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(54) Title: A PROCESS FOR TREATMENT AND/OR REMEDIATION OF WATER

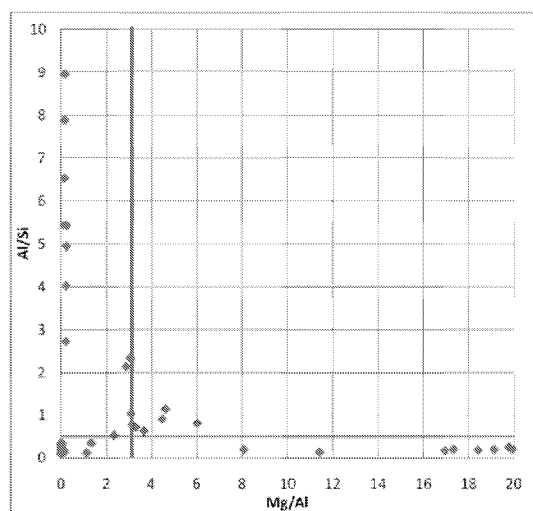


Figure 1.

(57) Abstract: A process for treating water containing one or more dissolved cation species and/or one or more dissolved anion species is described. The process comprises the steps of: adding a magnesium and/or aluminium containing silicate material in the water and dissolving at least a part of the silicate material in the water thereby leaching at least a part of the magnesium and/or aluminium from the silicate material into the water. The process also comprises controlling reaction conditions for achieving an appropriate Mg:Al ratio in the water for in situ formation of layered double hydroxide containing Mg and Al as predominant species in a lattice of the LDH; wherein at least one of the said dissolved cation and/or anion species is incorporated into the LDH formed in situ. Furthermore, Mg-containing compounds or Al-containing compounds may also be optionally added for achieving the appropriate Mg:Al ratio.

A PROCESS FOR TREATMENT AND/OR REMEDIATION OF WATER

TECHNICAL FIELD

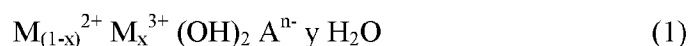
[0001] The present invention relates to a process for treatment and/or remediation of water including but not limited to natural water, waste water and process waters.

[0002] The process of the present invention refers to all of the waters, other liquids or solutes or solvents or mixtures whether miscible or immiscible and solids such as but not limited to natural water, waste waters or mineral processing/metallurgical streams and electronic waste (e-waste) streams that result from one or more processes including leaching or chemical extraction in acidic, neutral or alkali reagents may often contain a range of elements (as ions, molecules, complexes, micelles, aggregates, particulates or colloids etc) and metals or metallic species or other elements (such as and including metals, metalloids, lanthanide or rare earth elements, REE, actinides, transuranics and radionuclides) that may be considered both as commodities and contaminants.

BACKGROUND ART

[0003] Layered double hydroxides (LDH) are a class of both naturally occurring and synthetically produced materials characterised by a positively-charged mixed metal hydroxide layers separated by interlayers that contain water molecules and a variety of exchangeable anions. LDH is most commonly formed by the co-precipitation of divalent (e.g. Mg^{2+} , Fe^{2+}) and trivalent (e.g. Al^{3+} , Fe^{3+}) metal cation solutions at moderate to high pH (Taylor, 1984, Vucelic et al, 1997, Shin et al, 1996).

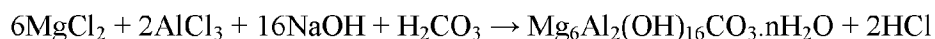
[0004] An LDH compound may be represented by the general formula (1):



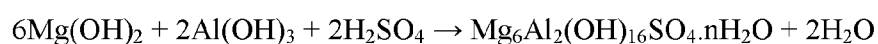
where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively and A^{n-} is the interlayer ion of valence n. The x value represents the proportion of trivalent metal ion to the proportion of total amount metal ion and y denotes variable amounts of interlayer water.

[0005] Common forms of LDH comprise Mg^{2+} and Al^{3+} (commonly known as hydrotalcites [HT]) and Mg^{2+} and Fe^{3+} (known as pyroaurites), but other cations, including Ni, Zn, Mn, Ca, Cr and La, are known. The amount of surface positive charge generated is dependent upon the mole ratio of the metal ions in the lattice structure and the conditions of preparation as they affect crystal formation.

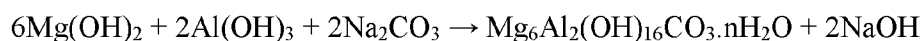
[0006] The formation of HT (the most commonly synthesised LDH frequently with carbonate as the principal “exchangeable” anion) may be most simply described by the following reaction:



[0007] Typically, ratios of divalent to trivalent cations in Hydrotalcites vary from 2:1 to 4:1. Other synthetic pathways to form HT (and other LDH) include synthesis from $\text{Mg}(\text{OH})_2$ (brucite) and MgO (calcined magnesia) via neutralisation of acidic solutions (eg. Albiston et al, 1996). This can be described by the following reaction:



[0008] A range of metals of widely varying concentrations may also be simultaneously co-precipitated, hence forming a polymetallic LDH. HT or LDH were first described over 60 years ago (Fron del, 1941, Feitknecht, 1942). Sometimes, they can also occur in nature as accessory minerals in soils and sediments (eg. Taylor and McKenzie, 1980). Layered double hydroxides may also be synthesised from industrial waste materials by the reaction of bauxite residue derived from alumina extraction (red mud) with seawater (eg. Thornber and Hughes, 1987), as described by the following reaction:



or by the reaction of lime with fly ash derived from fossil fuel (eg. coal fired power stations, Reardon and Della Valle, 1997).

[0009] Within the LDH or HT structure there are octahedral metal hydroxide sheets that carry a net positive charge due to limited substitution of trivalent for divalent cations as described above. As a consequence, it is possible to substitute a wide range of inorganic or organic anions into the LDH or HT structure. These anions are often referred to as “interlayer anions” as they fit between the layers of hydroxide material. Layered double hydroxides are generally unstable below a pH of approximately 5 (Ookubu et al, 1993) but may act as buffers over a wide range of solution pH (Seida and Nakano, 2002). Layered double hydroxides or HT, and in particular those that contain carbonate as the predominant anion, have also been demonstrated to have a considerable capacity to neutralise a range of mineral acids via consumption of both the hydroxyl and carbonate anions contained within the LDH structure (eg. Kameda et al, 2003).

[0010] A number of studies have been conducted to investigate ways to exploit the anion

exchange properties of LDH. These studies have focussed on the removal of phosphate and other oxyanions and humic substances from natural and wastewater(s) (Miyata, 1980, Misra and Perrotta, 1992, Amin and Jayson, 1996, Shin et al, 1996, Seida and Nakano, 2000). Phosphate is one of the many anions that may be exchanged into the interlayer space in LDH. Laboratory studies of phosphate uptake using synthetically prepared Mg-Al HT and a range of initial dissolved phosphate concentrations indicate an uptake capacity of from ca. 25-30 mg P/g (Miyata, 1983, Shin et al, 1996) to ca. 60 mg P/g with uptake also influenced by initial phosphate concentration, pH (with maximum phosphate absorption near pH 7), degree of crystallinity and the HT chemistry (Ookubo et al, 1993). A major obstacle to the use of HT for phosphate removal in natural and/or wastewaters is the selectivity for carbonate over phosphate, with a selectivity series in the approximate order $\text{CO}_3^{2-} > \text{HPO}_4^{2-} \gg \text{SO}_4^{2-}$, $\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{NO}_3^-$ (Miyata, 1980, 1983, Sato et al, 1986, Shin et al, 1986, Cavani et al, 1991). Many HT are also synthesised with carbonate as the predominant anion and thus require anion exchange before they are exposed to phosphate. When carbonate is also combined with sulphate, nitrate and chloride (as might commonly occur in natural or wastewaters) the reduction of phosphate absorption to the HT is further decreased (Shin et al, 1996).

[0011] A number of recent studies have focussed on the formation and study of synthetic LDH or specifically HT or similar and their subsequent reactivity to a range of anions, particularly silicate (e.g. Depege et al, 1996) with a view to forming polymetallic aluminosilicates, which as potential precursors to clay materials, are thought to limit metal mobility and bioavailability (eg. Ford et al, 1999). A potential also exists for the co-precipitation of silicate and aluminate anions as another precursor of analogue of clay minerals.

[0012] Thus, other structural elements or interlayer ions may be incorporated (both inorganic and organic) to assist in both substitution and/or incorporation of ions from solution and/or increased stability. Subsequent formation of chlorite- or phyllosilicate-like minerals from pure Mg-Al or predominantly Mg-Al HT which may be similar to the HT, or iso-chemical in composition when compared to the HT, or may possess a similar chemistry as the HT with substitution of some ions as determined by the nature of Mg and/or Al added or the nature and chemical composition of the natural or wastewater which may influence the final geochemical composition, crystallinity or mineralogy.

[0013] This increased stability of LDH or HT or chlorite-like minerals or other LDH or HT derivatives may also be achieved possibly in combination with chemical methods described above by partial or complete evaporation, calcination or vitrification leading to part or complete dehydration and partial/total recrystallisation. The use of co-amendments with, or encapsulation

of, the LDH or HT may also be an option to further increase physical or chemical stability.

[0014] The International Atomic Energy Agency (which is the international centre of cooperation in the nuclear field working with member states and multiple partners worldwide to promote safe, secure and peaceful nuclear technologies) published a report in 2004 summarising the state of the art in the field of treatment of effluents from uranium mines and mills. Importantly, the novelty of the invention as described herein using the addition of chemical compounds to modify solution chemistry to form LDH or HT is exemplified by the absence of any similar description or process for the treatment of effluents from uranium mines (IAEA, 2004).

[0015] It will be clearly understood that, if a prior art publication is referred to herein, this reference does not constitute an admission that the publication forms part of the common general knowledge in the art in Australia or in any other country.

BRIEF DESCRIPTION OF INVENTION

[0016] In one aspect, the invention provides a process for treating water containing one or more dissolved cation species and/or one or more dissolved anion species; the process comprising the steps of:

(a) adding a magnesium and/or aluminium containing silicate material to the water and dissolving at least a part of the silicate material in the water thereby leaching at least a part of the magnesium and/or aluminium from the silicate material into the water; and

(b) controlling reaction conditions for achieving an appropriate Mg:Al ratio in the water for formation/precipitation of layered double hydroxide (LDH) in situ containing Mg and Al as predominant species in a lattice of the LDH;

wherein at least one of the said dissolved cation and/or anion species is incorporated into the LDH formed in situ.

[0017] The applicants have realised that addition of magnesium and/or aluminium containing silicates such as, for example Mg-bearing sepiolite, vermiculite, attapulgite or talc or kaolinite or natural or synthetic minerals such as zeolite or other clay materials that may yield magnesium and/or aluminium ions into the water when at least a part of the silicate material is subjected to the dissolving step (step [a]) of the process of the present invention. Without being bound by theory, it is theorised that leaching of at least some of the magnesium and aluminium ions into the water results in the leached magnesium and/or aluminium ions being taken up for formation of the LDH material in situ.

[0018] The utilisation of magnesium containing and/or aluminium containing silicate materials as a source of magnesium and/or aluminium ions for the formation of the LDH material presents several advantages.

[0019] It is understood by the applicants that addition of the said silicate material to the water followed by dissolving at least a part of the silicate results in leaching of at least some of the magnesium and/or aluminium ions initially present in the silicate material. However the applicants have surprisingly found that the remaining undissolved silicate material provides nucleation sites for facilitating the formation or precipitation of the LDH material in situ thereby improving yield of the LDH formed in the water.

[0020] It is also understood that the undissolved silicate material also functions as an agent for increasing density and/or aggregate particle size of the LDH formed in situ thereby assisting in settling of the LDH in the water and/or dewatering or physical separation and recovery.

[0021] Another advantage presented by the process of the present invention is that the undissolved silicate material may also function as an additional cation or anion exchange agent in the water. This implies that in addition to the LDH material, the undissolved silicate material may contribute towards functioning as an adsorbent for ionic species dissolved in the water.

[0022] The silicate materials mentioned above may also include, but are not limited to one or more of the following: Attapulgite; Clinoptilolite; Sepiolite; Talc; Vermiculite, mineral aggregates or associations in the form of rocks (e.g. ground granite, greenstone or serpentinite), overburden, soils, sediments or waste materials, for instance from alumina refining (red mud) or coal combustion (fly ash).

[0023] In at least some embodiments, undissolved silicate material from step (a) and the LDH formed in situ in step (b) form an insoluble clay material mixture wherein the clay material mixture incorporates said at least one or more dissolved cation species and/or the one or more dissolved anion species. This mixture may be also referred to a hybrid clay mixture.

[0024] In one embodiment, the step of dissolving the magnesium and aluminium containing silicate material comprises leaching the magnesium and aluminium from the silicate material under acidic pH conditions. For example, the silicate material may be dissolved by way of introducing an acidic solution such as hydrochloric acid solution and/or sulphuric acid solution. The applicants have realised that acid treatment or acid leaching of silicate materials containing both aluminium and magnesium may result in the leaching or release of aluminium ions and magnesium ions from the silicate material into the water. Therefore, conducting the dissolving

step under acidic conditions in at least some embodiments can result in leaching of magnesium and aluminium ions into the water. The leached ions may be utilised for tailoring the Mg:Al ratio and using the magnesium and aluminium ions as building blocks for the LDH formed in situ.

[0025] In an alternative embodiment, the step of dissolving the magnesium and/or aluminium containing silicate material comprises leaching the magnesium and/or aluminium from the silicate material under alkaline conditions. Conducting the dissolving step for silicate materials (containing both magnesium and aluminium) under alkaline conditions results in low dissolution of magnesium and comparatively higher dissolution of aluminium ions into the water. Conducting the dissolving step under alkaline conditions in at least some embodiments can result in leaching of at least the aluminium ions into the water which may be utilised for tailoring the Mg:Al ratio and using the leached aluminium ions as building blocks for the LDH formed in situ.

[0026] Furthermore, in at least some embodiments, Si may also be leached into the water as a result of the dissolving step of the present invention. Excessive leaching of silica can potentially occupy the interlayer anion exchange site within the LDH during formation or may combine with the leached aluminium ions to form other compounds during the LDH formation. In some embodiments, the process also comprises controlling the leaching of silica into the water.

[0027] In at least some embodiments, the step of dissolving involves agitating the silicate material in the water for leaching said at least part of the magnesium and/or aluminium from the silicate material. The agitation may be carried out by way of one or more methods such as stirring and/or ultrasonication and/or any other desirable agitation means. It is also envisaged that a series of agitation steps may be utilised for agitating the silicate materials. The applicants have realised that agitating the silicate material results in increased leaching of the magnesium and/or aluminium ions from the silicate material into the water.

[0028] In at least some embodiments, the adding step comprises addition of a mixture comprising the said magnesium and/or aluminium containing silicate material and an additional silicate material. It is important to appreciate that by carefully combining one or more magnesium and/or aluminium containing silicate materials in desired proportions a modification of the divalent to trivalent ratio (Mg:Al) as required to form the LDH may be achieved. As a result, the required amount of additional Mg or Al to be added is reduced which can result in significant benefits.

[0029] In further embodiments the step of controlling the reaction conditions comprises addition of at least one Mg-containing compound and/or at least one Al-containing compound for achieving the appropriate Mg:Al ratio in the water for formation of the LDH in situ.

[0030] The Mg or Al dissolved in the water may comprise the leached magnesium and/or aluminium ions derived from the dissolved silicate materials and in at least some embodiments may also comprise magnesium and or aluminium ions forming a part of the dissolved cations in the water being subjected to the process of the present invention.

[0031] This recognises that many natural or in particular wastewaters may include dissolved magnesium and or aluminium ions. In the present invention, Mg ions and Al ions present in the water are taken up by the formation of LDH (containing Mg and Al as the predominant metal species in the lattice structure of the LDH). Advantageously, the LDH also can take up and largely immobilise other ions into the interlayer spaces between the lattice. Thus, other ions can also be removed from the water and largely immobilised.

[0032] For example, the said at least one aluminium containing compound may comprise aluminate ($\text{Al}(\text{OH})_4$ or $\text{AlO}_2 \cdot 2\text{H}_2\text{O}$) or aluminium sulphate, aluminium hydroxide or organometallic compounds containing aluminium.

[0033] Other inorganic compounds such as aluminium sulphate (e.g. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), aluminium hydroxide ($\text{Al}(\text{OH})_3$) or organometallic compounds (e.g. aluminium acetylacetonate $\text{C}_{15}\text{H}_{21}\text{AlO}_6$) may also be used where a source of Al is required. Preferably these sources of Al will be alkaline to raise solution pH to an appropriate level for LDH or HT formation, but also may be used where the final solution pH or the combination of these or other compounds is alkaline.

[0034] In some embodiments of the present invention, it may also be necessary to add additional Mg to the water in order to adjust the ratio of Al to Mg in the water to the desired level to obtain LDH or HT containing Mg and Al as predominant metal species in a lattice. This may be achieved, for example, by adding MgO or $\text{Mg}(\text{OH})_2$ to the water. Advantageously, MgO or $\text{Mg}(\text{OH})_2$ also assist in obtaining desirable pH characteristics that are suitable for the formation of LDH, such as HT.

[0035] In some embodiments of the present invention, it may be necessary or desirable to add additional alkaline or acid-neutralising material in addition to the at least one Mg-containing compound or the at least one Al-containing compound to the natural or wastewater. The additional alkaline or acid neutralising material may be selected from one or more of alkaline or

acid-neutralising solutes, slurries or solid materials or mixtures thereof, such as lime, slaked lime, calcined magnesia, sodium hydroxide, sodium carbonate, sodium bicarbonate or sodium silicate. This list is not exhaustive and other alkaline or acid-neutralising materials may also be added. The additional alkaline or acid-neutralising material may be added before the addition of the at least one Mg-containing compound or the at least one Al-containing compound to the natural or wastewater, together with the addition of the at least one Mg- containing compound or the at least one Al-containing compound to the natural or wastewater, or after the addition of the at least one Mg-containing compound or the at least one Al-containing compound to the natural or wastewater.

[0036] In some embodiments of the present invention, the order or sequence of addition of various alkalis or acid-neutralising materials to acid waters, wastewaters, slurries or process waters as described elsewhere in this specification may confer certain benefits. For example, the order of addition may confer geochemical and/or operational advantages to the neutralisation process and the formation of Layered Double Hydroxides (LDH) and other mineral precipitates.

[0037] Selective, partial or total removal of Layered Double Hydroxide (LDH) and/or other undissolved silicate materials and/or mineral precipitates or slurry components at various stages of the reactions whether via addition of various alkalis or acid-neutralising materials to acid waters, wastewaters or process waters or via addition of acid waters, wastewaters or slurries to various alkalis or acid-neutralising materials as described elsewhere in this specification may also be considered advantageous.

[0038] Such an example involves the removal of precipitates or existing solids or aggregates, mixtures or co-precipitates thereof prior to the introduction of reverse osmosis to remove some or all of remaining solutes or evaporation. This removal of Layered Double Hydroxide (LDH) and/or other mineral precipitates including the undissolved silicates at various stages of the reactions whether via addition of various alkalis or acid-neutralising materials to acid waters, wastewaters or process waters or via addition of acid waters, wastewaters or process waters to various alkalis or acid-neutralising materials as described elsewhere in this specification may be facilitated or enhanced by mechanical (e.g. centrifugation) or chemical (e.g. via addition of flocculants) means or a combination thereof

[0039] In some embodiments of the present invention, partial or total removal of water or other solvents or miscible or immiscible solutes, such as by partial or total evaporation or distillation, may be used to increase the concentrations of one or more of dissolved, colloidal or particulate constituents or additional added constituents such as Mg and/or Al, (e.g. to tailor the

appropriate Al to Mg ratio) to increase the concentration by a sufficient degree to induce the formation of LDH.

[0040] The present invention in at least some embodiments is also directed to water and water streams including process waters that may contain little or no Mg and/or Al or be dominated by other dissolved cations and/or anions. (e.g. such as those derived from some acid sulphate soils, industrial processes or nuclear power plants, weapons or research facilities). It is noted that not all waters (e.g. processing or wastewaters) have a major ion chemistry suitable for the formation of LDH or specific types of LDH such as Mg-Al HT or similar compositions. Thus, it may be necessary to tailor this chemistry for the formation of LDH or more specifically Mg-Al HT. The tailoring of the solution chemistry includes the step of adding the silicate material in a manner as set out in step (a) and may also addition of one or more reagents such as those containing Mg and/or Al to achieve a suitable Mg: Al ratio for promoting formation of the LDH *insitu*.

[0041] In some embodiments, at least one of the dissolved anions in the water from a stream such as process stream may comprise a complex anion such that at least one of the complex anions is intercalated into an interlayer of the LDH formed *in situ* and wherein one or more dissolved cations are incorporated into the LDH material's crystal structure or matrix. Preferably, the process may further comprise the steps of controlling pH levels in the water thereby controlling speciation of the complex anion.

[0042] It is recognised that cations such as metal cations may be incorporated into the metal oxide layers of the LDH that forms the crystal structure or matrix. The applicant has also recognised that some metallic constituents, particularly metals such as uranium (or vanadium or chromium in further embodiments) usually exist as large sized oxy-cations such as UO_2^{2+} that cannot be accommodated into the crystal structure or matrix. The applicant has discovered that by tailoring or controlling reaction conditions such as pH conditions and/or addition of reaction agents etc., such large size oxy-cations such as UO_2^{2+} maybe utilised for preferentially forming one or more complex anion species such as any of $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{UO}_2^{2+}\text{-SO}_4$. For example, at lower pH that $\text{UO}_2^{2+}\text{-SO}_4$ complexes (e.g. $\text{UO}_2(\text{SO}_4)_3^{4-}$) may predominate while at intermediate to higher pH $\text{UO}_2^{2+}\text{-CO}_3^{2-}$ anionic complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) may predominate. Given this speciation of the uranyl ion (UO_2^{2+}) as anionic complexes, these anionic complexes preferentially partition into the anionic interlayers of the LDH material. Therefore, if the aqueous solution comprises a mixture of metals such as Cu, Mn, Ni, Pb, Zn and rare earth elements (REE; 15 metallic elements with atomic numbers ranging from 57 to 71; The REE are often described as part of the

Lanthanide series and, for convenience, from time to time be represented as Ln^{3+}) and uranium, the process of the present invention would separate the uranium from the remaining metals, metalloids and rare earth elements by preferentially forming uranyl complex anionic complexes which would be intercalated into the interlayer of the LDH whereas at least some of the metals and rare earth elements would be incorporated into the crystal structure of the LDH. For example, REE as predominantly Ln^{3+} cations (Ce as +3 and +4 and Eu and +2 and +3 oxidation states) are strongly partitioned into the primary metal hydroxide layer of LDH materials substituting for other +3 cations such as Al and Fe. As a result of the process of the present invention, REE are for example contained within the metal hydroxide layers of the LDH and valuable uranium is contained as anionic complexes within the LDH interlayers.

[0043] The present embodiment also results in the formation of an LDH material that typically may contain in excess of 30% U and 0-50% REE. Such resulting quantities of uranium and rare earth metals is typically 100-300 times higher than typical ore grades of these elements thus allowing substantial enrichment of the commodities of value. Another significant benefit afforded by the present invention is that the process results in effective separation of potentially problematic ions such as Na, Cl and SO_4 or other additives or components from the mineral processing or aqueous stream, thus potentially facilitating simpler processing, further enrichment, recovery or purification). Yet another advantage of at least some embodiments of the present invention is the production of a cleaner effluent that may potentially be reused in mineral processing or other site applications or other operations without (or minimal) additional treatment.

[0044] The present invention in at least some embodiments therefore also provides a method or a process of treating process waters for recovering the selectively separated constituents of the water provided in the form of an aqueous solution wherein the different constituents have been taken up by the LDH by differing uptake mechanisms (for example uranium in the interlayer of the LDH, whereas REE in the crystal structure or metallic oxide layers of the LDH) by subjecting the LDH from step (b) to a further recovery treatment step. The various recovery treatment steps that may be utilised have been detailed in the foregoing passages of the present specification.

[0045] In some embodiments, the process comprises the recovery of the LDH from the aqueous stream before subjecting the separated LDH from step (b) to a recovery treatment step. Such recovery of the LDH may be carried out by recovery means such as sedimentation, flocculation or filtration.

[0046] In an embodiment, the process further comprises the step of controlling the pH levels of the aqueous solution thereby controlling speciation of the complex anion. The applicants have discovered that by tailoring the pH conditions speciation of the anionic complexes may be suitably tailored or controlled. For example, at lower pH that $\text{UO}_2^{2+}\text{-SO}_4$ complexes (e.g. $\text{UO}_2(\text{SO}_4)_3^{4-}$) may be preferentially formed whereas under intermediate to higher pH conditions $\text{UO}_2^{2+}\text{-CO}_3^{2-}$ anionic complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) may predominately formed.

[0047] The separated LDH may be treated to recover the constituents therefrom. In some further embodiments, the recovery treatment step may be carried by introducing the separated LDH to an ion-exchanging solution to cause ion-exchange to occur whereby the complex anion of the metallic constituent in the interlayer of the LDH is ion-exchanged with an anion in the ion-exchanging solution. In this manner the complex anion of the metallic solution goes into solution by carrying out the ion exchanging step. It will be appreciated that this ion-exchanging step involves the ion-exchange solution having at least one substituent anion such that the substituent ion displaces at least some of the intercalated anion or complex anion by an ion exchange mechanism thereby resulting in the anion or complex anion being released from the LDH interlayer into the ion-exchange solution. Whilst, the intercalated anion or complex anion of the metallic constituent is released from the interlayer of the LDH, the other metals (such as the REE/metals) that are present in the crystal structure or matrix of the LDH remain incorporated in the crystal structure or matrix of the LDH material.

[0048] The applicant has discovered that recovering the LDH from step (b) and then conducting an ion exchange process is particularly beneficial when the initial aqueous solution in step (a) comprises leaching solutions having high salt concentrations (such as those used in leaching processes for recovering uranium) because achieving optimal ion exchanging efficiencies in such leaching solutions such as mining waste solutions was found to be difficult. Adopting the process described in some embodiments that involves the step of separating the LDH from step (b) and as described above results in higher ion exchanging efficiencies thereby resulting in better separation of the intercalated metallic constituent from the LDH.

[0049] In a further embodiment, the ion exchanging step also comprises controlling pH conditions to promote displacement of the anion or complex anion from the interlayer and/or to promote speciation of a preferred type of anion or complex anion over other anions or complex anions. For example, a strong alkali may be added to displace $\text{UO}_2^{2+}\text{-SO}_4$ or $\text{UO}_2^{2+}\text{-CO}_3$ complexes by OH anions by increasing the pH. It would be appreciated that such a recovery treatment step involves the recovery of the uranium (in the form of the uranyl complex anion)

back into aqueous solution even though the REE remain incorporated in the LDH crystal structure. Alternatively, addition of a strong acid thereby reducing the pH such that charged or neutral UO_2^{2+} complexes are displaced from the interlayers of the LDH is also possible. In this, sustained acid addition may also sufficiently decompose the LDH crystal structure to liberate the REE or other metals or elements.

[0050] In some embodiments, the substituent agent may comprise one or more of the following nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) or a range of other complexing agents such as crown ethers or other organic or (complex) inorganic ligands and/or wherein the substituent agent is substantially more electronegative relative to the intercalated complex anion in the LDH material thereby resulting in the substituent agent such as EDTA and/or NTA displacing the complex anion from the interlayer.

[0051] In a further embodiment, the recovery step further comprises separating the LDH material after the ion exchanging step is completed. It may be appreciated that separating the LDH material after the ion-exchanging step is complete results in obtaining a separated LDH material which comprises the incorporated metallic cations or REE present in the crystal structure of the separated LDH material. The incorporated metallic cations or REE from the separated LDH may be recovered by methods such as heat treatment or thermal decomposition of the separated LDH material thereby resulting in the formation of a collapsed or metastable material.

[0052] In a further embodiment, the process may include the addition of a further additive (such as silica) to the LDH material prior to or during the heat treatment or thermal decomposition. Preferably, the process may involve controlling the ratio of the further additive to the LDH material for selectively controlling formation of oxide materials upon the heat treatment or thermal decomposition.

[0053] Additives such as silica may also be added to the LDH prior to or during the heat treatment or thermal decomposition step in a range of forms including crystalline silica (e.g. quartz), amorphous or chemically-precipitated silica, silicic acid, organic forms including tetra-ethylsilica(TEOS) or silica added to the LDH interlayers.

[0054] It is important to appreciate that in addition to recovering the LDH material, the undissolved silicate material from step (a) may also be recovered with the LDH and may be utilised. Controlling the ratio of the silica to the LDH and/or controlling the temperature of heat treatment may result in a series of reactions between the added forms of silica and the LDH

resulting in the formation of a range of materials like minerals such as (or in addition to spinel and periclase) pyroxenes such as enstatite, olivines including forsterite and other minerals including silica transformed into high temperature forms including cristobalite.

[0055] It will be appreciated that by varying the amount of silica or other elements in one or more forms relative to the LDH (by controlling the ratio of the silica to the LDH material) that different proportions or suites of minerals may form as a result of the heat treatment step. This process of including an additive as described above is particularly advantageous for two reasons. The first advantage is that secondary mineral oxides such as metallic silicates or pyroxenes may be formed that may constitute a suitable long-term repository for a range of contaminants including radionuclides. The second advantage is that given selected elements may be partitioned into materials formed as a result of the heat treatment, the materials formed (as determined by the composition of the LDH and the type and proportion of the additive) this may assist in the selective recovery of particular elements contained within selected minerals. Silica may be replaced by other additives in further embodiments and the embodiment described above is in no way limited by the addition of silica.

[0056] Therefore, the addition of the silicate materials in step (a) of the present invention may also assist in recovery of one or more dissolved species (cationic or anionic) from the LDH material.

[0057] In some alternative embodiments, the separated LDH may be subjected to a dissolution step wherein the separated LDH is dissolved in a dissolving solvent such as an acid that results in the release of the intercalated complex anion and the metal cations from the crystal structure of the separated LDH into the dissolving solvent. Capturing the metallic species from the initial aqueous solution containing low concentrations of metallic species in the LDH material in accordance with step (b), separating the LDH material and then redissolving the separated LDH in a dissolving solvent results in obtaining a solvent with relatively higher concentration levels of the metallic species (in comparison with the low concentration levels of the initial aqueous solution). It would be appreciated that recovery of metallic species from a solution containing relatively higher concentration levels of the metallic species is more desirable and cost-effective and therefore offers the skilled person an opportunity to use conventional metallurgical recovery methods which would otherwise be ineffective for capturing trace amounts of metallic species as present in at least some embodiments of the aqueous solution utilised in step (a) of the present invention. Therefore, this embodiment presents a significant commercial advantage by offering a viable method or process for recovering metallic species from aqueous solutions having low concentration of the metallic species.

[0058] In an alternative embodiment of the process, ion exchange of the intercalated complex anion may not be carried out. Instead, the LDH comprising the intercalated complex anion and the incorporated one or more metals and other materials obtained from step (b) may be separated and subsequently subjected to a heat treatment process as described above. Such a heat treatment process initially results in the collapsing of the LDH material resulting in the loss of the layered structural characteristics of the LDH material and subsequently results in recrystallisation of the LDH material. Specifically, the recrystallisation of the heat treated and collapsed LDH results in formation of a first oxide material comprising the metallic constituent and a second oxide material comprising one or more of the other metals. For example, the present applicants have surprisingly discovered that calcination of LDH comprising intercalated uranyl complex cations and rare earth metals incorporated in the crystal structure produce a first crystalline oxide material in the form of periclase that incorporates a proportion of uranium and a second crystalline oxide material in the form of a spinel oxide that incorporates other commodities such as the REE.

[0059] In further embodiments, the heat treatment may be carried out under substantially reducing conditions for reducing the intercalated complex anion present within the interlayers of the LDH material obtained in step (b). For example, during heat treatment of LDH comprising intercalated uranyl complex anions, the heat treatment may be carried out under anoxic conditions (e.g. N₂) or reducing (e.g. CO or C) conditions to form reduced U mineralogy, for example to produce uraninite (UO₂). In some alternative embodiments, other agents may be added to form UF₆ as a gas phase to assist in separation and recovery of U or specific U isotopes.

[0060] In some further embodiments, the process may comprise optimisation of the crystal structure or matrix of the LDH material for selectively incorporating one or more of the other metals into the crystal structure or matrix of the LDH. For example, the optimisation may be carried out by introducing additives to the aqueous solution such as carbonates in an alkaline liquor for tuning uptake of selected or specific rare earth elements in the crystal structure or matrix of the LDH. Without being bound by theory, it is theorised that amount/speciation of bicarbonate/carbonate in the aqueous solution may potentially endow the LDH material (such as hydrotalcite) with some selectivity given the increasing affinity of mid to heavy REE for carbonates or bicarbonates.

[0061] In an embodiment, the pre-determined metallic constituent comprises uranium or vanadium and wherein the one or more of the other metals comprises REE. As described earlier, the complex anion [anion] may comprise a uranyl complex anion such as but not limited to: UO₂(CO₃)₂²⁻, UO₂(CO₃)₃⁴⁻, CaUO₂(CO₃)₃²⁻, UO₂(SO₄)₃⁴⁻, VO₂(OH)²⁻, VO₃OH²⁻, V₁₀O₂₈⁶⁻,

$\text{Cr}_2\text{O}_7^{2-}$. In at least some embodiments the pH of the solution determines speciation of the uranyl complex anion.

[0062] In one embodiment the intercalated uranyl complex may be displaced from the interlayer of the LDH by the ion exchanging step described in the earlier section by the addition of a substituent agent such as EDTA, NTA, crown ethers, etc.

[0063] In alternative embodiments, the LDH material may be subjected to the heat treatment step in accordance such that the heat treatment results in the thermal decomposition of the LDH material to recrystallise as a first crystalline oxide and a second crystalline oxide such that the uranium is incorporated in the first metal oxide and one or more of the REE is incorporated in the second crystalline oxide. Preferably the heat treatment may be carried out under substantially reducing conditions for reducing the uranyl ion from a +6 to +4 oxidation state or a mixture thereof.

[0064] In at least some embodiment, the process comprises the step of contacting the separated LDH material with an aqueous solution for dissolving at least a part of the LDH material into the solution thereby obtaining dissolved LDH in the solution followed by controlling the reaction conditions in the aqueous solution for in situ precipitation of LDH material from the dissolved LDH material such that the complex anion is intercalated within interlayers of the LDH material formed in situ and wherein one or more of the other cations are incorporated into the crystal structure or matrix of the LDH material formed in situ. Preferably, the step of dissolving the LDH in the aqueous solution comprises controlling the pH of the aqueous solution preferably at pH levels of less than 7 and more preferably less than 5 and even more preferably less than 3. The in situ precipitation of the LDH from the dissolved LDH constituents may be carried out by controlling the reaction conditions in the aqueous solution comprises controlling the pH of the aqueous solution preferably at pH levels of greater than 8.

[0065] Any of the features described herein can be combined in any combination with any one or more of the other features described herein within the scope of the invention.

[0066] The reference to any prior art in this specification is not, and should not be taken as an acknowledgement or any form of suggestion that the prior art forms part of the common general knowledge.

BRIEF DESCRIPTION OF FIGURES

[0067] Figure 1 depicts Molar ratios of Al/Si and Mg/Al produced by 1 M HCl and 1 M NaOH after stirring (1-4 hours) and ultrasonication + stirring (1 hour) of filtered clay and zeolite solutions in accordance with an embodiment of the present disclosure. Red lines mark Al/Si molar ratio of 0.5 and Mg/Al molar ratio of 3 (see text).

[0068] Figure 2 depicts X-ray diffraction (XRD) spectrum of sepiolite/white clinoptilolite-hydrotalcite nanohybrid. Note peaks corresponding to sepiolite and clinoptilolite precursors and characteristic hydrotalcite (pale blue) /Mg-Al hydroxide (pink) peaks at ~13 and 26 degrees, Theta.

[0069] Figure 3 depicts phosphorus uptake capacity of a range of clay/zeolite nano-hybrid materials synthesised in this study.

[0070] Figure 4 is schematic flowchart of a process for separating one or more metallic commodities in an aqueous solution by adopting a process in accordance with a preferred embodiment of the present invention.

[0071] Figure 5 represents a speciation diagram for the system U-H₂O-SO₄-CO₃ from pH 2-10 in equilibrium with the atmosphere.

DESCRIPTION OF EMBODIMENTS

[0072] The passages below describe one or more embodiments in the form of examples in accordance with the present invention.

[0073] Raw materials, primarily Mg-Al or Al-bearing aluminosilicate clays (such as vermiculite, attapulgite, sepiolite, talc kaolinite) and zeolites (white and pink clinoptilolite), were procured from industrial and commercial sources. These clays and zeolites were used as sources of raw materials, principally Al and Mg, during acid and alkali dissolution experiments enhanced by the use of ultrasonication.

[0074] Initial batch decomposition reactions of the aluminosilicates in both acid and alkali and with the additional use of agitation including ultrasonication were completed. Results of ICP analyses to quantify the extent of dissolution due to acid or alkali in combination with stirring (1-4 hours) or ultrasonication + stirring (1 hour) are presented in Table 1 and Figure 1. These results indicate that substantial Mg and Al release (preferably >3:1 Mg/Al molar ratio) as required for hydrotalcite synthesis can be achieved from clays or zeolites during acid extraction.

In addition, some clays such as sepiolite (Table 1) yielded both high concentrations of Mg and Al and high Mg/Al molar ratios. Under acidic conditions, all clays and zeolites demonstrated incongruent dissolution with Mg/Al and Al/Si ratios higher in the solute than the solid. In contrast, under alkali conditions any incongruent dissolution was obscured by secondary precipitation reactions.

[0075] Table 1. Geochemistry of filtered solutions produced by 1 M HCl or 1 M NaOH digestion after stirring (1-4 hours) and ultrasonication + stirring (1 hour) of clay and zeolite suspensions.

Clay/zeolite	Al	Si	Mg	Ca	Fe	K	Na	Mg mM	Al mM	Si mM	Mg/Al	Al/Si
Attapulgite sonicated 1 hr in 1M HCl	88	172	183	206	52	61	143	8	3	6	2.3	0.5
Attapulgite sonicated 1 hr in 1M NaOH	31	176	0	3	0	34	24202	0	1	6	0.0	0.2
Attapulgite stirred 1 hr in 1M HCl	27	25	113	172	10	28	384	5	1	1	4.6	1.1
Attapulgite stirred 1 hr in 1M NaOH	7	70	0	6	0	31	22591	0	0	3	0.0	0.1
Attapulgite stirred 2 hr in 1M HCl	29	34	117	173	12	28	82	5	1	1	4.5	0.9
Attapulgite stirred 2 hr in 1M NaOH	8	81	0	6	0	32	22620	0	0	3	0.0	0.1
Attapulgite stirred 4 hr in 1M HCl	38	63	125	170	17	31	90	5	1	2	3.6	0.6
Attapulgite stirred 4 hr in 1M NaOH	10	103	0	5	0	32	21519	0	0	4	0.0	0.1
Clinoptilolite (pink) sonicated 1 hr in 1M HCl	192	74	35	139	32	17	114	1	7	3	0.2	2.7
Clinoptilolite (pink) sonicated 1 hr in 1M NaOH	54	158	0	2	1	13	25419	0	2	6	0.0	0.4
Clinoptilolite (pink) stirred 1 hr in 1M HCl	85	16	18	90	11	9	49	1	3	1	0.2	5.4
Clinoptilolite (pink) stirred 1 hr in 1M NaOH	10	32	0	19	0	7	23071	0	0	1	0.0	0.3
Clinoptilolite (pink) stirred 2 hr in 1M HCl	85	18	17	89	11	8	51	1	3	1	0.2	4.9
Clinoptilolite (pink) stirred 2 hr in 1M NaOH	10	35	0	17	0	17	23211	0	0	1	0.0	0.3
Clinoptilolite (pink) stirred 4 hr in 1M HCl	107	28	21	99	14	9	63	1	4	1	0.2	4.0
Clinoptilolite (pink) stirred 4 hr in 1M NaOH	13	41	0	11	0	10	22719	0	0	1	0.0	0.3
Clinoptilolite (white) sonicated 1 hr in 1M HCl	347	67	45	146	13	198	76	2	13	2	0.1	5.4
Clinoptilolite (white) sonicated 1 hr in 1M NaOH	160	777	0	1	0	160	24486	0	6	28	0.0	0.2
Clinoptilolite (white) stirred 1 hr in 1M HCl	151	18	21	75	4	157	49	1	6	1	0.2	9.0
Clinoptilolite (white) stirred 1 hr in 1M NaOH	13	98	0	3	0	120	22080	0	0	3	0.0	0.1
Clinoptilolite (white) stirred 2 hr in 1M HCl	152	20	22	78	4	162	49	1	6	1	0.2	7.9
Clinoptilolite (white) stirred 2 hr in 1M NaOH	22	130	0	2	0	119	22496	0	1	5	0.0	0.2
Clinoptilolite (white) stirred 4 hr in 1M HCl	178	28	24	85	5	163	49	1	7	1	0.2	6.5
Clinoptilolite (white) stirred 4 hr in 1M NaOH	31	182	0	2	0	120	23054	0	1	6	0.0	0.2
Sepiolite sonicated 1 hr in 1M HCl	18	75	326	22	6	7	5	13	1	3	19.8	0.3
Sepiolite stirred 1 h in 1M HCl	20	105	357	22	7	10	5	15	1	4	19.9	0.2
Sepiolite stirred 2 h in 1M HCl	23	125	374	22	16	13	4	15	1	4	18.4	0.2
Sepiolite stirred 4 h in 1M HCl	76	403	1312	26	50	19	8	54	3	14	19.1	0.2
Talc sonicated 1 hr in 1M HCl	10	53	71	11	4	6	57	3	0	2	8.1	0.2
Talc stirred 1 h in 1M HCl	1	5	16	9	1	3	7	1	0	0	17.3	0.2
Talc stirred 2 h in 1M HCl	1	8	18	9	1	3	6	1	0	0	16.9	0.2
Talc stirred 4 h in 1M HCl	4	30	40	9	2	2	7	2	0	1	11.4	0.1
Vermiculite sonicated 1 hr in 1M HCl	538	784	1605	19	57	532	28	66	20	28	3.3	0.7
Vermiculite sonicated 1 hr in 1M NaOH	2	15	0	1	1	59	25733	0	0	1	0.1	0.1
Vermiculite stirred 1 hr in 1M HCl	28	13	71	47	30	139	7	3	1	0	2.9	2.1
Vermiculite stirred 1 hr in 1M NaOH	1	3	1	3	1	37	22442	0	0	0	1.3	0.3
Vermiculite stirred 2 hr in 1M HCl	84	85	234	48	90	170	10	10	3	3	3.1	1.0
Vermiculite stirred 2 hr in 1M NaOH	1	3	0	3	0	46	22636	0	0	0	0.1	0.2
Vermiculite stirred 4 hr in 1M HCl	127	169	359	49	13	193	6	15	5	6	3.1	0.8
Vermiculite stirred 4 hr in 1M NaOH	0	4	0	4	0	55	22335	0	0	0	1.1	0.1

[0076] Importantly, the dissolution of Mg and Al is substantially enhanced using the combination of ultrasonication + stirring relative to stirring alone. During an acid digest, substantial Si and other elements such as Fe and Ca may also be released depending on the chemistry and purity of the clay or zeolite. This is undesirable as excess silica can potentially occupy the interlayer anion exchange site within the LDH or HT during formation or may combine with Al to form other compounds during LDH or HT synthesis. In particular, it is

desirable that the Al/Si molar ratio is <0.5 as depicted in Figure 1. In addition, abundant Fe may result in substitution for one or both of Mg and Al in the LDH or HT structure. If Fe is present in sufficient quantities this may lead to the formation of unstable green rusts.

[0077] Alkali dissolution using either stirring or ultrasonication + stirring, as expected, yielded a substantially different solution composition with enhanced dissolution of Si over that of Al, while Mg was low as it is likely to have precipitated as brucite - $\text{Mg}(\text{OH})_2$. Whilst excess silica is generally undesirable in the formation of LDH or HT as described above, potential exists to use the remnant clay or zeolite after dissolution as substrates for LDH or HT nucleation.

[0078] In cases where high Si is present, this may occupy at least part of the anionic interlayers of the LDH or HT structure. This property may be exploited if calcination is required to form other high temperature phases as described elsewhere.

[0079] Further clay dissolution experiments were undertaken with H_2SO_4 in place of HCl to investigate the effects, if any, of using a different acid. These results are presented in Table 2 and illustrate that relatively less dissolved Si is produced in the presence of H_2SO_4 yielding lower Al/Si ratios. As outlined above, this is considered important in the synthesis of LDH or HT from solutions produced by clay or zeolite dissolution. In addition, Mg/Al ratios generally increased using H_2SO_4 in place of HCl.

[0080] Table 2. Ratios of concentrations of Al, Si and Mg and Mg/Al and Al/Si in solutions produced by 1 M H_2SO_4 and 1 M HCl digestion using ultrasonication + stirring (1 hour) of clay and zeolite suspensions.

Clay/ zeolite	Al ($\text{H}_2\text{SO}_4/\text{HCl}$)	Si ($\text{H}_2\text{SO}_4/\text{HCl}$)	Mg ($\text{H}_2\text{SO}_4/\text{HCl}$)	Mg/Al ($\text{H}_2\text{SO}_4/\text{HCl}$)	Al/Si ($\text{H}_2\text{SO}_4/\text{HCl}$)
Vermiculite sonicated 1 hr in 1M HCl or H_2SO_4	0.7	0.5	0.7	1.0	1.4
Sepiolite sonicated 1 hr in 1M HCl or H_2SO_4	2.7	0.7	3.1	1.2	3.8
Attapulgite sonicated 1 hr in 1M HCl or H_2SO_4	0.6	0.6	0.8	1.3	1.0
Keolinite sonicated 1 hr in 1M HCl or H_2SO_4	1.5	1.4	5.0	3.3	1.1
Pink clinopt sonicated 1 hr in 1M HCl or H_2SO_4	0.4	0.2	0.4	1.1	1.9
White clinop sonicated 1 hr in 1M HCl or H_2SO_4	0.7	0.6	0.7	1.0	1.1

[0081] On the basis of the above dissolution experiments and supplementary experiments using H_2SO_4 in place of HCl, synthesis of the nano-hybrid materials was undertaken using a range of clay and zeolite. In addition, aluminate was also used as both a source of additional Al and as a neutralising agent. A list of the nano-hybrid material produced and their P-uptake capacity is given in Table 3.

[0082] Table 3. Phosphorus uptake capacity of a range of clay/zeolite nano-hybrid materials synthesised in this study.

Clay/zeolite	P-uptake mg/g
Unground vermiculite+white clinoptilolite ALL SOLIDS	4.6
Unground Vermiculite + aluminate ALL SOLIDS	5.4
Sepiolite + aluminate ALL SOLIDS	9.0
Unground vermiculite/white clinoptilolite NO SOLIDS	11.7
Sepiolite/white clinoptilolite ALL SOLIDS	13.2
Sepiolite+white clinoptilolite ALL SOLIDS	13.5
Vermiculite+white clinoptilolite ALL SOLIDS	13.7
Vermiculite + aluminate ALL SOLIDS	14.1
Unground vermiculite/white clinoptilolite ALL SOLIDS	14.3
Vermiculite/white clinoptilolite ALL SOLIDS	14.5
Unground vermiculite + aluminate NO SOLIDS	15.4
Vermiculite/white clinoptilolite NO SOLIDS	17.5
Vermiculite + aluminate NO SOLIDS	19.8
Sepiolite/white clinoptilolite NO SOLIDS	28.4
Sepiolite + aluminate NO SOLIDS	41.7

[0083] Mixing ratios of solutions both with and without residual clay or zeolite solids present were determined using the equation:

$$v_1/v_2 = (r [Mg]_2 - [Al]_2) / ([Al]_1 - r [Mg]_1)$$

where v_1 and v_2 are the volume ratio of the two clay or zeolite solutions required to give r which is the required Mg;Al ratio in the final solution (in this case 3), and $[Mg]_1$, $[Mg]_2$ and $[Al]_1$ and $[Al]_2$ are the concentrations of Mg and Al in solutions 1 and 2, respectively. Where aluminate was added, target Mg/Al molar ratios of 3 were calculated.

[0084] Mineralogical (XRD) analysis of the nano-hybrid materials indicated the presence of hydrotalcite in addition to the residual clay or zeolite mineral which acted as a scaffold for hydrotalcite nucleation and precipitation is depicted in Figure 2.

[0085] The significance of the examples presented here is that a new class of material has been synthesised using a novel preparation method utilising elements contained within commercial clays to produce nano-hybrids which contain LDH in the form of hydrotalcites grafted onto the original clay or zeolite substrate. The beneficiation process adds significant utility and value to commercially-mined clays and zeolites as demonstrated by the high P-uptake (as phosphate) achieved. The high P-uptake demonstrates that other simple or complex anions, for instance uranyl-carbonate complexes, may also be removed from solution using these materials.

[0086] Referring to the flow diagram illustrated in Figure 4, an ore body containing a plurality of metallic constituents such as uranium and REE may be introduced to an aqueous leaching solution to obtain a pregnant leaching solution or aqueous stream. Some of the metallic constituents such as uranium may form complex anions in the solution, such as uranyl anionic complexes, as described in previous sections. Some of the other metallic constituents particularly constituents such as the REE may typically form cations in the aqueous solutions. The liquid phase of the pregnant leach solution containing the dissolved anions and cations may be separated from the undissolved solids and directed to a reaction step. The reaction step may comprise steps such as pH control which determine the speciation of the uranyl complexes as illustrated in Figure 5. The reaction step may form complex anions containing the metallic constituent (eg. uranium). The reaction step may be followed by an LDH formation step or alternatively an LDH addition step or LDH addition and cycling of the pH to induce partial dissolution and then reformation of the LDH.

[0087] In the LDH formation step, additives such as divalent additives such as MgO may be added in combination with trivalent additives such as soluble alumina salts in specific ratios and under suitable pH (alkaline pH) to promote the in-situ formation of LDH material in the solution. Such an LDH formation step also results in intercalation of the complex anion (such as the uranyl complex anion) interlayers of the LDH material formed in-situ. The metallic cations are also incorporated into the metal oxide layers of the LDH material formed in situ thereby forming a part of the crystal structure or matrix of the LDH. Such separation of the metallic species is based upon the differing uptake mechanisms for different ions provided by the LDH material formed in situ.

[0088] As described earlier, the LDH formation step may be substituted or complemented by an LDH addition step in which pre-formed LDH material may be added to the solution containing the complex anions (uranyl complex anion) and the metallic cations. The step of adding pre-formed LDH material also results in intercalation of the complex anion (such as the uranyl complex anion) interlayers of the LDH material. This step may also include pH control so that part of the LDH may be initially dissolved at a pH of less than 9 and as low as pH 1, for specified time intervals as required to yield a sufficient degree of LDH dissolution, followed by an increase in the pH to promote reformation of the LDH material in situ. During this reformation step, other cations such as REE cations may be incorporated into the metal hydroxide layer substituting for the original cations in the initially added LDH. During this process, some anions, in particular those comprised of uranyl anionic complexes may also be substituted into the interlayer of the LDH material. Note that other techniques may also be used

in the dissolution or reformation steps including (ultra)sonication or the addition of other solvents or reagents as required.

[0089] The LDH material containing the intercalated complex anion and obtained from the LDH formation step or the LDH addition step may be separated by processes such as sedimentation, flocculation, filtration, cyclonic separation or other known separation methods. The separated LDH material may then be subjected to a further process for recovering the intercalated complex anion (the uranyl complex anion) such as an ion exchange process in accordance with the steps described in the preceding sections of the specification. Alternative methods of recovering the intercalated metallic constituent may also be employed in accordance with the process step detailed in the preceding sections. As discussed earlier, the recovery treatment step may not be limited to recovery of the intercalated metallic constituent such as the uranyl complex anion but may further include recovery of the metallic cations such as REE incorporated in the LDH matrix in the LDH formation step.

[0090] The presently described invention utilises the differing uptake mechanisms for different metallic ionic species as a way of separating the metallic species. In the present invention, desirable separation and recovery is achieved by intercalating at least one metallic constituent in the interlayer (such as the uranyl complex anion) of the LDH (formed in-situ or added to the solution) and subsequently recovering the metallic constituent from the LDH by a further recovery step.

EXAMPLES

Example 1

[0091] In a first exemplary embodiment (example 1) the process may be utilised for the processing of uranium-bearing ores. It is common in uranium bearing ores that a range of other elements are present in addition to uranium. The other elements may include elements such as As, Se, Cu and the rare earth elements (REE – Ln^{3+} comprising La-Lu + Sc + Y). Extensive work undertaken by the applicant has demonstrated that the REE predominantly exist as Ln^{3+} cations in a +3 oxidation state. Cerium exists in +3 and +4 oxidation states. Europium exists in +2 and +3 oxidation states. In the exemplary process, a uranium bearing solution derived from leaching of a uranium ore was contacted with LDH material.

[0092] There are two different ways in which intercalation of the uranyl complex anion may be achieved. In a first possible way, the uranyl complex anion would readily intercalate into the interlayer of the LDH material added to the solution. However, utilising such a method does not

result in uptake of the REE into the matrix or crystal structure of the LDH material added to the uranium.

[0093] In a more preferred way, the LDH material added to the uranium bearing solution was dissolved in the uranium bearing solution by reducing the pH of the solution to less than 3. Reducing the pH level resulted in dissolution of the LDH material thereby resulting in the release of divalent and trivalent cations (that form the metal oxide layers of the LDH material) into the solution. After dissolving the LDH material, the pH was increased to provide alkaline reaction conditions in the solution. Providing such alkaline conditions resulted in reformation of the LDH material as a result of precipitation of the LDH material in the solution. During the reformation of the LDH material the divalent and trivalent cations that were dissolved into the solution (as a result of the initial dissolving step) precipitated to form the metal oxide layer of the reformed LDH material. During the reformation step at least some of the REE cations were also incorporated into the crystal structure of the reformed LDH material. Anionic uranyl complexes were also intercalated into the interlayer of the reformed LDH material. Importantly it has been recognised that as the divalent to trivalent ratio of metals in the primary metal hydroxide layer of the LDH may typically vary between 2:1 and 4:1, changes in this ratio may occur in the reformed LDH due to incorporation of other cations from solution that still allow a stable LDH to form.

[0094] During the course of the process, the REE were shown to be strongly partitioned into the primary metal hydroxide layer of the reformed LDH material substituting for other +3 cations such as Al and Fe that were present in the initially added LDH material. Unlike the REE cations, the uranyl ion (uranium is known to exist as a UO_2^{2+} oxy-cation in solution) is considered too large to substitute for the +2 cations such as Mg $2+$ Alkaline earth and transition metals generally present in the metal hydroxide layers of LDH material. As shown in Figure 2, under low pH conditions, anionic uranyl complexes are formed especially UO_2^{2+} - SO_4 complexes (e.g. $\text{UO}_2(\text{SO}_4)_3^{4-}$). Under intermediate to higher pH UO_2^{2+} - CO_3^{2-} anionic complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) may predominate. Given this speciation of the UO_2^{2+} as anionic complexes, these uranyl anionic complexes preferentially partition into the anionic interlayers of LDH. As a result, the process of example 1 provides the following advantages:

- Valuable REE are contained within the metal hydroxide layers of the LDH
- Valuable U is contained as anionic complexes within the LDH interlayers. Separation of these two valuable commodities U and REE, not only from each other in terms of the way they are bound in the initial solution, but also from other components including

some contaminants, salts or ions etc that may otherwise interfere in the U or REE recovery process is highly beneficial for later separation, recovery and purification.

- A solid LDH is produced that typically may contain in excess of 30% U and 0-50% REE, typically 100-300 times typical ore grades of these elements thus allowing substantial enrichment of the commodities of value.
- Effective separation of potentially problematic ions such as Na, Cl and SO₄ or other additives from the mineral processing stream (with the potential to make for simpler processing, further enrichment or recovery).
- Production of a cleaner effluent that may potentially be reused in mineral processing or other site or other operations without (or minimal) additional treatment.

[0095] In addition to the above, given the different partitioning or separation of U from REE, several methods may be utilised for recovering a commodity of interest based upon the separation of commodities achieved, as elucidated above. Recovery of one or more commodities may be carried out effectively by one or more of the following further steps:

- the addition of a strong alkali to displace UO_2^{2+} -SO₄ complexes by OH anions, or reducing the pH such that less charged or neutral UO_2 complexes are displaced from the LDH interlayers.
- other complexing ligands or other anions (e.g. NTA, EDTA) may be added to the LDH to displace the UO_2 -complexes and form new NTA, EDTA complexes.
- addition of other chemical reagents such as phosphates, vanadates or inorganic or organic peroxides, or combinations thereof, to induce uranium precipitation.
- partial or complete dissolution of a U-, REE-metal-containing LDH by the addition of acid and recovery of the constituents by conventional means.
- addition of reducing agents, anoxia or gases (e.g. CO) to reduce uranyl complexes (U +6 oxidation state) to U (+4 oxidation state) for example as UO_2 to eliminate the uranyl complexation with carbonate on the basis of charge and allow recovery of U in the +4 oxidation state. Such recovery methods may include physical (e.g. ultrasonication) or otherwise chemical (solvent-based) delamination of the LDH to recover the reduced U or the application of other physicochemical methods as required.
- other methods of separation that may include calcination such that with heating, typically in the range 100-1200 C, there will be layer collapse and re-crystallisation of the LDH leading to the formation of discrete or intimately associated mineral phases such as spinel and periclase. These phases, by virtue of their chemistry and crystal structure, may accommodate one or more elements of interest or may provide enhanced opportunities

for recovery of particular elements given the different physicochemical properties of the mineral phases formed from calcination.

[0096] The methods of stabilisation described here may also find applications in the nuclear energy or weapons industries to assist in the containment of Uranium bearing materials or wastes including transuranics or daughter radionuclides.

Example 2

[0097] In a second exemplary embodiment (example 2) the process of the present invention may be utilised for the processing of uranium-bearing ores, in which LDH can be formed in situ within a mineral processing or metallurgical stream that includes the uranium bearing ores. The uranium ore containing stream was dosed, typically with one of or both of Mg and Al containing compounds, to achieve a desired ratio of Mg/Al in the stream which results in precipitation of LDH such as hydrotalcites. As explained in example 1, uranium bearing ores include a range of other elements that are present in addition to uranium which includes heavy metals, metalloids and/or REE. Forming the LDH material in situ also results in incorporation of the cations such as Ln^{3+} cations and/or Ce $3+$ and Ce $4+$ and/or Eu $2+$ or Eu $3+$ oxidation states. In situ formation of the LDH also results in REE cations being shown to be strongly partitioned into the primary metal hydroxide layer of LDH. As discussed earlier, since uranium exists as an oxy-cation commonly known as a uranyl (UO_2^{2+}) cation, the uranyl ion is too large to be substituted for $+2$ cations such as Mg $2+$ into the LDH. Alkaline earth and transition metals generally present in the metal hydroxide layers of the LDH. Once again, under low pH conditions, anionic uranyl complexes are formed, especially $\text{UO}_2^{2+}\text{SO}_4$ complexes (e.g. $\text{UO}_2(\text{SO}_4)_3^{4-}$). Under intermediate to higher pH $\text{UO}_2^{2+}\text{CO}_3^{2-}$ anionic complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) may predominate. Given this speciation of the UO_2^{2+} as anionic complexes, these uranyl anionic complexes preferentially partition into the anionic interlayers of LDH formed in situ. The process described in example 2 also provides one or more of the several advantages of the process of Example 1 as summarised above. The commodities of interest may also be recovered by one or more of the further recovery steps listed under Example 1.

Example 3

[0098] In a third exemplary embodiment (Example 3) the process of the present invention may be utilised for the processing of uranium-bearing ores, in which LDH can be formed in situ within a an alkaline mineral processing or metallurgical stream that includes the uranium bearing ores.

[0099] The uranium ore containing stream was dosed, typically with one of both of Mg and Al containing compounds, to achieve a desired ratio of Mg/Al in the stream which results in precipitation of LDH such as hydrotalcites. Due to the pre-existing alkaline conditions (pH of at least greater than 7 and preferably greater than 8) of the alkaline mineral processing or metallurgical stream, in situ formation of LDH is favourable when the desired ratio of Mg/Al is achieved. As explained in Example 1, uranium bearing ores include a range of other elements that are present in addition to uranium which includes heavy metals, metalloids and/or REE. Forming the LDH material in situ also results in incorporation of the cations such as Ln^{3+} cations and/or Ce^{3+} and Ce^{4+} and/or Eu^{2+} or Eu^{3+} oxidation states and a range of anions including oxo-metallic anions or oxyanions. Laboratory trials have demonstrated that the Al containing compound is preferably to be added first or in conjunction with any Mg containing compound to prevent the precipitation of the Mg as Mg carbonate compounds such as MgCO_3 rather than it being utilised in the formation of the LDH.

[00100] In situ formation of the LDH also results in REE cations being shown to be strongly partitioned into the primary metal hydroxide layer of LDH. As discussed earlier, since uranium exists as an oxy-cation commonly known as a uranyl (UO_2^{2+}) cation, the uranyl ion is too large to be substituted for +2 cations such as Mg^{2+} into the LDH. Alkaline earth and transition metals generally present in the metal hydroxide layers of the LDH. Once again, under the alkaline conditions of the stream, anionic uranyl complexes are formed. Under the intermediate to higher pH conditions of the stream, UO_2^{2+} - CO_3^{2-} anionic complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) may predominate. Given this selective speciation of the UO_2^{2+} as anionic complexes, these uranyl anionic complexes preferentially partition into the anionic interlayers of LDH formed in situ.

[00101] It is important to appreciate that under the reaction conditions of example 3, as explained above only carbonate complexes will predominate and some REE, particularly the mid (MREE) to heavy REE (HREE) may be preferentially retained in the solution due to the known preferential complexation of MREE and HREE by carbonate ligands. This preferential speciation under alkaline conditions may be used advantageously given that the MREE and HREE are generally considered the most valuable components of the REE due to their often low abundance.

[00102] In the present specification and claims (if any), the word 'comprising' and its derivatives including 'comprises' and 'comprise' include each of the stated integers but does not exclude the inclusion of one or more further integers.

[00103] Reference throughout this specification to ‘one embodiment’ or ‘an embodiment’ means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearance of the phrases ‘in one embodiment’ or ‘in an embodiment’ in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more combinations.

[00104] In compliance with the statute, the invention has been described in language more or less specific to structural or methodical features. It is to be understood that the invention is not limited to specific features shown or described since the means herein described comprises preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims (if any) appropriately interpreted by those skilled in the art.

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CLAIMS

1. A process for treating water containing one or more dissolved cation species and/or one or more dissolved anion species; the process comprising the steps of:
 - (a) adding a magnesium and/or aluminium containing silicate material in the water and dissolving at least a part of the silicate material in the water thereby leaching at least a part of the magnesium and/or aluminium from the silicate material into the water; and
 - (b) controlling reaction conditions for achieving an appropriate Mg:Al ratio in the water for in situ formation of layered double hydroxide containing Mg and Al as predominant species in a lattice of the LDH;
wherein at least one of the said dissolved cation and/or anion species is incorporated into the LDH formed in situ.
2. A process in accordance with claim 1 wherein the step of dissolving the magnesium and aluminium containing silicate material comprises leaching the magnesium and aluminium from the silicate material under acidic pH conditions.
3. A process in accordance with claim 1 wherein the step of dissolving the magnesium and/or aluminium containing silicate material comprises leaching the aluminium from the silicate material under alkaline conditions.
4. A process in accordance with any one of the preceding claims wherein the step of dissolving the silicate material further comprises leaching of at least a part of the silica from the silicate material.
5. A process in accordance with any one of the preceding claims wherein the step of dissolving involves agitating the silicate material in the water for leaching said at least part of the magnesium and/or aluminium from the silicate material.
6. A process in accordance with any one of the preceding claims wherein the adding step comprises addition of a mixture comprising the said magnesium and/or aluminium containing silicate material and an additional silicate material.
7. A process in accordance with any one of the preceding claims wherein the step of controlling the reaction conditions comprises addition of at least one Mg-containing compound and/or at least one Al-containing compound for achieving the appropriate Mg:Al ratio in the water for formation of the LDH in situ.

8. A process in accordance with claim 6 wherein said at least one aluminium containing compound comprises aluminate ($\text{Al}(\text{OH})_4$ or $\text{AlO}_2 \cdot 2\text{H}_2\text{O}$) or aluminium sulphate, aluminium hydroxide or organometallic compounds containing aluminium.
9. A process in accordance with claim 6 or claim 7 wherein said at least one Mg-containing compound comprises MgO or $\text{Mg}(\text{OH})_2$ or a mixture thereof.
10. A process in accordance with any one of the preceding claims wherein the step of controlling the reaction conditions further comprises providing substantially alkaline reaction conditions for formation of the LDH in situ.
11. A process in accordance with any one of the preceding claims wherein the step of controlling the reaction conditions further comprises addition of alkaline or acid-neutralising material for formation of the LDH in situ.
12. A process in accordance with claim 10 wherein the additional alkaline or acid neutralising material is selected from one or more of alkaline or acid-neutralising solutes, slurries or solid materials or mixtures thereof, including lime, slaked lime, calcined magnesia, sodium hydroxide, sodium carbonate, sodium bicarbonate or sodium silicate.
13. A process in accordance with any one of the preceding claims further comprising the step of removing at least a part of the hydrotalcite formed in situ, wherein the at least one of the said dissolved cation and/or anion species is incorporated in the hydrotalcite or the LDH.
14. A process in accordance with any one of the preceding claims wherein the silicate material comprises one or more of: Attapulgite; Clinoptilolite; Sepiolite; Talc; Vermiculite mineral aggregates or associations in the form of rocks such as ground granite, greenstone or serpentinite or overburden, soils, sediments or waste materials, for instance from alumina refining (red mud) or coal combustion (fly ash).
15. A process in accordance with any one of the preceding claims wherein at least a part of the silicate material from step (a) and the LDH formed in situ in step (b) forms an insoluble clay material mixture wherein the clay material mixture incorporates said at least one or more dissolved cation species and/or the one or more dissolved anion species.

16. A process in accordance with any one of the preceding claims wherein undissolved clay material particles from step (a) provide nucleation sites for formation of at least a part of the LDH formed in situ in step (b).
17. A process in accordance with any one of the preceding claims wherein the one or more dissolved cation species in the water comprises magnesium and/or aluminium cations such that at least a part of the dissolved magnesium and/or aluminium is incorporated into the lattice of the LDH formed in situ.
18. A process in accordance with any one of the preceding claims wherein at least one of the dissolved anions in the water is a complex anion such that at least one of the complex ions is intercalated in an interlayer of the LDH formed in situ.
19. A process in accordance with any one of the preceding claims wherein the LDH formed in situ comprises hydrotalcite.
20. A process in accordance with any one of the preceding claims for treating water containing a dissolved metallic complex anion and one or more dissolved cations such that the metallic complex anion is intercalated within interlayers of the LDH material and wherein one or more of the other cations are incorporated into the LDH material's crystal structure or matrix.
21. A process in accordance with 20 further comprising the step of controlling pH levels in the water thereby controlling speciation of the complex anion in the water.
22. A process in accordance with any one of claims 20 or 21 further comprising separating the LDH from the water in step (b) and recovering the metallic constituent from the interlayer of the LDH by subjecting the separated LDH to a recovery treatment step.
23. A process in accordance with claim 22 wherein the recovery treatment step comprises an ion exchanging step involving the addition of at least one substituent anion to an ion-exchanging solution and introducing the separated LDH to the ion exchanging solution such that the substituent anion displaces at least some of the intercalated complex anion by an ion exchange mechanism thereby resulting in the complex anion being released from the interlayer of the LDH into the ion exchange solution.
24. A process in accordance with claim 23 wherein the ion exchanging step further comprises controlling pH conditions to promote displacement of the complex anion from the

interlayer and/or to promote speciation of a preferred type of complex anion over other complex anions.

25. A process in accordance with claim 23 or claim 24 wherein the substituent agent comprises one or more of the following NTA, EDTA and/or wherein the substituent agent is substantially more electronegative relative to the intercalated complex anion in the LDH material.
26. A process in accordance with any one of claims 23 to 25 wherein the recovery step further comprises separating the LDH material after the ion exchanging step.
27. A process in accordance with any one of claims 20 to 22 wherein the recovery treatment step comprises subjecting the LDH material to heat treatment or thermal decomposition thereby forming a collapsed or metastable material.
28. A process in accordance with claim 27 when dependent upon any one of claims 20 to 22 wherein the heat treatment step results in recrystallisation of the LDH material after thermal decomposition resulting in formation of a first oxide material comprising the pre-selected metallic constituent and a second oxide material comprising one or more of the other metals.
29. A process in accordance with any one of claims 27 or 28 wherein the heat treatment is carried out under substantially reducing conditions.
30. A process in accordance with any one of claims 27 to 29 further comprising the addition of a further additive to the LDH material prior to or during the heat treatment or thermal decomposition.
31. A process in accordance with any one of claims 27 to 30 wherein the process further comprises controlling the ratio of the further additive to the LDH material for selectively controlling formation of oxide materials upon the heat treatment or thermal decomposition.
32. A process in accordance with any one of claims 20 to 31 wherein the recovery treatment step comprises optimisation of the crystal structure or matrix of the LDH material for selectively incorporating one or more of the other cations into the crystal structure or matrix of the LDH in step (b).

33. A process in accordance with any one of the preceding claims wherein the complex metallic anion comprises uranium or vanadium and wherein the one or more of the other metals comprises rare earth metals.
34. A process in accordance with any one of claims 20 to 33 wherein the complex anion comprises a uranyl complex anion such as $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{UO}_2(\text{SO}_4)_3^{4-}$.
35. A process in accordance with claim 34 when dependent upon claim 21 wherein controlling the pH of the solution determines speciation of the uranyl complex anion.
36. A process in accordance with claim 34 or claim 35 wherein the intercalated uranyl complex is displaced from the interlayer of the LDH by the ion exchanging step in accordance with any one of claims 23 to 27.
37. A process in accordance with any one of claims 33 or 34 wherein the LDH material is subjected to the heat treatment step in accordance with claims 27 to 30 such that the heat treatment is preferably carried out under substantially reducing conditions for reducing the uranyl ion to U^{4+} and/or U^{6+} .
38. A process in accordance with claim 22 or any one of claims 23 to 37 when dependent upon claim 22 further comprising the step of contacting the separated LDH material with an aqueous solution for dissolving at least a part of the LDH material into the solution thereby obtaining dissolved LDH in the solution followed by controlling the reaction conditions in the aqueous solution for in situ precipitation of LDH material from the dissolved LDH material such that the complex anion is intercalated within interlayers of the LDH material formed in situ and wherein one or more of the other cations are incorporated into the crystal structure or matrix of the LDH material formed in situ.
39. A process in accordance with claim 38 wherein the step of dissolving the LDH in the aqueous solution comprises controlling the pH of the aqueous solution preferably at pH levels of less than 7 and more preferably less than 5 and even more preferably less than 3.
40. A process in accordance with claim 38 or claim 39 wherein the step of controlling the reaction conditions in the aqueous solution comprises controlling the pH of the aqueous solution preferably at pH levels of greater than 8.

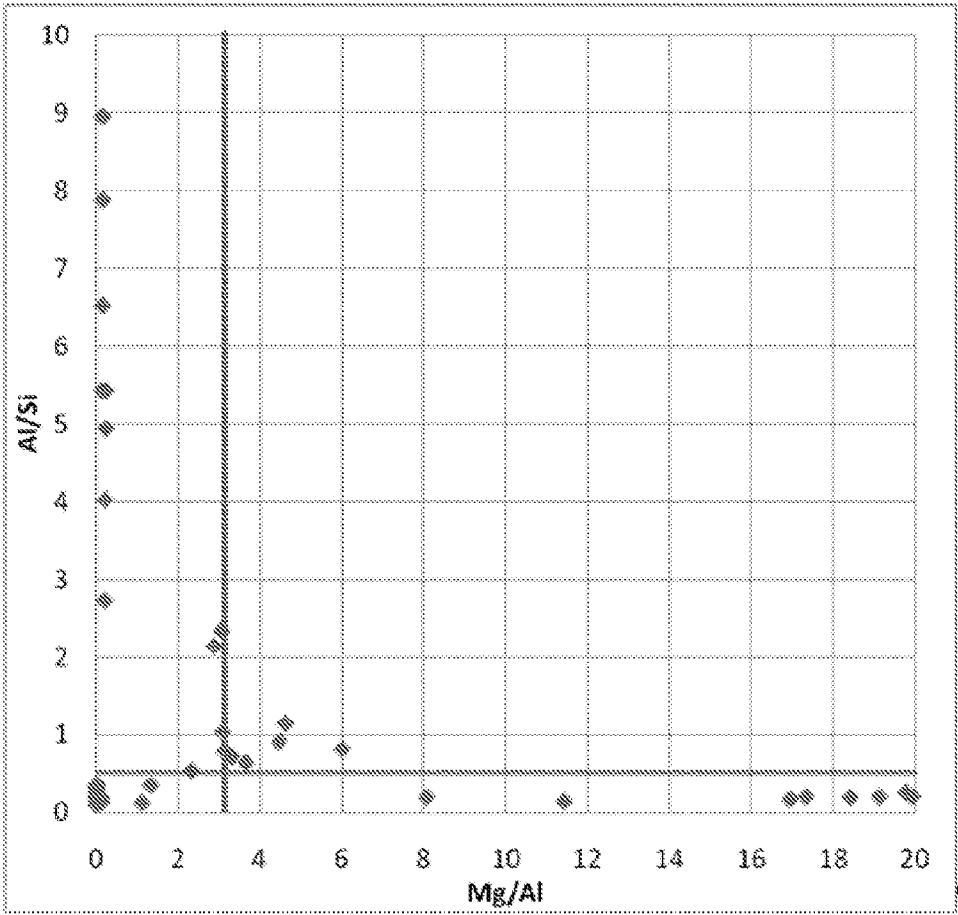


Figure 1.

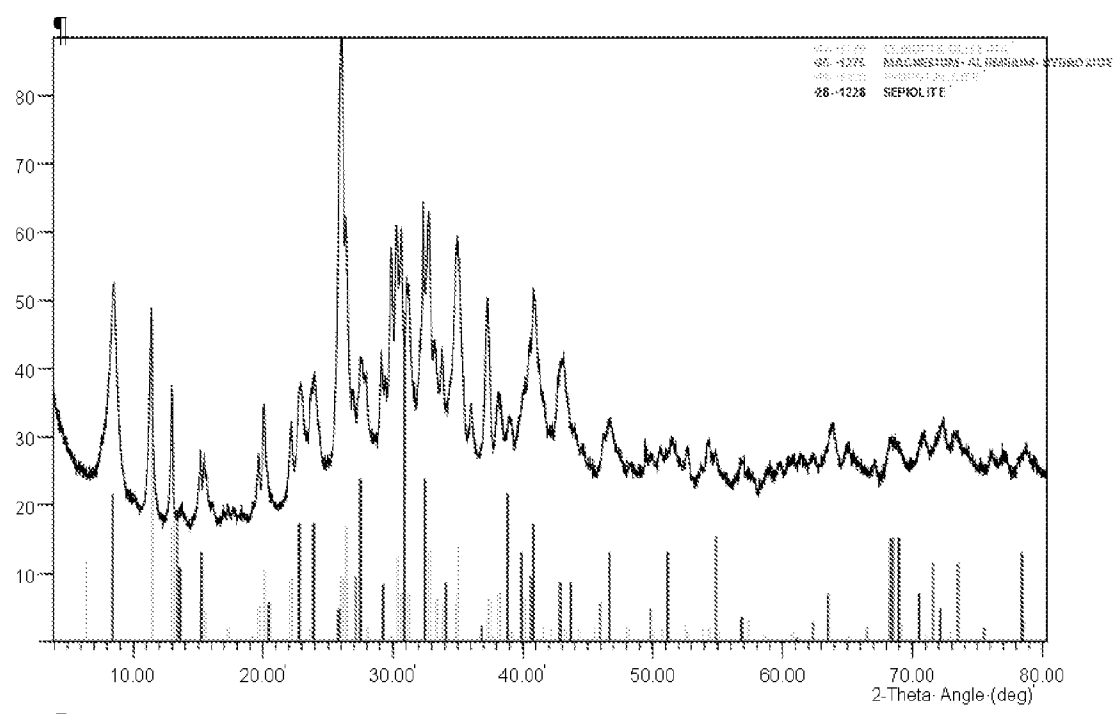


Figure 2

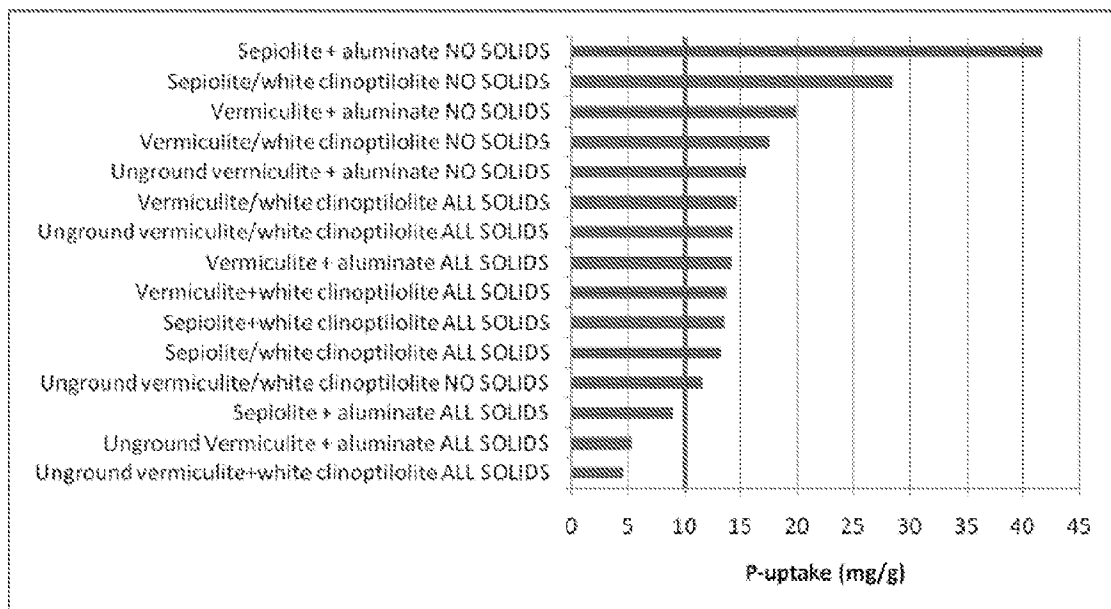


Figure 3

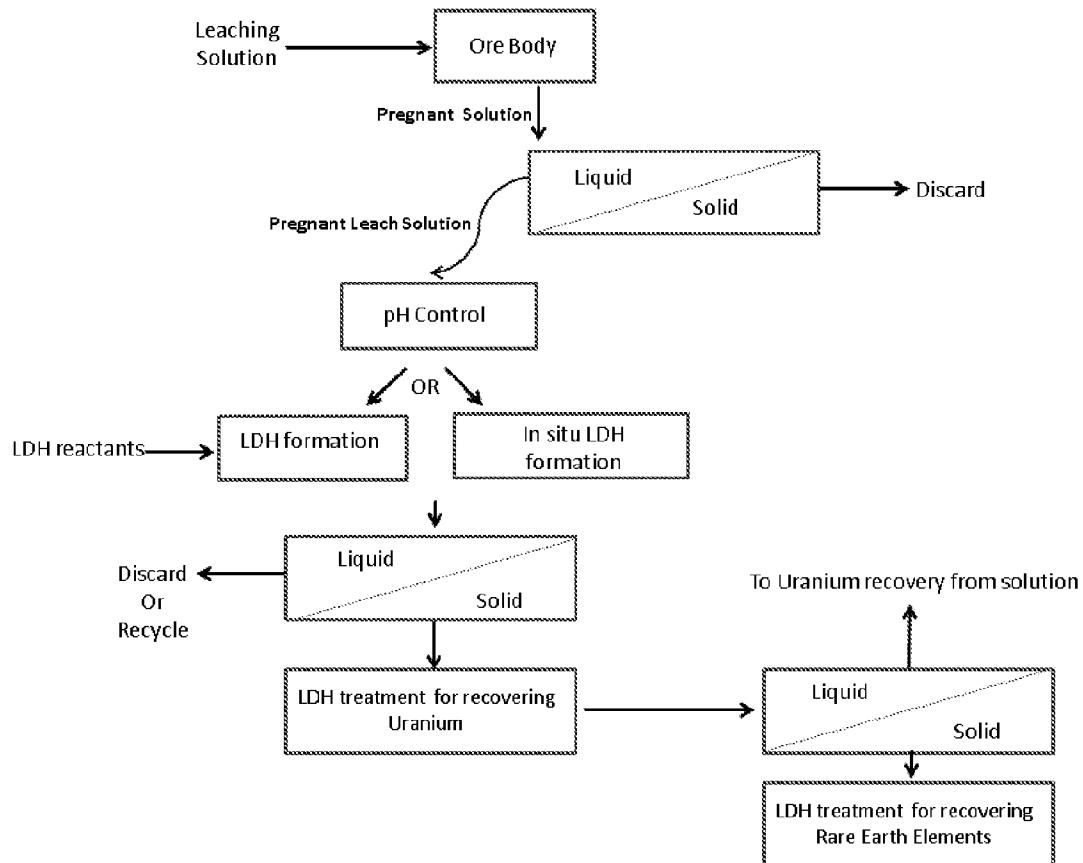


Figure 4

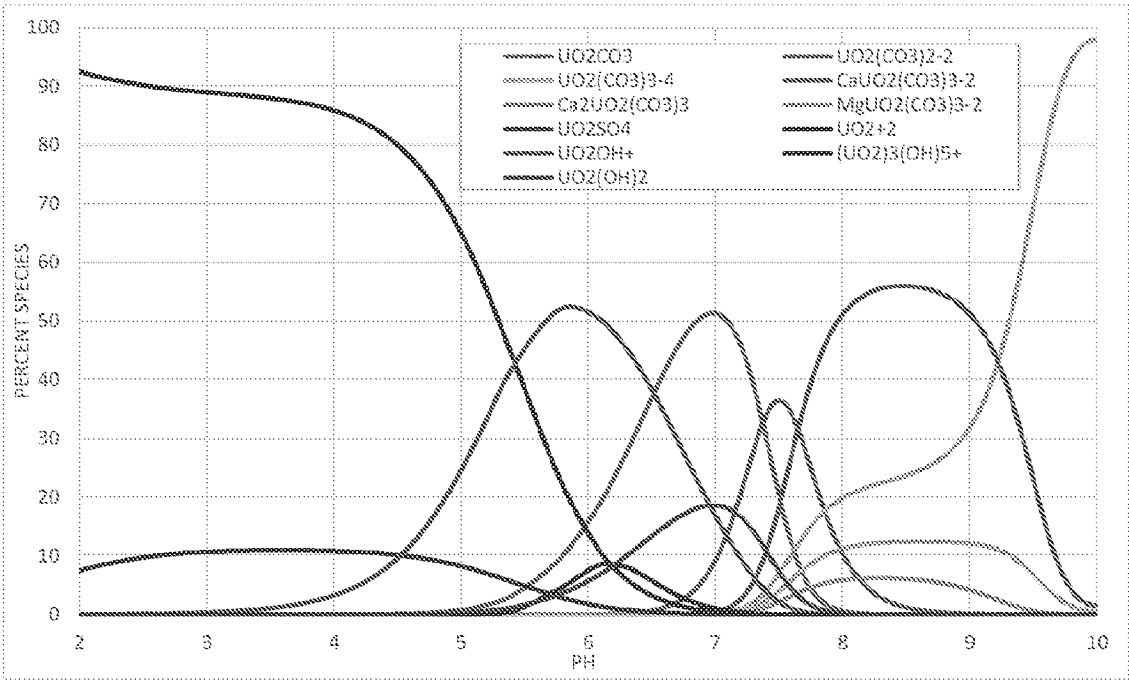


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2015/050175

A. CLASSIFICATION OF SUBJECT MATTER

C02F 1/42 (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)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIAP; EPODOC; TXTE: TXTUS5, TXTUS4, TXTUS3, TXTUS2, TXTUS1, TXTUS0, TXTEP1, TXTGB1, TXTWO1, TXTAU1, TXTCA1, TXTSG1; INSPEC; IPC and CPC Marks: IC/CC: C02F1/42, C02F9/04, C02F103/10, C02F/-; keywords: layered double hydroxide, LDH, hydrotalcite, magnesium, aluminium, aluminum, silicate, Mg, Al, Mg:Al, regulate, control, stabilise, stabilize, leach and similar search terms; Esp@cenet, USPTO, Google Scholar, ScienceDirect & Google Patents using similar search terms. "Applicant/Inventor name search": "COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION/DOUGLAS, Grant" through AusPat, Esp@cenet, WPIAP and EPODOC.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"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
25 May 2015

Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2015/050175
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/0184058 A1 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 23 July 2009 Abstract; paragraphs [0049], [0051], [0082]; claims 1, 4, 14, 17	1-40
A	US 2012/0228229 A1 (DOUGLAS) 13 September 2012 Abstract; paragraphs [0085], [0119]; claims 1-3, 5, 17, 24	1-40

Form PCT/ISA/210 (fifth sheet) (July 2009)

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2015/050175	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2009/0184058 A1	23 July 2009	AP 2420 A	06 Jun 2012
		AU 2007233585 A1	11 Oct 2007
		AU 2007233585 B2	18 Aug 2011
		CA 2643638 A1	11 Oct 2007
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		EA 017527 B1	30 Jan 2013
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