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(71) Demandeur/Applicant:
AUSTRALIAN NUCLEAR SCIENCE AND
TECHNOLOGY ORGANISATION, AU
(72) Inventeurs/Inventors:
DEMOL, JOHN, AU;
HO, ELIZABETH MARGARET, AU;
SOLDENHOFF, KARIN HELENE, AU
(74) Agent: GOWLING WLG (CANADA) LLP

(54) Titre : PROCEDE DE RECUPERATION DE TERRES RARES
(54) Title: PROCESS FOR RECOVERING RARE EARTHS

(57) Abrégé/Abstract:

A process for recovering rare earth elements from a rare earth element containing ore, the process comprising: adding an amount of a silicon containing source to the rare earth element containing ore to form a mixture; subjecting the mixture to an acid-bake process, wherein the mixture is subjected to temperatures above 150°C; and performing a leaching process on the mixture to produce a leach liquor with a high concentration of rare earth elements.

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Abstract:

A process for recovering rare earth elements from a rare earth element containing ore, the process comprising: adding an amount of a silicon containing source to the rare earth element containing ore to form a mixture; subjecting the mixture to an acid-bake process, wherein the mixture is subjected to temperatures above 150°C; and performing a leaching process on the mixture to produce a leach liquor with a high concentration of rare earth elements.

PROCESS FOR RECOVERING RARE EARTHS

Technical Field

[0001] The present disclosure relates to a process for recovering rare earths, in particular for an acid-bake process for recovering rare earths.

Background of the Disclosure

[0002] Rare earth elements (REE) are a group of 17 elements which have become critical for the production of many modern technologies, ranging from common electronic devices such as laptop hard drives, servo-motors and mobile phones to more specialised equipment such as solid state lasers and microwave communication devices. Correspondingly, the demand for rare earth elements is constantly increasing as these technologies become more widespread and new uses are found.

[0003] Rare earth elements are usually found dispersed in ion adsorption clays or within minerals. These minerals are commonly referred to as rare earth bearing minerals. While over 200 such minerals have currently been identified worldwide, the vast majority of commercial processing is carried out on three minerals: bastnasite, monazite and xenotime. Bastnasite is a carbonate-fluoride mineral while monazite and xenotime are both phosphate minerals. Other rare earth bearing minerals include euxenite, samarskite, fergusonite, loparite, allanite, eudialyte and pyrochlore.

[0004] The general process of extracting the rare earth elements from rare earth bearing minerals after mining and comminution of the ore typically occurs in three primary stages: Firstly, a beneficiation process is carried out in order to remove gangue minerals from the mined ore. This stage results in the formation of a rare earth mineral concentrate. In some processes, the ore is processed directly, without beneficiation. The next stage is a decomposition process to extract rare earth elements from the concentrate. Finally, further chemical processing is performed to remove impurities and to separate the rare earth elements into saleable products.

[0005] The main decomposition processes used on an industrial scale are alkali digestion, oxidative roasting followed by acid leaching, and acid bake. The choice of decomposition process will predominantly depend on the composition of the ore/concentrate following

beneficiation, although other factors such as cost and environmental considerations may also influence the decision.

[0006] The acid-bake process, also referred to in the art as a sulfation roast, acid digestion or calcination, is currently used around the globe on all three of the main mineral ores, most notably at the Bayan Obo deposit in Baotou, China which is responsible for around 57% of the rare-earth element production worldwide. Acid bake processes are a common choice for monazite and xenotime based ores or concentrates.

[0007] An issue that arises from these processes is that impurities present in the rare earth ore or concentrate can be solubilised during the bake process and report to the leach liquor with the rare earth elements. Two central impurities which are often found are thorium and phosphate. Phosphate in particular is an issue for the processing of monazite and xenotime as they are phosphate minerals. Additional sources of phosphate, for example apatite (calcium phosphate) are often also present alongside rare earth minerals in mined ores and may also result in a significant amount of phosphate being present in the rare earth ore or concentrate even if the rare earth mineral does not include phosphate. These impurities report to the leach liquor and must be removed through subsequent purification steps which can be lengthy, complex and costly.

[0008] In this specification, a significant amount of phosphate is taken to refer to an amount of phosphate which would, on performing a typical acid-bake process, require downstream processing for removal from the leach liquor to produce a saleable rare earth element product.

[0009] A number of approaches exist to achieve separation of rare earths from impurities when using the acid bake processing route.

[0010] One known method is to increase the bake temperature above 300°C. This results in the rejection of impurities including phosphate, thorium and iron and as a result less downstream processing is required. This is due to the impurities forming insoluble compounds at these temperatures, and as a result they remain as solids in the leach residue following the leaching step. However, a decrease in the extraction of rare earth elements is often seen at temperatures above 300°C. This may be due to a portion of the rare earth elements being contained within the insoluble impurity compounds. The extent of this decrease is dependent on the type and composition of the ore/concentrate. As an example, a rare earth ore/concentrate containing impurities of thorium and phosphates will form thorium polyphosphates above approximately

400°C which are insoluble and will not report to the leach liquor, however rare earth elements incorporated into the structure of these compounds will similarly remain in the leach residue. In many cases, the economic loss from the decreased rare earth element recovery outweighs the benefits achieved by having less downstream processing.

[0011] Another known method involves providing a pre-leach prior to the acid baking to remove impurities such as phosphate from the ore or concentrate. The additional processing steps and the cost of reagents for the pre-leach also reduce or nullify the benefits of less downstream processing.

[0012] Further known methods are to add additives or reagents such as a ferric source to the bake or to the leach solution to precipitate insoluble compounds such as iron phosphate on neutralization of the leach solution. Rare earth elements may also be partially incorporated in these compounds and the extraction of rare earth elements may decrease. A large volume of iron phosphate compounds are produced by this method. Another reagent that may be added to the leach liquor is sodium sulfate which is added to precipitate a rare earth double sulfate salt for further processing, leaving phosphate in the solution. For all these methods, the costs associated with large amount of reagents required and additional process steps often nullify any advantages of reduced downstream processing.

[0013] Accordingly, there remains a need to develop an improved acid-bake process wherein impurities are rejected while rare earth extraction remains high, and wherein the cost of the process is not substantially increased. The present invention seeks to at least partially meet these requirements.

Summary of the Invention

[0014] According to a first aspect, there is provided a process for recovering rare earth elements from a rare earth element containing ore, the process comprising: adding an amount of a silicon containing source to the rare earth element containing ore to form a mixture; subjecting the mixture to an acid-bake process, wherein the mixture is subjected to temperatures above 150°C; and performing a leaching process on the mixture to produce a leach liquor with a high recovery of rare earth elements.

[0015] In certain embodiments, the process further comprises: performing a beneficiation process on the ore to produce a rare earth concentrate prior to adding an amount of a silicon containing source.

[0016] In certain embodiments, the silicon containing source is a silicate mineral.

[0017] In certain embodiments, the rare earth element containing ore contains a significant amount of phosphate.

[0018] In certain embodiments, the acid-bake process is carried out using sulphuric acid.

[0019] In certain embodiments, the acid-bake process is carried out at a temperature between 150-800°C. In a preferred form, the acid-bake process is carried out at a temperature between 300-600 °C.

[0020] In certain embodiments, an iron source is added to the mixture prior to the acid-bake process.

[0021] In certain embodiments, the silicon containing source includes a silicate mineral selected from at least one of the following: muscovite, kaolinite, phlogopite or some other nesosilicate, sorosilicate, cyclosilicate, inosilicate, phyllosilicate or tectosilicate mineral.

[0022] In certain embodiments, the silicon containing source includes a naturally derived material such as diatomaceous earth, perlite or zeolite.

[0023] In certain embodiments, the silicon containing source is at least partially a silicate material or other silicon containing source present in the rare earth containing ore.

[0024] In certain embodiments, the process includes performing a beneficiation process on the ore to produce a rare earth concentrate prior to adding an amount of a silicon containing source and the silicon containing source is at least partially retained during the beneficiation process.

[0025] In certain embodiments, the acid-bake process comprises a two stage bake.

[0026] In certain embodiments, the two stage bake includes a first stage at a lower temperature between 150-300°C and a second stage at a higher temperature between 300-800°C.

[0027] In certain embodiments, the rare earth element containing ore contains an equal or lower rare earth: phosphate ratio relative to monazite.

[0028] In certain embodiments, the phosphate present is at least partially the result of apatite being present in the ore.

[0029] In certain embodiments, the silicon containing source is added to the rare earth element containing ore in a ratio ranging from 0.5:1 to 2:1.

[0030] In certain embodiments, the leaching process is performed at a controlled pH.

[0031] In certain embodiments the pH of the leaching solution of the leaching process is in the range of 0 to 4.5. In a preferred form, the pH of the leaching solution of the leaching process is in the range of 0 to 2.5. In a further preferred form, the pH of the leaching solution of the leaching process is in the range of 0.5 to 2.0.

[0032] In certain embodiments the process comprises a further step of carrying out chemical processing steps on the leach liquor to produce saleable rare earth element products.

[0033] According to a second aspect, there is provided a leach liquor with a high concentration of rare earth elements produced by a process according to the first aspect.

[0034] According to a third aspect, there is provided rare earth element products produced by a process according to the first aspect.

[0035] Other aspects, features, and advantages will become apparent from the following detailed description when taken in conjunction with the accompanying drawings, which are a part of this disclosure and which illustrate, by way of example, principles of the inventions disclosed.

Brief Description of the Figures

[0036] The present disclosure will become better understood from the following detailed description of various non-limiting embodiments thereof, described in connection with the accompanying figures, wherein:

[0037] Figure 1 shows a flow chart of a conventional acid-bake process.

[0038] Figure 2 shows a graph comparing the rare earth dissolution of a monazite concentrate with the dissolution of a mixture containing the monazite concentrate and a silicate mineral.

[0039] Figure 3 shows a graph comparing the dissolution of rare earth elements and a series of common impurities over a range of leach pH values.

Detailed Description

[0040] The inventors have found that a high rare earth element extraction and high impurity rejection can be maintained in acid bake processes regardless of baking temperature through the addition of silicate minerals or other silicon containing sources. In a preferred form, the silicate minerals, or other silicon containing sources are included to the mixture in a w/w ratio between 0.5:1 and 2:1. Advantageously, it was found that the addition of a silicon containing source to the rare earth element containing ore allows the subsequent acid bake process to be carried out at higher temperatures (>300°C) without the corresponding decrease in rare earth element extraction.

[0041] As used herein, the term 'a silicon (Si) containing source' is intended to encompass both silicate minerals as well as other suitable silicon containing sources and is not to be restricted to any specific silicate minerals described herein. Examples of suitable silicate minerals may include, but are not limited to: kaolinite, muscovite, phlogopite, nesosilicates, sorosilicates, cyclosilicates, inosilicates, phyllosilicates and tectosilicates. Examples of other silicon containing sources may include, but are not limited to: diatomaceous earth (i.e. kieselguhr), perlite and zeolite. The silicon containing source is added to the rare earth element containing ore in a ratio ranging from 0.5:1 to 2:1.

[0042] A large range of Si sources are widely available and relatively inexpensive compared to existing additives. Even more advantageously, Si sources are often present in the rare earth element ore before beneficiation and are removed, as the conventional thinking is that a higher initial grade will result in lower operating costs. Accordingly, applying the process as herein described to many existing mining operations will in fact decrease the amount of beneficiation required and as a result reduce costs throughout the extraction process.

[0043] As used herein, the term rare earth element (REE) is reference to one of a group of seventeen elements comprising the fifteen lanthanides, yttrium and scandium. Specifically, the

rare earth elements include: cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), promethium (Pm), samarium (Sm), scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb), and yttrium (Y).

[0044] As used herein, the term rare earth element containing ore refers to a naturally occurring solid material from which a rare earth bearing mineral can be extracted. Rare earth bearing minerals include: bastnasite, monazite, xenotime, euxenite, samarskite, fergusonite, loparite, allanite, eudialyte and pyrochlore. The rare earth element ore may contain a significant amount of phosphate

[0045] A typical acid bake process is shown in Figure 1. Either a rare earth concentrate, obtained following a beneficiation process or a rare earth containing ore is mixed with concentrated sulfuric acid, usually meaning $\geq 93\%$ sulfuric acid. In the exemplified process, $\sim 98\%$ sulfuric acid is added. It will be understood that any beneficiation process known in the art may be used to obtain the rare earth concentrate, for example by flotation separation, gravity separation or magnetic separation techniques, depending on the type and composition of the ore.

[0046] The mixture of rare earth ore or concentrate and sulfuric acid is then heated to an elevated temperature, resulting in the formation of rare earth sulfate products which are insoluble in concentrated sulfuric acid. These products remain soluble in water or a dilute acid, so they may be collected by a water or dilute acid leaching step, resulting in a rare earth containing leach liquor. This leach liquor can then undergo further processing to separate out impurities and individual rare earth elements for sale or use.

[0047] A large range of temperatures may be used for the acid-bake process. For monazite and xenotime, decomposition into rare earth sulfates occurs between 200°C and 300°C . Typical acid bake processes are carried out in this range, however higher temperature bakes up to 600°C are also practiced.

[0048] According to one embodiment, there is provided a process for recovering rare earth elements from a rare earth element containing ore, the process comprising: adding an amount of a silicon containing source to the rare earth element containing ore to form a mixture; subjecting the mixture to an acid-bake process using sulphuric acid, wherein the mixture is subjected to temperatures of above 150°C and less than 800°C ; and performing a leaching process on the

mixture to produce a leach liquor with a high recovery of rare earth elements. In a preferred form, the temperature of the acid-bake process ranges from above 300°C and less than 600°C.

[0049] In certain embodiments, the acid-bake process comprises a two stage bake. In this form, the two stage bake may include a first stage at a lower temperature between 150-300°C which is followed by a second stage which is set at a higher temperature between 300-800°C.

[0050] In accordance with the disclosure and without wishing to be bound by theory, a high rare earth extraction is thought to be obtained through the mechanism of silicate minerals reacting to sequester phosphate and thus preventing the formation of less soluble rare earth phosphate type phases, i.e. rare earth polyphosphates, allowing rare earth elements to pass into the leach liquor. At the same time, the acid bake may be carried out at a higher temperature to obtain the associated benefits, such as the conversion of impurities including phosphate and thorium to insoluble compounds providing both a high rare earth extraction and improved rejection of impurities compared with existing processes.

[0051] The inventors have also found that in a preferred form and to achieve a significant removal of major impurities such as phosphate and thorium using the process as herein described, the pH of the leach process and specifically the leach solution may be controlled. In particular, by adjusting the leach solution to a pH in the range of 0 to 4.5, and in a preferred form a pH in the range of 0 to 2.5, or even more preferably in the range of 0.5 and 2.0, the greatest rare earth extraction may be balanced with the greatest rejection of impurities during the leach process.

[0052] A number of advantages exist over the existing processes and methods of increasing rejection of impurities. The process requires no additional unit operation and many Si sources are both widely available and relatively inexpensive. As the addition of Si sources allows the bake to be carried out at higher temperatures, the process is also more robust with regard to temperature excursions in the kiln compared with existing processes. Further, the extraction of phosphate and thorium is decreased, so that more of the impurities are rejected to one solid waste stream in the form of the leach residue. This is particularly beneficial with regard to radioactive impurities such as thorium as the waste management is simplified.

[0053] The process may also involve adding both Si sources together with iron sources to the rare earth ore or concentrate before an acid-bake process. The combination of adding both Si

sources and iron sources provide additional benefits which overcome some of the previously discussed drawbacks of ferric reagents. In particular, the presence of silicate minerals sequesters phosphate and reduces the mass of ferric phosphate which is precipitated. This has two beneficial effects. Firstly, there is less rare earth loss in a ferric phosphate precipitation step, and secondly, the required size of filters in downstream processing decreases resulting in capital savings. Such a system also results in considerable ferric reagent savings owing to the fact that ferric does not have to be added to the neutralization step.

[0054] This process is particularly beneficial for ores or concentrates with a rare earth: phosphate (RE:P) ratio equal to monazite or lower, for example in circumstances where the ore consists of monazite or xenotime and an apatite, owing to the sequestering of phosphates by the silicate minerals. Monazite has a mole RE:P ratio close to but slightly lower than 1:1 owing to the Th content of monazite. It will be understood that this process may also be used on ores with an equal or even higher RE:P ratio compared to monazite.

[0055] The resultant rare earth element containing leach liquor can then be further processed by any methods known in the art, for example by solvent extraction or ion exchange methods.

Examples

[0056] The present disclosure will be better understood by the following experimental data. It will be understood that these examples represent non-limiting embodiments.

[0057] In a first experiment, the temperature of the acid-bake process was varied and the resultant effect on the rare earth element dissolution following leach was investigated. A rare earth concentrate derived from monazite was mixed with a silicate mineral in the form of kaolinite in a 1:1 w/w ratio as well as 1650 kg/t concentrated sulfuric acid. The mixture was then subjected to a two-stage bake, the first stage being carried out at 250°C for 2 hours and a second stage carried out at varied temperatures between 200°C and 800°C for 2 hours. Following the bake, a leaching step was carried out using dilute sulfuric acid (0.9 M) for 2 hours at ambient temperature and with an initial solids density of 2.5% (w/w). The rare earth dissolution in the leach liquor was then compared to the same rare earth concentrate without the addition of kaolinite.

[0058] A graph comparing rare earth dissolution in the leach versus bake temperature is shown in Figure 2. Rare earth extraction from the monazite concentrate without any silicate

mineral added increases with temperature up to a maximum approaching 100% at 300°C, above which the dissolution falls substantially. By contrast, rare earth extraction from the monazite concentrate with kaolinite added maintains close to 100% dissolution up to a bake temperature of 650°C. The monazite concentrate with kaolinite added resulted in a greater dissolution of rare earth elements in the resultant leach over the full range of temperatures.

[0059] In a second experiment, natural kaolinite was mixed with a monazite concentrate at a ratio of 1:1 (w/w) and subjected to an acid-bake process with 1650 kg/t concentrated sulphuric acid in a two stage bake consisting of a first stage at 250°C for 2 hours and a second stage at 500°C for 2 hours. The baked solids were then leached for 2 hours with leaches with a range of pH levels between 0 and 1.7 at ambient temperature and with an initial solids density of 2.5% (w/w).

[0060] A graph showing the comparative dissolution of rare earth elements and impurities of phosphate, thorium, aluminium and silicon is shown in Figure 3. The rare earth dissolution remains high at pH levels between 0 and 1, before falling at pH levels above 1. The dissolution of all impurities falls with increasing pH. At pH 1, silica and aluminium are almost completely rejected from the leach, and substantial rejection of both thorium and phosphate is achieved while maintaining high rare earth element dissolution.

[0061] In the foregoing description of certain embodiments, specific terminology has been resorted to for the sake of clarity. However, the disclosure is not intended to be limited to the specific terms so selected, and it is to be understood that each specific term includes other technical equivalents which operate in a similar manner to accomplish a similar technical purpose.

[0062] In this specification, the word “comprising” is to be understood in its “open” sense, that is, in the sense of “including”, and thus not limited to its “closed” sense, that is the sense of “consisting only of”. A corresponding meaning is to be attributed to the corresponding words “comprise”, “comprised” and “comprises” where they appear.

[0063] 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 acknowledgement or admission or any form of suggestion that prior publication (or information

derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

[0064] In addition, the foregoing describes only some embodiments of the invention(s), and alterations, modifications, additions and/or changes can be made thereto without departing from the scope and spirit of the disclosed embodiments, the embodiments being illustrative and not restrictive.

[0065] Furthermore, invention(s) have described in connection with what are presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the invention(s). Also, the various embodiments described above may be implemented in conjunction with other embodiments, e.g., aspects of one embodiment may be combined with aspects of another embodiment to realize yet other embodiments. Further, each independent feature or component of any given assembly may constitute an additional embodiment.

The claims:

1. A process for recovering rare earth elements from a rare earth element containing ore, the process comprising:
 - adding an amount of a silicon containing source to the rare earth element containing ore to form a mixture;
 - subjecting the mixture to an acid-bake process, wherein the mixture is subjected to temperatures above 150°C; and
 - performing a leaching process on the mixture to produce a leach liquor with a high concentration of rare earth elements.
2. The process of claim 1, wherein the process further comprises:
 - performing a beneficiation process on the ore to produce a rare earth concentrate prior to adding an amount of the silicon containing source.
3. The process according to either claim 1 or 2, wherein the silicon containing source is a silicate mineral.
4. The process according to any one of the preceding claims, wherein the rare earth element containing ore contains a significant amount of phosphate.
5. The process according to any one of the preceding claims, wherein the acid-bake process is carried out using sulphuric acid.
6. The process according to any one of the preceding claims, wherein the bake is carried out at temperatures between 300-800°C.
7. The process according to any one of the preceding claims, wherein an iron source is added to the mixture prior to the acid-bake process.
8. The process according to any one of the preceding claims, wherein the silicon containing source includes a silicate mineral selected from at least one of the following: muscovite,

kaolinite, phlogopite or some other nesosilicate, sorosilicate, cyclosilicate, inosilicate, phyllosilicate or tectosilicate mineral.

9. The process according to any one of the preceding claims, wherein the silicon containing source includes a naturally derived material such as diatomaceous earth, perlite or zeolite.
10. The process according to any one of the preceding claims, wherein the silicon containing source is at least partially a silicate material or other silicon containing source present in the rare earth element containing ore.
11. The process according to claim 10, wherein the process includes performing a beneficiation process on the ore to produce a rare earth concentrate prior to adding an amount of a silicon containing source and the silicon containing source is at least partially retained during the beneficiation process.
12. The process according to any one of the preceding claims, wherein the acid-bake process comprises a two stage bake.
13. The process according to claim 12, wherein the two stage bake includes a first stage at a lower temperature between 150-300°C and a second stage at a higher temperature between 300-800°C.
14. The process according to any one of the preceding claims, wherein the rare earth element containing ore contains an equal or lower rare earth: phosphate ratio relative to monazite.
15. The process according to claim 14, wherein the phosphate present is at least partially the result of apatite being present in the ore.
16. The process according to any one of the preceding claims, wherein the silicon containing source is added to the ore in a ratio ranging from 0.5:1 to 2:1.
17. The process according to any one of the preceding claims, wherein the leaching process is performed at a controlled pH.

18. The process according to claim 17, wherein the controlled pH is in the range of 0 to 4.5.
19. A leach liquor with a high concentration of rare earth elements produced by a process according to any one of claims 1 to 18.
20. The process according to any one of claims 1 to 18, wherein the process comprises a further step of:
carrying out chemical processing steps on the leach liquor to produce saleable rare earth element products.
21. A rare earth element product produced from a process according to claim 20.

1/3

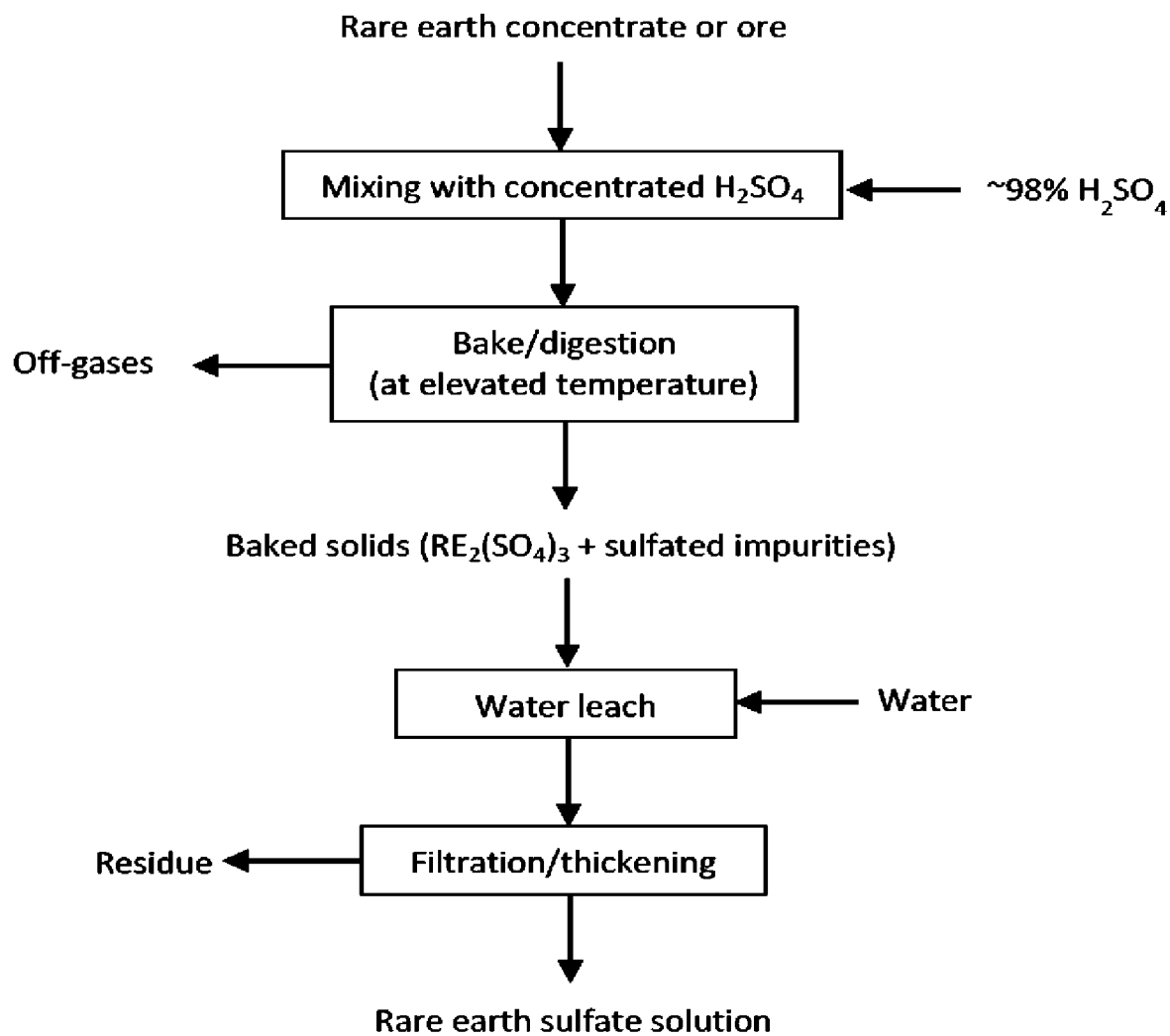


FIGURE 1

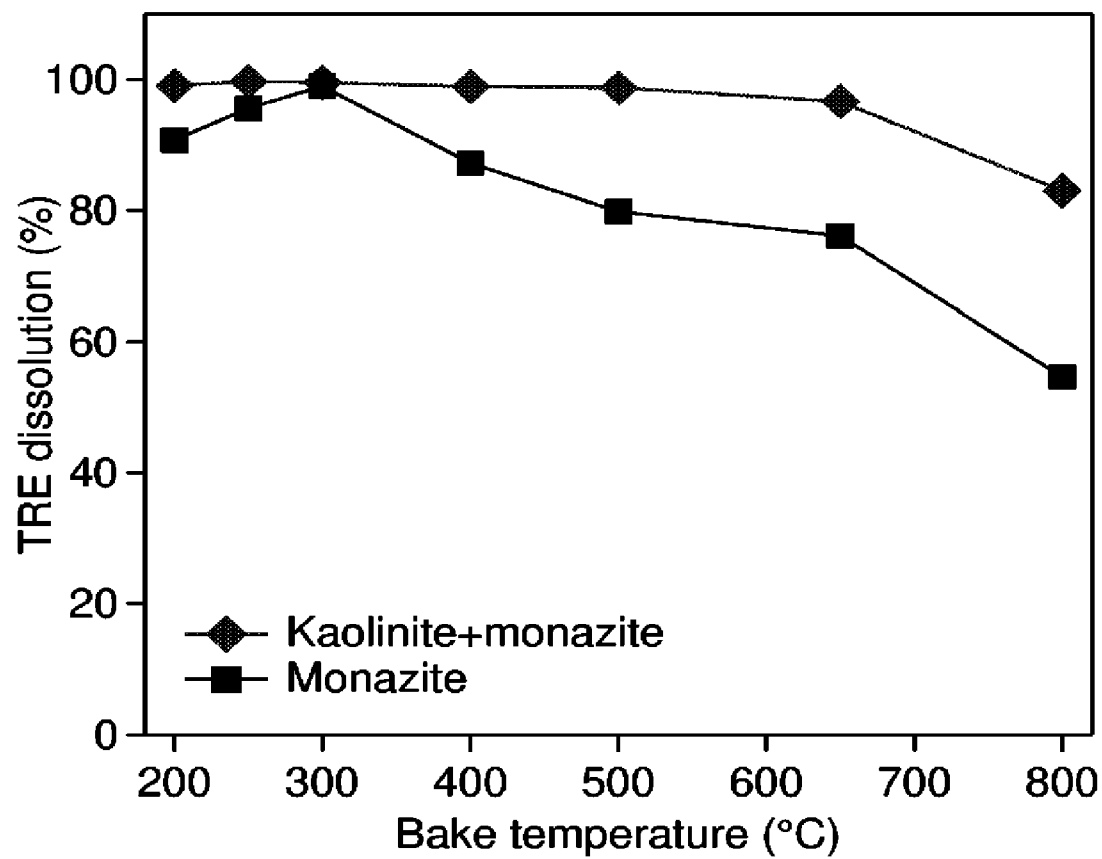


FIGURE 2

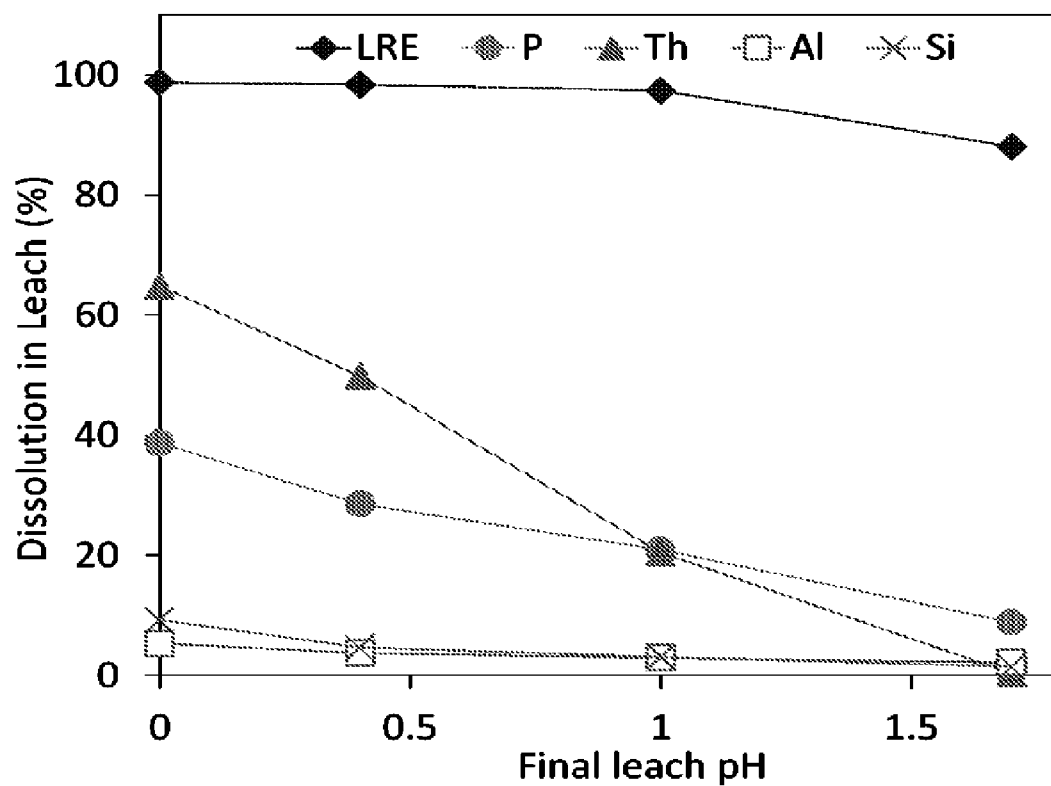


FIGURE 3