(54) **Title:** RARE EARTH ORE PROCESSING METHODS BY ACID MIXING, SULPHATING AND DECOMPOSING
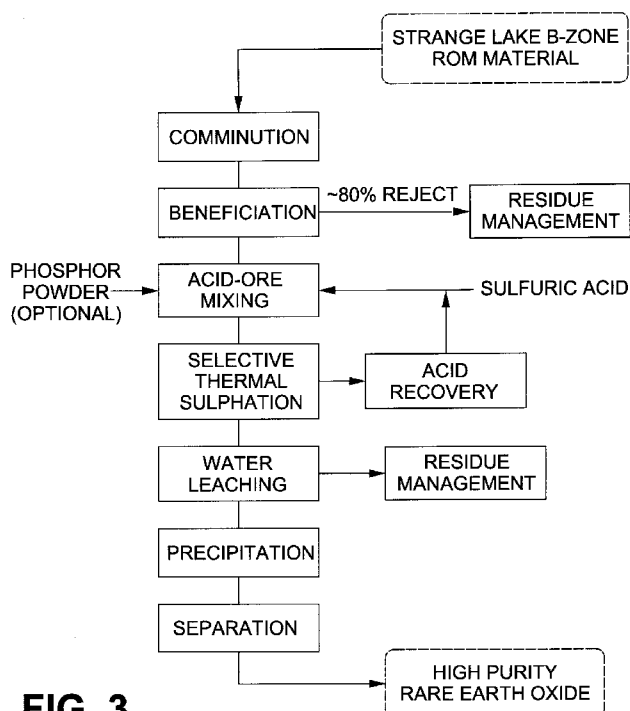
FIG. 3

(57) **Abstract:** Described is a process for the selective extraction of rare earth elements from an ore or mineral concentrate material containing one or more gangue-derived elements, such as, iron, aluminum, zirconium and niobium. The process comprises the steps of (i) preparing a mineral concentrate using one or more beneficiation methods to reduce the amount of ore processed and economically maximize the recovery of rare earth elements; ii) mixing concentrated sulphuric acid in super-stoichiometric amount to the mineral concentrate to produce a homogenous agglomerate or powder mixture; (iii) heating said mixture to promote the sulphation of the rare earth and non-rare earth metals in a first thermal vessel; (iv) increasing the temperature to selectively decompose non-rare earth metal sulphates in a second thermal vessel; (v) leaching the material formed in (iv) to produce a leach solution containing the rare earth elements, that is substantially free of gangue elements.

RARE EARTH ORE PROCESSING METHODS BY ACID MIXING, SULPHATING AND DECOMPOSING

FIELD OF THE INVENTION

[0001]   The present invention relates to processes and methods for the purification of rare earth metals and metal oxides from ore deposits.

BACKGROUND OF THE INVENTION

[0002]   Several rare earth elements (REEs), such as europium, gadolinium, dysprosium, terbium, holmium, erbium, thulium, ytterbium, lutetium, and yttrium or Eu-Lu+Y, are critical inputs to many clean technologies and generally in short supply. REEs are found around the world in varying concentrations in mineral deposits (for example, as fluorocarbonates, phosphates, or silicates) and often in association with various undesirable metals such as iron, aluminum, zirconium and niobium that require complex and uneconomical processing methods. Rare earth minerals can sometimes be substantially separated from associated gangue minerals to a degree sufficient to produce a mineral concentrate that is suitable for processing by methods well known by the industry, such as acid or caustic attacks. With state of the art processing methods, however, not all deposits are amenable to sufficient pre-concentration and separation of rare earth metals from gangue metals to enable economical extraction of rare earth metals. Separation of gangue metals from the rare earths is a major challenge for many types of rare earth bearing mineral deposits and is required for economic viability.

[0003]   Indeed it is appreciated in the mining industry that each rare earth deposit is unique and consists of different ore bodies, with many different elements in varying proportions. Accordingly, processes suitable for separating elements of value from gangue elements have been customized to one degree or another for each ore deposit based on the initial characterization of the ore deposit with an emphasis on a few core elements of interest from an industrial standpoint.

[0004]   The deportment of gangue metals to solution following acid or caustic attack, especially iron (Fe) and aluminum (Al), is a major driver for the cost and complexity of any hydrometallurgical process. If present, removal of Fe and other non-REE

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impurities from pregnant leach solutions (PLS) requires precipitation steps which frequently result in significant loss of valuable rare earth metals, or highly complex solvent extraction processes to recover the REE product from the impure solution, and can render the process uneconomical.

[0005]   Most rare earth minerals are insoluble in water, but can be rendered soluble for recovery by the addition of sulphuric acid (or alkali) and baking at temperatures up to 300°C, or up to 1000°C in the case of alkali cracking. An alkali cracking stage is normally followed by mineral acid leaching. A substantial portion of the gangue minerals are also converted to soluble sulphates during such state of the art treatment processes.

[0006]   Acid baking or roasting processes for the decomposition of REE ores to obtain REEs have been described wherein concentrated sulphuric acid is mixed with REE ore in 1:1 to 2:1 mass ratios and the mixture is heated within ranges of about 150°C to 600°C (see for example, CN Publication No. 102094116B and CN Publication No. 1173050C). These processes, as described, focus on the extent of the decomposition of REE ores following acid roasting, for example, by determining the REE content in leachates obtained by an aqueous leaching process applied to acid roasted ore material (calcine). These references do not describe or provide the details about the composition of the REE ores, nor are further purification steps described for separating industrially useable REEs from undesirable non-REE gangue materials, once the ore materials they originated from have been decomposed.

[0007]   CN Publication No. 102912117B describes a system and provides at a high level, a continuous acid roasting process for the decomposition of REE ore powder and iron powder ore. Given the focus of this reference on describing the configuration of the industrial system for decomposing REE ores and recycling heat and sulphuric acid, the acid roasting process supported by the system is not disclosed in any detail and no information is provided about the composition of the REE ore which may be processed by the system and process.

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[0008] As described in CN Publication No. 102912117B, REE ore may be mixed with sulphuric acid and heated to 300°C until a dried calcine is obtained comprising soluble rare earth ore sulphates. This material is then continuously and gradually heated to 800°C to complete the roasting decomposition which entails the decomposition of

5   sulphuric acid and ferric pyrophosphate, to facilitate removing iron, phosphorus, thorium and other impurities (not specifically elaborated on), enhance the decomposition of rare earth ore and improve the recovery of REEs. Following the higher temperature calcination, a dissolution step is applied to the decomposed roasted material to facilitate further processing.

10 [0009] In International Patent Application No. PCT/BR2013/000148 a process for purifying heavy REEs (HREEs) from ore is described wherein sub-stoichiometric amounts of sulphuric acid are used to obtain sulphates of iron and/or aluminum from partially processed ore materials and then submitting the mixture to temperatures of between 620°C and 750°C which triggers the sulphation of HREEs at the same time as

15 iron and aluminum sulphates are decomposed. The process is demonstrated using ore samples containing high levels of iron and very low levels of dysprosium, europium, erbium, holmium and lutetium. It is contemplated for the exploitation of low grade rare earth ores not amenable to conventional concentrating processes and acid baking techniques, due to the requirement for high amounts of acid and the resulting leachates

20 containing too many impurities which would require costly removal processes.

[0010] In International Patent Application No. PCT/AU2002/00538, a process for obtaining rutile (titanium oxide) from ilmenite is described using an acid bake process with sulphuric acid, wherein the roasting temperature is maintained below 650°C, followed by magnetic separation of the rutile together with iron. At temperatures above

25 640°C (e.g. 700°C), rutile crystallization led to lower yields of rutile in the magnetic fraction of leachates. In this process the primary impurity of concern is the presence of chromium which can interfere with the use of rutile in titania pigments.

[0011] Processes for the dissolution of elements into leachates following acid baking at 300°C (and in one instance at 500°C) are described in International Patent

30 Application No. PCT/EP2012/050188, with particular emphasis on the quantitative

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dissolution of niobium and/or tantalum, uranium and cerium, as specifically disclosed in the examples of the application, but not other light REEs (LREEs) or HREEs. Other elements which can apparently be dissolved into leachates derived from the acid bake calcine include iron, aluminum, thorium, manganese, and titanium. The dissolution process relies on the presence of iron in a ferric state at concentrations of at least 50 g/L and higher, up to about 120 g/L. This concentration of iron allows the Nb and Ta sulphates to remain in solution at restricted free acidity which would otherwise hydrolyze the sulphates.

[0012]   For the acid baking step, mass ratios of sulphuric acid to dry ore materials are described as ranging from 100 kg acid/t of dry ore material to 3000 kg acid/t of dry ore material. Upstream of roasting, the pre-treatment of ore is contemplated to physically concentrate or enrich the ore materials subjected to acid baking. For example, the process is described as being carried out on material exhibiting a particle size of less than 700 microns and advantageously less than 400 microns.

[0013]   The effective separation of REEs from one another and from gangue elements following acid roasting may be enhanced by using and combining various purification steps as described in CN 101012499 (such as ultrasonic extraction in combination with electrochemical oxidation and chemical treatments). The purification step protocols disclosed in this reference have been described as effective for the purification of cerium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium and yttrium oxides, but are numerous and cumbersome from an industrial applicability standpoint.

[0014]   Processes for the efficient and effective purification of a wide selection of REEs from different ore deposit sources using simple and economical processes continue to be required. More particularly, such processes are required for high HREE deposits as demand for HREEs grows for their application in permanent magnets used in an array of green, medical imaging and defense technologies.

[0015]   There also remains a need to improve state of the art acid baking and leaching processes for extracting a full range of LREEs and HREEs from different ore sources

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which are economical, efficient and which can reduce the environmental impact of industrial ore processing, by reducing the amount of acid used and recycling acid lost due to evaporation, or the generation of sulphur containing off gases arising as by-products of acid baking processes.

SUMMARY OF THE INVENTION

5   [0016] The present invention relates generally to processes and methods for selectively recovering rare earth metals from ore or mineral concentrates such as, but not limited to, those containing rare earth oxides, silicate, carbonate, fluorcorbonate, fluoride, or phosphate minerals. It is an object of the present disclosure to provide processes and methods suitable for the effective and economic purification of REE
10   ores, or mineral concentrates and more particularly from deposits rich in heavy rare earth elements (europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium), containing one or more of iron, aluminum, thorium, and which may also include one or more of scandium, and the light rare earth elements (lanthanum, cerium, praseodymium, neodymium, and samarium).

15   [0017] The processes and methods disclosed herein represent four stages of processing including a first stage comprising the beneficiation of ore to prepare a mineral concentrate (i.e. concentrated and/or enriched in REEs), a second stage comprising acid-ore (concentrate) mixing to substantial homogeneity and heating to sulphate the REEs and gangue elements in the mineral concentrate, a third stage
20   comprising the selective decomposition of gangue element sulphates at high temperatures into insoluble gangue element compounds; and a fourth stage to separate soluble REE compounds from insoluble gangue element compounds, comprising a leaching step and further downstream processing to extract REE oxides with a high recovery rate from the mineral concentrate with substantially reduced gangue element
25   impurities.

[0018] According to one aspect, there is provided a process for purifying REEs from an ore also comprising gangue elements, comprising the steps of: (i) preparing a mineral concentrate from ore material containing REEs and gangue elements; ii)

combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate to produce a homogeneous agglomerate or powder mixture; iii) heating the homogeneous agglomerate or powder mixture to temperatures between about 150°C and about 330°C to sulphate the REEs and gangue elements and produce a

5   first calcine; iv) heating the first calcine to temperatures between about 400°C to about 800°C to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially

10   free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

[0019]   In one embodiment the ore material comprises a mixture of LREEs, HREEs and one or more gangue elements selected from the group of iron, aluminum, niobium and zirconium.

15   [0020]   In another embodiment, the ore material is derived from a silicate, monazite, or bastnaesite deposit.

[0021]   In yet another embodiment the mineral concentrate is prepared by beneficiation of the ore material by one or more physical methods selected from sensor based sorting, flotation, magnetic separation, and gravity separation.

20   [0022]   In a further embodiment the concentrated sulphuric acid and the mineral concentrate are combined and mixed in a manner so as to obtain and maintain a granular mixture consistency throughout mixing

[0023]   In still a further embodiment the concentrated sulphuric acid is combined and mixed in batches or a stage-wise manner with the mineral concentrate.

25   [0024]   In one embodiment the step of combining and mixing the concentrated sulphuric acid and the mineral concentrate is done in whole or in part concurrently with the step of heating the homogeneous agglomerate or powder mixture to sulphate REEs and gangue elements to produce the first calcine.

[0025]   In another embodiment the homogeneous agglomerate or powder mixture is produced by adding a recycled amount of first calcine during mixing of the concentrated sulphuric acid and the mineral concentrate.

[0026]   In a further embodiment, the step of combining and mixing the concentrated sulphuric acid and the mineral concentrate is done in a high sheer mixer, pug mill, paddle mixer, ribbon mixer, or rotary drum mixer.

[0027]   In a related embodiment, the homogeneous agglomerate or powder mixture has a substantially uniform pellet diameter or particle size, produced in whole or in part by applying a pelletizing mixing action and particle removal method during mixing of the concentrated acid and mineral concentrate.

[0028]   In a further related embodiment the homogenous agglomerate or powder mixture has a substantially uniform particle size, produced in whole or in part by one or more cycles of grinding and screening.

[0029]   In one embodiment the homogenous agglomerate or powder mixture is heated to between about 150°C and about 330°C for about 15 to about 240 minutes.

[0030]   In a related embodiment, the homogenous agglomerate or powder mixture is continuously fed into a first thermal vessel for heating to produce the first calcine.

[0031]   In another embodiment the first calcine is heated to between about 400°C to about 800°C for about 15 to about 240 minutes.

[0032]   In a related embodiment, the first calcine is continuously fed from the first thermal vessel into a second thermal vessel for heating to produce the second calcine.

[0033]   In a further embodiment, concentrated sulphuric acid is produced or recovered from the gas stream and recycled to produce the homogeneous agglomerate or powder mixture.

[0034]   In yet another embodiment the leaching of the second calcine is done with dilute acid or water.

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[0035] In still another embodiment the sulphated REEs in the leachate solution are recovered out of solution as REE solids by pH adjustment, precipitation reactions and/or solvent extraction methods.

[0036] According to another aspect there is provided a process for purifying REEs from an ore also comprising gangue elements, comprising the steps of: (i) preparing a mineral concentrate from ore material containing REEs and gangue elements; ii) combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate in a manner so as to obtain and maintain a granular mixture consistency throughout mixing to produce a homogeneous agglomerate or powder mixture; iii) heating the homogeneous agglomerate or powder mixture to temperatures between about 150°C and about 330°C to sulphate the REEs and gangue elements and produce a first calcine; iv) heating the first calcine to temperatures between about 400°C to about 800°C to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

[0037] According to yet another aspect there is provided a process for purifying REEs from an ore also comprising gangue elements, comprising the steps of: (i) preparing a mineral concentrate from ore material containing REEs and gangue elements, using a combination of sensor-based sorting and flotation; ii) combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate in a manner so as to obtain and maintain a granular mixture consistency throughout mixing to produce a homogeneous agglomerate or powder mixture; iii) heating the homogeneous agglomerate or powder mixture to temperatures between about 200°C and about 300°C for one to two hours to sulphate the REEs and gangue elements and produce a first calcine; iv) heating the first calcine to temperatures between about 600°C to about 700°C for one to two hours to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and

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v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

[0038]   According to a related aspect there is provided a process for producing a homogeneous agglomerate or powder mixture of concentrated sulphuric acid and mineral concentrate containing REEs and gangue elements, comprising the step of combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to a mineral concentrate in a manner so as to obtain and maintain a granular mixture consistency throughout mixing to produce a homogeneous agglomerate or powder mixture.

[0039]   In one embodiment the concentrated sulphuric acid is combined and mixed in batches or a stage-wise manner with the mineral concentrate.

[0040]   In another embodiment the concentrated sulphuric acid is combined and mixed with the mineral concentrate in dosage amounts each ranging from about 200 kg to about 900 kg of acid per tonne of mineral concentrate until the super-stoichiometric amount of concentrated sulphuric acid has been combined and mixed with the mineral concentrate.

[0041]   In a further embodiment the super-stoichiometric amount of acid is about 800 kg to 1500 kg of acid per tonne of mineral concentrate.

[0042]   In yet another embodiment the homogeneous agglomerate or powder mixture is produced by adding an amount of calcine during mixing of the concentrated sulphuric acid and the mineral concentrate.

[0043]   In yet a further embodiment the mixing of concentrated sulphuric acid and mineral concentrate is carried out at temperatures ranging from about 150°C to about 330°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0044] These and other features of the invention will become more apparent in the following detailed description in which reference is made to the appended drawings.

[0045] **Figures 1:** is a schematic representation of an X-ray sensor based sorting system for the separation of ore material into fractions that are high and low in REE content. Sensor systems other than X-ray may be effective on other ores.

[0046] **Figures 2:** is a graphical representation of the data of Table 1, namely a comparison of the extraction of gangue metal elements using a two-step selective thermal sulphation process (represented by the circular data points plot) versus a non-selective single step acid bake process (represented by the triangular data points plot).

[0047] **Figure 3:** Block flow diagram of an exemplary process for purifying REEs from gangue elements staring with ore materials from Strange Lake Deposit (Zone B) in Quebec, Canada containing one of the largest rare earth, yttrium and zirconium deposits in the world. The Strange Lake Deposit has a HREO:TREO ratio of 50% in the enriched zone.

[0048] **Figure 4:** Graphical representation of the effect of ore material grind size on flotation recovery of REE in mineral concentrate. The data was generated using a Flotinor 1682 Collector (and reagent scheme).

[0049] **Figure 5:** Graphical representation of Mass Pull versus REE recovery using a Flotinor 1682 reagent scheme, comprising a sodium silicate depressant and citric/oxalic acid modifiers.

[0050] **Figure 6:** Effect of acid dosage on the consistency of concentrated sulphuric acid/mineral concentrate mixtures. At single stage acid dosages above 625 kg/T the consistency of the resulting mixtures becomes increasingly sticky and paste-like.

[0051] **Figure 7:** Formation of agglomerates using a multi-stage acid addition (A) and recycled calcine (B) methods and low intensity acid mixing. The recycled calcine method reduces stickiness and is therefore beneficial to the process.

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[0052]   **Figure 8:** Effect of mineral concentrate (particle) grind size on sulphated element recovery, including REEs (including Y) (diamond data points plot), iron, zirconium and niobium (triangular data points plot), after thermal sulphation under the following conditions: 300°C, 3 hour bake time, 600kg H2SO4/t ore, and followed by a 1 h leach at 22°C. The lower plot with square data points depicts the recovery of iron and the upper plot of square data points depicts zirconium recovery.

[0053]   **Figure 9:** An exemplary kiln configuration for carrying out a thermal sulphation protocol according to the disclosure.

[0054]   **Figure 10:** An elemental breakdown of the effect of mineral concentrate (particle) grind size on sulphated element recovery, following single stage, low temperature sulphation under the following conditions: 300°C, 3 hour bake time, 600kg H2SO4/t ore, and followed by a 1 h leach at 22°C. The particle sizes in the legend from top to bottom correspond to the order of bar groupings from left to right.

[0055]   **Figure 11:** Exemplary Dy recovery following single stage, low temperature sulphation at different concentrated sulphuric acid (kg) /mineral concentrate (T) ratios, temperatures and heating times (A: 600kg/T; B: 750 kg/T; C: 1200 kg/T; D: 1500 kg/T).

[0056]   **Figure 12:** Exemplary HREE recovery following single stage, low temperature sulphation at different concentrated sulphuric acid (kg) /mineral concentrate (T) ratios, temperatures and heating times (A: 600kg/T; B: 750 kg/T; C: 1200 kg/T; D: 1500 kg/T).

[0057]   **Figure 13:** Exemplary TREE recovery following single stage, low temperature sulphation at different concentrated sulphuric acid (kg) /mineral concentrate (T) ratios, temperatures and heating times (A: 600kg/T; B: 750 kg/T; C: 1200 kg/T; D: 1500 kg/T).

[0058]   **Figure 14:** High strength acid recovery at condensation temperatures between 180°C and 220°C. The results with respect to the bake (BK) samples listed in the

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legend from top to bottom correspond to the order of bars in each bar grouping from left to right.

[0059] **Figure 15:** An exemplary acid recovery gas condenser train configuration.

[0060] **Figure 16:** Schematic representation of an industrial system flow implementation for a two-step sulphation and selective sulphate decomposition process including multi-stage acid/mineral concentrate mixing. Also shown is a two stage acid bake with a first stage carried out at 280°C and a second stage carried out at 300°C. The abbreviations "LT" and "HT" stand for low temperature and high temperature, respectively.

[0061] **Figure 17:** Schematic representation of an industrial system flow implementation of a calcine recycling protocol in acid/mineral concentrate mixing.

DETAILED DESCRIPTION OF THE INVENTION

[0062] The present disclosure relates to processes and methods for separating REEs from gangue metals and other materials found in rare earth ores to provide substantially pure REEs which can be further processed for industrial application. There is provided a selective thermal sulphation process for separating REEs from gangue minerals and non-REE metals that can be applied to ore sources rich in REEs, but with varying compositions of LREEs, HREEs and gangue-related elements. An overall process and method flow diagram is provided at Figure 3. The process can also be applied for recovering REEs from secondary sources such as phosphor powder from fluorescent lighting devices.

[0063] Unlike state of the art processes, the processes and methods disclosed have been demonstrated to facilitate industrially significant recoveries for most REEs relative to their original ore source, such as Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu and Y.

[0064] An exemplary source of REEs is the ore, and concentrates derived therefrom, of the Strange Lake Deposit, Quebec, Canada. This is one of the largest and richest

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sources of rare earths (including yttrium) and zirconium in the world. The Strange Lake Deposit has a HREO content of 50% of the TREO in the enriched zone and a HREO content of about 35-38% in the granite domain of the deposit.

Definitions

[0065] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0066] The use of the word "a" or "an" when used herein in conjunction with the term "comprising" may mean "one," but it is also consistent with the meaning of "one or more," "at least one" and "one or more than one."

[0067] As used herein, the terms "comprising," "having," "including" and "containing," and grammatical variations thereof, are inclusive or open-ended and do not exclude additional, unrecited elements and/or method steps. The term "consisting essentially of" when used herein in connection with an apparatus, system, use or method, denotes that additional elements and/or method steps may be present, but that these additions do not materially affect the manner in which the recited apparatus, system, method or use functions. The term "consisting of" when used herein in connection with an apparatus, system, use or method, excludes the presence of additional elements and/or method steps. An apparatus, system, use or method described herein as comprising certain elements and/or steps may also, in certain embodiments consist essentially of those elements and/or steps, and in other embodiments consist of those elements and/or steps, whether or not these embodiments are specifically referred to.

[0068] As used herein, the term "about" refers to as much as a +/-10% variation from a given value. It is to be understood that such a variation is always included in any given value provided herein, whether or not it is specifically referred to.

[0069] The terms, "rare earths," "rare earth element(s)," "rare earth metal(s)," and abbreviation "REE(s)" as used herein refer to the industrially relevant elements of the periodic table including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium

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(Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), as well as scandium (Sc) and yttrium (Y). Promethium (Pm) is not included as it has no stable isotopes and does not exist in nature.

[0070]   These elements may be further referred to as "light" and "heavy" REEs to further delineate subsets of REEs based on their respective unpaired and paired electron configurations, namely (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd) as light rare earth elements ("LREE(s)") and terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), as heavy rare earth elements ("HREE(s)"). Yttrium is regarded as a HREE due to the similarity of its similar chemical properties, whereas scandium's properties are not similar enough to any LREEs or HREEs to be classified as such.

[0071]   It is understood that reference to REEs, LREEs and HREEs as used herein, may be a reference to the element, oxide or other compound forms of these elements as they may be found in ores, in the solid product of purification processes, or in a solubilized state in solution. To refer to the oxide forms of rare earth elements, the term "REO(s)" may be used interchangeably with REE(s) and reference to light and heavy REOs may be made as "LREO(s)" and "HREO(s)", and used interchangeably with LREE(s) and HREE(s), respectively.

[0072]   As used herein, the terms "TREE(s)" and "TREO(s)" may be interchangeably used to refer to the total REE/REO present in a given sample, batch or load of ore material, mineral concentrate, or recovered amount of solid material from one or more ore processing steps.

[0073]   The terms "ore(s)", or "ore material(s)" as used herein refer to (mining output) material as received from a mine before beneficiation, chemical treatment, or other selection and purification procedures applied to change the relative content of, composition, or chemical form of REEs in a given ore sample, batch or load received from the mine. Ore or mining output material may also include material which has been

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subjected to physical processing to break it up into smaller pieces for ease of management in transportation and for application in beneficiation procedures, such as, but not limited to, flotation, and/or (X-ray) sensor based separation techniques.

[0074] The term "partially processed ore material(s)" refer to ore material(s) which have been partially processed, but wherein substantially all or a portion of REEs are in their naturally occurring or original mineralized states, whether or not such mineralized states include matrix integration or composite structures with gangue and/or other non-REE elements. Partially processed ore materials can arise following physical processing (e.g. crushing or grinding into small particulate matter or powder), beneficiation to concentrate and/or enrich the REE content in the ore material (e.g. using recycled materials). In other words, partially processed ore materials have not undergone any substantial chemical processing to chemically modify, solubilize, extract or precipitate REEs. Partially processed ore material may have undergone limited chemical treatments as part of flotation methods to chemically alter ore mineral surfaces in order to facilitate the physical separation of desirable REEs minerals from undesirable sands/silica, silicate gangue or non-REE silicates.

[0075] As used herein, the term "beneficiation" refers to processes which can result in partially processed ore(s) where the content of REEs is concentrated or enriched. Concentration or enrichment can be achieved by the application of one or more processes or procedures which effect the physical separation of undesirable materials, such as sands, which are loosely associated with mineral matrices of REEs or REE composite structures in ore materials. The concentration of REE content may be achieved by magnetic separation, sensor based systems which scan pieces of ore for REE content and which can selectively sort and separate low REE content pieces from high REE content pieces (e.g. sensor based systems), and the removal of sands and non-REE silicates or other gangue minerals (e.g. through flotation procedures). REE content in a given sample of partially processed ore material can be further enriched by the addition of partially processed ore material from distinct sources, or the addition of recycled materials with REE content.

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[0076] The term "mineral concentrate" refers to partially processed ore material that is the product of one or more beneficiation processes that has resulted in the removal of gangue material, such as iron, aluminum and silicon compounds. It is characterized by having a higher concentration of desirable REEs compared to the ore or mine output

5   material it was derived from, and the material which is subjected to chemical processing, for example, acid baking with concentrated sulphuric acid. An exemplary mineral concentrate, derived from ore material of the Strange Lake Deposit, may contain a mixture of natural granite and pegmatite minerals containing rare earth minerals, zirconium, niobium, iron, calcium, trace beryllium and naturally occurring

10   radiological trace elements.

[0077] The term "gangue" as used herein refers to minerals, non-REE metal and non-metal elements, found in ore materials, which are targeted for separation from REEs. Gangue minerals containing elements such as silicon (Si), iron (Fe), aluminum (Al), zirconium (Zr), niobium (Nb), and titanium (Ti) may form matrices in which desirable

15   REE minerals are embedded, or otherwise form mineral composites with REEs which require chemical or physical processing methods to separate them from REEs.

[0078] The term "calcine" as used herein refers to the product of chemically processed mineral concentrate which has been subjected to thermally assisted acid treatment or thermally assisted sulphate decomposition process.

20   [0079] The terms "acid bake," "acid roast", "acid baking" and "acid roasting" refer to a thermal sulphation process consisting of heating a mixture of sulphuric acid and ore (or concentrate). This process may be conducted at temperatures ranging typically between about 150°C up to about 400°C. By contrast thermal sulphate decomposition processes are typically conducted at temperatures above about 500°C to about 800°C.

25   [0080] The terms "leaching" and "leachate" as used herein refer, respectively, to the process and product of dissolving desirable (REE) minerals into a liquid solution by using a lixiviant reagent of mixture of reagents such as water or a diluted/mild acid (typically, sulphuric acid or hydrochloric acid). Leachates contain solubilized REEs which have been, or can be separated from solubilized gangue elements and other

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impurities by way of selective decomposition and precipitation processes, such as, but not limited to selective sulphate decomposition. The selective leaching of soluble REEs (sulphates) into aqueous solution results in a "pregnant leach solution" abbreviated as "PLS" and is a liquor consisting of water soluble salts of desirable REEs. Pregnant

5   leach solutions according to the disclosure will typically have low free acid content and have an acidic pH of about 2.

[0081] The term "extract," "extracted," or "extraction" is used herein with reference to the process of recovering elements in one or more solid forms, such as metal oxides from a liquid or solid mixture. The recovered elements may be in solution or solid

10   materials that have been separated out from liquid suspensions, precipitated from liquid solutions, or mechanically separated from other solids.

[0082] The term "residue" refers to the solid faction of an ore processing or purification step that contains predominantly undesirable non-REE minerals or salts and is not processed in subsequent or downstream steps to obtain purified, concentrated

15   or enriched REE materials in solid (e.g. oxide) or liquid form (e.g. sulphated in solution).

[0083] The term "agglomerate" refers to the association of smaller (primary) particles to form larger particles in which the identity of the smaller particles is still detectable. The nature of agglomerates is affected by the chemical nature and interaction between

20   primary particles, as well as the mixing time, speed and intensity of a given process or method to produce them. A homogenous agglomerate as used herein denotes a mixture having a consistency amenable for being processed and/or fed continuously through different mineral concentrate processing stages. For example, a homogeneous agglomerate denotes an acid/mineral concentrate mixture that is sufficiently dry so as

25   not to be sticky or cause blockages in equipment it is fed through.

[0084] The terms "homogeneous" and "homogeneity" refer to the uniform composition and distribution of components in a mixture, such as the mixtures of concentrated sulphuric acid and mineral concentrate obtained according to the processes and methods disclosed herein. A mixture of acid and mineral concentrate can

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be wet and sticky and difficult to handle through process equipment. Under these circumstances, recycling calcine can be very beneficial and permit the relatively trouble-free processing of what would otherwise be material difficult to process. Achieving homogenous mixing of acid and mineral concentrate ensures complete

5   chemical processing of the mineral concentrate during heat-assisted sulphation and selective desulphation processing. Optimal proportions of acid and mineral concentrate that have been uniformly mixed to a state of homogeneity according to the present disclosure, are evidenced by the formation of sufficiently dry agglomerates or powders that can be fed continuously and at a controllable rate into one or more thermal vessels

10   without sticking or blockage, and with minimal operational disruptions, stoppages or adjustments to maintain the desired feed rate of material through different processing stages.

[0085]   It is contemplated that any embodiment discussed herein can be implemented with respect to any disclosed process, method, use, apparatus or system. For example,

15   an apparatus and/or system provided herein can be applied to carry out the disclosed processes and methods and said processes and methods can delimit the operational parameters and functional characteristics of a disclosed apparatus or system.

Beneficiation of Ore Material

Ore Sorting

20   [0086]   In one embodiment of the disclosed processes and methods, ore materials are crushed into smaller pieces (comminution) and sorted to reject coarse-grained quartz, feldspar and other pieces of ore material which are relatively low in REE content. Sorting may be done using X-ray sensor-based systems (e.g. the Tomra Com Tertiary XRT production scale sorting system) to remove low REE grade rock from higher

25   grade REE rock. The sorting protocol may include an initial screening to create more homogeneously sized fractions of ore material for sorting. In one embodiment fractions of ore material for sorting comprise rock pieces of about 10-20 mm or 20-40 mm. In another embodiment, ore materials may be fractionated into pieces of ore of about 12 to 20 mm, 10 to 19 mm or 19-38 mm in size. It will be understood by one

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skilled in the art that such ore fractions may also contain fines of ore material (i.e. particles less than 10 mm in size) arising from the crushing process.

[0087] With reference to Figure 1, an exemplary sorting protocol and apparatus comprises a belt feeding system 1 which facilitates the presentation of non-uniform feed, and particle stabilization before scanning with X-ray sensor transmission technology that recognizes and separates ore materials based on specific atomic density. A broad-band electrical x-ray source 3 is applied to the material to be sorted as it is carried on a moving belt. The sensor system including a X-ray camera 2 sits below the belt in the exemplary configuration shown in Figure 1, and produces a digital image of the material being sorted using two different energy bands. Depending on the thickness and density of the ore materials scanned, an image transformation of the density images of the two bands allows pixel classification relative to a reference atomic density. Scanned ore materials are either ejected or accepted as material streams A or B in a separation chamber 4, respectively. The material that is ejected may be either waste material (barren rock) or ore material targeted for further processing (e.g. beneficiation).

[0088] The results of sorting tests using two different ore fraction sizes is presented below in Table A:

Summary : fraction 10-20mm +fines

XRT sorter setting	95%	90%	90% LS	85%	80%	75%
mass pull	83.75%	78.11%	76.18%	70.29%	63.96%	56.10%
Total LREE	91.81%	88.13%	87.83%	83.04%	80.38%	72.90%
Total HREE	93.10%	89.08%	88.21%	84.49%	80.80%	76.59%
Total HREE +Y	93.13%	89.28%	89.31%	84.72%	81.75%	76.50%
Total REE +Y	92.52%	88.73%	88.57%	83.90%	81.07%	74.76%

Summary : fraction 19-38 mm +fines

XRT sorter setting	95%	90%	90% LS	85%	80%	75%
mass pull	85.62%	78.93%	76.81%	71.33%	64.49%	57.26%
Total LREE	92.90%	87.39%	86.22%	82.67%	76.84%	73.83%
Total HREE	92.98%	89.20%	87.34%	85.02%	78.70%	76.17%
Total HREE +Y	93.75%	90.29%	88.61%	85.74%	78.45%	76.76%
Total REE +Y	93.31%	88.87%	87.42%	84.23%	77.62%	75.29%

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[0089]   Such sorting methods allow for the more economical and environmentally sound processing of lower amounts of ore which contain the majority of REEs of interest and value. With reference to Table A, it is apparent that at ore particle sizes of about 10-20 mm and 19-38 mm respectively, a lower percentage XRT sorter setting of 75% reduces the mass pull of material, but increases the proportional amount of REE content in the material retained. The "mass pull" value indicated in Table A denotes the amount of ore material retained following scanning and sorting of an amount of ore material fed into the sorting apparatus system and thus comprises the sorter accept and the fines that bypassed the sorter and were not sorted, i.e., the -10 mm material in the upper portion of the above table and the -19 mm material in the lower portion of the table.

[0090]   It is understood by one skilled in the art that the final amount of material retained for further processing may be the result of multiple rounds of screening and sorting of ore material fractions. For example, a given input of ore material may be separated into fractions categorized as low and high in REE content, respectively. In subsequent sorting cycles, the low REE fraction may be further sorted into fractions categorized as low and barren/waste (in REE content), and the high REE fraction may be further sorted into medium and high REE fractions.

[0091]   Depending on the desired ore processing objectives, ore sorting using such a system may be sufficient to produce ore material which can be ground to a fine particulate consistency to produce a mineral concentrate for chemical treatment (e.g. acid baking). Accordingly, in one embodiment mineral concentrate is produced only by sensor-based sorting.

Flotation

[0092]   In another embodiment, a mineral concentrate is produced by applying a flotation protocol to (pre-sorted) ore materials. This method for separating desirable minerals from gangue minerals exploits the hydrophobic properties of different minerals using surfactants and wetting agents. Undesirable or gangue particles (e.g.

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sands and other silicon compounds) are carried by air bubbles to the surface of a flotation vessel and removed, while desirable REE minerals are wetted and remain in the liquid phase of a mineral/water slurry or vice versa.

[0093]   In a further embodiment, prior to subjecting ore material to a flotation protocol, ore material is ground into fine particulate matter (micron sized particles). In yet another embodiment, ore material is ground to a grind size of 80% passing ("k80") of about 40 μm. Figure 4 demonstrates a relationship between the grind size of ore material and the flotation recovery of REE in the resulting mineral concentrate where the level of recovery decreases as grind size increases..

[0094]   Figure 5 illustrates a relationship between mass pull and REE recovery following flotation where there is approximately a 10% increase in recovery for the indicated REE oxides when the mass pull is approximately doubled. In one embodiment, a 20% mass pull from flotation achieves 80% REE recovery and is used as a source of mineral concentrate in acid baking or a thermal sulphation protocol. In an alternative embodiment a mass pull of 20% to 55% from flotation is used as the source of mineral concentrate in an acid baking or thermal sulphation protocol.

[0095]   In another embodiment one or more beneficiation protocols can be applied to produce a mineral concentrate, such as sensor-based sorting and flotation.

[0096]   The mineral concentrate obtained following ore material beneficiation may require further adjustments to meet transport exemption activity levels for U and Th. In one embodiment flotation recovery is controlled such that the content of U and Th in a mineral (flotation) concentrate is below 10 Bq/g of U and Th combined and below a total calculated activity of 110 Bq/g. These levels are set and prescribed in accordance with the International Atomic Energy Agency/Canadian Nuclear Safety Commission (IAEA/CNSC) exempt activity for transportation and dangerous good (DG) classification purposes. In a related embodiment, the mass pull/recovery can be adjusted by changing flotation reagent dosages, and by dilution with lower REE grade material. An exemplary activity calculation for Strange Lake Mineral Concentrate is provided in Example 3.

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[0097] Prior to processing mineral concentrate to purify REEs, drying will prevent dilution of the concentrated sulphuric acid that is added to the mineral concentrate. Accordingly, in one embodiment beneficiated ore material is dried, as required, to reduce moisture content before being mixed with sulphuric acid. In a related embodiment the mineral concentrate moisture level after drying is less than 1%.

Sulphation of REEs and Other Metal Elements in Mineral Concentrates

[0098] The step of combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to mineral concentrate is conducted in such a way so as to ensure that there is material (i.e. a mixture of acid and mineral concentrate) that can be and is available to be continuously fed into a heated vessel without sticking or creating blockages. Combining and mixing acid and concentrate to obtain and maintain a granular or particulate consistency throughout the mixing process provides for the consistent flowability of material through an industrial processing system (e.g. a plant) for the purification of REEs from mineral concentrate. The amount of acid used is dependent on acid utilization efficiency, while acid/mineral concentrate mixing is integrally linked to acid dosage and the total amount of acid used. Using a super-stoichiometric amount acid to mineral concentrate (having regard to the amount of REEs therein) ensures substantially complete sulphation of REEs, and also accounts for acid usage/consumption by gangue and other elements.

[0099] One or more of the following strategies can be used to produce acid/mineral concentrate mixing conditions which optimizes acid utilization efficiency:

    a) Limitation of sulphuric acid addition (i.e. total acid is delivered in batches or dosage amounts for mixing with concentrate) so as to avoid formation of sticky, paste-like material;

    b) Adjustment of mixing intensity;

    c) Pelletization/agglomeration of the acid and mineral mixture;

    d) Addition of heat during mixing;

    e) Recycling of the heat treated acid and mineral mixture (calcine) to dilute the feed to the heated vessel and reduce the acid:solids ratio so as to maintain the desired mixture consistency; and/or

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f) Batch addition of acid concurrent with the thermal treatment process (for example, portions of the total acid added in advance of multiple and successive thermal treatment (sulphation) cycles so that the acid:solid ratio is maintained at a low enough level throughout the process to maintain a granular or particulate mixture consistency, while allowing sufficient total acid to be added to achieve high recovery of REEs).

Acid/Mineral Concentrate Mixing

[00100] The modulation of concentrated sulphuric acid addition to mineral concentrate at a rate and/or in dosages that provide for a granular or particulate mixture consistency upon mixing can be done in whole or in part by combining acid and concentrate, and optionally calcine, at intervals in between cycles of thermal sulphation or concurrently with thermal sulphation by controlling the rate of addition of acid to concentrate in a heated vessel. Mixture heating can be done in a single or in multiple thermal vessels (in kilns or fluidized bed reactors) to apply the strategies for optimizing acid utilization efficiencies and for optimizing material flowability during acid/concentrate mixing and thermal sulphation of the resulting mixture.

[00101] In one embodiment the dosage of acid combined with concentrate is selected from about 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475, 500, 525, 550, 575, 600, 625, 650, 675, 700, 725, 750, 775, 800, 825, 850, 875 and 900 kg of acid per tonne of mineral concentrate. At higher dosages of acid addition if a slurry of acid and mineral concentrate is initially formed, calcine may be added to obtain the desired granular or particulate consistency upon mixing

[00102] In one embodiment about 600 to 625 kg/t of concentrated sulphuric acid to mineral concentrate is used to produce a homogeneous agglomerate or powder. A homogeneous, agglomerate or powder has a sufficient level of mechanical integrity so that it can be continuously fed into a thermal (sulphation) vessel at a consistent flow rate without blockage or sticking. The effect of acid dosage and mixing on the resulting consistency of an acid/mineral concentrate mixture is illustrated in Figures 6 and 7.

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[00103] The formation of a homogeneous agglomerate in one embodiment is prepared by the stage-wise addition of acid at single dosages ranging between about 220 kg to about 625 kg of acid per tonne of mineral concentrate, with continuous mixing. In another embodiment, acid dosages for stage-wise mixing range between about 200 kg to about 900 kg of acid per tonne of mineral concentrate, Such protocols comprise making successive additions of acid, concurrently with or followed by thermal processing of acid/concentrate mixture after each stage of acid addition until a total of about 800 kg to about 1500 kg of concentrated sulphuric acid per tonne of mineral concentrate have been mixed. Using these and other variations of these protocols as would be appreciated by one skilled in the art, desirable particulate (e.g. agglomerate or powder-like) acid/concentrate mixture properties can be maintained.

[00104] In a further embodiment, the stage-wise mixing of acid and mineral concentrate is done concurrently with acid baking. In a related embodiment, stages of mixing during acid baking include the step of mixture cooling preceding the addition of successive doses of acid to partially sulphated mineral concentrate.

[00105] In yet another embodiment the formation of a homogeneous dry agglomerate or powder that is easy to handle is facilitated and promoted by recycling a portion of sulphated mineral concentrate following acid baking (calcine). Calcine is added into an acid/mineral concentrate mixture and remixed. Use of this protocol may require a larger vessel to achieve target throughputs.

[00106] In another embodiment concentrated sulphuric acid and mineral concentrate are mixed at a low intensity to form a homogeneous agglomerate or powder. In a further embodiment agglomeration is conducted in a concrete or other kind of rotary mixer. In still a further embodiment acid and concentrate are mixed at about 100 rpm.

[00107] In yet another embodiment the grind size of mineral concentrate particles mixed with concentrated sulphuric acid is about 40 μm. Figure 8 illustrates the effect of mineral concentrate (particle) grind size on sulphated element recovery. A more detailed breakdown of element recovery based on grind size is provided in Figure 10.

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[00108] In a further embodiment mixing of acid and mineral concentrate is carried out before feeding the mixture into a thermal sulphation vessel. In an alternative embodiment, mixing of acid and mineral concentrate is carried out in a thermal sulphation vessel. In yet another alternative embodiment, acid and mineral concentrate

5   mixing is carried out before and after feeding the mixture into a thermal sulphation vessel. In all of these embodiments temperature may be controlled to optimize the sulphation of mineral concentrate elements.

[00109] In a related embodiment, thermal sulphation or acid baking of an acid/mineral concentrate mixture is conducted in a rotary kiln, packed bed reactor, fluidized bed

10   reactor, moving fixed bed or grate, or a continuous stirred tank. An exemplary kiln configuration is provided in Figure 9, including a quartz kiln with lifters 10, operatively associated with an electric furnace 11, variable-speed kiln drive 12 and air source 13. Various temperature sensors and controls (14, 15 and 16) are provided for the furnace 14, gas inlet 15 and to track burden temperature 16.

15   *Thermal Sulphation*

[00110] In one embodiment, the acid and mineral mixture may be heated at a sustained temperature of 150°C, 200°C, 250°C, 300°C, or 350°C. Alternatively, in another embodiment, acid baking may be carried out over a variety of temperature ranges, including ranges such as 150°C to less than 400°C, 150°C to 330°C, 200°C to 310°C,

20   250°C to 330°C, 250°C to 300°C, 270°C to 300°C or 280°C to 300°C. At these temperatures, rare earth containing minerals react with the sulphuric acid to form water-soluble REE sulphates. Metals in gangue minerals, including but not limited to iron, aluminum, zirconium and niobium will also form water-soluble sulphates. These sulphates complicate and can render uneconomical the downstream processing of the

25   leach solution if not converted to insoluble compounds. Examples of reactions that can occur when the processes provided and described herein are applied to a silicate-based rare earth metal are presented below for sulphation and sulphate decomposition reactions.

[00111] *Examples of sulphation reactions at 300 °C:*

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Gadolinite Group

$$Y_2Fe_2Be_2Si_2O_{10} + 7H_2SO_4 \rightarrow Y_2(SO_4)_3 + 2BeSO_4 + 1/2Fe_2(SO_4)_3 + 2SiO_2 + 7H_2O + 1/2SO_2 \quad (1)$$

5 Allanite

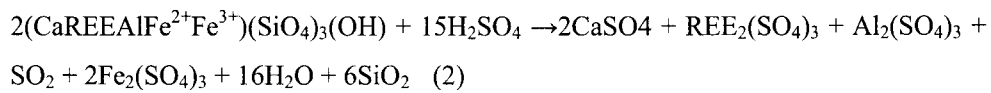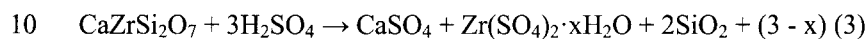$$2(CaREEAlFe^{2+}Fe^{3+})(SiO_4)_3(OH) + 15H_2SO_4 \rightarrow 2CaSO4 + REE_2(SO_4)_3 + Al_2(SO_4)_3 + SO_2 + 2Fe_2(SO_4)_3 + 16H_2O + 6SiO_2 \quad (2)$$

Gittinsite

10 $$CaZrSi_2O_7 + 3H_2SO_4 \rightarrow CaSO_4 + Zr(SO_4)_2 \cdot xH_2O + 2SiO_2 + (3 - x) \quad (3)$$

Zircon

$$ZrSiO_4 + 2H_2SO_4 \rightarrow Zr(SO_4)2 \cdot xH_2O + SiO_2 + (2 - x)H_2O \quad (4)$$

15 Pyrochlore

$$2CaNaNb_2O_6(OH) + 9H_2SO_4 \rightarrow Na_2SO_4 + 2CaSO_4 + 2Nb_2O_2(SO_4)_3 + 10H_2O \quad (5)$$

Hematite

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \quad (6)$$
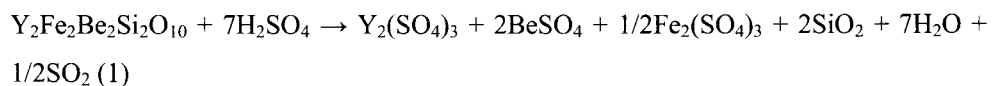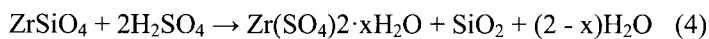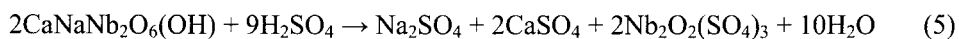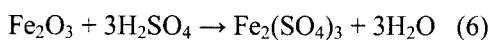
20 **[00112]** The completeness of the sulphation reactions will depend in part on the length of time the acid and mineral concentrate mixture is heated. In one embodiment the acid and mineral concentrate mixture is continuously fed into a first thermal vessel wherein the mixture is heated for a residence time, ranging from 15 to 240 minutes, 30 to 120 minutes or 60 to 90 minutes before the resulting calcine is subjected to a selective

25 thermal sulphate decomposition protocol.

[00113] Typical recoveries for desirable elements using different proportions of acid to mineral concentrate, expressed as kg/t, over time and with increasing temperature are shown in Figures 11 for Dy and Figure 12 for HREEs. Recoveries for other individual REEs, TREEs (as shown in Figure 13) and overall recovery value may be reasonably

30 extrapolated from such known recoveries using accepted calculation and statistical analysis methods known in the art. In this way, one skilled in the art can reasonably

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predict the efficacy of different mixing and heating parameters/conditions as illustrated in Table B, to design appropriate protocols for REE extraction from ore material. In Table B below, "A" stands for acid and "C" stands for concentrate:

	Max Value%	Temperature °C	A/C Kg/T	Time min
Dy	98.0	300	1500	120
HREE	96.3	300	1500	120
TREE	95.1	271	1097	120
Recovered Value	93.7	300	1424	120

5 [00114] In one embodiment, thermal sulphation of mineral concentrate elements is carried out at 300°C, using a total of 1400-1500 kg of concentrated sulphuric acid per tonne of mineral concentrate for 120 minutes.

[00115] In another embodiment, thermal sulphation or acid baking of mineral concentrate elements is carried out at 270°C to less than 300°C, using a total of about 10 1000 kg of concentrate sulphuric acid per tonne of mineral concentrate for 120 minutes to optimize total REE recovery.

[00116] In yet another embodiment thermal sulphation or acid baking is carried out by packing agglomerates of acid/mineral concentrate mixtures into a thermal vessel to reduce the evaporation of acid during heating (e.g. a packed bed reactor).

15 [00117] In a further embodiment, thermal sulphation or acid baking is conducted in a closed thermal vessel to reduce acid loss during the sulphation of mineral concentrate elements. In a related embodiment, the sulphation of mineral concentrate elements may be optimized by controlling the feed rate into and amount of acid/mineral concentrate agglomerate or powder mixture in the thermal vessel, the pressure in the vessel and the 20 atmospheric environment.

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[00118] In another embodiment, the heating rate applied to the acid/mineral concentrate mixture may be varied to optimize the completeness of mineral concentrate element sulphation.
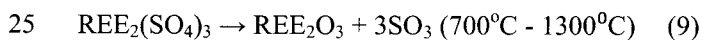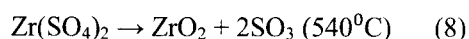
Selective Thermal Decomposition of Gangue (Derived) Element Sulphates

5   [00119] According to the present disclosure the mixture of rare earth sulphates and any gangue-derived, or non-REE metal sulphates present in the calcine product of an acid bake are subjected to a higher temperature heating protocol of at least about 400°C but not more than about 800°C.

[00120] In one embodiment the calcine product resulting from acid baking may be
10   heated at a sustained temperature of 400°C, 450°C, 500°C, 550°C, 600°C, 650°C, 700°C or 750°C. In an alternative embodiment, the calcine product resulting from acid baking may be heated over a variety of temperature ranges, including ranges of 400°C to no more than 800°C, 550°C to 750°C, 600°C to 750°C, 580°C to 680°C, and 650°C to 700°C. The high temperature provides thermodynamically favourable conditions for the
15   preferential decomposition of the gangue metal sulfates, such as those of iron, aluminum, niobium and zirconium, while minimizing the decomposition of REEs. This thermal sulphate decomposition protocol may be carried out in a separate thermal vessel than the lower temperature acid baking protocol.

[00121] *Examples of sulphate decomposition reactions:*
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$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3 \ (550^\circ C) \quad (7)$$

$$Zr(SO_4)_2 \rightarrow ZrO_2 + 2SO_3 \ (540^\circ C) \quad (8)$$

25     $$REE_2(SO_4)_3 \rightarrow REE_2O_3 + 3SO_3 \ (700^\circ C - 1300^\circ C) \quad (9)$$
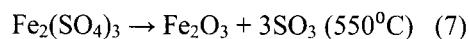
[00122] A comparison of REE and non-REE element recovery data obtained from a two-step selective thermal sulphation protocol and one-step non-selective acid bake protocols, is provided in Table C below (and plotted in Figure 2):

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Elements	Selective Process Extraction	Unselective Process Extraction
	Dot	Triangle
	Extractions, %	
La	87	95
Ce	89	95
Pr	91	95
Nd	91	95
Sm	90	93
Eu	89	90
Gd	90	90
Tb	88	87
Dy	86	85
Ho	84	83
Y	86	87
Er	83	82
Tm	81	81
Yb	80	81
Lu	79	81
Th	80	81
U	78	89
Zr	18	79
Nb	9	93
Fe	10	38
Al	10	11
Si	0	3
Mg	97	96
Ca	24	30
Na	18	11
K	11	5
Ti	11	69
P	28	31
Mn	48	48

[00123] The step of decomposing non-REE metal sulphates to insoluble compounds (for example oxides as in reaction (7) and (8)), while limiting the decomposition of rare

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earth sulphates, generates a second calcine material that when water leached will produce a PLS with improved purity and reduced processing costs when compared with state-of-the art standard acid baking methods.

[00124] In one embodiment, the first calcine product of thermal sulphation is removed from the thermal sulphation vessel and fed into a selective thermal sulphate decomposition vessel to produce a second calcine product. In a related embodiment, the first calcine product is pre-heated prior to being fed into the selective thermal sulphate decomposition vessel.

[00125] Coarser agglomerates containing non-REE sulphates (such as iron, zirconium, niobium and aluminum sulphates) exhibit less complete decomposition and have a grey colouring when crushed. Finer agglomerates of a similar composition have a reddish colour when crushed that is indicative of more complete selective iron sulphate decomposition. Accordingly, in another embodiment, the first calcine product is mechanically processed prior to or as it is fed into the selective thermal sulphate decomposition vessel to optimize agglomerate size and to maximize the completeness of selective thermal sulphate decomposition. In a related embodiment the optimized agglomerate size is between 3 to 10 mm.

[00126] In yet another embodiment, selective thermal sulphate decomposition is controlled to achieve maximum Fe sulphate decomposition with less than 5% REE sulphate decomposition. In a further embodiment, selective thermal sulphate decomposition is controlled to achieve 80%-90% Fe sulphate decomposition.

Heat and Acid Recovery

[00127] Processing costs may also be reduced by incorporating heat recovery and acid recovery methods as part of the processes disclosed herein.

[00128] In one embodiment heat from the selective thermal decomposition of non-REE sulphates may be captured and recycled to preheat the calcine product of acid baking as it is fed from the acid baking thermal vessel to a another thermal vessel to carry out the selective thermal decomposition of gangue element sulphates.

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[00129] The design of effective acid recovery methods requires consideration of the different processing steps in which acid losses occur. Super-stoichiometric quantities of sulphuric acid are usually required to achieve economic recoveries of rare earths in the typical acid attack process. Excess acid reports to off-gas during acid/mineral concentrate mixing, low temperature acid baking and high temperature selective sulphate decomposition. Residual acid is carried into aqueous solution during leaching, and acid is also consumed by gangue metals. Free acid lost to off-gas and aqueous solutions or reacted with gangue metals is typically neutralized with an alkaline chemical (such as lime or caustic reagents) and replaced with fresh acid. Acid replacement and neutralization represent significant costs and generates waste products that must be disposed of. By offering a method for recycling of excess acid and recovering acid consumed by gangue metals, the processes provided herein reduce acid requirements and the environmental footprint of rare earth processing.

[00130] *Acid Recovery Reactions*:

$$H_2SO_{4\,(liquid)} \rightarrow H_2SO_{4(vapour)} \quad (280\text{-}338°C) \quad (10)$$

$$H_2SO_{4\,(vapour)} \rightarrow SO_{3\,(gas)} + H_2O_{\,(gas)} \quad (>338°C \quad (11)$$

$$H_2SO_{4\,(vapour)} \rightarrow H_2SO_{4\,(liquid)} \text{(cooling to } 220°C) \quad (12)$$

$$SO_{3\,(gas)} + H_2O_{\,(gas)} \rightarrow H_2SO_{4\,(liquid)} \text{(cooling to } 220°C) \quad (13)$$
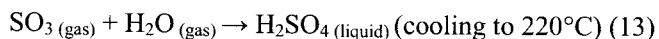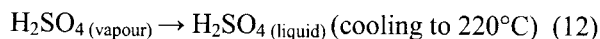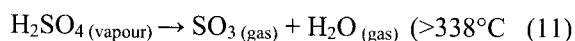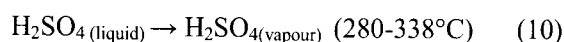
[00131] The present disclosure provides a method for the recovery of excess acid that is normally lost to the gas phase and PLS and is normally neutralized with alkaline chemicals. The majority of acid that is not used in the sulphation reactions, and SO_3 that is liberated according to reactions (7) and (8) is recovered according to the reactions (10) to (13). The SO_3 recovered can also be used together with concentrated sulphuric acid, or on its own as a sulphation agent. Use of SO_3 in the sulphation stage of the process for REE extraction from mineral concentrate could be carried out using a fluidized bed system configuration.

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[00132] In one embodiment high strength acid is recovered at condensation temperatures of 180°C to 220°C by passing off-gas through a primary condenser (see Figure 14). Figure 14 (including a bar graph and table) presents data tracing the presence of sulphur and acid in various process fractions, based on baking acid/concentrate agglomerate mixture to 40 microns, baking and evaporation at 300°C, drying and a 1 h leach at 22°C . Bar graph groupings A-D represent the amount of sulphur to calcine (A), sulphur to calcine titrated as free acid leach (B), sulphur to first condenser (C) and acid concentration in first condenser (D). Values shown above the bar groupings are average parameter values for 600 and 500 kg acid/t mineral concentrate (ore). In a related embodiment the strength of the recovered acid is 93-96% (i.e. concentrated sulphuric acid). In a further embodiment, low strength acid is recovered at temperatures of 40°C to 50°C.

[00133] In one embodiment, acid is recovered using equipment including, but not limited to, condensers, electrostatic precipitators, or absorption columns. In another embodiment an apparatus for the recovery of acid (see Figure 15) is configured as a gas train comprising one or more condensers 20, an electrostatic precipitator 21 operatively associated with a high voltage source, a scrubber 22 and glass fiber mist filter 23 operatively associated with a vacuum pump 24. One skilled in the art would appreciate that there may be other suitable gas train configurations and that the apparatus shown in in Figure 15 is one exemplary apparatus.

Separation of REEs from Gangue (Derived) Metal Elements (Calcine Leaching)

REE Recovery

[00134] The calcine product of selective thermal sulphate decomposition contains a mixture of REE sulphates and water insoluble non-REE compounds. To separate these two groups of compounds, a water or mild acid leaching protocol may be applied by successively adding the calcine to water or mild acidic water according to known methods in the art, for example, as described in Example 1 and 2. Further processing of the leachate to precipitate out purified REE compounds may also be done according to

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a number of protocols well known in the art to obtain mixtures of REE compounds, or to selectively isolate different REEs from one another.

[00135] In one embodiment, less than 15% of the original Fe content in a mineral concentrate is recovered in a leachate.

[00136] In another embodiment, more than 85% of REE content in a mineral concentrate is recovered in a leachate.

[00137] In still another embodiment the leachate is subjected to a hydromet (i.e. hydrometallurgy) protocol that does not require solvent extraction to produce mixed REE oxides.

[00138] In a further embodiment, the REE containing leachate solution contains 10%-20% Fe which is precipitated out of solution using $MgCO_3$.

System Configuration for the Extraction and Purification of REEs from Ore Materials

[00139] A pilot or industrial scale plant system can be configured to carry out the process for purifying REEs from an ore also comprising gangue elements comprising the steps of: (i) preparing a mineral concentrate from ore material; ii) adding concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate and mixing to produce a homogeneous agglomerate or powder mixture; iii) heating the mixture to temperatures between about 150°C and about 330°C to sulphate the REEs and gangue elements and produce a first calcine; iv) heating the first calcine to temperatures between about 400°C to about 800°C to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

[00140] The system implementation of the processes and methods of the disclosure are primarily dictated by the need to provide for:

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1) Acid/concentrate mixing (as exemplified in Figure 16) and/or calcine recycling
    acid/concentrate mixing (as exemplified in Figure 17);

2) The controlled and continuous operation of thermal sulphation and
    decomposition thermal vessels, including the feeding of material in and out of
    the vessels, temperature control and material residence time in thermal vessels;

3) The implementation of low acid use, and high strength acid recovery strategies;
    and

4) Heat recovery strategies to minimize energy consumption during heating and
    overall operations.

[00141] Based on pilot testing conducted, in one embodiment, an exemplary industrial
system and implementation protocol may comprise:

a. 3 Stages of acid/concentrate mixing @ 889 kg/t total acid addition
    across the stages to provide the ratios of acid/concentrate indicated in 'b'
    for each stage

b. 436 kg/T in stage 1; 665 kg/T stage 2; 889 kg/T stage 3

c. Heating at 273-291 °C (sulphation) following each acid addition stage
    in sequentially configured thermal vessels for a total of about one hour
    in each vessel

d. Promoting agglomeration in a rotary kiln

e. Heating to 673°C in a rotary kiln (selective sulphate decomposition) for
    about one hour

[00142] Based on other pilot tests, in another embodiment, the implementation of an
industrial calcine recycle protocol for acid/mineral concentrate mixing may comprise:

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    a. 809-840 kg/t Acid @ 47% calcine recycle ratio; calcine is obtained from a previous cycle of thermal sulphation and the remaining calcine product (53%) is subjected to further processing (desulphation)

    b. Heating to 296 °C

    c. A "one kiln" configuration for acid/concentrate mixing with recycled calcine

    d. Dry crushing of calcine for recycling

    e. Approximate calcine hot zone retention time of 99 min

    f. Low temperature calcine product charged as is for heating to 663-669 °C in a second kiln

    g. Approximate hot zone retention time of 71min

[00143] From pilot testing conducted according the above described protocols, the following results have been achieved:

Overall Extractions

    a. 81% TREE w/ 22% Zr and 17% Fe

    b. Both methods had similar extractions

Low Temperature Heating Off-Gas (sulphation stage)

    c. Sulphur: 50% SO_3/SO_4, 35% SO_2, 15% particulate sulphur

    d. Fluoride: All as HF

High Temperature Off-Gas (selective sulphate decomposition stage)

    e. SO_2 detected

Phosphor Addition (to enrich REE content in mineral concentrate)

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> f. No physical or chemical issues observed versus without Phosphor powder

[00144] In one embodiment, a system for implementing the above protocols comprises, a feed (concentrate and recycled material) delivery system; heated acid /feed mixing equipment; an acid delivery system; one or more thermal vessels (e.g. kilns or furnaces) for carrying out sulphation and sulphate decomposition reactions on feed materials; an acid recovery and regeneration system; one or more off-gas treatment units; calcine handling equipment; waste material handling systems and storage facilities, and an instrumentation, control and data acquisition system, all operatively associated in such a way so as to carry out the processes and methods of the disclosure.

[00145] In another embodiment the system for carrying out the processes and methods of the disclosure is configured to process about 3,550,000 Mt of mined ore material per year. In an alternative embodiment, mine output is controlled to achieve constant flotation concentrate volume or grade.

[00146] In yet another embodiment, the system for carrying out the processes and methods of the disclosure is configured to process about 1,850,000 Mt/yr of mill feed.

[00147] In a further embodiment, the system for carrying out the processes and methods of the disclosure is configured to process about 300,000 Mt/yr of flotation (mineral) concentrate.

[00148] In still a further embodiment, the system for carrying out the processes and methods of the disclosure is configured to input about 10,000 Mt/yr of lamp (phosphor) material.

[00149] In one embodiment, the system for carrying out the processes and methods of the disclosure is configured to produce about 11,270 Mt/yr of mixed REE concentrate.

[00150] In related embodiment, the system for carrying out the processes and methods of the disclosure is configured to produce about 11,050 Mt/yr of pure REOs.

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[00151] It is understood that reference to various embodiments of the processes of the present disclosure and related applications thereof, including those described in the Examples and in the Figures are illustrative of certain embodiments of the processes disclosed herein and are not intended to limit the scope of the invention in any way.

EXAMPLES

[00152] Embodiments of the invention are further illustrated in the following examples.

Example 1

[00153] 500 g of flotation concentrate (grade provided below in Table 1) was added to a glass reactor fitted with a polytetrafluoroethylene (PTFE) impeller to provide mixing. In four steps, with high intensity mixing in-between each step, a total of 236.7 g of concentrated (96%) sulphuric acid was added (909 kg acid/T concentrate) in a total time of one hour. During mixing (high intensity) the reactor was heated to 235-259 degrees C. At the completion of mixing, agglomerated solids had been formed and were removed from the glass reactor and placed in a tray, which was placed in pre-heated muffle furnace heated to 600 degrees C. The furnace temperature was allowed to return/stabilize to 600 degrees C, and the sample was kept in the furnace for an additional 30 min. During the baking in the furnace, gas flow of 3L/min was applied to promote the desulphation reactions. After baking the sample weighed 563 g and 187 g of this was added to 1470 mL of ambient temperature (25 degrees C) de-ionized (DI) water for leaching. Leaching was conducted in a glass reactor equipped with a PTFE impeller for 1hr. The pulp was weighed and filtered, and the cake washed with 271 mL of DI water. 1398 mL of final of leach filtrate and 260 mL of wash filtrate were collected. 159 g of dry residue was collected. Filtrate, washed and dry leached residue were analyzed. The results of the metallurgical balance are presented below. Dy and Nd extraction to solution were 86% and 91%, respectively, while Fe and Al extraction were both only 10%. The pH of the leach filtrate was only mildly acidic with about 1.3 g/L of free acid. The solution was later further processed for the recovery of high purity mixed rare earth oxide.

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[00154] **Table 1 – Feed Composition for Example 1**

Feed:	Concentrate #1	Unit
Mass:	166	g
Element:	**Assay**	
La	2020	g/t
Ce	4400	g/t
Pr	474	g/t
Nd	1630	g/t
Sm	390	g/t
Eu	23	g/t
Gd	414	g/t
Tb	89	g/t
Dy	629	g/t
Ho	141	g/t
Y	3680	g/t
Er	446	g/t
Tm	69	g/t
Yb	426	g/t
Lu	59	g/t
Sc	<25	g/t
Th	638	g/t
U	102	g/t
Zr	2.55	%
Nb	0.29	%
Ta	0.01	%
Si	29.4	%
Al	3.19	%
Fe	7.48	%
Mg	0.37	%
Ca	2.82	%
Na	2.62	%
K	2.29	%
Ti	0.45	%
P	0.03	%
Mn	0.21	%
F	1.36	%
Be	480	g/t

[00155] **Table 2 - Metallurgical balance for Example 1 products:**

Component:	Final PLS	Unit	Wash	Unit	Final residue	Unit	Extraction to Solution:	Unit
Quantity:	1389	mL	260	mL	159	g		
Element:	**Assay:**		**Assay:**		**Assay:**			
La	186	mg/L	83.5	mg/L	266	g/t	87	%

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Ce	406	mg/L	177	mg/L	480	g/t	89	%
Pr	48.1	mg/L	20.0	mg/L	47	g/t	91	%
Nd	166	mg/L	69.1	mg/L	153	g/t	91	%
Sm	38.0	mg/L	15.3	mg/L	38	g/t	90	%
Eu	2.25	mg/L	0.92	mg/L	3	g/t	89	%
Gd	41.5	mg/L	16.3	mg/L	44	g/t	90	%
Tb	8.44	mg/L	3.25	mg/L	11	g/t	88	%
Dy	59.9	mg/L	22.3	mg/L	89	g/t	86	%
Ho	12.8	mg/L	4.64	mg/L	22	g/t	84	%
Y	355	mg/L	127	mg/L	541	g/t	86	%
Er	40.9	mg/L	14.5	mg/L	81	g/t	83	%
Tm	6.04	mg/L	2.05	mg/L	13	g/t	81	%
Yb	37.6	mg/L	12.6	mg/L	88	g/t	80	%
Lu	4.99	mg/L	1.63	mg/L	12	g/t	79	%
Sc	<0.2	mg/L	<0.2	mg/L	<25	g/t	8	%
Th	55.4	mg/L	17.0	mg/L	127	g/t	80	%
U	8.78	mg/L	2.35	mg/L	23	g/t	78	%
Zr	509	mg/L	119	mg/L	2.12	%	18	%
Nb	27.0	mg/L	5.1	mg/L	0.26	%	9	%
Ta	<0.9	mg/L	<0.9	mg/L	0.01	%	9	%
Si	2.8	mg/L	3.2	mg/L	30.1	%	0	%
Al	326	mg/L	163	mg/L	2.91	%	10	%
Fe	845	mg/L	278	mg/L	7.06	%	10	%
Mg	372	mg/L	108	mg/L	0.01	%	97	%
Ca	667	mg/L	633	mg/L	2.14	%	24	%
Na	525	mg/L	167	mg/L	2.17	%	18	%
K	264	mg/L	114	mg/L	2.12	%	11	%
Ti	54.1	mg/L	11.8	mg/L	0.41	%	11	%
P	10.0	mg/L	<8	mg/L	0.03	%	28	%
Mn	116	mg/L	34.2	mg/L	0.12	%	48	%
F	31.0	mg/L	11.0	mg/L	0.27	%	10	%
Be	36.4	mg/L	10.7	mg/L	202	g/t	62	%

Example 2

[00156] A bench scale test was conducted to test the effect of multi-stage acid addition and selective thermal sulphation. 35 g of concentrated (96%) sulfuric acid was added to 50 g of dry flotation concentrate. The acid and concentrate were mixed by hand with a plastic stick in a glass crucible to achieve as homogeneous a mixture as possible. The crucible was placed in a muffle furnace where it was heated until the sample reached approximately 280°C, and it was maintained at this temperature for 30 minutes. The sample was removed from the furnace and allowed to cool slightly. An additional 25 g

of concentrated sulphuric acid was added and again mixed with the solids by hand. After mixing, the crucible was charged again into the muffle furnace. The sample was heated to 300°C and maintained at this temperature for an additional 30 min. The sample was then heated further to 650°C, and maintained at close to this temperature for 30 minutes, before being removed and allowed to cool. At all stages of the test, the mixture was either in dry powder or granular agglomerate form. Paste formation or adhesion was avoided by adding the acid in multiple stages with heating in between. After baking the sample weighed 60 g and 55 g of this was added to 406 mL of ambient temperature (25°C) de-ionized (DI) water for leaching. Leaching was conducted in a glass reactor equipped with a PTFE impeller for 1hr. The pulp was weighed and filtered, and the cake washed with 75 mL of DI water. 464mL of combined final leach and wash filtrate were collected. 39 g of dry residue was collected. Filtrate, and dry leached residue were analyzed. The results of the metallurgical balance are presented below. Dy and Nd extraction to solution were 82% and 92%, respectively, while Fe and Al extraction were 26 and 34%, respectively. The pH of the leach filtrate was only mildly acidic with about 1.3 g/L of free acid.

[00157] **Table 3 - Feed Composition for Example 2**

Feed:	20% MP Concentrate #4	Unit
Mass:	46	g
Element:	**Assay**	
La	5380	g/t
Ce	11400	g/t
Pr	1280	g/t
Nd	4000	g/t
Sm	1000	g/t
Eu	56	g/t
Gd	889	g/t
Tb	205	g/t
Dy	1390	g/t
Ho	306	g/t
Y	7540	g/t
Er	958	g/t
Tm	142	g/t
Yb	857	g/t
Lu	115	g/t
Sc	<25	g/t
Th	1520	g/t

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U	222	g/t
Zr	4.22	%
Si	21.0	%
Al	1.79	%
Fe	13.15	%
Mg	0.36	%
Ca	6.09	%
Na	3.34	%
K	0.88	%
Ti	0.92	%
P	0.10	%
Mn	0.33	%

[00158] Table 4 - Metallurgical balance for Example 2 products:

Component:	PLS+ Wash	Unit	Final residue	Unit	Extraction to solution	Unit
Quantity:	464	mL	39	g		
Metal:						
La	437	mg/L	403	g/t	93	%
Ce	912	mg/L	897	g/t	92	%
Pr	102	mg/L	99	g/t	93	%
Nd	353	mg/L	370	g/t	92	%
Sm	74.9	mg/L	108	g/t	89	%
Eu	4.37	mg/L	7	g/t	89	%
Gd	80.9	mg/L	135	g/t	88	%
Tb	15.4	mg/L	33	g/t	85	%
Dy	102	mg/L	276	g/t	82	%
Ho	21.9	mg/L	67	g/t	80	%
Y	596	mg/L	1520	g/t	83	%
Er	66.6	mg/L	229	g/t	78	%
Tm	9.68	mg/L	36	g/t	76	%
Yb	59.2	mg/L	225	g/t	76	%
Lu	7.39	mg/L	30	g/t	75	%
Sc	<0.2	mg/L	<25	g/t	9	%
Th	105	mg/L	342	g/t	79	%
U	14.3	mg/L	46	g/t	79	%
Zr	1310	mg/L	2.92	%	35	%
Si		mg/L	21.9	%	0	%
Al	559	mg/L	1.31	%	34	%
Fe	3100	mg/L	10.77	%	26	%
Mg	314	mg/L	0.04	%	90	%
Ca	823	mg/L	5.62	%	15	%
Na	688	mg/L	2.92	%	22	%
K	98	mg/L	0.84	%	12	%

Ti	237	mg/L	0.71	%	29	%
P	40.0	mg/L	0.06	%	44	%
Mn	147	mg/L	0.19	%	48	%

Example 3

[00159] Based on reasonable flotation performance targets set having regard to experimentations conducted and available mineral concentrate samples, an exemplary estimate of maximum uranium and thorium content and activity in projected flotation concentrate was calculated as set out below. Given the putative targets and available resources, no representation is made with respect to the estimated concentrations or applicability of the calculations below with respect to any other ore samples, or with respect to as of yet unknown mine plans or installations:

[00160] Table 5 - Estimated maximum U+Th concentrations for Strange Lake Mineral concentrate

Radionuclide	Max Concentration (ppm)
Uranium (U)	600
Thorium (Th)	4300

[00161] Table 6 -Specific Activity Constants for U and Th

Radionuclide	Specific Activity Constant (bq/g)
Uranium 238	12460
Thorium 232	4066

[00162] Based on the projected radionuclide levels in concentrate in Table 5 and the activity constants in Table 6, the following calculation can be made:

Max Calculated activity (U+Th only) = 600/10^6*12460 + 4300/10^6*4066 = 7.5 bq/g (U) + 15.5 bq/g (Th) = 23 bq/g (U+Th)

[00163] In the entire decay chain there are 10 Th232 daughter products and 14 U238 daughter products, allowing the following calculation to be made:

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Total estimated maximum activity = 600/10^6*12460*14 +4300/10^6*4066*10 = **75 bq/g (U series) + 155 bq/g (Th series) = 230 bq/g (Total U+Th series)**

[00164] **Radiation Dosage:**

A previous sample with a calculated activity (U + Th only) of 13.2 bq/g measured approximately 2.5 μSv/h near the surface of the sample. Assuming a linear relationship between dosage and U+Th activity, a sufficient quantity of this mineral concentrate could generate an activity of 4.4 μSv/h. An exposure of 227 hours directly adjacent to a material stockpile could possibly give rise to an annual external dose of 1 millisievert (the annual dose limit for a member of public). There is also a minor potential for internal dose from inhaled dust.

[00165] Although the invention has been described with reference to certain specific embodiments, various modifications thereof will be apparent to those skilled in the art without departing from the spirit and scope of the invention. All such modifications as would be apparent to one skilled in the art are intended to be included within the scope of the following claims.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for purifying REEs from an ore also comprising gangue elements, comprising the steps of: (i) preparing a mineral concentrate from ore material containing REEs and gangue elements; ii) combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate to produce a homogeneous agglomerate or powder mixture; iii) heating the homogeneous agglomerate or powder mixture to temperatures between about 150°C and about 330°C to sulphate the REEs and gangue elements and produce a first calcine; iv) heating the first calcine to temperatures between about 400°C to about 800°C to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

2. The process of claim 1, wherein the ore material comprises a mixture of LREEs, HREEs and one or more gangue elements selected from the group of iron, aluminum, niobium and zirconium.

3. The process of claim 1 or 2 wherein the ore material is derived from a silicate, monazite, or bastnaesite deposit.

4. The process of any one of claims 1 to 3 wherein the mineral concentrate is prepared by beneficiation of the ore material by one or more physical methods selected from sensor-based sorting, flotation, magnetic separation, and gravity separation.

5. The process according to claim 4, wherein the mineral concentrate is prepared using sensor-based sorting and flotation.

6. The process according to any one of claims 1 to 5, wherein the mineral concentrate contains at least 80% of the REEs from the ore material.

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7. The process of any one of claims 1 to 6 wherein the concentrated sulphuric acid and the mineral concentrate are combined and mixed in a manner so as to obtain and maintain a granular mixture consistency throughout mixing.

8. The process of any one of claims 1 to 7 wherein the concentrated sulphuric acid is combined and mixed in batches or a stage-wise manner with the mineral concentrate.

9. The process of any one of claims 1 to 8 wherein the step of combining and mixing the concentrated sulphuric acid and the mineral concentrate is done in whole or in part concurrently with the step of heating the homogeneous agglomerate or powder mixture to sulphate REEs and gangue elements to produce the first calcine.

10. The process of any one of claims 1 to 9 wherein the homogeneous agglomerate or powder mixture is produced by adding a recycled amount of first calcine during mixing of the concentrated sulphuric acid and the mineral concentrate.

11. The process of any one of claims 1 to 10, wherein the step of combining and mixing the concentrated sulphuric acid and the mineral concentrate is done in a high sheer mixer, pug mill, paddle mixer, ribbon mixer, or rotary drum mixer.

12. The process of any one of claims 1 to 11, wherein the homogeneous agglomerate or powder mixture has a substantially uniform pellet or particle size, produced in whole or in part by applying a pelletizing mixing action and particle removal method during mixing of the concentrated sulphuric acid and the mineral concentrate.

13. The process of any one of claims 1 to 11, wherein the homogenous agglomerate or powder mixture has a substantially uniform particle size, produced in whole or in part by one or more cycles of grinding and screening.

14. The process of claim 13, wherein the homogenous agglomerate or powder mixture is ground and screened to achieve a substantially uniform particle size of about 40 microns.

15. The process of any one of claims 1 to 14, wherein the homogenous agglomerate or powder mixture is heated to between about 150°C and about 330°C for about 15 to about 240 minutes.

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16. The process of any one of claims 1 to 15, wherein the homogenous agglomerate or powder mixture is heated to between about 200°C and about 300°C for about 60 to about 120 minutes.

17. The process of any one of claims 1 to 16, wherein the homogenous agglomerate or powder mixture is continuously fed into a first thermal vessel for heating to produce the first calcine.

18. The process of any one of claims 1 to 17, wherein the first calcine is heated to between about 400°C to about 800°C for about 15 to about 240 minutes.

19. The process of any one of claims 1 to 18, wherein the first calcine is heated to between about 600°C to about 700°C for about 60 to about 120 minutes.

20. The process of any one of claims 1 to 19, wherein the first calcine is continuously fed from the first thermal vessel into a second thermal vessel for heating to produce the second calcine.

21. The process of any one of claims 1 to 20, wherein concentrated sulphuric acid is produced or recovered from the gas stream and recycled to produce the homogeneous agglomerate or powder mixture.

22. The process of any one of claims 1 to 21, wherein the leaching of the second calcine is done with dilute acid or water.

23. The process of claims 1 or 22, wherein the sulphated REEs in the leachate solution are recovered out of solution as REE solids by pH adjustment, precipitation reactions and/or solvent extraction methods.

24. A process for purifying REEs from an ore also comprising gangue elements, comprising the steps of: (i) preparing a mineral concentrate from ore material containing REEs and gangue elements; ii) combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate in a manner so as to obtain and maintain a granular mixture consistency throughout mixing to produce a homogeneous agglomerate or powder mixture; iii) heating the homogeneous agglomerate or powder mixture to temperatures between about 150°C and about 330°C to sulphate the REEs and gangue elements and produce a first calcine; iv) heating the first calcine to temperatures between about 400°C to about 800°C to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue

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element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

25. The process of claim 24, wherein the ore material comprises a mixture of LREEs, HREEs and one or more gangue elements selected from the group of iron, aluminum, niobium and zirconium.

26. The process of claim 24 or 25 wherein the ore material is derived from a silicate, monazite, or bastnaesite deposit.

27. The process of any one of claims 24 to 26 wherein the mineral concentrate is prepared by beneficiation of the ore material by one or more physical methods selected from sensor-based sorting, flotation, magnetic separation, and gravity separation.

28. The process according to claim 27, wherein the mineral concentrate is prepared using sensor-based sorting and flotation.

29. The process according to any one of claims 24 to 28, wherein the mineral concentrate contains at least 80% of the REEs from the ore material.

30. The process of any one of claims 24 to 29 wherein the concentrated sulphuric acid is combined and mixed in batches or a stage-wise manner with the mineral concentrate.

31. The process of any one of claims 24 to 30 wherein the step of combining and mixing the concentrated sulphuric acid and the mineral concentrate is done in whole or in part concurrently with the step of heating to sulphate REEs and gangue elements to produce the first calcine.

32. The process of any one of claims 24 to 31 wherein the homogeneous agglomerate or powder mixture is produced by adding a recycled amount of the first calcine during mixing of the concentrated sulphuric acid and the mineral concentrate.

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33. The process of any one of claims 24 to 32, wherein the step of combining and mixing the concentrated sulphuric acid and the mineral concentrate is done in a high sheer mixer, pug mill, paddle mixer, ribbon mixer, or rotary drum mixer.

34. The process of any one of claims 24 to 33, wherein the homogeneous agglomerate or powder mixture has a substantially uniform pellet or particle size, produced in whole or in part by applying a pelletizing mixing action and particle removal method during mixing of the concentrated sulphuric acid and the mineral concentrate.

35. The process of any one of claims 24 to 34, wherein the homogenous agglomerate or powder mixture has a substantially uniform particle size, produced in whole or in part by one or more cycles of grinding and screening.

36. The process of claim 35, wherein the homogenous agglomerate or powder mixture is ground and screened to achieve a substantially uniform particle size of about 40 microns.

37. The process of any one of claims 24 to 36, wherein the homogenous agglomerate or powder mixture is heated to between about 150°C and about 330°C for about 15 to about 240 minutes.

38. The process of any one of claims 24 to 37, wherein the homogenous agglomerate or powder mixture is heated to between about 200°C and about 300°C for about 60 to about 120 minutes.

39. The process of any one of claims 24 to 38, wherein the homogenous agglomerate or powder mixture is continuously fed into a first thermal vessel for heating to produce the first calcine.

40. The process of any one of claims 24 to 39, wherein the first calcine is heated to between about 400°C to about 800°C for about 15 to about 240 minutes.

41. The process of any one of claims 24 to 40, wherein the first calcine is heated to between about 600°C to about 700°C for about 60 to about 120 minutes.

42. The process of any one of claims 24 to 41, wherein the first calcine is continuously fed from the first thermal vessel into a second thermal vessel for heating to produce the second calcine.

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43. The process of any one of claims 24 to 42, wherein concentrated sulphuric acid is produced or recovered from the gas stream and recycled to produce the homogeneous agglomerate or powder mixture.
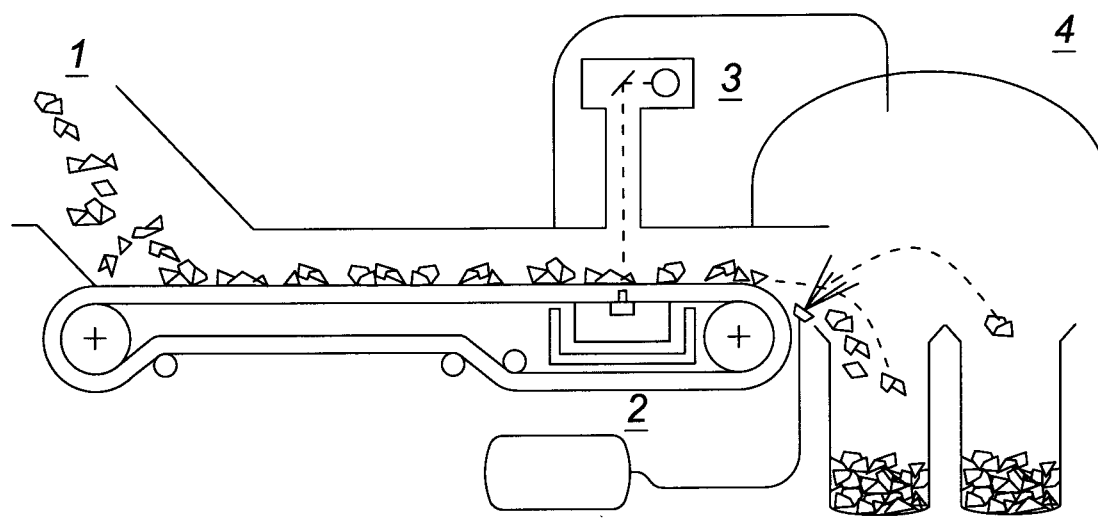
44. The process of any one of claims 24 to 43, wherein the leaching of the second calcine is done with dilute acid or water.

45. The process of claims 24 or 44, wherein the sulphated REEs in the leachate solution are recovered out of solution as REE solids by pH adjustment, precipitation reactions and/or solvent extraction methods.

46. A process for purifying REEs from an ore also comprising gangue elements, comprising the steps of: (i) preparing a mineral concentrate from ore material containing REEs and gangue elements, using a combination of sensor-based sorting and flotation; ii) combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to the mineral concentrate in a manner so as to obtain and maintain a granular mixture consistency throughout mixing to produce a homogeneous agglomerate or powder mixture; iii) heating the homogeneous agglomerate or powder mixture to temperatures between about 200°C and about 300°C for one to two hours to sulphate the REEs and gangue elements and produce a first calcine; iv) heating the first calcine to temperatures between about 600°C to about 700°C for one to two hours to decompose the sulphates of the gangue elements and produce a second calcine comprising insoluble gangue element compounds, soluble REE sulphates, and a gas stream comprising SO_3 and/or SO_2; and v) subjecting the second calcine to a leaching process to obtain a leachate solution of sulphated REEs that is substantially free of gangue element sulphates, and a solid residue comprising the insoluble gangue element compounds.

47. A process for producing a homogeneous agglomerate or powder mixture of concentrated sulphuric acid and mineral concentrate containing REEs and gangue elements, comprising the step of combining and mixing concentrated sulphuric acid in a super-stoichiometric amount to a mineral concentrate in a manner so as to obtain and maintain a granular mixture consistency throughout mixing to produce a homogeneous agglomerate or powder mixture.

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48. The process of claim 47 wherein the concentrated sulphuric acid is combined and mixed in batches or a stage-wise manner with the mineral concentrate.

49. The process according to claim 48 wherein the concentrated sulphuric acid is combined and mixed with the mineral concentrate in dosage amounts each ranging from about 200 kg to about 900 kg of acid per tonne of mineral concentrate until the super-stoichiometric amount of concentrated sulphuric acid has been combined and mixed with the mineral concentrate.

50. The process according to claim 49 wherein the super-stoichiometric amount of acid is about 800 kg to 1500 kg of acid per tonne of mineral concentrate.

51. The process of claim 49 or 50 wherein each of the dosage amounts is between 220 kg to about 625 kg of acid per tonne of mineral concentrate or less.

52. The process of any one of claims 47 or 49, wherein the homogeneous agglomerate or powder mixture is produced by adding an amount of calcine during mixing of the concentrated sulphuric acid and the mineral concentrate.

53. The process according to any one of claims 47 to 52, wherein the mixing of concentrated sulphuric acid with mineral concentrate is done continuously.

54. The process according to any one of claims 47 to 53, wherein the mixing of concentrated sulphuric acid and mineral concentrate is carried out at temperatures ranging from about 150°C to about 330°C.

55. The process according to claim 54, wherein the mixing of concentrated sulphuric acid and mineral concentrate is carried out at temperatures ranging from about 200°C to about 300°C.
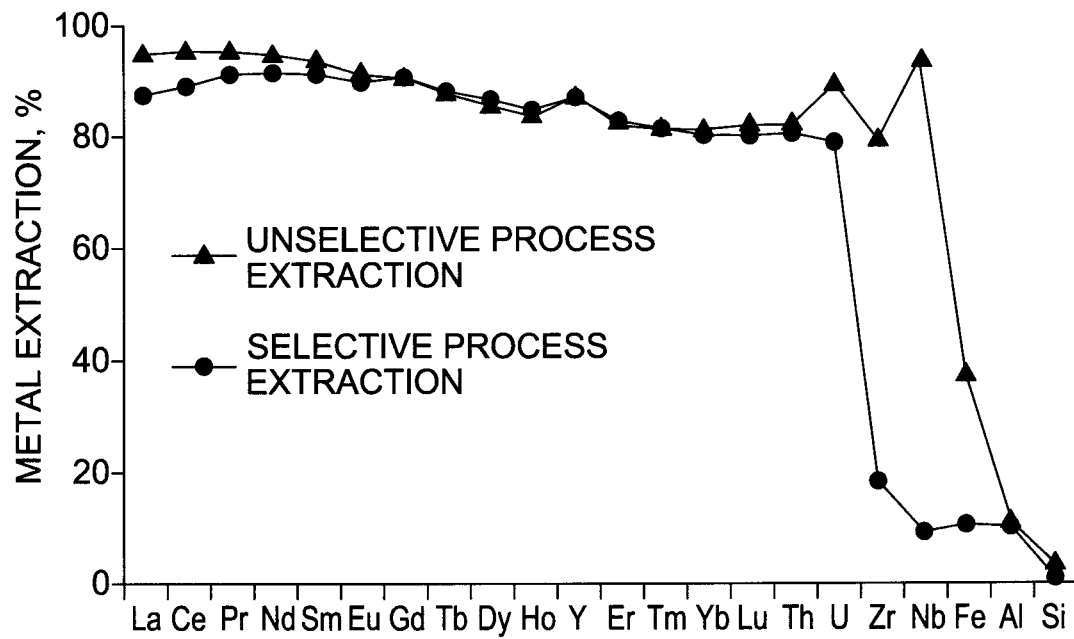
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3

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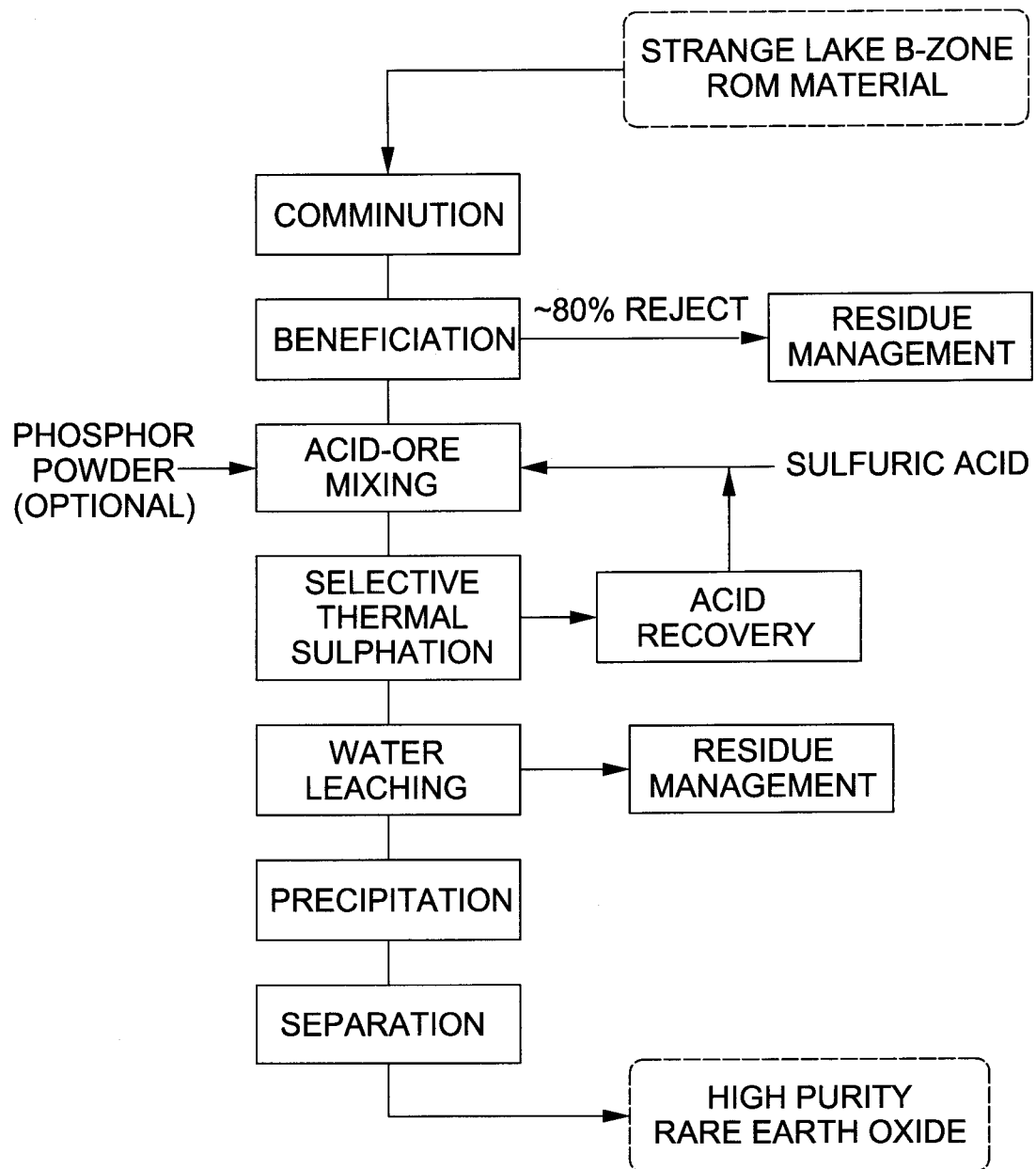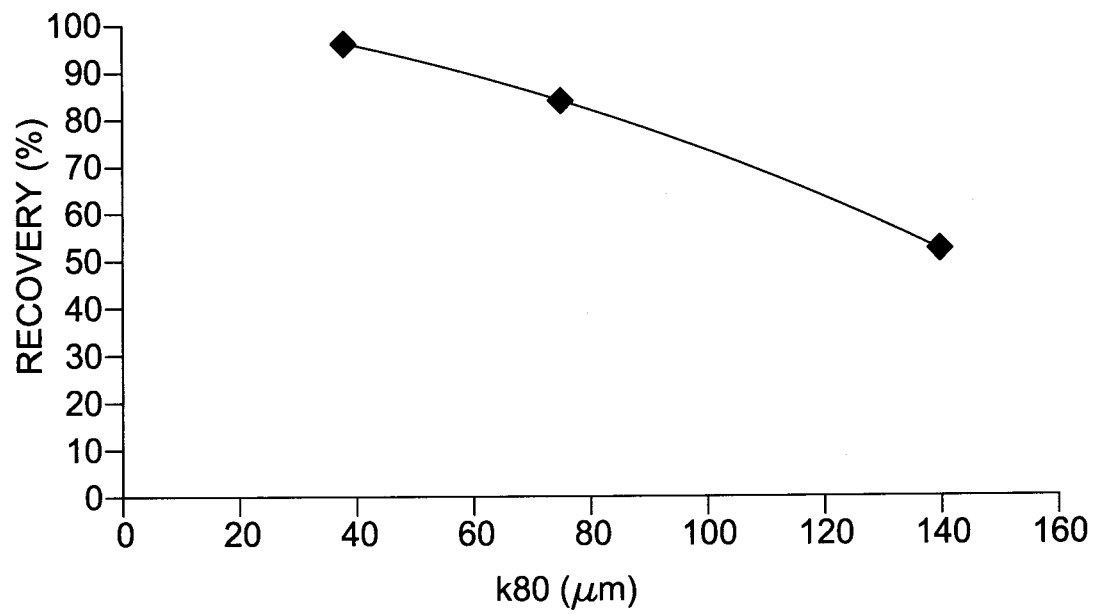*2*

_1_ FEEDING OF UNSORTED MATERIAL
_2_ X-RAY CAMERA
_3_ X-RAY SOURCE
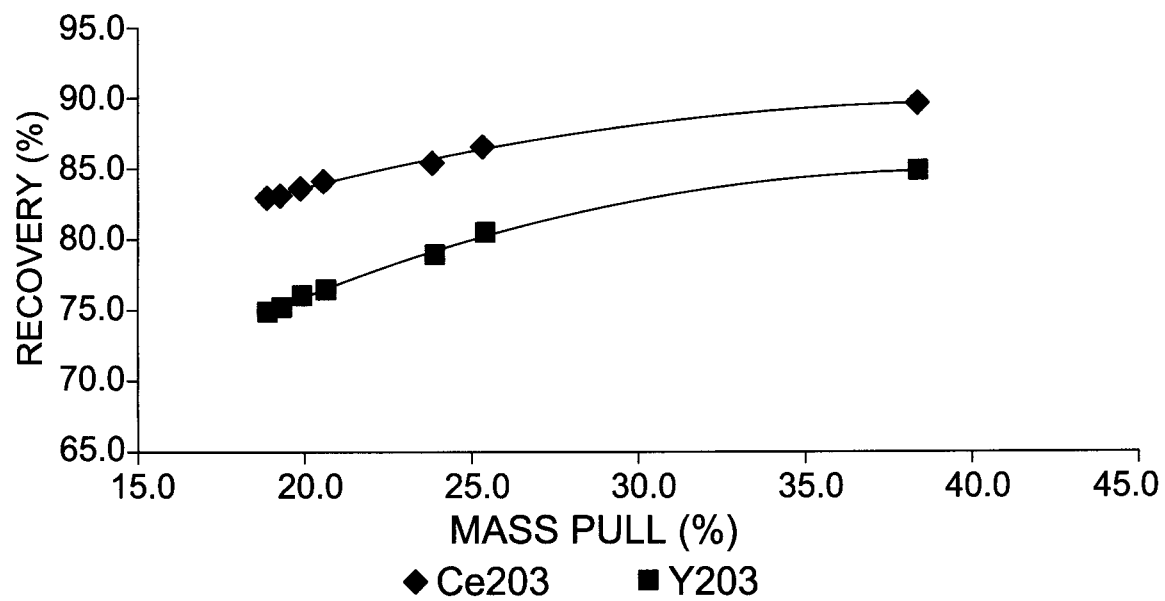_4_ SEPARATION CHAMBER

FIG. 1

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FIG. 2

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STRANGE LAKE B-ZONE
ROM MATERIAL

COMMINUTION

BENEFICIATION — ~80% REJECT → RESIDUE MANAGEMENT

PHOSPHOR POWDER (OPTIONAL) → ACID-ORE MIXING ← SULFURIC ACID

SELECTIVE THERMAL SULPHATION → ACID RECOVERY

WATER LEACHING → RESIDUE MANAGEMENT

PRECIPITATION

SEPARATION

HIGH PURITY RARE EARTH OXIDE

FIG. 3

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FIG. 4

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FIG. 5

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FIG. 6

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A   B

FIG. 7

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FIG. 8

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TO OFFGAS
HANDLING
SYSTEM
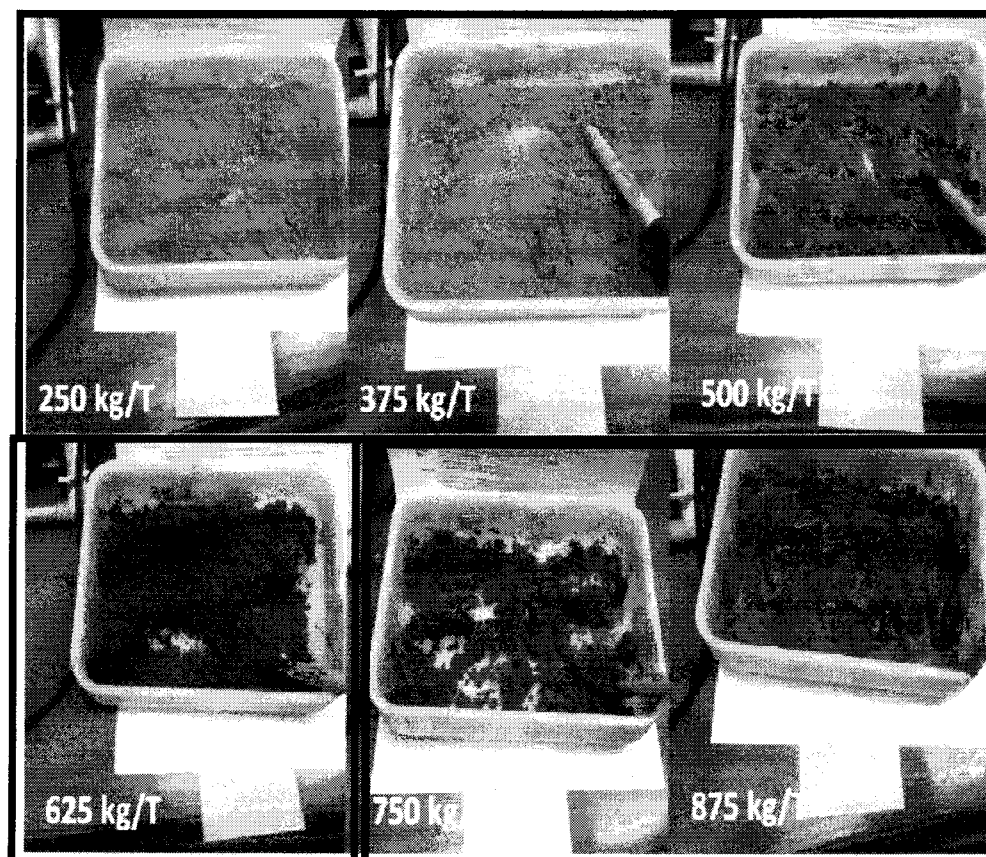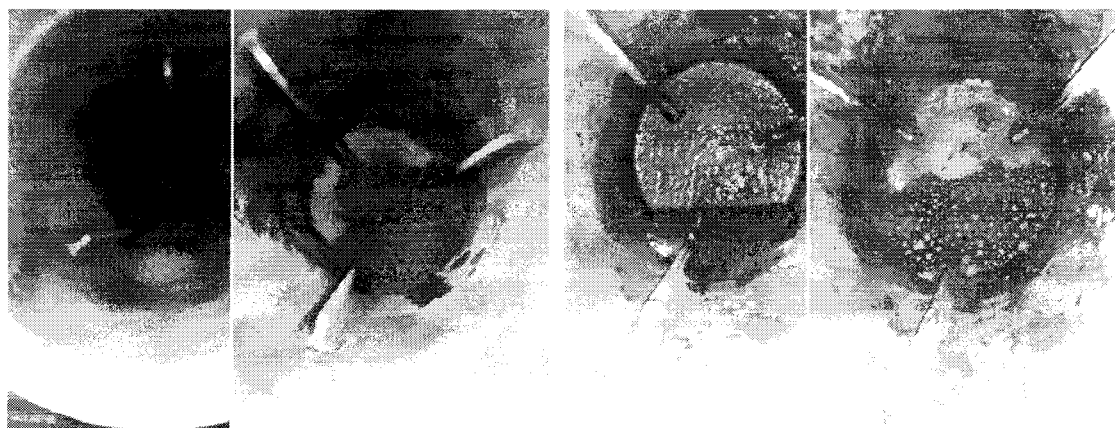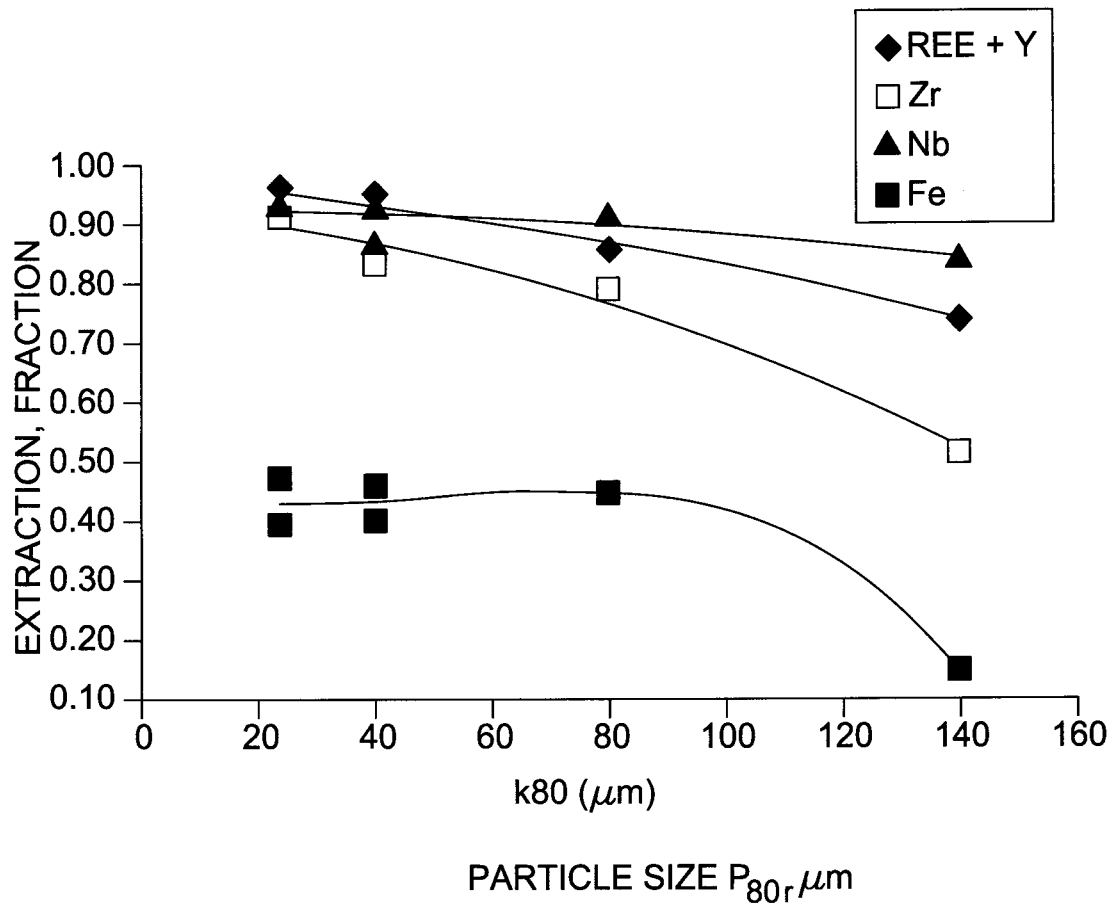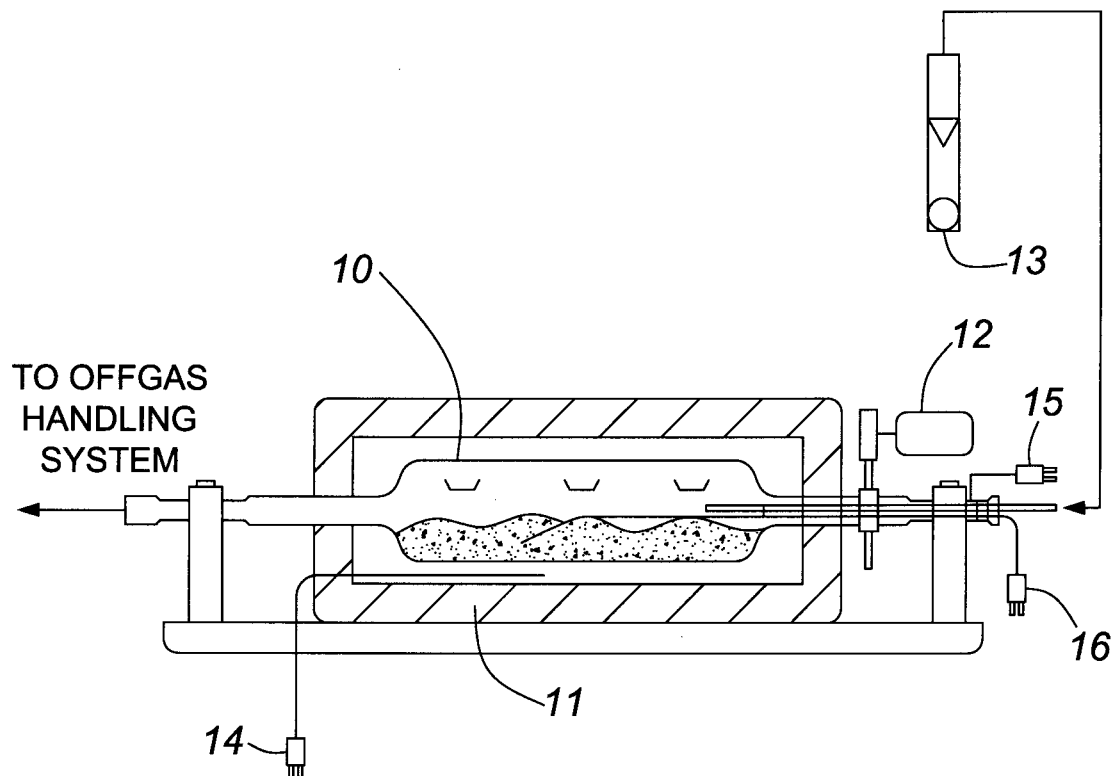
FIG. 9

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FIG. 10

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A

B

C

D

FIG. 11

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A

B

C

D

FIG. 12

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A

B

C

D

FIG. 13

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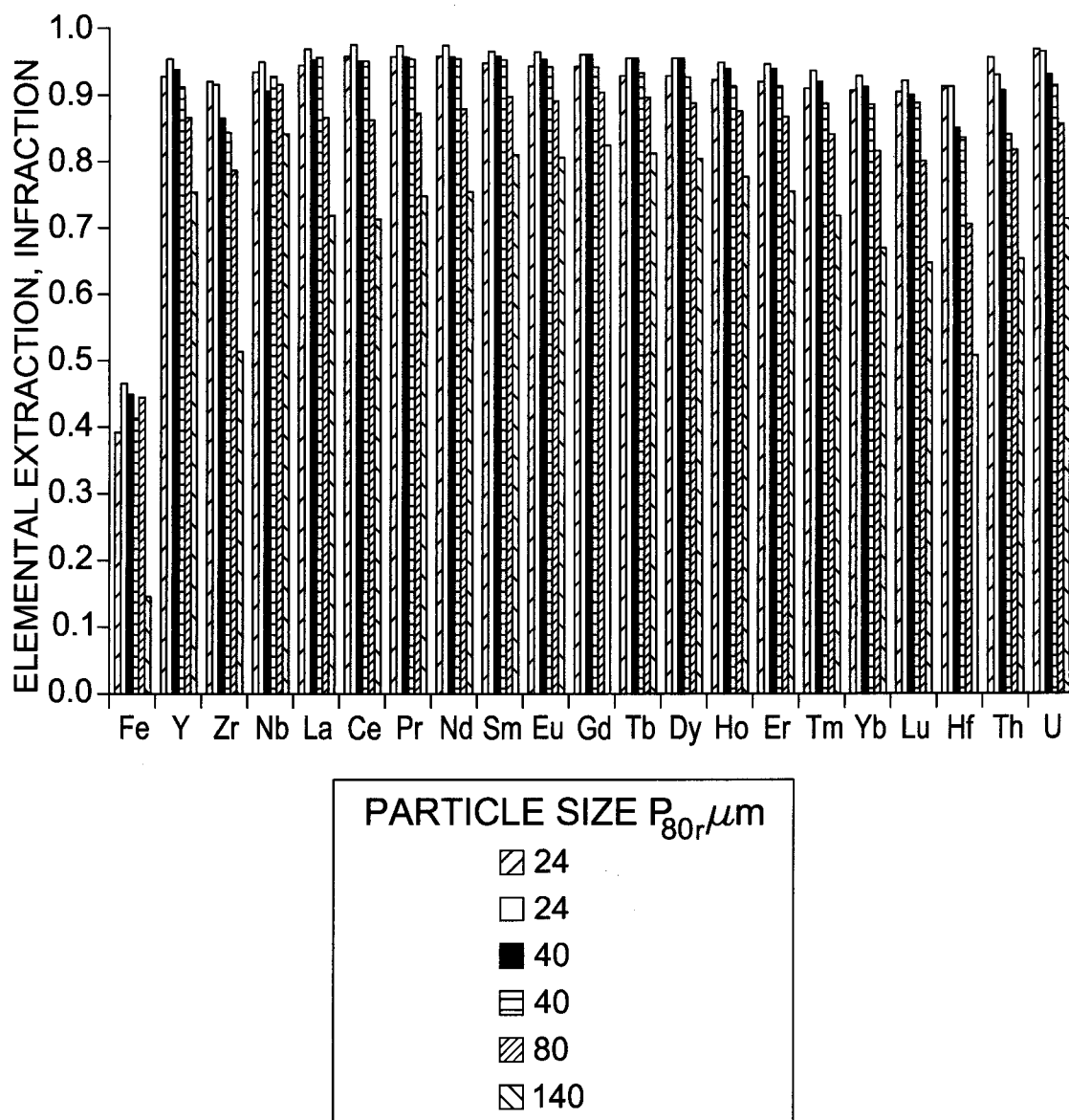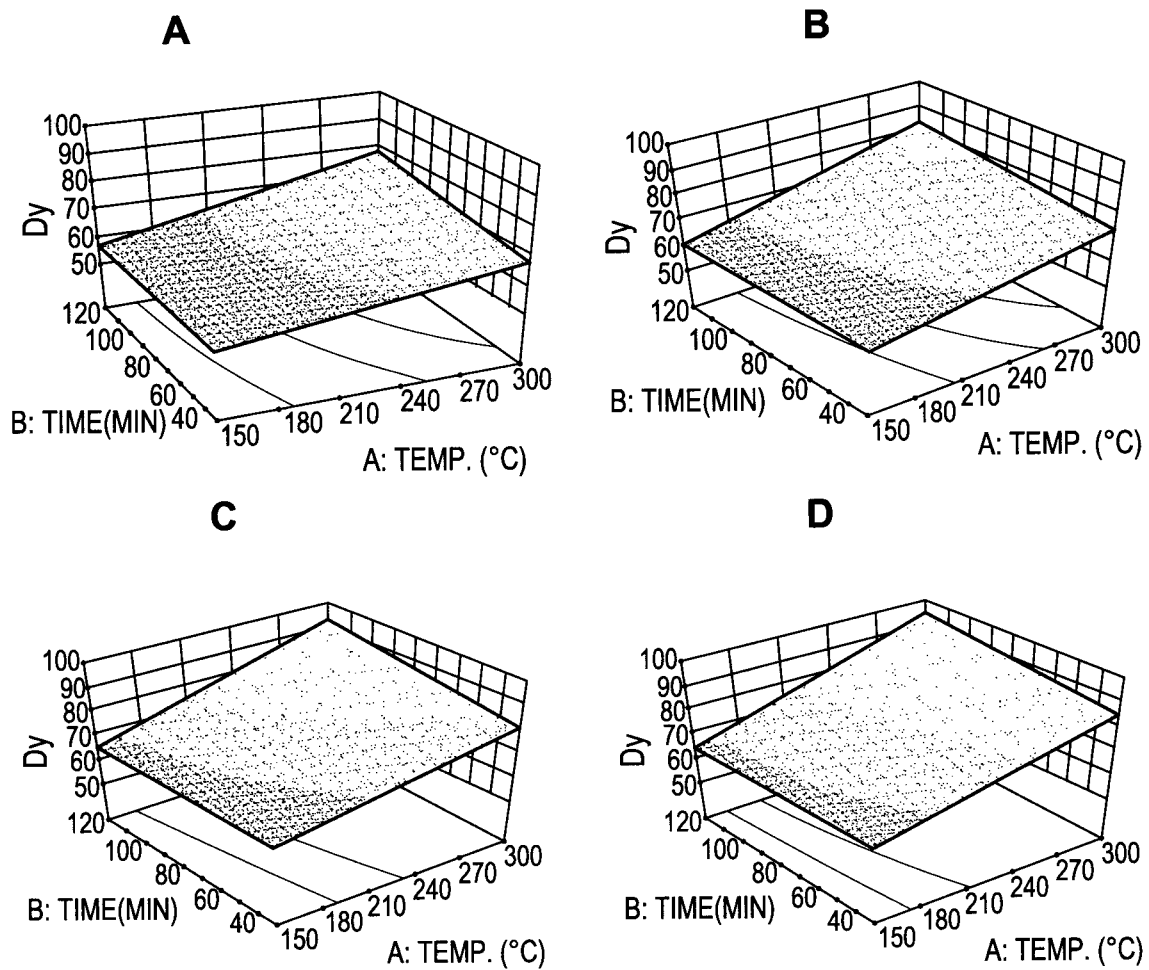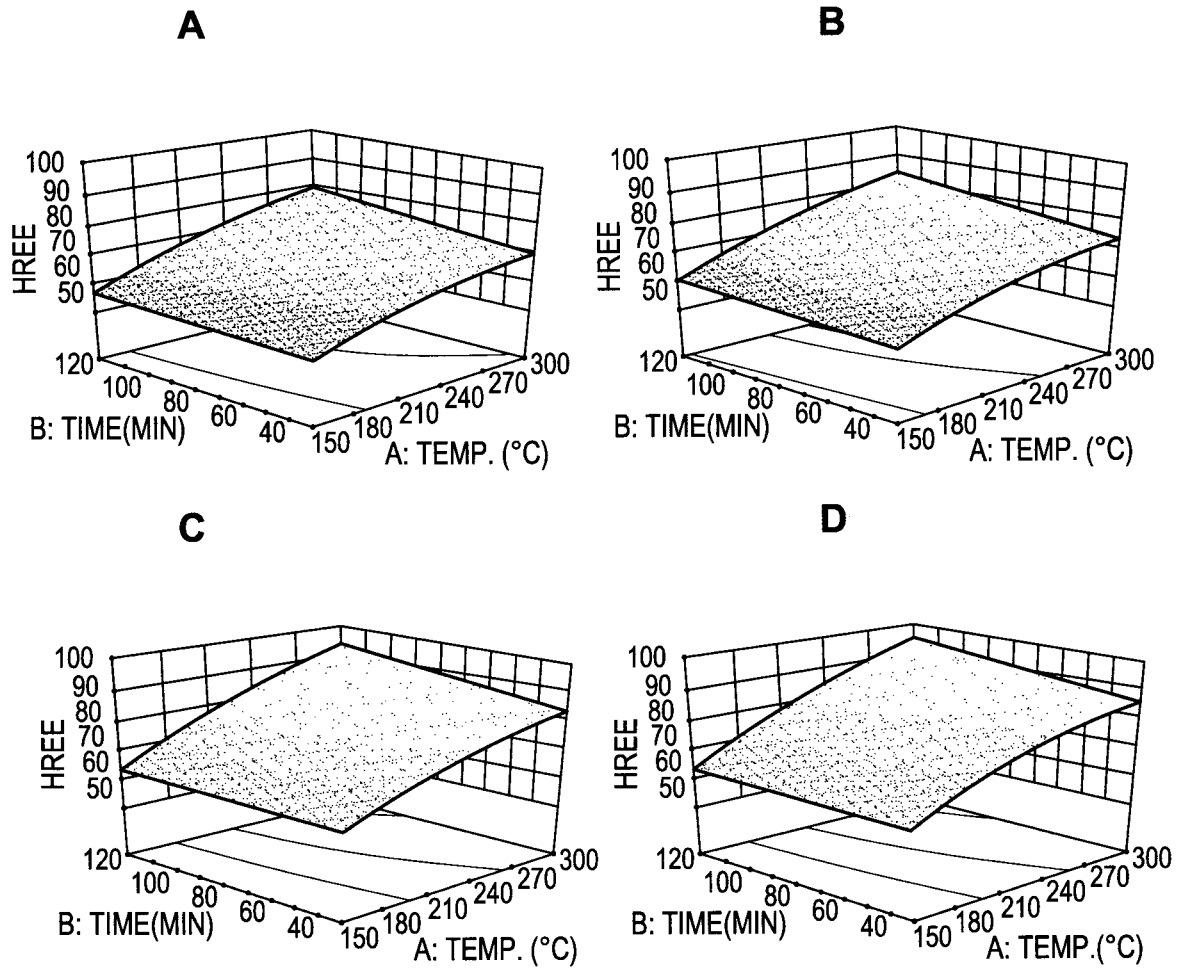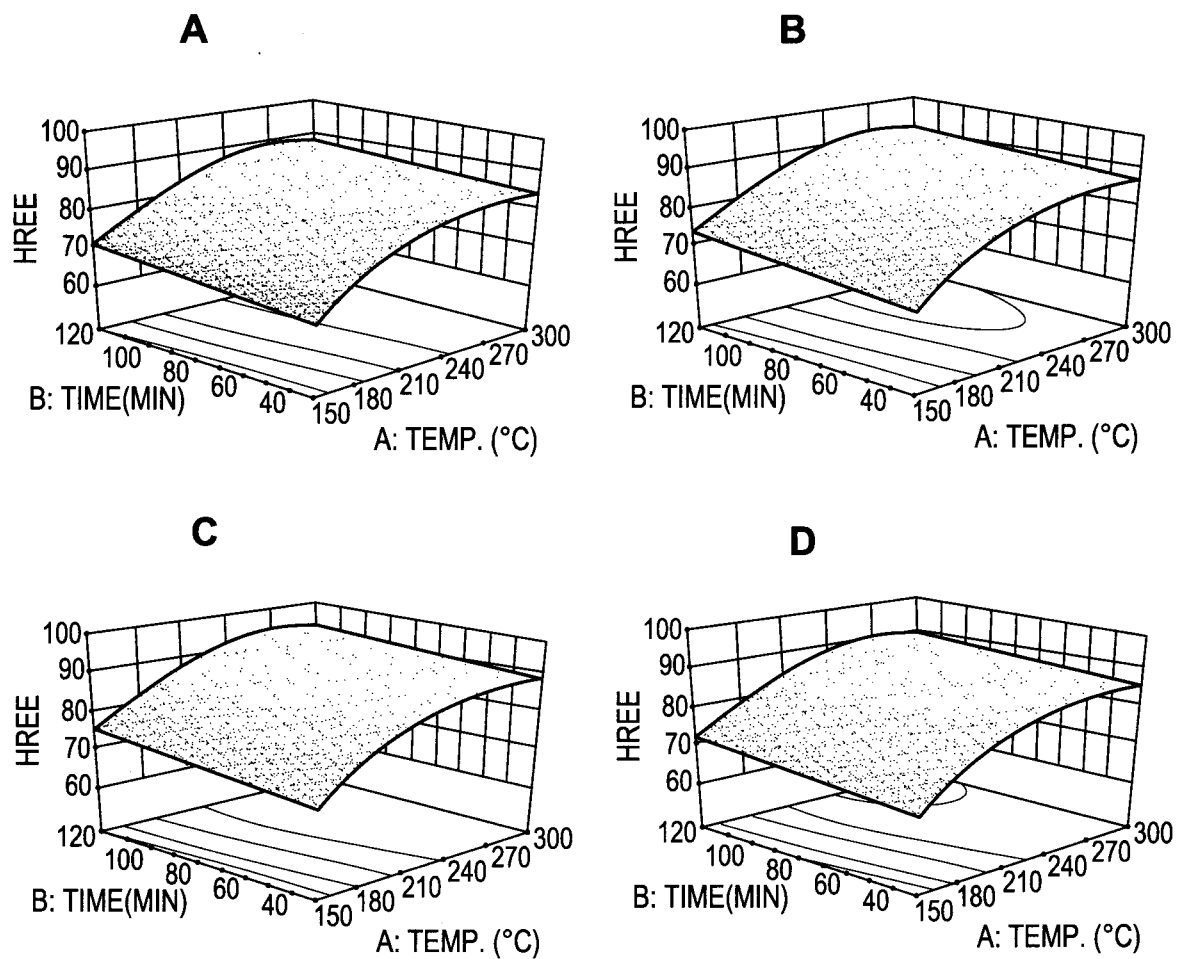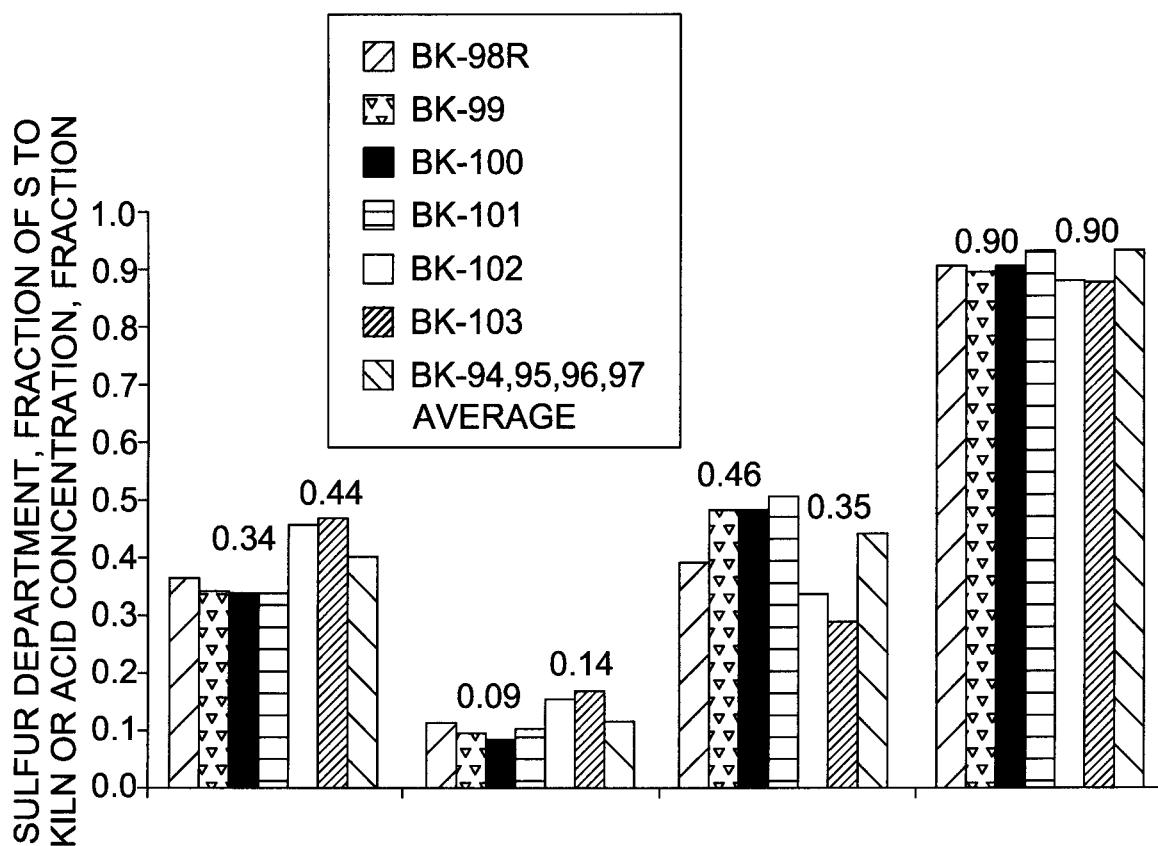
SULFUR DEPORTMENT AND ACID STRENGTH IN FIRST CONDENSER

	BK-98R	BK-99	BK-100	BK-101	BK-102	BK-103	BK-94-97
A)	600	590	600	590	500	500	500
B)	0	0.37	0	0.23	0	0.29	0
C)	3.0	3.0	1.5	1.5	3.0	3.0	1.5

A) H_2SO_4 ADDITION, kg/t ORE
B) H_2SO_4 RECYCLE, FRACTION OF TOTAL ADDED
C) BAKING TIME, h

FIG. 14

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FIG. 15

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CONCENTRATE $\downarrow H_2SO_4$ $\downarrow H_2SO_4$ $\downarrow H_2SO_4$

| BATCH MIXING | BATCH MIXING | BATCH MIXING |

| CONTINUOUS LT BAKE #1 (~280°C,ROTARY KILN) | CONTINUOUS LT BAKE #1 (~280°C,ROTARY KILN) | CONTINUOUS LT BAKE #2 (~300°C,ROTARY KILN) |

| PARTIALLY SULPHATED CALCINE (ACIDIC SOLIDS) | PARTIALLY SULPHATED CALCINE (ACIDIC SOLIDS) | SULPHATED CALCINE (ACIDIC SOLIDS) |

SO_2/SO_3 CAPTURE IN SCRUBBER

CONTINUOUS HT BAKE (~700°C,ROTARY KILN)

WATER → CONTINUOUS WATER LEACH (AMBIENT T)

WASH WATER → L / S →

LIQUOR FOR DOWNSTREAM PILOTING

FIG. 16

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CONCENTRATE H_2SO_4

BATCH MIXING

CRUSHING

CONTINUOUS LT BAKE
(~300°C, ROTARY KILN)   → SO_2/SO_3 CAPTURE IN SCRUBBER

SULPHATED CALCINE
(ACIDIC SOLIDS)

RECYCLED CALCINE

CONTINUOUS HT BAKE
(~700°C, ROTARY KILN)   → SO_2/SO_3 CAPTURE IN SCRUBBER

CRUSHING

WATER   → CONTINUOUS WATER LEACH (AMBIENT 1)

WASH WATER   → L / S

LIQUOR FOR
DOWNSTREAM PILOTING

FIG. 17

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A. CLASSIFICATION OF SUBJECT MATTER
    IPC: *C22B 1/06* (2006.01) , *B03B 9/00* (2006.01) , *C22B 3/04* (2006.01) , *C22B 3/22* (2006.01) ,
C22B 59/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: *C22B 59/00* (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
FAMPAT (Questel), Scopus, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR2826667A1 (RENOU et al.) 03 January 2003 (03-01-2003)	1-4, 6-7, 11, 13-16, 18, 22-27, 29, 33, 36-38, 40, 44-45, 47, 54-55
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Y		1-7, 9, 11, 13-16, 18, 22-29, 31, 33, 36-38, 40, 44-45, 47, 54-55
X	CN102864319A (WANG et al.) 09 January 2013 (09-01-2013)	1-4, 6-8, 11, 15-27, 29-30, 33, 35, 37-45, 47-51, 53
--		--
Y		1-4, 6-9, 11, 15-27, 29-31, 33, 35, 37-45, 47-51, 53

☑ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 February 2017 (20-02-2017)	14 March 2017 (14-03-2017)

Name and mailing address of the ISA/CA	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Jay Fothergill (819) 639-8455

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	FR2469462A1 (LAMBERT) 22 May 1981 (22-05-1981)	47-48, 53-55 -- 9, 31
Y	DE102014201939 (HANEBUTH et al.) 06 August 2015 (06-08-2015)	5, 28
A	JP2015187291A (SATO et al.) 29 October 2015 (29-10-2015)	
P, A	BORRA, C.R. et al. Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching. *Minerals Engineering* 92 (2016): 151-159.	

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
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CN102864319A	09 January 2013 (09-01-2013)	CN102864319A CN102864319B	09 January 2013 (09-01-2013) 04 February 2015 (04-02-2015)
FR2469462A1	22 May 1981 (22-05-1981)	FR2469462A1 FR2469462B1	22 May 1981 (22-05-1981) 11 December 1981 (11-12-1981)
DE102014201939	06 August 2015 (06-08-2015)	None	
JP2015187291A	29 October 2015 (29-10-2015)	None	