Extraction of Rare Earth Elements from non-Chinese Ion Adsorption Clays

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Abstract

Rare earth elements (REE) are required for several high tech devices like high performance magnets for wind turbines or lighting products for instance energy saving bulbs. Especially the more valuable heavy rare earth elements (HREE, Gadolinium – Lutetium) are a critical resource. These HREE are currently almost exclusively supplied by the ion adsorption clays (IAC) of southern China [1]. 90-60 % of the REE are absorbed on clay minerals [1] and can be recovered with high extraction yields by monovalent salt solutions using the concept of ion exchange. The remaining 10-40 % are not recovered to date because of the need of more aggressive leaching conditions and resulting less selectivity to major matrix elements.

This paper deals, in addition to the processing of non-Chinese IAC as a possible independent source for HREE, with the potential enhancing the recovery rates of REE from IAC in general. The investigated material mainly consists of the clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$ ~73-80- wt.%), quartz (SiO_2 ~4-18 wt.%) and iron (hydr-) oxides (~1.5-12 wt.%) with an average REE concentration of ~1100 ppm. As an approach, acidic conditions are used additionally to the ion exchange reaction with monovalent salt solutions to liberate the adsorptive ligated as well as the more strongly bound REE. This increases the REE recovery rates by 20 % up to over 90 % of the investigated material (best recovery rates with combination of 0.5 mol/L $(NH_4)SO_4$ and 0.1 mol/L H_2SO_4). In contrast, this leads to lower selectivity to impurities like iron, aluminum and silicon but a kinetic evaluation points out different leaching behaviors for the REE and the impurities, which can be used enhancing the selectivity.

1   Definition and formation of Ion Adsorption Clays

The term "Ion adsorption clay (IAC)" denotes a supergene ore that has been derived from lateritic weathering of rocks containing elevated amounts of Rare Earth Element (REE) bearing minerals. If these mineral phases are exposed to weathering under humid tropical conditions, they can be fully disintegrated [2]. During this process RE^{3+} ions are mobilized by the transfer into an aqueous solution which percolates through the weathering body and are adsorbed onto clay mineral surfaces. Clay minerals are progressively formed by the alteration of tectonosilicates (mainly feldspar). REE-enriched Ion Adsorption Clays (IAC) are currently exclusively mined in southern China and contribute a great amount (~80 % [1]) to the global supply with the more valuable Heavy Rare Earth Elements (HREE). The ore is primarily mined in two deposit areas in the Jiangxi province (Fig. 1A and B). HREE are particularly extracted in Longnan, whereas Xunwu is rather responsible for the supply of LREE (Light Rare Earth Elements) [3]. Orris and Grauch [4] mention 18 Chinese IAC deposits whereas over 200 have been reported by Chi and Tian (2008) [1]. However, several illegal mining sites are probably in production. The advantages of this ore type are a relatively low radioactivity in comparison to conventional ore minerals like monazite and bastnaesite as well as the postulated simple extraction and beneficiation process.
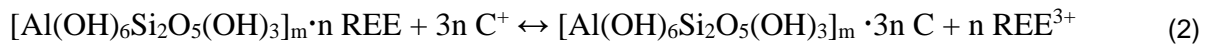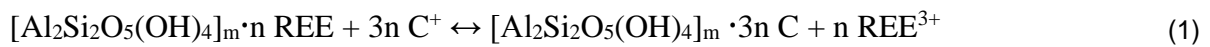

Figure 1:   A IAC deposit, Xunwu Longnan district, Jiangxi province, China [5]; B IAC deposit near Dingnan, Jiangxi province, China [6]

In addition to the adsorption onto clay mineral surfaces, REE are also attached to occurring Al-Fe-hydroxides for instance gibbsite (AlOOH) and goethite (FeOOH). Whereas adsorption is most probably the prevalent process of REE enrichment within Ion Adsorption clays, they are also incorporated into the crystal lattices of (secondary) oxides (hematite) and silicates (clay minerals, zircon) to a much lesser extend [7]. [1]

2   Theoretical background of REE-recovery from Ion Adsorption Clays

The leaching of rare earth elements (REE) from ion adsorption clays (IAC) has a long tradition in Chinese REE processing. The past 45 years several generations of leaching technologies were investigated to extract REE using the concept of ion-exchange leaching. In the IAC 60-90 % [1] of the REE are adsorbed onto the surface of phyllosilicate minerals like kaolinite [$Al_2Si_2O_5(OH)_4$], halloysite [$Al(OH)_6Si_2O_5(OH)_3$] or muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$]. These adsorbed REE can be easily recovered by leaching with monovalent electrolytic salt solutions as sodium or ammonium based systems (Eqn. 1-3). The leaching kinetic of the REE extraction via ion exchange is very fast e.g. reported by Moldoveanu with less than five minutes [8]. [1], [9], [10], [11], [12]

$$[Al_2Si_2O_5(OH)_4]_m \cdot n\ REE + 3n\ C^+ \leftrightarrow [Al_2Si_2O_5(OH)_4]_m \cdot 3n\ C + n\ REE^{3+} \qquad (1)$$

$$[Al(OH)_6Si_2O_5(OH)_3]_m \cdot n\ REE + 3n\ C^+ \leftrightarrow [Al(OH)_6Si_2O_5(OH)_3]_m \cdot 3n\ C + n\ REE^{3+} \qquad (2)$$

$$[KAl_2(AlSi_3O_{10})(OH)_2]_m \cdot n\ REE + 3n\ C^+ \leftrightarrow [KAl_2(AlSi_3O_{10})(OH)_2]_m \cdot 3n\ C + n\ REE^{3+} \qquad (3)$$

$$C^+ \triangleq e.g.\ Na^+\ oder\ NH_4^+$$

Although the leaching with monovalent salt solutions is very selective the solved REE are usually precipitated with oxalic acid or ammonium-bi-carbonate, following a thermal conversion to rare earth oxides via roasting and re-leaching with hydrochloric acid to receive a pure REE solution for single REE separation via solvent extraction or ion exchange. This separation of the major leaching impurities is needed to obtain sufficient REE product qualities. [10], [11]

Up to now 10-40 % of the REE are not recovered because they cannot be liberated by simple ion exchange reactions. These remaining REE are present in two further phases (first: in a colloid phase as REE-oxides, –hydroxides or as part of polymeric organometallic compounds, second: in the mineral phase). The REE of the colloid phase can be liberated by acid leach (Fig. 2, 2. Colloid phase) whereas breaking down the mineral structure needs more aggressive conditions (Fig. 2, 3. Mineral phase). Both ways are not implemented in the state of the art because of less selectivity to the major co-leached impurities like Al^{3+}, Fe^{3+}, Si^{4+} and Mg^{2+} but indicate high potentials with increasing REE recoveries [1], [10], [11], [12]
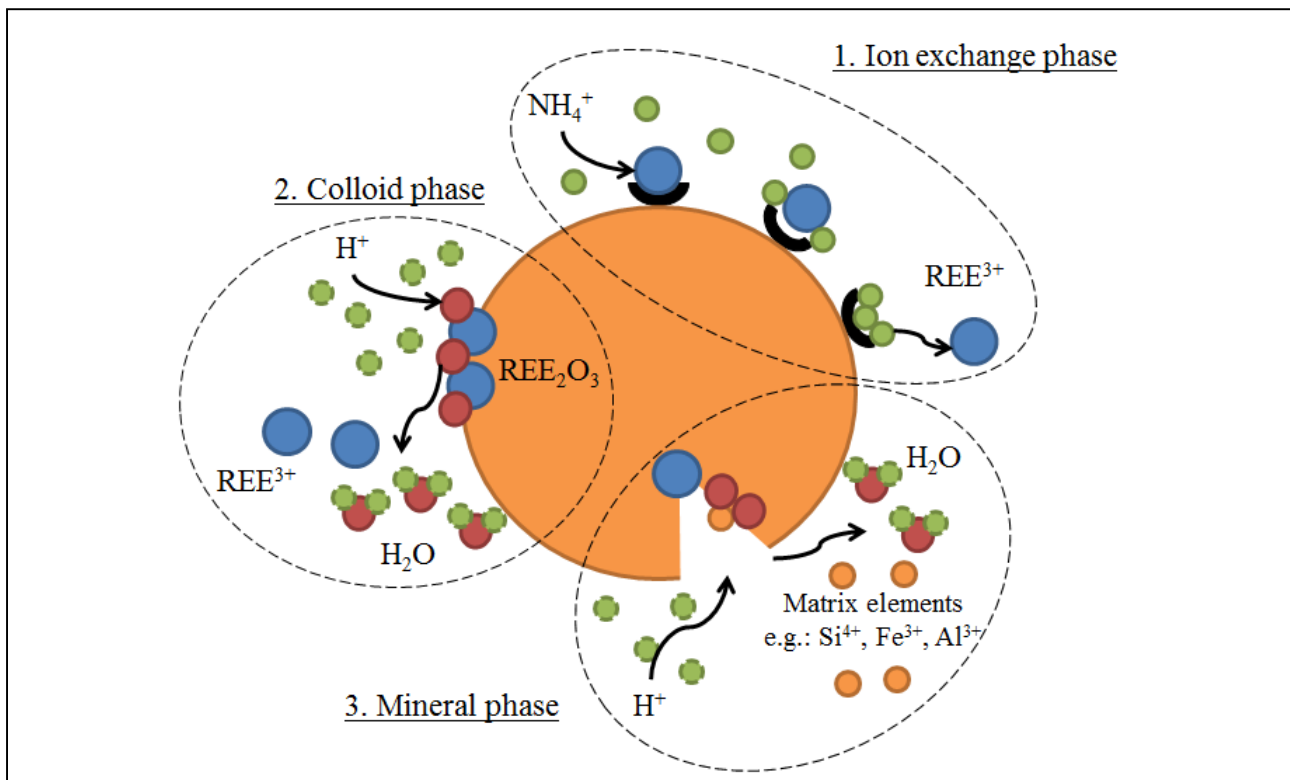
Figure 2:   Proposed leaching mechanisms for 1. Ion exchange phase, 2. Colloid phase, 3. Minerals phase

As a consequence, a detailed analysis of reaction mechanism of IAC is needed concerning high REE recovery rates taking into account the exchangeable phase as well as the colloid phase and the product quality regarding low impurities. Therefore, the leaching selectivity of the main impurities like iron, aluminium or silica implying their liberation mechanism is investigated as well as the following required cleaning process.

3   Experiments

3.1   Characterisation of investigated Ion Adsorption Clays

The acquired lateritic, respectively potential IAC samples consist of a loose, soil like brown to red coloured material (Fig. 3). Yellow and brown coloured specimen indicate the presence of Fe hydroxides ($FeO(OH)$, goethite), whereas red samples contain higher proportions of Fe_2O_3 (hematite). Hydrometallurgical methods were applied on red specimen (Lok18 and Lok45) because of higher total REE (TREE) concentrations within these samples (Fig. 2B). In order to conduct chemical and mineralogical analyses, specific samples were homogenized in a mortar as well as prepared onto thin sections. The major element chemistry was analysed by XRF. REE and additional trace elements were measured by ICP-MS. The mineralogy was investigated by SEM, XRD and quantified by Rietveld refinement.

Figure 3:   Ion Adsorption Clay raw material (left: Fe-hydroxide enriched material, right: hematite enriched material)

The analysed IAC samples primarily consist of SiO_2 (~48-58 %), Al_2O_3 (~27-38 %), Fe_2O_3 (~11-16 %) and TiO_2 (1-2 %). Alkali- and alkaline earth metals are below 1 %. The results of the ICP-MS analysis of the samples reveal an average REE concentration of ~1100 ppm. However, the IAC have a strong heterogeneity (~150 - ~ 1200 ppm). Chinese ores show a similar variability between ~500 and 3000 ppm [13]. The Light vs. Heavy Rare Earth Elements (LREE vs. HREE) ratio in investigated samples is approximately 5:1 (Tab. 1).

Table 1:   ICP-MS analysis of investigated IAC in ppm

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Σ(TREE)
LOK 18	287	311	65	278	44	8	36	5	26	157	5	14	2	11	2	1.250
LOK 45	211	469	41	150	23	2	17	3	13	70	2	7	1	7	1	1.016

XRD analysis and Rietveld quantification revealed consequentially a high abundance of clay minerals (kaolinite, ~73-80- wt.%) (Fig. 4). Quartz (SiO_2) contents reach from ~4-18 wt.%, iron (hydr-) oxides occur in terms of goethite (~7-12 wt.%) and hematite (~1.5-2.5 wt.%). Minor amounts of gibbsite indicate a very weak bauxitization (~0-1 wt.%). Figure 3 presents a typical spatial lateritic mineral assemblage in a bse image. Due to similar (low) mean atomic numbers, quartz and clay minerals appear dark or near black and were distinguished by EDX analysis and crystal shape.
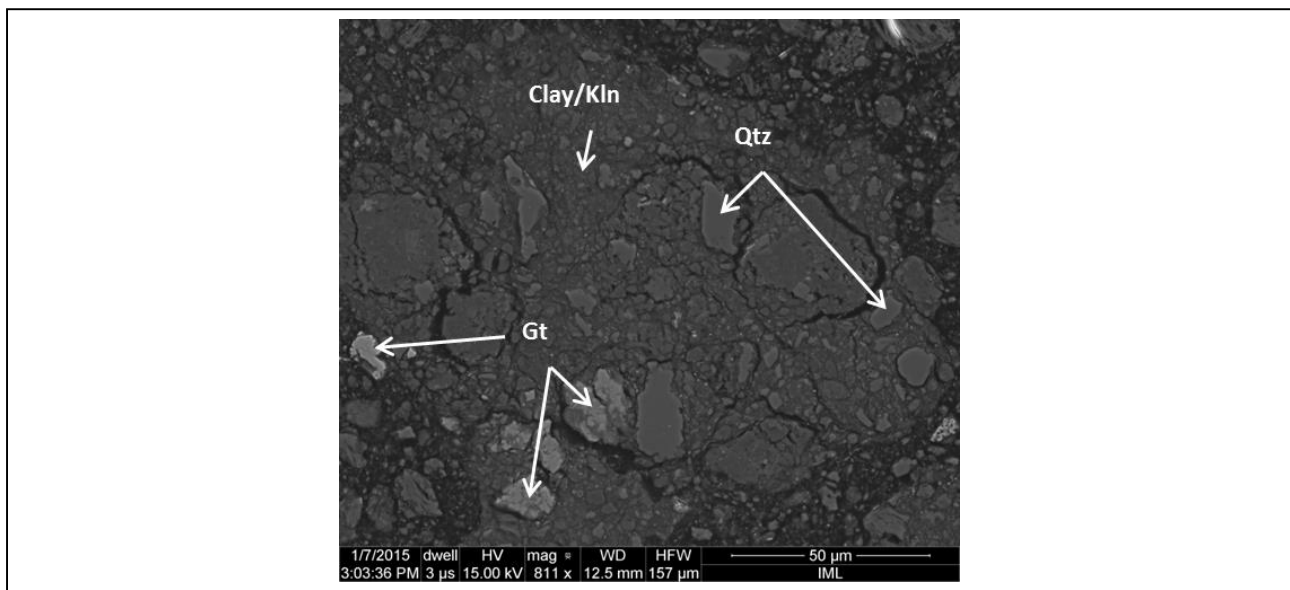
Figure 4:   BSE image of the lateritic Ion Adsorption clay with the dominating minerals kaolinite (Kln) and quartz (Qtz) in the presence of Fe-hydroxides (goethite - Gt)

3.2   Parameters of batch leaching tests with different lixiviates to extract rare earth elements

The batch leaching tests were performed in 250 mL beaker with a constant magnetic stirring speed of 300 rpm under standard conditions (25 °C, 1 bar). During reaction time, a continuous pH and temperature measurement was realised for the experiments by a Mettler Toledo InLab® Expert Din pH electrode. To verify the direct implementation of the studied IAC in state of the art process routes, leaching tests with pure salt solutions (Na^+ and NH_3^+ based, c = 0.5 mol/L) were carried out. To verify the single effect of, mineral acids HCl, HNO_3 and H_2SO_4 were used with different concentrations (0.1 mol/L). Further on, combinations of sulphate, chloride or nitrate salt and mineral acid solutions were investigated (c(salt) = 0.5 mol/L, c(acid) = 0.1 mol/L) to enhance REE recoveries because of co-liberation out of the exchangeable phase as well as the colloid phase. Constant parameters were the leaching time of one hour and a solid:liquid-ratio of 1:5. After leaching, the suspensions were filtrated under vacuum, the metal concentration of the filtrates were analysed with ICP-OES and the solids with XRF. Based on the elemental analysis, the REE extraction yield (R) and the selectivity (S) (Eqn. 4) to major matrix elements serve as evaluation criteria.

$$S(M_1 : M_2) = \frac{R(M_1)}{R(M_2)}$$

4

$R(M_1)$: e.g. metal yield of Nd
$R(M_2)$: e.g. metal yield of Fe, Al, Ti or Si

4   Results

The evaluation comparing the acid solutions (H_2SO_4, HCl and HNO_3) and the sodium based leaching agents (Na_2SO_4, NaCl and $NaNO_3$) indicates higher REE recoveries of 30-40 % absolute using sulfuric acid or sodium sulfate solution (Fig. 5). The first assumption is the divalence of sulfate ions which leads to lower pH-values for acid leaching solutions using 0.1 mol/L H_2SO_4 (pH 0.95 ± 0.05) in comparison to equal concentrated solutions of HCl (pH 1.25 ± 0.05) or HNO_3 (pH 1.05 ± 0.05). A similar explanation is the double input of sodium for ion exchange reaction (Eqn. 1) with 0.5 mol/L Na_2SO_4 solution. But previous papers point out no considerable effect of an excess stoichiometric addition for the ion exchange reaction in the investigated area (factor ~100 for chloride and nitrate salts and factor ~200 for sulfate salts in comparison to Moldoveanu: factor ~50-300 [14]). In the case of ammonium based systems ((NH_4)$_2SO_4$, NH_4Cl and NH_4NO_3) the REE recovery rates are similar, which shows that the double input of NH_4 using sulfates in contrast to using chlorides or nitrates is negligible with the used ratio of salt cations and exchangeable REE. All in all, the experiments with single mineral acids as well as with single salt solutions point out the sulfate based reagents as the favorable leaching system for further studies to extract REE from IACs.
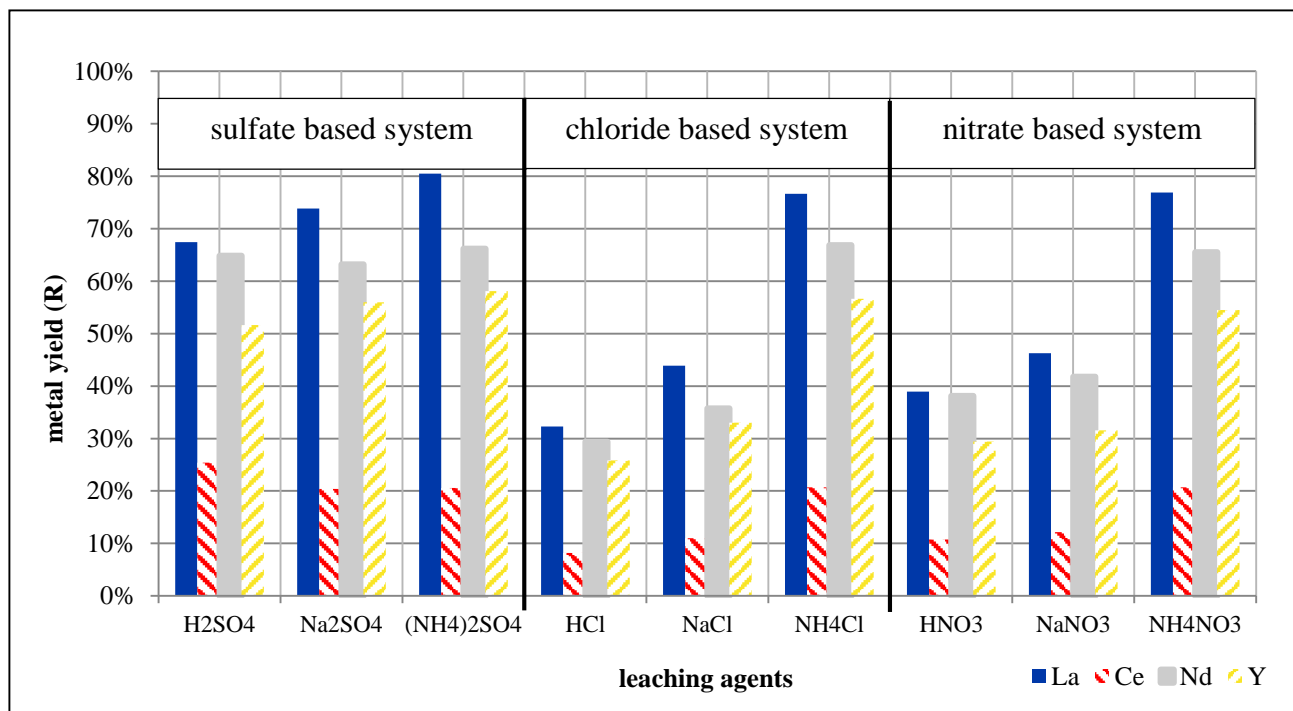

Figure 5:   Evaluation of sulfate-, chloride- and nitrate-based systems on REE metal yield (0.1 mol/L acid solutions or 0.5 mol/L salt solutions)

Comparing single sulfate salt solutions (0.5 mol/L) and single sulfuric acid (0.1 mol/L) with mixed leaching agents (Fig. 6) indicates an increasing REE metal yield of about 10 to 20 % absolute. This is attributed to the intended co-liberation of REE from the exchangeable phase as well as the colloid phase. Apart from this, impurities (e.g. Fe) are liberated increasingly with use of H_2SO_4 due to the

more acidic conditions (selectivity S(Nd:Fe) in Fig. 6). Especially iron can be leached from iron hydroxides that were identified in the studied material. A variation between pure acid and mixed leaching solutions is not noticed.
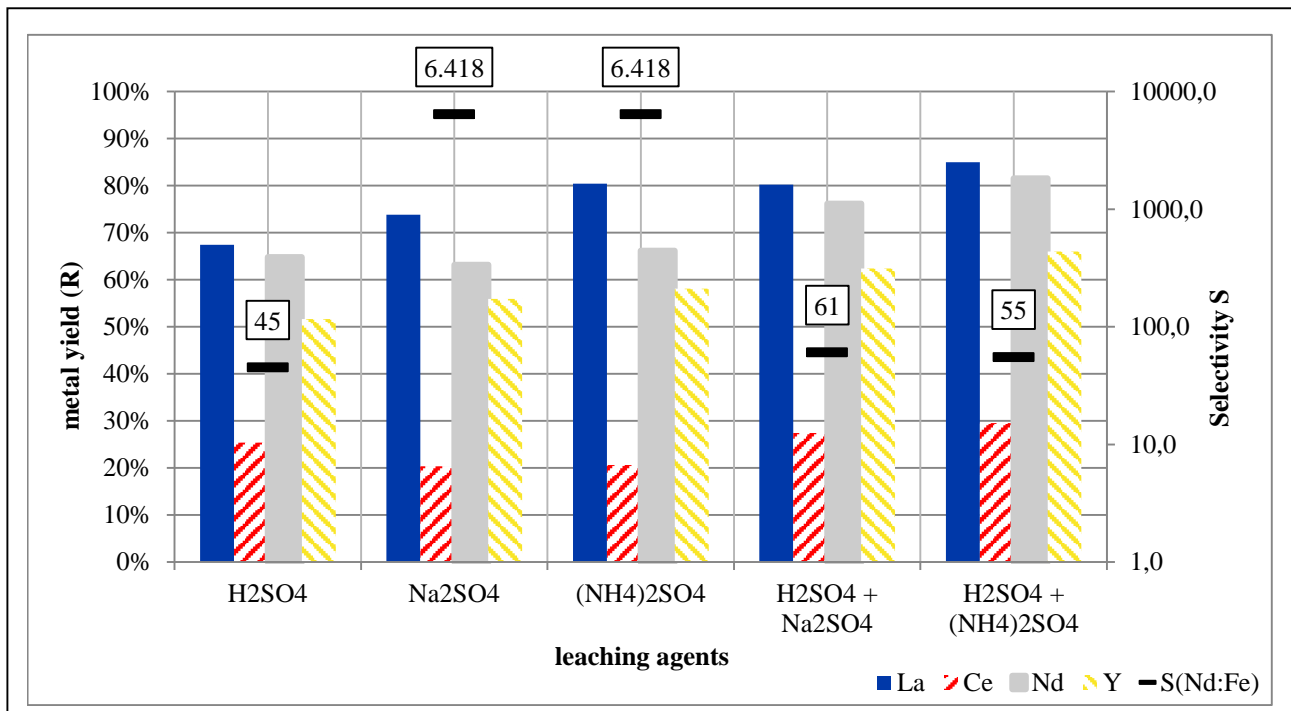

Figure 6:   Evaluation of sulfate based systems on REE metal yield (0.1 mol/L acid solutions, 0.5 mol/L salt solutions or composites of 0.1 mol/L acid and 0.5 mol/L salt solution)

To further investigate the REE recovery and the liberation of impurities a kinetic study of the best leaching system with highest REE extraction yields (0.1 mol/L H_2SO_4 + 0.5 mol/L $(NH_4)_2SO_4$) was carried out (Fig. 7). A direct comparison of these experiments with previous is not possible because of a change of material from LOK 45 to LOK 18. The REE extraction shows a fast leaching reaction caused by the instantaneous exchange kinetics with marginal increasing over time. The remaining REE are expected to be present in the mineralization like mentioned in chapter two. For additionally liberation a total decomposition is needed. Whereas is the liberation of impurities iron and silicon inhibited and for aluminum and titanium constant over time. As a consequence, a mixture of acid and salt solutions can increase the REE leaching efficiency and with short leaching times prohibit an excess liberation of matrix elements.
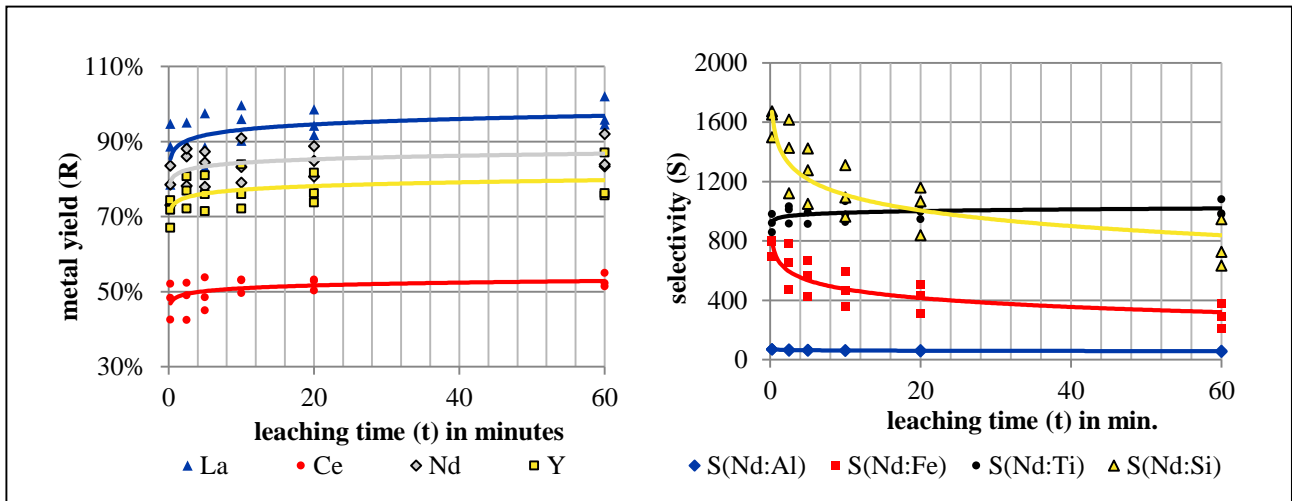
Figure 7: REE metal yield (left) and selectivity of Neodymium to major matrix elements (right) of direct leaching experiments (0.1 mol/L H_2SO_4 and 0.5 mol/L $(NH_4)_2SO_4$)

5   Summary and Outlook

The non-Chinese IAC consist of the major components kaolinite, quartz and iron (hydr-) oxides with an average REE concentration of ~1100 ppm and can be treated with ammonium and sodium based salt solutions. Using acidic conditions of pH one in combination with monovalent salt solutions enhances the REE recovery rates by 20 % up to 90 % (best recovery rates with combination of 0.5 mol/L $(NH_4)SO_4$ and 0.1 mol/L H_2SO_4). In contrast this leads to higher liberation of impurities and less selectivity. A kinetic evaluation points out a different leaching behavior of REE and impurities e.g. iron and silicon. Accordingly, a fast processing of IAC improves the selectivity in spite of only minor REE losses. In order to investigate the direct impact of the leaching process on individual mineral phases in the leachate/residue, automated mineralogy analyses, such as QEMSCAN, could provide insightful information on alteration reactions, leaching efficiency and environmental related considerations.

Further studies have to be focused on enhancing the inhibition of leaching impurities and the further processing of the leach solution to find out the limits of the following separation process with no decline in REE product quality.

Acknowledgement

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