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[Continued on next page]

(54) Title: PROCESS FOR UPGRADING TANTALUM AND NIOBIUM ORES AND CONCENTRATES WITH THE RECOVERY OF MANGANESE AND RARE EARTHS OXIDES

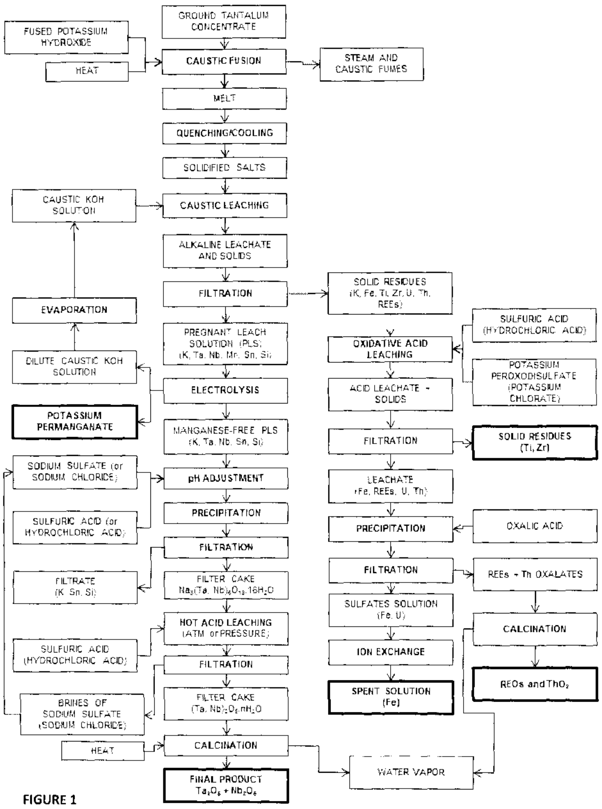

FIGURE 1

(57) **Abstract**: A process for upgrading tantalum and niobium ores and concentrates is described herein. The process comprising: a) submitting the ore or concentrate 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 an alkaline leaching step to produce an alkaline pregnant leaching solution comprising manganese values; c) recovering the manganese values from the alkaline pregnant leaching solution to produce a substantially manganese-free leach solution; and d) precipitating tantalum and niobium as an insoluble niobiate and tantalate from the manganese-free leach solution. The rare earth oxides are recovered from the insoluble residues obtained during alkaline leaching.

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TITLE

PROCESS FOR UPGRADING TANTALUM AND NIOBIUM ORES AND CONCENTRATES WITH THE RECOVERY OF MANGANESE AND RARE EARTHS OXIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority from co-pending U.S. provisional application no. 61/538,273 filed on September 23, 2011, the contents of which are incorporated herein by reference in their entirety.

FIELD

[0002] The present specification broadly relates to a process for upgrading tantalum and niobium ores and concentrates. More specifically, but not exclusively, the present specification relates to a process for upgrading tantalum and niobium ores and concentrates with the recovery of manganese and rare earth oxides and the electrochemical regeneration of reactants.

BACKGROUND

[0003] Tantalum and to a lesser extent niobium are two scarce refractory metals of the group VB(5) with a relative abundance in the Earth's crust of two parts per million by weight and twenty parts million by weight respectively. Both metals are used in various civilian and military applications.

METALLURGICAL AND CHEMICAL PROCESSES

[0004] The most important commercial niobium and tantalum minerals mined today constitute essentially the niobiate and tantalate of iron, manganese and tin. These minerals belong to three major groups; namely the pyrochlore, the columbite and wodginite groups.

[0005] The pyrochlore group minerals exhibit a cubic crystal lattice structure having the general formula: $AB_2O_6(O,OH,F)$ wherein A is at least one of K^+,

Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ln^{3+},Pb^{2+} and U^{4+}; and B is at least one of Nb^{5+}, Ta^{5+}, Ti^{4+}, Sn^{4+} and W^{6+}. The pyrochlore (sensu stricto) $[(Na,Ca)_2(Nb,Ta,Ti)_2O_4(OH,F)\cdot H_2O$ is of paramount commercial importance as the main niobium ore. When tantalum fully replaces niobium, the mineral is called microlite.

[0006] The columbite group minerals exhibit an orthorhombic crystal lattice structure having the general formula AB_2O_6 wherein A is at least one of Fe^{2+}, Mn^{2+} and Mg^{2+}; and B is at least one of Nb^{5+} and Ta^{5+} with complete isomorphic substitutions between the end members. The tantalum-rich end is called tantalite $[(Fe,Mn)Ta_2O_6)]$ and the niobium-rich end is named columbite $[(Fe,Mn)Nb_2O_6]$ with a continuous gradation between them yielding the common name columbo-tantalite or coltan in short that is extensively used in trade. Sometimes their names are preceded by the prefixes ferro-, mangano-, or magno- for indicating the predominance of one of the divalent cations.

[0007] The wodginite group minerals exhibit a monoclinic crystal lattice structure having the general formula ABC_2O_8 wherein A is at least one of Mn^{2+}, Fe^{2+} and Li^+; B is at least one of Sn^{2+}, Ti^{4+}, Fe^{3+} and Ta^{5+}; and C is at least one of Nb^{5+} and Ta^{5+}. Among them, only wodginite $[(Mn,Fe)(Sn,Ta)(Ta,Nb)_2O_8]$ is of commercial importance.

[0008] Other niobio-tantalate minerals such as samarskite $[(Y,Fe,U)(Nb,Ta)O_4]$ and euxenite $[(Y,Ca,Ce,U,Th)(Ta,Nb,Ti)_2O_6]$ are also mined, even though to a lesser extent.

[0009] Tantalum ores containing tantalum minerals such as tantalite, wodginite and euxenite are usually found in acidic igneous host rocks such as granite and pegmatite as well as in weathered, residual or alluvial deposits derived from such parent igneous rocks. Accordingly, they are frequently associated with silicate minerals such as albite, microcline, beryl, lepidolite, muscovite, spodumene, tourmaline and zircon, phosphates gangue minerals such as amblygonite, triphillyte and apatite as well as other heavy minerals such as cassiterite, wolframite, and samarskite, forming tantalum- and niobium-rich mineral sands. Typical premier tantalum deposits are those of the Tanco pegmatite, Bernic Lake in the Province of Manitoba, Canada and the Wodgina Mine in Western Australia.

[0010] The major commercial niobium deposits are mainly based on pyrochlore and columbite minerals that are usually found in ultramafic igneous rocks such as anorthosites and carbonatites. Typical premier pyrochlore deposits are those of the CBMM mine in Araxa, Brazil, the Lueshe deposit in the Congo, the Mabounie deposit in Gabon, and the two Canadian deposits of Niocan in Oka and the Niobec mine in Saint-Honoré, both located in the Province of Quebec, Canada.

[0011] At present, the world's main tantalite or wodginite production originates from Australia, with Brazil, Canada, China, Ethiopia and Central and Southern Africa largely accounting for the residual production. In 2008, the primary tantalum mine production worldwide was estimated at 2,500,000 pounds of Ta_2O_5. This represents only one third of the world's tantalum demand. Other significant sources of tantalum include tin slags from Malaysia and Thailand, as well as electronic scrap. As a result of the continuing shortage of tantalum production, several tantalum mining projects are under intense development worldwide. The temporary shutdown in 2008 of the largest underground Wodgina mine in Greenbushes Australia, and the closure in 2009 of the Tanco mine in Canada further strained the world's tantalum supply.

[0012] The metallurgical processing of tantalum ores and concentrates, currently performed by the two major tantalum producers such as Cabot Performance Materials (Boyertown, PA) or H.C. Starck GmbH (Goslar, Germany), poses serious technical, occupational and environmental issues that need to be resolved.

[0013] The ore material typically undergoes on-site beneficiation by means of common mineral dressing techniques such as gravity separation and magnetic separation to remove the silicate gangue minerals. The tantalum-rich concentrate is subsequently shipped to the metallurgical plant for further processing. As a result of the well-known chemical inertness of most niobio-tantalate minerals, the tantalum-rich concentrate is subjected to a chemical decomposition step (*i.e.* dissolution step), typically performed using mixtures of concentrated hydrofluoric and sulfuric acids (HF-

H_2SO_4). The use of these extremely corrosive and hazardous chemicals imposes harsh operating conditions with the inherent obvious and severe occupational risks. Moreover, due to the elevated vapor pressure of hydrofluoric acid, approximately 6-8% is lost as fumes during the decomposition process. The decomposition step is followed by a solid-liquid separation step order to remove the insoluble residues. The clear pregnant leach solution (PLS) is then typically transferred to the chemical processing plant. In view of similar chemical properties, the separation of tantalum and niobium requires an extensive solvent extraction (SX) processing.

[0014] Usually, both tantalum and niobium are co-extracted by solvent extraction using methyl-iso-butyl-ketone (MIBK) dissolved in kerosene. Both MIBK and kerosene are highly flammable and noxious organic solvents. This extraction process, under highly acidic conditions, provides for the selective extraction of both niobium and tantalum from deleterious manganese, iron, titanium, and other metallic impurities that are later discarded along with the original radionuclides in the processing wastes. The niobium is then stripped from the tantalum by contacting the organic phase with dilute hydrochloric acid (HCl). Subsequent adjustment of the pH provides for tantalum to be transferred into the aqueous phase. Tantalum can be recovered by two routes, depending on the final product required. The tantalum may be precipitated as hydrated tantalum pentoxide or tantalic acid ($Ta_2O_5.xH_2O$) by adding gaseous ammonia (NH_3). The precipitate can then be calcined to yield pure tantalum pentoxide (Ta_2O_5). Alternatively, the tantalum can be crystalized as potassium heptafluorotantalate (K_2TaF_7) by addition of potassium chloride (KCl) or potassium fluoride (KF) to a hot aqueous solution. Pure tantalum metal powder is obtained by sodiothermic reduction using sodium metal.

[0015] The liquid effluents (mostly waste waters) and solid wastes produced contain significant concentrations of fluoride ions. Since recycling of the fluorides at the extraction plant is not economical, these wastes are typically simply disposed of. The environmental problem is further compounded considering that all of the radionuclides originating from the ore, and that are responsible for its natural radioactivity, also end up in the wastes. These wastes are thus considered as technologically enhanced naturally occurring radioactive materials, (TENORM) that must be concentrated, stabilized and disposed of in accordance with local regulations, often at prohibitive costs.

[0016] Finally, from an economic perspective, the fact that the major metallic impurities such as manganese and iron and to a lesser extent tin and various rare earth elements are not recovered during the current processing conditions constitutes a significant loss of acid values. Moreover, as shortages of hydrofluoric acid occurred sporadically in the past, the supply of HF has always been a major concern to processors worldwide.

[0017] Additional processes consisting of either acid sulfate roasting or acid digestion of the ore materials or concentrates using concentrated sulfuric acid, oleum, or molten pyrophosphates all generate huge amounts of processing wastes mostly composed of ferric and ferrous sulfates that consume enormous quantities of acid values. As a result, these processes are not economically viable when carried-out on a large scale. This is especially the case when dealing with low grade ores.

[0018] The present specification refers to a number of documents, the contents of which are herein incorporated by reference in their entirety.

SUMMARY

[0019] The present specification broadly relates to a process for upgrading tantalum and niobium ores and concentrates.

[0020] In an embodiment, the present specification relates to a process for upgrading tantalum and niobium ores and concentrates, the process comprising: a) submitting the ore or concentrate 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 an alkaline leaching step to produce an alkaline pregnant leaching solution comprising manganese values; c) recovering the manganese values from the alkaline pregnant leaching solution to produce a substantially manganese-free leach solution; and d) precipitating tantalum and niobium as an insoluble niobiate and tantalate from the manganese-free leach solution.

[0021] In an embodiment of the present disclosure, the process further comprises separating the alkaline pregnant leaching solution from insoluble solid residues; recovering rare earth oxides and/or thorium oxides from the insoluble solid residues producing a spent acid filtrate; and recovering uranium from the spent acid filtrate.

[0022] In an embodiment of the present disclosure, the process further comprises acid-leaching the insoluble niobiate and tantalate producing a hydrated tantalum and niobium oxides; and calcining or roasting the hydrated tantalum and niobium oxides to yield tantalum metal and niobium oxides.

[0023] In an embodiment, the present specification relates to a process for upgrading tantalum and niobium ores and concentrates with the recovery of manganese and recovery of rare earths oxides and the electrochemical regeneration of reactants.

[0024] 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.

[0025] 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.

[0026] In an embodiment of the present specification, the caustic fusion or alkali fusion is performed using a potassium salt.

[0027] In an embodiment of the present specification, the caustic fusion or alkali fusion is performed using a sodium salt.

[0028] The foregoing and other objects, advantages and features of the present specification will become more apparent upon reading of the following non-restrictive description of illustrative embodiments thereof, given by way of example only with reference to the accompanying drawings/figures.

BRIEF DESCRIPTION OF THE DRAWINGS/FIGURES

[0029] In the appended drawings/figures:

[0030] **FIG. 1** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the caustic or alkali fusion is performed using a potassium salt such as potassium hydroxide. Moreover, the manganese value is recovered as potassium permanganate following alkaline leaching of the melt and electrochemical treatment of the pregnant leach solution.

[0031] **FIG. 2** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the caustic or alkali fusion is performed using a potassium salt such as potassium hydroxide. Moreover, the manganese value is recovered as manganese dioxide by precipitation following alkaline leaching of the melt.

[0032] **FIG. 3** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the caustic or alkali fusion is performed using a sodium salt such as sodium hydroxide. Moreover, the manganese value is recovered as manganese dioxide by precipitation following alkaline leaching of the melt.

[0033] **FIG. 4** is an illustration of a flowchart in accordance with an embodiment of the present specification. In this particular embodiment, the rare earth values are recovered as rare earth oxides and thorium from the air-dried or calcined residues.

[0034] **FIG. 5** is an illustration of the two-compartment electrolyzer and the electrodes and membrane reactions occurring inside the electrolyzer in accordance with an embodiment of the present specification. In this particular embodiment the electrolyzer is used for the preparation of potassium permanganate along with the concurrent regeneration of the potassium hydroxide lye.

[0035] **FIG. 6** is an image of a commercially available tantalite concentrate (**A**) and a mixed tantalum-niobium oxide produced in accordance with an embodiment of the present specification (63 wt.% Ta_2O_5 + 37 wt.% Nb_2O_5) (**B**).

DETAILED DESCRIPTION

I. Definitions

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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.

[0040] 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.

[0041] As used herein, the term "concentrate" or "ore concentrate" refers to a mineral product obtained after mineral dressing and beneficiation and from which most of the gangue minerals and waste rock have been removed and discarded as tailings. The concentrate is frequently the raw material for further metallurgical and chemical treatments such as roasting, leaching and smelting.

[0042] As used herein, the term "upgrading" refers to a chemical or electrochemical process, typically part of an upstream metallurgical process, for removing major impurities and other deleterious impurities from an ore or a concentrate in order to improve the grade, that is, the concentration of the valuable(s) metal(s).

[0043] 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.

[0044] The present specification broadly relates to a process for upgrading tantalum and niobium ores and concentrates. In an embodiment of the present specification, the process provides for substantially pure tantalum oxide, substantially pure niobium oxide and mixtures of these oxides to be produced. In an embodiment, the present specification relates to a pyrometallurgical and hydrometallurgical process for upgrading tantalum and niobium ores and concentrates with the concurrent electrochemical recovery of manganese metal, manganese oxides and other manganese-based materials as co-products and the regeneration of reactants. In an embodiment of the present specification, the process also provides for the recovery of a product comprising the rare earth metal oxides.

[0045] The process comprises a high temperature caustic fusion or alkali fusion step followed by a hydrometallurgical alkaline leaching step with the concurrent electrochemical recovery of manganese metal or manganese-based materials, non-limiting examples of which include manganese dioxide and potassium permanganate, as co-products of the process. The process further comprises precipitation steps, leaching steps and calcination steps ultimately yielding substantially pure tantalum oxide, substantially pure niobium oxide and mixtures of these oxides. Finally, the process comprises steps for recovering the product comprising the rare earth metal oxides as well as steps for regenerating at least some of the reactants such as the alkaline leaching solution and the alkali metal hydroxides.

[0046] The process comprises a high temperature caustic fusion or alkali fusion step. This high temperature pyrometallurgical step includes subjecting the tantalum or niobium ore or concentrate 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. In embodiments where the tin content of the ore starting material is elevated, an 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 of the tin content is oxidized to its tetravalent oxidation state (Sn^{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.

[0047] 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 hydroxides 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.

[0048] In an embodiment of the present disclosure, the tantalum or niobium ores and concentrates are ground prior to being used in the fusion step. In an embodiment of the present specification, the grinding produces a particle size distribution not higher than 80-mesh. Fine grinding of the ores and concentrates is typically not required in order to avoid dusting. In a further embodiment, the tantalum or niobium ores and concentrates are dried prior to being processed. In yet a further embodiment, the ground product is dried prior to being processed.

[0049] In an embodiment of the present disclosure, the ground and dried material is 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 ground and dried material is 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 ground and dried material is 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.

[0050] In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio of ore or concentrate mass (C) to mass of melt material (*i.e.* mass of molten hydroxide salt) (S) denoted as C:S or C/S 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.

[0051] 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.

[0052] 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.

[0053] 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.

[0054] 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. A certain number of materials suitable for use in the fusion step are described in the literature: i) Probst, H.B.; May, C.E.; and McHenry, H.T. - *Corrosion resistance of Ni-alloys in molten NaOH.* - National Advanced Committee for Aeronautics (NACA) Technical Note No. 4157, Washington DC January 1958; ii) Grayhead, C.M.; Smith, L.A.; and Jaffee, R.I. - *Screening Tests on Metals and Alloys in Contact with molten NaOH at 1000F and 1500F.* - Report BMI 706 Battelle Memorial inst. Nov. 6 (1951). Suitable materials include metals such as pure nickel (Ni), pure zirconium (Zr), and their alloys (*e.g.*, Duranickel® 201, Zircadyne® 702); 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 (*e.g.*, AISI 310); copper-nickel (*e.g.*, Monel®) and high nickel-alloys (*e.g.*, Hastelloys X® and Inconel® 601) 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, carborundum®), fused zirconia (ZrO_2), fused magnesia (MgO), fused ceria (CeO_2), fused calcia (CaO) and combinations thereof. The corrosion rates of at least some of the above-mentioned materials are illustrated hereinbelow in **Table 1**.

[0055] In an embodiment of the present disclosure, the caustic or alkali fusion step and the alkaline leaching step are performed using potassium hydroxide.

[0056] In an embodiment of the present disclosure, the caustic or alkali fusion step and the alkaline leaching are performed using sodium hydroxide.

[0057] Table 1: Corrosion Resistance of Various Materials to Molten KOH.

CORROSION RESISTANT MATERIAL		**CORROSION RATE AFTER IMMERSION OF COUPONS IN MOLTEN KOH AT 800°C FOR 2 HOURS (METAL-TO-MELT MASS RATIO OF 1:10)**
METALS	GOLD	OUTSTANDING (< 0.5 μm/year)
	SILVER	OUTSTANDING (< 0.5 μm/year)
	HAFNIUM	EXCELLENT (< 12.5 μm/year)
	ZIRCONIUM	EXCELLENT (< 12.5 μm/year)
	NICKEL	EXCELLENT (< 25 μm/year)
	IRON (ELECTROLYTIC)	GOOD (< 50 μm/year)
ALLOYS	INCONEL® 601	1.27 mm/year (INTER-GRANULAR ATTACK)
	MONEL® 500	1.27 mm/year (INTER-GRANULAR ATTACK)
	CAST IRON	3.30 mm/year
	NI-RESIST 2 and 3	3.50 mm/year
	STAINLESS STEEL 302	46 mm/year
	CHROMIUM STEEL (18.5%Cr)	69 mm/year
CERAMICS	DIAMOND AND DIAMOND LIKE CARBON	EXCELLENT
	TITANIUM CARBIDE (SiC)	GOOD
	ZIRCONIA (ZrO_2) (STABILIZED WITH YTTRIA)	GOOD
	CERIA (CeO_2)	GOOD
	CARBON AND GRAPHITE	EXCELLENT

[0058] POTASSIUM ROUTE - CAUSTIC FUSION AND ALKALINE LEACHING WITH POTASSIUM HYDROXIDE

[0059] In an embodiment of the present disclosure, the molten caustic fusion is performed using at least one potassium salt selected from the group consisting of potassium hydroxide, potassium peroxide, potassium carbonate and potassium nitrate. The chemical reactions and reaction products contained in the melt when potassium hydroxide is used as the salt for the caustic fusion step are illustrated hereinbelow in **Table 2**. A distinction is made between the soluble and insoluble reaction products. Deleterious impurities such as iron, titanium, zirconium, uranium, rare earth metals and thorium will remain locked as insoluble residues, while substantially all the tantalum, niobium, manganese values and to a lesser extent tin, tungsten, silica, aluminum will be completely dissolved into the melt. A significant amount of water is released as water vapor or as superheated steam as a result of the elevated operation temperatures. The steam release is at the origin of the effervescence or apparent boiling of the melt occurring following the introduction of the ore or concentrate into the melt. The steam evolution ceases once the chemical reactions are completed as is hence a good indicator of the completion of the caustic fusion reaction.

[0060] Table 2: Chemical Reactions and Products of KOH Caustic Fusion

	REACTION	**PRODUCT**
SOLUBLE REACTION	$3Ta_2O_5 + 8KOH \rightarrow \mathbf{K_8Ta_6O_{19}} + 4H_2O$	Potassium pertantalate

	$3Ta_2O_5 + 6KOH \rightarrow 2\mathbf{K_3Ta_3O_9} + 3H_2O$	Potassium metatantalate
	$3Nb_2O_5 + 8KOH \rightarrow \mathbf{K_8Nb_6O_{19}} + 4H_2O$	Potassium perniobiate
	$3Nb_2O_5 + 6KOH \rightarrow 2\mathbf{K_3Nb_3O_9} + 3H_2O$	Potassium metaniobiate
	$2MnO_2 + 6KOH + 0.5O_2 \rightarrow 2\mathbf{K_3MnO_4} + 3H_2O$	Potassium manganite
	$MnO_2 + 2KOH + 0.5O_2 \rightarrow \mathbf{K_2MnO_4} + H_2O$	Potassium manganate
	$SnO_2 + 2KOH \rightarrow \mathbf{K_2SnO_3} + H_2O$	Potassium metastannate
	$SiO_2 + 2KOH \rightarrow \mathbf{K_2SiO_3} + H_2O$	Potassium metasilicate
	$WO_3 + 2KOH \rightarrow \mathbf{K_2WO_4} + H_2O$	Potassium orthotungstate
	$Al_2O_3 + 2KOH \rightarrow 2\mathbf{KAlO_2} + H_2O$	Potassium aluminate
INSOLUBLE REACTION PRODUCTS	$Fe_2O_3 + 2KOH \rightarrow \mathbf{K_2Fe_2O_4} + H_2O$	Potassium ferrite
	$TiO_2 + 2KOH \rightarrow \mathbf{K_2TiO_3} + H_2O$	Potassium metatitanate
	$2TiO_2 + 2KOH \rightarrow \mathbf{K_2Ti_2O_5} + H_2O$	Potassium pertitanate
	$ZrO_2 + 2KOH \rightarrow \mathbf{K_2ZrO_3} + H_2O$	Potassium zirconate
	$UO_2 + 2KOH \rightarrow \mathbf{K_2UO_4} + H_2O$	Potassium uranate

[0061] Upon completion of the caustic fusion step, substantially all of the tantalum and niobium values initially contained in the ore or concentrate are dissolved into the melt while impurities remain in the solid residues. The melt is subsequently allowed to slowly solidify while cooling to room temperature. 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 an 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 an 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 an 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. The time required for the caustic or alkali fusion is typically dependent on the mass ratio between the caustic agent and the ground ore or concentrate. In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio of ore or concentrate mass (C) to mass of melt material (*i.e.* mass of molten potassium hydroxide salt) (S) denoted as C:S or C/S 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.

[0062] The melt produced following the caustic or alkali fusion step is subsequently subjected to an 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 scoping 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.

[0063] In an embodiment of the present disclosure, the solidified melt is subjected to an alkaline leaching step to produce an alkaline pregnant leach solution. In an embodiment of the present disclosure, the alkaline leaching step is performed using a dilute aqueous solution of potassium hydroxide (KOH). In an embodiment of the present disclosure, the aqueous potassium hydroxide solution comprises a concentration ranging from 50g/liter to 250g/liter. In a further embodiment of the present disclosure, the temperature of the potassium 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 potassium hydroxide solution is at least 13. In cases where the resulting dark green and strongly alkaline pregnant leach solution (PLS) contains a suspension of non-dissolved solids and particulates, it is subjected to common solid-liquid separation techniques, such as gravity settling, filtration and centrifugation. In an embodiment of the present disclosure, the solid-liquid separation is carried out while hot. The solid residues obtained following solid-liquid separation consist essentially of insoluble compounds of iron (III), titanium (IV), zirconium (IV), rare earths (*i.e.*, Y, Sc and lanthanides), and uranides (*e.g.*, uranium and thorium). 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 include mainly ferric oxides and hydroxides [*e.g.*, Fe_2O_3, $Fe(OH)_3$], as a result of the decomposition of potassium ferrite; potassium (IV) titanate [K_2TiO_3]; potassium (IV) zirconate [Zr_2TiO_3]; potassium (IV) uranate [K_2UO_4], hydroxides of rare earth elements (REEs) [$Ln(OH)_3$], as well as thorium hydroxide [$Th(OH)_4$].

[0064] In a further embodiment of the present disclosure, the wet filter cake obtained following solid-liquid separation was thoroughly washed with a hot aqueous solution of KOH (5 wt. %). The washed residue was subsequently subjected to oxidative acid leaching producing an acid leachate. In an embodiment of the present disclosure, the oxidative acid leaching was performed using sulfuric acid and an oxidizing agent selected from the group consisting of potassium peroxodisulfate ($K_2S_2O_8$), ammonium peroxodisulfate [$(NH_4)_2S_2O_8$], hydrogen peroxide (H_2O_2) and Caro's acid (H_2SO_5). This oxidative acid leaching oxidized substantially all the uranium (IV) to its hexavalent oxidation state which is highly soluble. In an embodiment of the present disclosure, hydrochloric acid is used as the acid with either hydrogen peroxide (H_2O_2), manganese dioxide (MnO_2), or potassium chlorate ($KClO_3$) as the oxidizing agent. The remaining insoluble solid residue, containing potassium titanate and potassium zirconate is disposed of in accordance with enforced regulations. The pH of the acid leachate is subsequently adjusted to a range from about 0.5 to 2.5. In an embodiment of the present disclosure, the pH of the acid leachate 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 1.2. Following pH adjustment, a saturated solution of oxalic acid (ca. 10 wt.% $H_2C_2O_4$) is added and the solution was allowed to stand overnight resulting in substantially all of the rare earth elements (REEs) along with thorium precipitating out of the solution in the form of insoluble metal oxalates. The precipitate is first rinsed using a dilute oxalic acid solution (2 wt.%) and then with either sulfuric acid or hydrochloric acid (1 wt.%). The residue is then oven dried at 100-110°C and subsequently calcined to yield a product containing rare earth oxides (REOs) and thoria (ThO_2). The remaining liquor contained substantially all of the uranium as uranyl cations (UO_2^{2+}) which could be readily recovered using selective ion exchange resins. The residual liquor contains substantially all of the ferric iron that can be either reduced to ferrous iron and recovered as iron metal by electrowinning or precipitated as ferric hydroxide and neutralized prior to disposal.

[0065] In an embodiment of the present specification, the calcined product comprises substantially all of the cerium oxidized to cerium(IV) along with other oxidized lanthanides such as Ln_2O_3, Pr_6O_{11}, Eu_2O_3 and Tb_4O_7 as well as thorium ThO_2. In order to remove the cerium values, the calcined product is acid leached with dilute hydrochloric acid at a pH ranging between 2 and 4. The insoluble CeO_2 is easily recovered by solid-liquid separation. The clear filtrate solution that contains all the thorium and the other lanthanides is then contacted with metallic zinc, aluminum or magnesium or mixtures thereof (*e.g.*, shot, flakes, chunks, or powder) in order to reduce substantially all the europium(III) to europium(II). An aqueous solution of barium chloride ($BaCl_2$) is then added to the clear solution and a stoichiometric amount of dilute sulfuric acid is subsequently added in order to co-precipitate the insoluble barium and europium sulfates [$(Ba,Eu)SO_4$]. 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)]. The europium is readily recovered from the wet insoluble $(Ba,Eu)SO_4$ precipitate by simply oxidizing it with concentrated nitric acid and by precipitating the europium (III) hydroxide from the neutralized solution by adding aqueous ammonia. The cerium- and europium-free liquor that contains the remaining lanthanides and thorium can eventually be treated to separate the remaining lanthanides from the thorium.

[0066] In an embodiment of the present disclosure, the clear alkaline pregnant leach solution obtained following solid-liquid separation comprises substantially all of the manganese values, mainly as brilliant-green potassium manganate (K_2MnO_4) and to a lesser extent blue-green potassium manganite (K_3MnO_4), both imparting a dark green color to the solution. The pregnant leach solution further contains substantially all of the soluble tantalum and niobium values, mainly as potassium pertantalate and perniobiate of general formula $K_8(Ta,Nb)_6O_{19}$ and to a lesser extent potassium meta-tantalate and meta-niobiate of general formula $K_3(Ta,Nb)_3O_9$. The potassium salts are highly soluble under the strongly alkaline conditions prevailing in the pregnant leach solution. Finally, the pregnant leach solution also contains tin, silicon and tungsten values as soluble potassium stannate (K_2SnO_3), potassium metasilicate (K_2SiO_3) and potassium orthotunsgtate or wolframate (K_2WO_4).

[0067] In an embodiment of the present disclosure, the alkaline pregnant leach solution is treated by batch or continuous electrochemical process in order to recover the manganese values. In an embodiment, the electrochemical process is performed using a divided electrolyzer including an anode compartment equipped with an anode consisting of pure nickel, nickel-plated copper or nickel-plated steel; a separator consisting of a diaphragm cloth or a cation exchange membrane (CEM) that is chemically resistant to both alkaline conditions and oxidizing conditions, non-limiting examples of which include NAFION® N324 or N424, or N438; and a cathode compartment equipped with a cathode consisting of pure iron, mild steel, austenitic stainless steels or nickel-plated copper. The pregnant leach solution is typically fed into the anode compartment where the potassium (VI) manganate is oxidized at the anode and converted to the less soluble potassium (VII) permanganate ($KMnO_4$). Any excess potassium cations released during the oxidation reaction migrate and diffuse across the membrane into the cathode compartment where they combine with hydroxyl anions, regenerating potassium hydroxide (KOH) that is subsequently reused for the alkaline leaching step. In an embodiment, the pregnant leach solution is at a temperature of at least room temperature when fed into the anode compartment of the electrolyzer. In a further embodiment, the pregnant leach solution is at 60°C when fed into the anode compartment of the electrolyzer. The electrochemical reactions occurring at the electrodes and the overall reactions are presented hereinbelow in **Table 3** as well as in **Fig. 5**.

[0068] **Table 3**: Electrochemical Reactions of Electrosynthesis of $KMnO_4$

ANODE (+)	$MnO_4^{2-} = MnO_4^- + e^-$
	$MnO_4^{2-} = MnO_4^- + 2e^-$
CATHODE (-)	$2H_2O + 2e^- = H_2(g) + 2OH^-$
OVERALL REACTION	$K_2MnO_4 + H_2O = KMnO_4 + KOH + 0.5H_2(g)$
	$K_3MnO_4 + 2H_2O = KMnO_4 + 2KOH + H_2(g)$

[0069] The potassium permanganate crystals ($KMnO_4$) are only sparingly soluble in alkaline solutions (ca. 64 g/L at 20°C) and are recovered from the anolyte by crystallization using a multistage vacuum crystallizer. The potassium permanganate product obtained following centrifugation and drying can be packaged and sold as a high value manganese chemical co-product.

[0070] In an embodiment of the present disclosure, the potassium hydroxide rich catholyte exiting the cathode compartment of the electrolyzer is further concentrated by thermal evaporation to yield a potassium hydroxide lye having a mass density of about 1,514 kg/m^3. Alternatively, the potassium hydroxide can be crystallized from the lye to produce anhydrous KOH flakes that are recycled back into the caustic fusion process. Moreover, the steam or water driven-off from the evaporator can optionally be condensed and reused as distilled water in the upstream process. In yet a further embodiment of the present disclosure, the potassium rich catholyte exiting the cathode compartment of the electrolyzer can be purified by causticization by adding calcium hydroxide (CaO) or spent lime [$Ca(OH)_2$] in order to precipitate calcium carbonate and other minor metallic impurities that can build-up during the recycling of the caustic leaching liquor.

[0071] In an embodiment of the present disclosure, the dark green alkaline pregnant leach solution is simply exposed to air and carbon dioxide (*i.e.* maturing) for several hours until the potassium manganate(s) are reduced and/or disproportionated, yielding a dense red-brown precipitate of manganese oxides (*e.g.*, MnO_2, Mn_2O_3). The dense precipitate is then separated by solid-liquid separation techniques, washed with water and oven dried. The maturing process constitutes an alternative to the electrochemical recovery of the manganese values. The dried oxide, consisting mostly of manganese dioxide (MnO_2), can be sold as a technical manganese dioxide product or as a raw material for the synthesis of chemical (CMD) or electrochemical grade (EMD) manganese dioxides, or even as feed for preparing manganese metal either by electrowinning or smelting.

[0072] In an embodiment of the present disclosure, the clear and manganese-free alkaline pregnant leach solution containing the tantalum and niobium values and to a lesser extent the tin and silicon values, is transferred to a plastic-lined steel tank for recovering the tantalum and niobium values. Non-limiting examples of plastic linings include high density polyethylene (HDPE), polypropylene (PP) and polyvinylidene chloride (PVDC). The temperature of the solution is raised to a temperature ranging from 30°C to 100°C. A saturated aqueous solution of sodium sulfate or sodium chloride is then added. The total amount of sodium added typically corresponds to the stoichiometric amount necessary to yield hydrated sodium tantalate ($Na_8Ta_6O_{19}.16H_2O$) and sodium niobiate ($Na_8Nb_6O_{19}.16H_2O$) respectively, while also providing an excess ranging from 10 to 50%.wt. The pH of the solution is then gradually adjusted to values ranging between 6 and 7 by adding concentrated sulfuric acid or hydrochloric acid. The solubility of sodium tantalate and sodium niobiate decreases as the pH is lowered. In fact, hydrated sodium tantalate starts to precipitate at pH values below 10, whereas hydrated sodium niobiate starts to precipitate at values below 7. Both precipitates quickly settle at the bottom of the reactor and can be recovered by standard solid-liquid separation techniques to yield a wet filter cake. The remaining solution, comprising the silicon and tin values, in addition to excess sodium sulfate or sodium chloride, is subsequently used for recovering the tin values by precipitating tin oxide.

[0073] In an embodiment of the present disclosure, the wet filter cake comprising the hydrated sodium tantalate and niobiate is transferred to a glass lined autoclave reactor where it is subjected to hot acid leaching using sulfuric acid (30 wt.% H_2SO_4) or hydrochloric acid (20 wt.% HCl) in order to leach out the sodium and any traces of metallic impurities. In a further embodiment, the leaching is performed at atmospheric pressure. In yet a further embodiment, the leaching is performed at pressures in excess of atmospheric. The hot acid leaching yields an insoluble mass comprising hydrated tantalum oxide ($Ta_2O_5.nH_2O$) and hydrated niobium oxide ($Nb_2O_5.nH_2O$), also called tantalic and niobic acids. The oxide products are thoroughly washed with a hot and dilute solution of sulfuric acid (or hydrochloric acid), followed by washing with deionized water and solid-liquid separation to provide a bright milky white wet filter cake.

[0074] In an embodiment of the present disclosure, the hydrated tantalum and niobium oxides are transferred into a long quartz boat or a large zirconium crucible, dried at 120°C for about 4 hours and calcined in a muffle or rotary kiln to yield a dense white powder of a mixture of pure tantalum and niobium oxides (Ta_2O_5 + Nb_2O_5). In an embodiment of the present disclosure, the calcination is performed at temperatures of about 800°C. The tantalum/niobium mass ratio in the oxide product is substantially identical to that found in the original starting material (*i.e.* ore or concentrate).

[0075] In an embodiment of the present disclosure, the brine solution by-produced during the acid leaching of the wet filter cake comprising the hydrated sodium tantalate and niobiate, is either concentrated to yield a concentrated brine or evaporated to yield a crystallized salt. The salt comprises either sodium sulfate decahydrate (*i.e.* Glauber's salt) or sodium chloride (*i.e.* Rock salt) depending on the type of sodium salt and mineral acid used in the precipitation and acid leaching steps respectively. The concentrated brine or crystallized salts can be reused in the precipitation process and the water driven-off from the evaporator can optionally be condensed and reused as distilled water in the process.

[0076] In an embodiment of the present disclosure, the clear and manganese-free alkaline pregnant leach solution containing the tantalum and niobium values and to a lesser extent the tin and silicon values (potassium stannate and silicate) in addition to free potassium hydroxide, is evaporated until the potassium niobiate and tantalate have crystallized out. The valuable potassium salts are then removed by common solid-liquid separation, while the concentrated caustic potassium hydroxide lye containing potassium stannate and silicate, can be further purified by adding quicklime or calcium hydroxide in order to precipitate the insoluble calcium stannate and silicate. The purified potassium hydroxide lye is then ready to be recycled into the process.

[0077] **SODIUM ROUTE - CAUSTIC FUSION AND ALKALINE LEACHING WITH SODIUM HYDROXIDE**

[0078] In an embodiment of the present disclosure, the molten caustic fusion is performed using at least one sodium salt selected from the group consisting of sodium hydroxide, sodium peroxide, sodium carbonate and sodium nitrate. The chemical reactions and reaction products contained in the melt when sodium hydroxide is used as the salt for the caustic fusion step are illustrated hereinbelow in **Table 4**. A distinction is made between the soluble and insoluble reaction products. Contrary to the potassium-based caustic fusion process, the tantalum and niobium values, along with deleterious impurities such as iron, titanium, zirconium, uranium, rare earth metals and thorium will remain locked as insoluble residues, while substantially all the manganese values and to a lesser extent tin, tungsten, silica, aluminum will be completely dissolved into the melt. A significant amount of water is released as water vapor or as superheated steam as a result of the elevated operation temperatures. The steam release is at the origin of the effervescence or apparent boiling of the melt following the introduction of the ore or concentrate into the melt. The steam evolution ceases once the chemical reactions are completed as is hence a good indicator of the completion of the caustic fusion reaction.

[0079] <u>Table 4</u>: Chemical Reactions and Products of NaOH Caustic Fusion

	REACTION	**PRODUCT**
SOLUBLE REACTION PRODUCTS	$2MnO_2 + 6NaOH + 0.5O_2 \rightarrow \mathbf{2Na_3MnO_4} + 3H_2O$	Sodium manganite
	$MnO_2 + 2NaOH + 0.5O_2 \rightarrow \mathbf{Na_2MnO_4} + H_2O$	Sodium manganate
	$SnO_2 + 2NaOH \rightarrow \mathbf{Na_2SnO_3} + H_2O$	Sodium metastannate

	$SiO_2 + 2NaOH \rightarrow \mathbf{Na_2SiO_3} + H_2O$	Sodium metasilicate
	$WO_3 + 2NaOH \rightarrow \mathbf{Na_2WO_4} + H_2O$	Potassium orthotungstate
	$Al_2O_3 + 2NaOH \rightarrow \mathbf{2NaAlO_2} + H_2O$	Sodium aluminate
INSOLUBLE REACTION PRODUCTS	$3Ta_2O_5 + 8NaOH \rightarrow \mathbf{Na_8Ta_6O_{19}} + 4H_2O$	Sodium pertantalate
	$3Ta_2O_5 + 6NaOH \rightarrow \mathbf{2Na_3Ta_3O_9} + 3H_2O$	Sodium metatantalate
	$3Nb_2O_5 + 8NaOH \rightarrow \mathbf{Na_8Ta_6O_{19}} + 4H_2O$	Sodium perniobiate
	$3Nb_2O_5 + 6NaOH \rightarrow \mathbf{2Na_3Ta_3O_9} + 3H_2O$	Sodium metaniobiate
	$Fe_2O_3 + 2NaOH \rightarrow \mathbf{Na_2Fe_2O_4} + H_2O$	Sodium ferrite
	$2TiO_2 + 2NaOH \rightarrow \mathbf{Na_2Ti_2O_5} + H_2O$	Sodium pertitanate
	$TiO_2 + 2NaOH \rightarrow \mathbf{Na_2TiO_3} + H_2O$	Sodium metatitanate
	$ZrO_2 + 2NaOH \rightarrow \mathbf{Na_2ZrO_3} + H_2O$	Sodium zirconate
	$UO_2 + 2NaOH \rightarrow \mathbf{Na_2UO_4} + H_2O$	Sodium uranate

[0080] Upon completion of the caustic fusion step, substantially all of manganese values initially contained in the ore or concentrate are dissolved into the melt, while the tantalum and niobium values along with the impurities remain in the solid residues. The melt is subsequently allowed to slowly solidify while cooling to room temperature. 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 an 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 an 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 an 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. The time required for the caustic or alkali fusion is typically dependent on the mass ratio between the caustic agent and the ground ore or concentrate. In an embodiment of the present specification, the caustic or alkali fusion step is performed using a dimensionless mass ratio of ore or concentrate mass (C) to mass of melt material (*i.e.* mass of molten sodium hydroxide salt) (S) denoted as C:S or C/S 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.

[0081] The melt produced following the caustic or alkali fusion step is subsequently subjected to an 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 scoping 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.

[0082] In an embodiment of the present disclosure, the solidified melt is subjected to an alkaline leaching step to produce an alkaline pregnant leach solution. In an embodiment of the present disclosure, the alkaline leaching step is performed using a dilute aqueous solution of sodium hydroxide (NaOH). In an embodiment of the present disclosure, the aqueous sodium hydroxide solution comprises a concentration ranging from 50g/liter to 250g/liter. In a further embodiment of the present disclosure, the temperature of the sodium 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 sodium hydroxide solution is at least 13. The resulting blue green and strongly alkaline pregnant leach solution (PLS) contains a suspension of non-dissolved solids and particulates, and is subjected to common solid-liquid separation techniques, such as gravity settling, filtration and centrifugation. In an embodiment of the present disclosure, the solid-liquid separation is carried out while hot. The solid residues obtained following solid-liquid separation consist essentially of insoluble compounds of tantalum (V), niobium (V), iron (III), titanium (IV), zirconium (IV), rear earths (*i.e.*, Y, Sc and lanthanides), and uranides (*e.g.*, uranium and thorium). 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 include hydrated sodium tantalate ($Na_8Ta_6O_{19}.16H_2O$) and sodium niobiate ($Na_8Nb_6O_{19}.16H_2O$); ferric oxides and hydroxides [*e.g.* Fe_2O_3, $Fe(OH)_3$], as a result of the decomposition of sodium ferrite; sodium (IV) titanate [K_2TiO_3]; sodium (IV) zirconate [Zr_2TiO_3]; sodium (IV) uranate [K_2UO_4], hydroxides of rare earth elements (REEs) [$Ln(OH)_3$], as well as thorium hydroxide [$Th(OH)_4$].

[0083] In a further embodiment of the present disclosure, the wet filter cake obtained following solid-liquid separation was thoroughly washed with a hot aqueous solution of NaOH (5 wt.%). The washed residue was subsequently subjected to oxidative acid leaching producing an acid leachate. In an embodiment of the present disclosure, the oxidative acid leaching was performed using sulfuric acid and an oxidizing agent selected from the group consisting of sodium peroxodisulfate ($Na_2S_2O_8$), ammonium peroxodisulfate [$(NH_4)_2S_2O_8$], hydrogen peroxide (H_2O_2) and Caro's acid (H_2SO_5). This oxidative acid leaching oxidized substantially all the uranium (IV) to its hexavalent oxidation state which is highly soluble. In an embodiment of the present disclosure, hydrochloric acid is used as the acid with either hydrogen peroxide (H_2O_2), manganese dioxide (MnO_2), or sodium chlorate ($NaClO_3$) as the oxidizing agent.

[0084] In an embodiment of the present disclosure, the insoluble residues remaining following oxidative acid leaching comprise the tantalum and niobium values as hydrated tantalum oxide ($Ta_2O_5.nH_2O$) and hydrated niobium oxide ($Nb_2O_5.nH_2O$) also called tantalic and niobic acids. The insoluble residues further comprise, to a lesser extent, hydrated oxides of titanium and zirconium which explains why the "sodium" process provides a final tantalum and niobium oxide product that is generally of a lesser purity than that obtained by the "potassium" process.

[0085] In an embodiment of the present disclosure, the hydrated tantalum and niobium oxides are transferred into a long quartz boat or a large zirconium crucible, dried at 120°C for about 4 hours and calcined in a muffle or rotary kiln to yield a dense white fluffy powder comprising a mixture of pure tantalum and niobium oxides (Ta_2O_5 + Nb_2O_5). The solid further includes oxides of titanium and zirconium. In an embodiment of the present disclosure, the calcination is performed at temperatures of about 800°C.

[0086] In an embodiment of the present disclosure, the pH of the acid leachate 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 a range from about 1.0 to 2.5. In an embodiment of the present disclosure, the pH of the acid leachate is adjusted to a range from about 1.2 to 1.5. Following pH adjustment, a saturated solution of oxalic acid (ca. 10 wt.% $H_2C_2O_4$) is added and the solution was allowed to stand overnight resulting in substantially all of the rare earth elements (REEs) along with thorium precipitating out of the solution in the form of insoluble metal oxalates. The precipitate is first rinsed using a dilute oxalic acid solution (2 wt.%) and then with either sulfuric acid or hydrochloric acid (1 wt.%). The residue is then oven dried at 100-110°C and subsequently calcined to yield a product containing rare earth oxides (REOs) and thoria (ThO_2). The remaining liquor contained substantially all of the uranium as uranyl cations (UO_2^{2+}) which could be readily recovered using selective ion exchange resins. The residual liquor contains substantially all of the ferric iron that can be either reduced to ferrous iron and recovered as iron metal by electrowinning or precipitated as ferric hydroxide and neutralized prior to disposal.

[0087] In an embodiment of the present disclosure, the clear alkaline pregnant leach solution obtained following solid-liquid separation comprises substantially all of the manganese values, mainly as blue-green sodium manganite (Na_3MnO_4) and to a lesser extent brilliant-green sodium manganate (Na_2MnO_4), both imparting a blue-green color to the solution. The pregnant leach solution further contains tin, silicon and tungsten values as soluble sodium stannate (Na_2SnO_3), sodium metasilicate (Na_2SiO_3) and sodium orthotunsgtate or wolframate (K_2WO_4). These sodium salts are soluble under the strongly alkaline conditions prevailing in the pregnant leach solution.

[0088] Contrary to the process in which an alkaline leaching using a potassium salt (*i.e.* potassium hydroxide) is performed, the sodium salts of manganese cannot be oxidized to sodium permanganate because: (i) substantially only sodium manganite (Na_3MnO_4) is produced during the caustic fusion process with only little sodium manganate (Na_2MnO_4); (ii) sodium manganite is chemically highly unstable, and; (iii) even if electrolysis were performed, the high solubility of sodium permanganate (*ca.* 900 g/L at room temperature) would preclude the harvesting of the crystals from the mother liquor.

[0089] In an embodiment of the present disclosure, the clear alkaline pregnant leach solution obtained following solid-liquid separation is simply exposed to air and carbon dioxide (*i.e.* maturing) for several hours until the sodium manganate(s) are reduced and/or disproportionated, yielding a dense red-brown precipitate of manganese oxides (*e.g.*, MnO_2, Mn_2O_3). The dense precipitate is then separated by solid-liquid separation techniques, washed with water and oven dried. The dried oxide, consisting mostly of manganese dioxide (MnO_2), can be sold as a technical manganese dioxide product or as a raw material for the synthesis of chemical (CMD) or electrochemical grade (EMD) manganese dioxides, or even as feed for preparing manganese metal either by electrowinning or smelting.

[0090] In an embodiment of the present disclosure, the clear and manganese-free alkaline pregnant leach solution comprising the silicon and tin values, is subsequently used for recovering the tin values by precipitating tin oxide.

[0091] In an embodiment of the present disclosure, the spent acidic solution by-produced during acid leaching of the solid residues can be further concentrated and subjected to electrowinning to recover the iron values and concurrently regenerate the acid values.

[0092] A number of examples are provided herein below, further illustrating the process of the present disclosure in upgrading tantalum and niobium ores and concentrates. The following non-limiting examples are illustrative of the present disclosure.

[0093] EXPERIMENTAL

[0094] EXAMPLE 1: MOLTEN KOH CAUSTIC FUSION (SAMPLE A)

[0095] An aliquot mass (1.2 grams) of an oven dried and ground tantalum concentrate (sample A), having the average chemical composition illustrated in **Table 5**, was weighed using a precision scale. Separately, potassium hydroxide flakes of technical grade (10 g) were pre-melted inside a 25 mL crucible made of nickel 200 and equipped with a zirconium lid to avoid losses by splashing. The intense heating was provided by means of a blast Bunsen burner supplied with propane gas. Once the residual moisture was driven off and the melt surface became quiet, the heating was stopped and the melt was cooled. The ground aliquot sample was subsequently cautiously 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 5 minutes indicating that all the chemical reactions are completed. The caustic fusion reaction was continued for an additional 25 minutes. The heating was stopped and the molten mass was allowed to solidify. The crucible containing the solidified melt (including the lid) was subsequently introduced into a 400 mL borosilicate glass beaker containing a warm aqueous solution of potassium hydroxide (50 g/L of KOH). As a result of the strong exothermicity of the excess caustic dissolution reaction occurring during the alkaline leaching, the temperature of the solution increased. The temperature of the alkaline solution was subsequently maintained at about 60°C by heating with a hot plate. The resulting strongly alkaline pregnant leach solution (PLS) had a dark green color and contained a suspension of non-dissolved solids and particulates. After cooling to room temperature, the PLS was filtered using hardened and ashless filter paper (Whatman #541). The brown solid residue was subsequently washed thoroughly with deionized water, oven dried and then calcined inside a porcelain capsule from CoorsTech to yield 0.219 grams of calcined mass. The clear alkaline pregnant leach solution obtained following the caustic alkaline leach and removal of the suspension of non-dissolved solids and particulates, was intentionally left to stand overnight exposed to air and carbon dioxide. This maturing or ageing step yielded a dense red-brown precipitate composed of manganese oxides. The dense precipitate was subsequently separated by filtration, washed with water and oven dried at 120ºC over a period of 4 hours to yield 0.148 grams of dried manganese dioxide. The clear and manganese-free alkaline pregnant leach solution, containing all the tantalum and niobium values, was transferred to 600-ml glass beaker and the temperature of the solution was raised to 60°C. A saturated aqueous solution of sodium chloride (12 mL) (25.4 wt.% NaCl) was subsequently added. The pH of the resulting solution was gradually increased by cautious dropwise addition of concentrated sulfuric acid (98 wt.% H_2SO_4) until the pH was in a range from about 6-7. In this pH range, a milky white, dense and voluminous precipitate composed of hydrated sodium tantalate and niobiate formed that quickly settled at the bottom of the beaker. The precipitate was recovered by filtration using hardened and ashless filter paper (Whatman #541) and was subsequently rinsed with dilute hydrochloric acid. The wet filter cake of hydrated sodium tantalate and niobiate, along with the filter paper, was transferred into an atmospheric acid leaching apparatus consisting of a 250-mL Erlenmeyer flask containing 100 mL of hydrochloric acid (20 wt.% HCl) connected to a condenser. The precipitate and filter paper were acid leached under reflux conditions over a period of 30 minutes in order to leach out all of the sodium as well as traces of metallic impurities. The filter paper was digested during this treatment, forming a pulp. The hot acid leaching yielded a dense milky white solid consisting of a hydrated mixture of tantalic and niobic acids that was subsequently thoroughly washed with a hot and dilute solution of hydrochloric acid followed by washing with deionized water. The resulting solid was subsequently recovered by filtration using hardened and ashless filter paper (Whatman #541). The hydrated tantalum and niobium oxides, along with the filter paper, were subsequently transferred into a fused silica crucible and dried at a temperature of 120°C over a period of 1 hour. The product was then calcined at 800°C until all the carbon values were burned off and the fumes ceased. The calcination yielded a dense white powder (0.913 grams). The average chemical composition of the white powder was determined to be 90.5 percent by mass of tantalum pentoxide (Ta_2O_5) and 9.5 percent by mass of niobium oxide (Nb_2O_5) with no detectable traces of other impurities. The overall recovery of the tantalum and niobium values as contained in the original concentrate was determined to be 99 percent by weight (**Table 6**).

[0096] EXAMPLE 2: MOLTEN KOH CAUSTIC FUSION (SAMPLE B)

[0097] An aliquot mass (1.5 grams) of an oven dried and ground tantalum concentrate (sample B), having the average chemical composition illustrated in **Table 5**, was weighed using a precision scale. Separately, potassium hydroxide flakes of technical grade (15 g) were pre-melted inside a 25 mL crucible made of nickel 200 and equipped with a zirconium lid to avoid losses by splashing. The intense heating was provided by means of a blast Bunsen burner supplied with propane gas. Once the residual moisture was driven off and the melt surface became quiet, the heating was stopped and the melt was cooled. The ground aliquot sample was subsequently cautiously 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 5 minutes indicating that all the chemical reactions are completed. The caustic fusion reaction was continued for an additional 25 minutes. The heating was stopped and the molten mass was allowed to solidify. The crucible containing the solidified melt (including the lid) was subsequently introduced into a 400 mL borosilicate glass beaker containing a warm aqueous solution of potassium hydroxide (50 g/L of KOH). As a result of the strong exothermicity of the excess caustic dissolution reaction occurring during the alkaline leaching, the temperature of the solution increased. The temperature of the alkaline solution was subsequently maintained at about 60°C by heating with a hot plate. The resulting strongly alkaline pregnant leach solution (PLS) had a dark green color and contained a suspension of non-dissolved solids and particulates. After cooling to room temperature, the PLS was filtered using hardened and ashless filter paper (Whatman #541). The brown solid residue was subsequently washed thoroughly with deionized water, oven dried and then calcined inside a porcelain capsule from CoorsTech to yield

0.520 grams of calcined mass. The clear alkaline pregnant leach solution obtained following the caustic alkaline leach and removal of the suspension of non-dissolved solids and particulates, was intentionally left to stand overnight exposed to air and carbon dioxide. This maturing or ageing step yielded a dense red-brown precipitate composed of manganese oxides. The dense precipitate was subsequently separated by filtration, washed with water and oven dried at 120ºC over a period of 4 hours to yield 0.193 grams of dried manganese dioxide. The clear and manganese-free alkaline pregnant leach solution, containing all the tantalum and niobium values, was transferred to 600-ml glass beaker and the temperature of the solution was raised to 60°C. A saturated aqueous solution of sodium chloride (12 mL) (25.4 wt.% NaCl) was subsequently added. The pH of the resulting solution was gradually increased by cautious dropwise addition of concentrated sulfuric acid (98 wt.% H_2SO_4) until the pH was in a range from about 6-7. In this pH range, a milky white, dense and voluminous precipitate composed of hydrated sodium tantalate and niobiate formed that quickly settled at the bottom of the beaker. The precipitate was recovered by filtration using hardened and ashless filter paper (Whatman #541) and was subsequently rinsed with dilute hydrochloric acid. The wet filter cake of hydrated sodium tantalate and niobiate, along with the filter paper, was transferred into an atmospheric acid leaching apparatus consisting of a 250-mL Erlenmeyer flask containing 100 mL of hydrochloric acid (20 wt.% HCl) connected to a condenser. The precipitate and filter paper were acid leached under reflux conditions over a period of 30 minutes in order to leach out all of the sodium as well as traces of metallic impurities. The filter paper was digested during this treatment, forming a pulp. The hot acid leaching yielded a dense milky white solid consisting of a hydrated mixture of tantalic and niobic acids that was subsequently thoroughly washed with a hot and dilute solution of hydrochloric acid followed by washing with deionized water. The resulting solid was subsequently recovered by filtration using hardened and ashless filter paper (Whatman #541). The hydrated tantalum and niobium oxides, along with the filter paper, were subsequently transferred into a fused silica crucible and dried at a temperature of 120°C over a period of 1 hour. The product was then calcined at 800°C until all the carbon values were burned off and the fumes ceased. The calcination yielded a dense white powder

(0.991 grams). The average chemical composition of the white powder was determined to be 63.1 percent by mass of tantalum pentoxide (Ta_2O_5) and 36.9 percent by mass of niobium oxide (Nb_2O_5). The overall recovery of the tantalum and niobium values as contained in the original concentrate was determined to be 99 percent by weight (**Table 6**).

[0098] EXAMPLE 3: MOLTEN NaOH CAUSTIC FUSION (SAMPLE A)

[0099] An aliquot mass (1.0 grams) of an oven dried and ground tantalum concentrate (sample A), having the average chemical composition illustrated in **Table 5**, was weighed using a precision scale. Separately, sodium hydroxide flakes of technical grade (12.4 g) were pre-melted inside a 25 mL crucible made of nickel 200 and equipped with a zirconium lid to avoid losses by splashing. The intense heating was provided by means of a blast Bunsen burner supplied with propane gas. Once the residual moisture was driven off and the melt surface became quiet, the heating was stopped and the melt was cooled. The ground aliquot sample was subsequently cautiously 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 5 minutes indicating that all the chemical reactions are completed. The caustic fusion reaction was continued for an additional 25 minutes. The heating was stopped and the molten mass was allowed to solidify. The crucible containing the solidified melt (including the lid) was subsequently introduced into a 400 mL borosilicate glass beaker containing a warm aqueous solution of sodium hydroxide (50 g/L of NaOH). As a result of the strong exothermicity of the excess caustic dissolution reaction occurring during the alkaline leaching, the temperature of the solution increased. The temperature of the alkaline solution was subsequently maintained at about 60°C by heating with a hot plate. The resulting strongly alkaline pregnant leach solution (PLS) had a blue green color and contained a suspension of non-dissolved solids and particulates. After cooling to room temperature, the PLS was filtered using hardened and ashless filter paper (Whatman

#541). The brown solid residue was subsequently washed thoroughly with deionized water and put aside for the subsequent recovery of the tantalum and niobium values. The clear alkaline pregnant leach solution obtained following the caustic alkaline leach and removal of the suspension of non-dissolved solids and particulates, was intentionally left to stand overnight exposed to air and carbon dioxide. This maturing or ageing step yielded a dense red-brown precipitate composed of manganese oxides. The dense precipitate was subsequently separated by filtration, washed with water and oven dried at 120°C over a period of 4 hours to yield 0.158 grams of dried manganese dioxide. The brown solid residue (along with the filter paper), containing the tantalum and niobium values as hydrated sodium tantalate and niobiate, as well as the iron, titanium and zirconium values, was transferred into an atmospheric acid leaching apparatus consisting of a 250-mL Erlenmeyer flask containing 100 mL of hydrochloric acid (20 wt.% HCl) connected to a condenser. The residue and filter paper were acid leached under reflux conditions over a period of 30 minutes in order to leach out all of the iron and sodium. The filter paper was digested during this treatment, forming a pulp. The hot acid leaching yielded a dense solid consisting of a hydrated mixture of tantalic and niobic acids that was subsequently thoroughly washed with a hot and dilute solution of hydrochloric acid followed by washing with deionized water. The resulting solid was subsequently recovered by filtration using hardened and ashless filter paper (Whatman #541). The hydrated tantalum and niobium oxides, along with the filter paper, were subsequently transferred into a fused silica crucible and dried at a temperature of 120°C over a period of 4 hours. The product was then calcined at 800°C until all the carbon values were burned off and the fumes ceased. The calcination yielded a dense off-white powder (0.782 grams). The average chemical composition of the white powder was determined to be 87.7 percent by mass of tantalum pentoxide (Ta_2O_5) and 9.2 percent by mass of niobium oxide (Nb_2O_5) in addition to 3.1 percent by mass of other metal oxides, mainly titanium dioxide and zirconium dioxide tainted by traces of ferric oxide. The overall recovery of the tantalum and niobium values as contained in the original concentrate was determined to be 98.9 percent by weight (**Table 6**).

[00100] EXAMPLE 4: MOLTEN KOH CAUSTIC FUSION (SAMPLE C)

[00101] An aliquot mass (2.44 grams) of an oven dried and ground columbite concentrate (sample C), having the average chemical composition illustrated in **Table 5**, was weighed using a precision scale. Separately, potassium hydroxide flakes of technical grade (20 g) were pre-melted inside a tall 200 mL crucible made of deep drawn pure zirconium (BJ Scientific). The intense heating was provided by means of a pair of blast Bunsen burners supplied with propane gas. Once the residual moisture was driven off and the melt surface became quiet, the heating was stopped and the melt was cooled. The ground aliquot sample was subsequently cautiously 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 5 minutes indicating that all the chemical reactions are completed. The caustic fusion reaction was continued for an additional 25 minutes. The heating was stopped and the molten mass was allowed to solidify. An aqueous solution of potassium hydroxide (150 mL; 50 g/L of KOH) was then poured directly into the crucible containing the solidified melt. As a result of the strong exothermicity of the excess caustic dissolution reaction occurring during the alkaline leaching, the temperature of the solution increased. The temperature of the alkaline solution was subsequently maintained at about 60°C by heating the zirconium crucible directly on a hot plate equipped with a magnetic stirrer. A PTFE-coated magnetic bar was subsequently introduced into the crucible to ensure proper agitation and mixing. The resulting strongly alkaline pregnant leach solution (PLS) had a dark green color and contained a suspension of non-dissolved solids and particulates. After cooling to room temperature, the PLS was filtered using hardened and ashless filter paper (Whatman #541). The brown solid residue was subsequently washed thoroughly with aqueous potassium hydroxide, deionized water, oven dried and then calcined inside a porcelain capsule from CoorsTech to yield 1.030 grams of calcined mass. The clear alkaline pregnant leach solution obtained following the caustic alkaline leach and removal of the suspension of non-dissolved solids and particulates, was intentionally left to stand overnight exposed to air and carbon dioxide. This maturing or ageing step yielded a dense red-brown precipitate composed of manganese oxides. The dense precipitate was subsequently separated by filtration, washed with water and oven dried at 120°C over a period of 4 hours to yield 0.276 grams of dried manganese dioxide. The clear and manganese-free alkaline pregnant leach solution, containing all the tantalum and niobium values, was transferred to 600-ml glass beaker and the temperature of the solution was raised to 60°C. A saturated aqueous solution of sodium chloride (10 mL) (25.4 wt.% NaCl) was subsequently added. The pH of the resulting solution was gradually increased by cautious dropwise addition of concentrated sulfuric acid (98 wt.% H_2SO_4) until the pH was in a range from about 6-7. In this pH range, a milky white, dense and voluminous precipitate composed of hydrated sodium tantalate and niobiate formed that quickly settled at the bottom of the beaker. The precipitate was recovered by filtration using hardened and ashless filter paper (Whatman #541) and was subsequently rinsed with water with dilute hydrochloric acid. The wet filter cake of hydrated sodium tantalate and niobiate, along with the filter paper, was transferred into an atmospheric acid leaching apparatus consisting of a 250-mL Erlenmeyer flask containing 60 mL of hydrochloric acid (36 wt.% HCl) connected to a condenser. The precipitate and filter paper were acid leached under reflux conditions over a period of 30 minutes in order to leach out all of the sodium as well as traces of metallic impurities. The filter paper was digested during this treatment, forming a pulp. The hot acid leaching yielded a dense milky white solid consisting of a hydrated mixture of tantalic and niobic acids that was subsequently thoroughly washed with a hot and dilute solution of hydrochloric acid followed by washing with deionized water. The resulting solid was subsequently recovered by filtration using hardened and ashless filter paper (Whatman #541). The hydrated tantalum and niobium oxides, along with the filter paper, were subsequently transferred into a fused silica crucible and dried at a temperature of 120°C over a period of 1 hour. The product was then calcined at 800°C until all the carbon values were burned off and the fumes ceased. The calcination yielded a dense white powder (1.650 grams). The average chemical composition of the white powder was determined to be 19.2 percent by mass of tantalum pentoxide (Ta_2O_5) and 80.8 percent by mass of niobium oxide (Nb_2O_5). The overall recovery of the tantalum and niobium values as contained in the original concentrate was determined to be 97.6 percent by weight (**Table 6**).

[00102] EXAMPLE 5: MOLTEN KOH CAUSTIC FUSION (SAMPLE D)

[00103] An aliquot mass (2.04 grams) of an oven dried and ground Samarskite concentrate (sample D), having the average chemical composition illustrated in **Table 5**, was weighed using a precision scale. Separately, potassium hydroxide flakes of technical grade (18 g) were pre-melted inside a tall 200 mL crucible made of deep drawn pure zirconium (BJ Scientific). The intense heating was provided by means of a pair of blast Bunsen burners supplied with propane gas. Once the residual moisture was driven off and the melt surface became quiet, the heating was stopped and the melt was cooled. The ground aliquot sample was subsequently cautiously 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 5 minutes indicating that all the chemical reactions are completed. The caustic fusion reaction was continued for an additional 25 minutes. The heating was stopped and the molten mass was allowed to solidify. An aqueous solution of potassium hydroxide (100 mL; 50 g/L of KOH) was then poured directly into the crucible containing the solidified melt. As a result of the strong exothermicity of the excess caustic dissolution reaction occurring during the alkaline leaching, the temperature of the solution increased. The temperature of the alkaline solution was subsequently maintained at about 60°C by heating the zirconium crucible directly on a hot plate equipped with a magnetic stirrer. A PTFE-coated magnetic bar was subsequently introduced into the crucible to ensure proper agitation and mixing. The resulting strongly alkaline pregnant leach solution (PLS) had a dark green color and contained a suspension of non-dissolved solids and particulates. After cooling to room temperature, the PLS was filtered using hardened and ashless filter paper (Whatman #541). The brown solid residue was subsequently washed

thoroughly with aqueous potassium hydroxide, deionized water, oven dried and then calcined inside a porcelain capsule from CoorsTech to yield 1.005 grams of calcined mass. The clear alkaline pregnant leach solution obtained following the caustic alkaline leach and removal of the suspension of non-dissolved solids and particulates, was intentionally left to stand overnight exposed to air and carbon dioxide. This maturing or ageing step yielded a dense red-brown precipitate composed of manganese oxides. The dense precipitate was subsequently separated by filtration, washed with water and oven dried at 120°C over a period of 4 hours to yield 0.109 grams of dried manganese dioxide. The clear and manganese-free alkaline pregnant leach solution, containing all the tantalum and niobium values, was transferred to 600-ml glass beaker and the temperature of the solution was raised to 60°C. A saturated aqueous solution of sodium chloride (10 mL) (25.4 wt.% NaCl) was subsequently added. The pH of the resulting solution was gradually increased by cautious dropwise addition of concentrated sulfuric acid (98 wt.% H_2SO_4) until the pH was in a range from about 6-7. In this pH range, a milky white, dense and voluminous precipitate composed of hydrated sodium tantalate and niobiate formed that quickly settled at the bottom of the beaker. The precipitate was recovered by filtration using hardened and ashless filter paper (Whatman #541) and was subsequently rinsed with water with dilute hydrochloric acid. The wet filter cake of hydrated sodium tantalate and niobiate, along with the filter paper, was transferred into an acid digestion Bomb (125 mL) having an inner PTFE-liner from Parr Instruments and charged with 50 mL of hydrochloric acid (20 wt.% HCl). The pressure acid leaching autoclave, once hermetically sealed, was progressively heated to 150°C in an oven and maintained at that constant temperature for two hours in order to leach out all of the sodium as well as traces of metallic impurities. The filter paper was digested during this treatment, forming a pulp. The hot pressure acid leaching yielded a dense milky white solid consisting of a hydrated mixture of tantalic and niobic acids that was subsequently thoroughly washed with a hot and dilute solution of hydrochloric acid followed by washing with deionized water. The resulting solid was subsequently recovered by filtration using hardened and ashless filter paper (Whatman #541). The hydrated tantalum and niobium oxides, along with the filter paper, were subsequently transferred into a tall platinum crucible and dried at a temperature of 120°C over a period of 1 hour. The product was then calcined at 800°C until all the carbon values were burned off and the fumes ceased. The calcination yielded a dense white powder (0.989 grams). The average chemical composition of the white powder was determined to be 22.5 percent by mass of tantalum pentoxide (Ta_2O_5) and 77.5 percent by mass of niobium oxide (Nb_2O_5). The overall recovery of the tantalum and niobium values as contained in the original concentrate was determined to be 98.9 percent by weight (**Table 6**).

[00104] EXAMPLE 6: RECOVERY OF RARE EARTH OXIDES AND THORIUM FROM INSOLUBLE ALKALINE RESIDUES

[00105] The wet filter cake consisting of the brown solid residue, obtained following caustic fusion and alkaline leaching (Example 5 -sample D), was transferred into an atmospheric acid leaching apparatus consisting of 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 under reflux conditions over a period of 120 minutes. Small crystals of solid potassium chlorate ($KClO_3$) were added regularly with caution due to the strong evolution of chlorine gas. During this step all the uranium was oxidized to uranium (IV). Once the acid leaching was completed and the leachate was cooled and filtered using hardened and ashless filter paper (Whatman #541), the isolated insoluble residue consisted essentially of titanium and zirconium oxide. After adjusting the pH of the yellow filtrate to about 1.2 by the stepwise addition of small volumes of an aqueous potassium hydroxide solution, a saturated solution of oxalic acid (ca. 10 wt.% $H_2C_2O_4$) was added and the solution was left stand overnight in order to precipitate all the insoluble rare earth values and thorium oxalates. The precipitate was subsequently thoroughly rinsed using a solution containing 2 wt.% oxalic acid and then air dried at 110°C over a period of several hours to yield a product containing the rare earth oxides (REOs) and thoria (ThO_2). The air dried rare earth oxide (REOs) product contained the cerium values as cerium(IV) along with other lanthanide hydroxides ($Ln(OH)_3$) and thorium hydroxide ($Th(OH)_4$.). The air-dried residue was subsequently acid leached using a diluted hydrochloric acid solution having a pH ranging between 2 and 4 leaving behind an insoluble cerium(IV) hydroxide which was easily recovered by filtration. The clear filtrate solution, containing all the thorium and the other lanthanides, was reacted with zinc powder in order to reduce Eu(III) to Eu(II). An aqueous solution of barium chloride (5 wt.% $BaCl_2$) was subsequently added to the clear solution followed by a stoichiometric amount of dilute sulfuric acid in order to co-precipitate the insoluble barium and europium sulfates [$(Ba,Eu)SO_4$]. The completion of the europium precipitation was 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)). The europium was recovered from the wet insoluble $(Ba,Eu)SO_4$ precipitate by simply oxidizing it with hot concentrated nitric acid and by precipitating the europium (III) hydroxide once the solution was neutralized with ammonia. The remaining cerium- and europium-free liquor contained the remaining lanthanides and most of the thorium.

[00106] EXAMPLE 7: ELECTROSYNTHESIS OF POTASSIUM PERMANGANATE AND CONCURRENT ELECTROCHEMICAL REGENERATION OF KOH

[00107] A filtered alkaline pregnant leach solution (150 mL), obtained after caustic fusion of 10 grams of sample B and hot alkaline leaching, was charged in the anode compartment of the electrolyzer. The electrolyzer consisted of a rectangular cell divided into two compartments by a cation exchange membrane (CEM) made of NAFION® N324 (E.I. DUPONT DE NEMOURS). The anode compartment was equipped with a rectangular plate anode composed of pure nickel grade 201 while the cathode compartment was equipped with a rectangular plate cathode composed of austenitic stainless steel grade AISI 304. Both anode and cathode exhibited exactly the same dimensions (*i.e.* 4-in tall and 2-in wide and 1/8-in thick; 10.16 cm x 5.08 cm x 3.175 mm). Once immersed inside their respective electrolyte (2 inches), the active cathode and anode surface areas were 4 square inches (25.81 cm^2). The distance between the cation exchange membrane and the anode and the cathode was 1 inch (2.54 cm) and the inter-electrode gap was 2 inches (5.08 cm). The catholyte consisted of a diluted alkaline solution of potassium hydroxide containing 112 g/L KOH (*i.e.* 2

mol/L KOH) as measured by acid-base titration. After electrolysis, the concentration of potassium permanganate in the anolyte was determined by redox titration using a standard solution of sodium oxalate 0.1N. Both the anolyte and catholyte were circulated at room temperature with a volume flow rate of 90 mL/min using a L/S peristaltic pump (MASTERFLEX). The electrolysis was performed under galvanostatic mode (*i.e.* at a constant current of 1.29 A corresponding to an absolute current density of 500 A/m^2 at both electrodes. The average cell voltage measured between the anode and cathode was 2.9 V and the electrolysis was conducted over a period of 10 minutes. Upon completion of the electrolysis, the anolyte color turned purple, characteristic of permanganate anions. The final concentration of potassium hydroxide in the catholyte was measured by acid-base titration to be 114.9 g/L KOH. The potassium permanganate concentration in the anolyte was measured by redox titration using oxalic acid to be 8.0 g/L $KMnO_4$. The cathode and anode current efficiencies were determined to be 97% and 95% respectively. The specific energy consumption was determined to be 1.43 kWh/kg of KOH and 0.52 kWh/kg of $KMnO_4$ respectively (**Table 7**).

[00108] Table 5: Average chemical composition of the tantalum and niobium concentrates (only the principal metal oxides are shown).

METAL OXIDE (wt.%)	SAMPLE A (WODGINITE)	SAMPLE B (TANTALITE)	SAMPLE C (COLUMBITE)	SAMPLE D (SAMARSKITE)
Ta_2O_5	69.60	42.13	13.30	11.00
Nb_2O_5	7.30	24.61	56.00	38.00
MnO	7.50	8.00	6.42	1.00
FeO	4.00	13.51	14.00	12.00
SnO_2	8.80	8.00	0.56	1.00
SiO_2	0.10	0.50	3.04	0.20
Ln_2O_3	0.02	0.18	0.01	20.14
Al_2O_3	0.08	1.40	1.18	0.20
TiO_2	1.10	0.27	0.66	0.50
ZrO_2	1.20	1.00	4.40	0.96
UO_2	0.30	0.40	0.43	11.00

[00109] Table 6: Recovery of tantalum and niobium from the concentrates (only the principal metal oxides are shown; DL = detection limit).

METAL OXIDE (wt.%)	Tantalum and niobium oxide product from example #1	Tantalum and niobium oxide product from example #2	Tantalum and niobium oxide product from example #3	Tantalum and niobium oxide product from example #4	Tantalum and niobium oxide product from example #5
Ta_2O_5	90.5	63.1	87.7	19.2	22.5
Nb_2O_5	9.5	36.9	9.2	80.8	77.5
MnO	<DL	<DL	<DL	<DL	<DL
FeO	<DL	<DL	0.03	<DL	<DL
SnO_2	<DL	<DL	<DL	<DL	<DL
SiO_2	<DL	<DL	<DL	<DL	<DL
Al_2O_3	<DL	<DL	<DL	<DL	<DL
TiO_2	<DL	<DL	1.38	<DL	<DL
ZrO_2	<DL	<DL	1.51	<DL	<DL
UO_2	<DL	<DL	<DL	<DL	<DL
Overall (Ta+Nb) oxide value recovery yield	99.0%	99.1%	98.9%	97.6%	98.9%

[00110] Table 7: Operating Conditions and Cell Performance for the Electrosynthesis of Potassium Permanganate and Concurrent Regeneration of Potassium Hydroxide.

PARAMETER(S)	DESCRIPTION
CATHODE MATERIAL	Stainless steel AISI 304
CATHOLYTE (INITIAL)	KOH 112 g/L
CATHOLYTE (FINAL)	KOH 114.9 g/L
CATION EXCHANGE MEMBRANE	NAFION® N324
ANODE MATERIAL	Pure nickel 201
ANOLYTE (INITIAL)	Filtered PLS (Dark green color)
ANOLYTE (FINAL)	Violet color solution with 8 g/L $KMnO_4$
TEMPERATURE	ROOM TEMPERATURE

OVERALL CELL VOLTAGE (AVG.)	2.90V
CATHODE CURRENT EFFICIENCY	97%
ANODE CURRENT EFFICIENCY	95%
CATHODE CURRENT DENSITY	-500 A/m^2
ANODE CURRENT DENSITY	+500 A/m^2
SPECIFIC ENERGY CONSUMPTION	1.43 kWh/kg of KOH 0.52 kWh/kg of $KMnO_4$

[00111] 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.

WHAT IS CLAIMED IS:

1. A process for upgrading tantalum and niobium ores and concentrates, the process comprising:

a) submitting the ore or concentrate 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 an alkaline leaching step to produce an alkaline pregnant leaching solution comprising manganese values;

c) recovering the manganese values from the alkaline pregnant leaching solution to produce a substantially manganese-free leach solution; and

d) precipitating tantalum and niobium as an insoluble niobiate and tantalate from the manganese-free leach solution.

2. The process of claim **1**, further comprising:

a) separating the alkaline pregnant leaching solution from insoluble solid residues;

b) recovering rare earth oxides and/or thorium oxides from the insoluble solid residues producing a spent acid filtrate;

c) recovering uranium from the spent acid filtrate.

3. The process of claim **1**, further comprising:

a) acid-leaching the insoluble niobiate and tantalate producing a hydrated tantalum and niobium oxides; and

b) calcining or roasting the hydrated tantalum and niobium oxides to yield tantalum metal and niobium oxides.

4. 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.

5. The process of claim **4**, wherein the molten alkali-metal hydroxide is selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide and mixtures thereof.

6. The process of claim **5**, wherein the caustic fusion or alkali fusion is performed using a mixture of alkali-metal hydroxides.

7. The process of claim **6**, 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.

8. The process of claim **6**, 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.

9. The process of claim **4**, wherein the melt comprises a blend of alkali-metal hydroxides.

10. The process of claim **9**, wherein the alkali-metal hydroxides are individually melted or melted together prior to being used in the caustic or alkali fusion step.

11. The process of claim **1**, wherein the ores or concentrates are ground and oven dried prior to being subjected to the caustic or alkali fusion step.

12. The process of claim **11**, wherein the ground and oven dried ores or concentrates are fed into the melt at fusion temperatures and continuously stirred.

13. The process of claim **11**, wherein the ground and oven dried ores or concentrates 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.

14. The process according to claim **5**, wherein the caustic or alkali fusion step is performed at a temperature of at least the melting point of the alkali metal salt.

15. The process according to claim **6**, wherein the caustic or alkali fusion step is performed at a temperature of at least the eutectic melt temperature of the mixture.

16. The process of claim **15**, wherein the melt temperature ranges from about 200°C to about 1200°C.

17. The process of any one of claims **1** to **16**, wherein the caustic or alkali fusion step is performed over a period of time ranging from 5 minutes to 6 hours.

18. The process of claim **17**, wherein the caustic or alkali fusion step is performed over a period of time ranging from 10 minutes to 4 hours.

19. The process of claim **17**, wherein the caustic or alkali fusion step is performed over a period of time ranging from 15 minutes to 2 hours.

20. The process of claim **17**, wherein the caustic or alkali fusion step is performed over a period of time ranging from 15 minutes to 1 hour.

21. The process of claim **1**, wherein the caustic or alkali fusion step is performed using a mass ratio of ore material to melt material denoted as C:S or C/S ranging from 1:1 to 1:20.

22. The process of claim **21**, 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.

23. The process of claim **22**, 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.

24. The process of claim **23**, 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.

25. The process according to claim **1**, wherein the caustic or alkali fusion step is performed using a furnace or a rotary kiln.

26. The process according to claim **25**, wherein the caustic or alkali fusion step is performed using a crucible furnace.

27. The process according to claim **25**, wherein the caustic or alkali fusion step is performed using a muffle furnace.

28. The process according to claim **25**, wherein the caustic or alkali fusion step is performed using a rotary heart furnace.

29. 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.

30. The process according to claim **29**, wherein the containment vessel or crucible comprises a material selected from the group consisting of composite metallic materials, bulk metals, alloys and ceramic materials.

31. The process according to claim **29**, 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.

32. The process of claim **30**, 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.

33. The process of claim **32**, 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.

34. The process of claim **30**, 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.

35. The process of claim **8**, wherein the caustic fusion or alkali fusion is performed using a potassium salt selected from the group consisting of molten potassium hydroxide, potassium peroxide, potassium carbonate, potassium nitrate and mixtures thereof.

36. The process of claim **1**, wherein the alkaline leaching step is performed using an aqueous potassium hydroxide solution.

37. The process of claim **36**, wherein the potassium hydroxide solution comprises a concentration ranging from 50g/liter to 250g/liter.

38. The process of claim **37**, wherein the temperature of the potassium hydroxide solution ranges from room temperature to the boiling point of the solution.

39. The process of claim **2**, wherein the alkaline pregnant leaching solution is subjected to solid-liquid separation to produce an alkaline pregnant leaching liquor.

40. The process of claim **39**, wherein the solid-liquid separation is selected from gravity settling, filtration and centrifugation.

41. The process of claim **2**, wherein the solid residues comprise compounds of iron (III), titanium (IV), zirconium (IV), rare earths and uranides.

42. The process of claim **41**, wherein the rare earths include Y, Sc and lanthanides and wherein the uranides include uranium and thorium.

43. The process of claim **41**, wherein the solid residues are subjected to oxidative acid leaching producing an acid leachate.

44. The process of claim **43**, wherein the oxidative acid leaching is performed using sulfuric acid and an oxidizing agent selected from the group consisting of potassium peroxodisulfate ($K_2S_2O_8$), ammonium peroxodisulfate [$(NH_4)_2S_2O_8$], hydrogen peroxide (H_2O_2) and Caro's acid (H_2SO_5).

45. The process of claim **43**, wherein the oxidative acid leaching is performed using hydrochloric acid and an oxidizing agent selected from the group consisting of hydrogen peroxide (H_2O_2), manganese dioxide (MnO_2) and potassium chlorate ($KClO_3$).

46. The process of any one of claims **43** to **45**, wherein the oxidative acid leaching is performed under atmospheric conditions or under pressure.

47. The process of claim **46**, wherein the oxidative acid leaching is carried-out in an autoclave.

48. The process of any one of claims **43** to **47**, wherein the acid leachate is filtered and the pH adjusted to values ranging from 1.2 to 1.5.

49. The process of claim **48**, further comprising precipitating values including rare earth elements and/or thorium as insoluble metal oxalates and producing a liquor comprising the uranides.

50. The process of claim **49**, wherein the precipitation is performed by adding a saturated solution of oxalic acid to the leachate.

51. The process of claim **49**, wherein the insoluble metal oxalates are washed with an aqueous acid solution selected from the group consisting of oxalic acid, sulfuric acid and hydrochloric acid to produce washed metal oxalates.

52. The process of claim **51**, wherein the washed metal oxalates are dried.

53. The process of claim **52**, wherein the dried metal oxalates are calcined to produce rare earth metal oxides and/or thoria (ThO_2).

54. The process of claim **53**, wherein the rare earth metal oxides and/or thoria are subjected to acid leaching to separate cerium as insoluble cerium(IV) compounds and to produce an acid leachate.

55. The process of claim **49**, wherein the liquor is treated with an ion exchange resin to recover the uranides as uranyl cations (UO_2^{2+}).

56. The process of claim **39**, wherein the alkaline pregnant leaching liquor comprises manganese values, tantalum values and niobium values.

57. The process of claim **56**, wherein the manganese values are recovered by electrolyzing the alkaline pregnant leaching liquor and wherein the electrolyzing produces a manganese-free leaching liquor.

58. The process of claim **57**, wherein the electrolysis is performed batch-wise or in continuous mode using a two-chamber electrolyzer equipped with a cation exchange membrane.

59. The process of claim **58**, wherein the manganese values are obtained as potassium permanganate.

60. The process of claim **58**, wherein potassium hydroxide is regenerated.

61. The process of claim **56**, wherein the alkaline pregnant leaching liquor is exposed to air and carbon dioxide to produce a precipitate of manganese dioxide and a manganese-free leaching liquor.

62. The process of claim **61**, wherein the manganese dioxide is isolated by solid-liquid separation.

63. The process of claim **57** or **61**, wherein the manganese-free leaching liquor is heated to a temperature ranging from 30°C to 100°C.

64. The process of claim **63**, wherein an aqueous solution of a sodium salt is added to the manganese-free leaching liquor to precipitate the tantalum values and niobium values as sodium salts.

65. The process of claim **64**, wherein the sodium salt is selected from the group consisting of sodium chloride and sodium sulfate and mixtures thereof.

66. The process of claim **64**, wherein an aqueous acidic solution is added to the liquor to adjust the pH of the liquor at values ranging from 5 and 10 and to produce hydrated sodium tantalate and hydrated sodium niobiate.

67. The process of claim **66**, wherein the aqueous acidic solution is selected from the group consisting of aqueous H_2SO_4, aqueous HCl and mixtures thereof.

68. The process of claim **67**, wherein the hydrated sodium tantalate and hydrated sodium niobiate are isolated by solid-liquid separation to produce a spent solution.

69. The process of claim **68**, wherein the hydrated sodium tantalate and hydrated sodium niobiate are acid leached to produce hydrated tantalum oxide and hydrated niobium oxide.

70. The process of claim **69**, wherein the acid leaching is performed using hot sulfuric acid or hydrochloric acid or mixtures thereof.

71. The process of claim **70**, wherein the acid leaching is performed under atmospheric conditions or under pressure.

72. The process of claim **71**, wherein the acid leaching is carried-out in an autoclave.

73. The process of claim **69**, wherein the hydrated tantalum oxide and hydrated niobium oxide are isolated by solid-liquid separation.

74. The process of claim **73**, wherein the hydrated tantalum oxide and hydrated niobium oxide are calcined to produce a mixture of tantalum and niobium oxides.

75. The process of claim **69**, wherein the acid leaching further produces a brine solution.

76. The process of claim **8**, wherein the caustic fusion or alkali fusion is performed using a sodium salt selected from the group consisting of molten sodium hydroxide, sodium peroxide, sodium carbonate, sodium nitrate and mixtures thereof.

77. The process of claim **76**, wherein the alkaline leaching step is performed using an aqueous sodium hydroxide solution.

78. The process of claim **77**, wherein the sodium hydroxide solution comprises a concentration ranging from 50g/liter to 250g/liter.

79. The process of claim **78**, wherein the temperature of the sodium hydroxide solution ranges from room temperature to the boiling point of the solution.

80. The process of claim **76**, wherein the alkaline pregnant leaching solution is subjected to solid-liquid separation to produce an alkaline pregnant leaching liquor.

81. The process of claim **80**, wherein the solid-liquid separation is selected from gravity settling, filtration and centrifugation.

82. The process of claim **8**, wherein the solid residues comprise sodium tantalate, sodium niobiate, compounds of iron (III), titanium (IV), zirconium (IV), rare earth metals and uranides.

83. The process of claim **82**, wherein the rare earth metals include at least an element selected from the lanthanides, yttrium and scandium and wherein the uranides include uranium and thorium.

84. The process of claim **82**, wherein the solid residues are subjected to oxidative acid leaching producing an acid leachate and an oxidized residue.

85. The process of claim **84**, wherein the oxidative acid leaching is performed using sulfuric acid and an oxidizing agent selected from the group consisting of potassium peroxodisulfate, ammonium peroxodisulfate, hydrogen peroxide and Caro's acid.

86. The process of claim **85**, wherein the oxidative acid leaching is performed using hydrochloric acid and an oxidizing agent selected from the group consisting of hydrogen peroxide, manganese dioxide and sodium chlorate.

87. The process of any one of claims **84** to **86**, wherein the oxidative acid leaching is performed under atmospheric conditions or under pressure.

88. The process of claim **87**, wherein the oxidative acid leaching is carried-out in an autoclave.

89. The process of any one of claims **84** to **88**, wherein the acid leachate is filtered and the pH adjusted to values ranging from 1.2 to 1.5.

90. The process of claim **89**, further comprising precipitating values including rare earth elements and/or thorium as insoluble metal oxalates and producing a liquor comprising the uranides.

91. The process of claim **90**, wherein the precipitation is performed by adding a saturated solution of oxalic acid to the leachate.

92. The process of claim **90**, wherein the insoluble metal oxalates are washed with an aqueous acid solution selected from the group consisting of oxalic acid, sulfuric acid and hydrochloric acid to produce washed metal oxalates.

93. The process of claim **92**, wherein the washed metal oxalates are dried.

94. The process of claim **93**, wherein the dried metal oxalates are calcined to produce rare earth metal oxides and/or thoria.

95. The process of claim **90**, wherein the liquor is treated with an ion exchange resin to recover the uranides as uranyl cations (UO_2^{2+}).

96. The process of claim **80**, wherein the alkaline pregnant leaching liquor comprises at least manganese values and tin values.

97. The process of claim **96**, wherein the alkaline pregnant leaching liquor is exposed to air and carbon dioxide to produce a precipitate of manganese dioxide and a manganese-free leaching liquor.

98. The process of claim **97**, wherein the manganese dioxide is isolated by solid-liquid separation.

99. The process of claim **84**, wherein the oxidized residue comprises hydrated tantalum oxide and hydrated niobium oxide.

100. The process of claim **99**, wherein the oxidized residue further comprises hydrated titanium and zirconium oxides.

101. The process of claim **99**, wherein the oxidized residue is washed with an aqueous acid solution selected from the group consisting of sulfuric acid and hydrochloric acid.

102. The process of claim **101**, wherein the hydrated tantalum oxide and hydrated niobium oxide are calcined to produce tantalum oxide and niobium oxide.

103. The process of claim **53**, wherein the acid leachate is subjected to zinc reduction using zinc powder.

104. The process of claim **103**, further comprising adding an aqueous barium chloride solution to produce a precipitate of insoluble barium and europium sulfates.

105. The process of claim **104**, further comprising oxidizing the insoluble barium and europium sulfates to produce a precipitate of europium (III) hydroxide.

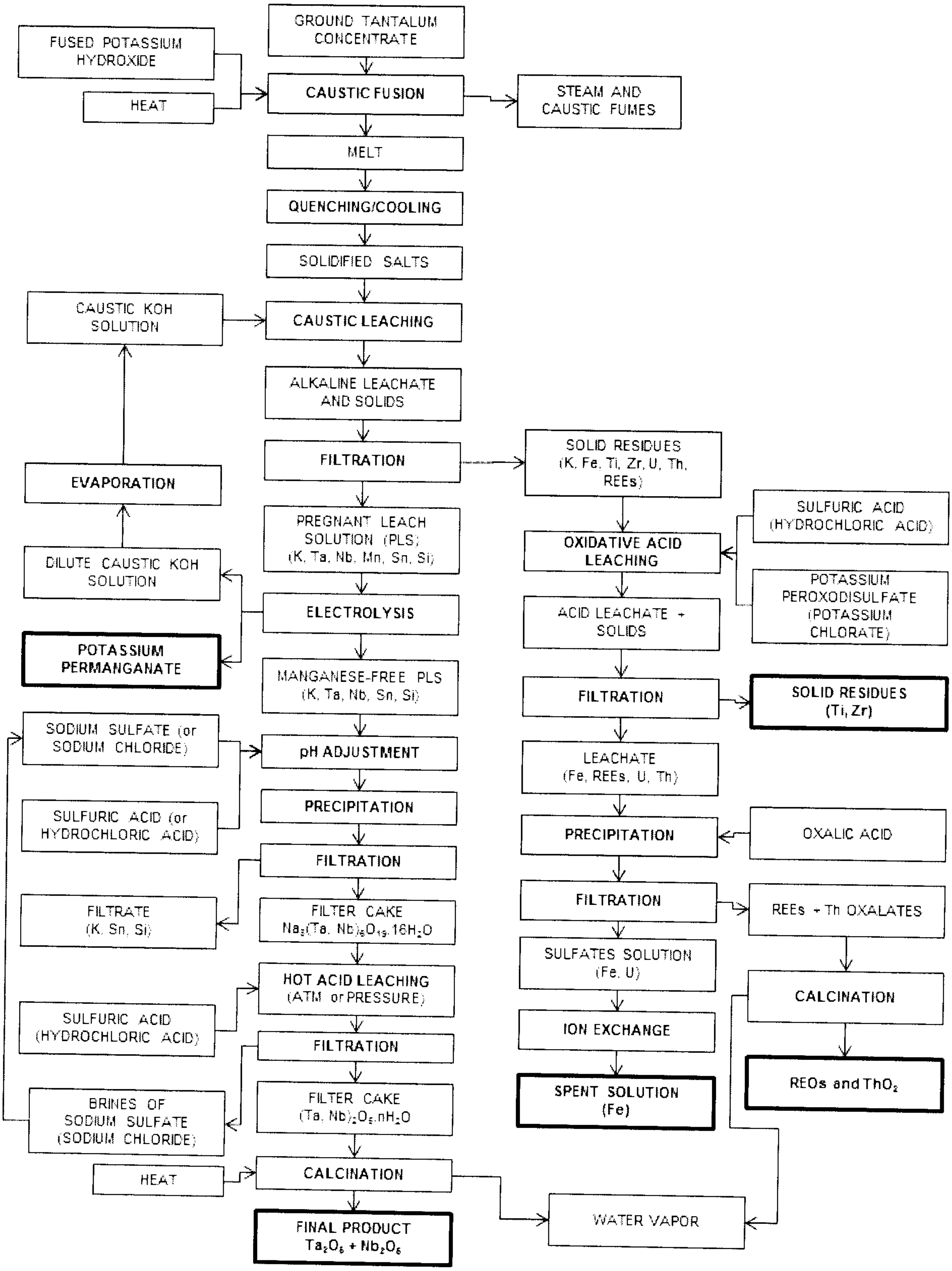

GROUND TANTALUM CONCENTRATE
FUSED POTASSIUM HYDROXIDE
HEAT
CAUSTIC FUSION
STEAM AND CAUSTIC FUMES
MELT
QUENCHING/COOLING
SOLIDIFIED SALTS
CAUSTIC KOH SOLUTION
CAUSTIC LEACHING
ALKALINE LEACHATE AND SOLIDS
FILTRATION
SOLID RESIDUES (K, Fe, Ti, Zr, U, Th, REEs)
EVAPORATION
PREGNANT LEACH SOLUTION (PLS) (K, Ta, Nb, Mn, Sn, Si)
SULFURIC ACID (HYDROCHLORIC ACID)
OXIDATIVE ACID LEACHING
DILUTE CAUSTIC KOH SOLUTION
ELECTROLYSIS
ACID LEACHATE + SOLIDS
POTASSIUM PEROXODISULFATE (POTASSIUM CHLORATE)
POTASSIUM PERMANGANATE
MANGANESE-FREE PLS (K, Ta, Nb, Sn, Si)
FILTRATION
SOLID RESIDUES (Ti, Zr)
SODIUM SULFATE (or SODIUM CHLORIDE)
pH ADJUSTMENT
LEACHATE (Fe, REEs, U, Th)
SULFURIC ACID (or HYDROCHLORIC ACID)
PRECIPITATION
PRECIPITATION
OXALIC ACID
FILTRATION
FILTRATE (K, Sn, Si)
FILTER CAKE $Na_8(Ta, Nb)_6O_{19}.16H_2O$
FILTRATION
REEs + Th OXALATES
SULFATES SOLUTION (Fe, U)
SULFURIC ACID (HYDROCHLORIC ACID)
HOT ACID LEACHING (ATM or PRESSURE)
CALCINATION
FILTRATION
ION EXCHANGE
BRINES OF SODIUM SULFATE (SODIUM CHLORIDE)
FILTER CAKE $(Ta, Nb)_2O_5.nH_2O$
SPENT SOLUTION (Fe)
REOs and ThO_2
HEAT
CALCINATION
WATER VAPOR
FINAL PRODUCT $Ta_2O_5 + Nb_2O_5$

FIGURE 1

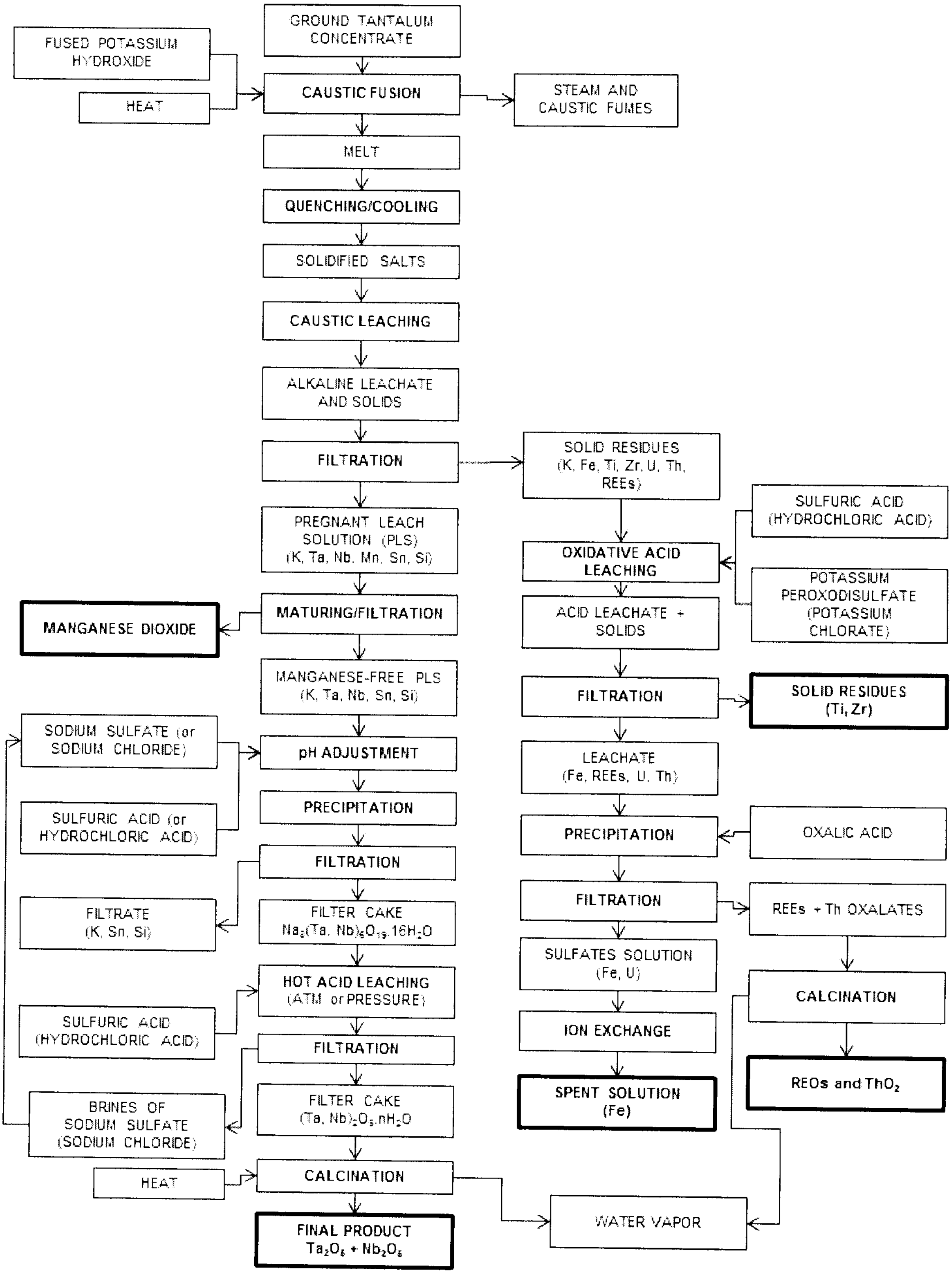

GROUND TANTALUM CONCENTRATE
FUSED POTASSIUM HYDROXIDE
HEAT
CAUSTIC FUSION
STEAM AND CAUSTIC FUMES
MELT
QUENCHING/COOLING
SOLIDIFIED SALTS
CAUSTIC LEACHING
ALKALINE LEACHATE AND SOLIDS
FILTRATION
SOLID RESIDUES (K, Fe, Ti, Zr, U, Th, REEs)
PREGNANT LEACH SOLUTION (PLS) (K, Ta, Nb, Mn, Sn, Si)
SULFURIC ACID (HYDROCHLORIC ACID)
OXIDATIVE ACID LEACHING
POTASSIUM PEROXODISULFATE (POTASSIUM CHLORATE)
MANGANESE DIOXIDE
MATURING/FILTRATION
ACID LEACHATE + SOLIDS
MANGANESE-FREE PLS (K, Ta, Nb, Sn, Si)
FILTRATION
SOLID RESIDUES (Ti, Zr)
SODIUM SULFATE (or SODIUM CHLORIDE)
pH ADJUSTMENT
LEACHATE (Fe, REEs, U, Th)
SULFURIC ACID (or HYDROCHLORIC ACID)
PRECIPITATION
PRECIPITATION
OXALIC ACID
FILTRATION
FILTRATE (K, Sn, Si)
FILTER CAKE $Na_8(Ta, Nb)_6O_{19}.16H_2O$
FILTRATION
REEs + Th OXALATES
SULFATES SOLUTION (Fe, U)
HOT ACID LEACHING (ATM or PRESSURE)
CALCINATION
SULFURIC ACID (HYDROCHLORIC ACID)
FILTRATION
ION EXCHANGE
BRINES OF SODIUM SULFATE (SODIUM CHLORIDE)
FILTER CAKE $(Ta, Nb)_2O_5.nH_2O$
SPENT SOLUTION (Fe)
REOs and ThO_2
HEAT
CALCINATION
WATER VAPOR
FINAL PRODUCT $Ta_2O_5 + Nb_2O_5$

FIGURE 2

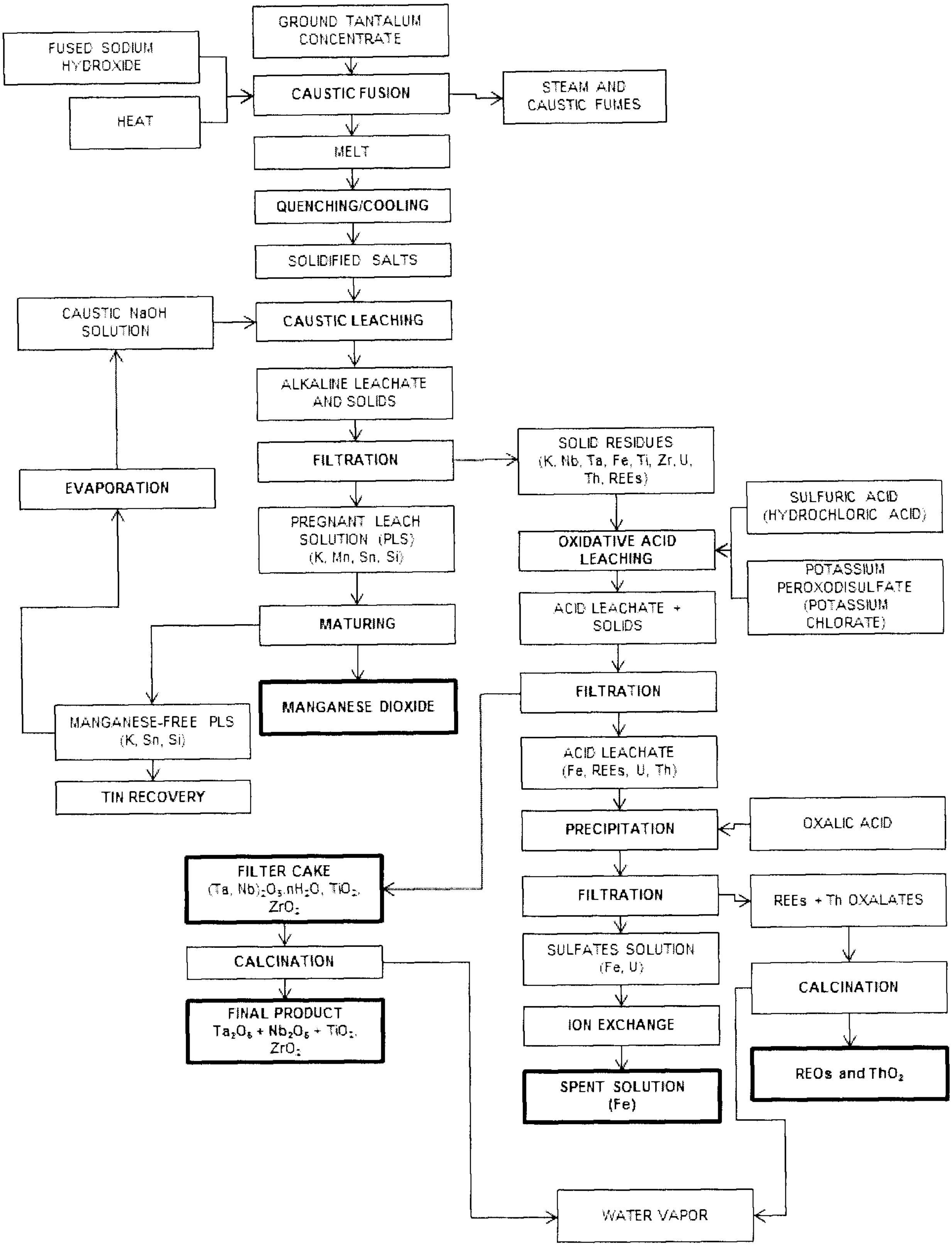

GROUND TANTALUM CONCENTRATE
FUSED SODIUM HYDROXIDE
HEAT
CAUSTIC FUSION
STEAM AND CAUSTIC FUMES
MELT
QUENCHING/COOLING
SOLIDIFIED SALTS
CAUSTIC NaOH SOLUTION
CAUSTIC LEACHING
ALKALINE LEACHATE AND SOLIDS
FILTRATION
SOLID RESIDUES (K, Nb, Ta, Fe, Ti, Zr, U, Th, REEs)
EVAPORATION
SULFURIC ACID (HYDROCHLORIC ACID)
PREGNANT LEACH SOLUTION (PLS) (K, Mn, Sn, Si)
OXIDATIVE ACID LEACHING
POTASSIUM PEROXODISULFATE (POTASSIUM CHLORATE)
ACID LEACHATE + SOLIDS
MATURING
MANGANESE DIOXIDE
FILTRATION
MANGANESE-FREE PLS (K, Sn, Si)
ACID LEACHATE (Fe, REEs, U, Th)
TIN RECOVERY
PRECIPITATION
OXALIC ACID
FILTER CAKE $(Ta, Nb)_2O_5.nH_2O$, TiO_2, ZrO_2
FILTRATION
REEs + Th OXALATES
CALCINATION
SULFATES SOLUTION (Fe, U)
CALCINATION
FINAL PRODUCT Ta_2O_5 + Nb_2O_5 + TiO_2, ZrO_2
ION EXCHANGE
REOs and ThO_2
SPENT SOLUTION (Fe)
WATER VAPOR

FIGURE 3

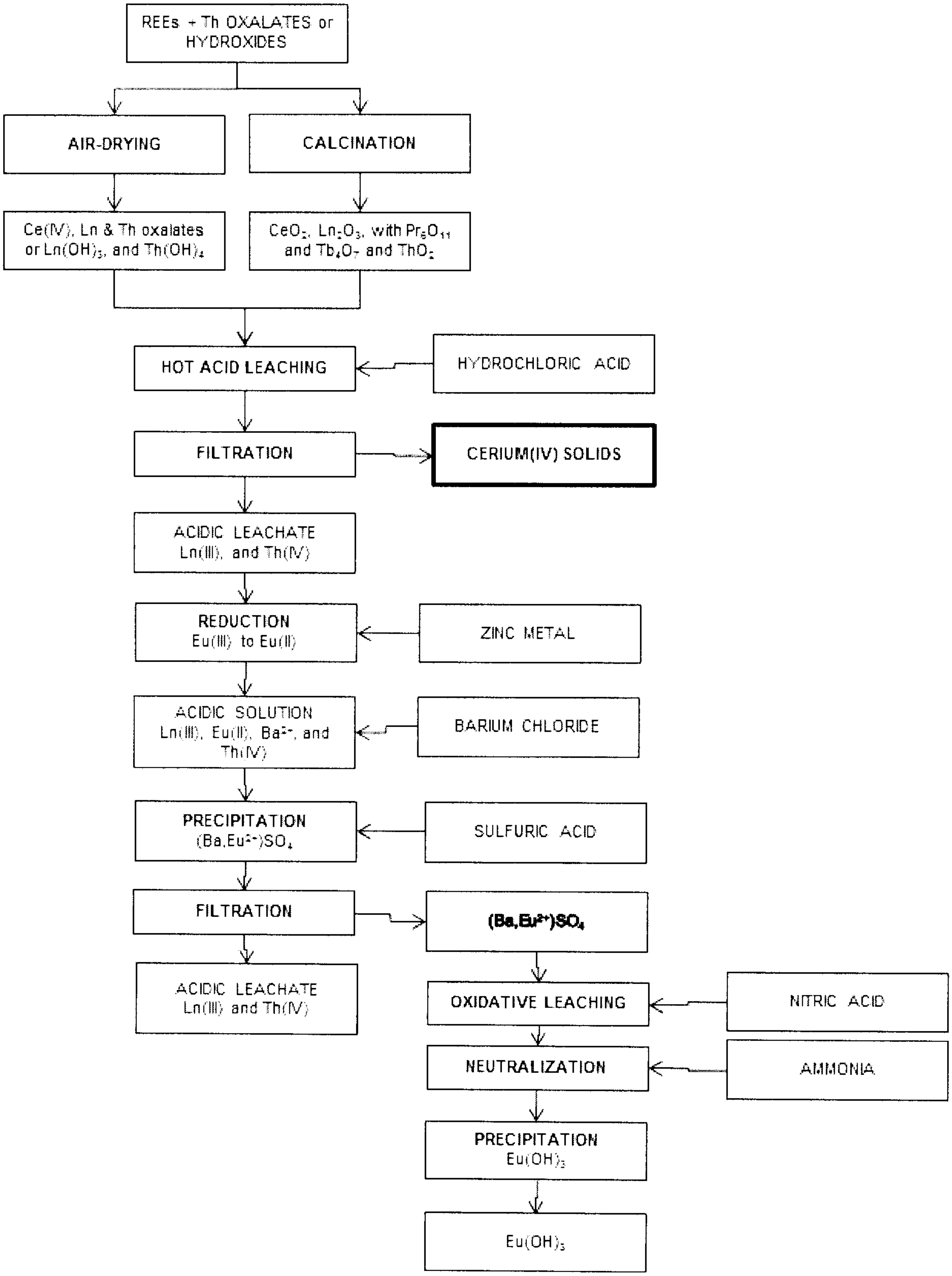
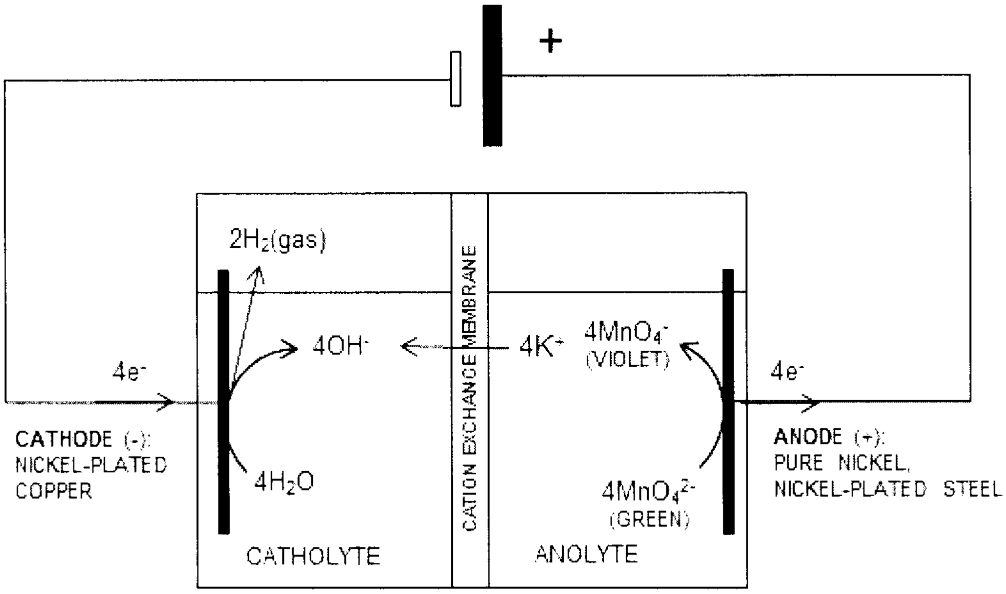

REEs + Th OXALATES or HYDROXIDES
AIR-DRYING
CALCINATION
Ce(IV), Ln & Th oxalates or $Ln(OH)_3$, and $Th(OH)_4$
CeO_2, Ln_2O_3, with Pr_6O_{11} and Tb_4O_7 and ThO_2
HOT ACID LEACHING
HYDROCHLORIC ACID
FILTRATION
CERIUM(IV) SOLIDS
ACIDIC LEACHATE Ln(III), and Th(IV)
REDUCTION Eu(III) to Eu(II)
ZINC METAL
ACIDIC SOLUTION Ln(III), Eu(II), Ba^{2+}, and Th(IV)
BARIUM CHLORIDE
PRECIPITATION $(Ba,Eu^{2+})SO_4$
SULFURIC ACID
FILTRATION
$(Ba,Eu^{2+})SO_4$
ACIDIC LEACHATE Ln(III) and Th(IV)
OXIDATIVE LEACHING
NITRIC ACID
NEUTRALIZATION
AMMONIA
PRECIPITATION $Eu(OH)_3$
$Eu(OH)_3$

FIGURE 4



ANODE : $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ CATHODE: $4MnO_4^{2-} \rightarrow 4MnO_4^{2-} + 4e^-$

OVERALL REACTION: $4K_2MnO_4 + 4H_2O \rightarrow 4KMnO_4 + 4KOH + 2H_2(g)$

FIGURE 5

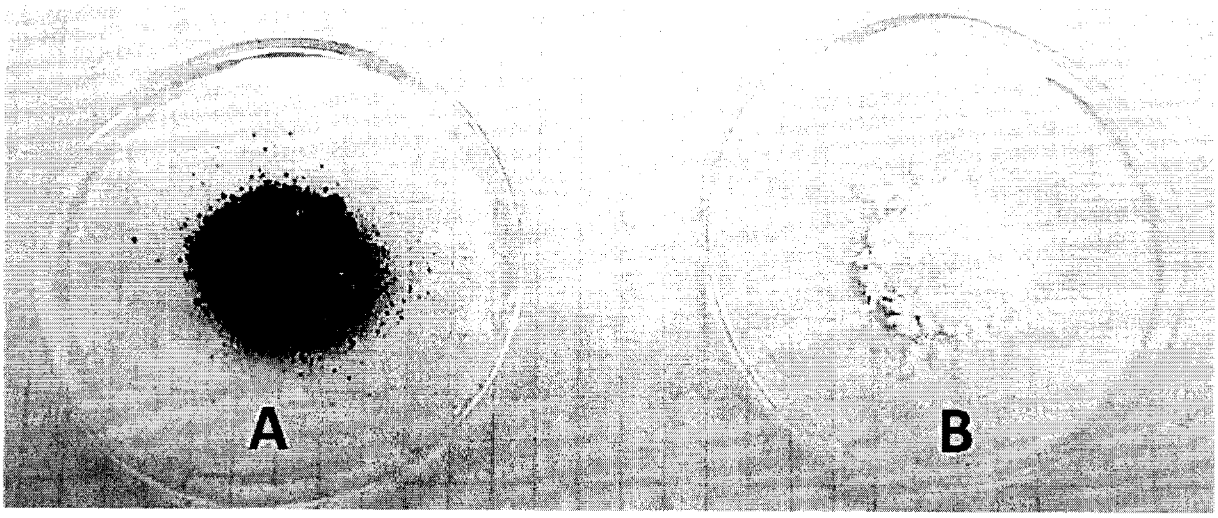


FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/000890

A. CLASSIFICATION OF SUBJECT MATTER

IPC: *C22B 1/00* (2006.01) , *C22B 3/12* (2006.01) , *C22B 3/22* (2006.01) , *C22B 3/06* (2006.01) , *C22B 34/24* (2006.01) , *C22B 60/02* (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/ECLA: C22B 34/24, C22B 60/02, C22B 59/00, C22B 47/00
USPC: 423/66, 423/67, 423/68, 75.clas.

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)

TotalPatent, WEST, Google Scholar, Scopus
Keywords: fus!/melt/molten, leach!/dissol!/digest!, alkali!/basic/naoh/koh/hydroxide/ammoni!, ore/concentrate/mineral, tantal!/niob!/colum!

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US3092448A (KENNEDY) 04 June 1963 (04-06-1963)	1, 4-5, 11-14, 17-29 and 36-38
Y	US2950966A (FOOS) 30 August 1960 (30-08-1960)	1, 4-5, 11-14, 17-29 and 36-38
Y	US1905882A (BALKE) 25 April 1933 (25-04-1933)	25-28
A	US2728633A (VICTOR et al.) 27 December 1955 (27-12-1955)	
A	SURI et al., Investigations on Flowsheet Development for the Treatment of Niobium-Tantalum Bearing Cassiterite. Mineral Processing and Extractive Metallurgy Review: An International Journal, Volume 9, Issue 1-4, 1992, pp. 293-303.	

[ ] Further documents are listed in the continuation of Box C. [X] See patent family annex.

*	Special categories of cited documents :
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Date of the actual completion of the international search

8 November 2012 (08-11-2012)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2012/000890

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US3092448A	04 June 1963 (04-06-1963)	None	
US2950966A	30 August 1960 (30-08-1960)	None	
US1905882A	25 April 1933 (25-04-1933)	None	
US2728633A	27 December 1955 (27-12-1955)	None	