(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 December 2024 (26.12.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/259535 A1

(51) International Patent Classification:
C01F 17/206 (2020.01) *B02C 23/18* (2006.01)
B01D 11/02 (2006.01) *C01B 33/20* (2006.01)
B02C 23/08 (2006.01) *C01F 17/10* (2020.01)

(21) International Application Number:
PCT/CA2024/050837

(22) International Filing Date:
21 June 2024 (21.06.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/509,560 22 June 2023 (22.06.2023) US

(71) Applicant: **CLAYSON ECOMINERAL INC.** [CA/CA]; 1761 des Amarantes, Carignan, Québec J3L 4Z8 (CA).

(72) Inventors: **FOURNIER, Joel**; c/o CLAYSON ECOMINERAL INC., 1761 des Amarantes, Carignan, Québec J3L 4Z8 (CA). **BADER, Najoua**; c/o CLAYSON ECOMINERAL INC., 1761 des Amarantes, Carignan, Québec J3L 4Z8 (CA).

(74) Agent: **ROBIC AGENCE PI S.E.C. / ROBIC IP AGENCY LP**; 630 Rene-Levesque Boulevard West, 20th Floor, Montreal, Québec H3B 1S6 (CA).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) Title: PROCESS AND SYSTEM TO EXTRACT RARE EARTH FROM CLAY AND CONVERT RESIDUE IN SUSTAINABLE BINDER FOR CONCRETE

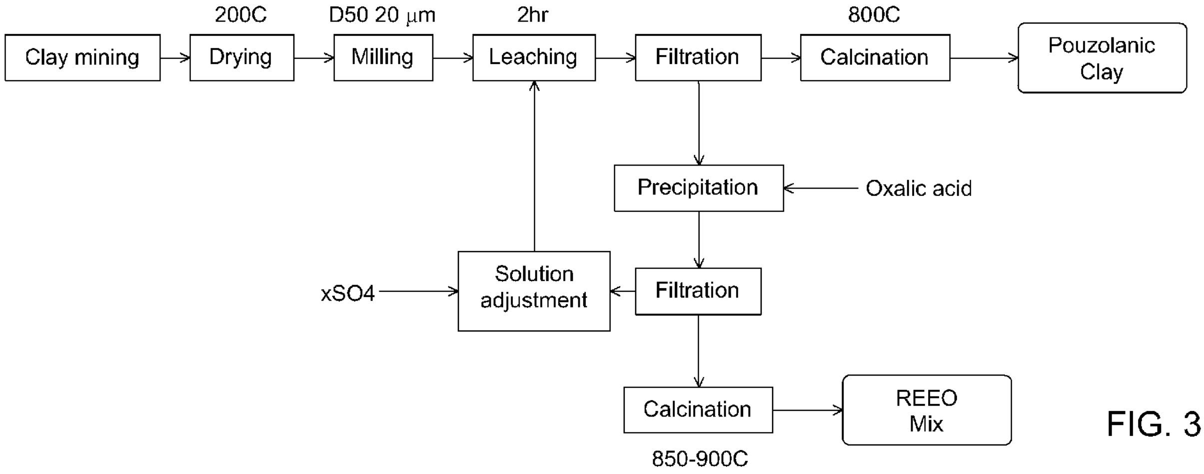


FIG. 3

(57) **Abstract:** The present description relates to a process that includes subjecting clay ore to pre- treatment; leaching the pre-treated clay to produce a leachate enriched in rare earth elements and a solid residue; calcining the solid residue to produce pozzolanic clay material suitable for use as a concrete binder; subjecting the leachate to precipitation to form precipitated rare earth element oxides (REEO) and a rare earth depleted solution; and calcining the precipitated REEO to form an REEO product mixture. Both REEO product and concrete binder material can thus be produced from clay ore.

WO 2024/259535 A1

PROCESS AND SYSTEM TO EXTRACT RARE EARTH FROM CLAY AND CONVERT RESIDUE IN SUSTAINABLE BINDER FOR CONCRETE

TECHNICAL FIELD

[001] The technical field generally relates to the extraction of rare earth from clay and the conversion of residues. In particular, the technical field relates to an integrated process and system for rare earth extraction from clay based materials and conversion of resulting residues in a sustainable binder for concrete.

BACKGROUND

[002] In various technologies and applications, there is an increasing need for rare earth elements. In certain countries, efforts to re-establish mining of rare earth elements have been undertaken. Supplies of rare earth elements may considerably depend upon economic viability of the extraction and production processes and technological innovations requiring such rare earth elements. In addition, global demand for cement and concrete has increased significantly in recent years with global cement production having increased almost four-fold since 1990. This has led to the expansion of industries connected to concrete as one of the leading construction industry components, starting from raw material extraction and increased fossil fuel consumption for material processing and cement production. Improvements in concrete sustainability have become a notable concern. Most of the binding materials used in concrete are based on Portland cement, which is the hydraulic binder that hardens when combined with water and is produced through an energy intensive process. While there have been some improvements in the cement and concrete industry, such initiatives have been outpaced by the dramatic increases in demand, and further developments are required to reduce the environmental impacts and costs. To address the sustainability problems facing the concrete industry, there is a need to develop concrete compositions with reduced cement content.

[003] There is indeed a need for a technology that facilitates sustainable production of rare earth elements as well as concrete binder materials.

SUMMARY

[004] In some implementations, there is provided a process comprising: subjecting clay ore to pre-treatment to produce a pre-treated clay material; leaching the pre-treated clay material to produce a leachate enriched in rare earth elements and a solid residue; separating the leachate from the solid residue; calcining the solid residue to produce pouzolanic clay material suitable for use as a concrete binder; subjecting the leachate to precipitation to form precipitated rare earth element oxides (REEO) and a rare earth depleted solution; separating the precipitated REEO from the rare earth depleted solution; and calcining the precipitated REEO to form an REEO product mixture.

[005] In some implementations, the pre-treatment comprises drying the clay ore to obtain a dried ore; the drying is performed at a drying temperature between 150°C and 250°C; the pre-treatment comprises milling the dried ore to obtain a milled ore that is subjected to the leaching; the milling is performed to a granulometric distribution (D50) between 5 and 30 microns, or between 10 and 25 microns; the separating of the leachate from the solid residue is performed by filtration; calcining the solid residue is performed at a residue calcining temperature of 700°C to 1000°C, 875°C to 1000°C, or 885°C to 950°C; the precipitation includes addition of a carboxylic acid to the leachate; the carboxylic acid comprises a dicarboxylic acid; the dicarboxylic acid comprises oxalic acid; separating the precipitated REEO from the rare earth depleted solution comprises filtration; calcining the precipitated REEO is performed at a REEO calcining temperature between 700°C and 1000°C; the process also includes recycling at least a portion of the rare earth depleted solution back into the leaching step as part of a leaching solution; the process also includes adjusting the rare earth depleted solution before recycling back into the leaching step; the adjusting comprises addition of a sulfate; the leaching is performed using magnesium sulfate; the leaching is performed at a solution pH of 3 to 5 or 1 to 3; the process also includes subjecting the REEO product mixture to dissolution in HCl and fractional solvent extraction to produce individual rare earther elements (REE); and/or the process also includes forming a concrete additive comprising the pouzolanic clay material as well as fly ash and/or silica fume.

[006] In some implementations, there is provided a system comprising: a drier configured to receive mined clay ore and produce a dried clay; a milling unit configured to receive the dried clay and produce a milled ore; a leaching unit configured to leach the milled ore to produce a leachate enriched in rare earth elements and a solid residue; a separation unit coupled to the leaching unit for separating the leachate from the solid residue; a clay calciner configured to receive and calcine the solid residue to produce pouzolanic clay material suitable for use as a concrete binder; a precipitation unit configured to receive the leachate and form precipitated rare earth element oxides (REEO) and a rare earth depleted solution; a separator configured for separating the precipitated REEO from the rare earth depleted solution; and an REEO calciner configured to receive and calcine the precipitated REEO to form an REEO product mixture.

[007] In some implementations, the milling unit is configured to mill to a granulometric distribution of at most D50 of 20 microns; the separation unit is a filtration unit; clay calciner is configured to operate at a residue calcining temperature of 700°C to 1000°C, 875°C to 1000°C, or 885°C to 950°C; the precipitation unit is configured to receive a precipitation solution that includes a carboxylic acid; the carboxylic acid comprises a dicarboxylic acid; the dicarboxylic acid comprises oxalic acid; the separator for separating the precipitated REEO from the rare earth depleted solution comprises a filter; the REEO calciner is configured for calcining the precipitated REEO at a REEO calcining temperature between 800°C and 1000°C; the system also includes a recycle system in fluid communication with the separator and configured for recycling at least a portion of the rare earth depleted solution back into the leaching unit as part of a leaching solution; the system also includes an adjustment unit coupled to the recycle system and the separator, and configured for adjusting the rare earth depleted solution before recycling back into the leaching unit; and/or the adjustment unit comprises a magnesium sulfate solution addition inlet.

[008] In some implementations, there is provided a use of a clay ore feedstock for extraction and co-production of rare earth element oxides (REEO) and a clay-based concrete binder. The use of the clay can include one or more features described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[009] The attached figures illustrate various features, aspects and implementations of the technology described herein.

[0010] Fig 1 is a graph and table of cumulative distribution versus particle size.

[0011] Fig 2 is a graph of weight versus temperature.

[0012] Fig 3 is a process flow diagram of a process for extracting rare earth elements and producing a concrete binder from the clay residues.

[0013] Fig 4 shows an X-ray diffraction graph and compositional information of a sample of Grande Vallée material.

[0014] Fig 5 is a bar graph of extraction percentage versus different elements.

DETAILED DESCRIPTION

[0015] Techniques described herein relate to systems, devices and methods for extracting rare earth elements from clay based materials and producing a concrete binder from the clay residues. In some implementations, the clay based material can be obtained from mining a clay deposit, pre-treating the clay ore which can include drying and milling, leaching the milled clay ore to produce a leachate enriched in rare earth elements and a solid residue, filtering or otherwise separating the leachate from the solid residue, calcining the solid residue to produce pouzolanic clay material, subjecting the leachate to precipitation to form precipitated rare earth element oxides (REEO), separating the precipitated REEO from the rare earth depleted solution, adjusting and recycling the solution back into the leaching step, and calcining the precipitated REEO to form an REEO product mixture. The process and system will be described in more detail further below.

[0016] The following provides additional context for the present technology. Rare-earth elements are incorporated in accessory minerals in various rocks, but the most commercially significant sources are:

> (1) Bastnäsite, is a fluorocarbonate mineral containing 65–75 wt.% light rare earth oxides (REO). They account for more than 80% of global REO production. The two major sources in the world for lanthanides are bastnäsite deposits at Mountain Pass, California (USA, owned by Molycorp Inc. devoted solely to REE production, and Bayan-Obo, Inner Mongolia (China) – mined primarily for iron ore and REE as a by-product (also containing monazite).

(2) Monazite, is a LREE phosphate containing 55–65 wt.% REO, associated with granites and beach sands in Australia, Brazil and India; the Mount Weld deposit in Western Australia, owned by Lynas Corp., contains one of the highest grades REE deposits in the world. Until about 1965 monazite was the main REE source; since then, the use of monazite has been considerably reduced due to radioactivity caused by thorium and radium.

(3) Xenotime, is an yttrium-rich phosphate containing 25–60 wt.% Y2O3 and other heavy REE. It is recovered mainly as a byproduct of mining for titanium, zirconium and tin in Malaysia, Indonesia and Thailand.

(4) Weathered crust elution-deposited rare earth ores (ion-adsorption ores) are aluminosilicate minerals (e.g. kaolinite, illite and smectite) containing 0.05–0.3 wt.% REEs physically adsorbed at sites of permanent negative charge. The ion-adsorption clay deposits are the result of in situ weathering of host rocks (mainly granitic), which, over geological timescales, results in the formation of aluminosilicate clays.

[0017] Clay minerals are part of the phyllosilicate class, containing layered structures of shared octahedral aluminium and tetrahedral silicon sheets, allowing water molecules and hydrated cations to move in and out of the interlayer spaces. Very commonly, isomorphous substitution of one cation with another (of similar size but with lesser charge, e.g., Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}) within crystal structures leads to a charge imbalance in silicate clays, which accounts for the permanent negative charge on clay particles, and thus the capability of adsorbing lanthanide ions released/dissolved from precursor REE-bearing minerals during weathering. Warm tropical and sub-tropical climates present ideal conditions for this process to occur. The best example of this formation process exists in Asia, where many such deposits are known to exist.

[0018] Regardless of the low grades, ion-adsorption clays account for ~35% of the China’s total REE output and ~80% of world’s HREE production. Some important deposit has recently been found in Canada in an area named Gaspésie (Québec).

[0019] Carbonate and phosphate sources, of high grade, are associated with elevated recovery costs due to separation, beneficiation and need for aggressive conditions to dissolve the REE. For example, bastnäsite is generally leached with concentrated H2SO4 or HCl, whereas monazite/xenotime concentrates need to be baked either in 98% H2SO4 or 70% NaOH to render the REE soluble. Other REE deposits in North America in addition to bastnäsite consist of the so-called “hard-rock” peralkaline ores including zircon, titanate, niobate, allanite, eudialyte, gadolinite; these deposits are enriched in HREE but require harsh conditions to break down the mineral matrix (e.g. caustic bake followed by acid leaching); the processing of these ores is directed mainly towards extraction of niobium, tantalum, and zirconium.

[0020] The route followed by ion-adsorption type deposits are substantially lower grade than other types of lanthanide sources, nominally requiring higher costs for REE extraction and recovery. However, this disadvantage is largely offset by the easier mining and processing costs, and the relatively low content of radioactive elements such as thorium and uranium. These deposits are mined by open-pit methods and no ore beneficiation is required. A simple leach using monovalent sulfate or chloride salt solutions at ambient temperature can produce a high-grade REO product. Because of their abundance in surface layers in nature, ease of mining and processing, these clays warrant a detailed study as important sources of rare earths.

[0021] In terms of Portland cement production for concrete, the process emits large amounts of greenhouse gases, an estimated 5–8% of the world’s anthropogenic CO_2. This trend is expected to increase in the coming decades as the countries continue to increase their concrete demand. It is predicted that cement production could represent 10% to 15% of global CO2 emissions by 2030. The cement industry has made substantial development in improving its production efficiency as well as reducing its environmental impact. Automation of the manufacturing of lime in modern cement kilns and increased use of alternative and sustainable fuel sources are the key improvements in the cement industry for reducing energy consumption and associated CO_2 emissions. However, these initiatives have been outpaced by the dramatic increases in demand, and further developments are required to reduce the environmental impacts and costs.

[0022] To address the sustainability problems facing the concrete industry, there is a need to develop concrete compositions with reduced cement content. Recent advancements in packing optimization and the development of water-reducing superplasticizers have already contributed to more sustainable concrete use. Furthermore, the cement industry has already achieved impressive improvements by developing supplementary cementitious materials (SCMs) and naturally sourced blending materials, such as silica fume (SF), natural pozzolan, fly ash, and limestone, to reduce the required cement content in concretes. Pozzolanic and filling effects are the two essential characteristics of these mineral admixtures. To date, a large variety of products have been used as cementitious materials, with a wide range of chemical compositions, which are placed in a $CaO–SiO_2–Al_2O_3$ ternary phase diagram. Although industrial by-products or waste (e.g., fly ashes and blast furnace slags) are widely used to replace part of the cement clinker, the availability of these SCMs is limited by their production as by-products of power plants or blast furnace industries. Furthermore, their efficiency to replace clinker has been studied by various researchers who have concluded that they cannot be considered a global alternative to cement. Thus, there is a growing tendency to find new alternative inorganic binders from local sources for replacing cement in concrete structures. Raw earth based materials are promising options for low-cost and environmentally friendly building materials. Among such materials, clays are an abundant option that can be effective as mineral additives or in blended concrete in many places of the world. Clays are a source of alumina and silica, which can cause a pozzolanic reaction under the proper conditions. Clays have already been shown to have excellent pozzolanic properties under specific calcination conditions or surface modifications.

[0023] The present technology relates to a new process and system to extract rare earth from clay while improving the pozzolanic activity of the resulting by-product material. Fig 3 illustrates one implementation of the process.

[0024] The clay mineral can be challenging to directly mine and introduce into a milling stage and thus can be subjected to pre-treatment. The typical composition of clay is present in Table 1. The REE and REEO content in the clay ore is presented in Table 2. The humidity content would generate a sticky mud. It is thus first passed through a drying step, which may be an air-drying step at 200C for 1 hr. The resulting loss in weight of this drying step is present in Table 3.

Table 1

SiO 2	%	56,55
Al2O3	%	20,55
Fe2O3	%	8,02
CaO	%	0,17
MgO	%	1,86
Na2O	%	1,4
K2O	%	3,74
Cr2O3	%	0,01
TiO 2	%	1,05
MnO	%	0,12
P2O5	%	0,151
SrO	%	0,02
BaO	%	0,06
LOI	%	5,93
Total	%	99,63
C organic	%	0,07

Table 2

# of Samples	26	18	44	96	13
Al203 (%)	24.4	24.2	24.3	19.9	24.7
TREE (ppm)	442.8	427.5	436.5	358.7	476.3
Ga (ppm)	33.2	33.8	33.4	28.5	37
Sc (ppm)	16.4	17.8	17.0	17.0	17.8
TREE+RM	492.4	479.1	486.9	404.2	531.1
TREO (ppm)	522.4	504.4	515.0	423.3	561.9
Ga203 (ppm)	44.6	45.4	44.9	38.3	49.7
Sc203 (ppm)	25.2	27.3	28.1	28.1	27.3
TREO+RMO	**592.2**	**577.1**	**588.0**	**489.7**	**638.9**
La (ppm)	80.3	76.9	78.9	67.3	88.4
Ce (ppm)	161.9	155.2	159.2	129.8	177.2
Pr (ppm)	20	19.5	19.8	15.9	21
Nd (ppm)	75	74.1	74.7	58.6	79.4
Gd (ppm)	14.3	13.9	14.1	11.1	15.2
Eu (ppm)	2.7	2.5	2.6	2.1	2.7
Sm (ppm)	11.5	10.9	11.2	9	11.2
Tb(ppm)	1.7	1.6	1.6	1.4	1.7
Dy (ppm)	10.1	9.7	9.9	8.1	9.5
Ho (ppm)	2	1.9	2	1.7	1.8
Er (ppm)	5.3	5.1	5.2	4.5	5.3
Tm (ppm)	0.8	0.7	0.75	0.7	0.7
Yb (ppm)	4.7	4.8	4.8	4.1	4.7
Lu (ppm)	0.7	0.7	0.7	0.6	0.7
y (ppm)	51.9	49.7	51	43.7	56.8
% HREE/TREE	20.6	20.5	20.6	21.2	20

Table 3

Drying			After milling
Test	Weight (g)		
	Humide	Dry	
1	3419,0	3094,0	
2	3562,0	3222,8	
3	3156,0	2841,8	
4	3283,0	2967,7	
5	3162,0	2851,7	
6	3282,0	2955,9	
7	3003,0	2723,9	
8	3268,0	2933,9	
Total	26135,0	23591,7	23300
	Average lost%	9,7	
	lost%		1,2

[0025] After drying, the dried clay material can be subjected to a size-reduction stage, such as a milling step, to reduce the particles size, e.g., to a D50 of 20um (see Figure 1). A weight loss of average 1.2% is related to the fine particles passing into the air filtration system (see Table 3).

[0026] The physisorbed REE ions can be readily displaced from the clay surface by monovalent cations (e.g., Na$^+$ and NH$_4^+$) following the below reaction mechanism:

(1) $\text{Clay} - \text{REE}^{3+} + 3\text{NH}_4^+ \rightarrow \text{Clay} - (\text{NH}_4^+)_3 + \text{REE}^{3+}$

[0027] An ammonium sulfate solution is typically employed for the ion-exchange leaching and the solution pH is maintained at between 3 and 5 or 1 to 3 to prevent the hydrolysis of REE^{3+} ions and minimize the dissolution of impurities such as aluminum- and iron-bearing minerals. The temperature of the leaching step could vary from 25°C to 85°C with a preference around 40°C to 60°C or at 50°C. It is noteworthy that in the current invention it is preferred to use magnesium sulfate instead of ammonium sulfate for the leaching step, although other leaching agents are possible. For example, leaching agents can include calcium sulfate, sodium sulfate, and ammonium sulfate can be used, and mixtures of two or more of such leaching agents can be used in combination. Magnesium based leaching agents can be preferred as it has been found that they can facilitate pouzolanic properties of the clay residue after calcination. The use of magnesium sulfate for leaching of ion-adsorption clays has the dual aim of replacing ammonium-based lixiviants to avoid environmental concern related to the next calcination step of the residue and improve the pozzolanic activity of this material. An additional benefit of using $MgSO_4$ instead of $(NH_4)_2SO_4$ is the 10-15% decrease in aluminum desorption, which translates into a lower solution impurity content to be processed or eliminated downstream.

[0028] There are other leaching agents and processes that can be used. For example, HCl, H_2SO_4 and HNO_3 can be employed in leaching steps and processes as described in WO 2012/149642 (Boudreault et al.), the contents of which are incorporated herein by reference, can be used in combination with techniques described in the present document. Processes described in WO'642 related to rare earth separation can also be used in combination with techniques described herein to separate rare earth compounds from each other, e.g., where rare earth oxides produced according to processes herein are dissolved (e.g., using an HCl solution) and then introduced into the rare earth separation process.

[0029] The dissolved REE are usually selectively precipitated with a carboxylic acid, such as oxalic acid, to form oxalates (see Equation 2) that are subsequently converted to REEO via calcination or roasting at 900°C.

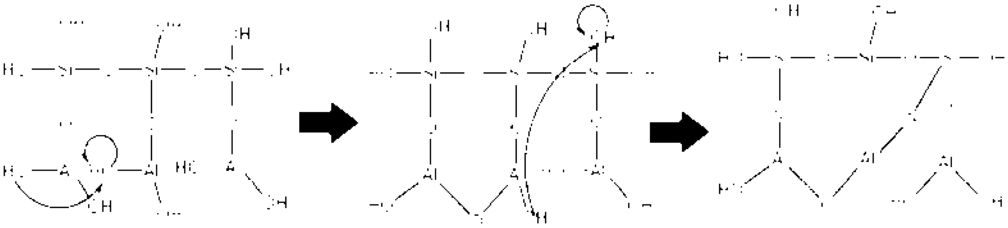
$$(2)\ \mathrm{REE}\ {}_2(SO_4)_3 + 3\ C_2O_4H_2 + 10\ H_2O \rightarrow \mathrm{REE}\ {}_2(C_2O_4)_3{*}10H_2O + H_2SO_4$$

[0030] Thermal decomposition of these oxalates gives the oxides, which is the most commonly marketed form of these elements.

$$(3)\ \mathrm{REE}\ {}_2(C_2O_4)_3{*}10H_2O \rightarrow \mathrm{REE}_2O_3 + 3CO + 3CO_2 + 10H_2O$$

[0031] Finally, the mixed REEO can be separated into individual REE by dissolution in HCl and fractional solvent extraction.

[0032] Turning to the clay reside treatment, the solid residue from the leaching stage can be conveyed to a calcination stage for processing. The calcination of clay minerals means the process of dehydroxylation of ultrafine clay by thermal activation in high temperature in a calciner kiln, which results in driving off the chemically bound water, breaking down the crystal structure, and changing the material into a highly reactive transition phase. Different temperatures are possible for the process of calcination and the preferred temperature can be between 700°C and 1000°C although others are possible and as disclosed herein. Below shows an example of dihydroxylation of kaolinite:



Schematic representation of kaolinite dehydroxylation producing increased disorder in the alumina sheet

[0033] Calcination temperature can affect the fresh/wet and hardened properties of cementitious material. One of the most applicable products of kaolinite ($Al_2Si_2O_5(OH)_4$) calcination is metakaolin as an anhydrous alumino-silicate ($Al_2Si_2O_7$). Metakaolin is a dehydroxylated form of the clay mineral kaolinite obtained by calcination. This reaction liberates water instead of CO_2 for a clinker.

$$\text{Kaolinite} \rightarrow \text{metakaolin: } Al_2Si_2O_5(OH)_4$$
$$- Al_2Si_2O_7 - 2H_2O \uparrow$$

[0034] The major constituents of residual clay are silica oxide (SiO_2) and alumina oxide (Al_2O_3). SiO_2 reacts with $Ca(OH)_2$ in concrete to produce secondary calcium silicate hydrate (CSH) gel at ambient temperature. Apart from that, the alumina in residual clay reacts with calcium hydroxide to produce additional alumina-containing phases, including C4AH13, C2ASH8, and C3AH6. MgO can be obtained by decomposition of $MgSO_4$. However, at 1500K, the temperature where this decomposition occurs, the pozzolanic properties of clay is strongly reduced. The thermodynamic study suggests that in the presence of reducing agents, such as carbon, hydrogen gas, aluminum or magnesium scrap, a decreased decomposition temperature is obtained for the $MgSO_4$ making the formed oxide (MgO) good for this use. Analyses performed with the variables of excess reducing agent (charcoal) and temperature showed that temperature is the variable that most influences the decomposition of $MgSO_4$. Experiments at 1173K and 20, 25 and 30 min were the conditions that indicated the best experimental results of conversion, reaching a conversion close to 100%.

[0035] MgO subjected to calcination temperatures (e.g., light burned MgO calcined at 700 - 1000°C) presents a great reactivity and early age expansion of concrete. Hydration reaction of MgO, which leads to the formation of $Mg(OH)_2$, is as follows :

$$MgO + H_2O = Mg^{2+} + 2\ OH^- = Mg(OH)_2$$

[0036] Since the volume of hydration products is higher than that of the reagents, the hydration of MgO leads to an expansion, which, if properly controlled, can be used to compensate the shrinkage typically observed in cementitious composites and their deformation due to creep as well. The compatible chemical nature of MgO with that of cement may produce beneficial expansive components capable of reducing the number of microcracks and contribute to strength gain under certain circumstances. Similar to that observed in the hydration of cement, after the formation of $Mg(OH)_2$, ensuing pozzolanic reactions can lead to the formation of magnesium silicate hydrates (e.g., $MgO\text{-}SiO_2\text{-}H_2O$ or M-S-H) capable of presenting considerable strength gain, if in the presence of amorphous silica-bearing mineral additions, such as fly ash or silica fume. Another practical feature of using reactive MgO-based cementitious composites is their ability to capture a considerable amount of CO_2, thereby further decreasing the material's environmental impact throughout its life cycle.

[0037] It is noted that various REEs can be extracted from the feedstock using the methods described herein. For example, in the context of the present description, REEs include the lanthanides as well as yttrium and scandium. For certain feedstocks, such as ion-adsorption clay materials, there is a higher concentration of heavy rare earth elements compared to conventional mineral deposits, and thus the process can be provided accordingly to obtain such REEs.

[0038] It is also noted that various integration techniques can be employed in the context of the present technology. For example, heat and material can be recycled at certain parts of the process to enhance efficiency, energy use, and sustainability. In one example, at least a portion of the vapors released from one or more of the calcination stages can be reused for preheating at least a portion of the material in the drying stage. The preheating can be done by direct contact of the hot vapours or using indirect heating. In addition, the partially cooled vapours that are withdrawn from the drying stage can be used to for heating purposes in the leaching stage (e.g., used to maintain the leaching temperature in the desired range or at around 50°C). It is also possible to use one of the calcination vapour streams for drying and the calcination vapour stream for leaching step heating.

[0039] Regarding the feedstock, it is noted that feedstock materials that are particularly suited to processing via this technology are high in degraded clay and high in clay mineral phases of kaolin, illite, and montmorillonite. Such clay materials can lead to better REE adsorption and kaolin rich materials can facilitate enhanced performance and properties after calcination for use in concrete. For example, analysis of the Grande Vallée clay has shown a composition containing a majority of Kaolinite, Illite/Mica muscovite and Quartz. See Fig 4 for X-ray diffraction of a sample of Grande Vallée material. It is preferred to have a composition of combined Kaolinite and Illite/Mica muscovite over 40% to have desired pozzolanic activity. For the concrete industry, the pozzolanic activity of the material after calcination should ideally have a minimum of 5 Mpa according to the CSA A3004 E1 test and obtain a score of 5g/100g of dried paste in the bound water measurements according to the ASTM C1897-20 Standard Test Methods. Of course, various other feedstocks and compositions are also possible in certain embodiments.

EXPERIMENTATION

[0040] Various tests were performed to assess materials and the technology described herein. Three samples of mortars were prepared with clays processed based on the present technology and calcined at different temperatures and lime according to standard CSA A3004-E1, Appendix A and the samples were tested after 7 days of curing. The composition of the mortars with the clays calcined at temperatures of 800°C, 850°C and 900°C, their fresh state, and their compressive strength after 7 days of curing are presented in Table 1 below:

Table 4

Sample	Sand (g)	Lime (g)	Clay (g)	E/ L	Water (g) Subsidence (mm)		Compression resistance (MPa)			
							C1	C2	C3	Average
S1 800	700	77,8	180	0,85	219,04	20,76	2,51	2,51	2,46	2,49
S1 850	700	77,8	177	0,81	206,69	21,2	3,89	3,6	5,07	3,75
S1 900	700	77,8	168	0,75	113,93	21,3	9,56	7,1	10,15	9,86
S2 800	700	77,8	173	0,81	203,48	21,4	0,89	0,89	0,94	0,91
S2 850	700	77,8	177	0,75	191,37	20,7	1,92	1,87	2,17	1,9
S2 900	700	77,8	180	0,70	180,74	20,8	8,57	9,8	8,38	8,92
S3 800	700	77,8	173	0,83	208,47	20,7	1,08	1,02	1,08	1,06
S3 850	700	77,8	178	0,77	196,99	21	2,56	2,51	2,22	2,43
S3 900	700	77,8	176	0,72	182,65	20,9	7,39	8,82	7,69	7,79

[0041] The CSA A 3001:23 standard requires that the minimum strength of the mortar tested at 7 days, according to the A3004 — Annex 4 standard, be at least 5 MPa. The analysis of the results showed that the three clays studied have very good potential as cementitious additions. The reactivity of the three clays was maximum at a calcination temperature of 900°C. The pozzolanic reactivity test, Canadian test CSA A3004-E1, Appendix A, shows results above the threshold necessary to consider cementitious additions as reactive.

[0042] It is noted that calcination temperatures between 875°C and 1000°C, optionally between 885°C and 950°C, can be used to provide a mortar strength of at least 5 Pa for the tested materials. It is also noted that the temperature and calcination conditions could be modified depending on clay composition and source as well as processing features such that the calcination results in a mortar strength of at least 5 Pa at other calcination operating conditions.

[0043] Referring now to Fig 5, leaching tests were performed to assess rare earth extraction. In such tests, the pH was approximately 2.57 (between 1 to 3) and the leaching solution was $(NH_4)_2SO_4$ with a leaching time of 30 minutes.

[0044] Several alternative implementations and examples have been described and illustrated herein. The implementations of the technology described above are intended to be exemplary only. A person of ordinary skill in the art would appreciate the features of the individual implementations, and the possible combinations and variations of the components. A person of ordinary skill in the art would further appreciate that any of the implementations could be provided in any combination with the other implementations disclosed herein. It is understood that the technology may be embodied in other specific forms without departing from the central characteristics thereof. The present implementations and examples, therefore, are to be considered in all respects as illustrative and not restrictive, and the technology is not to be limited to the details given herein. Accordingly, while the specific implementations have been illustrated and described, numerous modifications come to mind.

CLAIMS

1. A process comprising:

   subjecting clay ore to pre-treatment to produce a pre-treated clay material;

   leaching the pre-treated clay material to produce a leachate enriched in rare earth elements and a solid residue;

   separating the leachate from the solid residue;

   calcining the solid residue to produce pozzolanic clay material suitable for use as a concrete binder;

   subjecting the leachate to precipitation to form precipitated rare earth element oxides (REEO) and a rare earth depleted solution;

   separating the precipitated REEO from the rare earth depleted solution;

   calcining the precipitated REEO to form an REEO product mixture.

2. The process of claim 1, wherein the pre-treatment comprises drying the clay ore to obtain a dried ore.

3. The process of claim 2, wherein the drying is performed at a drying temperature between 150°C and 250°C.

4. The process of claim 2 or 3, wherein the pre-treatment comprises milling the dried ore to obtain a milled ore that is subjected to the leaching.

5. The process of claim 4, wherein the milling is performed to a granulometric distribution (D50) between 5 and 30 microns, or between 10 and 25 microns.

6. The process of any one of claims 1 to 5, wherein the separating of the leachate from the solid residue is performed by filtration.

7. The process of any one of claims 1 to 6, wherein calcining the solid residue is performed at a residue calcining temperature of 700°C to 1000°C, 875°C to 1000°C, or 885°C to 950°C.

8. The process of any one of claims 1 to 6, wherein calcining the solid residue is performed at a residue calcining temperature of 875°C to 1000°C.

9. The process of any one of claims 1 to 8, wherein the precipitation includes addition of a carboxylic acid to the leachate.

10. The process of claim 9, wherein the carboxylic acid comprises a dicarboxylic acid.

11. The process of claim 10-, wherein the dicarboxylic acid comprises oxalic acid.

12. The process of any one of claims 1 to 11, wherein separating the precipitated REEO from the rare earth depleted solution comprises filtration.

13. The process of any one of claims 1 to 12, wherein calcining the precipitated REEO is performed at a REEO calcining temperature between 700°C and 1000°C.

14. The process of any one of claims 1 to 13, further comprising recycling at least a portion of the rare earth depleted solution back into the leaching step as part of a leaching solution.

15. The process of claim 14, further comprising adjusting the rare earth depleted solution before recycling back into the leaching step.

16. The process of claim 15, wherein the adjusting comprises addition of a sulfate.

17. The process of any one of claims 1 to 16, wherein the leaching is performed using magnesium sulfate.

18. The process of any one of claims 1 to 17, wherein the leaching is performed at a solution pH of 3 to 5 or 1 to 3.

19. The process of any one of claims 1 to 18, wherein the leaching is performed at a solution pH of 1 to 3.

20. The process of any one of claims 1 to 19, further comprising subjecting the REEO product mixture to dissolution in HCl and fractional solvent extraction to produce individual rare earther elements (REE).

21. The process of any one of claims 1 to 20, further comprising forming a concrete additive comprising the pouzolanic clay material as well as fly ash and/or silica fume.

22. A system comprising:

    a drier configured to receive mined clay ore and produce a dried clay;

    a milling unit configured to receive the dried clay and produce a milled ore;

    a leaching unit configured to leach the milled ore to produce a leachate enriched in rare earth elements and a solid residue;

    a separation unit coupled to the leaching unit for separating the leachate from the solid residue;

    a clay calciner configured to receive and calcine the solid residue to produce pouzolanic clay material suitable for use as a concrete binder;

    a precipitation unit configured to receive the leachate and form precipitated rare earth element oxides (REEO) and a rare earth depleted solution;

    a separator configured for separating the precipitated REEO from the rare earth depleted solution;

    an REEO calciner configured to receive and calcine the precipitated REEO to form an REEO product mixture.

23. The system of claim 22, wherein the milling unit is configured to mill to a granulometric distribution of at most D50 of 20 microns.

24. The system of claim 22 or 23, wherein the separation unit is a filtration unit.

25. The system of any one of claims 22 to 24, wherein clay calciner is configured to operate at a residue calcining temperature of 700°C to 1000°C, 875°C to 1000°C, or 885°C to 950°C.

26. The system of any one of claims 22 to 24, wherein clay calciner is configured to operate at a residue calcining temperature of 875°C to 1000°C.

27. The system of any one of claims 22 to 26, wherein the precipitation unit is configured to receive a precipitation solution that includes a carboxylic acid.

28. The system of claim 27, wherein the carboxylic acid comprises a dicarboxylic acid.

29. The system of claim 28, wherein the dicarboxylic acid comprises oxalic acid.

30. The system of any one of claims 22 to 29, wherein separator for separating the precipitated REEO from the rare earth depleted solution comprises a filter.

31. The system of any one of claims 22 to 30, wherein the REEO calciner is configured for calcining the precipitated REEO at a REEO calcining temperature between 700°C and 1000°C.

32. The system of any one of claims 22 to 31, further comprising a recycle system in fluid communication with the separator and configured for recycling at least a portion of the rare earth depleted solution back into the leaching unit as part of a leaching solution.

33. The system of claim 32, further comprising an adjustment unit coupled to the recycle system and the separator, and configured for adjusting the rare earth depleted solution before recycling back into the leaching unit.

34. The system of claim 33, wherein the adjustment unit comprises a magnesium sulfate solution addition inlet.

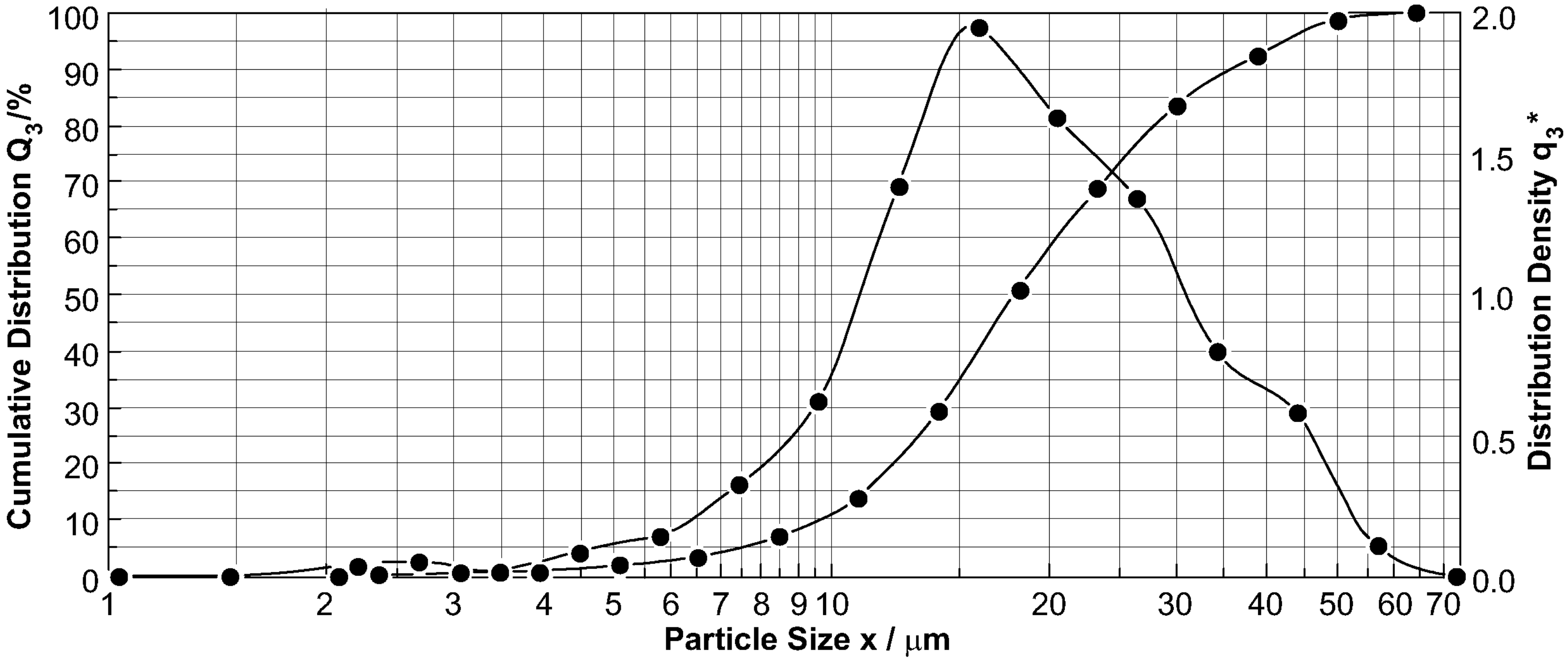
35. Use of a clay ore feedstock for extraction and co-production of rare earth element oxides (REEO) and a clay-based concrete binder.

36. The use of claim 35, further including one or more features of any one of claims 1 to 34 and/or as disclosed herein.

PARTICALE SIZE DISTRIBUTION PAQXOS 3.1.2 **EQPC**, sphere(EQPC), ISO

X_{10} =9.45 µm X_{50} =17.89 µm X_{90} =36.27 µm SMD =15.57 µm C_{opt} =0.00 %

X_{25} =13.12 µm X_{80} =28.35 µm X_{99} =51.90 µm VMD =20.63 µm Part. =3281



Cumulative Distribution

x_o / µm	Q_3 / %	x_o / µm	Q_3 / %
2.07	0.00	14.00	29.30
2.36	0.22	18.05	50.86
3.05	0.78	23.28	68.85
3.93	0.97	30.02	83.68
5.07	1.93	38.70	92.45
6.53	3.52	49.90	98.84
8.42	7.10	64.34	100.00
10.86	14.00	82.96	100.00

Distribution Density (LOG.)

x_m/ µm	$q_3$lg	x_m/ µm	$q_3$lg
1.46	0.000	12.33	1.386
2.21	0.038	15.90	1.953
2.68	0.050	20.50	1.630
3.46	0.017	26.43	1.344
4.46	0.087	34.08	0.795
5.75	0.144	43.95	0.579
7.42	0.325	56.66	0.105
9.56	0.625	73.06	0.000

FIG. 1

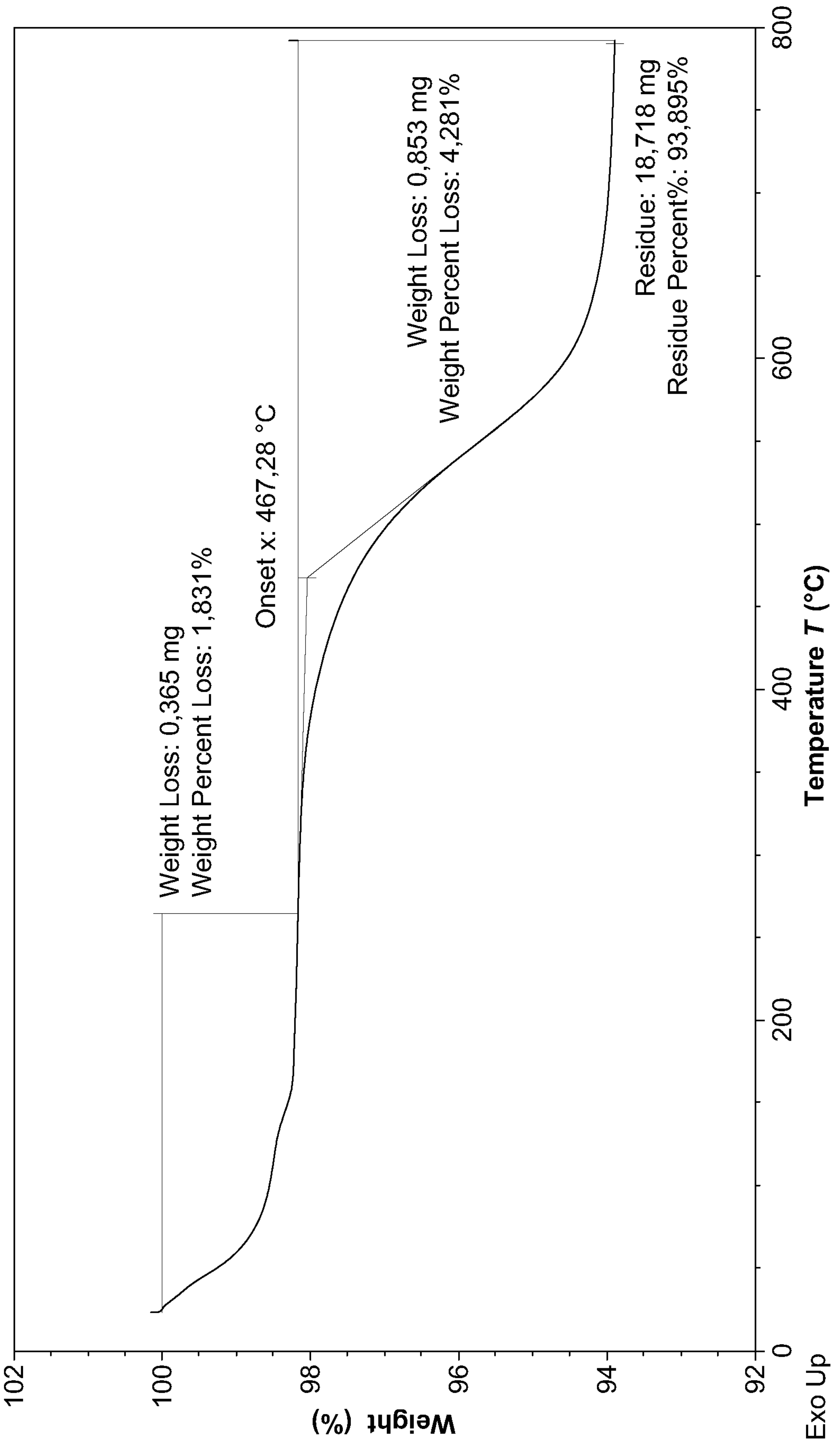

Weight Loss: 0,365 mg
Weight Percent Loss: 1,831%
Onset x: 467,28 °C
Weight Loss: 0,853 mg
Weight Percent Loss: 4,281%
Residue: 18,718 mg
Residue Percent%: 93,895%
Weight (%)
102
100
98
96
94
92
Exo Up
0
200
400
600
800
Temperature T (°C)

FIG. 2

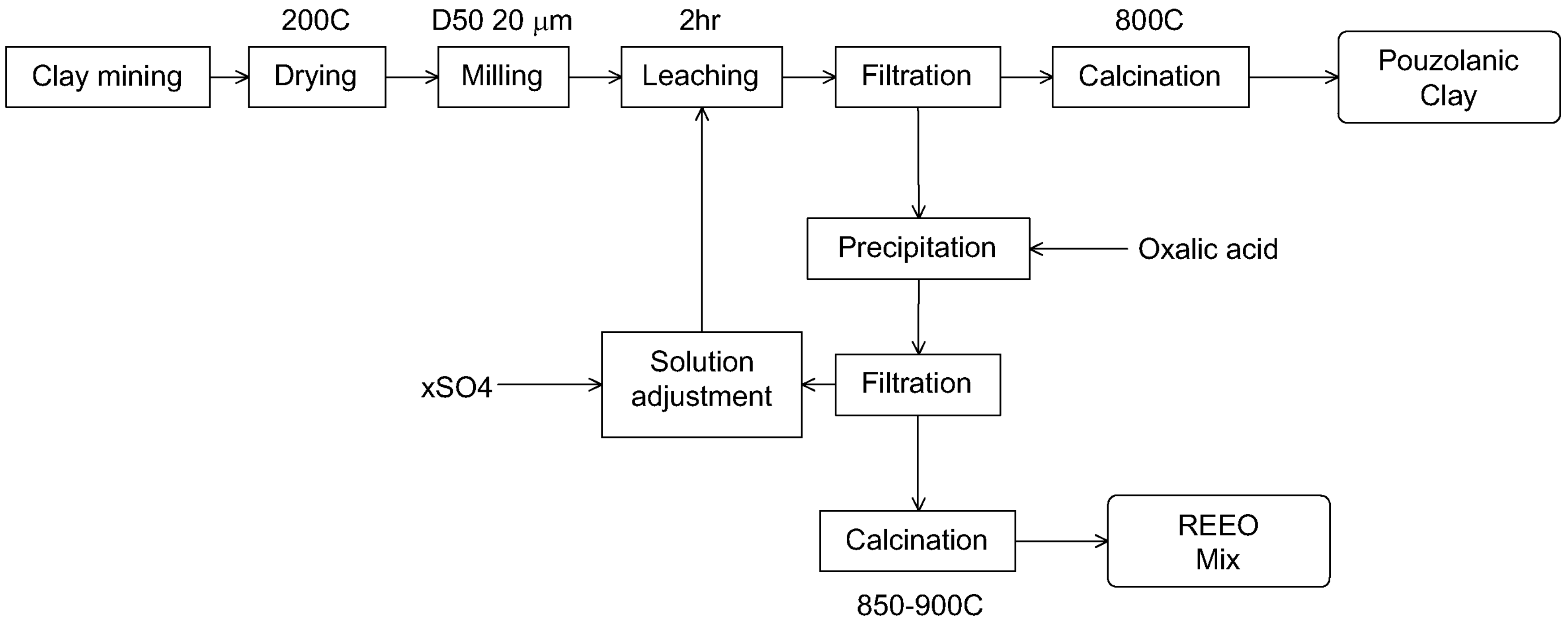
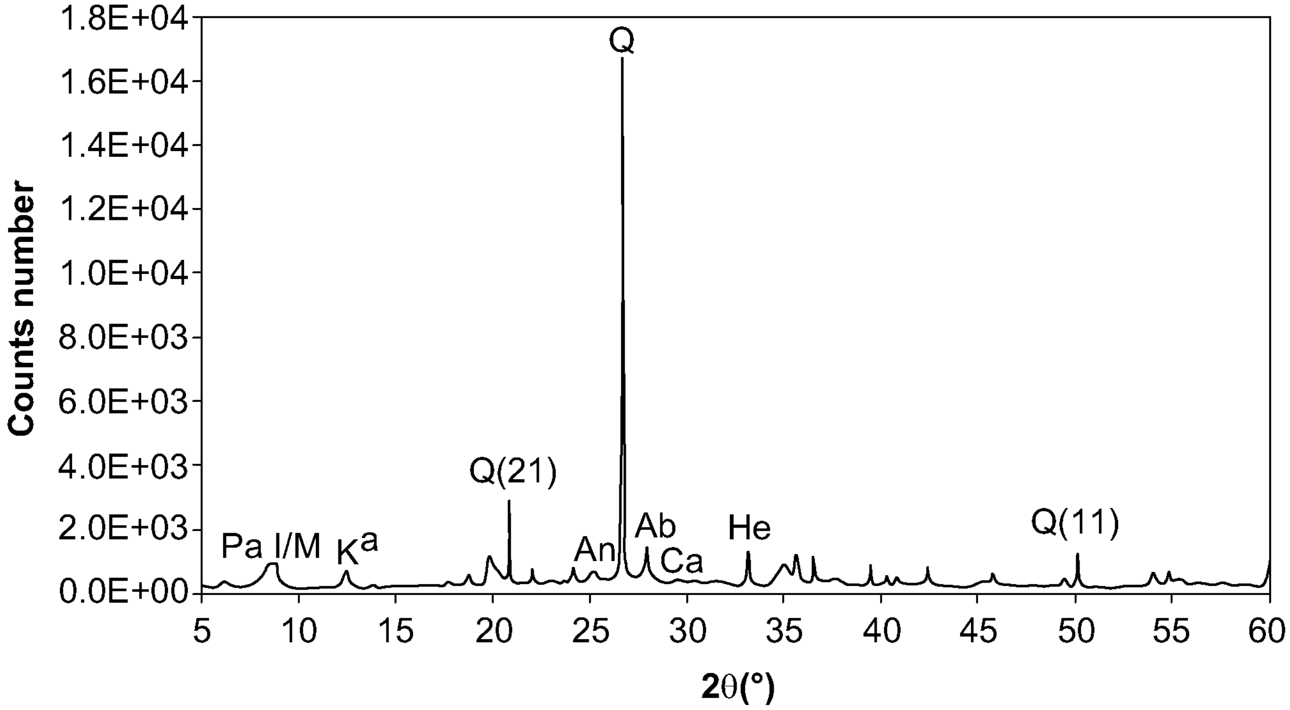

200C
D50 20 μm
2hr
800C
Clay mining
Drying
Milling
Leaching
Filtration
Calcination
Pouzolanic Clay
Precipitation
Oxalic acid
xSO4
Solution adjustment
Filtration
Calcination
REEO Mix
850-900C

FIG. 3



Sample 1: **Grand Vallée clay**

Crystalline structures identified:

-**K** = Kaolinite ($Al_2Si_2O_5(OH)_4$)
-**I/M** = Illite/M.Moscovite[1]($KAl_3Si_3O_{10}(OH)_2$)
-**Q** = Quartz (SiO_2)
-**Ab** = Albite ($NaAlSi_3O_8$)
-**He** = Hematite (Fe_2O_3)
-**Cl** = Clinochlore ($(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$)
-**Pa** = Palygorskite ($(Mg,Al)_2SI_4O_{10}(OH)\bullet 4(H_2O)$)
-**An** = Anatase (TiO_2)
-**Ca** = Calcite ($CaCO_3$)

Kaolinite	29%
Illite/Mica Moscovite	24%
Quartz	20%
Albite	9%
Hematite	8%
Clinochlore	5%
Palygorskite	2%
Calcite	1%
Anatase	1%
Others	1%

FIG. 4

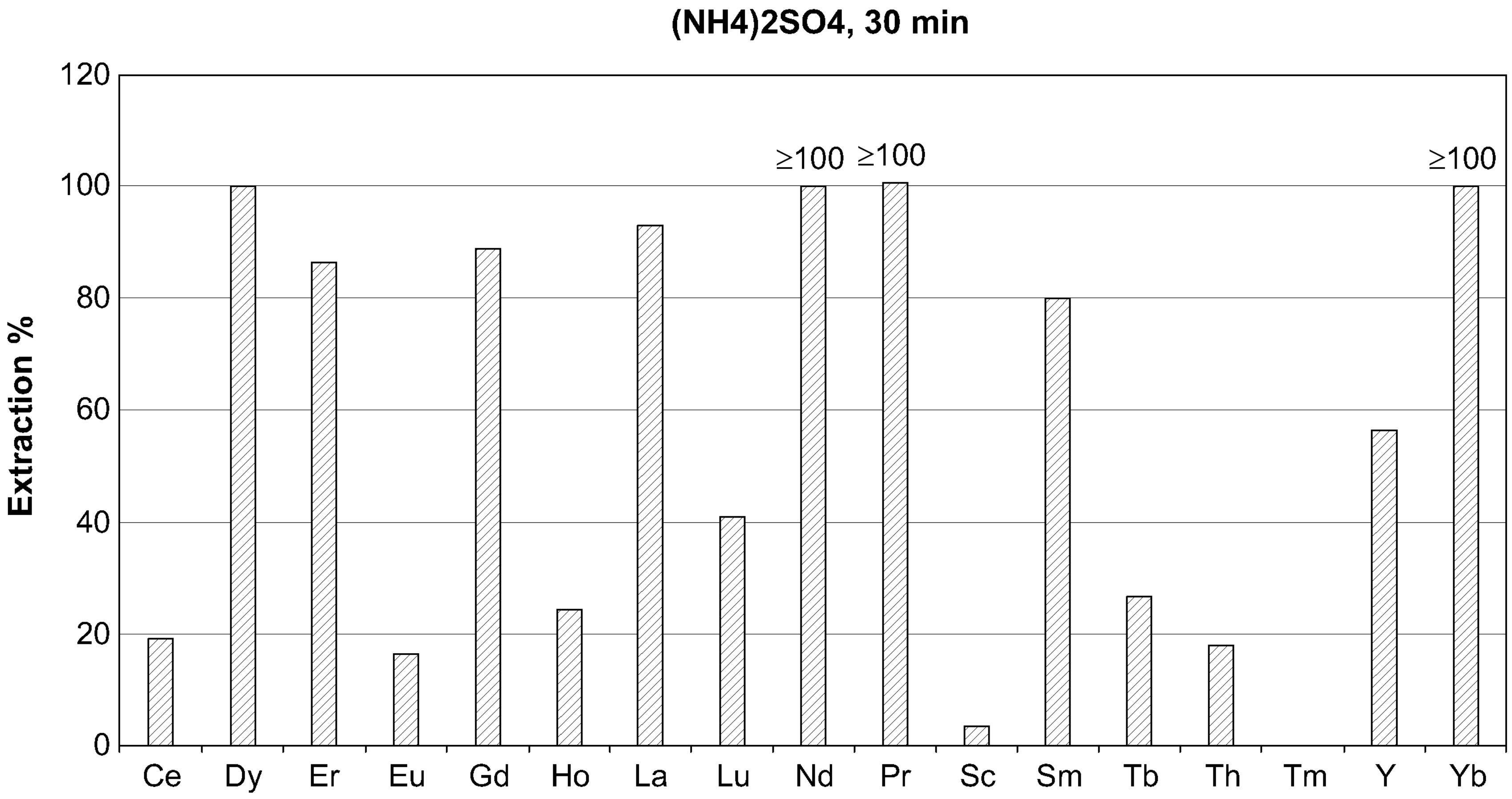

(NH4)2SO4, 30 min
Extraction %
0
20
40
60
80
100
120
Ce
Dy
Er
Eu
Gd
Ho
La
Lu
Nd
Pr
Sc
Sm
Tb
Th
Tm
Y
Yb
≥100
≥100
≥100

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2024/050837

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C01F 17/206*** (2020.01), ***B01D 11/02*** (2006.01), ***B02C 23/08*** (2006.01), ***B02C 23/18*** (2006.01), ***C01B 33/20*** (2006.01), ***C01F 17/10*** (2020.01)

CPC: B01D 11/02 (2020.01), B02C 23/08 (2020.01), B02C 23/18 (2020.01), C01B 33/20 (2020.01), C01F 17/10 (2022.01), C01F 17/206 (2022.01)

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: C01F 17/206 (2020.01), B01D 11/02 (2006.01), B02C 23/08 (2006.01), B02C 23/18 (2006.01), C01B 33/20 (2006.01), C01F 17/10 (2020.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases: Questel Orbit, Google Scholar SCOPUS

Keywords: clay, calcination, process, dry, precipitation, leachate, binder, rare earth, rare earth element, oxide, rare earth oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2016025928 A1 (BREWER) 18 February 2016 (18-02-2016) *Abstract; Claims; Paragraphs [0010]-[0015] and [0028]-[0045]; Figures 1-3*	1-36
Y	WO 2012149642 A1 (BOUDREAULT et al.) 8 November 2012 (08-11-2012) *Abstract; Claims; Paragraphs [0159]-[0195] and [0209]-[0215]; Examples; Figures 1-4*	1-36
Y	WO 2012126092 A1 (BOUDREAULT et al.) 27 September 2012 (27-09-2012) *Abstract; Claims; Paragraphs [0142]-[0190]; Examples; Figures 1-4*	1-36
Y	MOUSAVI et al., "*Clay as a Sustainable Binder for Concrete - A Review*". Constr. Mater., 29 September 2021 (29-09-2021), Vol. 1, pp. 134-168. *Entire Document*	1-36

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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

Date of the actual completion of the international search
05 August 2024 (05-08-2024)

Date of mailing of the international search report
23 September 2024 (23-09-2024)

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

Authorized officer
Jay Chi
778-847-1569

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2016025928A1	18 February 2016 (18-02-2016)	AU2015301415A1	02 February 2017 (02-02-2017)
		AU2015301415B2	31 January 2019 (31-01-2019)
		BR112017002928A2	05 December 2017 (05-12-2017)
		BR112017002928B1	29 March 2022 (29-03-2022)
		CA2955313A1	18 February 2016 (18-02-2016)
		CA2955313C	13 April 2021 (13-04-2021)
		CL2017000331A1	22 September 2017 (22-09-2017)
		CN106573792A	19 April 2017 (19-04-2017)
		CN106573792B	22 March 2019 (22-03-2019)
		DK3180290T3	27 July 2020 (27-07-2020)
		EA201790079A1	31 July 2017 (31-07-2017)
		EA036195B1	13 October 2020 (13-10-2020)
		EP3180290A1	21 June 2017 (21-06-2017)
		EP3180290A4	09 May 2018 (09-05-2018)
		EP3180290B1	22 April 2020 (22-04-2020)
		ES2807250T3	22 February 2021 (22-02-2021)
		HRP20201123T1	22 January 2021 (22-01-2021)
		HUE051507T2	01 March 2021 (01-03-2021)
		IL250527B	31 May 2021 (31-05-2021)
		JP2017532454A	02 November 2017 (02-11-2017)
		JP6622307B2	18 December 2019 (18-12-2019)
		KR20170042661A	19 April 2017 (19-04-2017)
		KR102441721B1	07 September 2022 (07-09-2022)
		LT3180290T	12 October 2020 (12-10-2020)
		MX2017000918A	07 August 2017 (07-08-2017)
		PE20170381A1	19 April 2017 (19-04-2017)
		PH12017500107A1	22 May 2017 (22-05-2017)
		PL3180290T3	02 November 2020 (02-11-2020)
		PT3180290T	23 July 2020 (23-07-2020)
		RS60628B1	30 September 2020 (30-09-2020)
		SG11201700280PA	27 February 2017 (27-02-2017)
		SI3180290T1	30 September 2020 (30-09-2020)
		UA118055C2	12 November 2018 (12-11-2018)
		US2017275732A1	28 September 2017 (28-09-2017)
		US10494694B2	03 December 2019 (03-12-2019)
WO2012149642A1	08 November 2012 (08-11-2012)	AU2012231686A1	18 April 2013 (18-04-2013)
		AU2012231686A8	26 September 2013 (26-09-2013)
		AU2012231686B2	27 August 2015 (27-08-2015)
		AU2012250460A1	02 May 2013 (02-05-2013)
		AU2012250460B2	26 November 2015 (26-11-2015)
		AU2012308068A1	09 May 2013 (09-05-2013)
		AU2012308068B2	05 February 2015 (05-02-2015)
		AU2013202318A1	25 July 2013 (25-07-2013)
		AU2013202318B2	05 November 2015 (05-11-2015)
		AU2013203668A1	03 October 2013 (03-10-2013)
		AU2013247339A1	16 October 2014 (16-10-2014)
		AU2016200411A1	11 February 2016 (11-02-2016)
		AU2016201013A1	03 March 2016 (03-03-2016)
		BR112013023907A2	24 September 2019 (24-09-2019)
		BR112013028371A2	14 February 2017 (14-02-2017)
		BR112014006275A2	11 April 2017 (11-04-2017)
		BR112014016732A2	13 June 2017 (13-06-2017)
		BR112014016732A8	04 July 2017 (04-07-2017)
		BR112015000626A2	27 June 2017 (27-06-2017)
		BR112015006536A2	08 August 2017 (08-08-2017)
		CA2820631A1	26 March 2014 (26-03-2014)

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
		CA2829049A1	27 September 2012 (27-09-2012)
		CA2829049C	02 December 2014 (02-12-2014)
		CA2834151A1	08 November 2012 (08-11-2012)
		CA2834151C	22 December 2015 (22-12-2015)
		CA2848751A1	21 March 2013 (21-03-2013)
		CA2848751C	21 April 2020 (21-04-2020)
		CA2857574A1	18 July 2013 (18-07-2013)
		CA2857574C	24 March 2015 (24-03-2015)
		CA2868363A1	26 September 2013 (26-09-2013)
		CA2869251A1	17 October 2013 (17-10-2013)
		CA2869251C	23 June 2020 (23-06-2020)
		CA2875776A1	18 July 2013 (18-07-2013)
		CA2878744A1	16 January 2014 (16-01-2014)
		CA2878744C	15 September 2020 (15-09-2020)
		CA2885255A1	03 April 2014 (03-04-2014)
		CA2885255C	22 December 2015 (22-12-2015)
		CA2913557A1	08 November 2012 (08-11-2012)
		CA2913682A1	03 April 2014 (03-04-2014)
		CA2913682C	13 June 2017 (13-06-2017)
		CN103534367A	22 January 2014 (22-01-2014)
		CN103857810A	11 June 2014 (11-06-2014)
		CN104039706A	10 September 2014 (10-09-2014)
		CN104245973A	24 December 2014 (24-12-2014)
		CN104302791A	21 January 2015 (21-01-2015)
		CN104302791B	15 March 2017 (15-03-2017)
		CN104603303A	06 May 2015 (06-05-2015)
		EP2686458A1	22 January 2014 (22-01-2014)
		EP2686458A4	15 April 2015 (15-04-2015)
		EP2705169A1	12 March 2014 (12-03-2014)
		EP2705169A4	15 April 2015 (15-04-2015)
		EP2755918A1	23 July 2014 (23-07-2014)
		EP2755918A4	01 July 2015 (01-07-2015)
		EP2802675A1	19 November 2014 (19-11-2014)
		EP2802675A4	13 July 2016 (13-07-2016)
		EP2802675B1	11 March 2020 (11-03-2020)
		EP2828415A1	28 January 2015 (28-01-2015)
		EP2828415A4	18 May 2016 (18-05-2016)
		EP2836616A1	18 February 2015 (18-02-2015)
		EP2836616A4	16 December 2015 (16-12-2015)
		EP3141621A1	15 March 2017 (15-03-2017)
		IN1918MUN2014A	10 July 2015 (10-07-2015)
		IN3007DEN2014A	08 May 2015 (08-05-2015)
		JP2014508863A	10 April 2014 (10-04-2014)
		JP2014513212A	29 May 2014 (29-05-2014)
		JP5894262B2	23 March 2016 (23-03-2016)
		JP2014526431A	06 October 2014 (06-10-2014)
		JP2015510483A	09 April 2015 (09-04-2015)
		JP6025868B2	16 November 2016 (16-11-2016)
		JP2015516507A	11 June 2015 (11-06-2015)
		JP2015535886A	17 December 2015 (17-12-2015)
		MY175471A	29 June 2020 (29-06-2020)
		MY190290A	12 April 2022 (12-04-2022)
		RU2013146790A	27 April 2015 (27-04-2015)
		RU2588960C2	10 July 2016 (10-07-2016)
		RU2013153535A	10 June 2015 (10-06-2015)
		RU2014114938A	27 October 2015 (27-10-2015)
		RU2014131946A	27 February 2016 (27-02-2016)

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
		RU2579843C2	10 April 2016 (10-04-2016)
		RU2014141795A	20 May 2016 (20-05-2016)
		RU2595178C2	20 August 2016 (20-08-2016)
		RU2015103833A	27 August 2016 (27-08-2016)
		RU2597096C2	10 September 2016 (10-09-2016)
		RU2016104423A	22 November 2018 (22-11-2018)
		US2016304987A1	20 October 2016 (20-10-2016)
		US10174402B2	08 January 2019 (08-01-2019)
		US2013283977A1	31 October 2013 (31-10-2013)
		US9115419B2	25 August 2015 (25-08-2015)
		US2014369904A1	18 December 2014 (18-12-2014)
		US9382600B2	05 July 2016 (05-07-2016)
		US2014369907A1	18 December 2014 (18-12-2014)
		US9023301B2	05 May 2015 (05-05-2015)
		US2014373683A1	25 December 2014 (25-12-2014)
		US9410227B2	09 August 2016 (09-08-2016)
		US2015104361A1	16 April 2015 (16-04-2015)
		US2015159239A1	11 June 2015 (11-06-2015)
		US9290828B2	22 March 2016 (22-03-2016)
		US2015225808A1	13 August 2015 (13-08-2015)
		US9353425B2	31 May 2016 (31-05-2016)
		US2015275330A1	01 October 2015 (01-10-2015)
		US9556500B2	31 January 2017 (31-01-2017)
		US2015307965A1	29 October 2015 (29-10-2015)
		US9260767B2	16 February 2016 (16-02-2016)
		US2016153067A1	02 June 2016 (02-06-2016)
		US2016153071A1	02 June 2016 (02-06-2016)
		US9945009B2	17 April 2018 (17-04-2018)
		US2016265082A1	15 September 2016 (15-09-2016)
		WO2012126092A1	27 September 2012 (27-09-2012)
		WO2013037054A1	21 March 2013 (21-03-2013)
		WO2013104059A1	18 July 2013 (18-07-2013)
		WO2013138900A1	26 September 2013 (26-09-2013)
		WO2013152423A1	17 October 2013 (17-10-2013)
		WO2014008586A1	16 January 2014 (16-01-2014)
		WO2014047728A1	03 April 2014 (03-04-2014)
		ZA201407202B	31 May 2017 (31-05-2017)
WO2012126092A1	27 September 2012 (27-09-2012)	AU2012231686A1	18 April 2013 (18-04-2013)
		AU2012231686A8	26 September 2013 (26-09-2013)
		AU2012231686B2	27 August 2015 (27-08-2015)
		AU2012250460A1	02 May 2013 (02-05-2013)
		AU2012250460B2	26 November 2015 (26-11-2015)
		AU2012308068A1	09 May 2013 (09-05-2013)
		AU2012308068B2	05 February 2015 (05-02-2015)
		AU2013202318A1	25 July 2013 (25-07-2013)
		AU2013202318B2	05 November 2015 (05-11-2015)
		AU2013203668A1	03 October 2013 (03-10-2013)
		AU2013247339A1	16 October 2014 (16-10-2014)
		AU2016200411A1	11 February 2016 (11-02-2016)
		AU2016201013A1	03 March 2016 (03-03-2016)
		BR112013023907A2	24 September 2019 (24-09-2019)
		BR112013028371A2	14 February 2017 (14-02-2017)
		BR112014006275A2	11 April 2017 (11-04-2017)
		BR112014016732A2	13 June 2017 (13-06-2017)
		BR112014016732A8	04 July 2017 (04-07-2017)
		BR112015000626A2	27 June 2017 (27-06-2017)

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
		BR112015006536A2	08 August 2017 (08-08-2017)
		CA2820631A1	26 March 2014 (26-03-2014)
		CA2829049A1	27 September 2012 (27-09-2012)
		CA2829049C	02 December 2014 (02-12-2014)
		CA2834151A1	08 November 2012 (08-11-2012)
		CA2834151C	22 December 2015 (22-12-2015)
		CA2848751A1	21 March 2013 (21-03-2013)
		CA2848751C	21 April 2020 (21-04-2020)
		CA2857574A1	18 July 2013 (18-07-2013)
		CA2857574C	24 March 2015 (24-03-2015)
		CA2868363A1	26 September 2013 (26-09-2013)
		CA2869251A1	17 October 2013 (17-10-2013)
		CA2869251C	23 June 2020 (23-06-2020)
		CA2875776A1	18 July 2013 (18-07-2013)
		CA2878744A1	16 January 2014 (16-01-2014)
		CA2878744C	15 September 2020 (15-09-2020)
		CA2885255A1	03 April 2014 (03-04-2014)
		CA2885255C	22 December 2015 (22-12-2015)
		CA2913557A1	08 November 2012 (08-11-2012)
		CA2913682A1	03 April 2014 (03-04-2014)
		CA2913682C	13 June 2017 (13-06-2017)
		CN103534367A	22 January 2014 (22-01-2014)
		CN103857810A	11 June 2014 (11-06-2014)
		CN104039706A	10 September 2014 (10-09-2014)
		CN104245973A	24 December 2014 (24-12-2014)
		CN104302791A	21 January 2015 (21-01-2015)
		CN104302791B	15 March 2017 (15-03-2017)
		CN104603303A	06 May 2015 (06-05-2015)
		EP2686458A1	22 January 2014 (22-01-2014)
		EP2686458A4	15 April 2015 (15-04-2015)
		EP2705169A1	12 March 2014 (12-03-2014)
		EP2705169A4	15 April 2015 (15-04-2015)
		EP2755918A1	23 July 2014 (23-07-2014)
		EP2755918A4	01 July 2015 (01-07-2015)
		EP2802675A1	19 November 2014 (19-11-2014)
		EP2802675A4	13 July 2016 (13-07-2016)
		EP2802675B1	11 March 2020 (11-03-2020)
		EP2828415A1	28 January 2015 (28-01-2015)
		EP2828415A4	18 May 2016 (18-05-2016)
		EP2836616A1	18 February 2015 (18-02-2015)
		EP2836616A4	16 December 2015 (16-12-2015)
		EP3141621A1	15 March 2017 (15-03-2017)
		IN1918MUN2014A	10 July 2015 (10-07-2015)
		IN3007DEN2014A	08 May 2015 (08-05-2015)
		JP2014508863A	10 April 2014 (10-04-2014)
		JP2014513212A	29 May 2014 (29-05-2014)
		JP5894262B2	23 March 2016 (23-03-2016)
		JP2014526431A	06 October 2014 (06-10-2014)
		JP2015510483A	09 April 2015 (09-04-2015)
		JP6025868B2	16 November 2016 (16-11-2016)
		JP2015516507A	11 June 2015 (11-06-2015)
		JP2015535886A	17 December 2015 (17-12-2015)
		MY175471A	29 June 2020 (29-06-2020)
		MY190290A	12 April 2022 (12-04-2022)
		RU2013146790A	27 April 2015 (27-04-2015)
		RU2588960C2	10 July 2016 (10-07-2016)
		RU2013153535A	10 June 2015 (10-06-2015)

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
		RU2014114938A	27 October 2015 (27-10-2015)
		RU2014131946A	27 February 2016 (27-02-2016)
		RU2579843C2	10 April 2016 (10-04-2016)
		RU2014141795A	20 May 2016 (20-05-2016)
		RU2595178C2	20 August 2016 (20-08-2016)
		RU2015103833A	27 August 2016 (27-08-2016)
		RU2597096C2	10 September 2016 (10-09-2016)
		RU2016104423A	22 November 2018 (22-11-2018)
		US2016304987A1	20 October 2016 (20-10-2016)
		US10174402B2	08 January 2019 (08-01-2019)
		US2013283977A1	31 October 2013 (31-10-2013)
		US9115419B2	25 August 2015 (25-08-2015)
		US2014369904A1	18 December 2014 (18-12-2014)
		US9382600B2	05 July 2016 (05-07-2016)
		US2014369907A1	18 December 2014 (18-12-2014)
		US9023301B2	05 May 2015 (05-05-2015)
		US2014373683A1	25 December 2014 (25-12-2014)
		US9410227B2	09 August 2016 (09-08-2016)
		US2015104361A1	16 April 2015 (16-04-2015)
		US2015159239A1	11 June 2015 (11-06-2015)
		US9290828B2	22 March 2016 (22-03-2016)
		US2015225808A1	13 August 2015 (13-08-2015)
		US9353425B2	31 May 2016 (31-05-2016)
		US2015275330A1	01 October 2015 (01-10-2015)
		US9556500B2	31 January 2017 (31-01-2017)
		US2015307965A1	29 October 2015 (29-10-2015)
		US9260767B2	16 February 2016 (16-02-2016)
		US2016153067A1	02 June 2016 (02-06-2016)
		US2016153071A1	02 June 2016 (02-06-2016)
		US9945009B2	17 April 2018 (17-04-2018)
		US2016265082A1	15 September 2016 (15-09-2016)
		WO2012149642A1	08 November 2012 (08-11-2012)
		WO2013037054A1	21 March 2013 (21-03-2013)
		WO2013104059A1	18 July 2013 (18-07-2013)
		WO2013138900A1	26 September 2013 (26-09-2013)
		WO2013152423A1	17 October 2013 (17-10-2013)
		WO2014008586A1	16 January 2014 (16-01-2014)
		WO2014047728A1	03 April 2014 (03-04-2014)
		ZA201407202B	31 May 2017 (31-05-2017)