

A resource recycling method for waste acids produced from surface treatment processes in electronics, semiconductors and photovoltaics industries

TECHNICAL FIELD

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[0001] Embodiments of the present disclosure are in the field of waste resource recycling and, in particular, methods of recycling waste acids produced from surface treatment processes in electronics, semiconductors and photovoltaics industries, and the resulting recovered acids.

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BACKGROUND OF THE INVENTION

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[0002] Electronic devices manufactured by industrial production, including the electronics industry, the semiconductor industry and the photovoltaics industry, provides essential services to meet common needs of modern livelihood. Generally, the substrate materials used for manufacturing the electronic devices in these industries involve a large amount of surface treatment processes that produce plenty of waste acids. Based on various specification requirements of the treated substrate surface during production, the components in the resulting waste acids are generally mixed acids. The resulting mixed acids commonly contains different kinds of acids, including two or more acids from the groups consisting of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid.

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[0003] For example, in the production of silicon based photovoltaic solar cells and semiconductor silicon wafers, a large amount of mixed waste acid containing fluorine acid and nitric acid is produced, wherein the fluorine concentration is 200 ppm to 20000 ppm and the proportion of nitric acid is 10% to 30%.

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[0004] For another example, many silicon devices used in semiconductors are coated with silicon nitride film as protection layer and require selective etching in subsequent processing. Ascribed to the good uniformity and high selectivity of silicon nitride etching by thermal phosphoric acid, the silicon nitride films are often etched with hot phosphoric acids. Furthermore, the nitric acid and hydrofluoric acid are usually added in to the hot phosphoric acid in order to expedite the etching reactions.

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[0005] Hydrochloric acid or sulfuric acid is also a common acid in the mixed acid. For a further example, in addition to the compulsory acids to be mixed required by designated specification of the surface processes, other kinds of acids, like hydrochloric acid, sulfuric acid or other organic/inorganic acids, are also required to

be used in some embodiments in the upstream and/or downstream of the production chain, for instance for the purpose of continuous production process or specific process design in the specification. In such cases, the resulting waste acid contains multiple acids with various pollution resources like fluoride ion, nitrogen ion and phosphoric ion, chlorine ion, sulfuric ion and other toxic and harmful substances.

[0006] In all the above-mentioned examples, the resulting mixed waste acid is of high acidity and complicated compositions which normally require pollution treatment before dismissal to the natural environment. Such pollution treatment is extremely difficult especially when the major components of the mixed acids contain more than two types of acids and the related treatment processes are generally costly.

[0007] The prior art techniques used in pollution treatment industry for eliminating the different pollutants in the mixed acids can roughly be classified into three categories described as follows.

[0008] 1) Lime neutralization method. Such type of method is to introduce the waste acids directly into lime powders for neutralization, where the phosphoric acid and fluorine acid can react with lime to form calcium phosphate and calcium fluoride precipitates, where the nitrogen ions will be removed when the waste acids when immersing passing the biochemical pool. However, due to the presence of large amount of sulfuric acid in the waste acids, the amount of produced solid waste from such method remains high and requires a secondary treatment that would increase the cost of the whole treatment process, meanwhile such type of method also leads to a great waste of fluorine, phosphorus and nitric acid resources.

[0009] 2) Distillation recovery method. Such type of method is particularly suitable for treatment of waste acid containing nitric acid, where the use of distillation process could recover the volatile nitric acid from the non-volatile acids in the waste acid solutions. However, such type of method cannot separate two or more volatile acids when they are collocated in the waste acid solutions. Generally the collection of the volatile acids from distillation still inevitably requires a continuous neutralization process. Therefore, a simple distillation process cannot solve the problem to maximization reuse of the mixed acid resources.

[0010] 3) Membrane treatment method. With the development of membrane technology, more and more membrane technology has been applied to the field of wastewater treatment, such as nanofiltration, ultrafiltration, reverse osmosis, electrodialysis and so on. These membranes can be used to separate hydrochloric acid, hydrofluoric acid, sulfuric acid, nitric acid and phosphoric acid. However, hydrochloric acid and hydrofluoric acid are difficult to be separated by the membrane treatment.

[0011] The prior art technologies are mainly focused on separation of the waste acids which typically contain two or three kinds acids selected from the group of hydrochloric acid, nitric acid, hydrofluoric acid,

sulfuric acid and phosphoric acid. For example, CN201410443526.7 provides a process for the separation of hydrofluoric acid and nitric acid from an electronic waste acid, and has developed a process for separating the targeted acids using one or two inorganic salts of cesium nitrate and its homologues. The method can effectively solve the problem of the separation of hydrofluoric acid and nitric acid from water as these two acids are liable to be distilled together and achieve the purpose of separation, recovery and reuse of the hydrofluoric acid and nitric acid. However, the invention does not deal with the problem of coexistence of these two acids and hydrochloric acid, and furthermore the recovery of hydrofluoric acid requires a specific reaction apparatus as the hydrofluoric acid is highly corrosive. For another example, CN 201410009187.1 discloses a method for producing calcium fluoride from the waste hydrofluoric acids containing sulfuric acid or the like. In this invention, the coprecipitate of calcium fluoride and calcium sulfate is firstly obtained using a traditional chemical production method, then the solid phase sulfate is transferred to the solution phase by adding a sulfate removal agent, and finally the calcium fluoride precipitates will be filtered and washed so as to meet the requirements of sulfur content in calcium fluoride in line with the standards of the steel plants. Using the disclosed method, the sulfuric ion or sulfate will be removed from the calcium fluoride obtained by the conventional calcium fluoride chemical production method, thus the fluorine-sulfur-containing sludge produced by such method would then become a useful resource, which aids to protect the environment while reutilize the resource. However, in such invention, the waste acid neutralization still requires a large amount of alkali and it would also cause waste of acid.

[0012] Therefore, it is necessary to develop a process for regenerating all acids from the waste acids that contains three or more acids selected from hydrochloric acid, nitric acid, hydrofluoric acid, sulfuric acid and phosphoric acid. It is also a demand to efficiently recover resources from the mixed waste acids so as to reduce industrial waste to protect the environment.

DETAILED DESCRIPTION

[0013] The following detailed description is merely illustrative in nature and is not intended to limit the embodiments of the subject matter or the application and uses of such embodiments. As used herein, the word “exemplary” means “serving as an example, instance, or illustration.” Any implementation described herein as exemplary is not necessarily to be construed as preferred or advantageous over other implementations.

Furthermore, there is no intention to be bound by any expressed or implied theory presented in the preceding

technical field, background, brief summary or the following detailed description.

[0014] This specification includes references to “one embodiment” or “an embodiment.” The appearances of the phrases “in one embodiment” or “in an embodiment” do not necessarily refer to the same embodiment. Particular features, structures, or characteristics may be combined in any suitable manner consistent with this disclosure.

[0015] Terminology. Certain terminology may also be used in the following description for the purpose of reference only, and thus are not intended to be limiting. The following paragraphs provide definitions and/or context for terms found in this disclosure (including the appended claims):

[0016] “Comprising.” and “comprise”. This term is open-ended. As used in the appended claims, this term does not foreclose additional structure or steps. Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[0017] “Configured To.” Various units or components may be described or claimed as “configured to” perform a task or tasks. In such contexts, “configured to” is used to connote structure by indicating that the units/components include structure that performs those task or tasks during operation. As such, the unit/component can be said to be configured to perform the task even when the specified unit/component is not currently operational. Reciting that a unit/circuit/component is “configured to” perform one or more tasks is expressly intended not to invoke 35 U.S.C. §112, sixth paragraph, for that unit/component.

[0018] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0019] As used herein, the term “about”, in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

[0020] Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be

considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[0021] Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0022] Such terminology may include the words specifically mentioned above, derivatives thereof, and words of similar import.

[0023] Methods of recycling waste acids produced from surface treatment processes in electronics, semiconductors and photovoltaics industries are described herein. In the following description, numerous specific details are set forth, such as specific process flow operations, in order to provide a thorough understanding of embodiments of the present disclosure. It will be apparent to one skilled in the art that embodiments of the present disclosure may be practiced without these specific details. In other instances, well-known fabrication techniques, such as lithography and patterning techniques, are not described in detail in order to not unnecessarily obscure embodiments of the present disclosure. Furthermore, it is to be understood that the various embodiments shown in the figures are illustrative representations and are not necessarily drawn to scale.

[0024] Disclosed herein are methods of recovering, or reutilizing, or separating, various kinds of acids from the mixed acids, or waste acids, or waste mixed acids, which typically contains the major components such as hydrochloric acid, nitric acid, fluoric acid, phosphoric acid and sulfuric acid. It should be noted that the source of the mixed acids is not limited, although it is preferably from the resulting waste acids from surface treatment processes in industries, especially from the electronics, semiconductors and photovoltaics industries, however the mixed acids can also resulted from university/institution laboratories or even mixed with waste waters from city or rural life.

[0025] Disclosed herein are methods for recycling, or reutilizing, or separating the mixed acids which contain two or more acids selected from the group comprising of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid. The disclosed methods herein comprises one or more operations or treatments or their combinations selected from the filtration, oxidation, separation, precipitation, reaction, conversion, electrodialysis and the like. The disclosed methods herein also comprise the introduction, or reuse,

of certain chemicals, or agents, additives, or medicament during the recycling processes of any of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid and other corresponding renewable products.

[0026] Disclosed herein are methods for recycling, or reutilizing, or separating, hydrochloric acid from the mixed acids which contain hydrochloric acid and at least one or more acids selected from the group comprising of nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid. Such methods comprise of at least a step of oxidizing the dissolved Cl^- in the mixed acid solution, or any intermediate solution separated from the mixed acid solution, stirring the mixed acid solution or any intermediate solution separated from the mixed acid solution, until the said dissolved Cl^- is about 100% oxidized to Cl_2 gas, and reducing the Cl_2 gas with reducing agent and water to obtain a hydrochloric acid regenerated product.

[0027] Disclosed herein are methods for recycling, or reutilizing, or separating, nitric acid from the mixed acids which contain nitric acid and at least one or more acids selected from the group comprising of hydrochloric acid, hydrofluoric acid, phosphoric acid and sulfuric acid. Such methods comprise of at least a step of separating, preferably distilling, the nitric acid from the mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain a nitric acid regenerated product. As an alternative, such methods comprise of at least a step of introducing calcium oxide or calcium hydroxide into the original mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain and separate calcium fluoride precipitate from a residual solution, wherein the residual solution is subjected to react with masking agent and to be distilled for obtaining a nitric acid regenerated product. Yet as another alternative, such methods comprise at least the aforementioned two steps to obtain a nitric acid regenerated product.

[0028] Disclosed herein are methods for recycling, or reutilizing, or separating, hydrofluoric acid from the mixed acids which contain hydrofluoric acid and at least one or more acids selected from the group comprising of hydrochloric acid, nitric acid, phosphoric acid and sulfuric acid. Such methods comprise of at least a step of separating, preferably distilling, the hydrofluoric acid from the mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain the volatile hydrofluoric acid regenerated product. As an alternative, such methods comprise of at least a step of introducing calcium oxide or calcium hydroxide into the original mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain and separate calcium fluoride precipitate out from a residual solution, wherein the calcium fluoride precipitate is subject to react with any non-volatile acids to obtain the volatile

hydrofluoric acid regenerated product. Yet as another alternative, such methods comprise at least the aforementioned two steps to obtain the volatile hydrofluoric acid regenerated product.

[0029] Disclosed herein are methods for recycling, or reutilizing, or separating, sulfuric acid phosphoric acid from the mixed acids which contain phosphoric acid and at least one or more acids selected from the group comprising of hydrochloric acid, nitric acid, hydrofluoric acid and sulfuric acid. Such methods comprise of at least a step of separating, preferably distilling, any volatile acids from the mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain the non-volatile phosphoric acid regenerated product. As an alternative, such methods comprise of at least a step of introducing calcium oxide, calcium hydroxide, calcium fluoride or any other calcium salts into the original mixed acid solution, or any intermediate solution separated from the mixed acid solution, preferably by high-temperature reaction, to obtain and separate calcium sulfate precipitate out from a residual solution, wherein the residual solution is separated from the precipitates for obtaining a phosphoric acid regenerated product. Yet as another alternative, such methods comprise at least the aforementioned two steps to obtain the non-volatile phosphoric acid regenerated product.

[0030] Disclosed herein are methods for recycling, or reutilizing, or separating, sulfuric acid from the mixed acids which contain sulfuric acid and at least one or more acids selected from the group comprising of hydrochloric acid, nitric acid, hydrofluoric acid and phosphoric acid. Such methods comprise of at least a step of separating, preferably distilling, any volatile acids from the mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain the non-volatile sulfuric acid regenerated product. As an alternative, such methods comprise of at least a step of introducing calcium oxide, calcium hydroxide, calcium fluoride or any other calcium salts into the original mixed acid solution, or any intermediate solution separated from the mixed acid solution, to obtain and separate calcium sulfate precipitate out from a residual solution, wherein the calcium sulfate precipitate reacts with hydroxide, preferably sodium hydroxide, to obtain water soluble sulfate, preferably sodium sulfate, whereby the obtained water soluble sulfate is subjected to electrodialysis for obtaining a non-volatile sulfuric acid regenerated product. Yet as another alternative, such methods comprise at least the aforementioned two steps to obtain the non-volatile sulfuric acid regenerated product.

[0031] The disclosed method herein can be applied to the treatments of any mixed acids containing the major components of all the said five acids, hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid, with the disclosed technical solutions in any combination. Such combination includes but is

not limited to the various methods, various aspects, claimed claims and deployed embodiments within the present specification and should be judged from the eyes of a skilled person to include any derivations or extensions from the disclosure herein.

[0032] The disclosed methods herein are also suitable for treating any mixed acids that contain combinations of two or more kinds of acids selected from the group comprising of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid as the major components. For separating a combination of two or more specific acids in the mixed acid solution, the corresponding treatment procedures disclosed herein for the specific acid resources that is not the major components in the acid solution could be omitted, or omitted in combination while the corresponding treatment procedures disclosed herein for the specific acid resources that is the major components in the acid solution could be configured, or configure in combination when treating the specific major components in the mixed acids accordingly. Such omission or combination includes but is not limited to the various methods, various aspects, claimed claims and deployed embodiments within the present specification and should be judged from the eyes of a skilled person to include any derivations or extensions from the disclosure herein.

[0033] Within the scope of above disclosure for treatments of the mixed acids, as some preferable embodiments, the technical solutions disclosed in the present invention at least includes but not limit to the following twenty aspects. In various preferable embodiments, it is possible to recover all the acid resources from the waste mixed acid solution that contains two or more acids selected from the group of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid, especially produced in the surface-treatment processes in electronics, semiconductors and photovoltaics industries.

[0034] According to a first aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising hydrofluoric acid and sulfuric acid, wherein the method comprising the steps of:

(1) separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;

(2) adding calcium hydroxide to the solution C obtained in step (1) to obtain a calcium fluoride precipitate;

(3) reacting the solution D obtained in step (1) with the calcium fluoride precipitate obtained in step (2)

and separate the reactant, preferably by distillation, to obtain a hydrofluoric acid regenerated product and a turbidity solution F;

(4) heating the turbidity solution F obtained in step (3) to obtain a calcium sulfate precipitate from a reaction conducted at a temperature higher than room temperature;

5 (5) reacting the calcium sulfate precipitate obtained in step (4) with a sodium hydroxide solution to obtain a calcium hydroxide precipitate and a sodium sulfate solution, wherein the calcium hydroxide precipitate is recycled to step (2);

(6) subjecting the sodium sulfate solution obtained in step (5) to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution, and the sodium hydroxide solution is recycled to step
10 (5).

[0035] According to a second aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising hydrofluoric acid and phosphoric acid, wherein the method comprising the steps of:

(1) separating the mixed acid solution A into a solution C containing volatile acid components, in
15 particular hydrofluoric acid, and a solution D containing non-volatile acid components, in particular phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;

(2) adding calcium hydroxide to the solution C obtained in step (1) to obtain a calcium fluoride precipitate;

20 (3) reacting the solution D obtained in step (1) with the calcium fluoride precipitate obtained in step (2) and separate the reactant, preferably by distillation, to obtain a hydrofluoric acid regenerated product and a turbidity solution F;

(4) adding sulfuric acid to the turbidity solution F obtained in step (3) and heating the turbidity solution F to obtain a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted
25 at a temperature higher than room temperature;

(5) reacting the calcium sulfate precipitate obtained in step (4) with a sodium hydroxide solution to obtain a calcium hydroxide precipitate and a sodium sulfate solution, wherein the calcium hydroxide precipitate is recycled to step (2);

(6) subjecting the sodium sulfate solution obtained in step (5) to electrodialysis to obtain a sulfuric acid
30 regenerated product and a sodium hydroxide solution, and the sulfuric acid is reused to step (4), the sodium

hydroxide solution is recycled to step (5).

[0036] According to a third aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising nitric acid and sulfuric acid, wherein the method comprising the steps of:

5 (1) separating the mixed acid solution A into a solution C containing volatile acid components, in particular to obtain a regenerated nitric acid product, and a solution D containing non-volatile acid components, in particular sulfuric acid to obtain a regenerated sulfuric acid product, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius.

10 [0037] According to a fourth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising nitric acid and phosphoric acid, wherein the method comprising the steps of:

(1) separating the mixed acid solution A into a solution C containing volatile acid components, in particular to obtain a regenerated nitric acid product, and a solution D containing non-volatile acid components, in particular phosphoric acid to obtain a regenerated phosphoric acid product, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius.

15 [0038] According to a fifth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising nitric acid and hydrofluoric acid, wherein the method comprising the steps of:

20 (1) adding a calcium oxide or calcium hydroxide into the mixed acid solution A to obtain a calcium fluoride precipitate and a residual solution E, and the residual solution E is added with a masking agent for distillation to obtain a nitric acid regenerated product;

(2) reacting the calcium fluoride precipitate obtained in step (1) with non-volatile acids and separate the reactant, preferably by distillation, to obtain a hydrofluoric acid regenerated product.

25 [0039] According to a sixth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising sulfuric acid and phosphorus acid, wherein the method comprising the steps of:

(1) adding calcium fluoride precipitate into the mixed acid solution A and heating the solution A to obtain a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a

temperature higher than room temperature;

(2) reacting the calcium sulfate precipitate obtained in step (1) with a sodium hydroxide solution to obtain a calcium hydroxide precipitate and a sodium sulfate solution;

(3) subjecting the sodium sulfate solution obtained in step (2) to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution, and the sodium hydroxide solution is recycled to step (2).

[0040] According to a seventh aspect of the present invention, provided is a resource recycling method for a mixed acid solution A, preferably comprising the acids according to any of the first to sixth aspects and further comprise hydrochloric acid, wherein the method comprising the steps of:

(1) oxidizing the dissolved Cl^- in the mixed acid solution A, stirring the mixed acid solution A until the said dissolved Cl^- is about 100% oxidized to Cl_2 gas, and reducing the Cl_2 gas with reducing agent and water to obtain a hydrochloric acid regenerated product.

[0041] According to an eighth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of proceeding aspects, especially the first aspect, preferably the mixed acid solution A further comprises phosphoric acid, characterized in that:

the step (1) is replaced by: separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid and phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;

the step (4) is replaced by: adding sulfuric acid to the turbidity solution F obtained in step (3) and heating the turbidity solution F to obtain a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature;

[0042] According to a ninth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of proceeding aspects, especially the first or eighth aspect, preferably the mixed acid solution A further comprises nitric acid, characterized in that:

the step (1) is replaced by: separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid and nitric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid and phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;

the step (2) is replaced by: adding a calcium oxide or calcium hydroxide into the mixed acid solution A

to obtain a calcium fluoride precipitate and a residual solution E, and the residual solution E is added with a masking agent for distillation to obtain a nitric acid regenerated product;

[0043] According to a tenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of proceeding aspects, especially the first, eighth and ninth aspects, preferably the mixed acid solution A further comprises hydrochloric acid, characterized in that:

adding step (1c) prior to step (1): oxidizing the dissolved Cl^- in the mixed acid solution A, stirring the mixed acid solution A until the said dissolved Cl^- is about 100% oxidized to Cl_2 gas, and reducing the Cl_2 gas with reducing agent and water to obtain a hydrochloric acid regenerated product;

the step (1) is replaced by: separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid and nitric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid and phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius.

[0044] According to an eleventh aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of proceeding aspects, especially the first, eighth to tenth aspects, characterized in that the mixed acid solution A is obtained from a raw waste acid solution by removing the solid particles after at least one filtration treatment with membrane module.

[0045] Provided in various embodiments, the membrane module could be any filtration membranes like filter bag, microfiltration or ultrafiltration membrane components that could conduct the solid-solution separation. Preferably, the membrane module can be one or more of functional units including coarse filter, reverse osmosis, nanofiltration, ultrafiltration and ion exchange membrane, furthermore, the membrane size of the filter medium is preferably 0.001 to 1 micron.

[0046] According to a twelfth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of proceeding aspects, especially the first, eighth to eleventh aspects, characterized in that, the said distillation in the involved steps is low pressure evaporation or atmospheric pressure evaporation.

[0047] Provided in various embodiments, when a low pressure evaporation is performed, the working vacuum degree for distillation is preferably at a range of 0.01 to 0.09, and the evaporator device is preferably at least one or more of MVR, single-effect device, multi-effect apparatus, and more preferably the material for evaporator apparatus contains at least one or more of enamel, stainless steel, Hastelloy C-276 and polytetrafluoroethylene.

[0048] According to a thirteenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of proceeding aspects, especially the first, eighth to twelfth aspects, characterized in that the oxidation treatment in step (1c) is electro-oxidation or chemical oxidation, and the reduction treatment is a chemical reduction.

5 [0049] Provided in various embodiments, the electro-oxidation is carried out at the conditions of a working voltage in the range of 0.5 V to 10 V, and more preferably, in a range of 1 V to 5 V.

[0050] Provided in various embodiments, the chemical oxidation is carried out using a chemical agent having a strong oxidizing capability. The chemical agent having strong oxidizing capability, the oxidizer, may be an oxidizing agent known to those skilled in the art, including organic oxidizing agent and/or inorganic oxidizing agent. Preferably, the inorganic oxidizer may be one or more oxidizing agent selected from the group comprising perchloric acid, permanganic acid and dichromic acid.

[0051] Provided in various embodiments, the chemical reducing treatment is carried out using a reducing agent known to those skilled in the art, including organic reducing agents and inorganic reducing agents.

15 Preferably, the organic reducing agent may be methanol or formic acid or their mixture thereof, and the inorganic reducing agent may be hydrogen peroxide or sulfurous acid or their mixture thereof.

[0052] Provided in various embodiments, the resulting regenerated hydrochloric acid is preferably with acidity in a range from 1% to 20% and preferably contains water in a range from 80% to 99% in weight.

[0053] According to a fourteenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to thirteenth aspects, characterized in that, in step (2), the concentration of calcium hydroxide in the mixed acid solution A is preferably in a range from 0.5% to 5% by weight.

20 [0054] Provided in various embodiments, the solution E may contain hydrofluoric acid or may not contain hydrofluoric acid. Optionally, the concentration of hydrofluoric acid in the solution E is in a range of 0.01-0.5% by weight.

25 [0055] Provided in various embodiments, the masking agent may be any masking agent, including organic masking agent or inorganic masking agent and the like, which are well known to those skilled in the art that has a masking effect capable of changing the fluorine ion present form. Preferably, the inorganic masking agent may be boric acid and ferric nitrate or their mixture. Preferably, the concentration of masking agent is in the range from 0.01% to 0.05% by weight.

30 [0056] Provided in various embodiments, the resulting regenerated nitric acid is preferably with acidity in

a range from 5% to 30% and preferably contains water in a range from 70% to 95% in weight.

[0057] According to a fifteenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to fourteenth aspects, characterized in that, in step (4), said turbidity solution F is preferably at least two of calcium sulfate, calcium dihydrogen phosphate, sulfuric acid and phosphoric acid. Optionally, calcium dihydrogen phosphate in an amount of 0.1% to 10% by weight may be added into the turbidity solution F according to the proportion of phosphoric acid in the turbidity solution F. Preferably, the concentration of calcium dihydrogen phosphate is 5% by weight.

[0058] Provided in various embodiments, the reaction of step (4) is carried out at a temperature higher than room temperature, preferably at a temperature of about 80°C to 120°C, more preferably at a temperature of about 90°C.

[0059] Provided in various embodiments, the separation method for obtaining a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature in step (4) may be selected from pressure filtration, centrifugation, filtration, and more preferably, the separation method is pressure filtration.

[0060] Provided in various embodiments, the resulting regenerated phosphoric acid is preferably with acidity in a range from 10% to 80% and preferably contains water in a range from 20% to 90% in weight.

[0061] According to a sixteenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to fifteenth aspects, characterized in that, in step (3), calcium fluoride precipitates and the solution D is mixed at a solid-solution ratio of 0.01:1 to 0.5:1, and more preferably, the calcium fluoride precipitate and the solution D are mixed at a solid-solution ratio of 0.1:1 to 0.3:1.

[0062] Provided in various embodiments, the resource recovery system disclosed in the present invention can achieve a closed-loop production without any intermediate external importation, especially in cases where the calcium fluoride precipitate and the solution D is mixed at a solid-solution ratio within a specific range of 0.15:1 to 0.25:1.

[0063] Provided in various embodiments, the reaction temperature of step (3) is controlled to be at a temperature in the range from about 60°C to about 120°C, preferably at a temperature of about 100°C.

[0064] Provided in various embodiments, the reaction equipment is made of one or more materials selected from enamel, stainless steel, Hastelloy C-276 and polytetrafluoroethylene.

[0065] Provided in various embodiments, the heating method is direct heating or indirect heating or the combination thereof.

[0066] Provided in various embodiments, the resulting regenerated hydrofluoric acid is preferably with acidity in a range from 1% to 15% and preferably contains water in a range from 85% to 99% in weight.

5 [0067] According to a seventeenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to sixteenth aspects, characterized in that, in step (5), the concentration of sodium hydroxide solution is in a range from 1% to 5% by weight, preferably 4% by weight.

[0068] According to an eighteenth aspect of the present invention, provided is a resource recycling method
10 for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to seventeenth aspects, characterized in that, in step (6), the preferred working conditions of electrodialysis includes an operating pressure of 0.5 to 3.0 kg/cm², an operating voltage of 100 to 250 V and an operating current of 1 to 3A.

[0069] Provided in various embodiments, the resulting regenerated sulfuric acid is preferably with acidity
15 in a range from 1% to 10% and preferably contains water in a range from 90% to 99% in weight.

[0070] According to a nineteenth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to eighteenth aspects, characterized in that, the resulting sodium hydroxide from electrodialysis in step (6) is reused to step (5) to reacted with calcium sulfate so as to produce calcium hydroxide for reusing in step (2).

20 [0071] Provided in various embodiments, the calcium hydroxide used in step (2) may alternatively be in whole or in part from the reaction product of step (5), or may alternatively be imported from external resources outside the system.

[0072] Provided in various embodiments, the sodium hydroxide used in step (5) may alternatively be in whole or in part from the reaction product of step (6), or may alternatively be imported from external resources
25 outside the system.

[0073] Provided in various embodiments, the calcium fluoride precipitate used in step (3) may alternatively be in whole or in part from the reaction product of step (2), or may alternatively be imported from external resources outside the system.

[0074] Provided in various embodiments, the calcium sulfate precipitate used in step (5) may alternatively
30 be in whole or in part from the reaction product of step (4), or may alternatively be imported from external

resources outside the system.

[0075] According to a twentieth aspect of the present invention, provided is a resource recycling method for a mixed acid solution A according to any of the proceeding aspects, especially the first, eighth to nineteenth aspects, characterized in that, the ratio of hydrofluoric acid radical and sulfuric acid radical is at a specific ratio which allows the calcium fluoride precipitate formed in step (2) to completely precipitate the sulfate ion in step (4) to form the calcium sulfate precipitates.

[0076] Provided in various embodiments, the preferable ratio of hydrofluoric acid radical and sulfuric acid radical in the mixed acid solution is 2:1.

[0077] Provided in various embodiments, the disclosed waste acid recycling method can achieve an efficiency of about 90% to about 95% for recycling the total calcium source, more preferably about 100% for recycling the total calcium source to achieve a closed loop production.

[0078] Provided in various embodiments, the disclosed waste acid recycling method can achieve an efficiency of about 90% to about 95% for recycling the total acid resource, more preferably about 100% of the total acid resource reuse to achieve a zero emissions production.

[0079] Provided in various embodiments, the auxiliary agents, for example the various calcium salts and metallic hydroxide, used in the methods as disclosed in the present invention does not introduce any obvious impurities into the mixed acid system. Provided in various embodiments, the auxiliary agents can be exported as high quality byproducts in a certain configurations of various acid components in the mixed acid solution. Provided in various embodiments, the whole system can achieve high efficiency closed loop production in a certain configurations of various acid components in the mixed acid solution.

[0080] For any ordinary person skilled in the art to which the present disclosure relates, the disclosed embodiments and the reasonable derivations and extensions would cover the separation, recycling and regeneration of any two or more types of acids in the mixed acid system, where the said acids are selected from the group comprising of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid. It is also obvious for the skilled person to be inspired by the present disclosure to configure or combine or omit the technical solutions disclosed herein to the separate, recycle and regenerate any two or more types of acids in the mixed acid system, where the said acids are selected from the group comprising of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid.

[0081] In addition, the mixed acid solution system according to the present disclosure is a mixture solution according to the solution composition but not from the solution resources. Therefore, the mixed acid solution

should not be confined to a specific industry and is also not limited to any specific industrial production or any waste acid solution produced in any specific producer, for example, any factory, any laboratory or any plant. It is also possible to make a number of simplification or re-combinations in the disclosed technical solutions for treating the mixed acid solutions, in which all the simplified or recombined technical solutions should be regarded as falling within the scope of the present invention.

[0082] The methods disclosed in the present invention have simple operation process and has significant economic benefits. The resource consumed in the disclosed methods is mainly electric energy and the disclosed methods do not generate any secondary pollution. The disclosed methods can realize a zero emission to protect the environment while at the same time recover all the mixed acids resources efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

[0083] Figure 1 is a process flow diagram illustrating the waste acid recycling methods for recycling the mixed waste acid containing the major components of hydrofluoric acid and sulfuric acid, in accordance with an embodiment of the present disclosure (Embodiment 1).

[0084] Figure 2 is a process flow diagram illustrating the waste acid recycling methods for recycling the mixed waste acid containing the major components of hydrofluoric acid, sulfuric acid and phosphoric acid, in accordance with an embodiment of the present disclosure (Embodiment 2).

[0085] Figure 3 is a process flow diagram illustrating the waste acid recycling methods for recycling the mixed waste acid containing the major components of hydrofluoric acid, sulfuric acid and nitric acid, in accordance with an embodiment of the present disclosure (Embodiment 3).

[0086] Figure 4 is a process flow diagram illustrating the waste acid recycling methods for recycling the mixed waste acid containing the major components of hydrofluoric acid, sulfuric acid, phosphoric acid and phosphoric acid, in accordance with an embodiment of the present disclosure (Embodiment 4).

EMBODIMENTS

[0087] The following will be described in further detail with reference to Figures 1-4 and specific preferred embodiments, and the specific embodiments of the invention are not to be construed as limited to such description. It will be apparent to those skilled in the art to which this invention pertains that various

modifications or substitutions may be made without departing from the spirit of the invention, and should be considered as falling within the scope of the present disclosure.

Embodiment 1

[0088] A mixed acid solution A1 is obtained from a solar company, after preliminary analysis, the major components are found to be hydrofluoric acid and sulfuric acid, the following steps, which are illustrated in Fig. 1, are used to recycle the waste acids from the mixed acid solution A1:

[0089] (1) The mixed acid solution A1 is obtained by removing the solid particles from the original waste acid solution using a solid-solution separation method, wherein the method includes a series of filtration with various membrane modules including the bag filter, microfiltration and ultrafiltration membrane module, coarse filter membrane module and reverse osmosis membrane module, in which the typical filter medium pore size is of 0.001-1 μ m;

[0090] (2) The volatile component solution C1 (the main component is hydrofluoric acid) and the non-volatile component solution D1 (the main component is sulfuric acid) are separated according to the volatilization of the different components in the mixed acid solution A1 by distillation, wherein the adopted distillation method is evaporation under reduced pressure or atmospheric pressure evaporation. When the reduced pressure distillation is used, the adopted working vacuum degree is in the range of 0.01-0.09, and the preferred evaporator apparatus is one or more of MVR, single effect apparatus, multi-effect apparatus. The deployed evaporator equipment is made of one or more materials selected from enamel, stainless steel, Hastelloy C-276 and polytetrafluoroethylene.

[0091] In another embodiment, the volatile component solution C1 (mainly composed of hydrofluoric acid) and the non-volatile component solution D1 (the main component is sulfuric acid) in the mixed acid solution can be separated by nanofiltration according to the difference in anion radius.

[0092] (3) Calcium hydroxide, preferably in a quality of industry pure level, is introduced to the solution C1 obtained in the step (2) to obtain a calcium fluoride precipitate.

[0093] (4) The solution D1 obtained in the step (2) and the calcium fluoride precipitate obtained in the step (3) are mixed for complete reaction to obtain a hydrofluoric acid regenerated product and a turbidity solution F1. In an embodiment, the calcium fluoride precipitate and the solution D1 are mixed at a solid-solution ratio of 0.01:1 to 0.5:1. In another embodiment, the calcium fluoride precipitate and the solution D1 are mixed at a solid-solution ratio of 0.1: 1 to 0.3: 1. In yet another embodiment, the production system can achieve a closed-

loop production in the cases where the calcium fluoride precipitate and the solid-solution ratio of the solution D1 are mixed at a specific ratio at the range of 0.15:1 to 0.25:1.

[0094] (5) The turbidity solution F1 obtained in step (4) is subjected to high-temperature reaction filtration to obtain calcium sulfate precipitate. In one embodiment, the reaction temperature is controlled at about 60°C to 120°C, preferably at temperature of 100°C. In another embodiment, the reaction equipment is made from any materials of enamel, stainless steel, Hastelloy C-276, polytetrafluoroethylene and the combination thereof. In yet another embodiment, the heating method is direct heating. In yet another embodiment, the heating method is indirect heating.

[0095] (6) The calcium sulfate precipitates obtained in step (5) is further mixed with a sodium hydroxide solution, preferably in a quality of industry level, introduced to the production system to obtain calcium hydroxide precipitate and sodium sulfate solution. In one embodiment, the calcium hydroxide precipitates is reused back to step (3). Preferably, the concentration of sodium hydroxide in the mixed acid solution is in a range from 1% to 5% by weight, more preferably 4% by weight.

[0096] (7) The sodium sulfate solution obtained in step (6) is then subjected to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution. In one embodiment, the sodium hydroxide solution is re-used back to the step (6) to react with calcium sulfate to form calcium hydroxide precipitate to be reused back in step (3). The preferred operating conditions for the electrodialysis process include an operating pressure of 0.5 to 3.0 kg/cm², an operating voltage of 100 to 250 V and an operating current of 1 to 3A.

[0097] The resulting regenerated hydrofluoric acid is with acidity in a range from 1% to 20% and contains water in a range from 80% to 99% in weight.

[0098] The resulting regenerated sulfuric acid is with acidity in a range from 1% to 10% and contains water in a range from 90% to 99% in weight.

Embodiment 2

[0099] A mixed acid solution A2 is obtained from a solar company, after preliminary analysis, the major components are found to be hydrofluoric acid, sulfuric acid and phosphoric acid, the following steps, which are illustrated in Fig. 2, are used to recycle the waste acids from the mixed acid solution A2:

[0100] (1) The mixed acid solution A2 is obtained by removing the solid particles from the original waste acid solution using a solid-solution separation method, wherein the method includes a series of filtration with various membrane modules including the bag filter, microfiltration and ultrafiltration membrane module,

coarse filter membrane module and reverse osmosis membrane module, in which the typical filter medium pore size is of 0.001-1 μ m;

[0101] (2) The volatile component solution C2 (mainly composed of hydrofluoric acid) and the non-volatile component solution D2 (the main component is sulfuric acid and phosphoric acid) in the mixed acid solution A2 are separated by nanofiltration according to the difference in anion radius. The separation apparatus is made from the materials selected from one or more of enamel, stainless steel, Hastelloy C-276 and polytetrafluoroethylene.

[0102] (3) Calcium hydroxide, preferably in a quality of industry pure level, is introduced to the solution C2 obtained in the step (2) to obtain a calcium fluoride precipitate.

[0103] (4) The non-volatile solution D2 obtained in the step (2) is mixed with the calcium fluoride precipitate obtained in the step (3) to obtain a regenerated hydrofluoric acid product and a turbidity solution F2. In an embodiment, the calcium fluoride precipitate and the solution D1 are mixed at a solid-solution ratio of 0.01:1 to 0.5:1. In another embodiment, the calcium fluoride precipitate and the solution D1 are mixed at a solid-solution ratio of 0.1: 1 to 0.3: 1. In yet another embodiment, the production system can achieve a closed-loop production in the cases where the calcium fluoride precipitate and the solid-solution ratio of the solution D1 are mixed at a specific ratio at the range of 0.15:1 to 0.25:1.

[0104] (5) The turbidity solution F2 obtained in step (4) is subjected to high-temperature reaction filtration to obtain calcium sulfate precipitate and a regenerated phosphoric acid product. The turbidity solution F2 is preferably at least two of calcium sulfate, calcium dihydrogen phosphate, sulfuric acid and phosphoric acid. Optionally, calcium dihydrogen phosphate in an amount of 0.1% to 10% by weight may be added into the turbidity solution F2 according to the proportion of phosphoric acid in the turbidity solution F2. Preferably, the concentration of calcium dihydrogen phosphate is 5% by weight.

[0105] In one embodiment, the reaction temperature is controlled at about 80°C to 120°C, preferably at temperature of 90°C. In another embodiment, the reaction equipment is made from any materials of enamel, stainless steel, Hastelloy C-276, polytetrafluoroethylene and the combination thereof. In yet another embodiment, the heating method is direct heating. In yet another embodiment, the heating method is indirect heating.

[0106] In yet another embodiment, the separation method for obtaining a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature in step (4) may be selected from pressure filtration, centrifugation, filtration, and more preferably, the

separation method is pressure filtration.

[0107] (6) The calcium sulfate precipitates obtained in step (5) is further mixed with a sodium hydroxide solution, preferably in a quality of industry level, introduced to the production system to obtain calcium hydroxide precipitate and sodium sulfate solution. In one embodiment, the calcium hydroxide precipitates is reused back to step (3). Preferably, the concentration of sodium hydroxide in the mixed acid solution is in a range from 1% to 5% by weight, more preferably 4% by weight.

[0108] (7) The sodium sulfate solution obtained in step (6) is then subjected to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution. In one embodiment, the sodium hydroxide solution is re-used back to the step (6) to react with calcium sulfate to form calcium hydroxide precipitate to be reused back in step (3). The preferred operating conditions for the electrodialysis process include an operating pressure of 0.5 to 3.0 kg/cm², an operating voltage of 100 to 250 V and an operating current of 1 to 3A.

[0109] The resulting regenerated hydrofluoric acid is with acidity in a range from 1% to 20% and contains water in a range from 80% to 99% in weight.

[0110] The resulting regenerated sulfuric acid is with acidity in a range from 1% to 10% and contains water in a range from 90% to 99% in weight.

[0111] The resulting regenerated phosphoric acid is with acidity in a range from 10% to 80% and contains water in a range from 20% to 90% in weight.

Embodiment 3

[0112] A mixed acid solution A3 is obtained from an electronic company, after preliminary analysis, the major components are found to be hydrofluoric acid, sulfuric acid, nitric acid and phosphoric acid, the following steps, which are illustrated in Fig. 3, are used to recycle the waste acids from the mixed acid solution A3:

[0113] (1) The mixed acid solution A3 is obtained by removing the solid particles from the original waste acid solution using a solid-solution separation method, wherein the method includes a series of filtration with various membrane modules including the bag filter, microfiltration and ultrafiltration membrane module, coarse filter membrane module and reverse osmosis membrane module, in which the typical filter medium pore size is of 0.001-1 μ m;

[0114] (2) The volatile component solution C3 (the main component is hydrofluoric acid and nitric acid) and the non-volatile component solution D3 (the main component is sulfuric acid and phosphoric acid) are

separated according to the volatilization of the different components in the mixed acid solution A1 by distillation, wherein the adopted distillation method is evaporation under reduced pressure or atmospheric pressure evaporation. When the reduced pressure distillation is used, the adopted working vacuum degree is in the range of 0.01-0.09, and the preferred evaporator apparatus is one or more of MVR, single effect apparatus, multi-effect apparatus. The deployed evaporator equipment is made of one or more materials selected from enamel, stainless steel, Hastelloy C-276 and polytetrafluoroethylene.

[0115] (3) Calcium hydroxide, preferably in a quality of industry pure level, is introduced to the solution C3 obtained in the step (2) to obtain a calcium fluoride precipitate and solution E3, the solution E3 is added to a masking agent for distillation to obtain a regenerated nitric acid product.

[0116] In one embodiment, wherein the concentration of calcium hydroxide added to the mixed acid solution A3 is preferably 0.5% to 5%, the solution E3 may not contain hydrofluoric acid or may contain hydrofluoric acid, and optionally, the hydrofluoric acid concentration of the solution E3 is 0.01-0.5%.

[0117] In one embodiment, the masking agent may be used as a masking agent, including an organic masking agent or an inorganic masking agent, etc., which are well known to those skilled in the art and capable of altering the presence of fluoride ions, and the preferred inorganic masking agent may be boric acid, A mixture or mixture of ferric nitrate. Preferably, the concentration of the masking agent is from 0.01% to 0.05%.

[0118] (4) The solution D3 obtained in the step (2) and the calcium fluoride precipitate obtained in the step (3) are mixed for complete reaction to obtain a hydrofluoric acid regenerated product and a turbidity solution F3. In an embodiment, the calcium fluoride precipitate and the solution D3 are mixed at a solid-solution ratio of 0.01:1 to 0.5:1. In another embodiment, the calcium fluoride precipitate and the solution D3 are mixed at a solid-solution ratio of 0.1:1 to 0.3:1. In yet another embodiment, the production system can achieve a closed-loop production in the cases where the calcium fluoride precipitate and the solid-solution ratio of the solution D3 are mixed at a specific ratio at the range of 0.15:1 to 0.25:1.

[0119] (5) The turbidity solution F3 obtained in step (4) is subjected to high-temperature reaction filtration to obtain calcium sulfate precipitate and a regenerated phosphoric acid product. The turbidity solution F3 is preferably at least two of calcium sulfate, calcium dihydrogen phosphate, sulfuric acid and phosphoric acid. Optionally, calcium dihydrogen phosphate in an amount of 0.1% to 10% by weight may be added into the turbidity solution F according to the proportion of phosphoric acid in the turbidity solution F3. Preferably, the concentration of calcium dihydrogen phosphate is 5% by weight.

[0120] In one embodiment, the reaction temperature is controlled at about 80°C to 120°C, preferably at

temperature of 90°C. In another embodiment, the reaction equipment is made from any materials of enamel, stainless steel, Hastelloy C-276, polytetrafluoroethylene and the combination thereof. In yet another embodiment, the heating method is direct heating. In yet another embodiment, the heating method is indirect heating.

5 [0121] In yet another embodiment, the separation method for obtaining a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature in step (4) may be selected from pressure filtration, centrifugation, filtration, and more preferably, the separation method is pressure filtration.

[0122] The calcium sulfate precipitates obtained in step (5) is further mixed with a sodium hydroxide
10 solution, preferably in a quality of industry level, introduced to the production system to obtain calcium hydroxide precipitate and sodium sulfate solution. In one embodiment, the calcium hydroxide precipitates is reused back to step (3). Preferably, the concentration of sodium hydroxide in the mixed acid solution is in a range from 1% to 5% by weight, more preferably 4% by weight.

[0123] In one embodiment, the reaction temperature is controlled at about 80°C to 120°C, preferably at
15 temperature of 90°C. In another embodiment, the reaction equipment is made from any materials of enamel, stainless steel, Hastelloy C-276, polytetrafluoroethylene and the combination thereof. In yet another embodiment, the heating method is direct heating. In yet another embodiment, the heating method is indirect heating.

[0124] In yet another embodiment, the separation method for obtaining a calcium sulfate precipitate and a
20 phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature in step (4) may be selected from pressure filtration, centrifugation, filtration, and more preferably, the separation method is pressure filtration.

[0125] (6) The calcium sulfate precipitates obtained in step (5) is further mixed with a sodium hydroxide solution, preferably in a quality of industry level, introduced to the production system to obtain calcium
25 hydroxide precipitate and sodium sulfate solution. In one embodiment, the calcium hydroxide precipitates is reused back to step (3). Preferably, the concentration of sodium hydroxide in the mixed acid solution is in a range from 1% to 5% by weight, more preferably 4% by weight.

[0126] (7) The sodium sulfate solution obtained in step (6) is then subjected to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution. In one embodiment, the sodium hydroxide
30 solution is re-used back to the step (6) to react with calcium sulfate to form calcium hydroxide precipitate to be

reused back in step (3). The preferred operating conditions for the electrodialysis process include an operating pressure of 0.5 to 3.0 kg/cm², an operating voltage of 100 to 250 V and an operating current of 1 to 3A.

[0127] The resulting regenerated hydrofluoric acid is with acidity in a range from 1% to 20% and contains water in a range from 80% to 99% in weight.

5 [0128] The resulting regenerated sulfuric acid is with acidity in a range from 1% to 10% and contains water in a range from 90% to 99% in weight.

[0129] The resulting regenerated phosphoric acid is with acidity in a range from 10% to 80% and contains water in a range from 20% to 90% in weight.

10 [0130] The resulting regenerated nitric acid is with acidity in a range from 5% to 30% and contains water in a range from 70% to 95% in weight.

[0131] Embodiment 4

15 A mixed acid solution A4 is obtained from a semiconductor company, after preliminary analysis, the major components are found to be hydrofluoric acid, sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid, the following steps, which are illustrated in Fig. 4, are used to recycle the waste acids from the mixed acid solution A4:

20 [0132] (1) The mixed acid solution A4 is obtained by removing the solid particles from the original waste acid solution using a solid-solution separation method, wherein the method includes a series of filtration with various membrane modules including the bag filter, microfiltration and ultrafiltration membrane module, coarse filter membrane module and reverse osmosis membrane module, in which the typical filter medium pore size is of 0.001-1μm;

25 [0133] (2) Oxidizing agents are introduced into the mixed acid solution A4, stirring the mixed acid solution A4 until the dissolved Cl⁻ is about 100% oxidized to Cl₂ gas and obtain the residual solution as the mixed acid solution B4, and reducing the Cl₂ gas with reducing agent and water to obtain a regenerated hydrochloric acid product;

30 [0134] The oxidation treatment in step (2) can be electro-oxidation or chemical oxidation, and the reduction treatment in step (2) is a chemical reduction. In one embodiment, the electro-oxidation is carried out at the conditions of a working voltage in the range of 0.5 V to 10 V, and more preferably, in a range of from 1 V to 5 V. In another embodiment, the chemical oxidation is carried out using a chemical agent having a strong oxidizing capability. The chemical agent having strong oxidizing capability, the oxidizer, may be an oxidizing

agent known to those skilled in the art, including organic oxidizing agent and/or inorganic oxidizing agent. Preferably, the inorganic oxidizer may be one or more oxidizing agent selected from the group comprising perchloric acid, permanganic acid and dichromic acid. In yet another embodiment, the chemical reducing treatment is carried out using a reducing agent known to those skilled in the art, including organic reducing agents and inorganic reducing agents. Preferably, the organic reducing agent may be methanol or formic acid or their mixture thereof, and the inorganic reducing agent may be hydrogen peroxide or sulfurous acid or their mixture thereof.

[0135] (3) The volatile component solution C4 (the main component is hydrofluoric acid and nitric acid) and the non-volatile component solution D4 (the main component is sulfuric acid and phosphoric acid) are separated according to the volatilization of the different components in the mixed acid solution B4 by distillation, wherein the adopted distillation method is evaporation under reduced pressure or atmospheric pressure evaporation. When the reduced pressure distillation is used, the adopted working vacuum degree is in the range of 0.01-0.09, and the preferred evaporator apparatus is one or more of MVR, single effect apparatus, multi-effect apparatus. The deployed evaporator equipment is made of one or more materials selected from enamel, stainless steel, Hastelloy C-276 and polytetrafluoroethylene.

[0136] (4) Calcium hydroxide, preferably in a quality of industry pure level, is introduced to the solution C4 obtained in the step (3) to obtain a calcium fluoride precipitate and solution E4, the solution E4 is added to a masking agent for distillation to obtain a regenerated nitric acid product.

[0137] In one embodiment, wherein the concentration of calcium hydroxide added to the mixed acid solution A4 is preferably 0.5% to 5%, the solution E4 may not contain hydrofluoric acid or may contain hydrofluoric acid, and optionally, the hydrofluoric acid concentration of the solution E4 is 0.01-0.5%.

[0138] In one embodiment, the masking agent may be used as a masking agent, including an organic masking agent or an inorganic masking agent, etc., which are well known to those skilled in the art and capable of altering the presence of fluoride ions, and the preferred inorganic masking agent may be boric acid, A mixture or mixture of ferric nitrate. Preferably, the concentration of the masking agent is from 0.01% to 0.05%.

[0139] (5) The solution D4 obtained in the step (3) and the calcium fluoride precipitate obtained in the step (4) are mixed for complete reaction to obtain a hydrofluoric acid regenerated product and a turbidity solution F4. In an embodiment, the calcium fluoride precipitate and the solution D4 are mixed at a solid-solution ratio of 0.01:1 to 0.5:1. In another embodiment, the calcium fluoride precipitate and the solution D4 are mixed at a solid-solution ratio of 0.1:1 to 0.3:1. In yet another embodiment, the production system can achieve a closed-

loop production in the cases where the calcium fluoride precipitate and the solid-solution ratio of the solution D4 are mixed at a specific ratio at the range of 0.15:1 to 0.25:1.

[0140] (6) The turbidity solution F4 obtained in step (5) is subjected to high-temperature reaction filtration to obtain calcium sulfate precipitate and a regenerated phosphoric acid product. The turbidity solution F4 is preferably at least two of calcium sulfate, calcium dihydrogen phosphate, sulfuric acid and phosphoric acid. Optionally, calcium dihydrogen phosphate in an amount of 0.1% to 10% by weight may be added into the turbidity solution F4 according to the proportion of phosphoric acid in the turbidity solution F4. Preferably, the concentration of calcium dihydrogen phosphate is 5% by weight.

[0141] In one embodiment, the reaction temperature is controlled at about 80°C to 120°C, preferably at temperature of 90°C. In another embodiment, the reaction equipment is made from any materials of enamel, stainless steel, Hastelloy C-276, polytetrafluoroethylene and the combination thereof. In yet another embodiment, the heating method is direct heating. In yet another embodiment, the heating method is indirect heating.

[0142] In yet another embodiment, the separation method for obtaining a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature in step (5) may be selected from pressure filtration, centrifugation, filtration, and more preferably, the separation method is pressure filtration.

[0143] The calcium sulfate precipitates obtained in step (6) is further mixed with a sodium hydroxide solution, preferably in a quality of industry level, introduced to the production system to obtain calcium hydroxide precipitate and sodium sulfate solution. In one embodiment, the calcium hydroxide precipitates is reused back to step (4). Preferably, the concentration of sodium hydroxide in the mixed acid solution is in a range from 1% to 5% by weight, more preferably 4% by weight.

[0144] In one embodiment, the reaction temperature is controlled at about 80°C to 120°C, preferably at temperature of 90°C. In another embodiment, the reaction equipment is made from any materials of enamel, stainless steel, Hastelloy C-276, polytetrafluoroethylene and the combination thereof. In yet another embodiment, the heating method is direct heating. In yet another embodiment, the heating method is indirect heating.

[0145] In yet another embodiment, the separation method for obtaining a calcium sulfate precipitate and a phosphoric acid regeneration product from a reaction conducted at a temperature higher than room temperature in step (5) may be selected from pressure filtration, centrifugation, filtration, and more preferably, the

separation method is pressure filtration.

[0146] (7) The calcium sulfate precipitates obtained in step (6) is further mixed with a sodium hydroxide solution, preferably in a quality of industry level, introduced to the production system to obtain calcium hydroxide precipitate and sodium sulfate solution. In one embodiment, the calcium hydroxide precipitates is reused back to step (4). Preferably, the concentration of sodium hydroxide in the mixed acid solution is in a range from 1% to 5% by weight, more preferably 4% by weight.

[0147] (8) The sodium sulfate solution obtained in step (7) is then subjected to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution. In one embodiment, the sodium hydroxide solution is re-used back to the step (7) to react with calcium sulfate to form calcium hydroxide precipitate to be reused back in step (4). The preferred operating conditions for the electrodialysis process include an operating pressure of 0.5 to 3.0 kg/cm², an operating voltage of 100 to 250 V and an operating current of 1 to 3A.

[0148] The resulting regenerated hydrofluoric acid is with acidity in a range from 1% to 20% and contains water in a range from 80% to 99% in weight.

[0149] The resulting regenerated sulfuric acid is with acidity in a range from 1% to 10% and contains water in a range from 90% to 99% in weight.

[0150] The resulting regenerated phosphoric acid is with acidity in a range from 10% to 80% and contains water in a range from 20% to 90% in weight.

[0151] The resulting regenerated nitric acid is with acidity in a range from 5% to 30% and contains water in a range from 70% to 95% in weight.

[0152] The resulting regenerated hydrochloric acid is with acidity in a range from 1% to 20% and contains water in a range from 80% to 99% in weight.

CLAIMS

1. A resource recycling method for a mixed acid solution A, comprising hydrofluoric acid and sulfuric acid, wherein the method comprising the steps of:

- 5 (1) separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;
- 10 (2) adding calcium hydroxide to the solution C obtained in step (1) to obtain a calcium fluoride precipitate;
- (3) reacting the solution D obtained in step (1) with the calcium fluoride precipitate obtained in step (2) and separate the reactant, preferably by distillation, to obtain a hydrofluoric acid regenerated product and a turbidity solution F;
- 15 (4) heating the turbidity solution F obtained in step (3) to obtain a calcium sulfate precipitate from a reaction conducted at a temperature higher than room temperature;
- (5) reacting the calcium sulfate precipitate obtained in step (4) with a sodium hydroxide solution to obtain a calcium hydroxide precipitate and a sodium sulfate solution, wherein the calcium hydroxide precipitate is recycled to step (2);
- 20 (6) subjecting the sodium sulfate solution obtained in step (5) to electrodialysis to obtain a sulfuric acid regenerated product and a sodium hydroxide solution, and the sodium hydroxide solution is recycled to step (5).

2. A resource recycling method for a mixed acid solution A according to claim 1, wherein the mixed acid solution A further comprises phosphoric acid, characterized in that:

25 the step (1) is replaced by: separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid and phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;

30 the step (4) is replaced by: adding sulfuric acid to the turbidity solution F obtained in step (3) and heating the turbidity solution F to obtain a calcium sulfate precipitate and a phosphoric acid

regeneration product from a reaction conducted at a temperature higher than room temperature.

3. A resource recycling method for a mixed acid solution A according to claims 1 or 2, wherein the mixed acid solution A further comprises nitric acid, characterized in that:

the step (1) is replaced by: separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid and nitric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid and phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius;

the step (2) is replaced by: adding a calcium oxide or calcium hydroxide into the mixed acid solution A to obtain a calcium fluoride precipitate and a residual solution E, and the residual solution E is added with a masking agent for distillation to obtain a nitric acid regenerated product.

4. A resource recycling method for a mixed acid solution A according to any one of claims 1 to 3, wherein the mixed acid solution A further comprises hydrochloric acid, characterized in that:

adding step (1c) prior to step (1): oxidizing dissolved Cl^- of the hydrochloric acid in the mixed acid solution A, stirring the mixed acid solution A until the said dissolved Cl^- is about 100% oxidized to Cl_2 gas, and reducing the Cl_2 gas with reducing agent and water to obtain a hydrochloric acid regenerated product;

the step (1) is replaced by: separating the mixed acid solution A into a solution C containing volatile acid components, in particular hydrofluoric acid and nitric acid, and a solution D containing non-volatile acid components, in particular sulfuric acid and phosphoric acid, which the separation is preferably conducted by distillation according to volatilization of acid components or by nanofiltration according to anion radius.

5. A resource recycling method for a mixed acid solution A according to any one of the preceding claims, characterized in that

the mixed acid solution A is obtained from a raw waste acid solution by removing solid particles after at least one filtration treatment with membrane module, preferably, the membrane module can be one or more of functional units including coarse filter, reverse osmosis, nanofiltration, ultrafiltration and ion exchange membrane.

6. A resource recycling method for a mixed acid solution A according to any one of the preceding claims, characterized in that

the said distillation in the involved steps is reduced pressure evaporation or atmospheric pressure evaporation.

7. A resource recycling method for a mixed acid solution A according to any one of claims 4-6, characterized in that

the oxidation treatment in the step (1c) is electro-oxidation or chemical oxidation, and the reduction treatment is a chemical reduction.

8. A resource recycling method for a mixed acid solution A according to any one of claims 4-7, characterized in that

in the step (2), the concentration of calcium hydroxide in the mixed acid solution A is preferably in a range from 0.5% to 5% by weight or the concentration of masking agent is in the range from 0.01% to 0.05% by weight.

9. A resource recycling method for a mixed acid solution A according to any one of claims 4-8, characterized in that

in the step (4), said turbidity solution F is preferably at least two of calcium sulfate, calcium dihydrogen phosphate, sulfuric acid and phosphoric acid.

10. A resource recycling method for a mixed acid solution A according to any one of claims 4-9, characterized in that

in the step (3), calcium fluoride precipitates and the solution D is mixed at a solid-solution ratio of 0.01:1 to 0.5:1, and more preferably, the calcium fluoride precipitate and the solution D are mixed at a solid-solution ratio of 0.1:1 to 0.3:1, and even more preferably, the calcium fluoride precipitate and the solution D are mixed at a solid-solution ratio of 0.15:1 to 0.25:1.

11. A resource recycling method for a mixed acid solution A according to any one of claims 4-10, characterized in that

in the step (5), the concentration of sodium hydroxide solution is in a range from 1% to 5% by weight, preferably 4% by weight.

12. A resource recycling method for a mixed acid solution A according to any one of claims 4-11, characterized in that

in the step (6), the preferred working conditions of electrodialysis includes an operating pressure of 0.5 to 3.0 kg/cm², an operating voltage of 100 to 250 V and an operating current of 1 to 3A.

13. A resource recycling method for a mixed acid solution A according to any one of claims 4-12, characterized

in that

the resulting sodium hydroxide from electrodialysis in the step (6) is reused to the step (5) to reacted with calcium sulfate so as to produce calcium hydroxide for reusing in the step (2).

14. A resource recycling method for a mixed acid solution A according to any one of claims 4-13, characterized

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in that

the ratio of hydrofluoric acid radical and sulfuric acid radical is at a specific ratio which allows the calcium fluoride precipitate formed in the step (2) to completely precipitate the sulfate ion in the step (4) to form the calcium sulfate precipitates.

ABSTRACT

The present invention discloses a method for recovering various acids in the mixed acid solution which comprises of two or more kinds of acids selected from the group of hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid and sulfuric acid, which are preferably produced in the process of surface treatment such as in the electronic, semiconductor and photovoltaics industries. The disclosed method comprises a series of treatment steps selected from filtering, oxidizing, separating, precipitating, reacting, transforming, electrodialysis, agent reuse and the like. All the resources in the mixed acid solution can be recycled and the auxiliary agents can be reused used during the production, under certain conditions the production system can achieve closed loop production. The method disclosed in the invention is simple for operation, the regeneration process has no secondary pollution and the resources in the mixed acid solution can be regenerated at high utilization level.

Fig. 1

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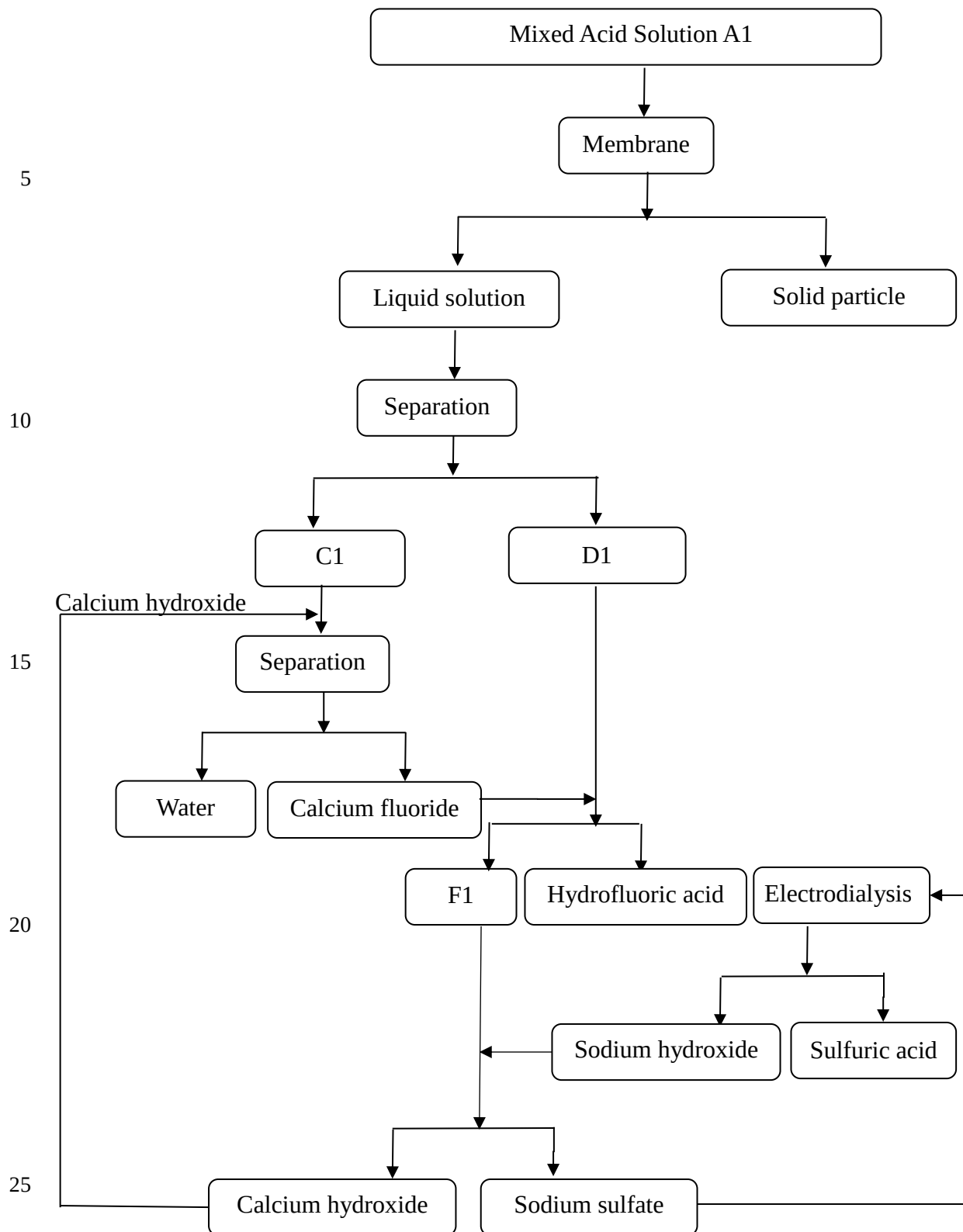


Fig.1

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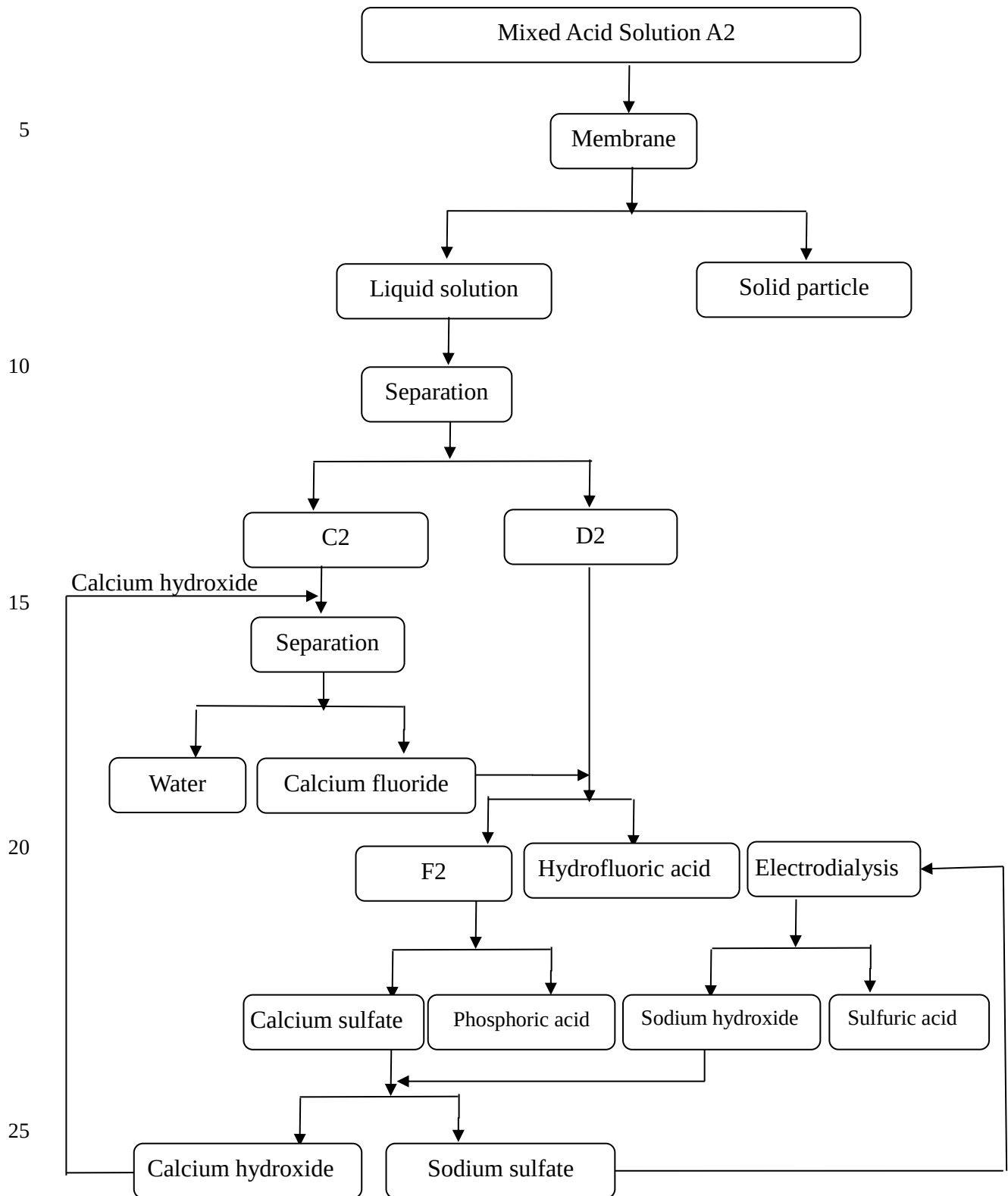


Fig.2

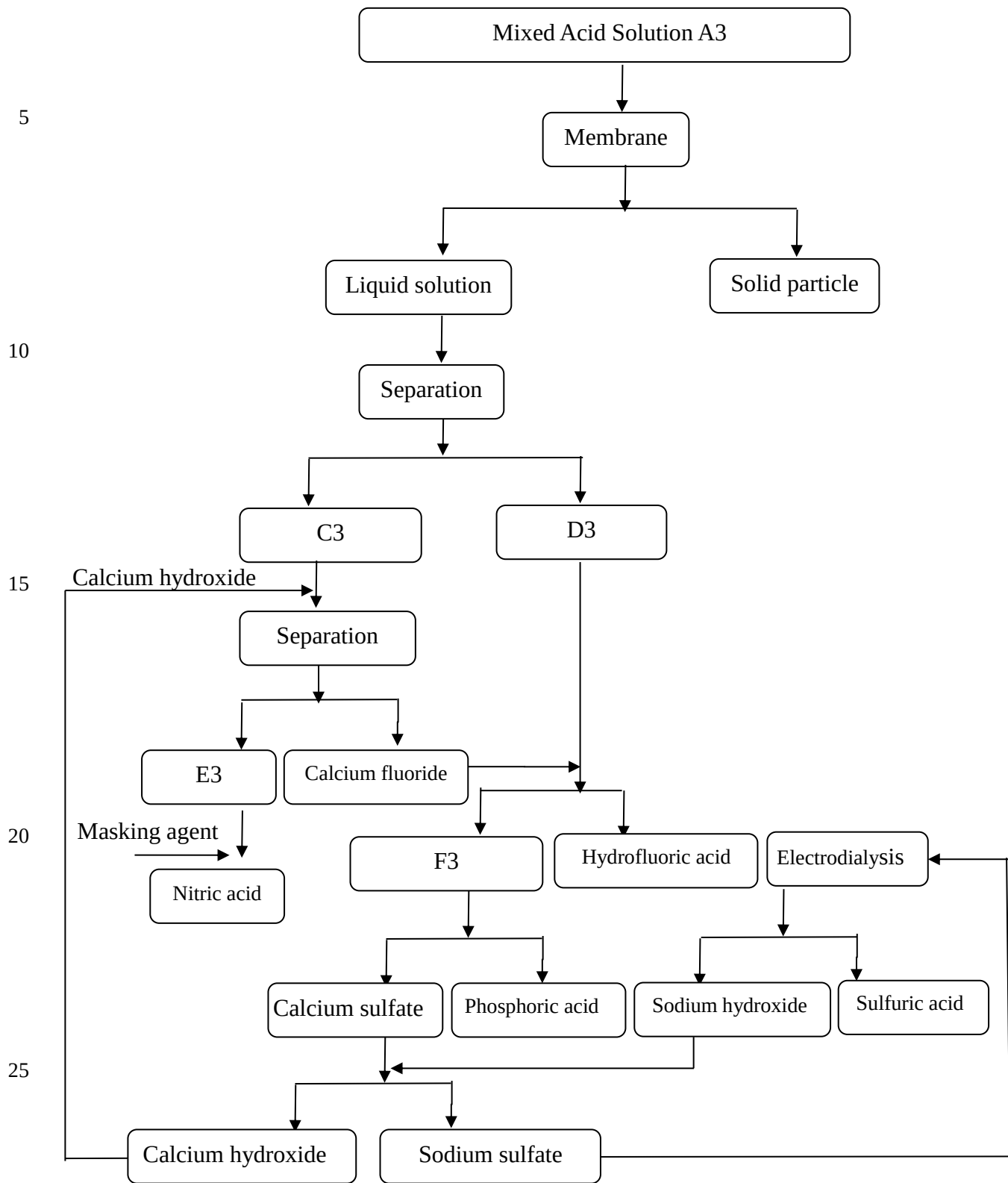


Fig.3

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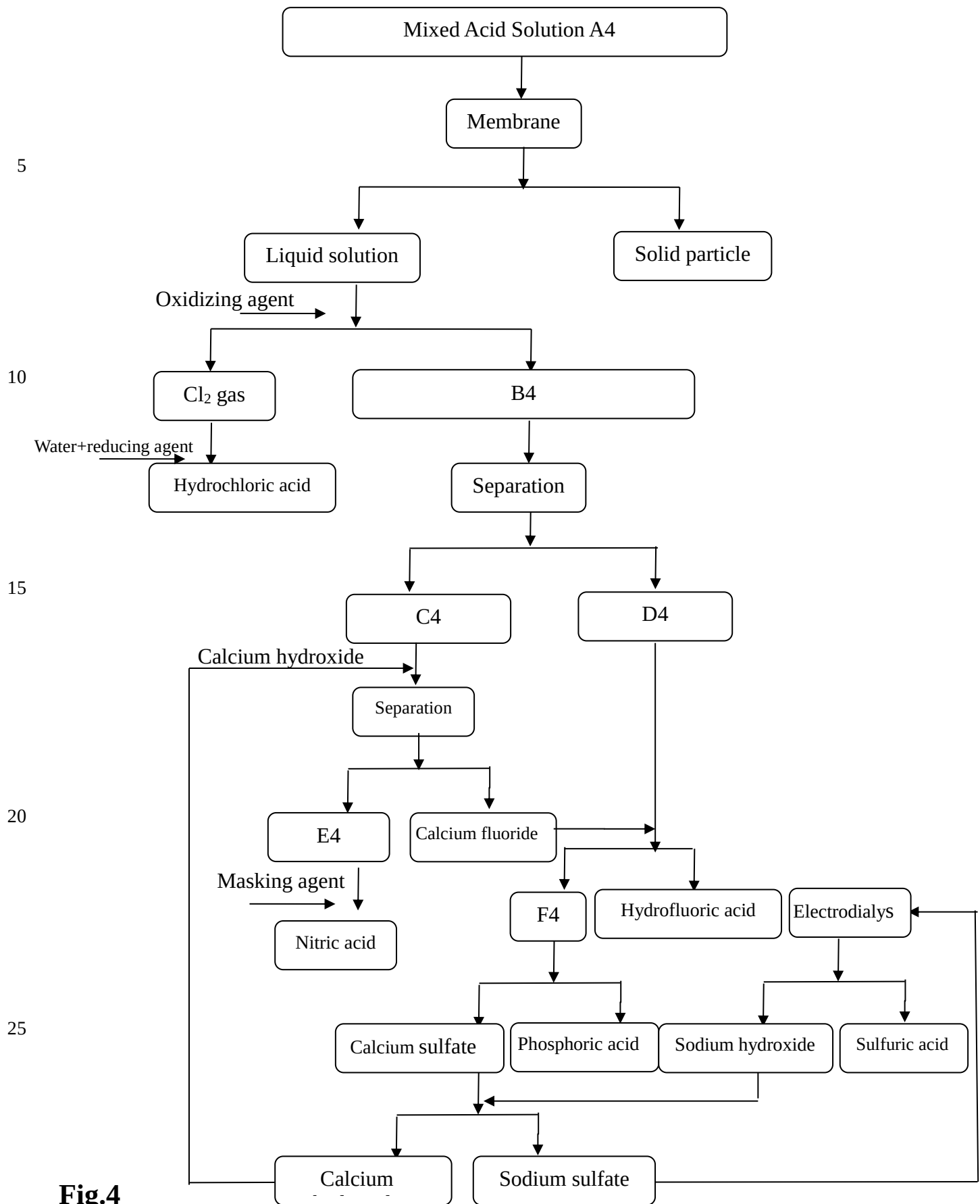


Fig.4