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(54) Process for preparing usable products from an impure ferric sulfate solution

Verfahren zur Herstellung von verwendbaren Produkten aus einer verunreinigten
Eisen(III)-Sulfatlösung

Procédé de préparation de produits utiles à partir d'une solution de sulfate ferrique

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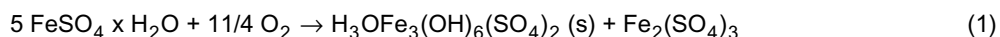
Description**Field of the invention**

5 **[0001]** The invention relates to a process for preparing usable products, in particular a water treatment solution which contains ferric iron, from an impure ferric sulfate solution, in particular a ferric sulfate solution formed in the process for preparing hydronium jarosite.

State of the art

10 **[0002]** US 3 816 593 discloses a process for regenerating a waste pickling liquor containing as impurity iron-sulfur compounds comprising ferrous sulfate. This process comprises the step (a) of oxidizing said iron-sulfur compounds comprising ferrous sulfate to ferric sulfate, and the step (b) of adding a caustic material to bring the pH to at least 2 to form precipitates comprising ferric hydroxide. Subsequently the precipitates are separated and the generated pickling liquor is returned to pickling service.

15 **[0003]** The applicant's earlier patent application WO 97/38944 discloses a process for preparing a pure product which contains ferric iron. In this process, the initial substance is hydrous ferrous sulfate produced as a byproduct in the process for preparing titanium dioxide. The ferrous sulfate is oxidized with oxygen in a pressurized vessel at an elevated temperature. During the oxidation the ferrous salt dissolves in its own crystal water, and simultaneously hydronium jarosite begins to precipitate. The reaction equation is



25 **[0004]** During the oxidation step, an equilibrium forms between the ferric sulfate solution and the hydronium jarosite. At this time approximately one-half of the iron is in the solution and the other half is in the form of precipitated hydronium jarosite. The solid jarosite is filtered out, and it is used for the preparation of pure water treatment chemicals. A solution containing ferric sulfate is left. The use of this solution has proved to be problematic, since it forms in a considerable amount in proportion to the amount of hydronium jarosite. Its storage is cumbersome and expensive. There is the additional difficulty that the solution contains most of the impurities of the original ferrous sulfate, in particular manganese.

Object of the invention

35 **[0005]** The problem is thus the further treatment of the impure ferric sulfate solution and its potential exploitation. It is therefore an object of the invention to find a method for the exploitation of the impure ferric sulfate solution in such a manner that no materials to be stored and/or eliminated are left from the process for the preparation of hydronium jarosite. It is thus an object to improve the profitability of the process for the preparation of hydronium jarosite.

Invention

40 **[0006]** According to the invention, there is provided a process for preparing a product, in particular a water treatment solution which contains ferric iron, from an impure ferric sulfate solution which contains at least one other metal as an impurity,; the process being characterized in that it comprises a first precipitation step, in which a base is added to the said impure ferric sulfate solution in order to raise the pH to 2-5, preferably approx. 3-4, whereupon ferric hydroxide precipitates; following the first precipitation step, a second precipitation step, in which there are added to the solution an oxidant and a base in order to raise the pH to 6-10, preferably approx. 8-9, whereupon the said impurity metal precipitates; and one or more separation steps for separating from the sulfate solution the solids precipitated during the first and the second precipitation steps; and possibly an additional step, in which the said separated solids, or a portion thereof, are treated further in order to form a usable product.

50 **[0007]** In the process according to the invention there is preferably used as the initial substance an impure ferric sulfate solution which is formed as a byproduct of the process for the preparation of hydronium jarosite and which contains as an impurity manganese, which precipitates as manganese oxide in the second precipitation step.

55 **[0008]** Thus the process according to the invention comprises two separate precipitation steps, ferric hydroxide being precipitated in the first precipitation step and the impurity metal, such as manganese dioxide, being precipitated in the second precipitation step.

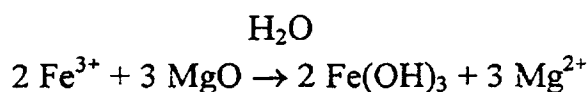
[0009] Alongside or in addition to manganese the impurity metal may be, for example, nickel and/or zinc. At the pH

concerned, these impurity metals precipitate as hydroxide.

[0010] According to one embodiment of the invention, the base added to the first precipitation step is added in the form of a solution or an aqueous suspension, which contains in part or entirely the sulfate solution obtained from the separation step. In this manner the amount of water circulating in the process can be regulated and thereby the concentration of the sulfate solution can be affected.

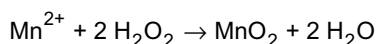
[0011] The base may be MgO, Mg(OH)₂, MgCO₃, NH₃, NaOH, KOH. In this case the said sulfate solution respectively contains soluble MgSO₄, (NH₄)₂SO₄, Na₂SO₄ or K₂SO₄.

[0012] One usable magnesium-containing base is an aqueous suspension prepared from calcined and ground magnesite. Another option is a suspension which contains magnesium hydroxide. As was pointed out, the suspending can be carried out in water or in the sulfate solution obtained as the final product of the process, or in a suitable mixture of these. Thus there is obtained a basic suspension, which is added to the ferric sulfate solution in order to precipitate iron. The pH of the ferric sulfate solution is originally approx. 1, and in the first precipitation step it is raised to the range of approx. 2-5, preferably approx. 3-4, at which iron precipitates in the form of ferric hydroxide. When magnesium oxide is used as the base in the first precipitation step, there thus occurs the reaction



[0013] The precipitated ferric hydroxide is in an amorphous state, in which state its solubility in acids is at its best.

[0014] In the second precipitation step, the pH of the solution is raised to approx. 6-10, preferably approx. 8-9, by adding a base, such as NaOH, KOH, Na₂CO₃ or NH₃, to the solution. In addition, an oxidant, such as H₂O₂, is added to the solution, whereupon the Mn²⁺ oxidizes and precipitates as manganese dioxide. Thus the reaction occurring in the second precipitation step is:



[0015] As the oxidant it is possible to use oxygen oxidants such as hydrogen peroxide, other peroxy compounds, or ozone. In addition it is possible to use chlorine, chlorine dioxide, chlorite, hypochlorite or chlorate.

[0016] According to one embodiment of the invention, the process comprises a joint separation step, in which the solids formed in both the first and the second precipitation steps are separated together from the sulfate solution.

[0017] According to another embodiment of the invention, the process comprises a first separation step, in which the solids precipitated in the first precipitation step are separated from the sulfate solution, and a second separation step, in which the solids precipitated in the second precipitation step are separated from the sulfate solution.

[0018] The solids precipitated in the first and second precipitation steps are preferably separated by filtration, but also other separation methods can be used.

[0019] The filtrate is a Mg sulfate solution the Mg content of which ranges from 0.5 to 5 %, depending on the composition of the basic suspension of the first step. Such a solution is suitable for use, for example, for the bleaching of cellulose. If the Mg content of the solution is sufficiently high, the magnesium sulfate can be separated from the solution by crystallization. Crystalline magnesium sulfate can be used, for example, as a trace element in fertilizers.

[0020] The separated solids contain as the principal component a ferric hydroxide precipitate which can be used for preparing an iron chemical suitable for the treatment of waste water. Since ferric hydroxide is a solid product, it can easily be transported to distant places, where it is dissolved in an acid in order to prepare a solution chemical suitable for waste water applications. Nitric acid is especially suitable. Ferric nitrate solutions are suitable for uses in which the water chemical is required to have oxidizing properties, for example, in the deodorization of waste waters which contain hydrogen sulfide.

[0021] In that embodiment of the process according to the invention which contains a joint separation step, the use of nitric acid is advantageous also for the reason that manganese dioxide present in ferric hydroxide does not readily dissolve in nitric acid. Thus most of the manganese dioxide remains undissolved and settles at the bottom of the container. Thus a solution is obtained which has a lower concentration of manganese. Another option is to remove the undissolved portion by filtration.

[0022] In addition to nitric acid it is also possible to use hydrochloric acid, sulfuric acid or an organic acid such as formic acid for the dissolving of the ferric hydroxide precipitate. The selection of the acid depends on the purpose for which the iron chemical is needed. For example in treatment use which includes a biologic treatment, ferric hydroxide dissolved in an organic acid would be highly usable, since both the anion and the cation present in the chemical would

be exploited in the treatment process.

[0023] The invention is described below with the help of preparation examples, with reference to the accompanying drawings, in which

Figure 1 depicts a block diagram of an embodiment of the process according to the invention and
Figure 2 depicts a block diagram of another embodiment of the process according to the invention.

[0024] Figure 1 depicts one embodiment of the process according to the invention, having first two successive precipitation steps and thereafter one separation step. The solid material obtained in the separation step contains in the main ferric hydroxide, but also manganese dioxide and possibly other impurities. The solid material is used for the preparation of an iron chemical by dissolving it in a suitable acid. The solution obtained from the separation step is a pure solution containing magnesium sulfate.

[0025] Figure 2 depicts another embodiment of the process according to the invention, having two precipitation steps and two separation steps in such a manner that a separation of solids is carried out after each precipitation step. Ferric hydroxide is separated after the first precipitation step. The ferric hydroxide precipitate thus obtained does not contain impurities and is therefore a highly useful raw material for the preparation of a pure iron chemical. The manganese and other impurities, if any, present in the solution are precipitated in the second precipitation step. They are separated in the second separation step and a waste precipitate is obtained which can be disposed of, for example, by taking it to a dump. What is left is a pure solution containing magnesium sulfate.

Example 1

Precipitation of iron

[0026] The experiments were carried out as continuous-working laboratory-scale processes. The initial solution was obtained from the process for the preparation of hydronium jarosite and its analysis was as follows: Fe 4 %, Fe^{2+} 0.08 % and Mn 490 ppm. For the precipitation of iron, a suspension having a Mg concentration of 2.4 % was prepared from a MgO powder and a water solution containing magnesium sulfate. This suspension was added to the solution continuously while maintaining the pH at 3.5, whereupon $\text{Fe}(\text{OH})_3$ precipitated. The reaction vessel was an open reactor equipped with a stirrer and a heating mantle. The temperature was maintained at 40 °C and the retention time was 1 h. A specimen taken from the reactor was filtered, and the filtrate was analyzed: Mg 1.9 %, Mn 311 ppm, Ni 1.9 ppm, $\text{Fe}^{2+} < 0.01$ %. The filter cake was dried and analyzed: Fe 47.4 %, Mg 1.5 %, state amorphous. The concentration of manganese in the precipitate was not analyzed, but a calculation showed that all of the Mn had passed into the filtrate.

[0027] The experiments carried out showed that the lower the temperature of the precipitation step, the higher the reactivity of the hydroxide precipitate obtained. The suitable temperature range was 20-40 °C and the most preferable range was 20-30 °C.

Example 2

Precipitation of manganese

[0028] To the suspension of Example 1, NaOH (25 % solution) and H_2O_2 (10 % solution) were added in order to precipitate the manganese. The base was fed deep under the surface of the solution, whereas the hydrogen peroxide was added directly to the surface. The pH was adjusted to 8-9. The retention time was approx. 1 h and the temperature was 40 °C. After the second precipitation step the solids were separated from the suspension by using a laboratory filter, and the filtrate was analyzed: Mg 1.1 %, Mn < 0.3 ppm, pH 9.15. The filtrate had thus been purified of impurities.

Example 3

Dissolving of iron precipitate

[0029] The following experiment was carried out to dissolve the ferric hydroxide precipitate obtained above. Water (30.3 g), ferric hydroxide precipitate (115.7 g, solids content 66 %) and nitric acid (172 g, concentration 65 %) were placed in a laboratory vessel. Owing to an exothermal reaction, the temperature rose to 50 °C, from which it was raised further to approx. 80 °C by heating the vessel. After approx. 15 min almost all of the ferric hydroxide had dissolved, and free acid remained in an amount of only 1.1 %. The dissolving was, however, continued until the total dissolving time was 2 h. The solution was analyzed: Fe 7.8 %, Mg 2.6 %, Mn 530 ppm, Ni 13 ppm, N 8 % (NO_3 35.4 %), free HNO_3 0.4 %, undissolved 0.13 %. The undissolved material was analyzed semi-quantitatively by X-ray fluorescence:

Fe was the principal component, Mg and Mn were present in an amount of approx. 5-10 %. This shows that the iron precipitate dissolved well in nitric acid.

Claims

1. A process for the preparation of a product, in particular a water treatment solution which contains ferric iron, from an impure ferric sulfate solution which contains at least one other metal as an impurity, **characterized in that** the process comprises

a first precipitation step, in which a base is added to the said impure ferric sulfate solution in order to raise the pH to 2-5, preferably approx. 3-4, whereupon ferric hydroxide precipitates;
following the first precipitation step, a second precipitation step, in which there are added to the solution an oxidant and a base to raise the pH to 6-10, preferably approx. 8-9, whereupon the said impurity metal precipitates; and one or more separation steps for separating from the sulfate solution the solids precipitated in the first and second precipitation steps; and
possibly an additional step, in which the said separated solids, or a portion thereof, are treated further in order to form a usable product.

2. A process according to Claim 1, **characterized in that** the impure ferric sulfate solution is a byproduct formed in the process for the preparation of hydronium jarosite.

3. A process according to Claim 1 or 2, **characterized in that** the said impurity metal is manganese, which precipitates as manganese dioxide in the second precipitation step.

4. A process according to any of the above claims, **characterized in that** the base added to the first precipitation step is magnesium oxide, magnesium hydroxide or magnesium carbonate, ammonia, sodium hydroxide or potassium hydroxide.

5. A process according to any of the above claims, **characterized in that** the oxidant added to the second precipitation step is an oxygen oxidant such as hydrogen peroxide, some other peroxy compound or ozone; chlorine, chlorine dioxide, chlorite, hypochlorite, or chlorate.

6. A process according to any of the above claims, **characterized in that** the base added to the second precipitation step is sodium hydroxide, potassium hydroxide, sodium carbonate or ammonia.

7. A process according to any of the above claims, **characterized in that** it comprises a joint separation step in which the solids precipitated during both the first and the second precipitation steps are separated together from the sulfate solution.

8. A process according to any of Claims 1-6, **characterized in that** it comprises a first separation step in which the solids precipitated in the first precipitation step are separated from the sulfate solution and a second separation step in which the solids precipitated in the second separation step are separated from the sulfate solution.

9. A process according to any of the above claims, **characterized in that** in the separation step or steps the solids are separated from the sulfate solution by filtration.

10. A process according to any of Claims 7-9, **characterized in that** the sulfate solution obtained from the joint separation step or the second separation step is recycled in part or entirely to the first precipitation step.

11. A process according to Claim 7, **characterized in that** the process comprises an additional step, in which the solids obtained from the joint separation step, containing ferric hydroxide and the impurity metal such as manganese dioxide, are dissolved in an acid in order to form a water treatment solution which contains ferric iron, the impurity metal such as manganese dioxide remaining undissolved.

12. A process according to Claim 11, **characterized in that** the water treatment solution which contains ferric iron is separated from the undissolved material.

13. A process according to Claim 8, **characterized in that** the process comprises an additional step in which the solids obtained from the first separation step, containing ferric hydroxide, are dissolved in an acid in order to form a water treatment solution which contains ferric iron.

14. A process according to Claim 11-13, **characterized in that** the acid is nitric acid, in which case the formed water treatment solution is a solution of ferric nitrate.

Patentansprüche

1. Verfahren für die Herstellung eines Produktes, insbesondere einer Wasserbehandlungslösung, welche Eisen(III) enthält, aus einer verunreinigten Eisen(III)-sulfatlösung, die wenigstens ein anderes Metall als eine Verunreinigung enthält, **dadurch gekennzeichnet, daß** das Verfahren umfaßt eine erste Ausfällungsstufe, in der eine Base zu dieser verunreinigten Eisen(III)-sulfatlösung zum Anheben des pH auf 2-5, bevorzugt annähernd 3-4, zugegeben wird, woraufhin Eisen(III)-hydroxid ausfällt; folgend auf die erste Ausfällungsstufe eine zweite Ausfällungsstufe, in der zu der Lösung ein Oxidationsmittel und eine Base zum Anheben des pH auf 6-10, bevorzugt annähernd 8-9, zugegeben wird, woraufhin dieses Verunreinigungsmetall ausfällt; und eine oder mehrere Trennstufen zum Abtrennen der in den ersten und zweiten Ausfällungsstufen ausgefällten Feststoffe von der Sulfatlösung; und möglicherweise eine zusätzliche Stufe, in der diese abgetrennten Feststoffe oder ein Teil hiervon zur Bildung eines brauchbaren Produktes weiter behandelt werden.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** die verunreinigte Eisen(III)-sulfatlösung ein Nebenprodukt ist, welches in dem Verfahren für die Herstellung von Hydroniumjarosit gebildet wurde.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** dieses Verunreinigungsmetall Mangan ist, welches als Mangandioxid in der zweiten Ausfällungsstufe ausfällt.

4. Verfahren nach einem der oben genannten Ansprüche, **dadurch gekennzeichnet, daß** die zu der ersten Ausfällungsstufe zugegebene Base Magnesiumoxid, Magnesiumhydroxid, oder Magnesiumkarbonat, Ammoniak, Natriumhydroxid oder Kaliumhydroxid ist.

5. Verfahren nach einem der oben genannten Ansprüche, **dadurch gekennzeichnet, daß** das zu der zweiten Ausfällungsstufe zugegebene Oxidationsmittel ein Sauerstoffoxidationsmittel, wie Wasserstoffperoxid, irgendeine andere Peroxyverbindung oder Ozon, Chlor, Chlordioxid, Chlorit, Hypochlorit oder Chlorat ist.

6. Verfahren nach einem der oben genannten Ansprüche, **dadurch gekennzeichnet, daß** die zu der zweiten Ausfällungsstufe zugegebene Base Natriumhydroxid, Kaliumhydroxid, Natriumkarbonat oder Ammoniak ist.

7. Verfahren nach einem der oben genannten Ansprüche, **dadurch gekennzeichnet, daß** es eine gemeinsame Trennstufe umfaßt, in der die Feststoffe, welche während der ersten und zweiten Ausfällungsstufe beide ausgefallen sind, zusammen von der Sulfatlösung abgetrennt werden.

8. Verfahren nach einem der Ansprüche 1-6, **dadurch gekennzeichnet, daß** es eine erste Trennstufe, in der die in der ersten Ausfällungsstufe ausgefällten Feststoffe von der Sulfatlösung abgetrennt werden, und eine zweite Trennstufe, in der die in der zweiten Ausfällungsstufe ausgefällten Feststoffe von der Sulfatlösung abgetrennt werden, umfaßt.

9. Verfahren nach einem der oben genannten Ansprüche, **dadurch gekennzeichnet, daß** in der Trennstufe oder den Trennstufen die Feststoffe von der Sulfatlösung durch Filtration abgetrennt werden.

10. Verfahren nach einem der Ansprüche 7-9, **dadurch gekennzeichnet, daß** die Sulfatlösung, welche aus der gemeinsamen Trennstufe oder der zweiten Trennstufe erhalten wurde, teilweise oder vollständig zu der ersten Ausfällungsstufe rückgeführt wird.

11. Verfahren nach Anspruch 7, **dadurch gekennzeichnet, daß** das Verfahren eine zusätzliche Stufe umfaßt, in der die Feststoffe, welche aus der gemeinsamen Trennstufe erhalten wurden, enthaltend Eisen(III)-hydroxid und das

Verunreinigungsmetall wie Mangandioxid, in einer Säure zur Bildung einer Wasserbehandlungslösung aufgelöst werden, welche Eisen(III) enthält, wobei das Verunreinigungsmetall wie Mangandioxid nicht aufgelöst verbleibt.

12. Verfahren nach Anspruch 11, **dadurch gekennzeichnet, daß** die Wasserbehandlungslösung, welche Eisen(III) enthält, von dem nicht aufgelösten Material abgetrennt wird.

13. Verfahren nach Anspruch 8, **dadurch gekennzeichnet, daß** das Verfahren eine zusätzliche Stufe umfaßt, in der die Feststoffe, welche aus der ersten Trennstufe erhalten wurden, enthaltend Eisen(III)-hydroxid, in einer Säure zur Bildung einer Wasserbehandlungslösung, welche Eisen(III) enthält, aufgelöst werden.

14. Verfahren nach Anspruch 11-13, **dadurch gekennzeichnet, daß** die Säure Salpetersäure ist, wobei in diesem Fall die Wasserbehandlungslösung eine Lösung von Eisen(III)-nitrat ist.

Revendications

1. Procédé de préparation d'un produit, en particulier une solution de traitement de l'eau contenant du fer ferrique, à partir d'une solution impure de sulfate ferrique, qui contient au moins un ou plusieurs métaux comme impureté, **caractérisé en ce que** le procédé comprend

une première étape de purification, dans laquelle une base est ajoutée à ladite solution impure de sulfate ferrique afin de porter le pH à 2-5, de préférence approximativement 3-4, ce qui déclenche la précipitation de l'hydroxyde ferrique,

à la suite de la première étape de précipitation, une deuxième étape de précipitation, dans laquelle on ajoute à la solution un oxydant et une base pour porter le pH à 6-10, de préférence approximativement 8-9, ce qui déclenche la précipitation de ladite impureté métallique,

et une ou plusieurs étapes de séparation pour séparer de la solution de sulfate les solides précipités dans les première et seconde étapes de précipitation,

et le cas échéant une étape additionnelle, dans laquelle lesdits solides séparés, ou une partie d'entre eux, sont à nouveau traités afin de former un produit utilisable.

2. Procédé selon la revendication 1, **caractérisé en ce que** la solution impure de sulfate ferrique est un produit secondaire formé dans le procédé de préparation de la jarosite d'hydronium.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** ladite impureté métallique est le manganèse, qui précipite sous forme de dioxyde de manganèse dans la deuxième étape de précipitation.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la base ajoutée lors de la première étape de précipitation est l'oxyde de magnésium, l'hydroxyde de magnésium ou le carbonate de magnésium, l'ammoniaque, l'hydroxyde de sodium ou l'hydroxyde de potassium.

5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'oxydant ajouté lors de la deuxième étape de précipitation est un oxydant oxygéné tel que le peroxyde d'hydrogène, un autre composé peroxy ou l'ozone, le chlore, le dioxyde de chlore, le chlorite, l'hypochlorite ou le chlorate.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la base ajoutée lors de la deuxième étape de précipitation est l'hydroxyde de sodium, l'hydroxyde de potassium, le carbonate de sodium ou l'ammoniaque.

7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'il** comporte une étape de séparation conjointe dans laquelle les solides précipités au cours des deux première et seconde étapes de précipitation sont séparés ensemble de la solution de sulfate.

8. Procédé selon l'une quelconque des revendications 1 à 6, **caractérisé en ce qu'il** comprend une première étape de séparation dans laquelle les solides précipités au cours de la première étape de précipitation sont séparés de la solution de sulfate, et une seconde étape de séparation dans laquelle les solides précipités au cours de la seconde étape de précipitation sont séparés de la solution de sulfate.

9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que**, dans la ou les étapes

de séparation, les solides sont séparés de la solution de sulfate par filtration.

5 10. Procédé selon l'une quelconque des revendications 7-9, **caractérisé en ce** la solution de sulfate obtenue de l'étape de séparation conjointe ou de la seconde étape de séparation est recyclée en partie ou en totalité vers la première étape de précipitation.

10 11. Procédé selon la revendication 7, **caractérisé en ce que** le procédé comporte une étape additionnelle dans laquelle les solides obtenus dans l'étape de séparation conjointe, contenant l'hydroxyde ferrique et l'impureté métallique telle que le dioxyde de manganèse, sont dissous dans un acide afin de former une solution de traitement de l'eau qui contient du fer ferrique, l'impureté métallique telle que le dioxyde de manganèse restant non dissoute.

12. Procédé selon la revendication 11, **caractérisé en ce que** la solution de traitement de l'eau qui contient du fer ferrique est séparée de la matière non dissoute.

15 13. Procédé selon la revendication 8, **caractérisé en ce que** le procédé comprend une étape additionnelle dans laquelle les solides obtenus dans la première étape de séparation, contenant de l'hydroxyde ferrique, sont dissous dans un acide pour former une solution de traitement de l'eau qui contient du fer ferrique.

20 14. Procédé selon la revendication 11-13, **caractérisé en ce que** l'acide est l'acide nitrique et dans ce cas la solution de traitement de l'eau formée est une solution de nitrate ferrique.

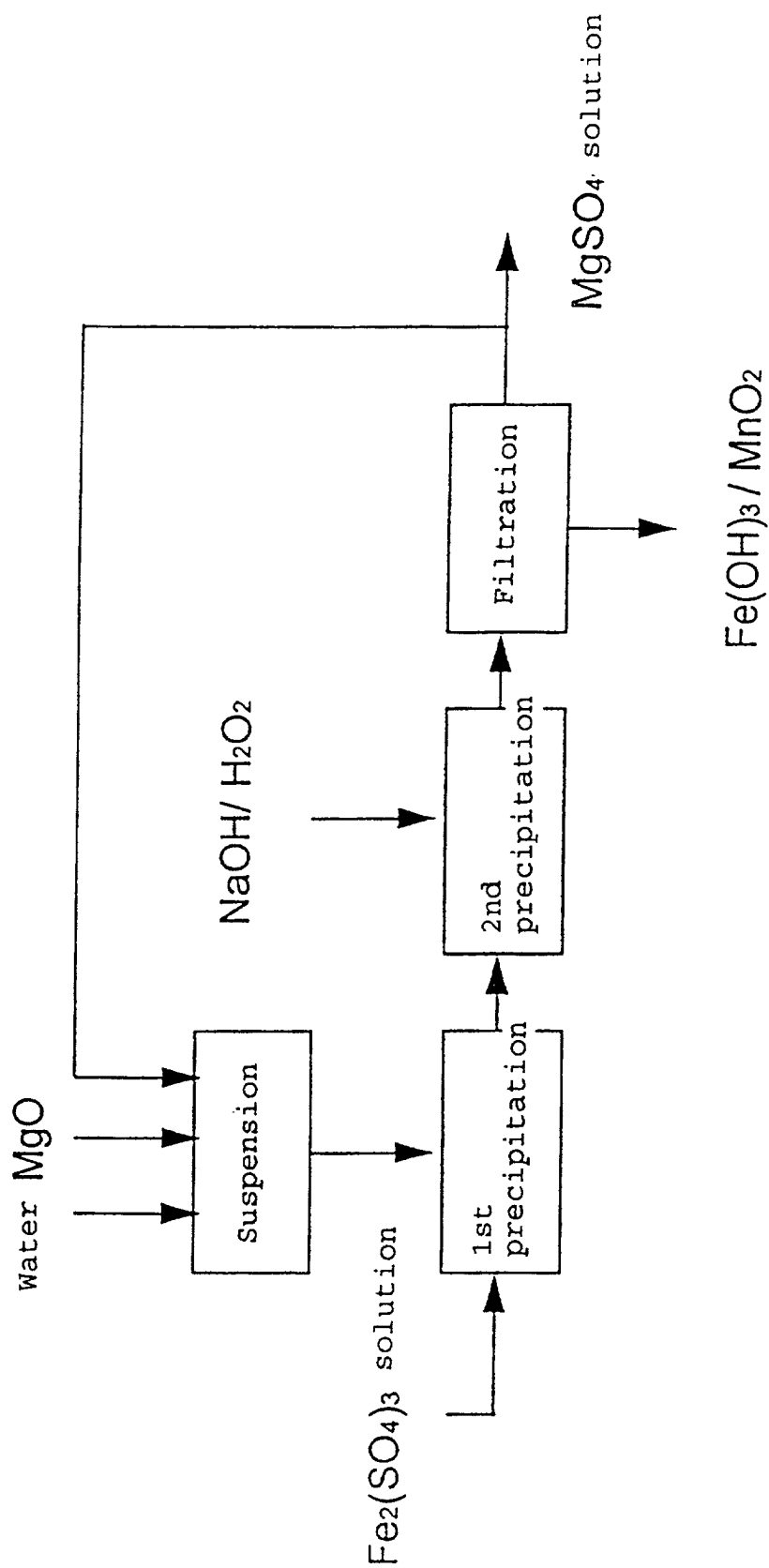


Fig. 1

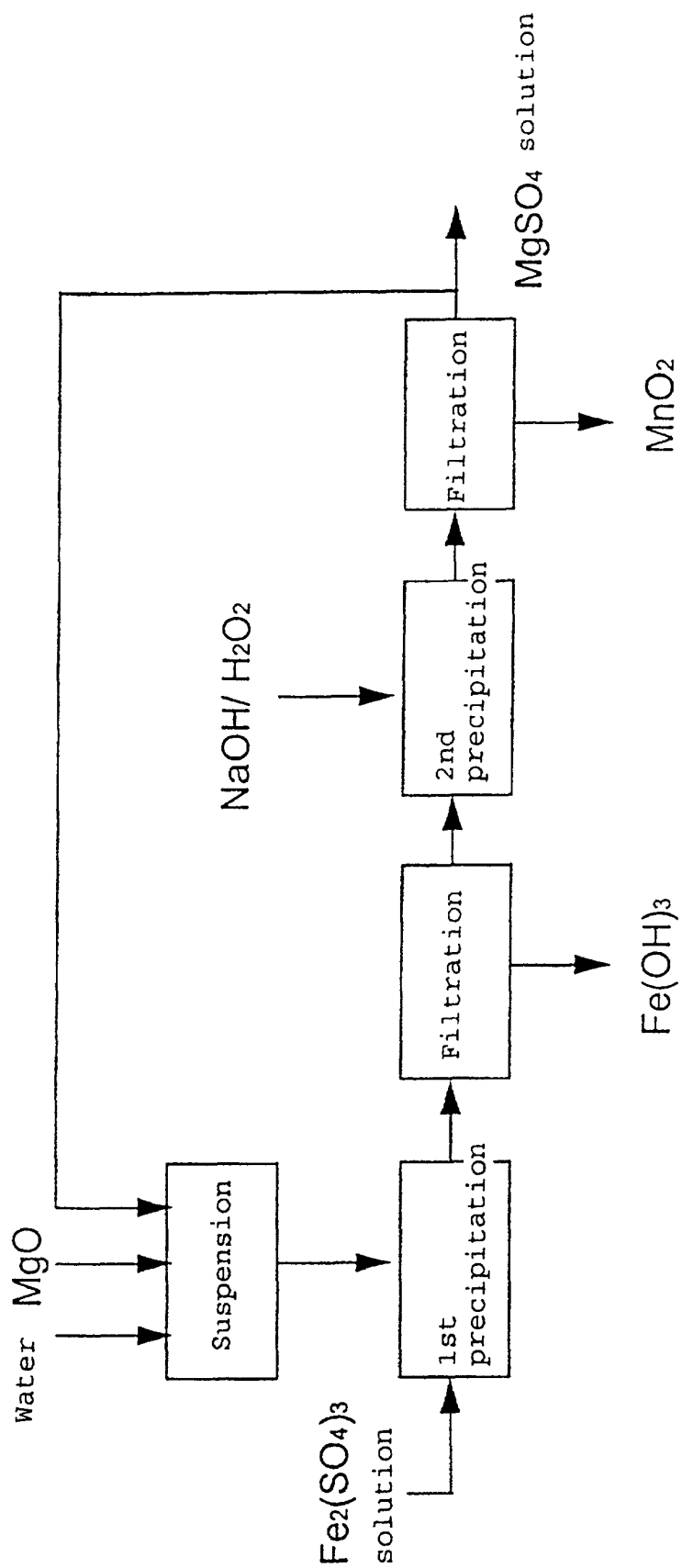


Fig. 2