a new method of decomposing sulphide ores by means of a comparatively simple heat treatment yielding a roasted product in which the metals are present in substantially a pure state, so that they can be separated out by simple methods of concentration or leaching.

Ores which cannot be metallurgically treated directly, are frequently subjected to concentrating processes in order to obtain concentrates which can be metallurgically treated economically.

Concentrating methods which may be employed are inter alia concentration by gravitation, concentration by flotation and magnetic concentration.

In the case of certain bituminous ores, however, concentration by these methods is not possible per se, as, inter alia the bitumen contained in the ores is obstructive. Such ores have heretofore in most cases been subjected to a process of smelting without previous concentration. Such a mode of procedure is however very expensive, as large quantities of fuel are consumed and economy is rendered questionable even in the case of high grade ores.

Attempts have not been wanting to overcome this difficulty. For example, it has been proposed to expel the bitumen from ores of this kind by heat treatment and to make it useful for the purpose of assisting the subsequent concentration of the material to be treated. According to a former proposal, this heat treatment was effected in the presence of a supply of air, a portion of the bitumen to be expelled being burned. Apart from the fact that the valuable bitumen is partially destroyed in this mode of procedure, and partially damaged, the bitumen-free ore product was also unfavourably acted on by the heat treatment in the presence of oxygen and, in particular, the uniformity of the product, which is important for the subsequent concentration thereof, was deleteriously affected.

In contradistinction to this, the subject matter of the present invention consists in a process for obtaining metals from bituminous ores of the kind above referred to, in which the treatment is performed with the complete exclusion of air. By such a heat treatment with exclusion of air the constituents which disturb the concentration are brought into a form in which they no longer cause interference. It has been found that the distillation products thus obtained are suitable for commercial exploitation in the usual way in the form of gases, or tar and oils, respectively.

The heat treatment may therefore be carried out in such a way that while maintaining the usual distillation temperature (which is around 500° C.) only the bitumen is removed, while the constituents of the ore, which are mostly present as sulphides, remain entirely unchanged or lose but little sulphur. The heated material may then, in many cases, be further treated according to known methods of concentration. In cases where the finest distribution of the ore in such a concentration is obstructive, the concentration is effected according to the method disclosed in the present applicant's United States patent application Ser. No. 249,774, according to which the material is reduced to colloidal fineness and suspended in a dispersing agent, preferably in the present of a peptizer, and then the various components or constituents of a colloidal suspension are individually and selectively precipitated, by modifying the electric charge so that as the isoelectric point for each constituent is reached, it and it alone is precipitated, whereby the succcessive precipitates represent the content of the treated ore in a particular constituent.

By the selection of suitable sizes of grain for the mass of ore to be treated and by suitable choice of the duration of heating and the temperature to which the material is heated, it is also possible so to decompose the metallic compounds contained in the particular ore, e. g. metallic sulphides, that the metals are completely, or for the most part, released therefrom. In this method, according to the invention, the temperature of the preferably fine-grained material should be raised, before distillation is complete, to more than 600° C.

In this way it is possible to obtain the various metals or metallic compounds separately. The concentration products obtained may be of such a pure nature that the process of smelting otherwise usual is rendered entirely or wholly, or in the main, superfluous and only a running down of the fine material of the various metals contained in the ore into the ordinary bars of commerce, or a simple refining of the smelted products, is required.

Example.—Mansfeld copper shale is reduced to grains of about 3 to 4 mm. in size and is subjected in a horizontal rotary distilling furnace to slow distillation at a temperature of from 600 to 700° C.

The gases evolved are carried off through pipes which are connected to the distilling furnace. The liquid hydrocarbons are collected in a receiver. After distillation has proceeded for several hours, the time depending on the amount of the charge, the material obtained is, after it has cooled down, removed from the distilling furnace. The copper, which is contained in the copper shale as sulphide, is converted by the distilling process into pure copper which is visible in the distilled material in the form of fine threads. The other metals contained in the copper shale, particularly silver and iron, are likewise converted from the sulphur compounds into the pure state. The lead ore originally present as lead glance is converted into the oxide, while the zinc ore contained in the copper shale remains unchanged as sulphide in the material obtained. This distilled material is ground to the fineness of dust and the metals or metallic oxides or sulphides are separately obtained therefrom in a pure state on rapid percussion-tables, so that they can be run down separately at slight cost into marketable products.

This concentration on rapid percussion-tables is possible because the previously ultramicroscopically fine particles of ore have been agglomerated into coarser threads, balls, leaflets or the like.

The applicant has also ascertained by experiments that the extraction of pure metals can be accelerated and augmented by the addition of certain catalysts. Gypsum has been found to be a suitable catalyst which, for example, may conveniently be applied by reducing it to a fine state of subdivision and adding it to the charge of ore in quantities of from say 1 to 2 per cent. Experiments have also shown that this catalyst works satisfactorily with pulverulent and even coarser charging material than was convenient according to previous experience with the process hereinbefore described and that it effects a total conversion of the metallic compounds into pure metals.

For the further treatment of the metal or metallic oxides obtained either with or without the addition of such a catalyst, electrolysis has been found to be convenient. The metals obtained are, as a matter of fact, in most cases so pure that the electrolysis takes only a very small amount of energy.

Furthermore it is possible to subject the concentrate obtained on the hearth to electrolysis directly without previously running it down into anode plates. For this purpose the electrolytic baths are divided up in the well known manner, by thin porous clay or porcelain plates, in such a way that boxes for the reception of the concentrate to be electrolyzed are formed, the internal diameter of which between two clay plates is about 8 to 10 cm. Into these is shot the concentrated metal powder and an anode is introduced thereinto. The cathode supports are suspended in the spaces between the boxes filled with the metal powder.

For the rest, the arrangement of the baths and the composition of the electrolyte may be such as are usual when anode plates are employed. The further working up of the anode sludge for recovery of any of the useful constituents that may still be contained therein, particularly the noble metals, may likewise be carried out by known methods. The sulphuric acid required for the electrolyte may be obtained from the sulphur dioxide contained in the distillation gases.

The extraction of electrolytic copper directly from the concentrate is particularly convenient if the concentration of the distilled material is not carried out to complete purity of the various constituents. In this case several of the metals may be still mixed with each other or one or more may be still permeated with gangue. In such case either one of the several mixed metal powders may be extracted electrolytically and the remainder subsequently smelted out or the various metals may be obtained in succession by electrolysis.

In the treatment of Mansfeld copper shale according to the process of this invention, there were obtained, from each ton of shale containing 3% of copper and 10% of bitumen, 80 to 100 cubic meters of gas with a calorific value of about 4000 units of heat per cubic meter. The yield of oil and tar amounted to about 1%.

The quantities of electricity required for the electrolysis of the copper can readily be obtained from the excess of gas. These quantities of gas would indeed also suffice for running down the copper dust with a subsequent slagging off or refining smelt. The excess of gas, which can be used for other purposes would however be considerably less. Furthermore only refined copper would be obtained and not the more valuable electrolytic copper. Finally the extraction of the noble metals is simpler and cheaper when the electrolytic process is employed.

Applicant has found that the method of the present invention can be usefully applied to the obtaining of metals from sulphide ores. For this purpose it has been found advantageous to employ a substantially similar process to that hereinbefore described as applied to obtaining metals from bituminous ores, by decomposing the bituminous ore under the action of the hydrocarbons and other constituents formed from the bitumen during heating in the rotary furnace until the metallic compounds are agglomerated into grains of pure metal. Among these effective other constituents there must be included inter alia sulphates (such as gypsum, sulphate of iron) and it may be lime.

The addition of gypsum as a catalyst also accelerates the process. In applying these methods to the treatment of sulphide ores to obtain pure metals therefrom, the procedure is as follows:—

Firstly, the sulphide ore to be treated is mixed with finely ground coal (pit coal or brown coal) which may conveniently be very rich in gas or bituminous, or with other substances which yield hydrocarbons when heated, amongst which mineral and other oils may be mentioned. The size of the grains of ore need not, in contradistinction to the added hydrocarbon-forming substances, be specially small; on the contrary coarser grains of metal are obtained when it is larger. Furthermore, finely ground sulphate of iron and if necessary a little lime are added to the ore and likewise thoroughly intermixed therewith. It has also been found beneficial to briquette the extremely fine grained mixture and then to reduce the briquettes to grains of from 5 to 10 cm. in size and treat them according to the above described methods of treatment. If the roasted product previously so treated be heated slowly to temperatures which are substantially below the temperature of reduction, e. g. to about 700° C. in a rotary furnace, the metallic sulphides will be decomposed in a few hours into pure metals, while the sulphur escapes in the form of sulphuretted hydrogen, organic sulphur compounds, flowers of sulphur and also sulphur dioxide with the hydrocarbons and other gases. The added sulphate of iron acts herein as a catalyst and the addition of lime is not absolutely necessary. Instead of sulphate of iron, other carriers of oxygen may also be employed, such, for example, as gypsum or hæmatite. Such bodies act as catalysts in facilitating and accelerating the separation of the metal, and may generally be described as having the property of sulphate of iron in transitorily liberating sulphur trioxide when heated with ore. The necessary hydrocarbons may also be introduced into the rotary furnace as gases and in such case lower temperatures will suffice. Suitable gases are illuminating gas, coke oven gas, water gas, air gas, acetylene gas and similar gases. The process can be applied to all sulphides, irrespective of whether they be simple or mixed sulphides (complex ores etc.) and also for other compounds such for example as arsenical ores. The various metals can be obtained therefrom by concentration by gravitation, by flotation or by leaching in so far as they are not carried off by the gases in a volatile state to become deposited in the gas outlet flues when sufficiently cooled. The metallic iron formed may also be obtained by magnetic concentration. It is a very pure product which is suitable for the manufacture of specially high grade steels. The process is specially suitable for poor ores which, on account of the fineness of the ore bearing material, cannot be concentrated without difficulty without such a previous treatment, but is in many cases suitable for rich ores also. The combustible gases which are obtained concurrently when coal, etc. is used may be used again to heat the rotary furnace, so that the process is in this way considerably cheapened. One well known process provides for expelling the oxygen, sulphur and phosphorus from ores by air and hydrogen or other gases in air-tight closed retorts. This process is mainly designed for iron ores, that is to say, therefore, for oxides. For other ores and in particular for sulphide ores it is useless, as in it (in contradistinction to the process according to this present invention) such high temperatures have to be used that it would be cheaper to obtain the metals by an ordinary smelting process. The advantage of the new process lies in the fact that heating temperatures suffice which are not considerably above the temperature of low temperature distillation of the bitumen and/or coal (which is around 500° C.) proper and are considerably below the normal reduction temperatures of the metal compounds (which are around 1300 to 1500° C.), and that furthermore the hydrocarbons added or formed from coal, etc. are not burned but can be used as high grade gases again for the most part.

Example.—A copper pyrites accompanied by much silicious and calcareous gangue and containing about 7% of copper was reduced to grains of about 1 mm. in size and intimately mixed with 10 parts by weight of finely ground bituminous brown coal and 1 part by weight of fine ground sulphate of iron. The mixture was roasted in a cylindrical electrical furnace, which was heated by a spirally arranged heating wire over its entire circumference, slowly and increasingly from 600° to 700° C. for some hours. From the roasted product so treated the iron contained therein could be obtained as metallic iron in grains of from 0.1–0.5 mm. in diameter by magnetic concentration and the copper contained therein as equally large pure copper granules by table concentration.

What I claim is:—

1. In a process for obtaining metals from bituminous copper shale, the steps of first disengaging the metals from the ores by direct heat treatment at a temperature exceeding 600 degrees C. and in the presence of solid hydrocarbon matters with the exclusion of air, and then subjecting the complex residual product of the heat treatment to concentration for the separate recovery of substantially pure metallic and other constituents thereof.

2. In a process for obtaining metals from bituminous ores of sulphidic nature, the steps of directly decomposing the bituminous ore under the action of heat in a closed chamber from which air is excluded and subsequently recovering substantially pure metals from the solid product of the heat treatment by concentration.

3. In a process for obtaining metals from bituminous ores of sulphidic nature, the steps of directly heat treating the ore in a closed chamber with the exclusion of air while continuously withdrawing the liquid and gaseous products of the distillation, cooling the solid residual matter of the ore, removing such solid matter from the closed vessel and separating the pure metallic and other constituents therein by concentration methods.

4. A process for working bituminous ores of sulphidic nature wherein the bitumen is expelled from the ore by heat treatment with the exclusion of air, the products of the distillation of the bitumen being recovered during the heat treatment, after which the bitumen-free residue of the ore is subjected to concentration for the separation of its contained pure metals and compounds.

5. A process according to claim 4 wherein the heat treatment is effected at temperatures between 500 and 700 degrees C.

6. A process according to claim 4 wherein the heat treatment is carried to a temperature exceeding 600° C.

7. In a process for obtaining metals from ores of sulphidic nature the steps of first directly subjecting the ore to heat treatment in the presence of hydrocarbon matter and a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore, with the exclusion of air and subsequently concentrating the solid products of such heat treatment.

8. In a process for obtaining metals from ores of sulphidic nature the steps of first directly subjecting the ore to heat treatment in the presence of hydrocarbon matter and a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore, with the exclusion of air subsequently concentrating the solid product of such heat treatment and finally subjecting the concentrated product to a metallurgical process for separation.

9. In a process for obtaining metals from ores of sulphidic nature the steps of first directly subjecting the ore to heat treatment in the presence of hydrocarbon matter and a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore with the exclusion of air, concentrating the solid product of the heat treatment and separately depositing several metallic constituents of the concentrate by electrolysis.

10. In a process for obtaining metals from ores of sulphidic nature the steps of first directly subjecting the ore to heat treatment in the presence of hydrocarbon matter and a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore with the exclusion of air, concentrating the solid product of the heat treatment separating out one of the constituents of the concentrate by electrolysis and separating out the other constituents by smelting.

11. In a process for obtaining metals from bituminous ores of sulphidic nature, the steps of directly decomposing the bituminous ore under the action of heat and in the presence of a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore in a closed chamber from which air has been excluded and subjecting the complex solid product of such heat treatment to concentration.

12. In a process for obtaining metals from bituminous ores of sulphidic nature, the steps of directly decomposing the bituminous ore under the action of heat and in the presence of a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore in a closed chamber from which air has been excluded subjecting the complex solid product of such heat treatment to concentration and then electrolyzing the concentrate.

13. In a process for obtaining metals from bituminous ores of sulphidic nature, the steps of directly decomposing the bituminous ore under the action of heat and in the presence of a catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore in a closed chamber from which air has been excluded,

subjecting the complex solid product of the heat treatment to concentration and then successively removing various metals from the concentrate by electrolytic means.

14. In a process for obtaining metals from bitumious ores of sulphidic nature, the steps of directly decomposing the bituminous ore under the action of heat and in the presence of a catalyst having the property of sulphate, of iron to liberate sulphurtrioxide transitorily when heated with the ore in a closed chamber from which air has been excluded subjecting the complex solid product of the heat treatment to concentration, removing one of the several constituents of the concentrate by electrolysis and finally separating the remaining constituents thereof by smelting.

15. A process for obtaining metals from sulphide ores comprising the direct heating of the ground ore in the presence of hydrocarbon matter and an oxygen carrying catalyst having the property of iron sulphate to liberate sulphurtrioxide transitorily when heated with the ore, at a temperature slightly above 500 degrees C. and considerably below 1300 degrees C. and then treating the roasted product to effect physical separation of the particular metals obtained therein from the other constituents.

16. A process for obtaining metals from sulphide ores, comprising the mixing of the ground ore intimately with coal and an oxygen carrying catalyst having the property of ferrous sulphate to liberate sulphurtrioxide transitorily when heated with the ore, heating the mixture in a rotary furnace to a temperature slightly above 500 degrees C. and considerably below 1300 degrees C. until the metallic compounds in the ore are decomposed into pure metals and effecting physical separation of such metals from the roasted product.

17. A process according to claim 16 wherein sulphate of iron is used as a catalyst.

18. A process for obtaining metals from sulphide ores, comprising the mixing of the finely ground ore intimately with coal and an oxygen carrying catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore, producing small briquetted lumps from the mixture, roasting the briquetted material in a rotary furnace at a temperature slightly above 500 degrees C. and substantially below 1300 degrees C. and treating the resulting mass to separate the pure metals therefrom.

19. A process for obtaining metals from sulphide ores comprising the mixing of the finely ground ore intimately with coal and an oxygen carrying catalyst having the propery of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore, roasting the mixture in the rotary furnace at a temperature slightly above 500 degrees C. but substantially below 1300 degrees C. while withdrawing the combustible gases evolved and utilizing the same for heating the furnace and then treating the complex mixture in the furnace for the separation of its metallic and other constituents.

20. A process for obtaining metals from sulphide ores comprising the mixing of the finely ground ore intimately with coal and an oxygen carrying catalyst having the property of sulphate of iron to liberate sulphurtrioxide transitorily when heated with the ore roasting the mixture in a rotary furnace at a temperature slightly above 500 degrees C. but substantially below 1300 degrees C. while withdrawing the gases evolved, recovering the volatile metallic constituents from such gases and subsequently separating the metallic and other constituents of the complex mixture remaining in the furnace after the heating treatment.

21. In a process of obtaining metals from bituminous ores of sulphidic nature, the steps of heating the ore in the form of course grains to a temperature between 500 degrees C. and 700 degrees C. with exclusion of air, and subsequently recovering by concentration the substantially pure metal from the residual solid products of the heat treatment.

22. A process such as in claim 1, in which an iron sulphate is mixed with the ore prior to the heating whereby to act as a catalyst for accelerating the extraction of the metal.

In testimony whereof I have signed my name to this specification.

DR. CARL GOETZ.