This invention is concerned with an improved pickling process and more particularly with the pickling of ferrous materials.

Ferrous metals acquire an adherent oxide coating at various steps in their fabrication. It is sometimes essential that this coating be removed prior to the next step in the processing operation and it is nearly always essential that the completed product be substantially free from the oxide coating. The conventional method employed to remove the coating is to dissolve it in a dilute bath of sulphuric acid. Sulphuric acid readily removes the oxide coating and a ferrous sulphate solution is formed. While the cost of the sulphuric acid is not inconsequential, the difficulty involved in the disposal of the large volume of acidic ferrous sulphate solution is the principal objection to this process.

Other acids can be employed to remove the oxide coating but as sulphuric acid is normally the cheapest available acid, there has been little point in employing any other acid, particularly as the waste disposal problem is not abated. Work which has been done using hydrochloric acid as a pickling reagent has proven that it very satisfactorily removed the oxide film. In view of the discrepancy in cost between the two reagents, only a small amount of hydrochloric acid has been used for pickling purposes.

It is an object of this invention to permit the use of hydrochloric acid as a pickling reagent at a cost substantially lower than the cost of the equivalent quantity of sulphuric acid.

It is a further object of this invention to completely avoid the formation of any waste product and hence eliminate the waste disposal problem completely.

It is a further object of this invention to recover the iron oxide removed in the pickling operation. These several objects and others to be stated below are accomplished by our novel pickling process.

In carrying out the novel process the material to be pickled is contacted with a relatively dilute hydrochloric acid solution at a temperature which is varied depending upon the type of steel or iron being treated, the equipment available for carrying out the process and the rate at which pickling is to be accomplished but usually at a temperature below 100°C. As the acid is consumed, additional hydrochloric acid is added to the solution. Hydrochloric acid or hydrogen chloride may be continuously added to the pickling bath until the volume of ferrous chloride solution becomes excessive or the ferrous chloride concentration becomes so high that the pickling action is inhibited. When the pickle is thus rendered inactive the ferrous chloride solution resultant from the pickling operation is then treated with magnesium oxide or hydroxide to form ferrous hydroxide. Due to the fact that magnesium hydroxide is not very soluble, it is not possible to convert all the iron to insoluble ferrous hydroxide. However, by blowing air through the solution while carrying out the treatment with magnesium oxide, iron can be quantitatively precipitated from the solution. The reactions involved may be represented as follows:

\[(1) \text{FeCl}_2 + \text{Mg(OH)}_2 = \text{Fe(OH)}_3 + \text{MgCl}_2\]

\[(2) 4\text{Fe(OH)}_2 + 2\text{H}_2\text{O} + \text{O}_2(\text{air}) = 4\text{Fe(OH)}_3\]

It can be seen that by carrying out the precipitation operation in one step, all the iron must be converted to ferric hydroxide before the iron is quantitatively removed from solution. However, by carrying out the iron removal in two steps, it is not necessary to oxidize all the iron, and still the iron can be quantitatively removed from solution. The two step operation is carried out as follows: The concentrated ferrous chloride solution from the pickling operation is treated with a slurry of magnesium hydroxide plus some ferric hydroxide whose source will be indicated below. Sufficient magnesium hydroxide should be added to convert as much of the ferrous chloride to ferrous hydroxide as possible. The amount, as will be understood, will depend upon the ferrous chloride concentration, the free hydrochloric acid present, the temperature of operation and the like. The amount that should be employed may be readily ascertained for the conditions existent in any particular installation by insuring the presence of a small amount of excess solid magnesium hydroxide in the ferrous hydroxide precipitate after the mixture has been contacted for a sufficient period to reach equilibrium. The ferrous hydroxide precipitate will contain a small amount of magnesium hydroxide and a small amount of ferric hydroxide. The solution will be composed of magnesium chloride plus some dissolved ferrous chloride.

The precipitate produced, as described above, is separated and the solution is then treated with an excess of magnesium oxide and blown with air. The magnesium oxide hydrates to form insoluble magnesium hydroxide. The air oxidizes some of the iron to the ferric state. As ferric hydroxide is much less soluble than magnesium hydroxide or ferrous hydroxide, the ferric iron precipitates as ferric hydroxide. This permits more ferrous iron.
to be oxidized and in this way the iron is progressively precipitated as the blowing with air continues. In a very short period of time, the small amount of iron initially present is quantitatively removed from solution. The iron-free solution of magnesium chloride is separated from the magnesium hydroxide and ferric hydroxide by filtration, settling or centrifuging. The mixed hydroxides are used to treat the ferrous chloride in the manner previously described.

The iron-free magnesium chloride solution is evaporated to form hydrated magnesium chloride. The hydrated magnesium chloride is then thermally decomposed to form magnesia and hydrochloric acid. This reaction may be represented as follows:

\[ \text{MgCl}_2.4\text{H}_2\text{O} = \text{MgO} + 2\text{HCl} + 3\text{H}_2\text{O} \]

The hydrochloric acid thus regenerated is absorbed and returned to the pickling operation. The magnesium oxide similarly is returned to the precipitation step. If desired, ferrous chloride solution may be circulated through the hydrochloric acid absorber. The ferrous chloride solution fortified with hydrochloric acid is returned to the pickling step. This permits the ferrous chloride concentration to be readily built up in the pickling step.

As will be perceived the process is eminently effective and simple to carry out. The only losses involved are those due to mechanical causes. Both the magnesium oxide and hydrochloric acid are substantially completely recovered. The iron hydroxides may be mixed with the incoming iron ore and recharged to the blast furnace. Obviously, it may be treated to produce other iron products if desired.

While preferred modifications of the invention have been described, it is to be understood that these are given to explain the underlying principles of the improved cyclic pickling method and not as limiting the useful scope of the invention except as such limitations are clearly imposed by the appended claims.

We claim:

1. In the regeneration of spent hydrochloric acid pickles derived from pickling ferrous metals that improvement which comprises, treating the solution with an excess of magnesium hydroxide to precipitate a quantity of the contained iron as ferrous hydroxide; separating the precipitate from the solution; treating the solution with magnesium oxide and air to precipitate further quantities of iron as ferric hydroxide; separating the precipitate; evaporating the solution to form hydrated magnesium chloride and thermally decomposing the magnesium chloride to regenerate magnesium oxide and hydrogen chloride.

2. In the regeneration of spent hydrochloric acid pickles derived from pickling ferrous metals that improvement which comprises, treating the solution with a slurry of magnesium hydroxide and ferric hydroxide to thereby precipitate a quantity of the contained iron as iron hydroxide; separating the precipitate from the solution; treating the separated solution with magnesium oxide and air to precipitate additional quantities of iron and some magnesium; separating the precipitate from the solution; utilizing said last-named precipitate for treating additional quantities of spent pickle; evaporating the last-named solution to form hydrated magnesium chloride; thermal dehydrating the hydrated magnesium chloride to form magnesium oxide and hydrogen chloride, utilizing the magnesium oxide to treat spent pickle and utilizing the hydrogen chloride for pickle make-up.

3. A method of pickling ferrous material which comprises, contacting the material with a hydrochloric acid solution derived from the thermal decomposition of hydrated magnesium chloride, utilizing such solution until it contains a substantial concentration of iron chloride, treating such iron chloride solution with magnesium oxide and air to precipitate most of the iron as ferric hydroxide, separating the precipitate from the magnesium chloride solution. Evaporating such chloride solution and heating the residue to effect the said thermal decomposition to produce the magnesium oxide and hydrochloric acid.

4. A method of pickling ferrous material which comprises, contacting the material with a hydrochloric acid solution derived from the thermal decomposition of hydrated magnesium chloride, utilizing such solution until it contains a substantial concentration of iron chloride, treating such iron chloride solution with magnesium oxide and air to precipitate most of the iron as ferric hydroxide, separating the precipitate from the magnesium chloride solution. Evaporating such chloride solution and heating the residue to effect the said thermal decomposition to produce the magnesium oxide and hydrochloric acid.

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