

**(12) STANDARD PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

(11) Application No. **AU 2016200606 B2**

(54) Title  
**A method for recovering phosphorus and rare earth from rare earth containing phosphorite**

(51) International Patent Classification(s)  
**C22B 3/06** (2006.01) **C22B 1/11** (2006.01)  
**C01B 25/01** (2006.01) **C22B 3/22** (2006.01)  
**C22B 1/00** (2006.01) **C22B 3/38** (2006.01)

(21) Application No: **2016200606** (22) Date of Filing: **2016.02.01**

(30) Priority Data

(31) Number	(32) Date	(33) Country
<b>201510080473.1</b>	<b>2015.02.13</b>	<b>CN</b>

(43) Publication Date: **2016.09.01**  
(43) Publication Journal Date: **2016.09.01**  
(44) Accepted Journal Date: **2021.05.13**

(71) Applicant(s)  
**Girem Advanced Materials Co., Ltd**

(72) Inventor(s)  
**Wang, Liangshi;Huang, Xiaowei;Dong, Jinshi;Zhao, Longsheng;Wu, Shengxi;Feng, Zongyu;Sun, Xu;Long, Zhiqi**

(74) Agent / Attorney  
**Davies Collison Cave Pty Ltd, Level 15 1 Nicholson Street, MELBOURNE, VIC, 3000, AU**

(56) Related Art  
**CN 102220488 B**

**Abstract**

The present disclosure discloses a method for recovering phosphorus and rare earth from rare earth containing phosphorite. The method includes the following steps: leaching a rare earth containing phosphorite by using a mixed acid solution, and filtering and obtaining a mono-calcium phosphate solution and a rare earth phosphate containing slag, the main component of the mixed acid solution is a phosphoric acid and the mixed acid solution further comprises a hydrochloric acid and/or a nitric acid; recovering the phosphorus of the mono-calcium phosphate solution, and recovering the rare earth of the rare earth phosphate containing slag. The method leaches the rare earth containing phosphorite by using the mixed acid solution so that the phosphorus in the phosphorite forms the higher soluble mono-calcium phosphate, at the same time by regulating and controlling the acidity in the leaching process to precipitate and enrich the rare earth in the form of a rare earth phosphate in the slag, if the rare earth containing phosphorite further contains a monazite, the monazite and the rare earth phosphate are enriched in the slag, thereby separating the phosphorus and the rare earth, simplifying recovery steps, improving the recovery rate of the rare earth, and achieving the purpose of comprehensive recovery of the rare earth with low cost.

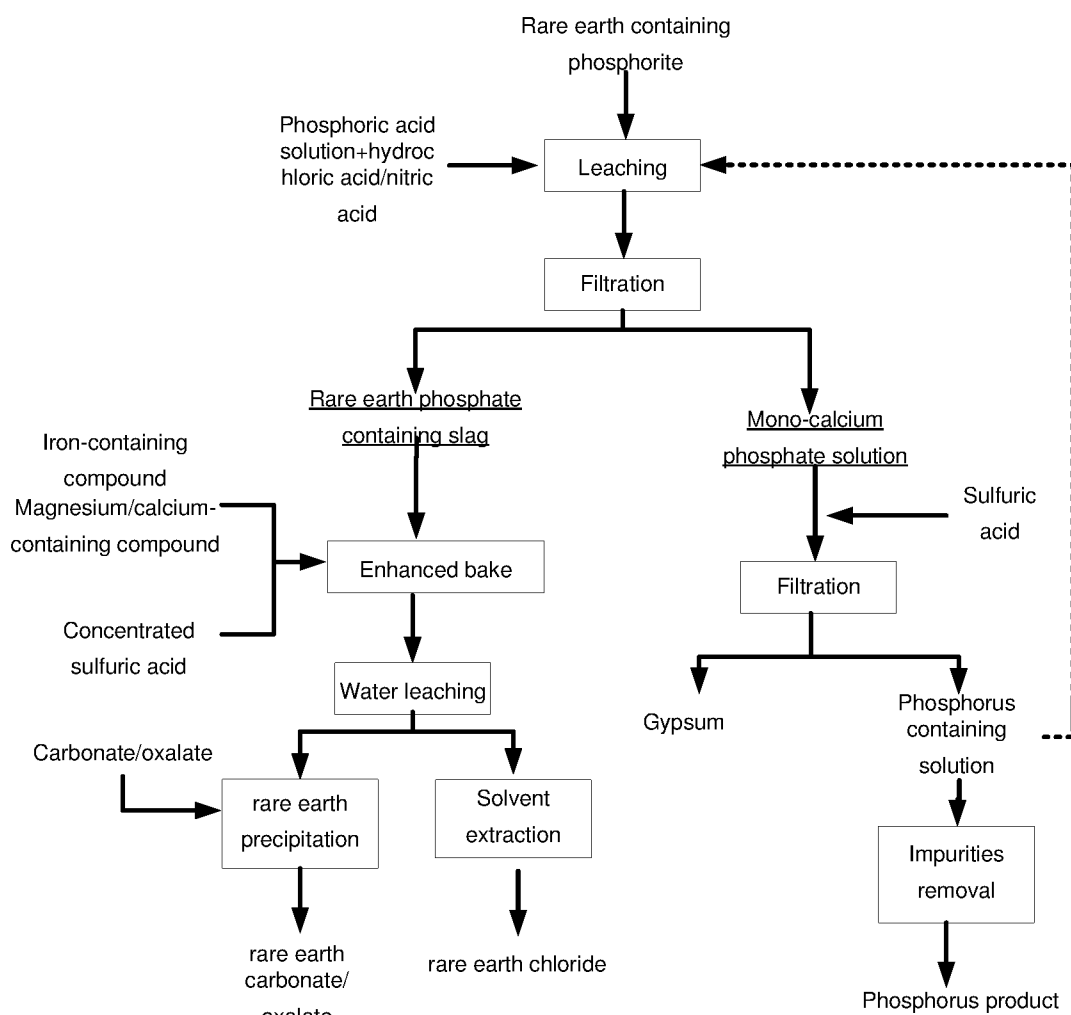


Fig. 1

## Technical field

☐ ☐ ☐ ☐ r ☐ ☐ ☐ ☐ d ☐ ☐ ☐ ☐ r ☐ ☐ r ☐ a ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ d ☐ ☐ ☐ r ☐ ar ☐ ☐ ar ☐ ☐ r ☐ ☐ ☐ ☐ ☐ ☐

☐ ar ☐ ☐ ☐ ar ☐ ☐ ☐ a ☐ ☐ ☐ ☐ d ☐ ☐ ☐ r ☐ ☐ ☐ r ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ r ☐ ☐ a ☐ d ☐ r ☐ ar ☐ ☐ ar ☐ ☐ ☐ ☐ r ☐ ☐ ☐ ☐ r ☐ ar ☐ ☐

☐ ar ☐ ☐ ☐ ☐ ☐ a ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ r ☐ ☐ ☐ ☐

☐

## Background

[illegible][illegible]

[illegible][illegible]





ra 1

ra a ra d a d 1

ra 1

ra a ra a r

d a d d a d a d r a r

a r a d a a d d r a 1 1

ra 1

ra a ra a r

d a d a a a r a r 1

ra a d a a r r a

r

ra a r a a



phosphate solution includes: adding a sulfuric acid into the mono-calcium phosphate solution, performing solid-liquid separation and obtaining a phosphorus containing solution and a calcium sulfate gypsum, and then recovering the phosphorus of the phosphorus containing solution.

Further, the step of recovering the phosphorus of the mono-calcium phosphate solution further includes: preparing a phosphoric acid from a portion of the phosphorus containing solution after impurities removal, then recycling the prepared phosphoric acid containing hydrochloric acid or nitric acid to the leaching step.

Further, the step of recovering the rare earth of the rare earth phosphate containing slag includes: adding an iron containing compound, a compound containing magnesium and/or calcium into the rare earth phosphate containing slag, then mixing with a concentrated sulfuric acid, with subsequent enhanced bake to obtain a calcination slag; leaching the calcination slag by water to obtain a rare earth containing water leach solution and an water leach slag; adjusting the pH value of the rare earth containing water leach solution to 3.8 to 5, filtering and obtaining a rare earth sulfate solution and a slag containing iron and thorium; adding a carbonate or an oxalate into the rare earth sulfate solution to precipitate the rare earth, and obtaining a rare earth carbonate or a rare earth oxalate, calcining the rare earth carbonate and the rare earth oxalate to obtain a rare earth oxide, or extracting the rare earth sulfate solution by using an acidic phosphorus extractant to obtain a mixed rare earth chloride or single rare earth compounds.

Further, the compound containing magnesium and/or calcium is at least one of an oxide of magnesium and/or calcium, a carbonate of magnesium and/or calcium or a mineral containing magnesium and/or calcium, preferably the mineral containing magnesium and/or calcium is at least one of dolomite, magnesite; the iron containing compound is at least one of an iron containing tailing and an iron containing slag, preferably a tailing containing rare earth and iron.

Further, the molar ratio of the magnesium and/or calcium of the compound containing magnesium and/or calcium to the fluorine of the rare earth phosphate containing slag is 1 to 2: 2.

Further, the mass ratio of the iron of the iron containing compound to the phosphorus of the rare earth phosphate containing slag is 2 to 4: 1, preferably 2.5 to 3.5: 1.

Further, during the enhanced bake, the concentrated sulfuric acid and the rare earth phosphate containing slag are mixed at a mass ratio of 1 to 2: 1, and the bake temperature during enhanced bake is 200 °C to 500 °C, preferably 250 °C to 400 °C.

Further, in the step of adjusting the pH value of the rare earth containing water leach solution, the pH value of the rare earth containing water leach solution is adjusted by using a magnesium oxide and/or a caustic calcined dolomite, and the pH value of the rare earth containing water leach solution is adjusted to 4 to 4.5.

By applying the technical solution of the present disclosure, the present disclosure leaches a rare earth containing phosphorite by using a mixed acid solution, so that the phosphorus in the phosphorite forms a highly-soluble mono-calcium phosphate with higher solubility, at the same time by regulating and controlling the acidity in the leaching process to precipitate and enrich the rare earth in the form of a rare earth phosphate in a slag, if the rare earth containing phosphorite further contains a monazite, the monazite and the rare earth phosphate are enriched in the slag, thereby separating the phosphorus and the rare earth. A hydrochloric acid or a nitric acid in the mixed acid solution is propitious to decompose apatite while ensuring that the rare earth is enriched in the slag in the form of a rare earth phosphate precipitate, thereby improving the leaching rate of the phosphorus in the apatite. Besides, the hydrochloric acid or the nitric acid can provide hydrogen ions  $H^+$ , and can reduce the content of phosphate radicals and the viscosity of the system with the same acid content, thus facilitating leaching of the phosphorus; in the

meanwhile, the existence of the chloride ions or the nitrate ions is propitious to increase the solubility of calcium ions in a solution and decomposition of the apatite. The rare earth and the phosphorus element can be separated effectively by a filtering process, thus improving the recovery rates of the rare earth and the phosphorus. At the same time, the rare earth enters the slag in the form of the rare earth phosphate, and is enriched with the insoluble monazite during the acid leaching process so as to recover the rare earth, thereby simplifying recovery steps, improving the recovery rate of the rare earth, and achieving the purpose of comprehensive recovery of the rare earth with low cost.

### **Brief description**

The accompanying drawings of the specification, which constitute a part of the present application, are used for providing further understanding to the present disclosure. The schematic embodiments of the present disclosure and description thereof are used for explaining the present disclosure, instead of forming improper limitation to the present disclosure. In the accompanying drawings:

Fig. 1 shows the flowchart of a method for recovering phosphorus and rare earth from a rare earth containing phosphorite according to an embodiment of the present disclosure.

### **Detailed description**

It needs to be noted that the embodiments in the present application and the characteristics in the embodiments may be combined with each other if there is no conflict. The present disclosure will be expounded hereinafter with reference to the accompanying drawings and in conjunction with the embodiments.

In the following description, the molar formula of monazite is  $(\text{Ln}, \text{Th})\text{PO}_4$ , where the Ln refers to at least one of rare earth elements except for

promethium.

As pointed out in the background art, the rare earth containing phosphorite has a lower rare earth grade and high impurities of phosphorus, the calcium and so on, thus it is difficult to efficiently separate the phosphorus and the calcium from the rare earth. It is more difficult to recover the phosphorus and the rare earth from a mixed phosphate mineral ore of a plurality of minerals including the apatite, the monazite and so on especially, the monazite and the phosphorite, which are phosphate minerals, have close mineralogical properties, and usually disseminate closely in the ore in which the monazite and the phosphorite coexist, thus the phosphorus and the rare earth in such a mixed ore of a plurality of minerals including the apatite, the monazite and so on are more difficult to recover.

To solve the above-mentioned technical problems, a method for recovering a phosphorus and a rare earth from a rare earth containing phosphorite is provided in an embodiment of the present disclosure. As shown in Fig. 1, the method includes the following steps: leaching the rare earth containing phosphorite by using a mixed acid solution, filterating and obtaining a mono-calcium phosphate solution and a rare earth phosphate containing slag, the main component of the mixed acid solution is a phosphoric acid and the mixed acid solution further comprises a hydrochloric acid and/or a nitric acid; recovering the phosphorus in the mono-calcium phosphate solution, and recovering the rare earth in the rare earth phosphate containing slag.

The method leaches the rare earth containing phosphorite by using the mixed acid solution, and forms the highly-soluble mono-calcium phosphate with the phosphorus in the phosphorite by using hydrogen ions in the mixed acid solution, at the same time by regulating and controlling the acidity in the leaching process to precipitate and enrich the rare earth in the form of a rare earth phosphate in the slag, if the rare earth containing phosphorite further contains a monazite, the monazite cannot be dissolved during the acid leaching process and enters into the slag together with the rare earth

phosphate, so as to separate the phosphorus from the monazite and the rare earth. The hydrochloric acid or the nitric acid in the mixed acid solution induces the decomposition of the apatite while ensuring that the rare earth is enriched in the slag in the form of a rare earth phosphate precipitate, thereby increasing the leaching rate of the phosphorus in the apatite. Besides, the hydrochloric acid or the nitric acid can provide hydrogen ions  $H^+$ , and can reduce the content of phosphate radicals and the viscosity of the system with the same acid content, thus facilitating leaching of the phosphorus; in the mean while, the existence of chloride ions or nitrate ions is propitious to increase the solubility of calcium ions in a solution and decomposition of the apatite. The rare earth and the phosphorus element in the rare earth containing phosphorite can be separated effectively by a filtering process, thus increasing the recovery rates of the rare earth and the phosphorus. At the same time, the rare earth enters the slag in the form of the rare earth phosphate to form the rare earth phosphate containing slag with the insoluble monazite during the acid leaching process and then the rare earth is recovered collectively, thereby simplifying recovery steps, increasing the recovery rate of the rare earth, and achieving the purpose of comprehensive recovery of the rare earth with low cost.

Applying the method above, the mono-calcium phosphate with higher solubility is formed by performing the leaching using the mixed acid solution, and the addition of the hydrochloric acid or the nitric acid induces the decomposition of the apatite, thereby improving the decomposition rate of the phosphorite and the yield of the phosphorus and reducing the slag rate. By means of regulating and controlling the leaching process, more than 95% of phosphorus in the apatite will enter into the solution, the rare earth is enriched in the slag to form the rare earth phosphate containing slag while ensuring a high phosphorus leaching rate, and more than 95% of rare earth in the mineral is enriched in the rare earth phosphate containing slag, the grade of rare earth in the mixed slag is significantly improved, and it is conducive to recovering

the rare earth subsequently.

The aim of the leaching using the mixed acid solution in the present disclosure is to dissolve the phosphorus in the rare earth containing phosphorite while keeping the rare earth in the slag to form the rare earth phosphate containing slag. In a preferred embodiment of the present disclosure, the rare earth containing phosphorite further contains a monazite, the monazite cannot be decomposed and remains in the slag to be enriched with the rare earth phosphate, the use amount of the acid is reduced. Preferably, in the step of leaching by using the mixed acid solution, the mixed acid solution and the rare earth containing phosphorite are mixed with a liquid-to-solid ratio of 2L to 10L: 1kg, preferably 4L to 8L: 1kg. The use amount of the acid is controlled so that the soluble mono-calcium phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ) is generated from the phosphorus and the calcium and enters the solution while reducing the use amount of the acid, the rare earth phosphate has a low solubility in a low-acidity condition, so that the rare earth in the apatite can be concentrated in the slag in the form of the rare earth phosphate, at the moment, the insoluble monazite will remain in the slag, thereby achieving the effective separation of the phosphorus from the rare earth and the monazite.

Preferably, based on the mole number of the anions, the proportion of the hydrochloric acid or the nitric acid in the mixed acid solution used in the leaching step using the mixed acid is 1% to 30%, preferably 2% to 15%. The content of hydrochloric acid or nitric acid used in the present disclosure is not limited to the ranges above, the solubility of the rare earth phosphate in the system increases with high content of hydrochloric acid or nitric acid, so that the rare earth is leached out and enters into the solution, thus the rare earth cannot be concentrated in the slag.

Preferably, the mass fraction of  $\text{P}_2\text{O}_5$  in the mixed acid used in the leaching step using the mixed acid is 15% to 50%, preferably 15% to 30%. The mass fraction of  $\text{P}_2\text{O}_5$  in the mixed acid used in the present disclosure is not

limited to the ranges above, a high acidity facilitates decomposition of the phosphorite when the mixed acid containing  $P_2O_5$  within the ranges above is applied, thereby improving the yield of the phosphorus, however, an excessively high content of the phosphoric acid results in problems including low mass transfer efficiency due to high viscosity and so on.

Preferably, in the leaching step using the mixed acid, the leaching temperature is  $55^{\circ}C$  to  $150^{\circ}C$ , and the leaching time is 0.5 to 8 hours. The leaching temperature and the leaching time in the leaching step using the mixed acid in the present disclosure are not limited to the ranges above, higher temperature facilitates the decomposition of the phosphorite, and the solubility product of the rare earth phosphate is smaller at the high temperature, so that the precipitate of the rare earth phosphate can be formed and enters the slag to be enriched therein. More preferably, the leaching temperature is  $60^{\circ}C$  to  $90^{\circ}C$ , and the leaching time is 2 to 5 hours. A method specifically applicable to the phosphorus recovery may be selected as a solution for recovering the phosphorus in the mono-calcium phosphate solution. In a preferred embodiment of the present disclosure, the step of recovering the phosphorus of the mono-calcium phosphate solution includes: adding a sulfuric acid into the leaching solution to remove the calcium, with subsequent solid-liquid separation to obtain a phosphorus containing solution and a calcium sulfate gypsum, recovering the phosphorus of the phosphorus containing solution. In this method, the phosphorus in the apatite may be recovered by applying a mature wet-process sulfuric acid technique, the technique has simple steps and a relatively high recovery yield.

Preferably, the step of recovering the phosphorus of the mono-calcium phosphate solution further includes: preparing a phosphorus product from the phosphorus containing solution after impurities removal, or recycling the phosphorus containing solution for leaching the phosphorite. In this method, the recycled phosphoric acid is used for decomposing and leaching the apatite, the whole process has reasonable links to effectively recover the rare earth

and the phosphorus at the same time with low consumption of the sulfuric acid and low cost. The impurity removal step in the step above includes, but is not limited to removal of iron, silicon, aluminum, calcium, magnesium, thorium and uranium from the phosphorus containing solution. These impurity removal steps may apply conventional processes in the prior art as required.

Similarly, the phosphorus has been separated from the rare earth before the step of recovering the rare earth in the rare earth phosphate containing slag in the present disclosure. The content of the rare earth in the rare earth phosphate containing slag, which is 3 to 10 times higher than that of the phosphorite, is still low, and the contents of the impurities including phosphorus, silicon, aluminum and so on are high, thus it is hard to recover the rare earth effectively by applying conventional sodium hydroxide decomposition, sulfuric acid decomposition. In a preferred embodiment of the present disclosure, the step of recovering the rare earth in the rare earth phosphate containing slag includes: adding an iron containing compound, a compound containing magnesium and/or calcium to the rare earth phosphate containing slag, then mixing with a concentrated sulfuric acid, with subsequent enhanced bake to obtain a calcination slag; leaching the calcination slag by water to obtain a rare earth containing water leach solution and a water leach slag; adjusting the pH value of the rare earth containing water leach solution to 3.8 to 5, filtering and obtaining a rare earth sulphate containing solution and a slag containing iron and thorium; adding a carbonate or an oxalate into the rare earth sulfate solution to precipitate the rare earth to obtain a rare earth carbonate or a rare earth oxalate, calcining the rare earth carbonate and the rare earth oxalate to obtain a rare earth oxide; or extracting the rare earth sulfate solution by using an acidic phosphorus extractant and obtaining a mixed rare earth chloride or single rare earth compounds.

The present disclosure may keep the monazite and the rare earth phosphate in the slag so as to enrich the monazite and the rare earth phosphate, thus increasing the grade of the rare earth in the slag, and



considerably reducing the amount of subsequent processing. Simple and unique processes including adding an iron to immobilize the phosphorus, adding a magnesium/calcium to immobilize fluorine and enhancing the calcination with the sulfuric acid so as to eliminate the interference of the phosphorus and the fluorine, thus effectively avoiding loss of rare earth precipitated in the form of a rare earth phosphate and a rare earth chloride during the leaching process, and avoiding environmental pollution caused by the fluorine escaping as a hydrogen fluoride gas during the calcination process. The method has low acid and alkaline consumption and the recovery rate of the rare earth may reach above 90%; in the meanwhile, the thorium is transformed into thorium pyrophosphate immobilized in the slag, thus preventing the radioactive thorium from being dispersed in the process to cause pollution. At the same time, the iron containing compound is added to immobilize the phosphorus in the slag, thus avoiding loss of the rare earth.

Preferably, the added compound containing magnesium and/or calcium is at least one of an oxide of magnesium and/or calcium, a carbonate of magnesium and/or calcium, or a mineral containing magnesium and/or calcium, preferably, the mineral containing magnesium and/or calcium is at least one of dolomite and magnesite, and the iron containing compound is at least one of an iron containing tailing and an iron containing slag, preferably a tailing containing rare earth and iron.

Preferably, in the step of adding the iron containing compound to the mixed slag, the mass ratio of the iron of the iron containing compound to the phosphorus of the rare earth phosphate containing slag is 2 to 4: 1, preferably 2.5 to 3.5: 1, an iron containing rare earth tailing is added in the ranges above to perform processing, which not only improves the yield of the rare earth, but also implements comprehensive utilization of an iron resource of the tailing, and implements recovery and utilization of rare earth in the tailing while largely reducing operation cost; besides, the mass ratio of Fe/P may be controlled in the subsequent impurity removal process with the pH value adjusted to 3.8 to 5,

so as to form an iron phosphate precipitate and effectively remove the phosphorus, while excess iron may be hydrolyzed at the pH value to form a precipitate to avoid formation of a rare earth phosphate precipitate, thereby avoiding the rare earth loss.

Preferably, in the step of adding the compound containing magnesium and/or calcium in the mixed slag, the molar ratio of magnesium and/or calcium in the compound containing magnesium and/or calcium to the fluorine in the rare earth phosphate containing slag is 1 to 2:2. The mixing ratio of the magnesium and/or calcium containing compound to the rare earth phosphate containing slag in the present disclosure is not limited to the range above, the two are mixed according to the molar ratio of 1 to 2:2, base on the premise the advantage of reducing the amount of the magnesium and/or calcium containing compound adding, the fluoride in the ore may be formed into a magnesium/calcium fluoride and magnesium/calcium fluorophosphate solid immobilized in the slag during the calcination process, thereby reducing environmental pollution caused by the escape of the fluoride as the hydrogen fluoride gas during the calcination process, while avoiding loss of the rare earth caused by a rare earth fluoride precipitate formed by the fluoride during the impurity removal process of the solution, so as to further improve the yield of rare earth. An available magnesium and/or calcium containing compound includes, but is not limited to a magnesium and/or calcium oxide, carbonate, or a magnesium and/or calcium containing mineral, such as dolomite, magnesite and so on.

Preferably, during the enhanced bake, the concentrated sulfuric acid and the rare earth phosphate containing slag are mixed with a mass ratio of 1 to 2:1, and the bake temperature is 200 to 500 °C, preferably 250 to 400 °C. The calcination is performed within the temperature ranges so that the thorium, the iron and the phosphoric acid are formed into a phosphate and a pyrophosphate precipitates immobilized in the slag without being leached. Meanwhile, the radioactive element thorium is also immobilized in the slag,

thus preventing the radioactive element thorium from being dispersed in the process to cause pollution. The concentration of the concentrated sulfuric acid used in the foregoing step is larger than or equal to 70%, preferably a concentrated sulfuric acid with the concentration of 98.3%.

Preferably, in the step of adjusting the pH value of the rare earth containing water leach solution, the pH value of the rare earth containing water leach solution is adjusted by using a magnesium oxide and/or a caustic calcined dolomite, and the pH value of the rare earth containing water leach solution is adjusted to 4 to 4.5, preferably. The pH value of the rare earth containing water leach solution is adjusted by the magnesium oxide and/or the caustic calcined dolomite to ensure that the phosphorus may be transformed to an iron phosphate and a thorium phosphate as much as possible without the precipitation of rare earth.

The beneficial effect of the present disclosure will be further described below in combination with Embodiment 1 to Embodiment 27.

#### Embodiment 1

100 g of phosphorite containing 1.5% rare earth is used as a raw material, and leached with a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 15% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 5% (based on the molar number of anions), the liquid-to-solid ratio of the system is controlled to 10: 1, 1000 mL of the mixed acid solution is added, a reaction is carried out for 6h at 55 °C , and filtering is performed to obtain a mono-calcium phosphate solution and 12.1 g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.6% and the leaching rate of phosphorus is 95.1%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for

leaching phosphorite.

#### Embodiment 2

100 g of phosphorite containing 3% rare earth is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 5% (based on the mole number of anions). The liquid-to-solid ratio of the system is controlled at 8: 1, 800 mL of the mixed acid solution is added, a reaction is carried out for 5h at 70°C, and filtering is performed to obtain a mono-calcium phosphate solution and 11.1g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.4% and the leaching rate of phosphorus is 98.1%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 3

100 g of phosphorite containing 3% rare earth is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 45% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 5% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 8: 1, 800 mL of the mixed acid solution is added, a reaction is carried out for 5h at 70°C, and filtering is performed to obtain a mono-calcium phosphate solution and 10.6g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 4.2% and the leaching rate of phosphorus is 98.1%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution

and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 4

100 g of phosphorite containing 3% rare earth is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 1% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 8: 1, 800 mL of the mixed acid solution is added, a reaction is carried out for 5h at 70°C, and filtering is performed to obtain a mono-calcium phosphate solution and 11.8g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 2.7% and the leaching rate of phosphorus is 95.5%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 5

100 g of phosphorite containing 3% rare earth is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 25% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 8: 1, 800 mL of the mixed acid solution is added, a reaction is carried out for 5h at 70°C, and filtering is performed to obtain a mono-calcium phosphate solution and 11.0g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 5% and the leaching rate of phosphorus is 98.5%. Sulfuric acid is added to the

obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus-containing solution and gypsum, phosphorus in the phosphorus-containing solution is recovered. And a portion of the phosphorus-containing solution is recycled and used for leaching phosphorite.

#### Embodiment 6

100 g of phosphorite containing 2% rare earth is used as a raw material, and leached by using a mixed acid solution of phosphoric acid, hydrochloric acid and nitric acid, the mass fraction of the phosphoric acid in the mixed acid is 40% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid and the nitric acid is 8% (based on the mole number of anions, the mole ratio of the hydrochloric acid to the nitric acid is 1:1), the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the mixed acid solution is added, a reaction is carried out for 4h at 80°C, and filtering is performed to obtain a mono-calcium phosphate solution and 9.7g rare earth phosphate-containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 4.5% and the leaching rate of phosphorus is 97.8%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus-containing solution and gypsum, phosphorus in the phosphorus-containing solution is recovered. And a portion of the phosphorus-containing solution is recycled and used for leaching phosphorite.

#### Embodiment 7

100 g of phosphorite containing 14.4% rare earth and 20% of monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 10% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 2: 1, 200 mL of the mixed acid solution is added, a reaction is carried out for 8h at 55°C, and filtering is

performed to obtain a mono-calcium phosphate solution and 33.4g rare earth phosphatecontaining slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 2.6% and the leaching rate of phosphorus is 95.0%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 8

100 g of phosphorite containing 14.4% rare earth and 20% of monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 10% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 7: 1, 700 mL of the mixed acid solution is added, a reaction is carried out for 8h at 55°C, and filtering is performed to obtain a mono-calcium phosphate solution and 31.1g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.1% and the leaching rate of phosphorus is 97.5%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 9

100 g of phosphorite containing 14.4% rare earth and 20% of monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric

acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 10% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 9: 1, 900 mL of the mixed acid solution is added, a reaction is carried out for 8h at 55°C, and filtering is performed to obtain a mono-calcium phosphate solution and 31.0g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.2% and the leaching rate of phosphorus is 98.2%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is returned and used for leaching phosphorite.

#### Embodiment 10

100 g of phosphorite containing 7.4% rare earth and 9.5% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 25% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 15% (based on the mole number of anions). The liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the mixed acid solution is added, a reaction is carried out for 2h at 70°C, and filtering is performed to obtain a mono-calcium phosphate solution and 17.8g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 2.7% and the leaching rate of phosphorus is 98.2%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.



## Embodiment 11

100 g of phosphorite containing 7.4% rare earth and 9.5% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and nitric acid, the mass fraction of the phosphoric acid in the mixed acid is 25% (based on  $P_2O_5$ ), and the proportion of the nitric acid is 15% (based on the mole number of anions). the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the mixed acid solution is added, a reaction is carried out for 2h at 70°C, and filtering is performed to obtain a mono-calcium phosphate solution and 18.9g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 2.9% and the leaching rate of phosphorus is 97.6%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

## Embodiment 12

100 g of phosphorite containing 9% rare earth and 11.9% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 25% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 20% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the mixed acid solution is added, a reaction is carried out for 4h at 57°C, and filtering is performed to obtain a mono-calcium phosphate solution and 20.7g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.5% and the leaching rate of phosphorus is 96.6%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution

and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 13

100 g of phosphorite containing 9.0% rare earth and 11.9% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 25% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 20% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the mixed acid solution is added, a reaction is carried out for 4h at 90°C, and filtering is performed to obtain a mono-calcium phosphate solution and 20.1g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.2% and the leaching rate of phosphorus is 98.3%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 14

100 g of phosphorite containing 9.0% rare earth and 11.9% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 25% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 20% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the mixed acid solution is added, a reaction is carried out for 4h at 120°C, and filtering is performed to obtain a mono-calcium phosphate solution and 19.9g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.2% and the leaching rate of phosphorus is 98.2%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 15

1000 g of phosphorite containing 8.1% rare earth and 10.6% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 20% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 15% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 6: 1, 6000 mL of the mixed acid solution is added, a reaction is carried out for 5h at 80°C, and filtering is performed to obtain a mono-calcium phosphate solution and 168.4g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.0% and the leaching rate of phosphorus is 98.5%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 16

100 g of phosphorite containing 11.4% rare earth and 15.5% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and hydrochloric acid, the mass fraction of the phosphoric acid in the mixed acid is 30% (based on  $P_2O_5$ ), and the proportion of the hydrochloric acid is 30% (based on the mole number of anions), the

liquid-to-solid ratio of the system is controlled at 3: 1, 300 mL of the mixed acid solution is added, a reaction is carried out for 1h at 110°C, and filtering is performed to obtain a mono-calcium phosphate solution and 24.7g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.3% and the leaching rate of phosphorus is 95.7%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Embodiment 17

100 g of phosphorite containing 6.5% rare earth and 8.2% monazite is used as a raw material, and leached by using a mixed acid solution of phosphoric acid and nitric acid, the mass fraction of the phosphoric acid in the mixed acid is 50% (based on  $P_2O_5$ ), and the proportion of the nitric acid is 2% (based on the mole number of anions), the liquid-to-solid ratio of the system is controlled at 4: 1, 400 mL of the mixed acid solution is added, a reaction is carried out for 0.5h at 150°C, and filtering is performed to obtain a mono-calcium phosphate solution and 19.5g rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 3.5% and the leaching rate of phosphorus is 95.0%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered. And a portion of the phosphorus containing solution is recycled and used for leaching phosphorite.

#### Comparison example 1

100 g of phosphorite containing 9.0% rare earth and 11.9% monazite is

used as a raw material, and leached by using a hydrochloric acid solution, the fraction of the hydrochloric acid is 20%, the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the hydrochloric acid is added, a reaction is carried out for 4h at 90°C, and filtering is performed to obtain a  $\text{CaCl}_2$  containing solution and 14.2g of a rare earth phosphate containing slag. It is tested that the leaching rate of the rare earth in the phosphorite is 78.2% and the leaching rate of phosphorus is 99.4%.

#### Comparison example 2

100 g of phosphorite containing 9% rare earth and 11.9% monazite is used as a raw material, and leached by using a phosphoric acid solution, the mass fraction of the phosphoric acid is 25%, the liquid-to-solid ratio of the system is controlled at 6: 1, 600 mL of the hydrochloric acid is added, a reaction is carried out for 4h at 90°C, and filtering is performed to obtain a mono-calcium phosphate solution and 43.1g of a rare earth phosphate containing slag.

It is tested that the leaching rate of the rare earth in the phosphorite is 2.5% and the leaching rate of phosphorus is 85.0%. Sulfuric acid is added to the obtained mono-calcium phosphate solution to remove the calcium, and solid-liquid separation is performed to obtain a phosphorus containing solution and gypsum, phosphorus in the phosphorus containing solution is recovered.

#### Embodiment 18

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing slag is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing slag to phosphorus in the rare earth phosphate containing slag is controlled to be 2.5, and magnesium oxide is added according to the fluorine content in the slag, the mole ratio of  $\text{Mg}/\text{F}$  is controlled to be 1: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1: 1, enhanced bake is performed at 200 °C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and an water leach slag.

Magnesium oxide is added to adjust the pH value of the rare earth containing water leach solution to 4.0, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.03g/L, P 0.005g/L, Th<0.06 mg/L); a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 91.5%.

#### Embodiment 19

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing slag is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing slag to phosphorus in the rare earth phosphate containing slag is controlled to be 2.5, and magnesium oxide is added according to the fluorine content in the slag, the mole ratio of Mg/F is controlled to be 1: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1: 1, enhanced bake is performed at 250°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Magnesium oxide is added to adjust the pH value of the rare earth containing water leach solution to 4.0, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.04g/L, P 0.005g/L, Th<0.05mg/L); a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 93.5%.

#### Embodiment 20

15 g of the rare earth phosphate containing slag obtained in Embodiment

15 is used as a raw material, an iron containing slag is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing slag to phosphorus in the rare earth phosphate containing slag is controlled to be 2.5, and magnesium oxide is added according to the fluorine content in the slag, the mole ratio of  $Mg/F$  is controlled to be 1: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1: 1, enhanced bake is performed at 500°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Magnesium oxide is added to adjust the pH value of the rare earth containing water leach solution to be 4.0, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution ( $Fe$  0.06g/L,  $P$  0.005g/L,  $Th < 0.05mg/L$ ); a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 95.1%.

#### Embodiment 21

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing rare earth tailing is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing rare earth tailing to phosphorus in the rare earth phosphate containing slag is controlled to be 2, and dolomite is added according to the fluorine content in the slag, the mole ratio of  $(Ca+Mg)/F$  is controlled to be 1.5: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1.5: 1, enhanced bake is performed at 350°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Caustic calcined dolomite is added to adjust the pH value of the rare earth containing water leach solution to 4.5, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.009g/L, P 0.005g/L, Th<0.05mg/L), a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 93.1%.

#### Embodiment 22

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing rare earth tailing is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing rare earth tailing to phosphorus in the rare earth phosphate containing slag is controlled to be 3, and dolomite is added according to the fluorine content in the slag, the mole ratio of (Ca+Mg)/F is controlled to be 1.5: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1.5: 1, enhanced bake is performed at 350°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Caustic calcined dolomite is added to adjust the pH value of the rare earth containing water leach solution to 4.5, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.02g/L, P 0.0009g/L, Th<0.03mg/L), a carbonate is added into the rare earth sulfate solution to precipitate rare earth, to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 95.4%.

#### Embodiment 23

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing rare earth tailing is added



according to the phosphorus content in the slag, the mass ratio of iron in the iron containing rare earth tailing to phosphorus in the rare earth phosphate containing slag is controlled to be 4, and dolomite is added according to the fluorine content in the slag, the mole ratio of  $(\text{Ca}+\text{Mg})/\text{F}$  is controlled to be 1.5: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1.5: 1, enhanced bake is performed at  $350^{\circ}\text{C}$  to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Caustic calcined dolomite is added to adjust the pH value of the rare earth containing water leach solution to 4.5, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution ( $\text{Fe}$  0.02g/L,  $\text{P}$  0.0008g/L,  $\text{Th}<0.04\text{mg/L}$ ); a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 96.2%.

#### Embodiment 24

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing tailing is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing tailing to phosphorus in the rare earth phosphate containing slag is controlled to be 3.5, and magnesite is added according to the fluorine content in the slag, the mole ratio of  $\text{Mg}/\text{F}$  is controlled to be 1, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 2: 1, enhanced bake is performed at  $400^{\circ}\text{C}$  to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Caustic calcined dolomite is added to adjust the pH value of the rare earth

containing water leach solution to 3.8, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.05g/L, P 0.007g/L, Th<0.05mg/L), a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 96.1%.

#### Embodiment 25

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing tailing is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing tailing to phosphorus in the rare earth phosphate containing slag is controlled to be 3.5, and magnesite is added according to the fluorine content in the slag, the mole ratio of Mg/F is controlled to be 1, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 2: 1, enhanced bake is performed at 400°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Caustic calcined dolomite is added to adjust the pH value of the rare earth containing water leach solution to 4.3, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.04g/L, P 0.001g/L, Th<0.04mg/L), a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate, calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 95.8%.

#### Embodiment 26

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing tailing is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing tailing to phosphorus in the rare earth phosphate containing slag is controlled

to be 3.5, and magnesite is added according to the fluorine content in the slag, the mole ratio of Mg/F is controlled to be 1, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 2: 1, enhanced bake is performed at 400°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Caustic calcined dolomite is added to adjust the pH value of the rare earth containing water leach solution to 5, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.01g/L, P 0.0008g/L, Th<0.04mg/L), a carbonate is added into the rare earth sulfate solution to precipitate rare earth to obtain a rare earth carbonate , calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 95.0%.

#### Embodiment 27

15 g of the rare earth phosphate containing slag obtained in Embodiment 15 is used as a raw material, an iron containing slag is added according to the phosphorus content in the slag, the mass ratio of iron in the iron containing slag to phosphorus in the rare earth phosphate containing slag is controlled to be 3, and calcium oxide is added according to the fluorine content in the slag, the mole ratio of Ca/F is controlled to be 1.5: 2, and then concentrated sulfuric acid is added and mixing is performed, the mass ratio of the concentrated sulfuric acid to the rare earth phosphate containing slag is 1.5: 1, enhanced bake is performed at 450°C to obtain a calcination slag.

The calcination slag is leached with 200mL of water, and filtered to obtain a rare earth containing water leach solution and a water leach slag.

Magnesium oxide is added to adjust the pH value of the rare earth containing water leach solution to 4, and filtering is performed to obtain an iron and thorium containing precipitate, and a rare earth sulfate solution (Fe 0.05g/L, P 0.002g/L, Th<0.05mg/L); a carbonate is added into the rare earth

sulfate solution to precipitate rare earth to obtain a rare earth carbonate , calcination is performed to obtain an rare earth oxide, the recovery rate of the rare earth is 95.8%.

It may be seen from the foregoing description that the embodiments of the present application have implemented the following technical effect: the present disclosure leaches a rare earth containing phosphorite by using a mixed acid solution so that the phosphorus in the phosphorite forms highly-soluble mono-calcium phosphate, at the same time by performing regulation and control in the leaching process to precipitate and enrich the rare earth in the form of a rare earth phosphate in a slag, if the rare earth containing phosphorite further contains a monazite, the monazite and the rare earth phosphate are enriched in the slag, thereby separating the phosphorus and the rare earth. A hydrochloric acid or a nitric acid in the mixed acid solution is propitious to decompose apatite while ensuring that the rare earth is enriched in the slag in the form of a rare earth phosphate precipitate, thereby improving the leaching rate of the phosphorus in the apatite. Besides, the hydrochloric acid or the nitric acid can provide hydrogen ions  $H^+$ , and can reduce the content of phosphate radicals and the viscosity of the system with the same acid content, thus facilitating leaching of the phosphorus; in the meanwhile, the existence of the chloride ions or the nitrate ions is propitious to increase the solubility of calcium ions in a solution and decomposition of the apatite. The rare earth and the phosphorus element in the rare earth containing phosphorite can be separated effectively by a filtering process, thus improving the respective recovery rate of the rare earth and the phosphorus. At the same time, the rare earth enters the slag in the form of the rare earth phosphate, and is enriched with the insoluble monazite during the acid leaching process so as to recover the rare earth collectively, thereby simplifying recovery steps, improving the recovery rate of the rare earth, and achieving the purpose of comprehensive recovery of the rare earth with low cost.

The above are only preferred embodiments of the present disclosure, but

are not used for limiting the present disclosure. For those skilled in the art, the present disclosure may have various modifications and changes. Any modifications, equivalent replacements, improvements and the like made within the spirit and principles of the present disclosure shall be included in the scope of protection of the present disclosure.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavor to which this specification relates.

**THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:**

1. A method for recovering phosphorus and rare earth from a rare earth containing phosphorite comprising the following steps:

leaching the rare earth containing phosphorite at a leaching temperature of 70 °C to 150 °C and for a leaching time is 0.5 to 8 hours using a mixed acid solution, filtering and obtaining a mono-calcium phosphate solution and a rare earth phosphate containing slag, wherein the main component of the mixed acid solution is a phosphoric acid and the mixed acid solution further comprises a hydrochloric acid and/or a nitric acid;

recovering (i) the phosphorus of the mono-calcium phosphate solution, and (ii) the rare earth of the rare earth phosphate containing slag.

2. The method according to claim 1, wherein the rare earth containing phosphorite contains a monazite.

3. The method according to claim 1 or 2, wherein based on a molar number of anions, a proportion of the hydrochloric acid and/or the nitric acid in the mixed acid solution is 1% to 30%.

4. The method according to claim 1 or 2, wherein a mass fraction of  $P_2O_5$  in the mixed acid solution is 15% to 50%.

5. The method according to claim 4, wherein in the step of leaching the rare earth containing phosphorite by using the mixed acid solution, the mixed acid solution and the rare earth containing phosphorite are mixed at a liquid-to-solid ratio of 2L to 10L: 1kg.

6. The method according to claim 1 or 2, wherein the leaching temperature is 60 °C to 90 °C and the leaching time is 2 to 5 hours.

7. The method according to claim 1 or 2, wherein the step of recovering the phosphorus of the mono-calcium phosphate solution includes: adding a sulfuric acid into the mono-calcium phosphate solution, performing solid-liquid separation and obtaining a phosphorus containing solution and a calcium sulfate gypsum, and then recovering the phosphorus of the phosphorus containing solution.

8. The method according to claim 7, wherein the step of recovering the phosphorus of the mono-calcium phosphate solution further includes: preparing a phosphoric acid from a portion of the phosphorus containing solution after impurities removal, then recycling the prepared phosphoric acid to the leaching step.

9. The method according to claim 1 or 2, wherein the step of recovering the rare earth of the rare earth phosphate containing slag includes:

adding an iron containing compound, a compound containing magnesium and/or a calcium into the rare earth phosphate containing slag, then mixing with a concentrated sulfuric acid, and performing an enhanced bake to obtain a calcination slag;

leaching the calcination slag by water to obtain a rare earth containing water leach solution and a water leach slag;

adjusting the pH value of the rare earth containing water leach solution to 3.8 to 5, filtering and obtaining a rare earth sulfate solution and a slag containing iron and thorium;

adding a carbonate or an oxalate into the rare earth sulfate solution to precipitate the rare earth, and obtaining a rare earth carbonate or a rare earth oxalate, calcining the rare earth carbonate and the rare earth oxalate to obtain a rare earth oxide; or extracting the rare earth sulfate solution by using an acidic phosphorus extractant to obtain a mixed rare earth chloride or single rare earth compounds.

10. The method according to claim 9, wherein the compound containing magnesium and/or calcium is at least one of an oxide, a carbonate or a mineral, and the iron containing compound is at least one of an iron containing tailing and an iron containing slag.

11. The method according to claim 9, wherein the molar ratio of the magnesium and/or calcium of the compound containing magnesium and/or calcium to the fluorine of the rare earth phosphate containing slag is 1 to 2: 2.

12. The method according to claim 9, wherein a mass ratio of the iron of

the iron containing compound to the phosphorus of the rare earth phosphate containing slag is 2 to 4: 1.

13. The method according to claim 9, wherein during the enhanced bake, the concentrated sulfuric acid and the rare earth phosphate containing slag are mixed with a mass ratio of 1 to 2: 1; and the bake temperature during the enhanced bake step is 200 °C to 500 °C.

14. The method according to claim 9, wherein in the step of adjusting the pH value of the rare earth containing water leach solution, the pH value of the rare earth containing water leach solution is adjusted by using a magnesium oxide and/or a caustic calcined dolomite, and the pH value of the rare earth containing water leach solution is adjusted to 4 to 4.5.

15. The method according to claim 1 or 2, wherein based on a molar number of anions, a proportion of the hydrochloric acid and/or the nitric acid in the mixed acid solution is 2% to 15%.

16. The method according to claim 1 or 2, wherein a mass fraction of  $P_2O_5$  in the mixed acid solution is 15% to 30%.

17. The method according to claim 4, wherein in the step of leaching the rare earth containing phosphorite by using the mixed acid solution, the mixed acid solution and the rare earth containing phosphorite are mixed at a liquid-to-solid ratio of 4L to 8L: 1kg.

18. The method according to claim 10, wherein the iron containing compound is a tailing containing rare earth and iron.

19. The method according to claim 9, wherein a mass ratio of the iron of the iron containing compound to the phosphorus of the rare earth phosphate containing slag is 2.5 to 3.5: 1.

20. The method according to claim 13, wherein the bake temperature during the enhanced bake step is 250 °C to 400 °C.



# **EDITORIAL NOTE**

**2016200606**

- There is 1 page of Drawings only

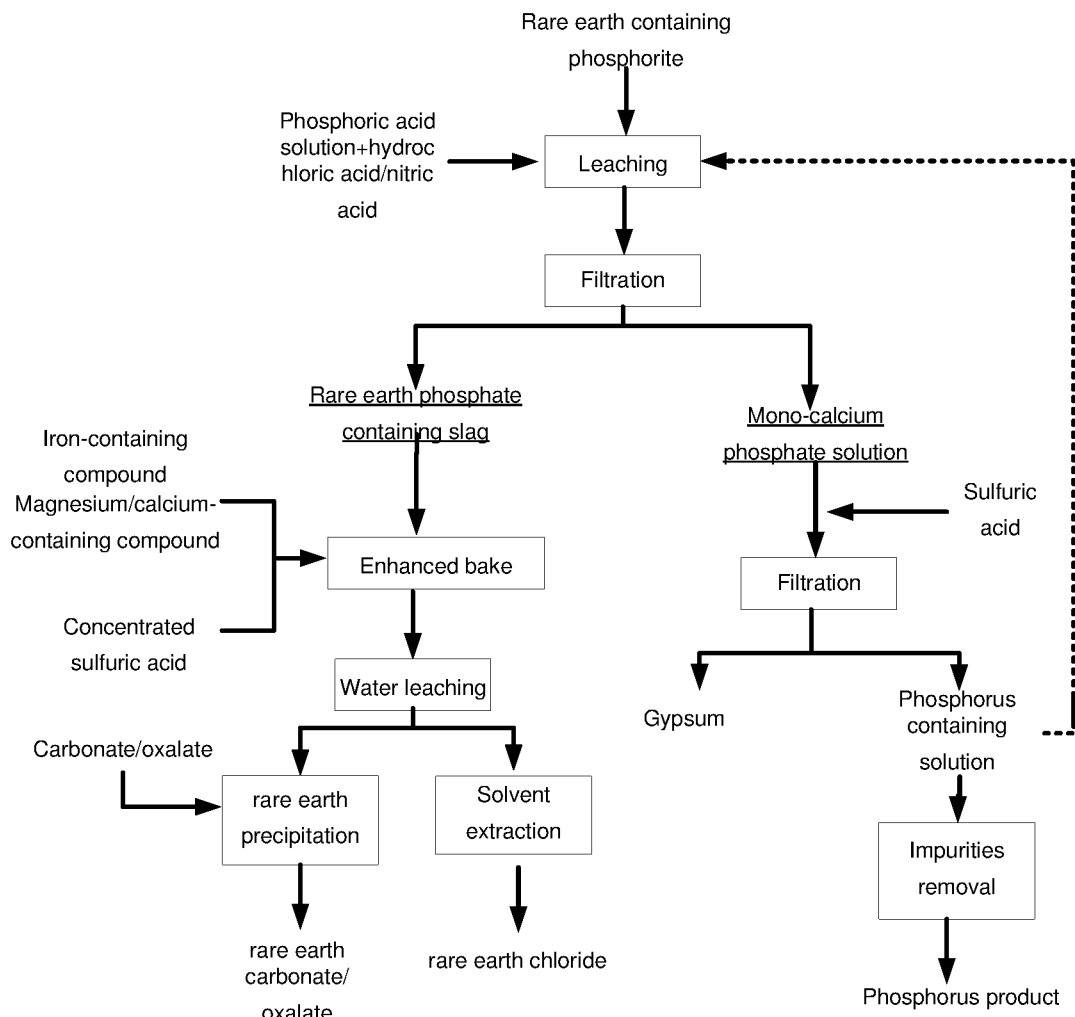


Fig. 1