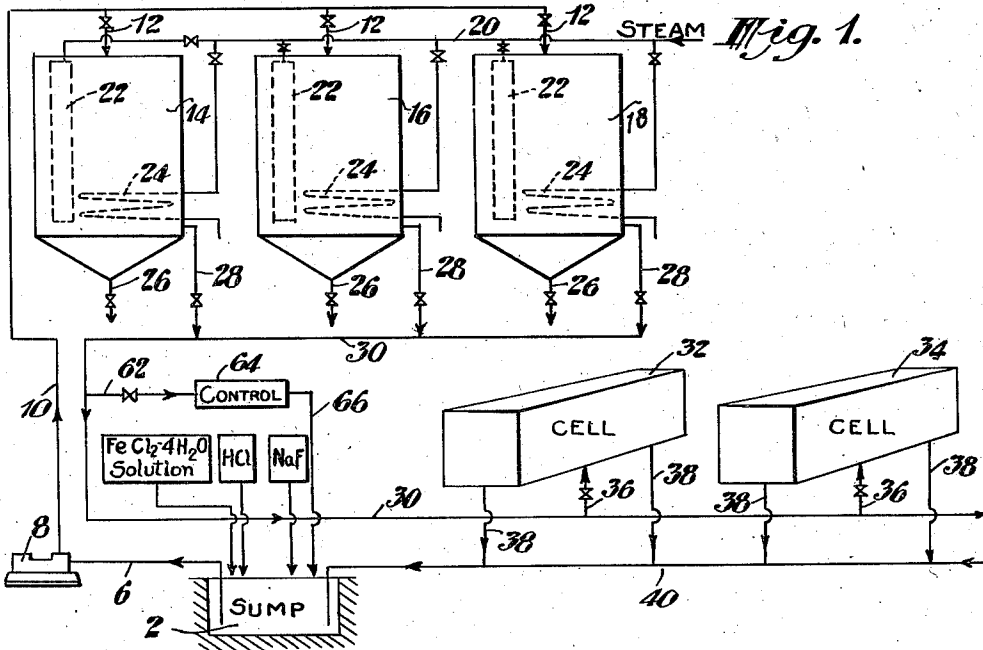
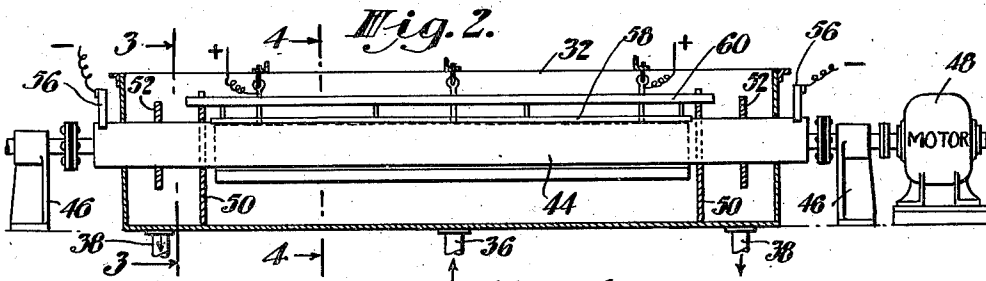
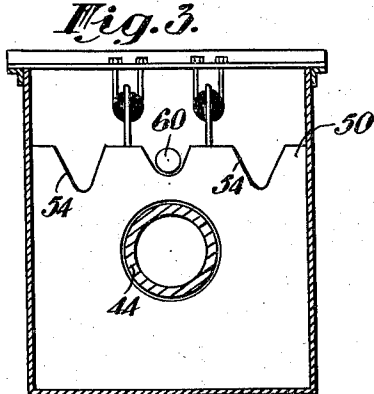
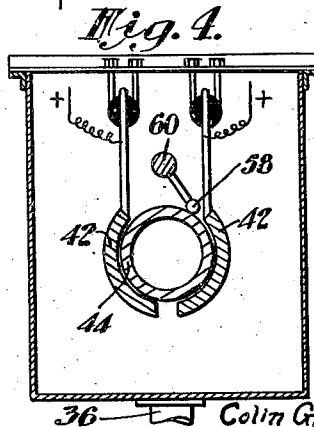


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ELECTROLYTIC IRON MANUFACTURE

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ELECTROLYTIC IRON MANUFACTURE

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This invention relates to the manufacture of electrolytic iron, particularly in the form of pipes or tubes.

The production of electrolytic iron has been a subject of investigation for many years, but up to the present time no commercial process has been sufficiently successful to establish and maintain itself as an industry. In the few processes which have been tried on any substantial scale, the high consumption of electrical energy, the low rate of iron deposit and the high investment cost have made operation unprofitable. Many attempts have been made to correct these difficulties by various changes in operative procedure of such as the use of various iron salts, the use of organic addition agents in the electrolyte, by the use of highly concentrated or dilute solutions, by changes in temperature of the electrolyte, by the use of oxidizing agents and by variously modifying other steps and factors involved in the process. Such changes while apparently improving the process in some respects have not materially aided in reducing the cost of production.

The primary object of the present invention is therefore to overcome the difficulties previously encountered and produce electrolytic iron tubes or other forms by a profitable commercial operation.

A further object of the present invention is to provide a commercial process for the manufacture of electrolytic iron tubes or sheets, by which a consistent smooth deposit of iron may be obtained in an economical manner.

A further object of the invention is the production of electrolytic iron sheets or tubes having a thickness suitable for present and future commercial uses. The greatest known thickness for tubes or sheets made by previously tried processes is only about 0.2 inch, while usually they were only 0.1 inch in thickness. Tubes of such thickness would not fulfill the requirements of modern boiler or oil still practice, or be suitable for high pressure gas and oil pipe lines. By the process of the present invention heavy walled tubes of any desired thickness may be made.

A further object of the invention is to provide a process whereby ores may be exploited where their content of phosphorus or of sulfur or both makes it impractical to use them in present ferrous metal production processes. Experiments have shown that an anode having a relatively high content of phosphorus or sulfur, or both, has no effect on the cell voltage, and that such an anode gives a cathode deposit well within the commercial limits for these substances.

A still further object of the invention is to provide a process for making electrolytic iron in which various important factors are so controlled that iron tubes may be produced on a commercial scale at a cost comparable with that for producing steel tubes.

Another object of the invention is the provision of a cell for the electro-deposition of iron which includes a specially controlled acid electrolyte and an anode having special properties.

With these and other objects in view the process of the present invention for the manufacture of electrolytic iron tubes or sheets comprises one in which the anode composition, the electrolyte composition, temperature and acidity, the circulation of the electrolyte, the spacing of the electrodes and other factors are accurately controlled.

Further objects and advantages of the process will be apparent to those skilled in the art from the following detailed description taken in connection with the accompanying drawing, in which:—

Fig. 1 is a diagrammatic showing of apparatus suitable for carrying out the process of the invention;

Fig. 2 is a longitudinal view partly in vertical section of one of the cells shown in Fig. 1;

Fig. 3 is a cross-section taken on the line 3—3 of Fig. 2, and

Fig. 4 is a cross-section of the cell shown in Fig. 2 taken on the line 4—4.

Referring to Fig. 1 of the drawing, the general features of the process will be described in connection with the elements of the apparatus shown. In accordance with the present invention the iron to be deposited electrolytically as tubes or sheets, is deposited from an acid solution of ferrous chloride also containing sodium fluoride. In starting the process the ferrous chloride solution, hydrochloric acid and sodium fluoride are introduced into a sump 2, from which the solution mixture is withdrawn through a pipe 6 and passed by a pump 3, pipe 10 and valved pipes 12 into a plurality of heating and storage tanks 14, 16 and 18. (Any suitable number may be used.) In these tanks the solution is heated to a suitable temperature by means of direct steam introduced from a steam main 20 through submerged tubes 22 mounted in each tank. The solution in tanks 14, 16 and 18 may also be heated electrically or by steam coils 24 which may be connected through valved pipes with the steam main 20. The storage tanks are also used as settling chambers for the removal of any suspended solid matter which may be pres-

ent in the electrolyte. Such deposits as may settle out in the tanks are withdrawn through valved drain pipes 26.

In carrying out the process electrolyte is usually supplied to only two (or less than all) of the tanks at any one time, and the heated electrolyte is continuously withdrawn from these tanks through valved discharge lines 28 and conducted by means of conduit 30 to a series of cells 32, 34, etc. The electrolyte is introduced into each cell from the line 30 through a valved connection 36. While electrolyte is continuously introduced into each cell it is also continuously withdrawn therefrom through drain pipes 38 into a pipe 40 which leads to the sump 2. During the operation of the process the electrolyte is circulated at a very rapid rate through the cells and back to the heating tanks in order to prevent any sediment settling out in the cells and to maintain the temperature and composition of the electrolyte in the cells substantially constant. Any convenient number of cells may be used in connection with the lines 30 and 40, only two being shown in Fig. 1 for purpose of illustration. A more detailed showing of the cells 32, 34, etc., is given in Fig. 2 to Fig. 4, from which it will be seen that the electrolyte is introduced at the bottom and near the middle of each cell and withdrawn from both ends thereof. Each cell comprises an anode composed of a pair of preferably semicylindrical cast iron pieces 42 suitably supported and insulated from the remainder of the cell as shown in the drawing. Within these semicylindrical anode elements is mounted a rotatable cathode 44, supported by blocks 46 outside the cell casing proper. The cathode may be rotated at any suitable speed by means of a motor 48.

The cell casing is divided into at least three compartments by means of partitions 50, through which the cathode extends. The cathode may be provided with deflector rings 52 adapted to prevent electrolyte which flows along the cathode through the partitions 50, from flowing outside the cell casing. The end compartments outside partitions 50 serve as collecting basis for the electrolyte, which is discharged through pipes 38. As shown in Fig. 3 the partitions 50 may be provided with overflow notches 54 to accommodate electrolyte in excess of that which flows through the relatively small space between the cathode 44 and the partitions 50. (Due to the relatively large amount of electrolyte circulated through the cells there may be a greater amount introduced than would flow through the space around the cathode.)

Electricity may be conducted to the anodes in any suitable manner, for example, by connections made to the anode supports as indicated in the drawing and from any suitable source not shown. Likewise current may be conducted to the cathode through brushes 56 or by any other suitable means.

In order to improve the iron deposit on the cathode the deposit is wiped during the rotation of the cathode by means of a wiping or rubbing block 58. This block rests on the cathode and is supported by a member 60 which in turn is supported by partitions 50. The wiping or rubbing block 58 may be suitably covered with rubber or other material.

One of the important features of the present invention is the method of manufacture and composition of the cast iron anode pieces 42. The high cost of producing electrolytic iron by previ-

ously tried processes was largely due to the necessary use of high cell voltage and relatively low current density. One process for example used a voltage of 5 in order to obtain a current density of 60 amps. per square foot. In this connection it has been discovered that an iron anode substantially free from carbon, silicon and manganese gives a much lower cell voltage than other iron. Furthermore, the presence of sulfur and phosphorus in the iron has no adverse effect on the cell. The iron for the process therefore may contain such quantities of sulfur and phosphorus as to be entirely unsuited for the manufacture of steel.

In preparing the anode pieces for the cells, a blast furnace iron which may be high in phosphorus, is subjected to a modified Bessemer treatment in that the iron is thoroughly blown with air to remove any carbon, silicon and manganese present. Then instead of recarburizing the iron as in the usual Bessemer process the iron is drawn at the end of the air blow and cast into anode pieces in substantially the form shown in Fig. 4. The cathode may comprise an ordinary steel tube having suitable mounting flanges substantially as shown in Fig. 2.

In starting up the apparatus a substantially clean solution of the desired composition is made up preferably in the sump 2 and then pumped into tanks 14, 16 and 18. The preferred solution comprises ferrous iron in a concentration equal to from 350 to 450 grams per liter of ferrous chloride tetrahydrate together with 10 to 20 grams per liter of sodium fluoride which probably acts as a buffer. The solution is made acid by the addition of hydrochloric, hydrofluoric or other acid until the solution has a pH value of from about 4 to 6, for example 5. The pH value of the electrolyte may be readily determined as follows: Take a 10 c. c. sample, dilute it with 40 c. c. of water and filter. To 10 c. c. of the filtrate add three drops of methyl orange; to a second 10 c. c. add 3 drops of methyl red. The methyl orange-tinted solution should be yellow, and the methyl red-tinted solution should be red to show a pH of about 5. This simple test is based on the fact that the neutral point of methyl orange is 4.2, while that for methyl red is 5.8. The dilution of the sample has substantially no effect on its pH because the solution is well buffered.

The use of a ferrous iron electrolyte of the particular concentration range referred to is preferred because the experimental work on this process has demonstrated that such a concentration range gives a lower cell resistance than either a more dilute or a more concentrated solution.

After the electrolyte has been made up and all tanks (14, 16 and 18) filled, the electrolyte in tanks 14 and 16 is heated to a temperature of from 65° to 106° C. (preferably 90° to 95° C.). Circulation of the electrolyte is then started from tanks 14 and 16 through lines 28 and 30 to cells 32, 34 etc., as previously referred to; the cells being cut into the circuit one at a time. During this operation (and before if desired to check its properties) a portion of the electrolyte is bypassed through a valved pipe 62 into a control box (or room) 64 then into sump 2 through a pipe 68. The temperature acidity and concentration of the electrolyte passing through the control box 64 may be determined by well-known instruments or tests, the results of which may be used as a basis for any necessary additions of acid or

of the salts referred to, or for the correction of any other property of the solution. Changes in temperature, concentration, gravity and acidity may be adjusted automatically from the control box by the use of well-known devices for this purpose. While satisfactory iron deposits may be obtained by maintaining the temperature of the electrolyte in the range of from 65° to 106° C. it has been found that at temperatures of from 90° to 95° C. the voltage is lower for a given current density than that required for the same current density at lower temperature. At the preferred temperature range (90° to 95° C.) the loss from evaporation of the solution is much less than at higher temperatures.

The electrolyte is circulated at a relatively high rate from the tanks through the cells for the purpose of maintaining the temperature and to keep the electrolyte in a high state of agitation in the cells. The rotation of the cathode is maintained at a peripheral speed of about 100 meters per minute. This rotation also serves to agitate the electrolyte and to assure a substantially constant supply of fresh hot electrolyte in the space between the cathode and anode. The anode pieces 42 are spaced so that all parts of the cathode are equally distant therefrom, and so that the space between the cathode and anode pieces is as short as possible. With the method of control used in accordance with the present invention it is possible to use a spacing between the electrodes as small as one half inch or less. The smaller the spacing the lower the resistance in the electrolyte and the lower the cell voltage becomes. As the anode material is removed by electrolysis the thickness of the iron deposited on the cathode increases, but if desired any necessary adjustment in the spacing between the electrodes may be made during a run by moving the anode pieces closer to or away from the cathode.

Under the conditions given above it has been found possible to maintain a current density of 100 amps. or higher per square foot and at the same time not have a cell voltage greater than one. The importance of this relationship is apparent when it is realized that the higher the current density the more rapid the rate of iron deposition, and the lower the voltage the more economical the process. In one specific run under substantially the conditions herein described the cell voltage was 0.84.

As the operation of the process proceeds the cells 32, 34, etc., may be alternately cut out of the system, the cathode removed and the deposited iron stripped therefrom in any suitable manner. For example the deposited iron may be removed by heating and rolling, a method commonly referred to in the art. It will be seen therefore with a number of cells connected to the lines 30 and 40 that cells will be constantly cut in and out of the circuit.

After about eight hours operation with tanks 14 and 16, tank 18 which is filled with electrolyte will be heated and cut into the system, while tank 14 will be cut out of system and the electrolyte therein allowed to settle. After the electrolyte in tank 14 has been allowed to stand and settle for a suitable period of time any sludge settled out therein may be withdrawn through the valved pipe 26 to any suitable storage. The relatively clear stratified solution may be drawn off and conducted into the circuit or other storage if the tank needs cleaning. After the tank 14 has been cleaned, it is then ready to be refilled, heated and used in place of tank 16. Instead of

using the settling tanks 14, 16 and 18 any other suitable means may be employed for heating the electrolyte and a filter may be used for removing any suspended material.

The salt (sodium fluoride) used in connection with the process of the present invention is very effective for maintaining the proper pH range, even though relatively large amounts of acid are added at a time. If sodium fluoride is not available other fluorides soluble in the electrolyte may be used, for example potassium fluoride or hydrofluoric acid.

It is the object of the present invention to operate the process under such conditions that the electrolyte will be protected as far as possible from oxidation, and to avoid the presence of organic impurities (or organic addition agents) in the electrolyte. In order to accomplish this result the cells, tanks and sump may be suitably covered and insulated which will also aid in decreasing the evaporation of the solution and aid in maintaining the temperature.

The features of this invention are applicable to the production of the other ferrous metals, cobalt and nickel, from their ores or from impure compositions of these metals, which are unsuited for use because of the presence of carbon, phosphorus or sulfur.

Having described the invention in its preferred form what is claimed as new is:

1. In the process of depositing iron electrolytically on a rotary cathode substantially surrounded by an iron anode submerged in a ferrous chloride electrolyte containing sodium fluoride, the improvement which comprises mechanically rubbing the cathode as it rotates, supplying electricity to the electrodes at a current density of about 100 amperes per square foot of cathode surface at a voltage of about one, maintaining the concentration of ferrous chloride in the electrolyte at from 350 to 450 grams per liter of ferrous chloride tetrahydrate and that of sodium fluoride at from 10 to 20 grams per liter, heating the electrolyte to a temperature of from 65° to 106° C., and maintaining the pH value of the electrolyte between about 4 and 6.

2. The process defined in claim 1 in which the cathode is rotated at a peripheral speed of about 100 meters per minute.

3. In the process of manufacturing electrolytic iron tubes in which iron is deposited on a rotating cathode substantially surrounded by a cast iron anode substantially free of carbon submerged in a ferrous chloride electrolyte contained in a cell chamber, the improvement which comprises continuously circulating the electrolyte from said chamber through a heating zone in which the electrolyte is heated to a temperature of from 90° to 95° C. and then back to the said chamber, maintaining all parts of the cathode substantially equidistant from the anode, said electrolyte containing from 10 to 20 grams per liter of a soluble fluoride, and controlling the concentration of the electrolyte to maintain it slightly acid and the content of ferrous chloride tetrahydrate between 350 and 450 grams per liter.

4. The process defined in claim 3 in which said cathode is rotated at a peripheral speed of about 100 meters per minute, and mechanically wiping said cathode during said rotation.

5. The process defined in claim 3 in which the acidity of the electrolyte is maintained at a pH value between 4 and 6 by the periodic addition of hydrochloric acid thereto.

6. An electrolyte for use in the manufacture of electrolytic iron, comprising from 350 to 450 grams per liter of ferrous chloride tetrahydrate, 10 to 20 grams per liter of sodium fluoride, said electrolyte having a pH value of from 4 to 6 and being substantially free of organic constituents.

7. The process of electrolytically converting a high sulfur, high phosphorus cast iron into a low sulfur, low phosphorus iron, which comprises using an iron of such high sulfur and phosphorus content but substantially free of carbon silicon and manganese as anode material in an electrolytic cell in which the electrolyte is slightly acid, contains from 350 to 450 grams per liter of ferrous chloride tetrahydrate and from 10 to 20 grams per liter of a soluble fluoride, and maintaining the temperature of said electrolyte between 65° and 106° C.

8. The process of electrochemically converting impure ferrous metals containing phosphorus or sulphur into the substantially pure metal, which comprises subjecting such an impure metal substantially free of carbon, silicon and manganese as an anode in an electrolytic cell to the action of an electric current and an acid electrolyte maintained at a temperature between 65° and 106° C., depositing the substantially pure metal on a cathode in said cell, and maintaining the hydrogen ion concentration in said electrolyte such that the electrolyte has a pH value of from 4 to 6 inclusive.

9. In the process of depositing iron electrolytically on a rotary cathode mounted between iron anode elements submerged in an electrolyte contained in a cell chamber, the improvement which comprises supplying electricity to the electrodes at a current density of approximately 100 amperes per square foot and at a voltage of about one, maintaining in the electrolyte a concentration of ferrous chloride tetrahydrate of from 350 to 450 grams per liter and maintaining the electrolyte at a temperature of from 65° to 106° C., and sufficiently acid to give a pH reading of from 4 to 6.

10. In the process of refining iron in which cast iron is used as anode material in an electrolytic cell for making electrolytic iron, the improvement which comprises electroplating the cast iron anode material on to a cathode mounted in an electrolyte in said electrolytic cell, said anode material comprising cast iron which has been air-blown while in a molten state until it is substantially free of carbon and thereafter cast into the desired anode shape, and said electrolyte comprising an acid ferrous iron solution containing a small proportion of a soluble fluoride buffer agent, and maintaining the pH value of the electrolyte between about 4 and 6.

11. The process of electrolytically depositing a firm smooth coat of iron on a cathode mounted in a body of an acidic ferrous electrolyte, which comprises passing an electric current having a voltage of about one at a current density of approximately 100 amperes per square foot of cathode surface between said cathode and a cast iron anode mounted in said body of electrolyte closely adjacent said cathode, said anode comprising cast iron substantially free of carbon silicon and manganese, and maintaining a small proportion of a soluble fluoride buffer agent in said electrolyte to control the pH value thereof.

12. A process for producing electrolytic iron, which comprises depositing iron on a cathode mounted in an acid ferrous chloride electrolyte maintained at a temperature of from 65° to 106° C. and containing a soluble fluoride in sufficient proportion to act as an inorganic buffer agent for maintaining the acidity of said electrolyte at from 4 to 6 pH value.

13. In the process of manufacturing electrolytic iron tubes in which the iron is deposited on a rotating cathode substantially surrounded by a cast iron anode substantially free of carbon and submerged in a slightly acid ferrous chloride electrolyte contained in a cell chamber, the improvement which comprises continuously circulating the electrolyte from said chamber through a heating zone in which the electrolyte is heated to a temperature of from 65° to 106° C. and then back to said chamber, maintaining all parts of the cathode substantially equidistant from the anode, controlling the concentration of the electrolyte to maintain the ferrous chloride content thereof equivalent to from 350 to 450 grams per liter of ferrous chloride tetrahydrate, said electrolyte also containing from 10 to 20 grams per liter of a soluble fluoride.

14. An electrolyte for use in the manufacture of electrolytic iron, comprising an acid ferrous chloride solution containing a relatively small proportion of a soluble fluoride compound but in sufficient proportion to act as a buffer for the electrolyte for maintaining it at a pH value of from 4 to 6.

15. A process for producing electrolytic iron, which comprises depositing iron on a cathode mounted in an acid ferrous electrolyte maintained at a suitable temperature for electrolysis, said electrolyte containing sufficient fluoride in solution to act as a buffer agent to aid in controlling the pH value of the electrolyte, adding acid to the electrolyte during the electrolysis, and maintaining the pH value of the electrolyte at from 4 to 6 during the electrolysis.

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