

## UNITED STATES PATENT OFFICE.

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## METHOD OF PRODUCING VOLATILE METALS FROM THEIR SULPHIDES.

No Drawing.

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The present invention relates to a method of producing such metals from their sulphides, which are capable of being liberated from their sulphides by iron, such as zinc, lead and silver, while using metallic iron as sulphur-binding agent. Our new process is especially suitable for producing zinc from zinc sulphide, for instance from complex zinc ores, but it may also be applied for producing for instance lead from lead sulphide.

It has been previously proposed, for instance for the production of zinc out of zinc blende, to heat the ore together with molten iron, but this process has not met with any success, inasmuch as it has been impossible to cause the conversion to take place in even an approximately complete manner. The molten materials show so great a difference in their specific gravities that they will settle in different layers reacting only very incompletely on each other.

It has also been proposed, for the production of zinc out of sulphide of zinc to melt a mixture of finely divided sulphide of zinc and finely divided iron in an electric furnace, whereupon the sulphide of iron thus obtained is roasted, the ferric oxide being then reduced, and the iron obtained again used as a sulphur-binding agent. It has been found, however, that a mixture of the charge thus produced outside the furnace is not sufficient to secure, from a technical point of view, a good yield of the zinc out of the zinc ore, because the mixture within the furnace will only too readily disintegrate into its constituents, before the process of conversion is completed.

According to another proposal for producing zinc from zinc sulphide in retort furnaces a mixture of unroasted zinc sulphide with iron and with carbonaceous material suitable for coking is formed into briquettes, which are distilled under such conditions that the briquettes are first coked into coherent masses, and finally the zinc is reduced and volatilized, while the resulting iron sulphide is retained in minute particles throughout the coke, thus preventing the retorts from being destroyed by the iron sulphide. Nor has this process, however, gained any practical use as the conversion between the materials is very incomplete on account of the great quantity of carbonaceous material which necessarily must be added.

The main object of our present invention is to provide a method of the type described in which the reaction between the sulphide and the iron will be substantially complete and a good yield of the metal from the sulphide material will be obtained.

Another object of our invention is to provide a method of the type described in which the metal is distilled and condensed and the condensation takes place without the difficulties arising in electric zinc processes hitherto employed, permitting of producing a metal of extreme pureness.

Still another object of our invention is to provide a method of the type described in which certain steps are taken for the purpose of carrying out the reaction in most suitable manner so as further to increase the output.

With these and other objects in view our invention consists essentially in heating in a closed electric furnace, i. e. a furnace the interior of which is held free from air, a charge of solidified briquettes of a mixture of a finely divided material containing a sulphide of a metal capable of being liberated from the sulphide by iron, with metallic iron in finely divided state, said charge being of such a nature that in the briquettes the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, said charge being heated to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

The expression "briquettes" is in that connection understood to comprise not only what is usually termed briquettes, that is to say bodies of a more or less regular form, but also other bodies of more or less irregular form, provided, however, that each body consists of several small particles of sulphide ore and iron. Further the size of such bodies may vary from that of a grain of sand to larger lumps.

For the heating any electric furnace may be used, but furnaces of the resistance type, for instance electrode furnaces in which heat is developed by electric resistance in the slag, are to be preferred.

According to a preferred embodiment of our new method applied to the production of zinc from zinc sulphide, ore or material containing zinc sulphide, such as zinc blende, 5 complex zinc ore or the like, is finely crushed and intimately mixed with finely divided metallic iron, preferably in the form of spongy iron, although also iron in the form of pig-iron, broken cast iron or the like as 10 well as ferro-alloys may be used, provided the iron has the requisite degree of fineness which may be effected by crushing, grinding, trituration or any similar process. By forming the spongy iron from finely divided 15 ferric oxides, such as concentrates of iron ore, the spongy iron may be obtained directly in a sufficiently fine-grained state by carrying out the reduction in a suitable manner, for instance in a revolving furnace, and 20 in such cases crushing or grinding of the spongy iron is, of course, not necessary. This mixture is transformed into briquettes or equivalent bodies by any known method. When spongy iron is used as a sulphur-binding agent, the comparatively soft particles of the spongy iron will at the same time act as a binder in the briquetting process, but when iron in other form is used, a 30 suitable binder is preferably added to the mixture, such binder being, for instance, water-glass, lime-white, clay, carbonaceous glutinous substances or the like.

The briquettes are then fed into an electric furnace and heated by means of electric 35 current to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated. During the reaction in the furnace the different particles in the briquettes will remain in 40 intimate contact with one another and fixed in their relative positions, and no separation of the ore and iron particles will set in prior to the reaction. In heating to the reaction temperature which, as a rule, may lie 45 below the melting temperature of the materials, one may thus rest assured that, on properly adapting the admixture of iron, the suitable quantity of iron required to bind the sulphur of the sulphide combined with 50 the zinc will be present everywhere, a liberation of the zinc as complete as possible being thus attained. The zinc may then, subject to its boiling point, either escape in a gaseous state at once, or be caused to do so 55 by further heating of the charge.

In several cases it may be preferable to cause the material to melt and to carry out the heating and melting with the briquettes floating on top of a slag bath in the furnace. 60 If required, suitable fluxes should then be added to the charge in a finely divided state, or be introduced into the furnace directly, so that a slag suitable for carrying out the process is obtained in the 65 furnace. If the briquettes sink entirely un-

derneath the surface of the slag bath prior to the reaction of the metal sulphide with the iron, the briquettes will easily burst by the violent development of gaseous metal taking place on the rapid heating in the slag 70 bath. The homogeneousness of the briquettes will then be destroyed, which is a very great drawback for a complete conversion. By admixing suitable substances 75 in the briquettes or with the same, for instance lime, dolomite, quartz, clay or the like, said substances being accommodated to the gangue of the ore, or by suitably adapting the degree of pressing of the briquettes, 80 the briquettes may be given such a specific gravity relative to the slag that they will float on top of the slag, which latter may at the same time be given such a toughness as to aid in preventing the briquettes from sinking 85 below the surface of the slag bath.

The zinc gases leaving the furnace are condensed in any suitable manner and apparatus, or may be directly burnt to zinc oxide which may be used as dye stuff or for 90 any other purpose.

Instead of mixing finely divided sulphide ore of the metal in question, for instance zinc, and finely divided iron, that is to say 95 instead of fine-crushing the ore and the iron separately, it may be preferable to effect said fine-crushing simultaneously and in the same apparatus with both the iron and the ore, the sharp-edged particles of the ore thereby 100 aiding in the grinding and crushing of the iron, especially in case of using quartziferous ores.

The method according to the invention is obviously adaptable also for producing 105 metal capable of being liberated from its sulphide from material or ore containing the metal in the form of sulphide as well as of oxide. The quantity of iron should then be proportioned to the quantity of sulphur to be combined, in addition to which a requisite quantity of carbon should be added to 110 the mixture before transforming into briquettes in order also to transfer the oxide into metal, a suitable quantity of flux being also added, if desired. If the carbon is added 115 in the form of liquid carbonaceous substances, such as tar, molasses, sulphite waste liquor or the like, a very accurate distribution of the carbon is obtained in the briquettes or the pieces of material, while at 120 the same time the liquid substance also serves as a binding agent.

In a number of ores requiring so high a heating temperature that the charge is caused to melt, it may be preferable to expel 125 the metal or metals combined with sulphur and that or those combined with oxygen in different stages. In such a case, the ore-iron mixture in the form of pieces or briquettes is first heated to such a temperature 130 that the metal combined with sulphur is

liberated, after which the remainder is heated, after having been mixed with carbon and, if required, with flux, in the same or another furnace, to the temperature required to reduce the oxides. This latter mixture may preferably also be transformed into briquettes before heating.

If the material or the ore treated, such as complex zinc ore, contains, in addition to sulphide of zinc, one or more sulphides of metals which also are capable of being liberated from their sulphides by iron but which are comparatively more difficult to volatilize than zinc, such as lead and silver, these latter sulphides are also reacted on by the iron causing the metal or metals to be liberated. As a relatively low temperature is sufficient to expel the volatile zinc, a very small portion of the comparatively non-volatile metals is transformed into a gaseous state, whereas the major portion may be accumulated in the form of molten metal at the bottom of the furnace, whence the molten metal or metals are tapped off and utilized. Consequently, the gases escaping from the furnace will, by carrying out the process at a relatively low temperature, contain vapours of zinc of a high degree of pureness, and the products obtained in condensing the gases or treating them in any other way will be much purer than in the electric methods hitherto employed. In order to draw off both kinds of metal as completely as possible, it is preferable to incorporate in the briquettes so great a quantity of iron that all metals will be liberated.

In order to bring about a complete conversion between the metal sulphides and the iron, it is, as mentioned before, of the utmost importance that the two materials on being heated are brought into contact with one another as intimately as possible. According to a modified embodiment of our new method, this object may be attained by producing the metallic iron in the briquettes directly, before they are heated to the temperature required for the reaction between the metal sulphides and the iron. In such a case, the finely divided sulphide ore is mixed, instead of with iron, with oxide of iron of some kind or other, such as iron ore concentrates, and with carbon proportioned to its reduction, and to the reduction of any metal oxide that may be present in the sulphide ore, the iron oxide and the carbon being both finely divided, whereupon the mixture is transformed into briquettes which are then heated to the proper temperature, the iron oxide being then converted into iron, while the carbon absorbs the oxygen and escapes in a gaseous state as carbon monoxide or carbon dioxide or both. By this means the briquettes will then contain metallic iron in the form of spongy iron finely divided and intimately mixed with the

sulphide material. The briquettes are then treated as set forth above.

If the production of spongy iron is effected in the same furnace wherein the distillation is taking place, the furnace should be provided with means preventing the gases generated in the production of the spongy iron from entering the condensers for the volatile metal gases, the former gases being drawn off separately.

In the reaction the iron is combined with the sulphur of the metal sulphide as sulphide of iron and accumulates at the bottom of the furnace, perhaps on top of any separated metal less volatile than the metal to be produced, such as lead and silver. The sulphide of iron may of course be tapped off and be used as such for any purpose, for instance by treating the same with air or with some other gas containing oxygen, such as steam, which gas may be heated, or not, for the oxidation of the sulphur as well as of the iron, the sulphur being then transformed into sulphurous acid and somewhat to sulphuric anhydride and the iron being oxidized to ferrous oxide or ferric oxide. The treatment may for instance be carried out in such a manner that air or gas under pressure is caused to meet and finely divide the flow of sulphide of iron (matte), or is blown through the latter in converters or the like. The oxides of iron may be restored by reduction to a metallic state in the form of spongy iron, pig iron or the like, in order to be used anew as a sulphur-binding agent in the process or for other purposes. If the ore, in addition to sulphide of a metal capable of being liberated from the sulphide by iron, also contains sulphide of a metal not having this property, for instance if the ore is cupriferous, copper will be found in the form of sulphide in the sulphide of iron formed during the reaction and may be extracted in known manner from this matte in some form or other. If the iron is caused to circulate in the process, a steady concentration of the copper contents of this iron will take place. Thus, after circulation for some time, the sulphides of iron and the oxides of iron or the iron respectively may in known manner advantageously be treated for the recovery of copper, even if the initial sulphide ore has a low percentage of copper. Should the ore also contain silver, the cupriferous matte will also contain some silver and, of course, in higher degree if the sulphide of iron or the iron is circulated.

If in addition to metal or metals capable of being liberated from the sulphide by iron, the material or the ore also contains iron pyrites, the one sulphur atom of the pyrites will be dissociated on the charge being heated. If the temperature is sufficiently high, nearly all of this sulphur will combine with the iron in the charge; otherwise the

same will escape wholly or partly in a gaseous state, and combine with zinc vapours, that may be present, into sulphide of zinc which deposits in the form of crusts in the gas outlet of the furnace. If in the latter case no zinc vapours are present in the furnace chamber, the sulphur will escape unaltered in a gaseous state to the condensers, which again will result in drawbacks. The major part of the sulphur, however, combines with the iron, if the temperature is sufficiently high, and consequently consumes a portion of the latter. Thus the charge must contain a sufficient quantity of iron in order also to bind the free sulphur of iron pyrites that may be present in the material. In order to avoid this consumption of metallic iron, it is preferable, at least if the content of iron pyrites is considerable, to subject the ore prior to its admixture with the iron to a preliminary heating to about 700° C., that is to say to the temperature at which the one sulphur atom of the iron pyrites is expelled. This sulphur may then be recovered in known manner.

The method according to the invention offers very great advantages as compared with the methods hitherto used in practice. In the latter methods only roasted ores could be used to advantage, whereas, according to the present invention, our novel method may also be applied to non-roasted sulphide ores permitting a ready utilization of the sulphur contents of such ores. The tedious and frequently very expensive roasting of the sulphide ores is thus eliminated, which is of great importance particularly with respect to the complex zinc ores that are difficult to roast, if the roasting is at all possible to accomplish, and on roasting lose a great portion of their metal contents on account of metal gases escaping with the roast gases.

Another very great advantage in the present method results from the fact that practically no gas, or at any rate an exceedingly small amount of gas, is obtained in addition to the metal gases. If by reactions in the furnace chamber gases other than the metal gases are also produced, the condensation is rendered very difficult and products will be obtained that are partly of an undesirable character. For example, in the production of zinc from roasted zinc ores according to the methods known hitherto, great quantities of gas (carbon monoxide and carbon dioxide) will form on the oxide of the ore being reduced with carbon, such gases involving very great drawbacks in the condensation of the zinc gases, and resulting in that the zinc is obtained only partly in the form of so-called fluid zinc, while the remainder forms so-called poussières (blue powder). Particularly in the production of zinc in an electric furnace such production or blue pow-

der is considerable, in that 30% or more of the zinc is obtained in this form. Such powder must then be transferred into fluid zinc at a considerable cost, or, it must be subjected to renewed treatment in the process. On the contrary, when using the method according to the invention, the condensation will take place without such difficulties, whereby the capacity of the condensing apparatus is correspondingly increased, and practically the whole quantity of zinc is obtained as fluid zinc, in addition to which such zinc can be obtained in a high degree of pureness. If the sulphide ore used also contains metal oxide, then, obviously, when said oxide is reduced with carbon, carbon monoxide will be produced also in our process, but the amount of gas will nevertheless always be smaller than in producing the metal solely out of oxide.

The invention is not restricted to the material, ores, metals or substances above enumerated as examples, but comprises all materials, ores, metals and substances fulfilling the conditions set forth. It is also of no consequence, whether the ore or the material contains one or more sulphides of one or more metals not having the property of being capable of being liberated from the sulphide by iron, provided only that said ore or material contains some sulphide of a metal having such a property.

When in this description and the appending claims ore is spoken of, this word is to be understood also to cover all other materials containing one or more sulphides of metal or metals capable of being liberated from the sulphide by iron and, perhaps, also sulphides of other metals, such as products, wastes or the like obtained from other processes.

What we claim as new and desire to secure by Letters Patent of the United States of America is:—

1. A method of producing metals from their sulphides, comprising heating in a closed electric furnace a charge of solidified briquettes of a mixture of a finely divided material containing a sulphide of a metal capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, said charge being of such a nature that in the briquettes the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, said charge being heated to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

2. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, and spongy iron as a bind-

ing agent, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions; and heating said briquettes in a closed electric furnace to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

3. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a volatile metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, and heating said briquettes in a closed electric furnace to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated and distilled.

4. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a volatile metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, heating said briquettes in a closed electric furnace to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated and distilled, and condensing said volatilized metal.

5. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, feeding said briquettes into a closed electric furnace, heating and melting same by means of electric current whilst floating on a slag bath to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

6. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, feeding said briquettes into a closed electric furnace, and

heating and melting same whilst floating on a slag bath with heat at least in part developed by electric resistance in the slag to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

7. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, feeding said briquettes into a closed electric furnace together with a suitable slag-forming material of such a nature that the specific gravity of the molten slag will be greater than that of the briquettes, and heating and melting the charge by means of electric current whilst floating on said slag bath to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

8. A method of producing metals from their sulphides, comprising mixing a finely divided material containing a sulphide of a metal, capable of being liberated from the sulphide by iron, with metallic iron in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, feeding said briquettes into a closed electric furnace together with a suitable slag-forming material of such a nature that the slag formed during the melting process will be given such a toughness that it will aid in preventing the briquettes from sinking below the surface of the slag bath prior to the reaction between the metal sulphide and the iron, heating and melting the charge by means of electric current whilst floating on said slag bath to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.

9. A method of producing metals from their sulphides, comprising mixing a finely divided material containing sulphide of a metal, capable of being liberated from the sulphide by iron and oxide of said metal, with metallic iron and carbonaceous material both in a finely divided state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, and heating said briquettes in a closed electric furnace to such a temperature that the sulphur and oxygen combined with the metal is given off to the iron and to the carbon respectively and the metal is liberated.

10. A method of producing metals from their sulphides, comprising mixing a material containing a sulphide of a metal, capable of being liberated from the sulphide  
5 by iron, with metallic iron, exposing said mixture to a fine-crushing process, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and  
10 fixed as regards their relative positions, and heating said briquettes in a closed electric furnace to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated.
- 15 11. A method of producing metals from their sulphides, comprising mixing a finely divided material containing sulphide of a metal, capable of being liberated from the sulphide by iron and sulphide of another metal with metallic iron in a finely divided  
20 state, transforming said mixture into briquettes of such a nature that the particles of the materials are in intimate contact with one another and fixed as regards their relative positions, heating said briquettes in a  
25 closed electric furnace to such a temperature that the sulphur combined with the metal is given off to the iron and the metal is liberated, desulphurizing the matte obtained and using the metallic iron thus produced again  
30 in the process until the matte contains the desired percentage of said other metal.
- In testimony whereof we affix our signatures.
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