

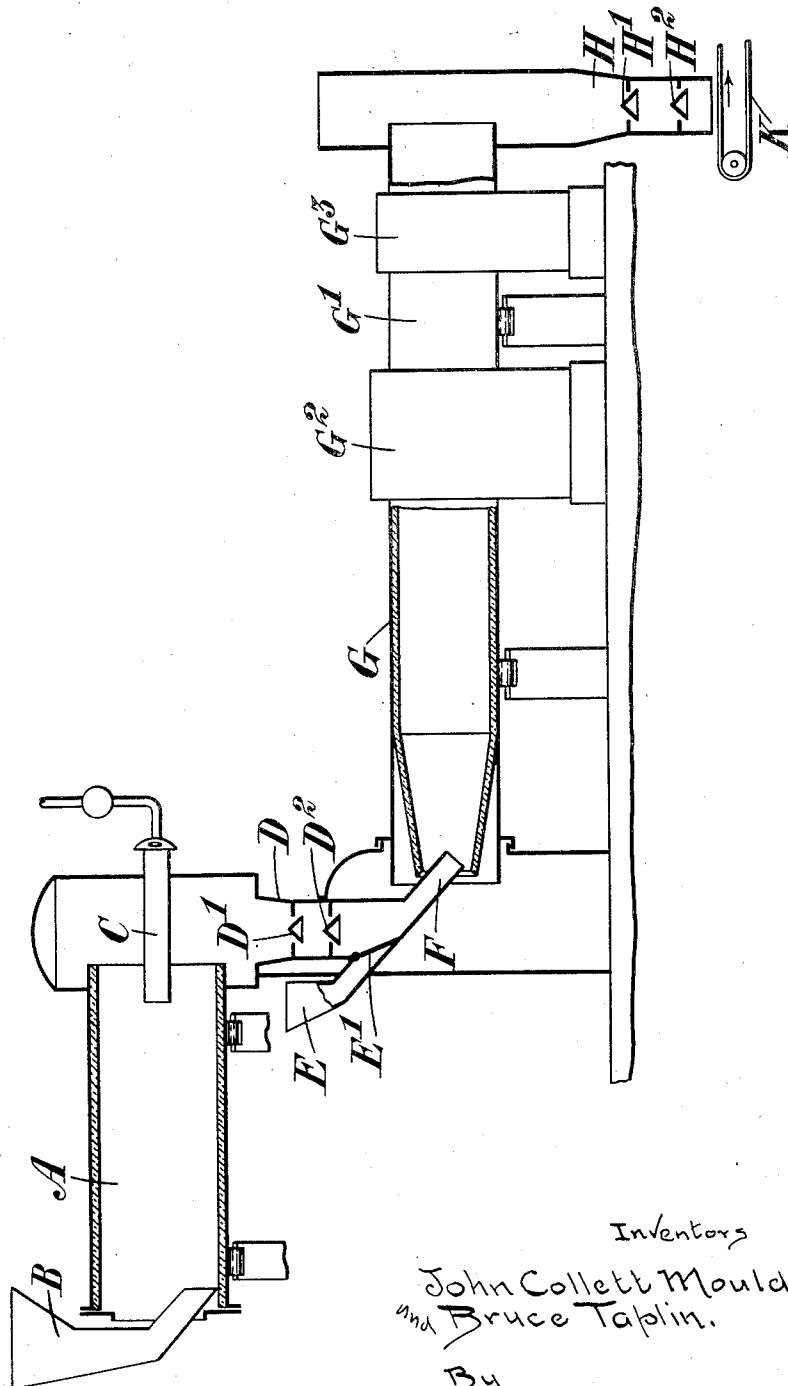
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HEAT TREATMENT AND CONCENTRATION OF COPPER ORES

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## UNITED STATES PATENT OFFICE.

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## HEAT TREATMENT AND CONCENTRATION OF COPPER ORES.

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This invention relates to the heat treatment and concentration of oxidized ores of copper, that is to say chrysocolla (copper silicate), malachite and azurite (copper carbonate) cuprite and melaconite (copper oxide) and the like, and has for an object to render the copper therein readily recoverable.

In previous United States specification No. 1,440,186, a process is disclosed of attaining this end by heating in a reducing gas at a temperature of about 400° C. In attempting to effect a similar reduction of a particular chrysocolla ore by admixture of the ore with a solid fuel, in a proportion of about 2½% with exclusion of oxygen, but without introduction of a separately generated reducing gas, we have found that upon heating to a temperature of 400° C. the chrysocolla showed no marked change in appearance: it retained its characteristic appearance, sometimes with a slight reddish superficial coating. This material was found to be sparingly soluble in a solution of ammonium carbonate and ammonia; when leaching was carried out by agitation, the maximum amount that could be dissolved amounted to 36-39%.

When however the mixture of ore and carbonaceous material had been heated for one hour at a temperature of 700° C. in a vessel from which oxygen was excluded, a very remarkable change was observed. The particles of chrysocolla had now acquired a greyish tint and copper with its characteristic pink colour was found in a very finely divided condition outside the particles. It was very noticeable that the copper had apparently migrated from the ore particles and was found in finely divided condition outside them.

When the ore was heated in a rotary tube furnace the copper showed a marked tendency to segregate into reddish friable balls, sometimes as large as a quarter of an inch in diameter.

None of the material showed the characteristic appearance of silicate reduced under the conditions specified in the specification of U. S. Patent No. 1,440,186.

The friable copper was found to be readily soluble in a solution of ammonia and ammonium carbonate, an extraction of 97.6% being obtained.

The reduced ore was cooled in a reducing or non-oxidizing gas to a temperature at which no appreciable oxidation occurred in the air; in the tests in question the cooling was effected to about 100° C. or lower.

The ore on which these tests were made was obtained from the Sagasca mine in Chile and it was found to contain a small proportion of sodium chloride. Removal of the chloride by washing it out with water previous to the heat treatment was found to prevent the effect above referred to, namely the formation of friable copper.

In the course of our experiments it has been found that when ores which contain oxidized copper uncombined with sulphur (hereinafter referred to as oxidized copper ores) are heated at a proper temperature in admixture with solid carbonaceous matter and in the presence of a haloid, the copper migrates out of the ore particles which originally contained it and is found outside them admixed with the charge. When the ore contains oxidized compounds of copper other than chlorides or oxychlorides and the haloid is present as a salt of a metal other than copper, the reaction can be carried to a point at which practically all the copper in the said oxidized compounds is found in the product in the metallic state. The copper in the product can be extracted by leaching with an ammoniacal solvent.

Accordingly the invention comprises a process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature (for example a red heat) lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

According to a feature of the invention the process may comprise the combination of steps which consists in heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid to a temperature (for example a red heat) lower than the melting point of copper and yet adequate to produce the reaction described so that the copper is caused to come out of the

ore particles which originally contained it and is found outside them amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to  
5 extract the copper.

In carrying the process into effect the atmosphere in which the ore is heated should be neutral so as not to interfere with the reaction, although small amounts of reducing gases may be liberated from the fuel  
10 without detriment to the process.

Apparently the ore should not contain marked amounts of either alkali or acid which are free at the temperature of the  
15 reaction, and according to the present invention the material may be subjected to the step of removing or neutralizing free alkalinity or acidity prior to the heating steps. Free alkalinity is, however, much  
20 more harmful than free acidity because it may entirely prevent the reaction.

Alkaline matter can be washed out of the ore with water, or, alternatively may be neutralized with acid, for example sulphuric  
25 acid. It has also been found that commercial ammonium sulphate may be used in place of sulphuric acid, but sulphuric acid gives the best results.

Preferably after the heat treatment the  
30 ore is cooled in a non-oxidizing medium to a temperature at which the copper is not readily re-oxidized on exposure to air.

A preliminary heating of the ore (for example to 700° C.) in a neutral or an oxidizing atmosphere may be effected with advantage before admixture with the fuel. One  
35 practical advantage of such a preliminary heating step lies in the fact that the ore may thus be heated rapidly and economically by direct contact with combustion gases to a  
40 temperature sufficient to effect the reaction when the haloid salt and the solid fuel are subsequently admixed with it. Consequently the supply of heat to the ore after  
45 admixture with the reagents can be reduced or obviated.

The process is found to be effectively carried out at temperatures lying between  
50 500° and 700° C.

The time required for the heat treatment may be reduced by suitable procedure. Thus the ore may be disposed in layers of such thickness, or so agitated, that the  
55 charge readily becomes uniformly heated throughout, when the reaction is completed in from one to two hours from the time of introduction of the haloid salt and the fuel. A shorter time, say three-quarters of an hour or less may be effective.

60 Preferably the haloid salt is a chloride of an alkali or of an alkaline earth metal, for example sodium chloride or calcium chloride. Haloids other than chlorides, however, are effective. For example, fluorspar may  
65 be used. Even hydrochloric acid and also

gaseous chlorine have been employed with success and the use of organic halogen compounds is not outside the scope of the invention. With any particular ore a simple preliminary trial will suffice to determine  
70 whether a proposed reagent is suitable for the process. The amount of the haloid salt present may be less than that which would be necessary to convert all of the copper present into cuprous chloride. For example  
75 0.2 to 0.3% of common salt reckoned on the weight of the ore has been employed with success with ores containing 4% copper and over.

It is evident that some ores, such as the  
80 Sagasca ore mentioned above, may already contain the necessary amount of sodium chloride or its equivalent, while in other cases it is necessary to incorporate such a reagent with the ore. The ore may be  
85 either soaked with salt solution or the salt may be added dry.

Sulphide ores of copper can be treated according to the process but these ores must be subjected to an oxidizing roast before  
90 submitting them to the process.

The carbonaceous matter employed may be bituminous coal, graphite, coke, or wood charcoal. In fact it appears that any solid  
95 fuel will suffice.

According to the invention there may be combined with the steps above set forth leaching the ore with ammoniacal carbonate solution for extraction of the reduced  
100 copper.

As alternatives, various means of physical concentration have been found to be effective. The reduced copper appears to collect upon the solid carbonaceous fuel so that in the final product the copper-bearing particles consist of a copper skin or outer sheet on a core of coke-like material. When the process is conducted in a rotating tubular furnace under suitable conditions, the copper-bearing particles can be caused to aggregate into large granular masses which may be separated by sifting. They may also be separated by gravity concentration and this may be effective even when large aggregates are not formed.  
115

In the preferred form of the process the ore, with or without preliminary heating is admixed with solid carbonaceous fuel and common salt and fed continuously into a zone which is maintained at a low red heat  
120 (for example 500 to 700° C.) in a neutral atmosphere and caused to pass therethrough at such a rate that on emergence the copper contents will have been segregated as described and thereafter the product is fed  
125 through a cooling zone in which the atmosphere is non-oxidizing and from which the product emerges sufficiently cooled to avoid re-oxidation of the reduced copper by atmospheric air. The apparatus employed may  
130

be that described in United States specification No. 1,510,956 with suitable modifications.

A suitable apparatus is indicated diagrammatically in the accompanying drawing.

In the drawing, A represents a rotatable tubular preheating furnace lined with refractory material. The ore is introduced at one end from a hopper B and heating is effected by an internal gas flame from a burner C. The ore is thereby raised to a good red heat of say about 700° C. and it falls in this condition into a closed charging hopper D provided with regulating valves D<sup>1</sup>, D<sup>2</sup>, which are preferably made of chrome steel. A mixture of solid carbonaceous fuel and common salt, is introduced into a hopper E provided with a regulating flap E<sup>1</sup> at the bottom for admission of fuel to the space below the valve D<sup>2</sup>. The ore from the valve D<sup>2</sup> and fuel and salt from the flap E<sup>1</sup> mix with one another in the chute F and are delivered thereby into a second rotating tubular furnace G lined with refractory material and provided, if necessary, with a spiral conveyor and lifting bars (not shown). Means (not shown) may be provided to heat the furnace G externally if it is found that the temperature in this furnace tends to become too low for the reaction. The furnace G is prolonged at G<sup>1</sup> to provide a cooling zone and means indicated at G<sup>2</sup>, G<sup>3</sup> are provided for cooling its exterior surface. The cooled ore may thereby be reduced in temperature to 100° C. or less and in this condition it is discharged through a hopper H and valves H<sup>1</sup>, H<sup>2</sup> on to a conveyor K which carries it away for further treatment, e. g. leaching.

The following are examples of results obtained according to the process.

#### Example 1.

In this case the ore was obtained from the Sagasca mine in Chile and contained 4.7% copper almost exclusively in the form of chrysocolla. This ore contains naturally a small proportion (about 0.5%) of sodium chloride. About 300 grams of the ore was crushed to 10 mesh and was preheated for half an hour to a temperature of about 400° C. Bituminous coal or charcoal was then mixed with it in a proportion of about 2½% of the weight of ore and the mixture was introduced into a rotary tubular furnace. Oxidizing gases were swept out by means of a current of carbon dioxide which was then stopped.

The tubular furnace had a diameter of 5 inches and was rotated at the rate of 7 to 8 revolutions per minute. The furnace was heated externally for one hour, at the end of which time heating was discontinued and the furnace together with its charge was allowed to cool. The ore was then found

to contain finely disseminated copper, much of which was in the form of friable balls with carbon nuclei distributed throughout the charge and produced by the rotary motion of the furnace. The material was leached by agitation with a cold solution containing 5% ammonia and 4% carbon dioxide and a small amount of copper, for 116 hours. When the leaching solution was removed the residues were washed with an aqueous solution of ammonia and the tailings were found to assay 0.12% copper. The recovery of the copper amounted to 97.6%.

#### Example 2.

Flue dust from the furnace of Lubumbashi, Katanga, Belgian Congo, was found to contain about 13% copper in an oxidized form together with a considerable amount of coarse grain carbon.

When this material was heated in a rotating cylindrical furnace in the presence of additional carbon and a suitable quantity of common salt, it was found that friable copper balls were produced, but these were of too fragile a constitution to be screened from the residues. The cause of this was traced to the coarse carbon in the crude material, and in order to remove this coarse carbon the material was roasted in air to a temperature of about 700° C. After it had cooled it was found that it contained a perceptible amount of free alkali. The cooled product was wetted with salt solution and then dried, mixed with fresh finely divided carbon and heated in a rotary furnace. Balls of copper were not produced and it was suspected that the free alkali was a source of trouble. The free alkali was therefore removed by washing it out with water, and salt solution was added and the material dried. Excellent copper balls were now produced by heating the material in a rotating furnace to between 600 and 700° C. in the presence of 2% of carbon crushed to pass a screen of 40 mesh (Institution of Mining and Metallurgy Standard). The quantity of salt added amounted to one-half of one per cent of the weight of the ore. The copper balls contained 54% of Cu and on separation from the ore by screening showed a recovery of 91.6%. Similar results were obtained by moistening the ore with a dilute solution of sulphuric acid containing 1% of H<sub>2</sub>SO<sub>4</sub> reckoned on the weight of the material, extraction of the alkali by washing being omitted.

In this specification the term "ores and the like" is intended to include not only naturally occurring ores but also copper-bearing materials which have been subjected to various commercial operations such as concentration, roasting and the like.

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

1. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

2. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

3. In the heat treatment of oxidized copper ores of the kind defined, the combination of steps which consists in heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid to a temperature lower than the melting point of copper and yet adequate to produce the reaction described so that the copper is caused to come out of the ore particles which originally contained it and is found outside them amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to extract the copper.

4. In the heat treatment of oxidized copper ores of the kind defined, the combination of steps which consists in heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to extract the copper.

5. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge and subsequently cooling the ore in a non-oxidizing medium to a temperature at which the reduced copper is not readily reoxidized on exposure to air.

6. In a process for the separation of copper from gangue in ores and like materials of the kind defined, the combination of first

heating the ore in a non-reducing atmosphere to a temperature sufficient to facilitate the subsequent reaction, and thereafter treating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

7. In a process for the separation of copper from gangue in ores and like materials of the kind defined, the combination of first heating the ore in a non-reducing atmosphere to a temperature sufficient to facilitate the subsequent reaction, and thereafter treating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

8. In a process for the separation of copper from gangue in ores and like materials of the kind defined, the combination of first heating the ore in a non-reducing atmosphere to a temperature sufficient to facilitate the subsequent reaction, and thereafter treating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to extract the copper.

9. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper but exceeding 500° C. so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

10. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge the treatment being so carried out that the

reaction is complete in from one to two hours.

11. In the process for the separation of copper from gangue in ores and like materials of the kind defined, the combination of first heating the ore in a non-reducing atmosphere to a temperature sufficient to facilitate the subsequent reaction, and thereafter treating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge the treatment being so carried out that the reaction is complete in from one to two hours.

12. A process for the separation of copper from gangue in ores and like materials of the kind described characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a chloride of an alkali metal at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

13. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a chloride of an alkali metal at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

14. In the heat treatment of oxidized copper ores of the kind defined, the combination of steps which consists in heating the ore in admixture with solid carbonaceous matter and in the presence of a chloride of an alkali metal to a temperature lower than the melting point of copper and yet adequate to produce the reaction described so that the copper is caused to come out of the ore particles which originally contained it and is found outside them amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to extract the copper.

15. In the heat treatment of oxidized copper ores of the kind defined, the combination of steps which consists in heating the ore in admixture with solid carbonaceous matter and in the presence of a chloride of an alkali metal at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to extract the copper.

16. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore in admixture with solid carbonaceous matter and in the presence of a chloride of an alkali metal at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge and subsequently cooling the ore in a non-oxidizing medium to a temperature at which the reduced copper is not readily re-oxidized on exposure to air.

17. In a process for the separation of copper from gauge in ores and like materials of the kind defined, the combination of first heating the ore in a non-reducing atmosphere to a temperature sufficient to facilitate the subsequent reaction, and thereafter treating the ore in admixture with solid carbonaceous matter and in the presence of a chloride of an alkali metal at a red heat so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

18. A process for the separation of copper from gangue in ores and like materials of the kind defined characterized by heating the ore after de-alkalination in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a reaction so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

19. In the heat treatment of oxidized copper ores of the kind defined, the combination of steps which consists in heating the ore after de-alkalination in admixture with solid carbonaceous matter and in the presence of a haloid to a temperature lower than the melting point of copper and yet adequate to produce the reaction described so that the copper is caused to come out of the ore particles which originally contained it and is found outside them amongst the charge, thereafter cooling the ore and finally leaching it with an ammoniacal solvent to extract the copper.

20. In a process for the separation of copper from gangue in ores and like materials of the kind defined, the combination of first heating the ore in a non-reducing atmosphere to a temperature sufficient to facilitate the subsequent reaction, neutralizing the ore, and thereafter treating the ore in admixture with solid carbonaceous matter and in the presence of a haloid at a temperature lower than the melting point of copper and yet adequate to produce a re-

action so that the copper is caused to come out of the ore particles which originally contained it and is found outside them in the metallic condition amongst the charge.

- 5 21. A process for the recovery of copper from oxidized copper ores wherein the ore is admixed with solid carbonaceous fuel and common salt and fed continuously into a zone which is maintained at a red heat in a  
10 neutral atmosphere and caused to pass there-through at such a rate that on emergence

the copper contents will have been segregated as described and thereafter the product is fed through a cooling zone in which the atmosphere is non-oxidizing and from 15 which the product emerges sufficiently cooled to avoid re-oxidation of the reduced copper by atmospheric air.

In testimony whereof we have signed our names to this specification.

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