

A simultaneous regeneration and utilization method of waste phosphating slag with waste phosphorus and sulfur binary acid liquid

5 [001] TECHNICAL FIELD

 [002] The invention relates to the field of secondary utilization of waste resources, in particular to a comprehensive regeneration and utilization method of waste phosphating slag and waste phosphorus and sulfur binary acid liquid. Specifically, the invention relates to a simultaneous regeneration and utilization
10 method of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, wherein the waste phosphating slag is produced from a phosphating process on steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium.

15 [003] BACKGROUND

 [004] Presently, in the technical fields for manufacturing electronic devices and equipment, it is usually necessary to perform chemical etching, polishing, or fine texturing treatments on the surface of aluminium-based matrix to ensure the surface properties and performance of the aluminium material
20 meet a certain specific requirement. During such surface treatments process, a large amount of waste phosphorus and sulfur binary acid liquid is produced. At the same time, surface treatments such as phosphating process is usually performed to the surface of steel-based material before painting or other anti-corrosion processes, a certain amount of waste phosphating slag, such as in
25 forms of precipitates, comprising iron phosphate would be produced.

 [005] For example, Chinese patent application CN 106148960 A discloses methods of etching aluminium matrix. This application discloses three technical solutions to ensure the etching performance: (1) adjust the temperature and pressure conditions inside the reaction chamber during dry etching process,
30 maintain aluminium chloride in a gaseous state and suppress the generation of

aluminium chloride particles. After exhausting the gas, the residue of aluminium chlorine particles inside the reaction chamber is insignificant and thereby the amount of aluminium-containing compounds and the generation of aluminium-containing particles is at a low level; or (2) implement a gas flushing step after the dry etching process but before the fluoro-chlorine displacement process so as to reduce the amount of aluminium compounds inside the reaction chamber; or (3) performing a certain cleaning steps in the reaction chamber before the dry etching process, in order to reduce the amount of aluminium compounds and the aluminium-containing particles subsequently generated. All these three approaches would reduce the quantity of aluminium-containing particles during the dry etching process, which reduces the deposition probability of such particles onto the film layer to be etched. The problem of residues and short circuits in the precision processing would be released and production yield is thus improved.

[006] Chinese patent application CN 102206821 A discloses an adjusted composition for etching and regulating aluminium alloy and a method for etching aluminium alloy. The adjusted composition composed of a component A and a component B. The component A is an etching solution, and the component B is a regulating solution. The component A comprises ferric chloride, phosphoric acid, pH regulator, corrosion inhibitor and defoaming agent; and the component B comprises phosphoric acid and sulfuric acid. The application also provides a method for etching aluminium alloy, which comprises the following steps of etching an aluminium alloy substrate in the said etching solution at 20-40 °C, and regulating the aluminium alloy in the said regulating solution at 60-80 °C. By using a two-step acidic etching system, the risk associating with the uneasily removal of abundant black ash, rough surface, edge burr and serious lateral erosion during the etching process with the etching solution is reduced.

[007] Chinese patent application CN 114806581 A discloses a method for recycling waste phosphorus and sulfur binary acid liquid, which comprises the

following steps: (1) adding acid liquor into the binary waste acid for treatment, and then carrying out solid-liquid separation to obtain aluminium fluoride precipitate and primary purified liquid; (2) distilling the primary purified liquid obtained in the step (1) to obtain secondary purified liquid and the acid liquid; and (3) carrying out nanofiltration treatment on the secondary purified liquid obtained in the step (2) to obtain binary acid liquid and phosphoric-sulfur binary acid etching liquid. However, the recycling method merely recycles the binary waste acid generated in the aluminium etching but is not capable to recycle two or more different types of waste produced from various sources.

[008] Conventionally, the waste phosphating slag produced from a phosphating process on steel and the waste phosphorus and sulfur binary acid liquid produced from a surface treatment process on aluminium contain large amounts of metallic ions, particularly aluminium ions, it is difficult to achieve a high recovery efficiency. These two types of waste, being one in solid state and the other in liquid state, are often recovered separately in the form of solid-liquid separation. In particular, to achieving a simultaneous comprehensive recycling for the said two types of waste resources is still a challenge.

[009] DETAILED DESCRIPTION

[010] The following detailed description is merely illustrative in nature and is not intended to limit the embodiments of the subject matter of the application or uses of such embodiments.

[011] 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.

[012] 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.

[013] Terminology. The following paragraphs provide definitions and/or context for terms found in this disclosure (including the appended claims):

[014] “Comprising”. This term is open-ended. As used in the appended claims, this term does not foreclose additional structure or steps.

[015] “First”, second, third, fourth” etc. As used herein, these terms are used as labels for nouns that they precede, and do not imply any type of ordering (e.g. spatial, temporal, logical, etc.). For example, reference to a “first” acid liquid does not necessarily imply that this absorption liquid is the first acid liquid in a sequence; instead, the term “first” is used to differentiate this absorption liquid from another acid liquid (e.g., a “second” acid liquid).

[016] “Based on”. As used herein, this term is used to describe one or more factors that affect a determination. This term does not foreclose additional factors that may affect a determination. That is, a determination may be solely based on those factors or based, at least in part, on those factors. Consider the phrase “determine A based on B.” While B may be a factor that affects the determination of A, such a phrase does not foreclose the determination of A from also being based on C. In other instances, A may be determined based solely on B.

[017] In addition, certain terminology may also be used in the following description for the purpose of reference only, and thus are not intended to be limiting. For example, terms such as “upper”, “lower”, “above”, and “below” refer to directions in the values in a range or ranges to which reference is made.

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

description, numerous specific details are set forth, such as specific 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
5 instances, well-known techniques are not described in detail in order to not unnecessarily obscure embodiments of the present disclosure.

[019] In view of the problems existed in the prior art, the object of the present invention is to provide a comprehensive simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary
10 acid liquid, particularly, the waste phosphating slag is produced from a phosphating process on steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process, such as etching or polishing, on aluminium. The present invention adopts a method of introducing the phosphating slag produced during the steel phosphating process into the
15 waste phosphorus and sulfur binary acid liquid produced by the aluminium surface treatment processes, whose main components composed of iron phosphate and manganese phosphate, and etc., to effectively generate products of fluoroaluminate and simultaneously to regenerate recycled phosphorus and sulfur binary acid liquid being products for direct usage in chemical polishing
20 process, which achieves extreme high efficiency in regeneration and utilization of the above two types of wasted resources in a reduced unit cost.

[020] As a first aspect, the invention provides a method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, wherein the waste phosphating slag is produced
25 from a phosphating process on steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium, the method comprises the following steps:

[021] (1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a

mixed acid solution, wherein the first acid liquid comprises sulfuric acid in a mass ratio of 30-40%;

[022] (2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, wherein the second acid liquid comprises hydrofluoric acid in a mass ratio of 1-10%, the fluoroaluminate product comprises at least one of manganese fluoroaluminate, iron fluoroaluminate and zinc fluoroaluminate;

[023] (3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2);

[024] (4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur binary acid product and a residue as a fourth acid liquid, wherein the fourth acid liquid is recycled as a component of the first acid fluid in step (1).

[025] The regeneration method provided by the invention realizes the simultaneous regeneration and utilization of waste phosphating slag and waste phosphorus and sulfur binary acid liquid. For reaching the above procedure combinations, combination sequences and the respective operation conditions, the inventor has conducted massive optimization experiments and completed large number of analysis and finalization, and the optimal conditions and combinations suitable for the two types of waste resources are determined, particularly on the selection of Zeta potential of the nano filter membrane.

Preferably, when the Zeta potential of the nano filter membrane is within a range from -60 mV to -20mV, a recovery efficiency of the waste phosphating slag reaches 98% or above and a recovery efficiency of the waste phosphorus and sulfur binary acid liquid reaches 95% or above could be realized simultaneously.

[026] The following technical solutions are preferred technical solutions of the present invention and do not limit the scope of the technical solutions provided by the gist of the present invention. Through the following technical solutions, the technical objectives and technical effects of the present invention
5 can be better achieved and realized.

[027] Preferably, the first acid liquid comprises sulfuric acid. Preferably, the mass ratio of the sulfuric acid solution is 30-40%, for example, can be 30%, 31%, 32%, 33%, 34%, 35%, 36%, 37%, 38%, 39%, 40%, etc., and is not limited to the specified values, other unspecified values within the value range are also
10 applicable.

[028] Preferably, the second acid liquid comprises hydrofluoric acid solution. Preferably, the mass ratio of the hydrofluoric acid solution is 1-10%, for example, can be 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 5.5%, 6%, 6.5%, 7%, 7.5%, 8%, 8.5%, 9%, 9.5% or 10%, etc., and is not limited to the
15 specified values, other unspecified values within the value range are also applicable.

[029] Preferably, the third acid liquid can be returned to step (1) or step (2) for reprocessing. Preferably, the third acid liquid can be returned to step (2) and added to the second acid liquid for a cyclic iterative processing.

[030] Preferably, the fourth acid liquid can be returned to step (1) or step (2) for reprocessing. Preferably, the fourth acid liquid can be returned to step (1) and added to the first acid liquid for a cyclic iterative processing.

[031] Preferably, the temperature of the distillation is controlled and maintained at a range between 90 °C and 120 °C, preferably, between 94 °C and
25 114 °C, for example, can be 90 °C, 92 °C, 94 °C, 96 °C, 98 °C, 100 °C, 102 °C, 104 °C, 106 °C, 108 °C, 110 °C, 112 °C, 114 °C, 116 °C, 118 °C or 120 °C, etc., and is not limited to the specified values, other unspecified values within the value range are also applicable.

[032] Preferably, the pressure of the distillation is increased and could be controlled to be within a range between 20 kPa and 30 kPa, preferably, between 24 kPa and 28 kPa, for example, can be 20 kPa, 20.5 kPa, 21 kPa, 21.5 kPa, 22 kPa, 22.5 kPa, 23 kPa, 23.5 kPa, 24 kPa, 24.5 kPa, 25 kPa, 25.5 kPa, 26 kPa, 26.5 kPa, 27 kPa, 27.5 kPa, 28 kPa, 28.5 kPa, 29 kPa, 29.5 kPa or 30 kPa, etc., and is not limited to the specified values, other unspecified values within the value range are also applicable.

[033] Preferably, as an essential parameter of the present invention, the zeta potential of the nano filter membrane used in the nanofiltration treatment is between -60 mV and -20 mV, more preferably, between -55 mV and -25 mV, even more preferably, between -50 mV and -30 mV, for example, can be -60 mV, -57.5 mV, -55 mV, -52.5 mV, -50 mV, -47.5 mV, -45 mV, -42.5 mV, -40 mV, -37.5 mV, -35 mV, -32.5 mV, -30 mV, -27.5 mV, -25 mV, -22.5 mV, -22 mV, etc., and is not limited to the specified values, other unspecified values within the value range are also applicable.

[034] Preferably, the pore size of the nano filter membrane is specified to be between 8 nm and 10 nm, preferably, between 8.5 nm and 9.5 nm, for example, can be 8 nm, 8.1 nm, 8.2 nm, 8.3 nm, 8.4 nm, 8.5 nm, 8.6 nm, 8.7 nm, 8.8 nm, 8.9 nm, 9 nm, 9.1 nm, 9.2 nm, 9.3 nm, 9.4 nm, 9.5 nm, 9.6 nm, 9.7 nm, 9.8 nm, 9.9 nm or 10 nm, etc., and is not limited to the specified values, other unspecified values within the value range are also applicable.

[035] Preferably, the pressure in nanofiltration is specified to pressure in the nanofiltration treatment is between 80 bar and 100 bar, preferably, between 90 bar and 95 bar, for example, can be 80 bar, 81 bar, 82 bar, 83 bar, 84 bar, 85 bar, 86 bar, 87 bar, 88 bar, 89 bar, 90 bar, 91 bar, 92 bar, 93 bar, 94 bar, 95 bar, 96 bar, 97 bar, 98 bar, 99 bar or 100 bar, etc., and is not limited to the specified values, other unspecified values within the value range are also applicable.

[036] Preferably, membrane permeability, or alternatively named as the membrane flux, of the nano filter membrane is in a range from 6 L/(m²·h) to 7

L/(m²·h), preferably, from 6.3 L/(m²·h) to 6.8 L/(m²·h), for example, can be 6 L/(m²·h), 6.1 L/(m²·h), 6.2 L/(m²·h), 6.3 L/(m²·h), 6.4 L/(m²·h), 6.5 L/(m²·h), 6.6 L/(m²·h), 6.7 L/(m²·h), 6.8 L/(m²·h), 6.9 L/(m²·h) or 7 L/(m²·h), etc., and is not limited to the specified values, other unspecified values within the value
5 range are also applicable.

[037] On a second aspect, as a preferred technical solution of the present invention, the present invention provides a method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, wherein the waste phosphating slag is produced from a
10 phosphating process on steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium, the method comprises the following steps:

[038] (1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a
15 mixed acid solution, wherein the first acid liquid comprises sulfuric acid in a mass ratio of 30-40%;

[039] (2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, wherein the second acid liquid
20 comprises hydrofluoric acid in a mass ratio of 1-10%, the fluoroaluminate product comprises at least one of manganese fluoroaluminate, iron fluoroaluminate and zinc fluoroaluminate;

[040] (3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified
25 solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2), wherein a temperature of the distillation in step (3) is within a range between 90 °C and 120 °C and a pressure of the distillation in step (3) is within a range between 20 kPa and 30 kPa;

[041] (4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur binary acid product and a residue as a fourth acid liquid, wherein the fourth acid liquid is recycled as a component of the first acid fluid in step (1),

5 [042] wherein a Zeta potential of the nano filter membrane is within a range from -60 mV to -20 mV,

[043] wherein pore size of the nano filter membrane is between 8 nm and 10 nm, a pressure in the nanofiltration treatment of step (4) is between 80 bar and 100 bar and

10 [044] wherein membrane permeability, or alternatively named as the membrane flux, of the nano filter membrane is in a range from 6 L/(m²·h) to 7 L/(m²·h).

[045] Compared with the prior art, the methods disclosed in the present invention has the following technical effects and benefits:

15 [046] (1) After analysis, the regenerated phosphorus and sulfur binary acid product obtained from the disclosed processes of the present invention meets the quality requirements of surface polishing liquid for aluminium materials, realizing the recycling of waste phosphorus and sulfur binary acid liquid.

20 [047] (2) Reduce the overall operating costs for resourcing the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid that are required to be outsourced for recycling separately, achieving simultaneous regeneration of the two types of waste in two states of solid and liquid.

[048] (3) The recovery efficiency of the regenerated acid is increased.
25 The recovery efficiency using a conventional scheme is usually around 70% whereas the recovery efficiency using the scheme of the present invention can reach up to 90% and above.

[049] (4) The aluminium ions in the waste phosphorus and sulfur binary acid liquid are vastly separated and resourced, and high pure and value-added products of fluoroaluminate are obtained.

[050] The present invention illustrates the detailed methods of the present invention through the above embodiments, but the present invention is not limited to the above detailed methods, that is, it does not mean that the present invention must rely on the above detailed methods to be implemented. Those skilled in the art should understand that any improvements to the present invention, related replacements of the methods of the present invention, addition of auxiliary method steps, selection of specific methods, etc., all fall within the scope of protection and disclosure of the present invention.

[051] BRIEF DESCRIPTION OF THE DRAWINGS

[052] Figure 1 is a process flow chart of the method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid of the present invention.

[053] EMBODIMENTS

[054] The technical solutions of the present invention will be further described in detail below, merely for facilitating a better understanding of the present invention. However, the following embodiments are only exemplary embodiments of the present invention and do not represent or limit the scope of protection of the present invention. The scope of protection of the present invention should be the same as the claims.

[055] Example 1

[056] This embodiment provides a method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, the waste phosphating slag is produced from a phosphating process on stainless steel and the waste phosphorus and sulfur binary acid liquid

is produced from a surface treatment process on aluminium, the efficient process flow chart of the method is shown in Figure 1 and the method comprises the following steps:

[057] (1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a mixed acid solution, the first acid liquid comprises sulfuric acid in a mass ratio of 40%.

[058] (2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, the second acid liquid comprises hydrofluoric acid in a mass ratio of 6%, the fluoroaluminate product comprises manganese fluoroaluminate, iron fluoroaluminate and zinc fluoroaluminate.

[059] (3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2), the temperature of the distillation is 108 °C and the pressure of the distillation is 25 kPa.

[060] (4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur binary acid product and a residue as a fourth acid liquid, the fourth acid liquid is recycled as a component of the first acid fluid in step (1), the Zeta potential of the nano filter membrane is -50 mV, pore size of the nano filter membrane is 9 nm, the pressure in the nanofiltration treatment is 90 bar and the membrane permeability of the nano filter membrane is 6.5 L/(m²·h).

[061] The waste phosphorus and sulfur binary acid liquid used in this embodiment comprises mass ratio of 20% sulfuric acid, 35% phosphoric acid, 40% water and 2.5% aluminium.

[062] The values of the purity of obtained fluoroaluminate product and the recovery efficiencies of both the waste phosphating slag and the waste

phosphorus and sulfur binary acid liquid are shown in Table 1. As compared to the comparative example 1 that also shown in Table 1, an effective simultaneous regeneration and utilization of these two types of waste resources is achieved.

[063] Example 2

5 [064] This embodiment provides a method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, the waste phosphating slag is produced from a phosphating process on stainless steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium, the efficient
10 process flow chart of the method is shown in Figure 1 and the method comprises the following steps:

[065] (1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a mixed acid solution, the first acid liquid comprises sulfuric acid in a mass ratio
15 of 35%.

[066] (2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, the second acid liquid comprises hydrofluoric acid in a mass ratio of 1%, the fluoroaluminate product comprises
20 manganese fluoroaluminate and iron fluoroaluminate.

[067] (3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2), the temperature of the distillation is 90 °C and the
25 pressure of the distillation is 20 kPa.

[068] (4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur binary acid product and a residue as a fourth acid liquid, the fourth acid liquid is recycled as a component of the first acid fluid in step (1), the Zeta potential of the nano

filter membrane is -60 mV, pore size of the nano filter membrane is 10 nm, the pressure in the nanofiltration treatment is 100 bar and the membrane permeability of the nano filter membrane is 6 L/(m²·h).

[069] The waste phosphorus and sulfur binary acid liquid used in this embodiment comprises mass ratio of 20% sulfuric acid, 35% phosphoric acid, 40% water and 4% aluminium.

[070] The values of the purity of obtained fluoroaluminate product and the recovery efficiencies of both the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid are shown in Table 1. As compared to the comparative example 2 that also shown in Table 1, an effective simultaneous regeneration and utilization of these two types of waste resources is achieved.

[071] Example 3

[072] This embodiment provides a method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, the waste phosphating slag is produced from a phosphating process on stainless steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium, the efficient process flow chart of the method is shown in Figure 1 and the method comprises the following steps:

[073] (1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a mixed acid solution, the first acid liquid comprises sulfuric acid in a mass ratio of 30%.

[074] (2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, the second acid liquid comprises hydrofluoric acid in a mass ratio of 10%, the fluoroaluminate product comprises manganese fluoroaluminate and iron fluoroaluminate.

[075] (3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2), the temperature of the distillation is 120 °C and the pressure of the distillation is 30 kPa.

[076] (4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur binary acid product and a residue as a fourth acid liquid, the fourth acid liquid is recycled as a component of the first acid fluid in step (1), the Zeta potential of the nano filter membrane is -30 mV, pore size of the nano filter membrane is 8 nm, the pressure in the nanofiltration treatment is 80 bar and the membrane permeability of the nano filter membrane is 7 L/(m²·h).

[077] The waste phosphorus and sulfur binary acid liquid used in this embodiment comprises mass ratio of 15% sulfuric acid, 35% phosphoric acid, 45% water and 4% aluminium.

[078] The values of the purity of obtained fluoroaluminate product and the recovery efficiencies of both the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid are shown in Table 1. As compared to the comparative example 3 that also shown in Table 1, an effective simultaneous regeneration and utilization of these two types of waste resources is achieved.

[079] Comparative example 1

[080] This comparative example 1 differs from Example 1 only in that the zeta potential of the nano filter membrane is -100 mV. The purity of obtained fluoroaluminate product and the recovery efficiencies of both the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid are shown in Table 1.

[081] Comparative example 2

[082] This comparative example 2 differs from Example 2 only in that the zeta potential of the nano filter membrane is -10 mV. The purity of obtained

fluoroaluminate product and the recovery efficiencies of both the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid are shown in Table 1.

[083] Comparative example 3

5 [084] This comparative example 3 differs from Example 3 only in that the zeta potential of the nano filter membrane is 20 mV. The purity of obtained fluoroaluminate product and the recovery efficiencies of both the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid are shown in Table 1.

10 Table 1

	REBAL [*]	REPS [#]	PUR ^{\$}
Example 1	95%	98%	98%
Example 2	98%	96%	99%
Example 3	92%	97%	99%
Comparative example 1	70%	88%	98%
Comparative example 2	65%	85%	98%
Comparative example 3	50%	75%	98%

* Recovery efficiency of the waste phosphorus and sulfur binary acid liquid

Recovery efficiency of the waste phosphating slag

\$ Purity of obtained fluoroaluminate product

15 [085] The results of the Examples and Comparative examples indicate that it is essential to precisely control the Zeta potential of the nano filter membrane to enable the effective simultaneous regeneration and utilization of both the waste phosphating slag and the waste phosphorus and sulfur binary acid liquid.

20 [086] Although specific embodiments have been described in detail above, these embodiments are not intended to limit the scope of the present disclosure, even where only a single embodiment is described with respect to a

particular feature. Examples of features provided in the disclosure are intended to be illustrative rather than restrictive unless stated otherwise. The above description is intended to cover such alternatives, modifications, and equivalents as would be apparent to a person skilled in the art having the benefit of this disclosure. The scope of the present disclosure includes any feature or combination of features disclosed herein (either explicitly or implicitly), or any generalization thereof, whether or not it mitigates any or all of the problems addressed herein.

[087] Accordingly, new claims may be formulated during prosecution of this application (or an application claiming priority thereto) to any such combination of features. In particular, with reference to the appended claims, features from dependent claims may be combined with those of the independent claims and features from respective independent claims may be combined in any appropriate manner and not merely in the specific combinations enumerated in the appended claims.

[088] In addition, the various embodiments of the present invention can also be combined arbitrarily, and as long as they do not damage the idea of the present invention, they should also be regarded as the disclosed content of the present invention.

Claims

1. A method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, wherein the waste phosphating slag is produced from a phosphating process on steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium, the method comprises the following steps:

(1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a mixed acid solution, wherein the first acid liquid comprises sulfuric acid in a mass ratio of 30-40%;

(2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, wherein the second acid liquid comprises hydrofluoric acid in a mass ratio of 1-10%, the fluoroaluminate product comprises at least one of manganese fluoroaluminate, iron fluoroaluminate and zinc fluoroaluminate;

(3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2);

(4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur binary acid product and a residue as a fourth acid liquid, wherein the fourth acid liquid is recycled as a component of the first acid fluid in step (1),

characterized in that, a Zeta potential of the nano filter membrane is within a range from -60 mV to -20mV, further characterized in that a recovery efficiency of the waste phosphating slag reaches 98% or above and a

recovery efficiency of the waste phosphorus and sulfur binary acid liquid reaches 95% or above.

2. The method as claimed in claim 1, characterized in that a temperature of the distillation in step (3) is within a range between 90 °C and 120 °C, preferably, between 94 °C and 114 °C.

3. The method according to any one of claims 1-2, characterized in that a pressure of the distillation in step (3) is within a range between 20 kPa and 30 kPa, preferably, between 24 kPa and 28 kPa.

4. The method according to any one of claims 1 to 3, characterized in that the Zeta potential of the nano filter membrane used in the nanofiltration treatment of step (4) is between -55 mV and -25 mV, preferably, between -50 mV and -30 mV.

5. The method according to any one of claims 1 to 4, characterized in that pore size of the nano filter membrane used in the nanofiltration treatment of step (4) is between 8 nm and 10 nm, preferably, between 8.5 nm and 9.5 nm.

6. The method according to any one of claims 1 to 5, wherein a pressure in the nanofiltration treatment of step (4) is between 80 bar and 100 bar, preferably, between 90 bar and 95 bar.

7. The method according to any one of claims 1 to 6, characterized in that membrane permeability of the nano filter membrane is in a range from 6 L/(m²·h) to 7 L/(m²·h), preferably, from 6.3 L/(m²·h) to 6.8 L/(m²·h).

8. A method of simultaneous regeneration and utilization of waste phosphating slag with waste phosphorus and sulfur binary acid liquid, wherein the waste phosphating slag is produced from a phosphating process on steel and the waste phosphorus and sulfur binary acid liquid is produced from a surface treatment process on aluminium, the method comprises the following steps:

(1) dissolving the waste phosphating slag with a first acid liquid and mixing with the waste phosphorus and sulfur binary acid liquid to obtain a mixed acid solution, wherein the first acid liquid comprises sulfuric acid in a mass ratio of 30-40%;

5 (2) adding a second acid liquid into the mixed acid solution obtained in step (1) to obtain a fluoroaluminate product and a primary purified solution through solid-liquid separation, wherein the second acid liquid comprises hydrofluoric acid in a mass ratio of 1-10%, the fluoroaluminate product comprises at least one of manganese
10 fluoroaluminate, iron fluoroaluminate and zinc fluoroaluminate;

(3) distilling the primary purified solution obtained in step (2) to obtain a distillate as a third acid liquid and a residue as the secondary purified solution, wherein the third acid liquid is recycled as a component of the second acid liquid in step (2), wherein a temperature of the distillation in
15 step (3) is within a range between 90 °C and 120 °C and a pressure of the distillation in step (3) is within a range between 20 kPa and 30 kPa;

(4) filtering the second purified solution obtained in step (3) with a nano filter membrane to obtain a regenerated phosphorus and sulfur mixed acid product and a residue as a fourth acid liquid, wherein the fourth
20 acid liquid is recycled as a component of the first acid fluid in step (1),

characterized in that, a Zeta potential of the nano filter membrane is within a range from -60 mV to -20mV, further characterized in that pore size of the nano filter membrane is between 8 nm and 10 nm, a pressure in the nanofiltration treatment of step (4) is between 80 bar and 100 bar and
25 membrane permeability of the nano filter membrane is in a range from 6 L/(m²·h) to 7 L/(m²·h).