April 11, 1950 J. R. CAIN 2,503,234

METHOD OF MAKING ELECTROLYTIC IRON

Filed March 13, 1946

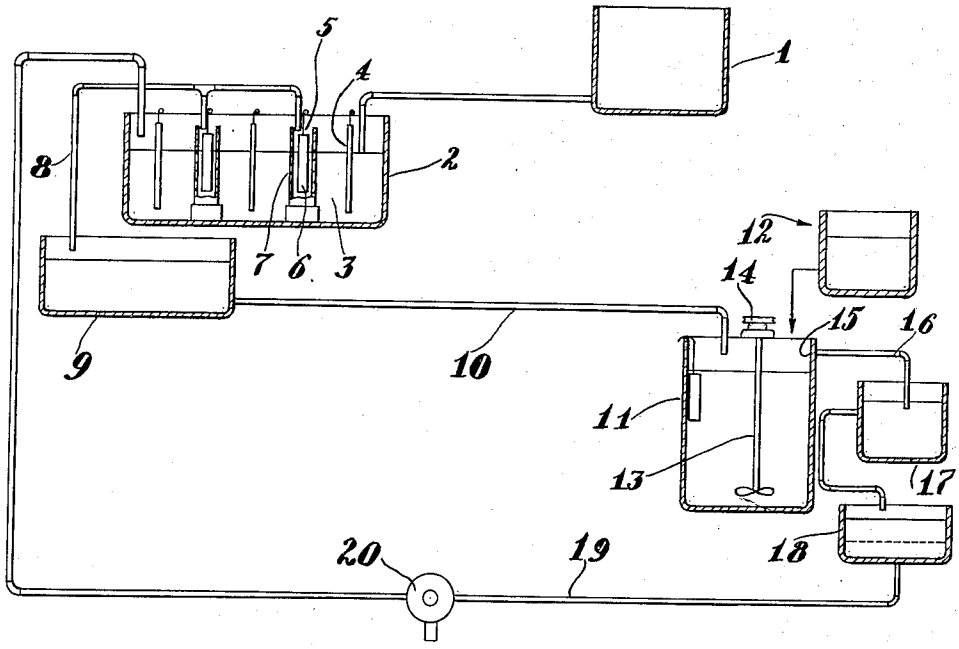


Fig. 1

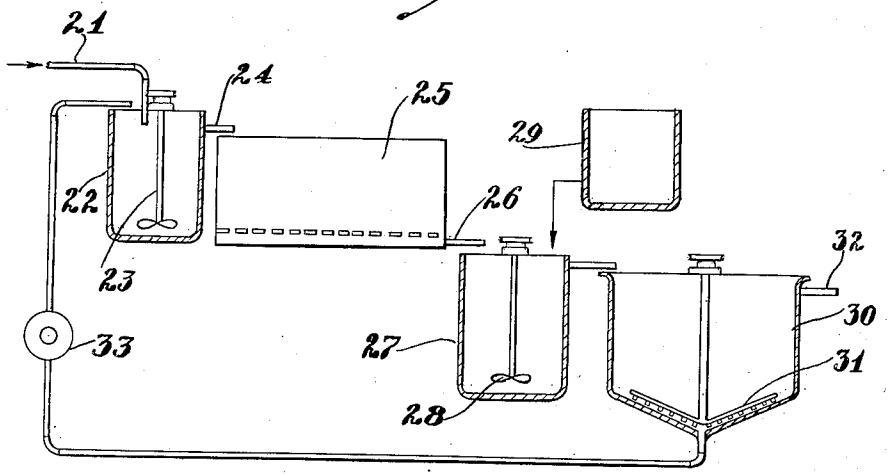


Fig. 2

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Patented Apr. 11, 1950 2,503,234

UNITED STATES PATENT OFFICE

2,503,234

METHOD OF MAKING ELECTROLYTIC IRON

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Application March 13, 1946, Serial No. 654,074

1 Claim. (Cl. 204—113)

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The present invention relates to a method of treating iron ores and of recovering electrolytic iron and other values therefrom.

While it is known that iron may be obtained from its soluble salts by electrolysis, in very pure form, it is also known that the conditions and composition of the electrolytic bath from which it is deposited determine its quality. It would of course be possible to prepare the electrolytic bath by dissolving relatively pure iron therein, which would go far to insure the obtainment of a pure electrolytically deposited product. But the commercial demand for electrolytic iron in quantity would not support a sufficient price to pay for such operations except upon a very small scale of operations.

It may therefore be assumed that the production of electrolytic iron, to be successful upon a commercial scale, must be accomplished by a method which is applicable directly to certain ores of iron, substantially in the condition in which they are found in nature. Native or metallic iron, though sometimes found in relatively pure condition, in the form of meteorites, is of such small and scattered occurrence as to be practically negligible. Oxide ores of iron do not lend themselves to chemical reaction to soluble form, except after preliminary reduction to metallic iron. Accordingly the pyrrhotitic sulphide ores of iron offer the best source for electrodeposition methods of operation.

As is well known, the presence of sulphur in ore, whether free or combined with the metallic components of the ore in the form of a sulphide or sulphides, renders the ore difficult to reduce and separate into its free metal constituents by smelting metallurgical methods, especially when high quality or purity is required. A general cause of these difficulties is found in the physical and chemical properties of sulphur to fuse, to burn, and to recombine chemically with the metallic components, formed during smelting under various conditions, leading to products which are weak and brittle and which, if included in the smelted metal produced, would greatly depreciate its value.

For example, iron pyrites, which is a common ore of iron, in marked crystalline form and widely distributed, contains sulphur in the proportion of two atoms of sulphur to one of iron. It accordingly has the chemical formula FeS_2. It is relatively stable to chemical action, being resistant to the weather and insoluble in hydrochloric acid. Upon heating in air however, it breaks down, liberating part of its sulphur, which fuses readily and at higher temperatures burns to sulphur dioxide. Upon complete combustion the iron may be oxidized to one of its various oxides or sulphates. Similar results may be encountered with other sulphides of iron, if subjected to smelting or oxidizing conditions.

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But it is found by the present invention that these reactions and results may be avoided both with certain sulphide ores of iron, per se, and with sulphide ores which contain other metal values which are sought to be recovered, as well as the iron, as will be hereinafter disclosed.

For example, certain deposits of copper ores, such as those of chalcopyrite, in the Appalachian regions and many others, and various foreign countries, contain copper sulphides associated with iron sulphides. In many places the iron sulphide appears as pyrrhotite. These pyrrhotitic sulphides of iron are characterized by containing a lower proportion of sulphur than iron pyrites. Thus, whereas iron pyrites has the formula FeS_2, the pyrrhotite ores of iron have the generic formula Fe_nS_{n+1}. The formula for iron pyrites would conform to this generic formula, if $n=1$, for then the formula would become Fe_1S_{1+1} or FeS_2. But for any value of n, other than one (e. g., from 5 to 16), it will be observed that the molecular ratio of iron to sulphur will be less than 1:2 and in fact will decrease with increasing complexity of the molecular formula. A significant relationship exists however, between iron pyrites of the formula FeS_2 and all of the iron sulphide compounds in which the iron:sulphur ratio is less than 1:2; namely, that iron pyrites, FeS_2, is difficultly affected by acids while all of the succeeding sulphides having an iron to sulphur ratio less than 1:2 are readily reacted upon by free acids, or by solutions of ferric salts, the iron component being dissolved as one of its ferrous salts and the sulphur being liberated as hydrogen sulphide or free sulphur.

In sulphide ores naturally containing other metal sulphides as well as iron sulphide in pyrrhotitic form, such as chalcopyrites, from the above sources, separation may be effected by fine crushing or grinding, flotation and separation of the other metal sulphides from the iron sulphide components. The latter are segregated in the form of finely divided sludge or concentrates. In this form, they are especially suitable for dissolution of the iron component, segregation and separation of the sulphur in desirable commercial forms, and efficient winning of the iron by electrodeposition in especially desirable condition and high purity, as electrolytic iron.

Moreover, it is an observation of the present invention that by dissolving iron sulphides, which are of pyrrhotitic composition, by means of aqueous solutions containing ferrous and ferric chlorides, in approximately the proportions 100:0.1 to 100:30, the resulting solution constitutes an improved electrolyte to serve for the electrodeposition of free metallic iron therefrom.

In all of the prior art of the electrodeposition

of iron, it has been taken as a fundamental premise that the presence of acid or ferric chloride (and especially of both together) produces a poor deposition of iron, and hence a poor product, and also that it militates against efficiency with respect to the energy input or electric current required. It has accordingly been common practice to avoid such conditions in the electrolytic bath, and many devices in the apparatus, electrolyte composition and procedure have been resorted to for this purpose.

The reason for this practice and belief has seemed perfectly sound and, furthermore, in a general sense it is probably true. For instance, it is well known that aqueous solutions containing free acids or ferric salts, or both, are active to dissolve free metallic iron and take it into solution in the form of a ferrous salt. Since such action is clearly opposite to the separation and electrodeposition of free metallic iron from a solution by electrolysis, it is manifest that the tendency toward dissolution of the iron into solution would appear to prevent or at least offset the tendency toward segregation and electrodeposition of free iron from solution.

Nevertheless, although such reasoning seems plausible, and no certain explanation is offered to account for the result, it is now found that limited amounts of ferric chloride or of free hydrochloric acid, or both, are desirable in the electrolytic bath and lead to an improved electrolytic action and deposition of iron from such solutions and also to an improved product.

It may be that the solvent action of ferric salts and acids upon iron, as mentioned above, is offset by the cathodic potential of the cell. In any event, the effective deposition of the metal is found not to be adversely affected and is in fact promoted and rendered more certain and controllable to the production of a satisfactory electrodeposited product when a limited amount of ferric chloride is present therein.

By the present invention, it is found that electrolytic iron may be effectively recovered directly from sulphide ores by segregating (and converting the iron sulphide component to pyrrhotitic form, if necessary) and leaching the same preferably in finely divided condition with an aqueous solution of ferrous and ferric chlorides in a ratio of 100:0.1, to 100:30 and a free acid, at a pH value below 2.0, and with an excess of the pyrrhotitic sulphide in contact with the leaching liquor, until the ferrous and ferric salts are in the ratio of approximately 100:2 to 100:0.1 delivering the resulting solution to an electrolytic cell and electrodepositing iron therefrom.

The procedure is promoted as a continuous cyclic operation by conducting the electrodeposition until the ratio of ferric to ferrous chloride is an optimum for such electrodeposition and/or for the dissolution of pyrrhotitic sulphides. It is also promoted, and the ductility of the electrodeposited iron is greatly enhanced, by heating the electrolyte or maintaining its temperature at an elevated temperature. This also increases its solvent action upon the fresh ore or previously treated ore residues as the case may be.

It is further found that the leaching action of such leach liquors is made more efficient not only by maintaining an excess of the pyrrhotitic iron sulphide in contact with the liquor, but also by maintaining (or returning) some partially or previously leached ore material in the leaching vat, in countercurrent relationship. The latter is especially effective upon sulphide ores of iron which have been aged or weathered, and thus oxidized.

A typical example of the invention will be described with reference to its application to a chalcopyrite ore with a pyrrhotite gangue, such as occurs in the Appalachian Mountains, and in apparatus diagrammatically illustrated in the accompanying drawings in which:

Fig. 1 is substantially a flow sheet of the complete cycle of procedure; and

Fig. 2 illustrates more particularly a modified type of apparatus used for leaching the ore and preparing the resulting solution for return to the electrolytic cell.

In operation, the supply tank 1, is provided with a solution of ferrous chloride, of a concentration between 90 and 120 grams per liter, and made up to a pH value below 2.0 with free hydrochloric acid.

To commence the operation of the electrolytic cell 2, enough of the acidified ferrous chloride solution is run from the tank 1 to fill the catholyte compartment 3, having the cathodes 4, and the anolyte compartments 5, having insoluble carbon anodes 6 therein, and preferably surrounded by permeable partitions such as the anode bags 7.

The anodes and cathodes are connected to a suitable source of direct current to impress a cathodic current density, for example, of 25 to 100 amperes per square foot.

The conduct of the electrodeposition may be controlled in known ways, and so regulated as to produce deposits of the required characteristics. If ductile deposits of iron are to be made, the electrolyte is heated and maintained in a temperature range between 80° and 100° C., with a low current density, e. g., 25 to 50 amperes per square foot. If brittle deposits are desirable, suitable for ready conversion to electrolytic iron powders for use in powder metallurgy, low temperatures, e. g. 20° to 45° C., are maintained and higher current densities, employed, e. g., 50 to 100 amperes per square foot.

The electrolytic deposits of iron may be withdrawn periodically or continuously, by means of well known devices or apparatus for this purpose, or simply by replacing the cathodes.

In the course of the electrolysis, the anolyte in the anode compartments 5, tends to increase in respect of its ferric:ferrous iron ratio. When or as this exceeds approximately 2 to 100 (to 30 to 100) the anolyte is withdrawn from the anode chamber (periodically or continuously) through pipes or the like 8, to a storage tank 9. At this stage, it is to be observed that an electrolytic solution of such composition, containing ferric chloride and/or free hydrochloric acid, with a pH not over 2.0, is only slowly oxidized by the air, with the formation of insoluble precipitates, usually regarded as oxychlorides. It does not, therefore, rapidly deteriorate in storage nor introduce variable factors which are commonly experienced with solutions of ferrous chloride not containing ferric chloride, and which are accordingly encountered with pure ferrous iron solutions as electrolytes.

The electrolyte, as thus withdrawn, may therefore be led directly, or periodically or continuously from the storage tank 9, through pipes 10 to a leaching vat 11, where it comes into contact with the finely divided pyrrhotite concentrates, as from chalcopyrite flotation separation above described, introduced from a suitable storage bin or tank 12.

As a matter of convenience, the pyrrhotitic

tailings or concentrates will be used as currently produced from the separation of the chalcopyrite ore. They are in most suitable condition for leaching when in such condition, being more reactive and hence more readily and more completely soluble. However, if they have been allowed to stand for some days or weeks, and especially if allowed to dry and exposed to the atmosphere they are found to be less reactive and less soluble. This condition may, however, be offset or overcome as hereinafter disclosed.

In any event, the finely divided ore or concentrates are agitated in the vat 11, with the leaching liquor, which is preferably hot, and hence may be advantageously introduced therein directly from the electrolytic cell, when hot electrolysis is being carried out for the electrodeposition of the iron.

Otherwise, provision may be made for heating the leaching liquor before or during the leaching operation (preferably above 90° C.). A stirring paddle 13 may be positioned near the bottom of the vat 11, driven from the pulley 14.

In the leaching vat, reactions of the following characteristics take place:

$$Fe_nS_{n+1}+2nFeCl_3+HCl+H_2O\rightarrow 3nFeCl_2+S_{n+1}+HCl+H_2O$$

The ferrous chloride goes into solution readily. The hydrochloric acid remains unaltered. The sulphur separates out in substantially molecular to colloidal condition. The reaction is rapid and is capable of going to completion. Moreover, it is promoted by providing at all times for an excess of the iron sulphide concentrates (in pyrrhotitic form) relative to the solvent leach liquor. On the other hand, complete reaction, according to the above equation is not permitted, (that is, at any one time, in the batch). This is desirable if not essential for two reasons. If all of the ferric iron present is reduced to ferrous iron, the resulting solution of ferrous chloride is sensitive to oxidation by contact with the air tending to form oxygen compounds of iron which are generally insoluble, troublesome to remove and may be deleterious upon the cathode if subsequently subjected to electrolysis for the deposition of iron. Moreover, as soon as the ferric iron is substantially or completely reduced to ferrous form, the hydrochloric acid becomes reactive upon the iron sulphides and liberates hydrogen sulphide gas which is deleterious both outside as well as within the solution, and both as leach liquor and for subsequent use in the electrolytic cell.

Both of these difficulties are therefore avoided by shortening the leaching period, as by withdrawing the leaching liquor from the concentrates, before such reactions have been induced, or by continuously withdrawing the leaching liquor at such a rate as to maintain the ferric:ferrous ratio of its dissolved iron contents above .1% (.01% to 30%), preferably .5% to 2.0%. On the other hand, of course, the farther down this ratio is carried to this limiting value, the more iron will have been dissolved and the greater the ferrous chloride concentration of the leach liquor obtained.

The leach liquor from the leaching tank is drawn off through outlet 15 at the top, after the stirring operation has been stopped for a sufficient time to permit settling, thus effectively separating it from the heavy undissolved, constant supply of solids which will accumulate and may be periodically withdrawn, from the bottom.

The effluent from outlet 15 is led through pipe 16 to a settling tank 17 and thence to a filter 18, therefore, at suitable times or at a sufficient rate to control the degree of reaction effected in the leaching tank and also to regulate the composition of the effluent liquor to the desired range of ferric to ferrous iron, the desired concentration of ferrous iron in solution, and to avoid reaction and consequent loss and depletion of the free acid concentration therein.

In the filter 18 any undissolved solid matter (consisting almost exclusively, however, of colloidal, or coagulated sulphur) is separated from the leach liquor, leaving a clear solution which is drawn off through pipe 19 by a pump 20 which may return it directly to the electrolysis tank 2, where it is preferably delivered into the catholyte compartment, and not only maintains the supply of ferrous iron, but also the prescribed ratio of ferric iron thereto, and the concentration of free hydrochloric acid and pH value of the electrolyte substantially constant and below 2.0.

As above pointed out, it is sometimes advantageous to contact the fresh leach liquor with particles of ore which have already been subjected to such reaction. This is especially desirable and effective, with pyrrhotitic iron sulphide ores which have been exposed, after mining, for some considerable time to oxidation or weathering. (This may happen in stock piles, transportation or for adjustment of operations, for example.) This may be effected with the apparatus shown in Fig. 2, in which the anolyte from the electrolytic cell (not shown in this figure) is introduced through pipe 21 into a mixing chamber 22, having a stirrer 23 therein, and an overflow 24 leading to the filter 25. The filtrate from the filter 25 is led through outlet 26 into a second mixing chamber or leaching tank 27, having a stirrer 28, into which the fresh pyrrhotitic ore is introduced, in finely divided condition from the vat or tank 29. The mixture is agitated to suspend the solids in the leach liquor and to effect the reaction therebetween as described above, and withdrawn periodically or continuously, accordingly, into the thickener 30. This is provided with a stirrer, 31 in the bottom, mounted and driven for slow rotation, and with an outlet 32 at the top from which the clear solution of dissolved ferrous and ferric chlorides and hydrochloric acid may be withdrawn and returned to the electrolytic cell directly for re-use as the electrolyte therein, of proper composition and properties. The sludge, settling to the bottom and containing insoluble impurities as well as some sulphur and partially reacted and/or dissolved sulphides, etc., as above described, is pumped off by the pump 33 and returned to the mixing chamber 22 wherein the latter are contacted with the fresh, incoming anolyte as withdrawn from the anode compartment of the electrolytic cell, from which iron is being electrodeposited.

Supplemental to the above procedure it is found that with copper bearing ores such as chalcopyrites, some copper may be taken into solution and be retained through the several operations sufficiently to reach the electrolytic tank. When and if this occurs, it is discovered as a part of the present invention that the copper tends to be deposited upon the cathode along with the electrodeposition of the iron. Such deposition not only contaminates the electrolytic iron and constitutes a loss of copper values, but may introduce the more serious physical defect of inducing nodular formation of the electrodeposited iron itself, which is very serious if not disruptive of the satisfactory

operation and the obtaining of a satisfactory electrolytic iron product.

It is now found that an effective correction of this condition is accomplished by removing the dissolved copper content to a degree represented by the solubility of copper sulphide. This may be done in practice by subjecting the electrolyte containing the copper in solution to contact with a sulphide ore, such as pyrrhotitic iron sulphide ore and subjecting to temperatures approximating the boiling point, for example 95°–100° C., or boiling.

For example, in the operations above described this reaction and separation of the copper content of the electrolyte may be effected by heating the electrolyte in a separate tank or in the leaching tank 11 or in the leaching tank 21, or the tank 22, above 90° C. while in contact with the pyrrhotitic iron sulphide. In this way the dissolved copper is converted to copper sulphide which is highly insoluble and separates. It settles to the bottom of the tank and may be withdrawn with the sludge of other residues and separated, by concentration, flotation, dissolving and electro-deposition or like procedures, for the recovery of the concentrated copper values contained therein.

It may also be practiced to remove and recover such dissolved copper values by providing a separate procedure from those above described and running the electrolyte solution containing copper into a separate tank and heating it to 95° C. or above, adding sulphide ore in sufficient amount to provide the sulphur required to precipitate the copper content as copper sulphide and preferably actively boiling the solution. This promotes the reaction and also the coagulation of liberated sulphur to a readily filterable form. By then filtering off the free sulphur and copper sulphide, the filtered electrolyte may be returned to the system for re-use. This may be done with the electrolyte as it is withdrawn from the anolyte of the cell or with the leach liquor coming from contact with the pyrrhotitic ore in the leaching tanks. In either case it may then be returned to the electrolytic cell or to the leaching tanks as the case may be.

I claim:

Method of making electrolytic iron, comprising the steps of subjecting an electrolyte containing ferrous and ferric chlorides to electrolysis between an insoluble anode in the anolyte, which has a pH value below 2.0 and contains ferrous and ferric chlorides in proportions of from 100 to 2 to 100 to 30, and is separated from the catholyte, which contains ferrous and ferric chlorides in proportions of from 100 to 0.1 to 100 to 2.0, withdrawing a portion of the anolyte, leaching an ore characterized by containing iron sulphide in pyrrhotitic form therewith, said ore being always in excess with respect to the solvent leach liquor thereby to dissolve the iron of the iron sulphide as ferrous chloride and to reduce the ferric chloride of the solution to ferrous chloride until the proportion of ferrous and ferric chlorides is between 100 to 2 and 100 to 0.5, then heating to the boiling point to remove any copper which may be in the solution, separating the resulting reduced solution from residual solids and undissolved iron sulphide, and delivering the same into the catholyte.

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