

The present invention relates to a process for the preparation of ferric chloride from dilute hydrochloric acid. It relates more particularly to the preparation of ferric chloride in aqueous solution whose analysis by titration is between 35 and 45% by weight. This ferric chloride formulation is employed as a flocculating agent in water treatment. Reference may be made to Kirk-Othmer, 3rd edition, volume 24, pages 394-396 (1984) and to volume 10, page 498 (1980), where this application appears. The simplest process consists in digesting iron with concentrated hydrochloric acid; a solution containing approximately 36% by weight of ferrous chloride (FeCl_2) is thus obtained, and this is chlorinated to obtain a solution of ferric chloride (FeCl_3) analysing by titration at approximately 41% by weight and capable of being employed directly as a flocculating agent. This 41% solution is the usual commercial form. A concentrated solution of FeCl_2 must be obtained, because in the course of a concentration by evaporation FeCl_2 and FeCl_3 can undergo a partial hydrolysis, giving HCl . The presence of HCl in FeCl_3 interferes with the water treatment. This process requires the use of concentrated hydrochloric acid.

US Patent 4,066,748 describes a process starting with a solution of FeCl_2 originating from a descaling bath. This process makes it necessary to concentrate the ferrous chloride and requires a two-step chlorination.

US Patent 3,682,592 describes a process which is similar to the preceding one but the ferrous chloride solution is brought into contact with oxygen.

No simple process starting with dilute acid is known. A remarkable point in the solution of hydrochloric acid is the water- HCl azeotrope concentration of 20.5% by weight at atmospheric pressure. To obtain ferrous chloride solutions containing at least 36% by weight it is necessary to start with an acid solution of approximately 24% by weight. The present invention makes it possible to employ acid of a concentration lower than the azeotrope

and avoids the disadvantages of having to concentrate the solutions of HCl and/or of ferrous chloride and/or of ferric chloride.

5 The present invention consists in preparing ferric chloride from dilute hydrochloric acid and comprises the following steps.

a) Iron is placed in contact with a solution containing dilute hydrochloric acid until the said hydrochloric acid has disappeared.

10 b) The solution obtained is chlorinated to obtain a solution of ferric chloride.

c) The solution obtained in b) is decompressed.

d) The liquid phase obtained in c) is partially recycled to step b), the remaining part forms the ferric
15 chloride output.

Iron or iron oxides or a mixture of iron and of iron oxides are employed. It is convenient to employ iron cuttings, such as wastes from the machining of steel components, turnings resulting from the boring of steel
20 components, or stamping residues. This recovered iron is oxidised to a greater or lesser extent. The solution containing dilute hydrochloric acid may be an aqueous solution of hydrochloric acid containing between 15 and 25% by weight of hydrochloric acid. The use of a higher
25 concentration would not constitute a departure from the scope of the invention, but it would be much simpler in this case to employ a conventional process such as described in the prior art. The invention is particularly useful for so-called residual acids which cannot be
30 concentrated beyond the azeotrope. In general, these acids are at a concentration of between 15% by weight and the azeotrope. The use of an acid containing less than 15% by weight of hydrochloric acid would not constitute a departure from the scope of the invention, but it would
35 be much simpler to concentrate this acid to above 15% by a conventional distillation. The solution containing dilute hydrochloric acid may also contain ferrous chloride and possibly already a little ferric chloride.

This step a) may be carried out in any manner, but the operation is advantageously carried out at atmospheric pressure in vessels, and arrangements are made such that there is always an excess of iron, to ensure that no hydrochloric acid remains in the ferrous chloride solution which is obtained at the end of this step a). The reaction between iron and hydrochloric acid is complete and stoichiometric. Although the solution containing the hydrochloric acid may be at any temperature, a solution is advantageously employed between 20 and 50°C and preferably between 35 and 45°C. The residence time of the acid may be of any length, but advantageously it is between 2 minutes and 30 hours, and preferably between 3 and 15 hours. It would not constitute a departure from the scope of the invention to add in this step a), in addition to a solution of dilute hydrochloric acid, a solution containing hydrochloric acid and ferrous chloride or only ferrous chloride, this being, for example, a solution originating from a descaling bath. It is preferable that the quantity of a solution of this kind does not represent more than 20% and, better, 10% by weight of the solution of residual hydrochloric acid. Using only a solution originating from a descaling operation and which contains FeCl_2 and HCl would not constitute a departure from the scope of the invention, but this solution must not contain an excess of heavy metals, which are a hindrance in the ferric chloride intended for the preparation of drinking water. Before chlorinating the solution obtained in a) it is advantageous to filter it or to decant it.

Step b) is performed by bringing the solution of ferrous chloride obtained in a) into contact with chlorine and a solution of ferric chloride. Liquid or gaseous chlorine, or a fluid containing chlorine may be employed. The contacting may be carried out in any manner; it suffices to ensure contact between the chlorine and the ferrous chloride. The device employed may have a number of stages operating in parallel or in

series and fed concurrently or countercurrentwise or in any combination of these principles.

For example, a stirred reactor or a column of the distillation column or absorption column type may be employed. Advantageously, a column equipped with contact devices such as plates or packing rings or a number of these devices may be employed. The ferrous chloride solution and the ferric chloride solution feed the column at the top and the chlorine is introduced at the bottom of this column. A little chlorine is collected at the top of this column if an excess thereof has been employed (relative to the quantity of ferrous chloride), together with the gases which may have accompanied the chlorine and a little water vapour entrained by its vapour pressure. A solution of ferric chloride is obtained at the bottom of the column. It would not constitute a departure from the scope of the invention to introduce the ferrous chloride and ferric chloride solutions at a number of points in the column, the same applying in the case of the chlorine, which may be introduced at a number of points.

The ferric chloride solution obtained is next decompressed and the liquid phase collected during this decompression is partly recycled into step b), the remainder forming the ferric chloride output. During the decompression, a gaseous phase consisting essentially of water vapour is obtained.

The chlorination of ferrous chloride to ferric chloride is complete and stoichiometric. Advantageously, a ferrous chloride residence time of at least 10 seconds, and preferably shorter than 4 hours is observed. It is not necessary to chlorinate all the FeCl_2 , and the specifications for FeCl_3 sometimes allow from 0.1 to 1% by weight of FeCl_2 in the ferric chloride solution. The use of an excess of chlorine would not constitute a departure from the scope of the invention. The temperature of the ferrous chloride solution originating from step a) is advantageously between 40 and 100°C, and preferably

between 60 and 90°C. The temperature of the ferric chloride solution which is recycled and which originates from the decompression in step c) results from the temperature at the outlet of step b) and from the pressure at which the decompression takes place. This temperature of the recycled ferric chloride at the entry to step b) is advantageously between 50 and 90°C, and preferably between 55 and 80°C. The temperature of the ferrous chloride originating from step a), and the temperature of the ferric chloride recycled to the top of step b) may be modified, for example with the aid of heat exchangers; preferably, these solutions are employed without their temperature being modified. The temperature of the outlet ferric chloride solution depends essentially on the temperatures of the solutions at the entry and on the quantity of ferrous chloride to be converted into ferric chloride, but also on whether the apparatus employed to perform this step b) is adiabatic, isothermal, etc.

An adiabatic apparatus is preferred; the outlet temperature of the solution at the end of this step b) is advantageously between 60 and 95°C, and preferably 65 and 90°C. Although the operation may be carried out at any pressure, it is simpler to perform this step b) at atmospheric pressure or at a pressure close to it, and this solution is decompressed from atmospheric pressure to a pressure of between 0.3 and 0.05 bar absolute. This decompression is carried out in a vessel of any kind; it merely suffices that it is possible to separate the gaseous phase and the liquid phase which results therefrom. The vacuum is provided, for example, by a pump or a steam ejector.

In a stationary regime, the quantity of ferric chloride forming the output corresponds, in the number of moles, to the quantity of ferrous chloride at the entry of step b). The quantity of ferric chloride solution recycled to step b) is advantageously between 5 and 10 times the quantity of the ferric chloride solution

forming the output in a stationary regime.

According to another form of the invention, the ferric chloride solution originating from step b) may also be heated before being decompressed.

5 The exchangers which may be installed in the ferrous chloride solution at the entry to step b) in the ferric chloride solution at the outlet of step b) and in the recycled ferric chloride solution may also be used to extract the heat energy in the case where the reaction
10 becomes excessively exothermic, for example if the concentration of hydrochloric acid drifts towards high values.

 According to another preferred embodiment of the invention, and provided that the temperature levels are
15 compatible, the heat energy from the production of ferric chloride may be transferred towards the ferrous chloride solution feeding step b).

 The single plate shows a particular embodiment of the invention. For the sake of clarity, the pumps, the
20 valves, etc. have not been shown.

 (1) shows the vessel for mixing iron (5) with a solution of hydrochloric acid (6). A solution (7) of ferrous chloride is obtained and is filtered in (2). Column (3) is fed with a stream of ferrous chloride (8)
25 and with a solution of ferric chloride (9). This column is fed with a stream of gaseous chlorine (14). The ferric chloride solution (10) is decompressed in the pot (4), a ferric chloride solution (12) is obtained and is divided into an output (13) and a fraction which is recycled (9).
30 The decompression pot (4) is connected via the pipe (11) to a steam ejector, not shown. The inerts and any unreacted chlorine are removed in the stream (15).

 The following examples illustrate the invention without limiting it.

35 EXAMPLE 1

 A device in accordance with the enclosed single plate is employed, in which the column 3 is made of glass, with an inner diameter of 0.35 m, and has a

packing height of 10 m.

A solution containing 170 kg/h of hydrochloric acid in 680 kg/h of water is introduced at 5. A quantity of iron turnings which is greatly in excess relative to the quantity of HCl has been introduced beforehand at 6. The ferrous chloride solution is filtered and then introduced at 8 into the column 3; its temperature is 70°C. A flow of 82.7 kg/h of gaseous chlorine is introduced at 14, together with 5 kg/h of inerts which are found again at the outlet 15. The column 3 operates at 1.1 bars absolute. The ferric chloride solution at 82°C is conveyed by the pipe 10 to the decompression pot 4, where it is decompressed to 0.2 bars; its temperature drops to 70°C. At 13, the output is 379 kg/h of FeCl₃ diluted in 545 kg/h of water. 2272 kg/h of FeCl₃ diluted in 3269 kg/h of water are recycled via 9.

EXAMPLE 2

The procedure is as in Example 1, but the solution of hydrochloric acid is more dilute, that is to say 170 kg/h of HCl in 963 kg/h of water; the temperature of the stream 8 is 60°C. The ferric chloride solution obtained at 10 is at 84°C; it is heated to 93°C before decompression to 0.12 bars. After the decompression, the same concentrated solution as in Example 1 is obtained at 13, but at 57°C and a quantity of 3032 kg/h of FeCl₃ diluted with 4360 kg/h of water is recycled. This solution is heated to 75°C before returning at 9 into the column 3.

CLAIMS

1. Process for the preparation of ferric chloride from dilute hydrochloric acid, characterised in that it comprises the following steps:

5 a) iron is placed in contact with a solution containing dilute hydrochloric acid until the said hydrochloric acid has disappeared,

b) the solution obtained is chlorinated to obtain a solution of ferric chloride,

10 c) the solution obtained in b) is decompressed,

d) the liquid phase obtained in c) is partially recycled to step b); the remaining part forms the ferric chloride output.

2. Process according to Claim 1, characterised in that a solution analysing by titration between 15% by weight of hydrochloric acid and the composition of the water-HCl azeotrope is employed in step a).

3. Process according to either of Claims 1 and 2, characterised in that the quantity of ferric chloride
20 which is recycled is between 5 and 10 times the output.

