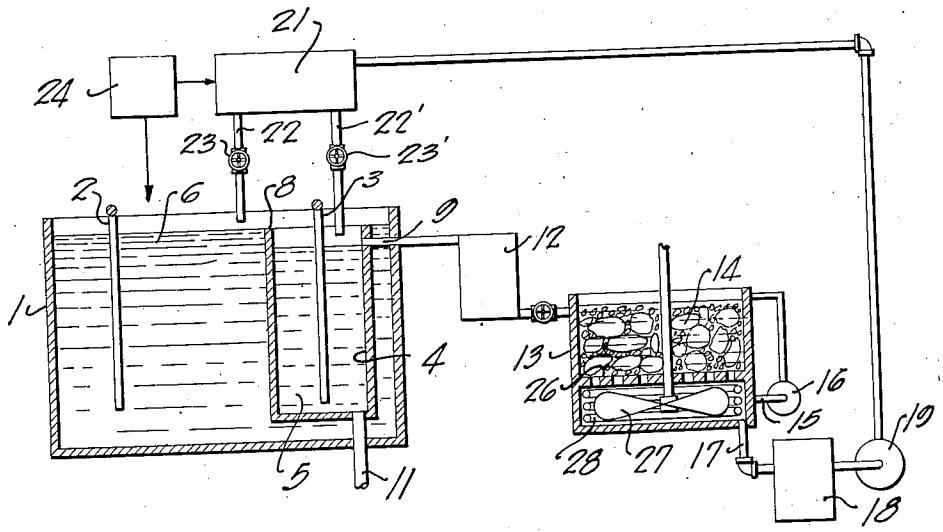
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METHOD OF MAKING DUCTILE ELECTROLYTIC IRON

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METHOD OF MAKING DUCTILE ELECTROLYTIC IRON

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This invention relates to ductile electrolytic iron and to an improved method of preparing the same from various raw materials, including the sulfide and oxide ores of iron, as well as scrap steel, commercial iron, and the like.

It has heretofore been proposed, as described and claimed in my copending application, Serial No. 387,097, filed August 19, 1929 to deposit iron electrolytically in ductile form,—i. e., so that it can be bent, rolled or drawn, within reasonable limits, just as it comes from the bath of electrolyte and without prior annealing,—by suitably controlling the pH value of the electrolyte, preferably between 1.0 and 3.0, during the electrolysis.

The procedure as there described, however, practically requires soluble anodes of steel, cast-iron or commercially pure iron, etc., for convenient and continuous operation. Iron sulfide, for example, can not be employed in the anodes nor can granular or powdered ore materials serve therein as such or when made into electrodes. It is nevertheless frequently desirable to be able to make use of sulfide or oxide of iron, or both, without subjecting them to the metallurgical treatment which is necessary to reduce them to metallic iron or steel.

It is therefore an object of the present invention to provide a method of preparing ductile electrolytic iron, wherein the anodes need not be wholly composed of metallic iron, but may also contain or consist of soluble ferrous sulfide,—either in the form of solid anodes cast therefrom in the molten state or in granular or powdered condition, or of iron chips or borings cemented together by ferrous sulfide—or in which the anodes may be insoluble, as of graphite.

It is a further object to render hematite or other oxide ores of iron as well as insoluble sulfide ores such as iron pyrites, available for use as a part of the raw material,—and in such a way that the operations may form a complete cycle for the regeneration or recovery of the reagent chemicals involved. This is done by the reduction of the oxide ores of iron in combination with pyrite materials, as described in my pending applications Serial Nos. 173,793 and 270,751.

A further object is to control the progress of the electrolytic deposition and the condition of the electrolyte, so that uniformity of the deposited iron may be assured and operation may be substantially continuous.

It is also an object to avoid the rapid consumption of acid and liberation of hydrogen sulfide gas, which tends to occur with anodes containing ferrous sulfide in an acid electrolyte and also tends to produce brittle deposits on the cathode. On the other hand, it is an object to avoid the accumulation and hydrolysis of ferric salts at the anode, which tend to disturb the pH value of the electrolyte and cause it to vary from the preferred range for making ductile iron and also to produce insoluble sediments which in turn may cause the formation of brittle deposits of iron on the cathode.

Other objects will appear from the following disclosure.

It is now found that ductile electrolytic iron may be prepared, with insoluble anodes or with soluble anodes of iron, including ferrous sulfide or the like, by subjecting to electrolysis an acid electrolyte containing a ferrous salt solution and having a pH value of 1.0 to 3.00 while maintaining the "anolyte" (or electrolyte surrounding the anode) separate from the remainder of the electrolyte, as by a permeable partition, and controlling the ferric iron content thereof, preferably so as not to exceed one-fourth of the total iron content of the anolyte, as by periodical or continuous replacement with ferrous salt solution. Such replacement may be effected with a separately prepared solution or with electrolyte from the cathode compartment of the cell.

It is now further found that ductile electrolytic iron may be conveniently and continuously prepared from various sources of raw materials (such as sulfide ores or oxide ores of iron, or both) by preliminary treatment of the same to produce ferrous sulfide or metallic iron (or both) and introducing such reduced material either into the anolyte, to serve as a soluble anode of the electrolytic cell or in a cyclic treatment with the electrolytic action of the cell to provide fresh ferrous salt solution for addition to the anolyte, as above described, or both.

In this way, not only is an immediately ductile electrolytic iron obtained from iron or iron ores, but substantial continuity of operations is made possible. A small amount of chemical reagents is consumed, the greater part being regenerated to useful condition within the process. Moreover, insoluble residues obtained during the process provide a concentrate which may contain other values sufficient in amount to permit their economical recovery, even though they are contained in the original raw materials employed in very small proportions.

Typical instances of carrying out the invention in actual practice will be described with reference to the accompanying drawing, in which the

figure is a more or less diagrammatic illustration of a suitable electrolytic cell, in side elevation.

Briefly, the apparatus may consist of an electrolytic chamber or tank 1 having a cathode 2 and anode 3 which are suitably connected to an appropriate source of electricity (not shown). The anode 3 is preferably enclosed by a porous diaphragm or cell 4, separating the electrolyte 5 therein (or anolyte) from the rest of the electrolyte 6 which hence constitutes the catholyte.

The porous cup or diaphragm 4 separating the anode 3 from the cathode 2 must have these qualities: (1) suitable porosity consistent with necessary mechanical strength; (2) resistance to corrosive or disintegrating action by hot strong solutions of ferric chloride; (3) freedom from tendency to give off shreds or fibers into the electrolyte surrounding the cathode. The porosity should be such as to interpose a low resistance to the current in passing from anode to cathode, but the pores should not be so large as to permit excessive interdiffusion to take place between the electrolyte within (5) and without (6) the cup. In practice I have found it satisfactory to use a cup made of sand, calcined clay, alundum or similar refractory particles of suitable size and bonded with proper binders. Such vessels are formed and burned at high temperatures by practices more or less standardized in the ceramic arts which need not be detailed here. Porous cups or diaphragms of asbestos cloth may be used but must be of such quality that they do not give off shreds or fibers into the outer electrolyte (hereafter called the catholyte) because even when a good filter is used such fibers cause rough deposits and also seem to contribute to the formation of brittle deposits. Asbestos cups or diaphragms are therefore less preferable owing to their gradual deterioration, and diaphragms of linen, cotton, silk, etc. are scarcely of any use.

The liquid level of the catholyte is preferably maintained at or above the top edge 8 of the porous cell 4 so that there may be a slight positive pressure thereon, tending to prevent appreciable transmission of the anolyte therethrough into the catholyte, or so that the catholyte may, periodically or continuously at a controlled rate, flow into the anolyte. There is also provided an overflow 9, whereby the anolyte may also, periodically or continuously be withdrawn, and a draw-off 11 through which accumulations of insoluble residues may be removed from the anode compartment of the cell. The overflow 9 may lead to a filter (not shown) or directly to storage tank 12 and thence to a series of leaching tanks of which one is indicated at 13 where the solution contacts with ferrous sulfide 14, or other source of soluble, reduced, iron as above described. Agitation or circulation of the solution over the raw material may be provided, as through the by-pass 15 and pump 16 or other suitable equipment. The solution from tank 13, when in sufficiently reduced condition, may be drawn through pipe 17 and filter 18, as by pump 19 or by gravity, to storage 21 and thence through pipe 22, controlled by valve 23, in such quantities as required to the cathode compartment of the cell or through pipe 22' and valve 23' to the anode compartment 5. It contains or consists substantially entirely of ferrous salts and if not of the desired acidity is corrected in this respect to control the pH value of the catholyte, by addition of hydrochloric acid from tank 24, in the required amounts.

The procedure may be followed, whether the anode is insoluble such as graphite or a soluble electrode such as iron or iron sulfide is used.

The anolyte is initially ferrous chloride solution with or without other chlorides such as calcium, magnesium or sodium chlorides, and usually of the same strength as the catholyte. Just as soon as electrolysis begins, the ferrous chloride of the anolyte begins to be converted to ferric chloride by the chlorine evolved at the anode 3. If the anode is completely insoluble (graphite) all of the ferrous chloride in the anolyte would thus be converted after current has passed for a sufficient time. If the anode is soluble (i. e., iron, iron sulfide, or iron sulfide and iron) a certain proportion of ferric chloride is also present in the anolyte, varying with the conditions. These changes in composition of the anolyte impose the second condition for securing ductile deposits, namely that the anolyte must be replaced with fresh ferrous chloride solution long before it has been completely converted to ferric chloride. If this is not done a point is reached during continuous electrolysis where the pH of the catholyte changes relatively rapidly to a range unsuitable for giving good ductile deposits and also there is likely to be a heavy deposition of sediments which interfere with maintaining ductile deposits. In order to avoid these difficultes and continue to get ductile iron deposits, it sufficies to change the anolyte when approximately one-fourth its iron has been converted to ferric iron. This proportion is given merely for convenience and is something that has been found simple to do in practice; however, a greater or less proportion of ferric iron may be present in the anolyte when the change is made without departing from the invention.

Without limiting myself to a definite theory to explain or justify this procedure, I believe that essentially what happens is that, when the proportion of ferric chloride in the anolyte reaches a certain figure the chlorine evolved at the anode is no longer used up practically instantaneously as was the case up to that time, but is then dissolved as such or possibly as hypochlorous or other oxygen-chlorine acid in the anolyte. From this solution the dissolved chlorine or chlorine-bearing compounds diffuse to a slight extent into the catholyte and immediately disturb the pH relations there and cause the precipitation of sediments of hydrolyzed ferric chloride. As long as this harmful action of chlorine is prevented by changing the electrolyte as directed and by suitably regulated porosity of the porous cup, the slight diffusion of ferric chloride into the catholyte seems to be helpful rather than harmful, since it is evidently reduced to ferrous chloride by some of the hydrogen that is always being evolved from the cathode during electrolysis. Such reduction generates a small amount of hydrochloric acid which seems to be enough to compensate for the small amount of free acid that is neutralized during electrolysis. Whatever the explanation, the observed fact is that when using a diaphragm of suitable porosity as herein directed little or no hydrochloric acid need be added to the catholyte over periods of several hours continuous electrodeposition of iron when using an insoluble anode. In fact, occasionally there is an increase in free acid that has to be neutralized by a small addition of alkali solution. This contrasts with the phenomena described in my application Serial No. 387,097, where hydrochloric acid has to be added at frequent intervals during electrolysis in order to retain the desired pH

range. If a soluble ore anode is used in the present invention hydrochloric acid has to be added more often than where an insoluble anode is used, but not so frequently or in such amounts as when practicing the invention of application Serial No. 387,097.

In carrying out the process of my invention continuously, it is necessary to renew the anolyte as directed and to maintain the iron content of the catholyte since iron is being removed from the latter by electrolysis. Both objects are accomplished by allowing the anolyte as removed to act on one or more of the above mentioned raw materials, such as ferrous sulfide, steel scrap, cast iron scrap, etc., whereby the ferric chloride is reduced to ferrous chloride and at the same time its iron content is increased by dissolving iron from the raw materials, which iron is subsequently removed as ductile electrolytic iron when the solution is returned to the cathode portion of the cell. The catholyte is removed and becomes the anolyte, and this cycle is repeated indefinitely.

In carrying out such cycle, if a soluble anode process is being used, the period of digestion of core or scrap is short because there is little ferric chloride to be handled. Usually, also, the anolyte is filtered before proceeding with the digestion, so as to recover sulfur liberated from it. Also, the anodes are occasionally taken out and scraped free of sulfur deposits which are added to the sulfur on the filter. This sulfur is then treated for purification and recovery of metals other than iron by steps that will not be detailed here.

With soluble anodes it may be desirable to filter the anolyte; but, if insoluble anodes are being used no filtration is required before digestion although the digestion process must be longer. Usually three to eight hours will suffice to reduce all but insignificant amounts of ferric chloride. The digestion of the ore takes place in tanks fitted with mechanical stirrers that give good agitation and means are provided for maintaining the solvent at 90° C. or above. Means are also provided for filtering off the materials unacted upon by the solvent before the latter is returned to the cathode compartment (as shown). The residue on the filter contains the sulfur and in certain cases metals other than iron and should be treated for sulfur purification and recovery of such of the metals as can be recovered economically.

Thus, as shown in the drawing, the raw material in the solution tank 13 may be retained upon a false bottom 26, beneath which is provided an agitator 27 and heating coils 28.

Such procedure and apparatus is applicable whether the raw material consists of scrap iron or an iron sulfide ore. It is also applicable with an insoluble anode such as graphite as well as with soluble anodes such as iron, ferrous sulfide, which may be in the form of castings or in sintered or briquetted form, if required,—or other form of soluble iron anode.

I will now describe more particularly the steps in carrying out my invention, starting from a catholyte made from such raw materials and by such leaching, etc. cycles as just outlined. As already stated, the initial anolyte will usually be similar to the catholyte in composition.

In carrying out my invention I prefer to start with anolyte and catholyte of ferrous chloride solution that is 80% or more saturated at room temperature. The pH of the catholyte is then adjusted by the addition of hydrochloric acid until it comes within the range of pH 1.5 to 2.5; a convenient figure is 2.0. The adjustment is effected with the aid of color indicators or by electrometric pH measurements such as are now well known. The catholyte is placed in the electrolytic tank which is provided with means (not shown) for maintaining the temperature at 95 to 100° C.—the preferred working temperature range for this method. The anolyte is placed in the porous cups at the same level as the catholyte. In the simplest cases, i. e., with freely soluble anodes to supply iron to the electrolyte, the pump 19 may be used for circulating the catholyte, and the filter 18, if necessary, through which the anolyte is continuously circulating or is passed occasionally, to clarify the liquid which is returned in the desired quantities after passing over metallic iron, to the electrolytic tank with such additions of acid as required to control the pH value of the catholyte. I have used a sand filter and a rotary pump with success for this work. It may also be practiced intermittently by regularly removing the anolyte and renewing the catholyte from a stock tank.

A plurality of anodes, in their respective porous cups, and cathodes of a size appropriate to the size of the tank and the scale of the operation may be used. Nothing in the nature of this invention is apparent that would limit the number of electrode pairs or their size. The spacing can be quite close and such close spacing permits me to realize the practical advantage of a small voltage drop between electrodes.

For anodes, as heretofore stated, iron sulfide or other ore anodes or iron sulfide-iron anodes or graphite or other carbon anodes may be used. After a certain length of time it is desirable to replace the ore anodes with clean ones while the accumulated coating (largely sulfur) is removed by iron brushes or otherwise so that the cleaned anodes may be put back again.

For cathodes there may be used sheets or plates and these may be of materials: (*a*) which allow the deposited sheet or bar of ductile iron to be removed by mechanical means, as by using materials for the cathode blanks which hold the deposited iron loosely, or by applying films of such materials to the face of the cathode blank; (*b*) which permit the cathode blank to be stripped chemically or electrochemically with or without regeneration of the blank from the solution; (*c*) which become integral with the electrodeposited iron, e. g., cathode blanks of electrolytic (ductile) iron or of pure copper. Furthermore, the cathode blank may be a cylinder or mandrel of any of the above types. There may or may not be mechanical movement of the cathode blank. The advantages of a ductile deposit of iron are very great with nearly all these types of cathodes, as shown by experiments with many of them, and I do not therefore wish to be limited as to cathode type.

Having the electrolytic tank and porous cups filled with electrolyte at 95 to 100° C. the pump and filter connected, and the anode and cathode pairs connected to a dynamo with voltage and amperage appropriate for the desired rate of making iron and the system of electrical connections for anodes and cathodes, I proceed to operate my bath at a cathode current, preferably at a density of 50 to 150 amperes per square foot of cathode, or more, the rate of circulation of electrolyte by the pump being adjusted in accordance with the current density as shown best by experience. One hundred amperes per square

foot has been found a convenient current density (cathodic) in most of my work. Cathodic current density has not been found a fundamental factor in producing ductile iron by my method, inasmuch as a satisfactory degree of ductility can be obtained with a wide variation in current density. After iron has deposited for a while a pH test in the catholyte may show that the pH has changed. If the test shows that the pH is much removed from 2.0, the figure herein set as a desirable mean, enough dilute hydrochloric acid or dilute alkali solution is added (as determined by outside test of a portion of the electrolyte) to bring the main body of the electrolyte back to the pH desired. Such tests and adjustments are made as often as experience shows necessary and once a routine is worked out for a given set of operating conditions, viz, current density in relation to volume of electrolyte, and rate of circulation, the procedure being standardized for any number of repetitions of the same set of conditions.

A more satisfactory way to keep the pH adjustment is by means of an outfit for determining pH values continuously and automatically, as by electrometric devices. This may be used in conjunction with reservoirs of the adjusting reagents from which the latter are admitted as needed to the catholyte by a valve controlled by the automatic electrolytic pH indicator. Apparatus of this kind lends itself well to the purpose and is standardized and in commercial use for similar operations.

Since large amounts of sulfates (of the order of 25% of the total acid in combination with the iron) interfere with production of ductile iron by my method, means must be taken for removing these if there is any occasion for them to form. Calcium chloride precipitation may be used to advantage for this purpose.

In case the ore or raw materials contain impurities such as copper beyond small percentages tending to give rough deposits, these must be first removed from the catholyte, as described in my application of even date with this.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

I claim:

1. Method of making ductile electrolytic iron, comprising as steps subjecting a solution of a ferrous salt to electrolysis between a pair of electrodes, while maintaining the solution surrounding the anode separate from the solution surrounding the cathode by a porous wall, and controlling the hydrogen ion concentration of the solution surrounding the cathode to a pH value between 1.0 and 3.0.

2. Method of making ductile electrolytic iron, comprising as steps subjecting a solution of a ferrous salt to electrolysis between a pair of electrodes, while maintaining the solution surrounding the anode separate from the solution surrounding the cathode by a porous wall, and controlling the hydrogen ion concentration of the solution surrounding the cathode to a pH value between 1.5 and 2.5.

3. Method of making ductile electrolytic iron, comprising as steps subjecting a solution of a ferrous salt to electrolysis between a pair of electrodes, while maintaining the solution surrounding the anode separate from the solution surrounding the cathode by a porous wall, and controlling the hydrogen ion concentration of the solution surrounding the cathode to a pH value of approximately 2.0.

4. Method of making ductile electrolytic iron, comprising as steps, subjecting an electrolyte of a ferrous salt to electrolysis while controlling the hydrogen ion of the solution surrounding the cathode and the proportion of ferric to ferrous iron in that portion of the solution surrounding the anode.

5. Method of making ductile electrolytic iron, comprising as steps, subjecting an electrolyte of a ferrous salt to electrolysis while controlling the hydrogen ion of the solution surrounding the cathode and the proportion of ferric to ferrous iron in that portion of the solution surrounding the anode while maintaining said portions of the solution separate by a porous partition.

6. Method of making ductile electrolytic iron, comprising as steps, subjecting an electrolyte of a ferrous salt to electrolysis while controlling the hydrogen ion of the portion of the solution surrounding the cathode to a pH value of 1.0 to 3.0 and the proportion of ferric iron to ferrous iron in that portion of the solution surrounding the anode to a value of approximately 1 to 3, more or less.

7. Method of making ductile electrolytic iron, comprising as steps subjecting an electrolyte containing a ferrous salt and having a pH value of 1.0 to 3.0, to electrolysis, removing that portion of the solution surrounding the anode, reducing said solution to ferrous condition, and returning the resulting solution to the electrolyte.

8. Method of making ductile electrolytic iron, comprising as steps subjecting an electrolyte containing a ferrous salt and having a pH value of 1.0 to 3.0, to electrolysis, removing that portion of the solution surrounding the anode, reacting the same with iron in reduced condition, and returning the resulting solution to the electrolyte.

9. Method of making ductile electrolytic iron, comprising as steps subjecting an electrolyte containing a ferrous salt and having a pH value of 1.0 to 3.0, to electrolysis, removing that portion of the solution surrounding the anode, reacting the same with metallic iron, and returning the resulting solution to the electrolyte.

10. Method of making ductile electrolytic iron, comprising as steps subjecting an electrolyte containing a ferrous salt and having a pH value of 1.0 to 3.0, to electrolysis, removing that portion of the solution surrounding the anode, reducing said solution to ferrous condition, and returning the resulting solution to the electrolyte and an acid or alkali to maintain the desired pH value.

11. Method of making ductile electrolytic iron, comprising as steps subjecting an electrolyte containing a ferrous salt and having a pH value of 1.0 to 3.0, to electrolysis, removing that portion of the solution surrounding the anode, reducing said solution to ferrous condition, and returning the reduced solution to the electrolyte.

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