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(54) **Method for solidifying and stabilizing waste acid**

Verfahren zum Verfestigen und Stabilisieren von Abfallsäuren

Procédé de solidification et de stabilisation d'acide usagé

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Description

BACKGROUND OF THE INVENTION

Field of Invention

[0001] This invention relates to a method for treating waste acid, and especially, to a method for solidifying and stabilizing waste acid. The method of the present invention can improve efficiency of the solidifying steps and stability of the solidified waste acid.

Related Art

[0002] In general, the radioactive-contaminated metal wastes include stainless steel and carbon steel which are used in the construction of the nuclear power plant. Since of the well worn piping of the nuclear power plant has to be replaced, a large amount of the radioactive-contaminated stainless steel should be treated. Decontaminants and methods for decontaminating have been improved and are applied, such as mechanical decontaminating by hydraulic giant; electrochemical decontaminating by a mixture of phosphoric acid, sulfuric acid, and nitric acid; and chemical decontaminating by decontaminant containing fluoroboric acid. The radioactive-contaminated metal wastes can reach regulations on final disposal of low-level waste after treated by the above-mentioned methods.

[0003] Decontaminant containing phosphoric acid and fluoroboric acid are widely applied in the decontamination of the radioactive metal wastes. For example, the mixture of phosphoric acid and nitric acid is applied for decontaminating of the metal wastes containing copper and aluminum; the mixture of phosphoric acid, sulfuric acid and nitric acid is applied to electrochemical decontamination suitable for the stainless steel wastes; and the decontaminant containing fluoroboric acid is applied to chemical decontamination. During the decontamination process, the metal ions accumulate in the decontaminant gradually. Then, the metal salts precipitate after reaching the saturated concentration. The precipitated material in the decontaminant is disadvantageous to the decontamination process. Moreover, if the decontaminant is contaminated by the nuclides and the radioactivity thereof raises, the decontaminant should be regenerated. Metal ions of the recycled decontaminant containing phosphoric acid and fluoroboric acid can be removed by way of oxalic acid selective precipitation, electrolysis recovery, and cation exchange, so that the decontaminant can be recovered and reused thereafter. After several times of the regenesis, decontaminant has to be eliminated since the radioactivity thereof is high. The used decontaminant becomes waste acid.

[0004] At the present day, the treatment of radioactive waste acid still makes progress. In the conventional process, the used decontaminant containing fluoroboric acid is treated by destroying the BF_4^- chelate therein so that CaF_2 can be precipitated. BF_4, which is stable at room temperature, can be hydrolyzed to form HF by aluminum salt as the catalyst, and then CaF_2 is formed after addition of calcium ion. The aforementioned reactions are the following formulas:

$$3HBF_4 + Ah(SO_4)3 + 9H_2O \Leftrightarrow 2H_3AlF_6 + 3H_2SO_4 + 3H_3BO_3 ;$$

and

$$H_3AlF_6 + 3Ca(OH)_2 \Leftrightarrow 3CaF_2 + Al(OH)_3 + 3H_2O.$$

In the formulas, the amount of aluminum salts has to add more than the concentration of fluoroboric acid so that the efficiency of eliminating fluoroboric acid can be ensured. The conventional method for eliminating fluoroboric acid in waste acid is effective but, however, the amount of the secondary waste will increase.

[0005] The conventional methods for treating used decontaminant containing phosphoric acid include selectively precipitating and directly neutralizating. In the method of selectively precipitating, for example, in order to treat 2500 L of used decontaminant containing phosphoric acid, 117 kg of iron powder and 1558.5 kg of oxalic acid is necessary to make phosphoric acid precipitate; 7089 L of water is necessary for solid-liquid separation; and the separated water is needed to neutralize and to eliminate oxalic acid by ultraviolet and ozone. After that, the treated decontaminant has to eliminate the radioactivity further. As described in the US patent no. 5,645,518 which is titled "Method for stabilizing low-level mixed wastes at room temperature", the phosphate ceramic material is applied to treat the solid and liquid wastes. The solid waste is grinded to a size in a range between 4 and 75 micrometers, the grinded powder is contacted with phosphate-containing solution to create phosphates of the oxide in a sol-gel, and the sol-gel is solidified. The solidified waste is convenient for follow-up treatment.

[0006] As described above, the conventional methods for treating waste acid have disadvantages including: (1) a large amount of the neutralizer is necessary to mix with the same amount of waste acid so that the effect of compaction of waste acid is undesired; (2) the solid sludge and liquid waste generated during treating of waste acid have to be

treated by another process so that the secondary contamination and the large amount of waste is undesired; (3) heat generated during the treatment of waste acid is hard to control so that the rapid setting caused by heat is disadvantageous to waste acid; and (4) applying neutralizers separately to waste acid is adverse for stabilization of waste acid. The aforementioned disadvantages should be eliminated to improve the solidification and stabilization of waste acid.

[0007] In this regard, it is important to provide a method for solidifying and stabilizing waste acid which prevents formation of secondary contamination, has low cost, simplifies the processes, and improves the efficiency of solidification to eliminate the foregoing drawbacks.

SUMMARY OF THE INVENTION

[0008] Accordingly, it is an object of the present invention to provide a method for treating radioactive waste acid to solidify and stabilize by adding barium hydroxide to adjust the pH of waste acid so that radioactive waste acid can be stabilized and the corrosion thereof can be reduced.

[0009] Another object of the present invention is to provide a method for solidifying waste acid by applying at least one solidifying agent to radioactive waste acid so that numerous granules in radioactive waste acid are formed. The granule is advantageous to reduce the volume of the solidified waste and to improve the mechanical strength thereof.

[0010] Yet another object of the present invention is to provide a method for solidifying radioactive waste acid which can prevent the formation of ettringite. The expansion and chap of the solidified waste caused by ettringite can be prevented and the stabilization thereof can be improved.

[0011] Still another object of the present invention is to provide a method for solidifying radioactive waste acid by adding barium hydroxide to form barium hydrogen phosphate. The formed granule of barium hydrogen phosphate is firm, tiny, solid to coagulate and easy to disperse in radioactive waste acid. Radioactive Waste acid containing granules is easy to flow and to mix with other chemicals.

[0012] In order to achieve the above objects, the present invention provides a method for solidifying and stabilizing radioactive waste acid including the steps of condensing radioactive waste acid containing phosphoric acid; adding barium hydroxide to the condensed radioactive waste acid and adjusting the pH thereof to form barium hydrogen phosphate; and adding solidifying agents to solidify barium hydrogen phosphate. The step of adding barium hydroxide is for adjusting the pH of radioactive waste acid and for stabilizing radioactive waste acid. The adjusted pH of radioactive waste acid can improve the formation of barium hydrogen phosphate. In the step of adding the solidifying agents, the solidifying agents are added in batches or continuously so that heat, which is generated by the intense reaction and is disadvantageous to solidification, can be prevented. In the method of present invention, radioactive waste acid containing phosphoric acid can form granules by adding solidifying agents to reduce the volume of waste acid. Moreover, radioactive waste acid containing phosphoric acid can be mixed with another waste acid containing fluoroboric acid. The pH of the mixed radioactive waste acid can be adjusted by adding barium hydroxide so that the stability of the mixed waste acid can be kept. The concentration of the solution and metal ions will not obstruct the solidifying reaction of the mixed radioactive waste acid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The invention can be more fully understood by reading the subsequent detailed description and examples with references made to the accompanying drawings, wherein:

[0014] Fig. 1 shows a basic flow diagram of one embodiment of the present invention;

[0015] Fig. 2 shows a basic flow diagram of another embodiment of the present invention; and

[0016] Fig. 3 shows a basic flow diagram of another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0017] A method for solidifying and stabilizing radioactive waste acid of the present invention is to improve the efficiency of the solidifying radioactive waste acid, to solve the problem of heat generated by the acid-base reaction, and to keep the efficiency of solidification which may be influenced by concentration of waste acid metal ions contained therein. The conventional method for adjusting pH is adding lime (calcium hydroxide) or sodium hydroxide. Calcium phosphate is formed by adding calcium hydroxide in radioactive waste acid containing phosphoric acid. However, during the solidifying reaction of radioactive waste acid, low-density ettringite is formed by calcium, which is from calcium phosphate, reacting with tricalcium aluminate in cement. The formed ettringite makes the volume of the solidified product of radioactive waste acid expended gradually so that the solidified product becomes chapped. In order to eliminate expansion and chapping of the solidified product of radioactive waste acid, mass of the solidified product should be increased with undesired volume. Besides, crystal of phosphoric acid is easily formed in radioactive waste acid. Crystal is disadvantageous to deliver solidified waste acid in a duct. During the solidifying step of the present invention, granules can be formed so

that volume of the solidified waste acid can be reduced and mechanical strength thereof can be improved. The present invention will be apparent from the following detailed description, which proceeds with reference to the accompanying drawings.

[0018] Fig. 1 shows a basic flow diagram of one embodiment of the present invention. In the embodiment, waste acid containing phosphoric acid can be a mixed radioactive waste acid, for example a solution of phosphoric acid and nitric acid, or a solution of nitric acid mixed with phosphoric acid or sulfuric acid. In step 100 shown in Fig. 1, waste acid containing waste acid is condensed by heating and stirring so that water therein is evaporated. After step 100, waste acid in the condensed waste is condensed to a concentration of 50% to 65% which is suitable for further solidification. Next, in the step S110, a conversion of phosphate is proceeded. Barium hydroxide is added to the condensed radioactive waste acid. During the addition of barium hydroxide, the condensed radioactive waste acid is kept stirring so that phosphoric acid can react with barium hydroxide to form barium hydrogen phosphate ($BaHPO_4$) completely. Furthermore, the pH of the mixed waste acid can be adjusted to 2.5-4.5. In the embodiment, the preferred pH is 3. In step 120, when pH of the mixed waste acid is in a range of 2.5 to 4.5, a solidifying agent is added so that the radioactive waste acid containing barium hydrogen phosphate can be solidified. The solidifying agent should be added to the mixed waste acid in batches or continuously. Temperature of the mixed waste acid during the addition of the solidifying agent should be kept in a range of 30 to 45°C. In the embodiment, the preferred way for adding solidifying agents is three times in batches. In the first batch, a half of total weight of the solidifying agent is added. In the second and the third batch, one-fourth of total weight of the solidifying agent is added, respectively.

[0019] The following is a detailed description of the embodiment shown in Fig. 1. In the step S100, 3510 g of radioactive waste acid containing phosphoric acid, in which the initial concentration of phosphoric acid is 45%, is held in a beaker, heated by a heating plate and stirred by an automatic stirrer so that water in waste acid is vaporized and the weight percent of water in waste acid is reduced. After the heating step, 2700 g of the condensed waste acid is obtained and the concentration of phosphoric acid in the condensed radioactive waste acid is in a range between 50 % and 65%. In the step of S110, the obtained 2700 g of the condensed waste acid is divided into two parts. Two parts of 1350 g of the condensed waste acid are held in two mixers, and 189 g and 181.6 g of barium hydroxide are added to the mixers, respectively. The mixer is kept running for one hour so that phosphoric acid in the condensed radioactive waste acid is converted to generate barium hydrogen hydroxide. In this step, barium hydroxide is used for adjusting pH of the condensed radioactive waste acid and for stabilizing thereof. After addition of barium hydroxide, barium hydrogen hydroxide is generated and pH of the condensed radioactive waste acid raises to 3.

[0020] As mentioned before, in the result of adding 181.6 g of monohydrous barium hydroxide which is used as a neutralizer, the applied amount of the solidifying agent is 310 g, and pH of the solidified product produced from radioactive waste acid containing phosphoric acid is 3.8 The compression strength of the solidified product which is formed after 12 days and after 28 days are 7.8 and 61.2 kg/cm^2, after 28 days are 7.8 and 61.2 kg/cm^2, respectively. Besides, in the result of adding 189 g of monohydrous barium hydroxide which is used as a neutralizer, the applied amount of solidifying agents is 404.5 g, and pH of the solidified product produced from radioactive waste acid containing phosphoric acid is 3.9. The compression strength of the solidified product which formed after 12 days and after 28 days are 101.9 and 112.2 kg/cm^2, respectively. As shown in Table 1 below, the method for solidifying and stabilizing radioactive waste acid of the present invention can steadily increase the compression strength of the solidified product. The additional amounts of the solidifying agent and the neutralizer make a better characteristic of the solidified product of radioactive waste acid.

Table 1 Results of radioactive solidification of waste acid containing phosphoric acid

Conditions				Result of solidification		
Applied amount of the neutralizer (monohydrous barium hydroxide) (g)	Total weight before condensing (g)	Total weight after condensing (g)	Applied amount of the solidifying agent (g)	pH of the solidified product of waste acid	Compression strength after 12 days (kg/cm^2)	Compression strength after 28 days (kg/cm^2)
181.6	1755	1350	310.0	3.8	7.8	61.2
189	1755	1350	404.5	3.9	101.9	112.2

[0021] Assuming that the total weight of radioactive waste acid containing phosphoric acid before condensing is 1755 g and total volume thereof is 1013.3 ml. After adding barium hydroxide, and adding the solidifying agent in batches, radioactive waste acid is solidified to form a solidified product. The total weight and volume of the solidified product is 1572.5 g and 834 ml, respectively. As shown in Table 2 below, the weight and volume of radioactive waste acid can be

reduced by the method for solidifying and stabilizing radioactive waste acid of the present invention.

Table 2 Results of solidification of radioactive waste acid containing phosphoric acid

Conditions			Result of solidification				
Total weight of waste acid before condensing (g)	Total weight of waste acid after condensing (g)	Volume of waste acid before condensing (ml)	Weight of the solidifying agent (g)	Volume of the solidifying agent(ml)	Specific gravity of the solidifying agent	Weight ratio of IER/ solidifying agent	Volume ratio of IER/ solidifying agent
1755	1350	1013.3	1572.5	834	1.88	1.116	1.215

[0022] Fig. 2 shows a basic flow diagram of another embodiment of the present invention. The difference between Fig. 1 and Fig. 2 is that in the steps of Fig. 1, barium hydroxide and the solidifying agent are added to solidify radioactive waste acid, but in the steps of Fig. 2, barium hydroxide is firstly added to waste acid containing fluoroboric acid and then mixed with radioactive waste acid containing phosphoric acid to form a mixed waste acid. A granule is formed by adding a first solidifying agent to the mixed waste acid, and a solidified product of the mixed waste acid is formed by adding a second solidifying agent. In the step of S200 shown in Fig.2, waste acid containing phosphoric acid is condensed to a concentration of 55%. In the step of S210, barium hydroxide is added to radioactive waste acid containing fluoroboric acid to form a precipitation of barium fluoride (BaF_2), and then, is mixed with the condensed radioactive waste acid containing phosphoric acid in the concentration of 55% to form a stable mixed radioactive waste acid. In the mixed radioactive waste acid, the weight ratio of waste acid containing phosphoric acid to waste acid containing fluoroboric acid is six. In the step 220, a first solidifying agent is added to the mixed waste by dropping so that a plurality of small granules in the mixed waste acid are formed. The first solidifying agent is consisted of cement, slag, and fly ash. In the step of S230, the formed granules are added to another half of the mixed radioactive waste acid which is kept stirring. Next, a second solidifying agent is added to another half of the mixed radioactive waste acid to solidify. After that the granules in the mixed waste acid are as an aggregate in the solidified product. Weight of the formed solidified product can be reduced. In the embodiment, the second solidifying agent is cement.

[0023] The following is a detailed description of the embodiment shown in Fig. 2. In the step of S200, 6282 g of waste acid containing phosphoric acid is condensed to 5140 g with a concentration of 55%. In the step of S210, barium hydroxide is added to radioactive waste acid containing fluoroboric acid, and then is mixed with the condensed radioactive waste acid containing phosphoric acid to form a mixed waste acid. In the embodiment, weight of radioactive waste acid containing fluoroboric acid is 860 g, and the applied amount of barium hydroxide is 396 g. In the step of S220, 3029 g of the solidifying agent is mixed with the mixed radioactive waste acid to form the granules. After the granulating, weight of liquid in the mixed radioactive waste acid reduced to 68.91% in comparison with the mixed radioactive waste acid before granulating. In contrast, the steps shown in Fig. 2 are carried out by 6747 g of radioactive waste acid containing phosphoric acid with a concentration of 50%, 1122 g of waste acid containing fluoroboric acid, 524 g of barium hydroxide, and 4223 g of the first solidifying agent. After the granulating, weight of liquid in the mixed radioactive acid reduced to 77.72% in comparison with the mixed radioactive waste acid before granulating. The foregoing results are listed in the Table 3. The weight of liquid in radioactive waste acid can be reduced by the method for solidifying and stabilizing radioactive waste acid of the invention.

Table 3 Results of granulation of waste acid containing phosphoric acid mixed with fluoroboric acid

Concentration of waste acid containing phosphoric acid after condensed (%)	Conditions					Results of granulation	
	Total weight of waste acid containing phosphoric acid beforecondensing (g)	Total weight of waste acid containing phosphoric acid after condensed (g)	Total weight of waste acid containing fluoroboric acid (g)	Applied amount of the neutralizer (monohydrous barium hydroxide) (g)	Applied amount of the solidifying agent	Total weight of the granule after granulation	Total weight of the granule after granulation/ mixted waste acid + Applied amount of the neutralizer
55	6282	5140	860	396	3029	7282.2	68.91
50	7500	6747	1122	524	4223	10391	77.72

[0024] In the step of S230, the weight of radioactive waste acid containing phosphoric acid before condensing is 1571 g, total weight of radioactive waste acid containing fluoroboric acid is 215 g applied amount of barium hydroxide is 210 g, and the weight ratio of the applied amount of the total solidifying agent to the mixed radioactive waste acid is 30.1%. After solidifying, the compression strength of the solidified product which formed after 3 days and after 28 days are 25 kg and 28 kg/cm^2, respectively. Furthermore, in the water-resistance test of the sample which the compression strength is 74 kg per square centimeter, the result of compression strength after dipping in water for three months is 53.5 kg/cm^2. It indicated that the solidified product of radioactive waste acid formed by the method of the invention has improved weather resistance and water resistance characteristics. As shown in Table 4, the granule is formed by the first solidifying agent and the efficiency of solidification would not be influenced. In the steps shown in Fig. 2, a half of radioactive waste acid is inactivated, and then another half of radioactive waste acid is combined therewith to solidify. Heat of acid-base reaction and rapid setting caused by heat can be prevented to influence the quality of the solidified product of waste acid so that the compression strength of the solidified product can be improved.

Table 4 Results of solidification and granulation of radioactive waste acid containing phosphoric acid mixed with fluoroboric acid

Conditions						Results of solidification			
Weight of granule after partially granulation (g)	Mixed waste acid			Applied amount of cement (g)	Applied amount of solidifying agent/Mixed waste acid (%)	Compression strength (kg/cm^2)			Compression strength after dipping 3 months (kg/cm^2)
	Total weight of phosphoric acid before condensing (g)	Total weight of waste acid containing fluoroboric acid (g)	Applied amount of neutralizer (monohydrous barium hydroxide) (g)			After 3 days	After 14 days	After 28 days	
1875	1571	215	210	-	30.1	25		28	
1875	1393	189	210	-	31.9	35		51	
1657	1231	167	186	-	30.1	21		29	
Results of dipping the solidified product									
5195	3750	561	262.2	340	34.1	67.5	78.5	74	53.5
4097	2810	423	197	318	31.6	33	52	64	42.5
4097	2810	423	197	283.3	31.2	33.5	48	45	38.3

[0025] Fig. 3 shows a basic flow diagram of another embodiment of the present invention. In the steps of Fig. 2, barium hydroxide is added to radioactive waste acid containing fluoroboric acid, and mixed with radioactive waste acid containing phosphoric acid to form a mixed waste acid. In the steps of Fig. 3, the difference is that radioactive waste acid containing fluoroboric acid is mixed with radioactive waste acid containing phosphoric acid to form a mixed waste acid, and then added barium hydroxide to the mixed waste acid. In the step of S300, the waste acid containing phosphoric acid is condensed to a concentration in a range of 50% to 65%. In the step of S310, the condensed waste acid, of which the concentration is from 50% to 65%, is mixed with waste aid containing fluoroboric acid to form a mixed waste acid. In the mixed waste acid, the weight ratio of waste acid containing phosphoric acid to waste containing fluoroboric acid is six. In the step of S320, barium hydroxide is added to the mixed waste acid to adjust the pH of the mixed waste acid. Next, the mixed waste acid is held by stirring for one hour so that barium hydroxide can completely react with phosphoric acid and fluoroboric acid in the mixed waste acid which pH is 2.5 to 4.5. In step of S330, a solidifying agent is added in bathes when the mixed waste acid is stirring. In the embodiment, the preferred way for adding the solidifying agent is three times in batches. In the first batch, a half of total weight of the solidifying agent is added. In the second and the third batch, a one-fourth of total weight of the solidifying agent is added, respectively. The solidifying agent is consisted of cement, slag, silicon ash, and fly ash. Temperature of the mixed radioactive waste acid during the addition of the solidifying agent should be kept in a range of 30 to 45 °C.

[0026] The following is a detailed description of the embodiment shown in Fig. 3. In the step of S300, 5711 g of radioactive waste acid containing phosphoric acid, which is indicated as No. B5, is condensed by heating and stirring. The condensed radioactive waste acid is 5140 g. In the step of S310, the condensed radioactive waste acid is mixed with 860 g of waste acid containing fluoroboric acid to form a mixed waste acid. In the step of S320, 840 g of barium hydroxide is added to the mixed waste acid. The mixed radioactive waste acid is held for one hour so that the added barium hydroxide can completely react with the mixed radioactive waste acid. Next, in the step of S30, a solidifying agent is added to the mixed radioactive waste acid in batches. The solidifying agent, which the total weight is 1560 g, includes 1200 g of cement, 96 g of slag, 172 g of silicon ash, and 504 g of fly ash. The weight ratio of the applied solidifying agent to the mixed radioactive waste acid is 23.74%, and the weight ratio of the solidifying agent with a neutralizer to the mixed radioactive waste acid is 36.83%. The compression strength of the solidified product formed after 28 days is 27.0 kg/cm^2. The compression strength of the solidified product after dipped three months is 60 kg/cm^2.

[0027] The result of foregoing steps is shown in Table 5. Besides, two results which indicated as Nos. B6 and B7 shown in Table 5 are similar to the result of No. B5. As the results shown in Table 5 indicated, the solidified product of radioactive waste acid formed by the method of the invention has improved weather resistance and water resistance characteristics. Moreover, the method of the invention prevents intensely exothermic reaction and rapid setting caused by adding the solidifying agents to influence the efficiency and quality of solidification.

Table 5 Results of indirect solidification of radioactive waste acid containing phosphoric acid mixed with fluoroboric acid

Conditions					Results				
No.	Total weight of waste acid containing phosphoric acid before condensing (g)	Total weight of waste acid containing phosphoric acid after condensed (g)	Total weight of waste acid containing fluoroboric acid (g)	Applied amount of neutralizer (monohydrous barium hydroxide) (g)	Applied amount of solidifying agent (%)	Applied amount of solidifying agent/Total weight of mixed waste acid (%)	Applied amount of solidifying agent + neutralizer/fotal weight of mixed waste acid (%)	Compression strength after 28 days (kg/cm^2)	Compression strength after dipping 3 months (kg/cm^2)
B5	5711	5140	860	840	1560	23.74	36.83	27.0	60
B6	5711	5140	860	640	1560	23.74	33.48	16.0	43
B7	5711	5140	860	840	1705	25.95	39.73	48.5	103

[0028] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by the way of example in the drawings and are herein described in detail.

Claims

1. A method for treating radioactive waste acid containing phosphoric acid comprising steps of:

   condensing the radioactive waste acid to a concentration of at least 50% of phosphoric acid;
   adding barium hydroxide to the condensed radioactive waste acid and adjusting the pH of the radioactive waste acid to generate barium hydrogen phosphate; and
   adding a solidifying agent to react with the barium hydrogen phosphate so that a solidified product of the radioactive waste acid can be formed.

2. The method as recited in claim 1, wherein the step of adding the solidifying agent is adding in batches or continuously so that the radioactive waste acid can be controlled in a temperature of 30 to 45 °C.

3. The method as recited in claim 1, wherein adjusting the pH of the radioactive waste acid is adjusting the pH to a range between 2.5 and 4.5.

4. A method for treating radioactive waste acid containing phosphoric acid and fluoroboric acid comprising steps of:

   condensing a radioactive waste acid containing phosphoric acid to a concentration of at least 50% of phosphoric acid;
   adding barium hydroxide to another radioactive waste acid containing fluoroboric acid, mixing the radioactive waste acid containing fluoroboric acid with the condensed radioactive waste acid containing phosphoric acid to form a mixed radioactive waste acid, and dividing the mixed waste into two parts;
   dropping one part of the mixed radioactive waste acid in a stirrer which contained a first solidifying agent to form at least a granule;
   mixing the formed granule with another part of the mixed radioactive waste by stirring; and
   adding a second solidifying agent to the radioactive mixed waste by stirring, placing in stationary so that a solidified product of the mixed radioactive waste acid can be formed.

5. The method as recited in claim 4, wherein the first solidifying agent is consisted of cement, slag, and fly ash.

6. The method as recited in claim 4, wherein the second solidifying agent is consisted of cement.

7. The method as recited in claim 4, wherein a weight ratio of the condensed radioactive waste acid containing phosphoric acid to the radioactive waste acid containing fluoroboric acid is six.

8. A method for treating radioactive waste acid containing phosphoric acid and fluoroboric acid according to claim 1, wherein
   the condensed radioactive waste acid containing phosphoric acid is mixed with a radioactive waste acid containing fluoroboric acid to form a mixed radioactive waste acid;

9. The method as recited in claim 8, the step of adding the solidifying agent is adding in batches or continuously so that the mixed radioactive waste acid can be controlled in a temperature of 30 to 45 °C.

10. The method as recited in claim 8, wherein adjusting the pH of the mixed radioactive waste acid is adjusting the pH to a range between 2.5 and 4.5.

Patentansprüche

1. Verfahren zum Behandeln eines radioaktiven Säureabfalls, der Phosphorsäure enthält, das die folgenden Schritte aufweist:

   Kondensieren des radioaktiven Säureabfalls bis zu einer Konzentration von mindestens 50 % Phosphorsäure;

Zugeben von Bariumhydroxid zu dem kondensierten, radioaktiven Säureabfall und Einstellen des pH-Wertes des radioaktiven Säureabfalls, so daß Bariumhydrogenphosphat erzeugt wird; und
Zugeben eines Verfestigungsmittels, damit es mit dem Bariumhydrogenphosphat reagiert, so daß ein verfestigtes Produkt des radioaktiven Säureabfalls erzeugt werden kann.

2. Verfahren nach Anspruch 1, wobei der Schritt des Zugebens des Verfestigungsmittels in Chargen oder kontinuierlich erfolgt, so daß der radioaktive Säureabfall bei einer Temperatur von 30 bis 45°C gesteuert werden kann.

3. Verfahren nach Anspruch 1, wobei das Einstellen des pH-Wertes des radioaktiven Säureabfalls das Einstellen des pH-Wertes in einem Bereich von 2,5 bis 4,5 ist.

4. Verfahren zum Behandeln eines radioaktiven Säureabfalls, der Phosphorsäure und Fluorborsäure enthält, das die folgenden Schritte aufweist:

Kondensieren eines radioaktiven Säureabfalls, der Phosphorsäure enthält, bis zu einer Konzentration von mindestens 50 % Phosphorsäure;
Zugeben von Bariumhydroxid zu einem weiteren radioaktiven Säureabfall, der Fluorborsäure enthält,
Mischen des radioaktiven Säureabfalls, der Fluorborsäure enthält, mit dem kondensierten radioaktiven Säureabfall, der Phosphorsäure enthält, so daß ein gemischter radioaktiver Säureabfall entsteht, und Aufteilen des gemischten Abfalls in zwei Teile;
Einfüllen von einem Teil des gemischten radioaktiven Säureabfalls in einen Rührer, der ein erstes Verfestigungsmittel enthält, so daß zumindest ein Granulat erzeugt wird;
Mischen des erzeugten Granulats mit dem anderen Teil des gemischten radioaktiven Abfalls unter Rühren; und
Zugeben eines zweiten Verfestigungsmittels zu dem gemischten radioaktiven Abfall unter Rühren, Ruhenlassen, so daß aus dem gemischten radioaktiven Säureabfall ein verfestigtes Produkt entstehen kann.

5. Verfahren nach Anspruch 4, wobei das erste Verfestigungsmittel aus Zement, Schlacke und Flugasche besteht.

6. Verfahren nach Anspruch 4, wobei das zweite Verfestigungsmittel aus Zement besteht.

7. Verfahren nach Anspruch 4, wobei das Gewichtsverhältnis zwischen dem kondensierten radioaktiven Säureabfall, der Phosphorsäure enthält, und dem radioaktiven Säureabfall, der Fluorborsäure enthält, 6 beträgt.

8. Verfahren zum Behandeln von radioaktivem Säureabfall, der Phosphorsäure und Fluorborsäure enthält, nach Anspruch 1, wobei
der kondensierte radioaktive Säureabfall, der Phosphorsäure enthält, mit einem radioaktiven Säureabfall gemischt wird, der Fluorborsäure enthält, so daß ein gemischter radioaktiver Säureabfall erzeugt wird.

9. Verfahren nach Anspruch 8, wobei der Schritt des Zugebens des Verfestigungsmittels in Chargen oder kontinuierlich erfolgt, so daß der radioaktive Säureabfall bei einer Temperatur von 30 bis 45°C gesteuert werden kann.

10. Verfahren nach Anspruch 8, wobei das Einstellen des pH-Wertes des radioaktiven Säureabfalls das Einstellen des pH-Wertes in einem Bereich von 2,5 bis 4,5 ist.

Revendications

1. Procédé destiné à traiter un acide usé radioactif qui contient de l'acide phosphorique, comprenant les étapes consistant à :

condenser l'acide usé radioactif jusqu'à obtenir une concentration en acide phosphorique au moins égale à 50 % ;
ajouter de l'hydroxyde de baryum à l'acide usé radioactif condensé et régler le pH de l'acide usé radioactif de façon à générer du phosphate d'hydrogène de baryum ; et
ajouter un agent solidifiant pour qu'il réagisse avec le phosphate d'hydrogène de baryum de sorte qu'un produit solidifié de l'acide usé radioactif puisse être formé.

2. Procédé selon la revendication 1, dans lequel l'étape consistant à ajouter l'agent solidifiant consiste à ajouter par lots ou de manière continue de sorte que l'acide usé radioactif puisse être contrôlé à une température allant de 30

°C à 45 °C.

3. Procédé selon la revendication 1, dans lequel le réglage du pH de l'acide usé radioactif consiste à régler le pH dans une plage comprise entre 2,5 et 4,5.

4. Procédé destiné à traiter un acide usé radioactif qui contient de l'acide phosphorique et de l'acide fluoroborique, comprenant les étapes consistant à :

condenser un acide usé radioactif qui contient de l'acide phosphorique jusqu'à obtenir une concentration en acide phosphorique au moins égale à 50 % ;
ajouter de l'hydroxyde de baryum à un autre acide usé radioactif qui contient de l'acide fluoroborique, mélanger l'acide usé radioactif qui contient de l'acide fluoroborique à de l'acide usé radioactif condensé qui contient de l'acide phosphorique de façon à former un acide usé radioactif mélangé, et diviser l'acide usé radioactif mélangé en deux parties ;
déposer une partie de l'acide usé radioactif mélangé dans un agitateur qui contient un premier agent solidifiant de façon à former au moins un granule ;
mélanger, en agitant, le granule formé à une autre partie de l'acide usé radioactif mélangé ; et
ajouter, en agitant, un second agent solidifiant à l'acide usé radioactif mélangé, laisser reposer pour laisser se former un produit solidifié de l'acide usé radioactif mélangé.

5. Procédé selon la revendication 4, dans lequel le premier agent solidifiant consiste en ciment, scories et cendres volantes.

6. Procédé selon la revendication 4, dans lequel le second agent solidifiant consiste en ciment.

7. Procédé selon la revendication 4, dans lequel le rapport en poids de l'acide usé radioactif condensé contenant de l'acide phosphorique sur l'acide usé radioactif contenant de l'acide fluoroborique est égal à six.

8. Procédé destiné à traiter un acide usé radioactif contenant de l'acide phosphorique et de l'acide fluoroborique, selon la revendication 1, dans lequel :

l'acide usé radioactif condensé contenant de l'acide phosphorique est mélangé à un acide usé radioactif contenant de l'acide fluoroborique de façon à former un acide usé radioactif mélangé.

9. Procédé selon la revendication 8, dans lequel l'étape consistant à ajouter l'agent solidifiant consiste à ajouter par lots ou de manière continue de sorte que l'acide usé radioactif mélangé puisse être contrôlé à une température allant de 30 °C à 45 °C.

10. Procédé selon la revendication 8, dans lequel le réglage du pH de l'acide usé radioactif mélangé consiste à régler le pH dans une plage comprise entre 2,5 et 4,5.

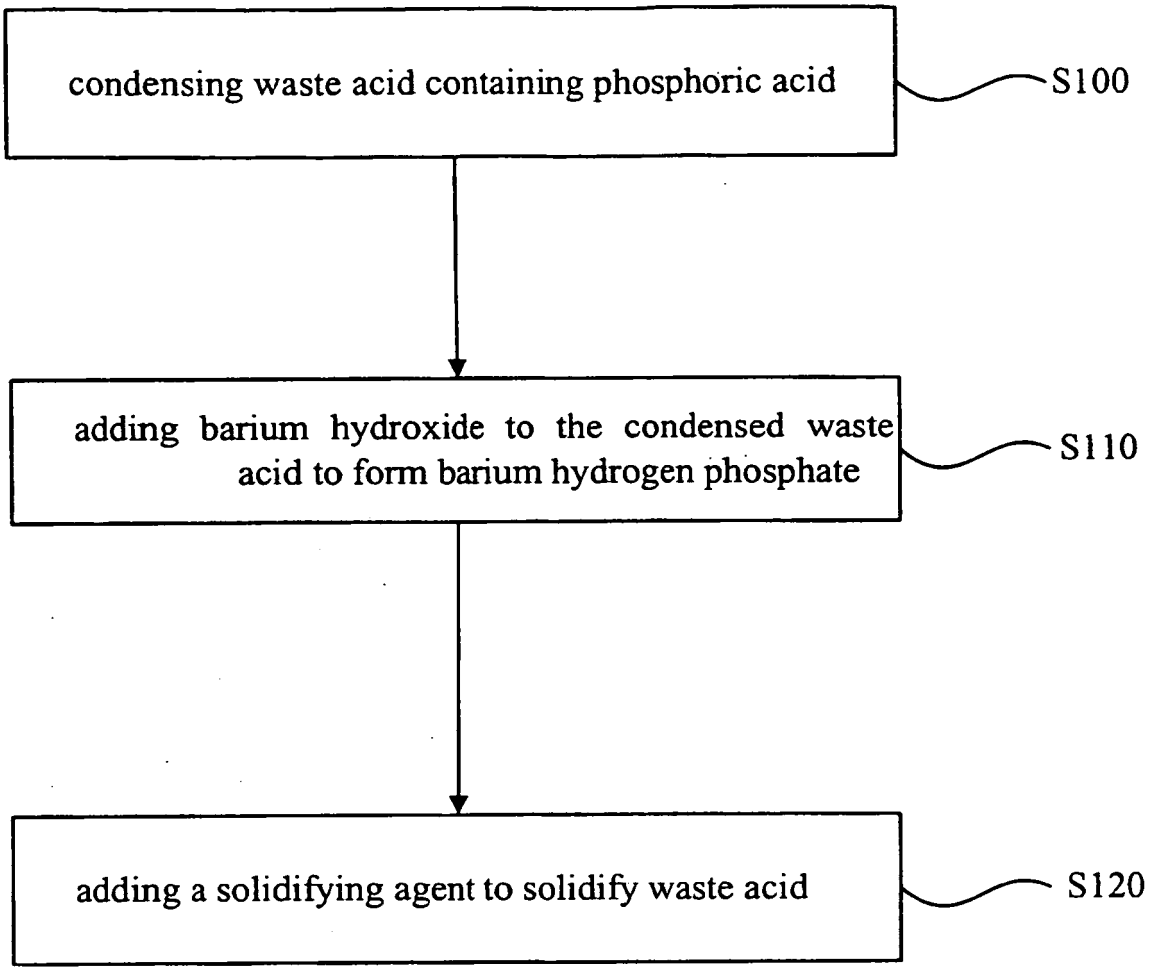

condensing waste acid containing phosphoric acid
S100
adding barium hydroxide to the condensed waste acid to form barium hydrogen phosphate
S110
adding a solidifying agent to solidify waste acid
S120

Fig. 1

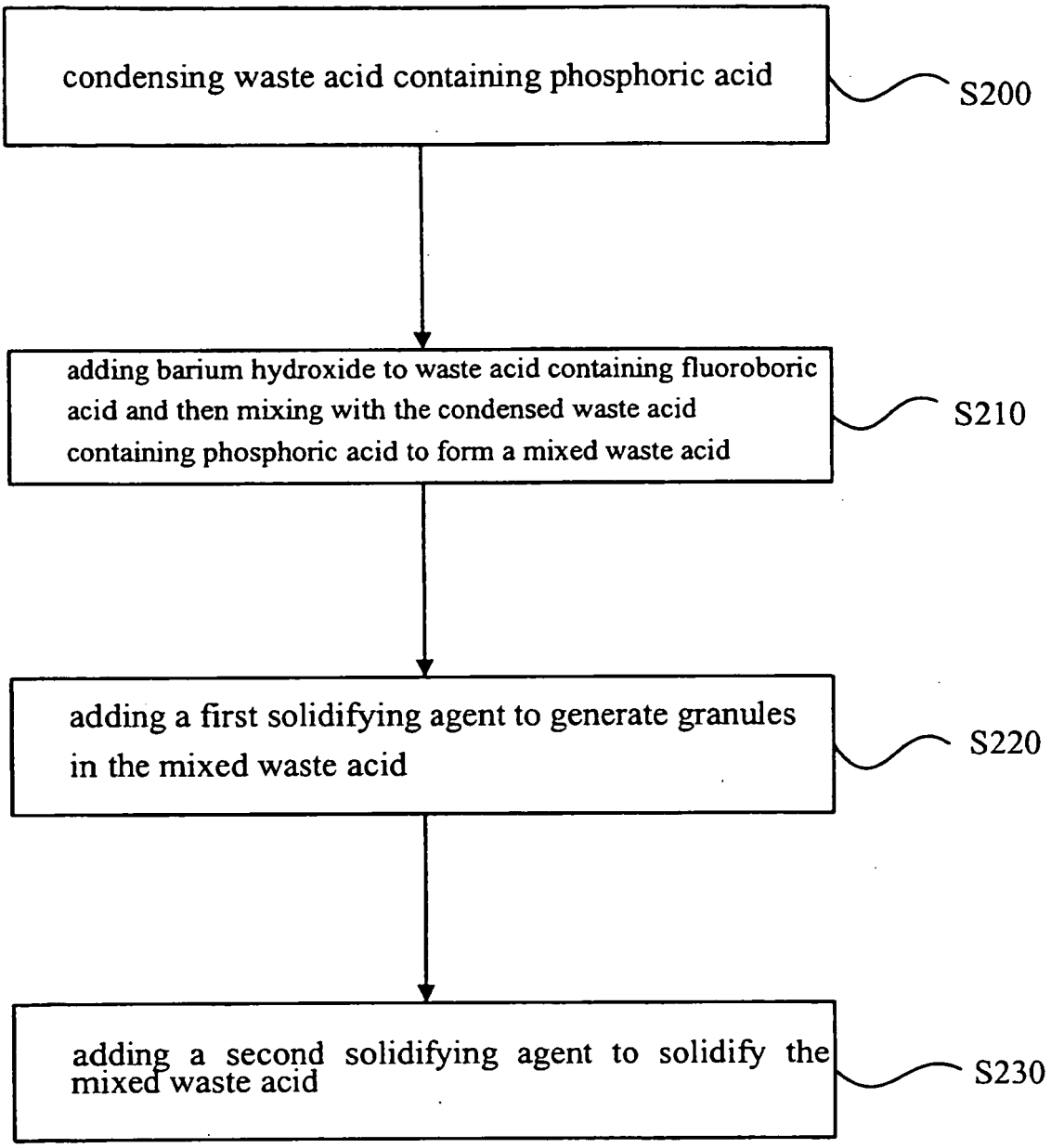

condensing waste acid containing phosphoric acid
S200
adding barium hydroxide to waste acid containing fluoroboric acid and then mixing with the condensed waste acid containing phosphoric acid to form a mixed waste acid
S210
adding a first solidifying agent to generate granules in the mixed waste acid
S220
adding a second solidifying agent to solidify the mixed waste acid
S230

Fig. 2

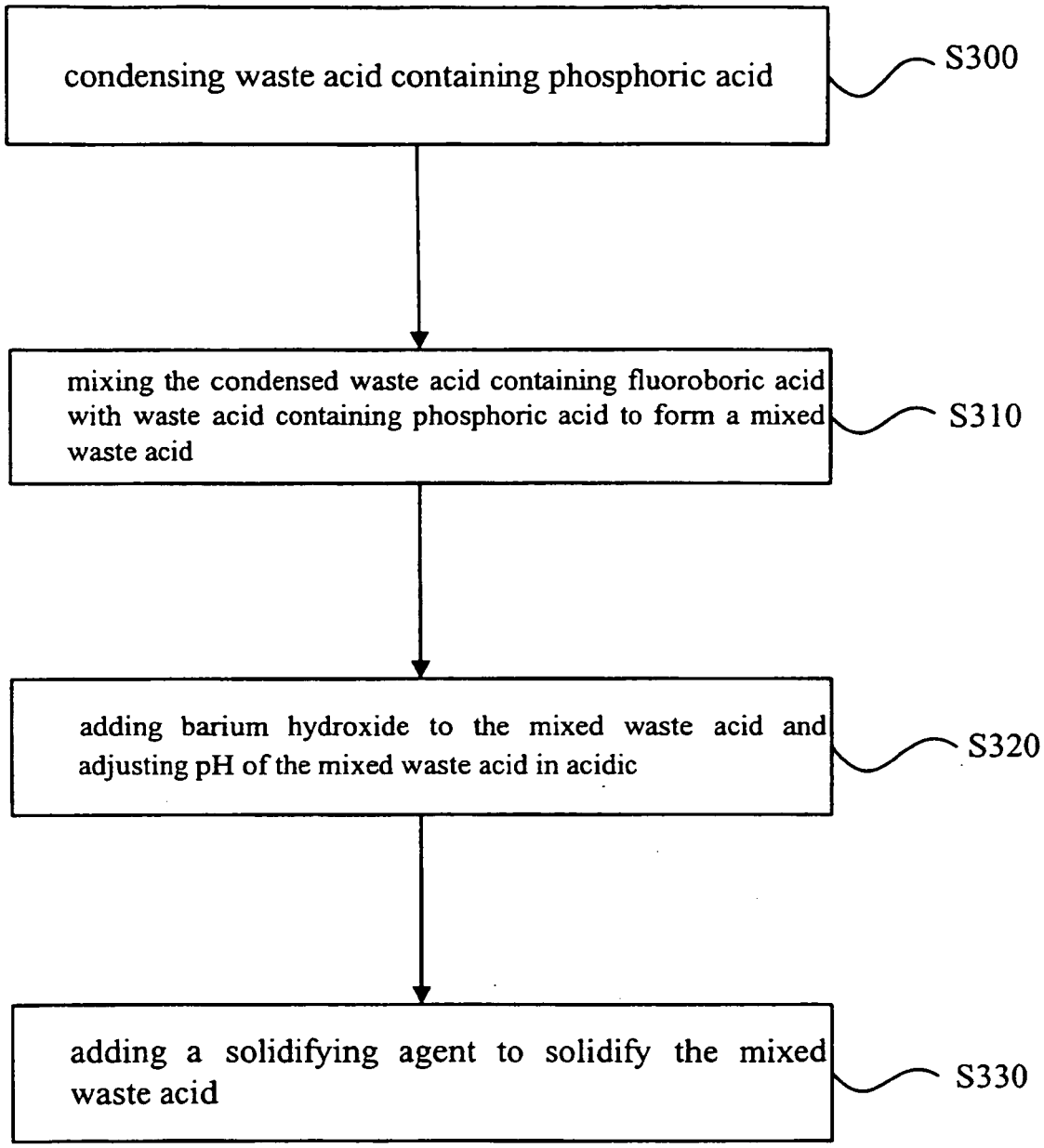

condensing waste acid containing phosphoric acid
S300
mixing the condensed waste acid containing fluoroboric acid with waste acid containing phosphoric acid to form a mixed waste acid
S310
adding barium hydroxide to the mixed waste acid and adjusting pH of the mixed waste acid in acidic
S320
adding a solidifying agent to solidify the mixed waste acid
S330

Fig. 3

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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