



- (51) International Patent Classification:  
C22B 3/04 (2006.01) H01J 9/52 (2006.01)  
C09K 11/01 (2006.01) C22B 59/00 (2006.01)
- (21) International Application Number:  
PCT/CA2013/000954
- (22) International Filing Date:  
8 November 2013 (08.11.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
61/724,022 8 November 2012 (08.11.2012) US
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:  
— with international search report (Art. 21(3))

(54) Title: PROCESS FOR RECOVERING RARE EARTH OXIDES FROM PHOSPHORS, FLUORESCENT LAMPS AND LIGHT BULBS, CATHODE RAY TUBES AND OTHER INDUSTRIAL WASTES

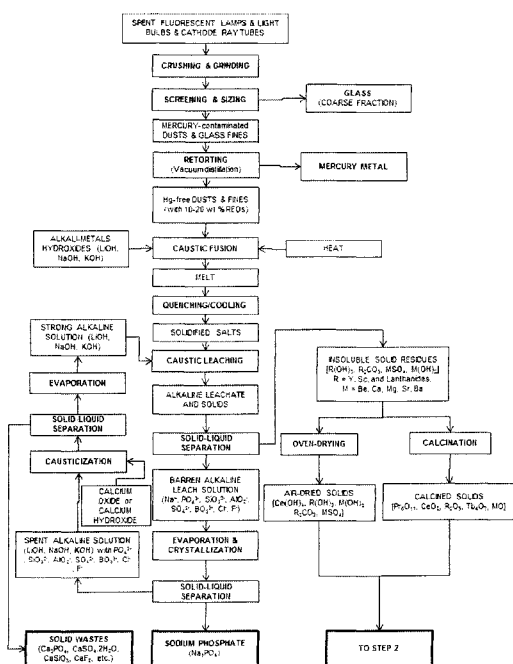


FIG. 1

(57) Abstract: The present disclosure broadly relates to a novel process for the recovery of rare earths oxides from phosphors, fluorescent lamps and light bulbs, cathode ray tubes and other industrial wastes containing rare earths elements in the form of halophosphates, tri-band phosphors and other fluorescent materials, the process comprising: a) submitting the wastes or spent materials to either caustic fusion or hot alkaline leaching; b) submitting the solidified melt to hot alkaline leaching step to produce insoluble solid residues and a barren alkaline leaching solution; c) crystallizing the tri-sodium phosphate from the barren solution; d) oven-drying or calcining the residues; e) acid leaching the oven-dried or calcined solids; f) recovering the cerium (IV) oxide from insoluble solids; g) reducing the cerium-free solution, precipitating, acid leaching, precipitating, calcining and recovering the europium (III) oxide; h) precipitating the remaining rare earths as oxalates; i) calcining the rare earths oxalates and dissolving the rare earths oxides in acid; j) separating the yttrium, gadolinium, terbium and erbium by ion exchange (IX) or solvent extraction (SX); h) precipitating and calcining to yield pure yttrium (III) oxide, gadolinium (III) oxide, terbium (III, IV) oxides, and erbium (III) oxide; i) regenerating and recycling the spent alkaline solution after causticization with calcium oxide or hydroxide.

WO 2014/071510 A1

**TITLE**

**PROCESS FOR RECOVERING RARE EARTH OXIDES FROM PHOSPHORS, FLUORESCENT LAMPS AND LIGHT BULBS, CATHODE RAY TUBES AND OTHER INDUSTRIAL WASTES**

**CROSS-REFERENCE TO RELATED APPLICATIONS**

**[0001]** The present application claims the benefit of priority from co-pending U.S. Provisional Application No. 61/724,022 filed on November 8, 2012, the contents of which are incorporated herein by reference in their entirety.

**FIELD**

**[0002]** The present disclosure relates to the combination of pyrometallurgical and hydrometallurgical processes for recovering rare earths oxides from phosphors, fluorescent lamps and light bulbs, cathode ray tubes, and other industrial wastes containing rare earths elements in the form of halophosphates, tri-band phosphors and other fluorescent materials.

**BACKGROUND**

**[0003]** Nowadays, the utilization of fluorescent lamps and fluorescent light bulbs is widely spread as these new lighting devices offer a cost effective alternative to former incandescent light bulbs. These light bulbs rely on the conversion of ultraviolet light, emitted by a low pressure electric discharge in a mercury vapor, to visible white light by means of inorganic luminophors also called simply phosphors. These phosphors consist mainly of doped inorganic compounds, the dopants are usually rare earth elements denoted by the commonly adopted acronym, REEs, consisting of the fifteen chemical elements of the lanthanide group with atomic number ranging from  $Z = 57$  for lanthanum (La) to  $Z = 71$  for Lutetium (Lu) plus the two elements scandium, Sc ( $Z = 21$ ) and yttrium, Y ( $Z = 39$ ). Among them yttrium, lanthanum, cerium, europium, gadolinium, terbium, and erbium as the most often used as dopants.

**[0004]** The technical difficulties encountered in the past for recovering efficiently the high valued rare earths elements (i.e., Y, Eu, Gd, Tb, Er) is mostly related to the fact that several types of phosphors chemistries are currently used and encountered in the spent fluorescent lamps and light bulbs.

**[0005]** First of all, former phosphors consisted of halophosphates, that is, a fluoro- or chloroapatite doped with Sb(III) or Mn(II)  $[\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl}):\text{Sb}^{3+},\text{Mn}^{2+}]$  and that emitted in the white spectrum. Since the 1960s the introduction of phosphors based on yttrium oxide or yttrium oxysulfide both doped with Eu(III) with the following chemical formula:  $\text{Y}_2\text{O}_3:\text{Eu}^{2+}$  and  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{2+}$ . These phosphors were mostly used in cathode ray tubes (CRTs). Today, most of the fluorescent lamps and light bulbs rely for their fabrication on three groups of phosphors also called tri-band phosphors. For the red color, the yttrium (III) oxide doped with Eu(II)  $[\text{Y}_2\text{O}_3:\text{Eu}^{2+}]$  that emits at a wavelength of 611 nm, for the green color, the xenotime type structure consisting of cerium and lanthanum phosphate  $(\text{Ce},\text{La})\text{PO}_4:\text{Tb}^{3+}$  and the spinel type cerium magnesium aluminum  $[\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}]$  both doped with Tb(III) and emitting at 543 nm, and finally for the blue color the barium magnesium aluminum spinel doped with Eu(II)  $[\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}^{2+}]$ .

**[0006]** More extensively, it is possible to group the chemical compounds identified in the fluorescent lamps and fluorescent light bulbs, cathode ray tubes from various origins and history into seven groups according to the anion chemistry, namely: inert silicates mainly the soda-lime glass from the broken tubes and slivers, halophosphates, phosphates, aluminates, oxides, and in a lesser extent borates, vanadates, fluorides and chlorides.

**[0007]** We can see clearly from Table 1, the complex chemistry that can be encountered during the processing of such industrial wastes. From a cations standpoint, apart the trivalent rare earth elements such as Y, Ce, La, Eu, Gd, Tb, and Er, we will have the divalent cations of the alkali-earths metals such as Mg, Ca, Sr, and Ba, together with Al, B, and V, along with some Fe and Mn together with Sb. On the anion side, we will have to deal with silicates, aluminates, phosphates and in lesser extent borates, sulfates, vanadates, fluorides and chlorides.

**[0008]** Industrially, at the end-of-life, the spent fluorescent lamps and light bulbs collected by hazardous wastes recyclers in North America and Europe are all sent to specialized processing facilities for the removal of mercury that poses environment, health, and safety issues for their disposal. During the processing, the spent fluorescent lamps and light bulbs are crushed by means of roller mill followed by screening and sizing using for instance vibrating screens of various size apertures. The coarse fraction (ca. 70 wt.%) consists mostly of soda-lime glass from slivers together with metals (e.g., filaments, electrodes, caps), plastics (caps, seals) and cement, while the remaining fine fraction (ca. 30 wt.%) contains phosphors dusts and glass fines. Afterwards, the removal of mercury from both fractions is usually performed by retorting that consists to evaporate under vacuum the mercury vapor and condensing it to yield pure liquid mercury metal which is sold on the market while mercury-free dusts and glass fines remain. This mercury-free fine fraction consists essentially of soda-lime glass fines together with halophosphates, tri-band phosphors and other fluorescent materials that contains most of the valuable rare earths elements mixed with an inert matrix made of silicates, together with phosphates, aluminates, and lesser extent borates, sulfates, vanadates, fluorides and chlorides compounds based on the typical composition described previously. Actually, the total content of rare earths elements of these mercury-free dusts and glass fines, expressed as rare earth oxides (REOs), ranges usually from 10 to 20 wt.%. Among these REOs, the concentration of yttrium (III) oxide ranges from 70 wt.% to 80 wt.% with the remaining 20-30 wt.% consisting of oxides of lanthanum, cerium, europium, gadolinium, terbium, and erbium. This complex chemistry renders the extraction and recovery of rare earths troublesome as some of these materials are refractory to most chemical treatments especially silicates and aluminates or they generate large volume of wastes upon chemical treatment that poses disposal issues because they contains deleterious compounds such as barium, lead, antimony, phosphates, and fluorides.

**[0009]** From the economic standpoint, such industrial wastes contain significant concentrations of europium, gadolinium, terbium, and erbium that are ranging, when expressed as a percentage of the total rare earths oxides (TREOs), from 1 to 5 wt.%. In the particular case of europium and terbium, this is well above the concentrations of

these rare earths elements in the best known ores occurring in nature. For comparison, in the Chinese ion-absorption clays, the maximum concentration of europium oxide ( $\text{Eu}_2\text{O}_3$ ) is 1 wt.% of TREOs, while for xenotime, the maximum concentration of terbium oxide ( $\text{Tb}_4\text{O}_7$ ) is 6 wt.% of TREOs. Hence a particular attention must be made to address the proper recovery and separation of europium, gadolinium, terbium, and erbium.

**[0010]** Therefore, the final REOs product obtained that will contain in addition to the light rare earths elements (LREEs) such as lanthanum, cerium and europium, the heavy rare earths elements (HREEs) present (i.e., Y, Gd, Tb, and Er) will yield a heavy rare earths oxides (HREOs) product with a much higher commercial value than most of the REOs concentrates currently obtained from natural ores (e.g., monazite and bastnaesite) and it might even compete with other naturally occurring HREE-sources mentioned previously such as ion exchange clays, and xenotime.

**[0011]** From the previous description, we see clearly that the processing of spent fluorescent lamps and light bulbs poses today serious economic, occupational, environmental and technical issues.

**[0012]** Several patents describe the chemical treatment of such industrial wastes. In WO2010/118967 to RHODIA, the process described is rather complicated. Actually, it consists first to perform an acid leaching of a mixture of halophosphates followed by the precipitation of the rare earths phosphates for separating them from alkaline-earth metals, and aluminum that remain in solution. Afterwards, a hot alkaline digestion is conducted on the wet solid residues with a concentrated solution of caustic soda in an autoclave in order to dissolve the refractory rare earth phosphates. The alkaline pregnant leach solution contains mostly all phosphates and fluoride anions and sodium cations, while the rare earths are precipitated as metal hydroxides and recovered by solid-liquid separation. Finally, the rare earths hydroxides are dissolved in nitric acid in order to be separated by common solvent extraction techniques that are currently used commercially.

**[0013]** In US patent 7,796,798 to OSRAM GmbH, the treatment of spent fluorescent light bulbs starts also with an acid leaching step that selectively dissolves the rare earths compounds based on their different dissolution behavior in various acidic and alkaline reagents.

**[0014]** First of all, all the processes described in the prior art, the processing starts by performing a mandatory acid leaching step with various acids such as hydrochloric or nitric or mixtures of these acids. The utilization of acid leaching process as disclosed in the prior art is not suitable for wastes containing halophosphates because of their elevated content of phosphates that produces large amount of phosphoric acid that yields to the precipitation of several rare earths elements. Moreover, the possible presence of sulfides requires an oxidative treatment to oxidize them into soluble sulfates and avoid the evolution of noxious hydrogen sulfide gas that poses serious occupational and environmental issues.

**[0015]** Secondly, the recovery of rare earths oxides is strongly impacted by the nature of the anions present. Apart the issue related to the phosphates discussed above, the presence of silicates, sulfates, borates, vanadates, chlorides and fluorides also impact negatively the processing and a processing route with a step for removing them in the early stage is mandatory to improve the extraction efficiency.

**[0016]** Thirdly, from an economic standpoint, the aim is to recover the critical rare earths elements especially europium, gadolinium, terbium and erbium that are the most valuable.

**[0017]** Finally, due to increased environmental concerns and stringent regulations, the regeneration of reactants and the recycling of spent or depleted solutions and waste streams are mandatory to minimize the environmental footprint.

**[0018]** Not only a technically improved, safer and environmentally friendly processing route will reduce the processing cost significantly, but the novel process will also greatly improve the life cycle of the rare earths elements.

**[0019]** There thus remains a need for a unique, simple, cost effective, less energy demanding and safer process allowing for recovering rare earths oxides from

spent phosphors, spent fluorescent lamps and light bulbs, cathode ray tubes and other electronic wastes containing rare earths elements in the form of halophosphates, tri-band phosphors and fluorescent materials.

**[0020]** The present description refers to a number of documents, the content of which is herein incorporated by reference in their entirety.

### **SUMMARY**

**[0021]** The present disclosure broadly relates to a novel process for recovering rare earths oxides from phosphors, fluorescent lamps and light bulbs, cathode ray tubes and other electronic wastes containing rare earths elements in the form of halophosphates, tri-band phosphors and fluorescent materials.

**[0022]** In an embodiment, the present specification relates to a process for recovering rare earths oxides from spent fluorescent lamps and light bulbs, the process comprising: a) submitting the mercury-free phosphors dusts and glass fines that contains the rare earths elements to a caustic fusion or an alkali fusion using a melt comprising at least one salt of an alkali metal to produce a solidified melt; b) submitting the solidified melt to hot alkaline leaching step either under atmospheric conditions or under pressure to produce insoluble solid residues and a barren leaching solution comprising mostly the phosphates anions and in a lesser extent silicates, aluminates, borates, vanadates, sulfates, chlorides, and fluorides anions;

**[0023]** In an embodiment of the present disclosure, the caustic fusion can be omitted and the mercury-free phosphors dusts and glass fines undergoing directly a hot alkaline leaching step either under atmospheric conditions or under pressure to produce insoluble solid residues and an alkaline barren leaching solution comprising mostly the phosphates anions and in a lesser extent silicates, aluminates, borates, vanadates, sulfates, chlorides, and fluorides anions.

**[0024]** In an embodiment of the present disclosure, the process further comprises separating by solid-liquid separation techniques the insoluble solid residues containing the oxides and hydroxides of rare earth elements (REEs) [e.g.,  $R(OH)_3$  with

R = Sc, Y, and lanthanides], rare earths elements carbonates [e.g.,  $R_2(CO_3)_2$  with R = Sc, Y, and lanthanides], alkali-earth metals hydroxides [e.g.,  $M(OH)_2$ ], alkali-earth metals carbonates [e.g.,  $MCO_3$ ] and oxides, hydroxides and carbonates of iron [e.g.,  $Fe_2O_3$ ,  $Fe(OH)_3$ ,  $FeCO_3$ , etc.] and eventually insoluble alkali-earth metals sulfates [ $MSO_4$ ] with M being an alkali-earth metal such as calcium, barium or strontium.

**[0025]** In an embodiment of the present disclosure, the process further comprises recovering the crystals of tri-sodium phosphate ( $Na_3PO_4$ ) by evaporation, followed by crystallization and solid-liquid separation from the barren alkaline leach solution produced after the caustic leaching.

**[0026]** In an embodiment of the present disclosure, the process comprises recycling the spent and depleted solution after the crystallization and separation of tri-sodium phosphate. This step consists by performing the causticization by adding calcium hydroxide or calcium oxide for precipitating the residual phosphates anions together with silicates, sulfates, borates and fluorides anions as insoluble calcium salts. After solid-liquid separation of the precipitated solids, the replenished and strong alkaline solution is suitable for performing the caustic leaching step.

**[0027]** In an embodiment of the present disclosure, the process further comprises oven-drying or calcining in air the insoluble solid residues from the alkaline leaching to oxidize all the cerium (III) into cerium (IV) while the oxidation state of the remaining rare earths elements remains unaffected as trivalent cations ( $R^{3+}$ ), together with the oxides and/or hydroxides of alkali-earths metals.

**[0028]** In an embodiment of the present disclosure, the process further comprises performing the acid leaching of the oven-dried or calcined solids.

**[0029]** In an embodiment of the present disclosure, the process further comprises separating by solid-liquid separation techniques the cerium (IV) compounds [e.g.,  $Ce(OH)_4$  and  $CeO_2$ ] as insoluble solids.

**[0030]** In an embodiment of the present disclosure, the process further comprises calcining the cerium (IV) compounds to yield pure cerium (IV) oxide ( $CeO_2$ ).

**[0031]** In an embodiment of the present disclosure, the process further



comprises reducing the trivalent europium (III) cations into divalent europium (II) cations in the acidic filtrate by adding a reducing agent such as zinc, magnesium or aluminum metals or their alloys.

**[0032]** In an embodiment of the present disclosure, the process further comprises adding barium chloride and then sulfuric acid or a soluble alkali-metal sulfate in order to co-precipitate barium and europium sulfates  $[(Ba, Eu)SO_4]$ .

**[0033]** In an embodiment of the present disclosure, the process further comprises separating the co-precipitate of barium and europium sulfates by solid-liquid separation techniques.

**[0034]** In an embodiment of the present disclosure, the process further comprises performing an oxidative acid leaching of the co-precipitate of barium and europium sulfates by for instance with nitric acid to fully oxidize europium (II) to europium (III).

**[0035]** In an embodiment of the present disclosure, the process further comprises separating by solid-liquid separation the insoluble barium sulfate from the acidic solution containing all the soluble europium (III) cations.

**[0036]** In an embodiment of the present disclosure, the process further comprises precipitating the europium (III) hydroxide from the acidic solution by neutralizing and adjusting the pH by adding for instance a neutralizing agent such as ammonia or sodium hydroxide.

**[0037]** In an embodiment of the present disclosure, the process further comprises performing the calcination of the europium (III) hydroxide  $[Eu(OH)_3]$  to yield europium (III) oxide  $(Eu_2O_3)$ .

**[0038]** In an embodiment of the present disclosure, the process further comprises precipitating the remaining rare earths elements from the cerium-free and europium-free acidic pregnant leach solution as rare earths oxalates by adjusting the pH and by adding a solution of containing oxalic acid or an alkali-metal oxalate;

**[0039]** In an embodiment of the present disclosure, the process further

comprises separating by solid-liquid separation and performing the calcination of the precipitate of rare earths oxalates to yield cerium-free and europium-free mixture of rare earths oxides (REOs) containing mostly scandium, yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium as rare earths (III) oxides (e.g.,  $Y_2O_3$ ,  $Ln_2O_3$ ) or complex rare earths oxides (e.g.,  $Pr_6O_{11}$ ,  $Tb_4O_7$ ).

**[0040]** In an embodiment of the present disclosure, the process further comprises dissolving the cerium-free and europium-free mixture of rare earths oxides in hot hydrochloric or hot nitric acid and performing the selective separation of yttrium, gadolinium, terbium and erbium by means of ion exchange (IX) or solvent extraction (SX).

**[0041]** In an embodiment of the present disclosure, the process further comprises precipitating from each individual stream the oxalates of yttrium, gadolinium, terbium and erbium followed by the calcination of each single oxalates to yield pure yttrium (III) oxide ( $Y_2O_3$ ), pure gadolinium (III) oxide ( $Gd_2O_3$ ), pure erbium (III) oxide ( $Er_2O_3$ ), and pure terbium (III, IV) oxides ( $Tb_4O_7$ ).

**[0042]** In an embodiment of the present specification, the caustic fusion or alkali fusion comprises using a molten alkali-metal hydroxide of formula MOH, wherein M is selected from the group consisting of Li, Na and K.

**[0043]** In an embodiment of the present specification, the molten alkali-metal hydroxide is selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide and mixtures thereof.

**[0044]** The foregoing and other objects, advantages and features of the present disclosure will become more apparent upon reading of the following nonrestrictive description of illustrative embodiments thereof, given by way of example only with reference to the accompanying drawings, and which should not be interpreted as limiting the scope of the present disclosure.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0045]** In the appended drawings/figures:

**[0046]** **FIG. 1** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the mercury-free dusts and glass fines undergo a caustic fusion with molten alkali-metal hydroxides. Moreover, the melt once solidified is submitted to the caustic leaching with an aqueous solution of alkali-metal hydroxides; afterwards the recovery of tri-sodium phosphate by crystallization, the regeneration of the spent and depleted alkaline solution by causticization, and the recovery of rare earths oxides is performed.

**[0047]** **FIG. 2** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the mercury-free dusts and glass fines undergo directly a hot caustic leaching either at atmospheric pressure or under pressure with an aqueous solution of alkali-metal hydroxides; afterwards the recovery of tri-sodium phosphate by crystallization, the regeneration of the spent and depleted alkaline solution by causticization, and the recovery of rare earths oxides product is performed.

**[0048]** **FIG. 3** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the first separation and recovery of cerium (IV) oxide, the second separation recovery of europium (III) oxide and finally the separation of other rare earths oxides especially yttrium (III) oxide, gadolinium (III) oxide, terbium (III, IV) oxides, and erbium (III) oxide is performed from the rare earth oxides product obtained from the oven-dried or calcined solid residues obtained at the end of STEP 1A or 1B.

### **DETAILED DESCRIPTION**

#### **DEFINITIONS**

**[0049]** In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein

have the same meaning as commonly understood by one of ordinary skill in the art to which this specification pertains.

**[0050]** Unless otherwise indicated, the definitions and embodiments described in this and other sections are intended to be applicable to all embodiments and aspects of the application herein described for which they are suitable as would be understood by a person skilled in the art.

**[0051]** The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one”, but it is also consistent with the meaning of “one or more”, “at least one”, and “one or more than one”. Similarly, the word “another” may mean at least a second or more.

**[0052]** As used in this specification and claim(s), the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), having (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “include” and “includes”), or “containing” (and any form of containing, such as “contain” and “contains”), are inclusive and open-ended and do not exclude additional, unrecited elements or process steps.

**[0053]** The term “about” is used to indicate that a value includes an inherent variation of error for the device or the method being employed to determine the value.

**[0054]** As used herein, the term “rare earths elements”, with the acronym REEs and symbol R used in chemical formulas, denotes the two chemical elements scandium (Sc) and yttrium (Y) plus the fifteen chemical elements of the lanthanide group also called lanthanides or lanthanoids with atomic number ranging from Z =57 (Lanthanum) to Z = 71 (Lutetium) and denoted with the symbol Ln in chemical formulas.

**[0055]** As used herein, the term “rare earths oxides” with the acronym REOs denotes the oxides of the two chemical elements scandium (Sc) and yttrium (Y) plus the oxides of the fifteen chemical elements of the lanthanide group also called lanthanides with atomic number ranging from Z =57 (Lanthanum, La) to Z = 71 (Lutetium, Lu).

**[0056]** As used herein, the term "light rare earths oxides" with the acronym LREOs denotes the oxides of the chemical elements scandium (Sc) the oxides of the seven chemical elements of the lanthanide group with atomic number ranging from Z =57 (Lanthanum, La) to Z = 63 (Europium, Eu).

**[0057]** As used herein, the term "heavy rare earths oxides" with the acronym HREOs denotes the oxides of the chemical elements yttrium (Y) plus the oxides of the eight chemical elements of the lanthanide group with atomic number ranging from Z =64 (Gadolinium, Gd) to Z = 71 (Lutetium, Lu).

**[0058]** As used herein, the term "dusts and glass fines" refers to the intimate mixture of dusts of spent phosphors and glass fines obtained after the crushing and screening the spent fluorescent lamps and light bulbs, or cathode ray tubes that consists essentially of soda-lime glass fines together with halophosphates, tri-band phosphors and other fluorescent materials that contains most of the rare earths elements values.

**[0059]** As used herein, the term "mercury-free dusts and glass fines" refers to the previously described "dusts and glass fines" by-produced after the vacuum retorting for removing the mercury. In the following description, all the processed wastes will be assumed to be mercury-free materials.

**[0060]** The term "substantially" as used herein with reference to the process steps disclosed herein means that the process steps proceed to an extent that conversion or recovery of the material is maximized. For example, with reference to recovery of a given metallic value, recovery means that at least 90% of the value is recovered.

**[0061]** The present specification broadly relates to a process for recovering rare earths oxides from spent luminophors and phosphors, spent fluorescent lamps and light bulbs, cathode ray tubes and other electronic wastes containing halophosphates, tri-band phosphors and other fluorescent materials that contain most of the rare earths elements.

**[0062]** In an embodiment, the present specification relates to a process for recovering rare earths oxides from spent fluorescent lamps and light bulbs, by submitting the mercury-free dusts and glass fines, to a molten caustic fusion or an alkali fusion using a melt comprising at least one alkali metal hydroxides;

**[0063]** The process comprises a high temperature caustic fusion or alkali fusion step followed by a hydrometallurgical alkaline or caustic leaching step with the production of insoluble solid residues containing most of the rare earth elements and alkali-metals together with a barren alkaline leach solution containing mostly sodium phosphate and other sodium salts such as silicates, borates, aluminates, vanadates, chlorides and fluorides. The process further comprises precipitation steps, leaching steps, ion exchange steps and calcination steps ultimately yielding substantially cerium oxide, europium oxide, yttrium oxide, erbium oxide and terbium oxides or mixtures of these oxides. Finally, the process comprises steps for the recovery of sodium phosphate and the regeneration of at least some of the reactants such as the spent alkaline leaching solution by performing a causticization with calcium oxide or calcium hydroxide.

**[0064]** In an embodiment of the present disclosure, in certain cases the caustic fusion can be omitted and the mercury-free dusts and glass fines undergo directly a hot alkaline leaching step either under atmospheric pressure or under pressure inside an autoclave in order to produce insoluble solid residues and an alkaline barren leaching solution comprising mostly the sodium and phosphates anions and in a lesser extent silicates, aluminates, sulfates, borates, vanadates, chlorides and fluorides anions;

**[0065]** The process comprises a high temperature caustic fusion or alkali fusion step. This high temperature pyrometallurgical step includes subjecting the mercury-free dusts and glass fines to a molten caustic fusion or a molten alkali fusion using a melt comprising an alkali-metal hydroxide. The alkali-metal hydroxide has the general formula MOH, wherein M is selected from the group consisting of Li, Na and K. Accordingly, non-limiting examples of alkali-metal hydroxides include potassium hydroxide, sodium hydroxide, lithium hydroxide and mixtures thereof. Eventually, alkali metal peroxide is added to the melt. The alkali-metal peroxide has the general formula

$M_2O_2$ , wherein M is selected from the group consisting of Li, Na and K. The alkali-metal hydroxide and peroxide typically have the same M value (i.e. both are either Li, Na or K). The addition of the peroxide ensures that essentially all the cerium content is oxidized to its tetravalent oxidation state ( $Ce^{4+}$ ). In a further embodiment, an alkali-metal carbonate of formula  $M_2CO_3$  or an alkali-metal nitrate of formula  $MNO_3$  are added to the melt, wherein M is selected from the group consisting of Li, Na and K. The addition of the alkali-metal carbonate or alkali-metal nitrate improves the fluxing properties of the melt by lowering the melting temperature of the alkali mixture and by increasing the fluidity of the melt.

**[0066]** In an embodiment of the present disclosure, the melt comprises more than one alkali-metal hydroxide (alkali-metal hydroxide blend). In this embodiment, the individual alkali-metal hydroxide can be melted individually and then combined, or melted together to produce the melt to be used in the fusion step. This prior melting drives-off all residual moisture and hydration water. In a further embodiment, the alkali-metal hydroxide blend is allowed to cool prior to be used in the fusion step.

**[0067]** In an embodiment of the present disclosure, the mercury-free dust and glass fines are fed directly into the melt once the desired operating temperature is reached and subsequently continuously stirred. In a further embodiment of the present disclosure, the mercury-free dusts and fines are added on top of a solidified melt comprising at least one alkali-metal hydroxide followed by raising the temperature until melting of the mixture has occurred. In yet a further embodiment of the present disclosure, the mercury-free dusts and glass fines are mixed with at least one alkali-metal hydroxide that has been previously ground followed by raising the temperature until melting of the mixture has occurred.

**[0068]** In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio of dusts and fines (F) to mass of melt material (i.e. mass of molten hydroxide salt) (M) denoted as F:M or F/M ranging from 1:1 to 1:20. In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio maintaining a low melt viscosity and allowing for substantially complete dissolution of the products. In an

embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio ranging from 1:1 to 1:15. In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio ranging from 1:1 to 1:10. In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio ranging from 1:1 to 1:6.

**[0069]** In an embodiment of the present disclosure, the caustic or alkali fusion step is performed at a temperature of at least the melting point of the alkali metal salt (i.e. alkali metal hydroxide). In cases where the melt comprises more than one alkali-metal hydroxide, the caustic or alkali fusion step is performed at a temperature of at least the eutectic temperature of the alkali mixture. In an embodiment of the present disclosure, the melt temperature ranges from about 200°C to about 1200°C. In a further embodiment of the present disclosure, the melt temperature ranges from about 300°C to about 1000°C. In a further embodiment of the present disclosure, the melt temperature ranges from about 300°C to about 1000°C. In a further embodiment of the present disclosure, the melt temperature ranges from about 400°C to about 900°C. As the fusion reaction typically proceeds with evolution of steam and caustic fumes, the operating temperature is sometimes increased in order to compensate for heat losses and to keep the charge fully liquid. The maximum operating temperatures are typically dictated so as to prevent losses in molten salts by intense evaporation of caustic fumes and by the limited number of corrosion resistant materials commercially available in which to perform the fusion reaction.

**[0070]** In an embodiment of the present disclosure, the caustic or alkali fusion step is performed over a period of time ranging from 5 minutes to 6 hours. In a further embodiment of the present disclosure, the caustic or alkali fusion step is performed over a period of time ranging from 10 minutes to 4 hours. In a further embodiment of the present disclosure, the caustic or alkali fusion step is performed over a period of time ranging from 15 minutes to 2 hours. In a further embodiment of the present disclosure, the caustic or alkali fusion step is performed over a period of time ranging from 15 minutes to 1 hour.



**[0071]** In an embodiment of the present disclosure, the caustic or alkali fusion step is performed either batch wise using a crucible furnace or a muffle furnace or in continuous mode using a rotary kiln or a rotary heart furnace. In a further embodiment of the present disclosure, the caustic or alkali fusion step is performed by means of direct flame heating, gas fired burners, radiant gas heaters, external electrical heaters, Joule heating by immersed AC or DC electrodes, or by induction heating of the crucible used as susceptor. Other suitable heating means for performing the caustic or alkali fusion step are known in the art, and are within the capacity of a skilled technician.

**[0072]** In an embodiment of the present disclosure, the caustic or alkali fusion step is performed using a containment vessel or crucible comprising a construction material capable of withstanding both the high operating temperatures as well as the inherent corrosiveness of the molten alkali-metal hydroxide(s) without contaminating the melt by releasing deleterious metallic impurities. Suitable materials include metals such as pure nickel (Ni) and nickel alloys, pure zirconium (Zr) and zirconium alloys, and their alloys; pure iron (Fe), nickel cast iron, cast irons; mild steels; and non-metals such as graphite and carbon-based materials. Further suitable materials include metallic composite materials comprising inexpensive bulk commercial alloys such as heat resistant stainless steels; copper-nickel and high nickel-alloys coated with an inert, protective and impervious metal lining composed of a highly corrosion resistant pure metal or alloy. Protective lining materials include gold (Au), gold alloys, silver (Ag), silver alloys, nickel (Ni), nickel alloys, iron (Fe), iron alloys, zirconium (Zr), and zirconium alloys, hafnium (Hf), hafnium alloys and combinations thereof. The protective lining materials can be applied by various techniques such as electroplating, electroless plating, physical or chemical vapor deposition, mechanical cladding, loose lining and explosion bonding. Yet further suitable materials include advanced ceramic materials useful as refractory brick linings, castables and coatings. Non-limiting examples of such ceramic materials include graphite, diamond like carbon (DLC), carbon-carbon composites, silicon carbide (SiC), fused zirconia (ZrO<sub>2</sub>), fused magnesia (MgO), fused ceria (CeO<sub>2</sub>), fused calcia (CaO) and combinations thereof.

**[0073]** The melt produced following the caustic or alkali fusion step is

subsequently subjected to a hot alkaline leaching step. In an embodiment of the present disclosure, the melt produced as a result of the caustic or alkali fusion step is transferred while hot into alkaline water. The transfer may be accomplished by either pouring or scooping the melt into the cold alkaline water. In a further embodiment, the melt, once cooled and still in the crucible, is demoulded onto a hard surface acting as a heat sink and is subsequently transferred into alkaline water. In a further embodiment, the crucible comprising the melt is cooled after which alkaline water is added to the crucible.

**[0074]** In an embodiment of the present disclosure, the solidified melt is subjected to a hot alkaline leaching step either under atmospheric conditions or under pressure. In an embodiment of the present disclosure, the alkaline leaching step is performed using an aqueous solution of alkali-metal hydroxide (MOH) with M being an alkali-metal such as sodium, potassium or lithium, or a mixture thereof. In an embodiment of the present disclosure, the aqueous alkaline solution comprises a concentration ranging from 5 mass percent up to 50 mass percent MOH. In a further embodiment of the present disclosure, the temperature of the alkali-metal hydroxide solution ranges from room temperature to the boiling point of the solution. In yet a further embodiment of the present disclosure, the pH of the alkaline solution is at least 13.

**[0075]** In an embodiment of the present disclosure, and under certain circumstances, the first caustic fusion step can be omitted and the mercury-free spent dusts and glass fines can be directly treated by hot alkaline leaching step either under atmospheric conditions or under pressure performed inside an autoclave in order to produce insoluble solid residues and an alkaline barren leaching solution comprising mostly sodium phosphate and in a lesser extent silicates, aluminates, borates, sulfates, vanadates, chlorides, and fluoride salts.

**[0076]** In an embodiment of the present disclosure, the hot alkaline leaching step performed directly on the mercury-free dusts and glass fines using a concentrated aqueous solution of alkali-metal hydroxide (MOH) with M being an alkali-metal such as sodium, potassium or lithium, or a mixture thereof. In an embodiment of the present

disclosure, the aqueous alkaline solution comprises a concentration ranging from 5 mass percent MOH up to 50 mass percent of MOH. In a further embodiment of the present disclosure, the temperature of the alkali-metal hydroxide solution ranges from room temperature to the boiling point of the solution.

**[0077]** In an embodiment of the present disclosure, the hot alkaline leaching step is performed either batch wise or in continuous mode.

**[0078]** In an embodiment of the present disclosure, the caustic fusion and/or alkaline leaching step are performed using a containment vessel or autoclave comprising a construction material capable of withstanding both the high operating temperatures as well as the inherent corrosiveness of the concentrated alkali-metal hydroxide(s) solution without contaminating the liquor by releasing deleterious metallic impurities. Suitable materials include metals such as pure nickel (Ni) and nickel alloys, pure zirconium (Zr) and zirconium alloys, and their alloys; pure iron (Fe), nickel cast iron, cast irons; mild steels; and non-metals such as graphite and carbon-based materials. Further suitable materials include metallic composite materials comprising inexpensive bulk commercial alloys such as heat resistant stainless steels; copper-nickel and high nickel-alloys coated with an inert, protective and impervious metal lining composed of a highly corrosion resistant pure metal or alloy. Protective lining materials include gold (Au), gold-alloys, silver (Ag), silver-alloys, nickel (Ni), nickel-alloys, iron (Fe), iron-alloys, zirconium (Zr), zirconium-alloys, hafnium (Hf), hafnium-alloys and combinations thereof. The protective lining materials can be applied by various techniques such as electroplating, electroless plating, physical or chemical vapor deposition, mechanical cladding, loose lining and explosion bonding. Yet further suitable materials include advanced ceramic materials useful as refractory brick linings, castables and coatings. Non-limiting examples of such ceramic materials include graphite, diamond like carbon (DLC), carbon-carbon composites, silicon carbide (SiC), fused zirconia (ZrO<sub>2</sub>), fused magnesia (MgO), fused ceria (CeO<sub>2</sub>), fused calcia (CaO) and combinations thereof.

**[0079]** The alkaline leach solution together with a suspension of non-dissolved solids and particulates produced by the hot alkaline leaching is subjected to common

solid-liquid separation techniques, such as gravity settling, filtration or centrifugation. The solid residues obtained following solid-liquid separation consist essentially of insoluble compounds rare earths (i.e., Y, Sc, and lanthanides), alkali-earths metals, and in a lesser extent iron if present as an impurity. These solid residues are typically insoluble under the strongly alkaline conditions prevailing in the pregnant leach solution. Examples of non-soluble compounds found in the solid residues are oxides and hydroxides of rare earth elements (REEs) [e.g.,  $R(OH)_3$ ], rare earths elements carbonates [e.g.,  $R_2(CO_3)_2$ ], alkali-earth metals hydroxides [e.g.,  $M(OH)_2$ ], alkali-earth metals carbonates [e.g.,  $MCO_3$ ] and iron oxides, hydroxides and carbonates [e.g.,  $Fe_2O_3$ ,  $Fe(OH)_3$ ,  $FeCO_3$ , etc.] and eventually insoluble alkali-earth metals sulfates [ $MSO_4$ ] with M being an alkali-earth metal such as calcium, barium or strontium.

**[0080]** In a further embodiment of the present disclosure, the wet filter cake obtained following solid-liquid separation is thoroughly washed with a hot aqueous solution of alkali metal hydroxides.

**[0081]** The barren alkaline leach solution that contains mostly sodium phosphate together with silicates, aluminates, sulfates, borates, vanadates, chlorides and fluorides salts is subjected to a concentration step performed by evaporation, followed by the crystallization for separating the crystals of tri-sodium phosphate ( $Na_3PO_4$ ) by solid-liquid separation.

**[0082]** In an embodiment of the present disclosure, the process further comprises recycling the spent alkaline solution remaining after the crystallization and separation of tri-sodium phosphate. The regeneration consists to perform the causticization by adding calcium hydroxide or calcium oxide in order to precipitate all the residual phosphates anions together with silicates, aluminates, sulfates, borates, vanadates, and fluorides anions as insoluble calcium salts and to obtain a replenished and concentrated alkaline solution of alkali-metal hydroxide suitable to be reused for the caustic leaching step.

**[0083]** The washed insoluble solid residues obtained after alkaline leaching are subsequently either oven-dried in air between 60°C and 200°C or calcined in air high temperature ranging from 300°C until 1200°C. The purpose of these steps is to

completely oxidize all the cerium (III) to its tetravalent oxidation state as cerium (IV) which forms insoluble compounds such as cerium (IV) hydroxide or cerium (IV) oxide.

**[0084]** In an embodiment of the present specification, the oven-dried product consists mainly of a mixture of hydroxides of rare earth elements (REEs) [e.g.,  $\text{Ce}(\text{OH})_4$ ,  $\text{R}(\text{OH})_3$ ], rare earths elements carbonates [e.g.,  $\text{R}_2(\text{CO}_3)_2$ ], alkali-earth metals hydroxides [e.g.,  $\text{M}(\text{OH})_2$ ], alkali-earth metals carbonates [e.g.,  $\text{MCO}_3$ ] and iron oxides, hydroxides and carbonates [e.g.,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{FeCO}_3$ , etc.] and eventually insoluble alkali-earth metals sulfates [ $\text{MSO}_4$ ] with M being an alkali-earth metal such as calcium, barium or strontium.

**[0085]** In an embodiment of the present specification, the calcined product comprises substantially all of the cerium oxidized to cerium (IV) [e.g.,  $\text{CeO}_2$ ] along with other rare earths oxides (REOs) [e.g.,  $\text{R}_2\text{O}_3$ ] with R being a lanthanide element from La up to Lu together with complex lanthanide oxides [e.g.,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Tb}_4\text{O}_7$ ], alkali-earth metals oxides [e.g.,  $\text{MO}$ ], and iron oxides [e.g.,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ] and eventually alkali-earth metals sulfates [ $\text{MSO}_4$ ] with M being an alkali-earth metal such as calcium, barium or strontium.

**[0086]** In an embodiment of the present disclosure, the oven-dried or calcined solids are then subjected to acid leaching performed with dilute acid at a pH ranging between 0 and 4, for dissolving most of the rare earths elements (REEs) values yielding an acidic pregnant leach solution (PLS) and an insoluble solid residue containing all the cerium values as cerium (IV) compounds [e.g.,  $\text{Ce}(\text{OH})_4$ ,  $\text{CeO}_2$ ].

**[0087]** In an embodiment of the present disclosure, the acid leaching is performed using either hydrochloric acid or nitric acid or a mixture thereof.

**[0088]** In an embodiment of the present disclosure, the insoluble solid residues containing all the cerium values as cerium (IV) compounds [e.g.,  $\text{Ce}(\text{OH})_4$ ,  $\text{CeO}_2$ ] is separated by usual solid liquid separation such as gravity settling, filtration, or centrifugation, thoroughly washed with diluted acid and then with deionized water.

**[0089]** In an embodiment of the present disclosure, the washed cerium (IV) compound is oven-dried between  $60^\circ\text{C}$  and  $150^\circ\text{C}$  and then calcined in air between

300°C and 1200°C to yield pure cerium (IV) oxide [e.g., CeO<sub>2</sub>].

**[0090]** In an embodiment of the present disclosure, the cerium-free acidic solution that contains all the other lanthanides is then contacted with a reducing agent such as metallic zinc, aluminum or magnesium or alloys thereof (e.g., shot, flakes, chunks, or powder) in order to reduce substantially all the europium (III) to europium (II).

**[0091]** In an embodiment of the present disclosure, an aqueous solution of barium chloride (BaCl<sub>2</sub>) is then added to the reduced solution and a stoichiometric amount of dilute sulfuric acid or alkali-metal sulfate is subsequently added in order to co-precipitate the insoluble barium and europium sulfates [(Ba,Eu)SO<sub>4</sub>]. The completion of the europium precipitation is verified by visible spectrophotometry by measuring the absorbance of the supernatant at the characteristic wavelength of 394 nm [i.e., peak of maximum absorption for Eu(II)].

**[0092]** In an embodiment of the present disclosure, the process further comprises separating the co-precipitate of barium and europium sulfates by solid-liquid separation techniques.

**[0093]** In an embodiment of the present disclosure, the process further comprises performing an oxidative acid leaching of the co-precipitate of barium and europium sulfates for instance with hot nitric acid to fully oxidize europium (II) to europium (III) cations that are soluble.

**[0094]** In an embodiment of the present disclosure, the process further comprises separating by solid-liquid separation the insoluble barium sulfate from the acidic solution containing all the soluble europium (III) cations.

**[0095]** In an embodiment of the present disclosure, the process further comprises neutralizing the acidic solution containing the europium (III) and precipitating europium as europium (III) hydroxide by adding a neutralizing agent such as ammonia, or alkali-metal hydroxide (e.g., NaOH, KOH, LiOH).

**[0096]** In an embodiment of the present disclosure, the process further comprises performing the separation of the precipitated europium (III) hydroxide,

washing, oven-drying between 60°C and 200°C, calcining between 300°C and 1200°C the europium (III) hydroxide [Eu(OH)<sub>3</sub>] to yield europium (III) oxide (Eu<sub>2</sub>O<sub>3</sub>);

**[0097]** In an embodiment of the present disclosure, the cerium- and europium-free acidic solution that contains the remaining lanthanides especially all the yttrium, gadolinium, terbium and erbium values is subjected to a precipitation of the rare earths as rare earths oxalates by adding a saturated solution of oxalic acid (ca. 10 wt.% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) or an alkali-metal oxalate in order to separate them from impurities such as magnesium, sodium, sulfates, etc.

**[0098]** In an embodiment of the present disclosure, the pH of the cerium- and europium-free acidic solution is subsequently adjusted to a range from about 0.5 to 2.5. In an embodiment of the present disclosure, the pH of the solution is adjusted to a range from about 1.0 to 2.0. In an embodiment of the present disclosure, the pH of the acid leachate is adjusted to about 1.5. Following pH adjustment, a saturated solution of oxalic acid (ca. 10 wt.% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is added and the solution is allowed to stand overnight resulting in substantially all of the rare earth elements (REEs) and eventually alkali-earth metals (M = Ca, Sr, Ba) precipitating out of the solution in the form of insoluble metal oxalates [e.g., R<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and MC<sub>2</sub>O<sub>4</sub>]. The metals oxalates precipitate is first rinsed using a dilute oxalic acid solution (2 wt.%) and then with dilute hydrochloric acid (1 wt.%).

**[0099]** In an embodiment of the present disclosure, the rare earths oxalates precipitate is then oven dried at 100-110°C and subsequently calcined between 300°C and 1200°C to yield a product containing the rare earth oxides (REOs) product containing mostly yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium as rare earths (III) oxides (e.g., Y<sub>2</sub>O<sub>3</sub>, Ln<sub>2</sub>O<sub>3</sub>) or mixed rare earths oxides (e.g., Pr<sub>6</sub>O<sub>11</sub>, Tb<sub>4</sub>O<sub>7</sub>).

**[00100]** In an embodiment of the present disclosure, the process further comprises dissolving the cerium-free and europium-free calcined rare earths oxides in hot hydrochloric acid or hot nitric acid and performing the selective separation of heavy rare earths such as yttrium, gadolinium, terbium and erbium by means of ion exchange

(IX) or solvent extraction (SX).

**[00101]** In an embodiment of the present disclosure, the process further comprises precipitating the individual oxalates of yttrium, gadolinium, terbium and erbium from the individual solutions, separating them by solid-liquid separation techniques, and finally calcining the individual oxalates between 300°C and 1200°C to yield separately pure yttrium (III) oxide ( $Y_2O_3$ ), gadolinium (III) oxide ( $Gd_2O_3$ ), erbium (III) oxide ( $Er_2O_3$ ), and terbium (III, IV) oxides ( $Tb_4O_7$ ).

### **EXPERIMENTAL**

**[00102]** The example provided herein below, illustrates the efficiency of the process of the present disclosure for the recovery of rare earths oxides from phosphors, fluorescent lamps and light bulbs, and cathode ray tubes or other industrial wastes containing rare earths elements.

**[00103]** **Example 1:** A sample of 10 grams of mercury-free dusts and glass fines that consists essentially of soda-lime glass fines together with halophosphates, tri-band phosphors and other fluorescent materials that contains most of the rare earths elements values with the composition breakdown reported in Table 2 was weighed using a precision scale. Separately, 60 grams of flakes of sodium hydroxide technical grade were pre-melted inside a tall 200 mL pure zirconium crucible. The heating was provided by means of propane burners. Once the residual moisture was driven off and the melt surface became quiet, the heating was stopped and the melt was cooled. The dusts and glass fines sample was subsequently poured on top of the solidified melt and heating was resumed to bring the crucible temperature to red-dull heat (ca. 800°C) over a period of 30 minutes in order to perform the molten caustic fusion. A significant amount of steam and caustic fumes initially evolved, producing a strong effervescence or apparent boiling of the melt. The effervescence or apparent boiling ceased after about 10 minutes indicating that all the chemical reactions were completed. The caustic fusion was continued for an additional 25 minutes. The heating was stopped and the molten mass was allowed to solidify. Then, 100 mL of an aqueous solution of sodium hydroxide (5 wt.% NaOH) was then poured directly into the crucible containing



the solidified melt. As a result of the strong heat generation due to the dissolution reaction, the temperature of the solution increased. The temperature of the alkaline solution was subsequently maintained at about 80°C by heating the zirconium crucible directly onto a hot plate equipped with a magnetic stirrer. The resulting strong alkaline leach solution contained a suspension of non-dissolved solids and particulates. After cooling to room temperature, the solution was filtered. The insoluble solid residues were subsequently washed thoroughly with deionized water, oven-dried at 120°C and then calcined at 800°C for one hour inside a platinum crucible to yield 2.060 grams of calcined materials. The calcined mass was transferred into a 250-mL round borosilicate glass flask containing 150 mL of hydrochloric acid (20 wt.% HCl) connected to a condenser. The residue was then acid leached boiling the solution under reflux conditions at atmospheric pressure during 60 minutes. Once the hot acid leaching was completed, the leachate was cooled and filtered; the isolated insoluble residue was oven-dried and then calcined at 800°C during one hour to yield 0.060 gram of cerium (IV) oxide ( $\text{CeO}_2$ ). Afterwards, 0.5 gram of zinc metal powder was added to the acidic solution. After all the zinc had dissolved and the hydrogen gas evolution ceased, 20 ml of an aqueous solution of barium chloride (5 wt.%  $\text{BaCl}_2$ ) were added to the still acidic solution. Afterwards, ca. 2 ml of sulfuric acid (30 wt.%  $\text{H}_2\text{SO}_4$ ) were added drop wise in order to co-precipitate the barium and europium (II) sulfates. The completion of the europium (II) precipitation was measured by spectrophotometry by measuring the absorbance of the solution at the characteristic wavelength of 394 nm (*i.e.*, peak of maximum absorption for  $\text{Eu(II)}$ ). The co-precipitate was then filtered and washed thoroughly with dilute sulfuric acid. Afterwards, the wet co-precipitate was transferred into a 250 mL Erlenmeyer flask containing 50 mL of nitric acid (50 wt.%  $\text{HNO}_3$ ) and acid leached at the boiling point during 30 minutes under reflux. Then once the solution cooled, the insoluble barium sulfate residue left behind was separated by filtration and discarded. The acidic filtrate containing the  $\text{Eu(II)}$  was neutralized with an aqueous ammonia solution added drop wise until the precipitate of europium (III) hydroxide was completed. The europium (III) hydroxide was separated by filtration, oven-dried, and calcined inside a platinum crucible at 800°C during one hour. The mass of europium (III) oxide recovered was 0.055 grams. The pH of cerium-free and

europium-free pregnant leach solution was adjusted to about 1.5 by the drop wise addition of an aqueous solution of sodium hydroxide, then a saturated solution of oxalic acid (ca. 10 wt.%  $\text{H}_2\text{C}_2\text{O}_4$ ) was added and the solution was left stand overnight in order to precipitate all the insoluble rare earths oxalates. The precipitate was subsequently thoroughly rinsed using a solution containing 2 wt.% oxalic acid and then oven-dried at  $110^\circ\text{C}$  and calcined at  $800^\circ\text{C}$  during two hours in a platinum crucible. The calcined heavy rare earths oxides (HREOs) produced weighed 0.840 gram and contained a mixture of yttrium (III) oxide ( $\text{Y}_2\text{O}_3$ ), lanthanum (III) oxide ( $\text{La}_2\text{O}_3$ ), gadolinium (III) oxide ( $\text{Gd}_2\text{O}_3$ ), and terbium (III,IV) oxides ( $\text{Tb}_4\text{O}_7$ ). On the other and, the filtered alkaline barren leach solution obtained after alkaline leaching was evaporated to reduce its volume by half and left to stand overnight to allow the crystallization and settling of crystals of tri-sodium phosphate. After removing the tri-sodium phosphate crystals by gravity settling and decantation, calcium oxide powder was added to the spent alkaline solution in slight excess. After completion of the exothermic reaction, the solution was filtered to remove the insoluble calcium salts yielding a replenished alkaline solution of sodium hydroxide.

**[00104]** It is to be understood that the specification is not limited in its application to the details of construction and parts as described hereinabove. The specification is capable of other embodiments and of being practiced in various ways. It is also understood that the phraseology or terminology used herein is for the purpose of description and not limitation. Hence, although the present invention has been described hereinabove by way of illustrative embodiments thereof, it can be modified, without departing from the spirit, scope and nature of the subject disclosure as defined in the appended claims.

[00105] **Table 1** – Chemistry compounds found in phosphors and mercury-free residues obtained after retorting fluorescent lamps and light bulbs.

| ANION CHEMICAL GROUP   | CRYSTAL STRUCTURE                        | COMPOUNDS  |
|------------------------|--|--|
| INERT SILICATE MATRIX  | Amorphous                                | Soda-lime glass  |
| HALOPHOSPHATES         | Fluoro-apatite structure                 | Sr <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl:Eu <sup>2+</sup><br>Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,Cl):Sb <sup>3+</sup> ,Mn <sup>2+</sup> |
| PHOSPHATES             | Xenotime structure<br>Monazite structure | (Ce,La)PO <sub>4</sub> :Tb <sup>3+</sup>   |
| ALUMINATES             | Spinel structure                         | CeMgAl <sub>11</sub> O <sub>19</sub> : Tb <sup>3+</sup><br>BaMg <sub>2</sub> Al <sub>16</sub> O <sub>27</sub> :Eu <sup>2+</sup>                                  |
| OXIDES AND OXYSULFIDES | Corundum structure                       | Y <sub>2</sub> O <sub>3</sub> :Eu <sup>2+</sup> and Y <sub>2</sub> O <sub>2</sub> S:Eu <sup>2+</sup>   |
| BORATES                | Colemanite structure<br>Borax structure  | (Gd,Mg)B <sub>5</sub> O <sub>10</sub> :Ce <sup>3+</sup> Tb <sup>3+</sup><br>SrB <sub>4</sub> O <sub>7</sub> :Eu <sup>2+</sup>                                    |
| VANADATES              | Xenotime structure                       | Y(P,V)O <sub>4</sub> : Eu <sup>2+</sup><br>YVO <sub>4</sub> : Eu <sup>2+</sup>   |

[00106] **Table 2** - Chemical composition breakdown of the mercury-free dusts and glass fines.

| COMPONENT       | wt. %        | SUB-COMPONENT                  | wt. %        | OXIDES                         | wt. %        | BREAKDOWN                      | wt. %         |
|-----------------|--------------|--------------------------------|--------------|--------------------------------|--------------|--------------------------------|---------------|
| SODA-LIME GLASS | 63.2         |                                |              |                                |              | SODA-LIME GLASS                | 63.20         |
| PHOSPHOR DUSTS  | 36.8         | VARIOUS OXIDES                 | 72.8         | CaO                            | 36.1         | CaO                            | 13.28         |
|                 |              |                                |              | P <sub>2</sub> O <sub>5</sub>  | 28.0         | P <sub>2</sub> O <sub>5</sub>  | 10.30         |
|                 |              |                                |              | Al <sub>2</sub> O <sub>3</sub> | 5.9          | Al <sub>2</sub> O <sub>3</sub> | 2.17          |
|                 |              |                                |              | Sb <sub>2</sub> O <sub>3</sub> | 0.5          | Sb <sub>2</sub> O <sub>3</sub> | 0.18          |
|                 |              |                                |              | MnO                            | 2.3          | MnO                            | 0.85          |
|                 |              | RARE EARTHS OXIDES (REOs)      | 27.2         | Y <sub>2</sub> O <sub>3</sub>  | 20.7         | Y <sub>2</sub> O <sub>3</sub>  | 7.62          |
|                 |              |                                |              | CeO <sub>2</sub>               | 1.7          | CeO <sub>2</sub>               | 0.63          |
|                 |              |                                |              | La <sub>2</sub> O <sub>3</sub> | 1.1          | La <sub>2</sub> O <sub>3</sub> | 0.41          |
|                 |              |                                |              | Eu <sub>2</sub> O <sub>3</sub> | 1.6          | Eu <sub>2</sub> O <sub>3</sub> | 0.59          |
|                 |              |                                |              | Gd <sub>2</sub> O <sub>3</sub> | 1.4          | Gd <sub>2</sub> O <sub>3</sub> | 0.52          |
|                 |              | Tb <sub>4</sub> O <sub>7</sub> | 0.7          | Tb <sub>4</sub> O <sub>7</sub> | 0.26         |                                |               |
| <b>TOTAL =</b>  | <b>100.0</b> | <b>TOTAL =</b>                 | <b>100.0</b> | <b>TOTAL =</b>                 | <b>100.0</b> | <b>TOTAL =</b>                 | <b>100.01</b> |

**WHAT IS CLAIMED IS:**

1. A process for recovering rare earths oxides from spent phosphors, fluorescent lamps and fluorescent light bulbs, cathode ray tubes and other industrial wastes containing rare earths elements, the process comprising:
  - a) submitting the wastes or spent materials to a pyrometallurgical step performing a caustic or alkali fusion with molten salts of alkali metals;
  - b) recovering the solidified melt;
  - c) submitting the solidified melt to an alkaline leaching;
  - d) separating by solid-liquid separation the insoluble solid residues from the alkaline barren leach solution;
  - e) recovering the sodium phosphate values from the alkaline barren leach solution by evaporation and crystallization;
  - f) regenerating the spent alkaline leach solution by adding calcium oxide or calcium hydroxide;
  - g) oven-drying or calcining the insoluble solid residues obtained from the alkaline leaching;
  - h) leaching the oven-dried or calcined solids with an acid;
  - i) recovering the insoluble solids containing all the cerium (IV) from the acidic pregnant leach solution;
  - j) reducing the europium (III) to europium (II) in the acidic pregnant leach solution with a reducing agent;
  - k) co-precipitating the europium (II) sulfate by adding a barium salt and sulfuric acid;
  - l) separating by solid-liquid separation the co-precipitate of europium and barium sulfates;
  - m) performing the oxidative acid leaching of the co-precipitate of europium and barium sulfates with nitric acid to extract soluble europium (III) cations;

- n) separating by solid-liquid separation the barium sulfate from the acidic solution containing the europium (III) cations;
  - o) performing the neutralization, pH adjustment of the acidic solution and the precipitation of the europium (III) hydroxide with a neutralizing agent;
  - p) separating by solid-liquid separation and calcining the europium (III) hydroxide to yield europium (III) oxide;
  - q) treating the cerium-free and europium-free acidic pregnant leach solution with oxalic acid to precipitate the remaining rare earths elements as oxalates;
  - r) separating by solid-liquid separation and calcining the rare earths oxalates to yield rare earth oxides;
  - s) dissolving the rare earths oxides in an acid;
  - t) separating the yttrium, gadolinium, terbium and erbium from the acidic leaching solution by ion exchange (IX) or solvent extraction (SX);
  - u) precipitating individually the oxalates of yttrium, gadolinium, terbium and erbium from each individual streams; and
  - v) calcining individually the oxalates of yttrium, gadolinium, terbium and erbium to yield the corresponding pure yttrium (III) oxide, gadolinium (III) oxide, terbium (III, IV) oxides, and erbium (III) oxide.
2. The process of claim 1, wherein the caustic fusion or alkali fusion comprises using a molten alkali-metal hydroxide of formula MOH, wherein M is selected from the group consisting of Li, Na and K.
3. The process of claim 2, wherein the molten alkali-metal hydroxide is selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide and mixtures thereof.
4. The process of claim 3, wherein the caustic fusion or alkali fusion is performed using a mixture of alkali-metal hydroxides.

5. The process of claim 4, wherein alkali-metal peroxides of formula  $M_2O_2$  are optionally added to the melt to fully oxidize any excess tin content, wherein M is selected from the group consisting of Li, Na and K.
6. The process of claim 4, wherein alkali-metal carbonates of formula  $M_2CO_3$  or alkali-metal nitrates of formula  $MNO_3$  are added to the melt, wherein M is selected from the group consisting of Li, Na and K, the alkali-metal carbonates or alkali-metal nitrates improving the fluxing properties of the melt.
7. The process of claim 2, wherein the melt comprises a blend of alkali-metal hydroxides.
8. The process of claim 7, wherein the alkali-metal hydroxides are individually melted or melted together prior to being used in the caustic or alkali fusion step.
9. The process of claim 1, wherein the dusts and glass fines are fed into the melt at fusion temperatures and continuously stirred.
10. The process of claim 1, wherein the dusts and glass fines are mixed with the at least one alkali metal salt to produce a mixture, the mixture being subsequently heated to a temperature at which fusion of the mixture occurs.
11. The process according to claim 3, wherein the caustic or alkali fusion step is performed at a temperature of at least the melting point of the alkali metal salt.
12. The process according to claim 4, wherein the caustic or alkali fusion step is performed at a temperature of at least the eutectic melt temperature of the mixture.
13. The process of claim 12, wherein the melt temperature ranges from about 200°C to about 1200°C.
14. The process of any one of claims 1 to 13, wherein the caustic or alkali fusion step is performed over a period of time ranging from 5 minutes to 6 hours.

15. The process of claim 14, wherein the caustic or alkali fusion step is performed over a period of time ranging from 10 minutes to 4 hours.
16. The process of claim 14, wherein the caustic or alkali fusion step is performed over a period of time ranging from 15 minutes to 2 hours.
17. The process of claim 14, wherein the caustic or alkali fusion step is performed over a period of time ranging from 15 minutes to 1 hour.
18. The process of claim 1, wherein the caustic or alkali fusion step is performed using a mass ratio of dusts and glass fines material to the molten hydroxides denoted as F:M or F/M ranging from 1:1 to 1:20.
19. The process of claim 18, wherein the caustic or alkali fusion step is performed using a mass ratio of ore material to melt material ranging from 1:1 to 1:15.
20. The process of claim 19, wherein the caustic or alkaline fusion step is performed using a mass ratio of ore material to melt material ranging from 1:1 to 1:10.
21. The process of claim 20, wherein the caustic or alkali fusion step is performed using a mass ratio of ore material to melt material ranging from 1:1 to 1:6.
22. The process according to claim 1, wherein the caustic or alkali fusion step is performed using a furnace or a rotary kiln.
23. The process according to claim 22, wherein the caustic or alkali fusion step is performed using a crucible furnace.
24. The process according to claim 22, wherein the caustic or alkali fusion step is performed using a muffle furnace.
25. The process according to claim 22, wherein the caustic or alkali fusion step is performed using a rotary heart furnace.

26. The process of claim 1, wherein the caustic or alkali fusion step is performed in a containment vessel or crucible resistant to the fusion conditions.
27. The process according to claim 26, wherein the containment vessel or crucible comprises a material selected from the group consisting of composite metallic materials, bulk metals, alloys and ceramic materials.
28. The process according to claim 26, wherein the bulk metals and alloys are selected from the group consisting of iron, iron alloys, cast irons, steels, nickel, nickel alloys, zirconium and zirconium alloys.
29. The process of claim 27, wherein the composite metallic materials are selected from the group consisting of cast iron, steel, heat resistant stainless steels and nickel alloys clad with an inert, protective and impervious metal lining of a corrosion resistant metal or alloys.
30. The process of claim 29, wherein the corrosion resistant metal or alloys are selected from the group consisting of gold, gold alloys, silver, silver alloys, nickel, nickel alloys, iron, iron alloys, zirconium, zirconium alloys, hafnium, hafnium alloys and combination thereof.
31. The process of claim 27, wherein the ceramic materials are selected from the group consisting of graphite, diamond like carbon, carbon products, carbon-carbon composites, silicon carbide, zirconia, magnesia, ceria, calcia and combinations thereof.
32. The process of claim 1, wherein the alkaline leaching step is performed using an aqueous solution of alkali-metal hydroxide.
33. The process of claim 32, wherein the solution of alkali-metal hydroxide comprises a concentration ranging from 5 mass per cent to 50 mass per cent.
34. The process of claim 33, wherein the temperature of the solution of alkali-metal hydroxide ranges from room temperature to the boiling point of the solution.



35. The process of claim 1, wherein the hot alkaline leaching step is performed either under atmospheric pressure or under pressure inside an autoclave.
36. The process of claim 1, wherein the hot alkaline leaching step is performed batch wise or in continuous mode.
37. The process of claim 1, wherein the alkaline pregnant leaching solution is subjected to solid-liquid separation to produce an alkaline barren leaching solution.
38. The process of claim 1, wherein the caustic fusion step is omitted and the wastes and spent materials containing the rare earths elements can be directly treated by hot alkaline leaching step.
39. The process of claim 35, wherein the solid-liquid separation is selected from gravity settling, filtration and centrifugation.
40. The process of claim 1, wherein the solid residues consist essentially of insoluble compounds made of oxides and hydroxides of rare earths elements (REEs) [e.g.,  $\text{CeO}_2$ ,  $\text{R}(\text{OH})_3$ ], carbonates of rare earths elements [e.g.,  $\text{R}_2(\text{CO}_3)_2$ ], hydroxides of alkali-earth metals [e.g.,  $\text{M}(\text{OH})_2$ ], carbonates of alkali-earth metals [e.g.,  $\text{MCO}_3$ ] and iron oxides, hydroxides and carbonates [e.g.,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{FeCO}_3$ , etc.] and eventually insoluble alkali-earth metals sulfates [ $\text{MSO}_4$ ] with R being a rare earth element and M being an alkali-earth metal such as calcium, barium or strontium.
41. The process of claim 40, wherein the rare earths elements include Y, Sc and lanthanides.
42. The process of claim 40, wherein the insoluble solid residues are subjected to oven-drying or calcination in air.
43. The process of claim 42, wherein the oven-dried or calcined solids are acid leached for producing an acidic pregnant leach solution.

44. The process of claim 43, wherein the acid leaching is performed using hydrochloric acid, nitric acid, sulfuric acid or a mixture thereof.
45. The process of any one of claims 43 to 44, wherein the acid leaching is performed under atmospheric conditions or under pressure.
46. The process of claim 43, wherein the acid leaching is carried-out in an autoclave.
47. The process of any one of claims 43 to 46, wherein the insoluble solids are made of cerium (IV) compounds and are then separated by solid-liquid separation techniques.
48. The process of claim 47, further calcining in air the cerium (IV) compounds at a temperature ranging from 300°C to 1200°C to yield pure cerium (IV) oxide (CeO<sub>2</sub>).
49. The process of claim 48, further treating the cerium-free acidic pregnant leach solution with a reducing agent such as zinc, aluminum, or magnesium metal or their alloys in order to reduce the europium (III) to europium (II).
50. The process of claim 49, wherein barium chloride is added to the reduced acidic solution together with sulfuric acid in order to co-precipitate the insoluble barium and europium (II) sulfates.
51. The process of claim 50, wherein the co-precipitate of barium and europium (II) sulfates is separated by solid-liquid separation.
52. The process of claim 51, wherein the co-precipitate of barium and europium (II) sulfates is acid leached with hot nitric acid to oxidize the europium (II) to form soluble europium (III).
53. The process of claim 51, wherein the solution containing the europium (III) is neutralized with ammonia to precipitate the europium (III) hydroxide.

54. The process of claim 53, wherein the europium (III) hydroxide precipitate is calcined in air at a temperature ranging from 300°C to 1200°C to yield pure europium (III) oxide.
55. The process of claim 51, wherein a solution of oxalic acid or an alkali-metal oxalate is added to the cerium-free and europium-free solution to precipitate the rare earths oxalates.
56. The process of claim 55, wherein the precipitate of rare earths oxalates is washed with an aqueous acid solution selected from the group consisting of oxalic acid, sulfuric acid and hydrochloric acid to produce washed rare earths oxalates.
57. The process of claim 56, wherein the washed rare earths oxalates are oven-dried between 60°C and 150°C.
58. The process of claim 57, wherein the oven-dried metal oxalates are calcined in air at a temperature ranging from 300°C to 1200°C to produce rare earths oxides (REOs).
59. The process of claim 58, wherein the rare earths oxides are dissolved into hydrochloric acid or nitric acid.
60. The process of claim 59, wherein the acidic pregnant solution that contains the rare earths elements is subjected to the separation of yttrium, gadolinium, terbium, and erbium salts either by ion exchange (IX) or by solvent extraction (SX).
61. The process of claim 60, wherein the yttrium, gadolinium, terbium, and erbium oxalates or hydroxides are precipitated from each individual streams and calcined in air between 300°C and 1200°C to yield pure yttrium (III) oxide, gadolinium (III) oxide, erbium (III) oxide, and terbium (III, IV) oxide ( $Tb_4O_7$ ).

62. The process of claim 1, wherein the spent alkaline solution remaining after the crystallization and separation of tri-sodium phosphate is regenerated by causticization by adding either calcium hydroxide or calcium oxide for precipitating the residual phosphate anions together with the silicates, aluminates, sulfates, borates and fluorides anions as insoluble calcium salts and to obtain a replenished and concentrated alkaline solution of alkali-metal hydroxide suitable to be reused for the caustic leaching step.
63. A process for recovering rare earths oxides from spent phosphors, fluorescent lamps and fluorescent light bulbs, cathode ray tubes and other industrial wastes containing rare earths elements, the process comprising:
- a) submitting the wastes or spent materials to a pyrometallurgical step performing a caustic or alkali fusion with molten salts of alkali metals to produce a solidified melt;
  - b) submitting the solidified melt to an alkaline leaching to produce a leach solution comprising a solid residue;
  - c) separating the solid residue from the leach solution;
  - d) drying or calcining the solid residue; and
  - e) leaching the oven-dried or calcined solids with an acid.

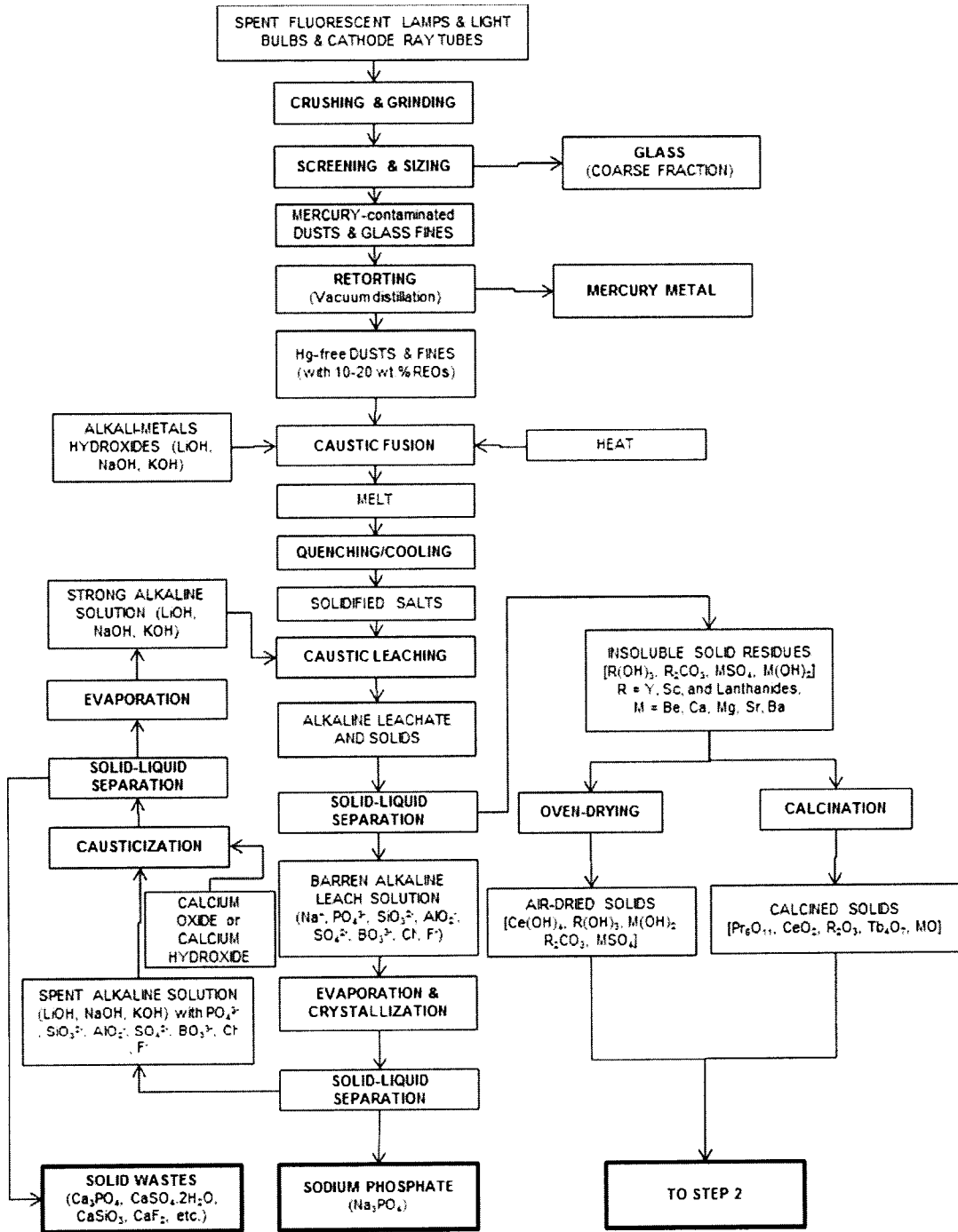


FIG. 1

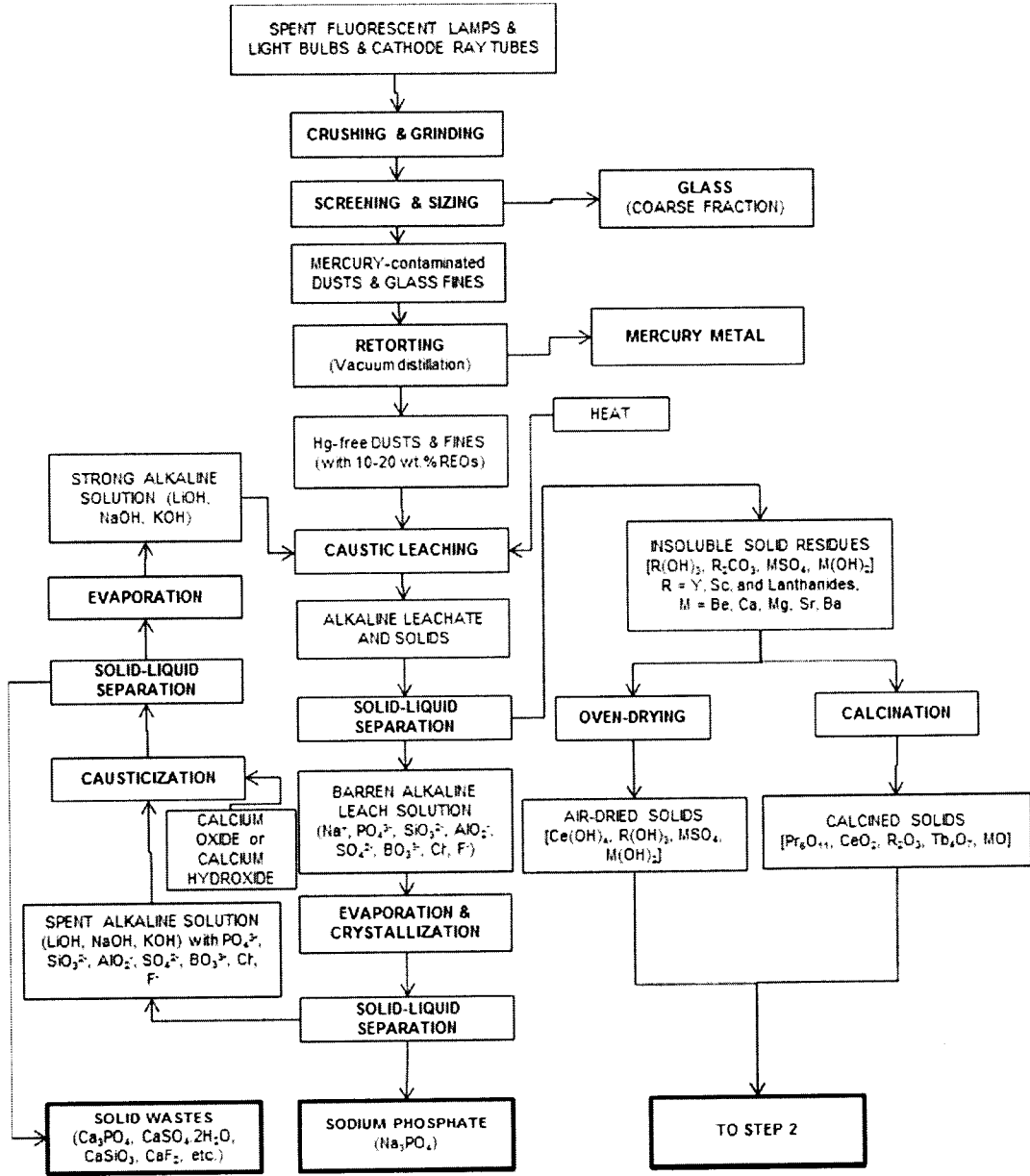


FIG. 2

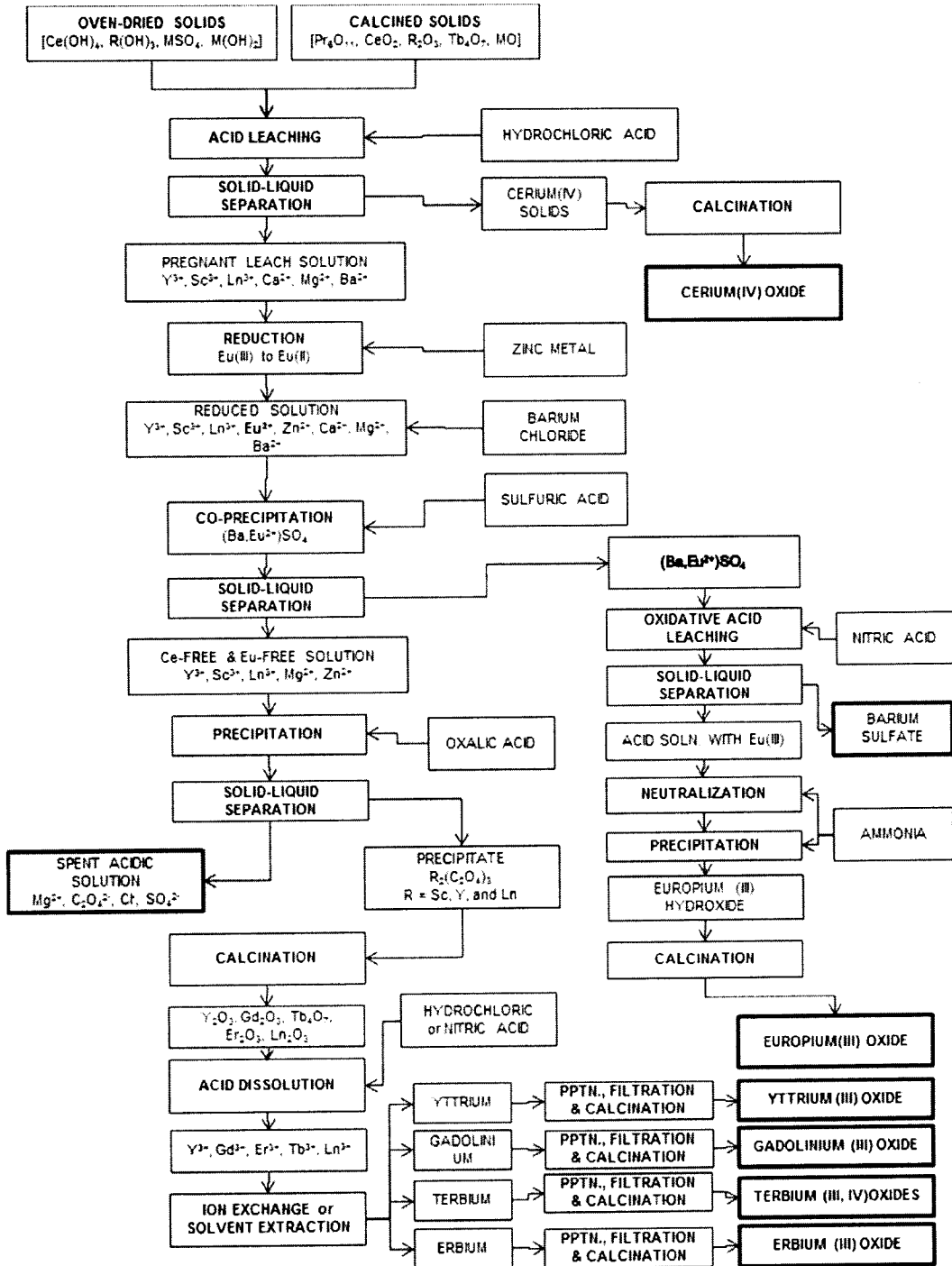


FIG. 3

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CA2013/000954

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC: **C22B 3/04** (2006.01) , **C09K 11/01** (2006.01) , **H01J 9/52** (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 3/04** (2006.01) , **C09K 11/01** (2006.01) , **H01J 9/52** (2006.01) , **C22B 59/00** (2006.01) in combination with keywords.

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  
 Canadian Patent Database, USPTO West, Google Scholar, TotalPatent. Search words: rare earth oxides, recovery, phosphors, fluorescent lamps, waste, alkali fusion, alkaline leaching.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant                        | Relevant to claim No. |
|----------|--|-----------------------|
| A        | US 2011/0206580 (POROB ET AL)<br>25 August 2011 (25-08-2011) *Abstract and claims 1, 2 and 10-14 | 1-63                  |
| A        | US 2012/0027651 (OTTO ET AL)<br>02 February 2012 (02-02-2012) *Abstract and Fig. 1               | 1-63                  |
| A        | US 4432948 (HEYTMEIJER)<br>21 February 1984 (21-02-1984) *Abstract and claim 1                   | 1-63                  |
| A        | WO 2010/118967 (BRACONNIER ET AL)<br>21 October 2010 (21-10-2010) *Abstract                      | 1-63                  |
| A        | WO 96/00698 (GREENBERG)<br>11 January 1996 (11-01-1996) *Abstract                                | 1-63                  |

 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  |
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| "P" document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

27 January 2014 (27-01-2014)

Date of mailing of the international search report

06 February 2014 (06-02-2014)

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/CA2013/000954**

| Patent Document Cited in Search Report | Publication Date              | Patent Family Member(s)  | Publication Date  |
|--|-------------------------------|--|---|
| US2011206580A1                         | 25 August 2011 (25-08-2011)   | US2011206580A1<br>US8137645B2<br>WO2011106167A1  | 25 August 2011 (25-08-2011)<br>20 March 2012 (20-03-2012)<br>01 September 2011 (01-09-2011)   |
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| WO9600698                              | 11 January 1996 (11-01-1996)  | None   |   |