Pilot-Plant Investigation of the Leaching Process for the Recovery of Scandium from Red Mud

**Maria Th. Ochsenkühn-Petropoulou,*,[†] Konstantinos S. Hatzilyberis,[‡]
Leonidas N. Mendrinos,[†] and Constantinos E. Salmas[‡]**

*Laboratory of Inorganic and Analytical Chemistry and Chemical Process Engineering Laboratory,
Department of Chemical Engineering, National Technical University of Athens, 9 Iroon Polytechniou Street,
15780 Athens, Greece*

A pilot-plant process has been developed based on an innovative laboratory-scale method for the recovery of scandium that exists in economically interesting concentrations in red mud, the main byproduct of alumina production. This method includes acid leaching of the red mud pulp, ion-exchange separation of scandium and lanthanides from the co-leached main elements such as iron, and subsequent liquid–liquid extraction of the eluate for further scandium purification and enrichment. In this work, experimental and theoretical investigation of the pilot-scale leaching process was performed. The following parameters were tested: mode of agitation, solid-to-liquid ratio, acidity of the leachate, number of stages in the process, and pretreatment of red mud with concentrated acids in order to achieve optimum scandium recovery combined with low iron dissolution. Furthermore, by theoretical interpretation of the experimental data, a predictive correlation for the scandium leaching efficiency was developed.

Introduction

Scandium (Sc) is a rare and very expensive metal but is very important as well from an industrial point of view. It is increasingly used in the metallurgy of Mg,[1] Al,[2] and Fe. Moreover, new applications for Sc have been developed such as laser crystals, coatings, cathode materials for color cathode-ray tubes, advanced ceramics, nuclear materials, and catalysts for automobiles.[3] In addition, Sc has attracted the attention of the optical industry,[4] astronavigation,[5] and production of advanced materials.[3] All of these applications have heightened the demand for Sc in both quantity and quality; however, it remains difficult to obtain because it is associated in trace amounts with natural minerals and the resources of Sc mineral deposits often exist in complicated mineral forms.[6]

The most attractive worldwide Sc deposits for commercial exploitation[7] have been discovered in Zhovti Vody, Ukraine (Sc content of 105 g/tons in a hardly treatable rock placed at a depth of 1000 m; exploitation by Ashurst Technology Group, USA[8]), and in Houston-Mitchel North, Port Macquarie, New South Wales, Australia (Sc content of 76 g/tons in a surface deposit, increasing with depth; exploitation by Jervois Mining N.L., Australia[7]).

Furthermore, there is no single mineral source for Sc known to exist; thus, it is mainly obtained as a byproduct of uranium and tungsten production, as well as from apatite and titanomagnetic mining.[9,10] In all cases the Sc content does not exceed 0.02% as Sc_2O_3, while in the case of uranium wastes, high radioactivity levels make the extraction of Sc hazardous to the environment.[11]

It has been found that during bauxite processing by the Bayer method for the production of alumina the Sc,

Y, and lanthanides content accumulates and is enriched in the red mud, the byproduct of this method.[12] Red mud (RM) pulp has pH $\approx$ 12, and it mainly consists of iron (Fe), calcium (Ca), aluminum (Al), silicon (Si), titanium (Ti), and sodium (Na) compounds (main elements = ME) and is comprised of small quantities of elements of economical interest such as vanadium (V), zirconium (Zr), niobium (Nb), and rare-earth elements (REE), viz., yttrium (Y), scandium (Sc), and lanthanides (Ln).[12,13] In Greece the annual production of RM, by the company Aluminium of Greece (Pechiney Group),[14] is about 6×10^8 kg, and its Sc concentration is high and uniform, about 130 g of Sc/ton of dry RM corresponding to 0.02% Sc_2O_3.[12] According to recent survey in the international market[15] and taking into account the concentration of Sc, Y, and lanthanides in the Greek RM,[12] Sc represents 95% of the economic value of this RM regarding the REE. The comparison between the Greek RM and the most attractive worldwide Sc deposits is evidence for the advantage of this Sc source for commercial exploitation.

The procedures used so far for the selective recovery of REE from bauxites and RM include thermal reduction of RM in an electric furnace for the separation of pig iron and treatment of the residue with various concentrations of H_2SO_4[16–18] or almost complete acidic dissolution of RM with aqua regia and HF, H_3BO_3, and H_2SO_4. All of these methods are either energy-consuming or too complicated and thus not economically viable to be applied on a large scale.[19]

Alcan International has patented a selective leaching process for the recovery of lanthanides and Y[20] by introducing gaseous SO_2, into an aqueous slurry of RM in two or three stages, by carefully reducing and adjusting the pH between them. In the first one or two stages, the ME and other impurities are separated from the insoluble REE that are leached in the last one. However, they reported extraction yields in the leachate solutions referring only to Y and supposing it as being typical of the extraction behavior of the other REE.[19]

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* To whom correspondence should be addressed. E-mail: oxenki@central.ntua.gr. Tel: +301 0 7723094. Fax: +301 0 6724471.
    [†] Laboratory of Inorganic and Analytical Chemistry.
    [‡] Chemical Process Engineering Laboratory.

An innovative method for the recovery of REE from RM and the separation of Sc was developed on a laboratory scale.[19,21] The method is based on the hydrometallurgical treatment of RM by leaching with dilute nitric acid and leads to a selective and efficient recovery of REE. Further separation of REE from the small percentage of the ME present in the leachate is achieved by an ion-exchange procedure, while separation of Sc from the other REE is accomplished by a liquid−liquid extraction procedure.

This innovative method was up-scaled to a pilot plant in order to investigate and optimize the various steps of the whole procedure toward industrial-scale production.[22] In this work, the leaching process of the pilot-scale procedure that is of critical importance for the whole method economics is theoretically and experimentally investigated, while the various parameters affecting the efficiency of this process are optimized.

Leaching Process

Leaching is a mass-transfer operation employed in the extraction of one or more soluble constituents from a solid by means of a solvent.[23] The mass-transfer rate within the porous solid residue is difficult to assess because it is impossible to define the shape of the channels through which transfer must take place. However, it is possible to obtain an approximate estimation of the rate of transfer from the particles to the bulk of the liquid. On the basis of the assumption of a thin film being responsible for the resistance to transfer, we can write the equation for mass transfer as

$$\frac{dm}{dt} = \frac{K'A(c_s - c)}{b} \tag{1}$$

where A is the area of the solid−liquid interface, b is the effective thickness of the liquid film surrounding the particles, c is the concentration (w/v) of the solute in the bulk of the solution at time t, c_s is the concentration (w/v) of the saturated solution in contact with the particles, m is the mass of solute transferred in time t, and K' is the diffusion coefficient. It is approximately equal to the product of the liquid-phase diffusivity D_L and the ratio of the total molar concentration of solvent and solute to the logarithmic mean value of the solute concentration at each side of the film.[23] It will be taken here as approximately constant. Therefore, the mass-transfer coefficient K_L is $K_L = K'/b$.

Considering the batch process of this work in which V is the total volume of solution, which will be assumed to remain constant:

$$dm = V dc \quad \text{and} \quad \frac{dc}{dt} = \frac{K_L A(c_s - c)}{V}$$

The time t taken for the concentration of the solution to rise from its initial value $c_0 = 0$ (pure solvent is used initially) to c is found by integration, on the assumption that both K_L and A remain constant.

Rearranging and integrating,

$$c = c_s(1 - e^{-(K_L A/V)t}) \tag{2}$$

This shows that the solution approaches a saturated condition exponentially.

In most cases the interfacial area will tend to increase during the extraction, and when the soluble material
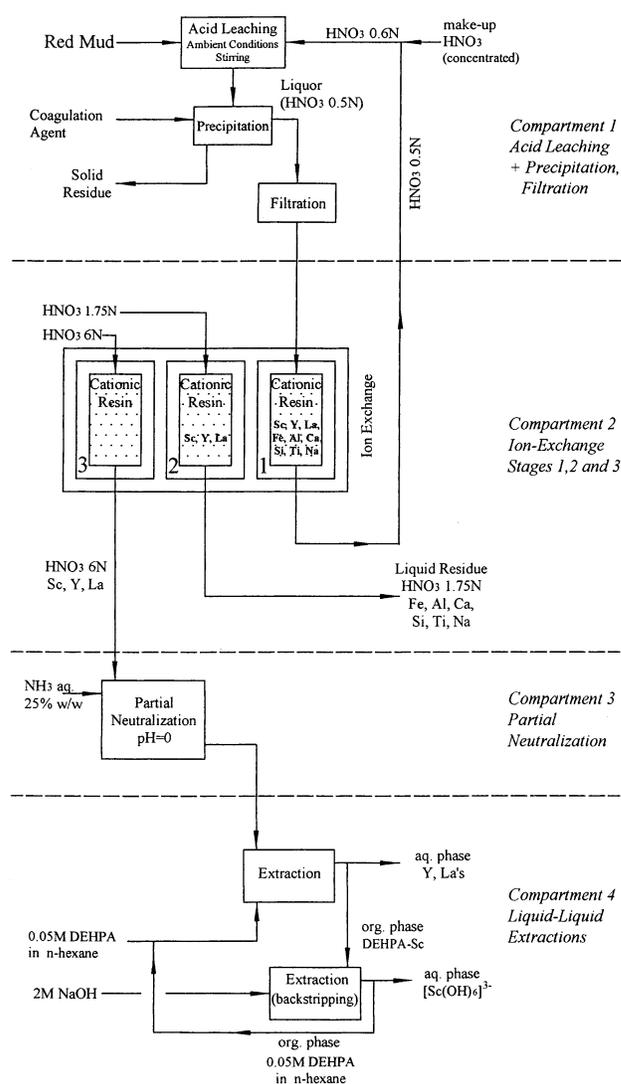
Figure 1. Schematic presentation of the Sc separation method.

forms a very high proportion of the total solid, complete disintegration of the particles may occur. Although this results in an increase in the interfacial area, the rate of extraction will probably be reduced because the free flow of the solvent will be impeded and the effective value of b will be increased.

Experimental Section

Separation Method. The flow diagram of the laboratory-scale Sc separation method used, based on the innovative method described in detail elsewhere,[19,21] is presented in Figure 1. A batch of RM is thoroughly stirred with dilute nitric acid (0.6 N HNO_3) under ambient temperature and pressure (acid leaching). During this process the alkaline content of the RM is neutralized by the acid solution whose normality decreases to 0.5 N. Sc, Y, and lanthanides are transferred from the RM solid particles to the liquid phase with an efficiency ranging from 50% to 75% depending on the element investigated. The ME of RM and especially iron are transferred in a small fraction to the liquid phase. The selection of the leaching acid and its normality was found to be very important for the efficient recovery of Sc and the minimization of the efficiency of Fe transfer from solid to liquid (<4%); Fe is an element hardly separable from Sc because of their similar ionic radii.[19]

Table 1. Technical Data of the Leaching Process Equipment

symbol in Figure 2	kind of equipment	trade name	capacity	materials of construction
V1	spherical vessel with a mechanical stirrer of 0.37 kW	QVF/Iludest Gmbh	100 L	glass vessel. stirrer: SS shaft coated with PTFE, PTFE paddles (140 mm)
V2	cylindrical vessel	NALGENE	100 L	LDPE
V3	spherical vessel	QVF/Iludest Gmbh	50 L	glass
V15	cylindrical vessel	NALGENE	100 L	LDPE
F1	filter with a cylindrical textile cartridge	filter shell: Iludest Gmbh	height: 0.5 m	glass
		cartridge: SARTORIUS, SARTOPURE PP2 (depth filter)	porosity: 8 μm	
F2	filter with a cylindrical textile cartridge	filter shell: Iludest Gmbh	height: 0.5 m	glass
		cartridge: SARTORIUS, SARTOPURE PP2 (depth filter)	porosity: 1.2 μm	
VP	diaphragm vacuum pump	Vacuubrand ME 4C	3.4 m^3/h, P > 80 mbar-a	wetted parts: PTFE
pipes		Iludest GmbH	o.d. 11 mm (i.d. 9 mm)	PTFE
piping instruments (valves, tees, etc.)		miscellaneous		PTFE, PE, PP, PVC

After the stirring stage, the suspension is allowed to rest and a coagulation agent (polymer electrolyte Praestol of 1‰ (w/v), Stockhausen) is added in a ratio of 1:200 (v/v), enabling the rapid precipitation of the solid particles. Then the liquid phase is directly led to a filtration unit consisting of two filters, a prefilter of 8 μm porosity and a filter of 1.2 μm porosity, appropriately selected as a result of a particle size investigation of the RM after the leaching process.

The clear liquid product of the leaching process flows through a column containing a strong acid cationic resin of the hydrogen form (Purolite C-100H; first stage of the ion-exchange process; Figure 1, Ion Exchange No. 1), resulting in the quantitative retention of the cations. HNO$_3$ (0.5 N) without impurities is obtained as the effluent, which by mixing with the proper proportion of concentrated HNO$_3$ can be reused as the leaching solvent of the process. In the second stage of the ion-exchange process (Figure 1, Ion Exchange No. 2), 1.75 N HNO$_3$ passes through the cationic resin and elutes the ME from the resin, leaving Sc, Y, and lanthanides in the column. This acidic solution could find a potential use as a neutralization medium of the alkaline waste RM of a nearby installed alumina production plant. The third stage of the ion-exchange process (Figure 1, Ion Exchange No. 3) is the elution of Y, Sc, and lanthanides by using 6 N HNO$_3$. Subsequently, the effluent of the third stage is partially neutralized up to pH = 0, through the addition of the appropriate proportion of an aqueous NH$_3$ solution [25% (w/w)]. This value of pH = 0, which in this case is very critical for the separation of Sc from Y and the lanthanides, was established through laboratory-scale extraction process testing.[21] The final acid solution (pH = 0) is transferred to a mixer−settler, where it is thoroughly mixed in countercurrent with a 0.05 M solution of DEHPA in n-hexane. The best ratio of the aqueous-to-organic phase is found to be 10:1 (v/v) and the contact time at least 5 min.[19,21] At pH = 0, during mixing, Sc cations are extracted with DEHPA, while the other REE remain in the aqueous phase. The extracted Sc in the organic phase is then backstripped with 2 M NaOH (i.e., organic-to-aqueous phase = 1:1) for a contact time of at least 5 min. Therefore, an alkaline solution of the scandium hydroxo complex [Sc(OH)$_6^{3-}$] is produced, and the organic phase containing DEHPA/n-hexane is recycled. The Sc-rich aqueous solution leads, by use of appropriate processes, to scandium oxide or metallic Sc.

Pilot-Plant Setup. The pilot plant corresponding to the flow diagram (Figure 1) was designed and built in the Semi-Industrial Laboratory of the NTUA Chemical Engineering Department (Athens, Greece). NTUA personnel performed the design, and the construction was accomplished in collaboration with the German company Iludest Destillationsanlagen GmbH. All of the main parts of the pilot plant were made of glass (QVF; Table 1). The plant has a nominal capacity (batch) of 5 kg of RM in pulp form (∼50% water content), and it operates under ambient pressure and temperature conditions. It is supplied with safety devices, emergency sprinklers, and a ventilation system (chemical gases exhauster), as well as with two auxiliary networks: a compressed air one, which is used for the agitation of the liquids contained in the vessels, and a vacuum network, which is used for filling of the plant vessels with liquids from external tanks.

The pilot plant has been designed for batch operation. The processes comprising a full operation cycle (i.e., full treatment of a RM batch) are performed in series (one after the other). The plant performance is based on the principle of compartmentalization. According to this principle, a specific process is performed in a specific part of the total equipment (compartment, shown in Figure 1) which can be isolated from the rest of the units of the plant through the proper opening or closing of vanes. This mode of operation allows the safe and cost-effective investigation of the different processes comprising the whole separation method.

Leaching Procedure. The investigation of the leaching process has been performed in the respective isolated compartment shown in Figure 2. After the RM batch has been put in the vessel V1 and the full compartment has been air-sealed from the external environment, the vacuum pump (VP) operates in order to apply the necessary vacuum inside the vessels V3 and V1 (∼ −0.4 bar·g at PI of F2). Thus, the 0.6 N HNO$_3$
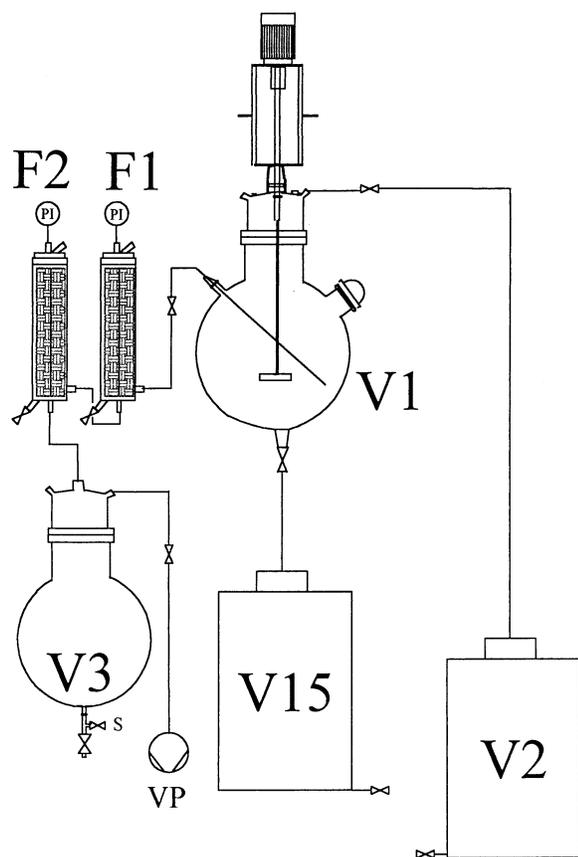
Figure 2. Leaching process compartment in detail.

solution contained in the V2 vessel that is open to the atmosphere is sucked to the V1, and it is dropped onto the mud under mechanical stirring. The suction of the solution is stopped, by stopping the VP and unsealing the V1 exhaust pipes, when the desired solid-to-liquid ratio is achieved in the V1 vessel. Then, a compressed air upstream (6−8 bar·g) is introduced into the mixture through the bottom of the V1, while the mechanical stirrer is still operated at low speed. After the combined agitation of the mixture for the desired period, the suspension was allowed to become calm and a coagulation agent (polymer electrolyte) was added. The addition of the polymer electrolyte allows the rapid precipitation of the solid particles (∼5 min). By operation again of the vacuum pump and having the V3 air-sealed and the V1 open to the atmosphere, the liquid phase of the mixture is sucked from V1 to V3. During this transportation, the liquid phase is channeled through the filters F1 and F2, yielding a clear solution in the V3. In some experimental runs, the same batch of RM is leached with a second amount of a 0.6 N HNO₃ solution (second stage of the leaching process) by following the above-described procedure. The liquid phase of the second stage is drained through the filters into the V3, which contains the first-stage product. Both products are mixed to one uniform solution by using compressed air flow into V3 after the unsealing of its exhaust pipes. The technical data of the leaching process equipment are listed in Table 1.

Analytical Instrumentation and Procedure. The composition of RM before and after the leaching process and the purity of the products were measured using various analytical methods in order to optimize the parameters of the leaching process. More specifically, the measurements of REE were carried out by induc-

tively coupled plasma-atomic emission spectrometry (ICP-AES)[12,24,26] and X-ray fluorescence spectroscopy (XRF),[12,25] while the measurements of Al, Fe, Si, Ti, Ca, V, and Na were carried out by XRF and atomic absorption spectroscopy (AAS). It should be noted that the precision of each method and the reliability of the measurements were first tested by standard samples [standard bauxite BX-N (ANRT)[27]].

(i) Reagents. Standard solutions of Y, Sc, and lanthanides, purity > 99.999% (CPI Int., USA), and of Al, Fe, Si, Ti, Ca, V, and Na (Fluka), 1000 μg/mL each, were used.

(ii) Instrumentation−Analytical Procedure. The XRF measurements were carried out with a X-ray fluorescence spectrometer (ARL, 8680S SIM/SEQ), the ICP-AES ones with a sequential analysis spectrometer (Jobin-Yvon 138 Ultrace) and the AAS ones with a Perkin-Elmer 3300 spectrometer. The dissolving of the samples for the ICP-AES and AAS measurements was achieved by a suitably developed fusion method with the ratio of sample/eutectic material = 1:3 (eutectic material: Li₂B₄O₇), at 1100 °C for 30 min.

Results and Discussion

Leaching Efficiency. A series of RM leaching runs was performed in the first from the feed end compartment of the pilot plant. The following process parameters were investigated: (i) the mode of agitation of the mixture (i.e., mechanical stirring and/or compressed air bubbling upstream), (ii) the ratio of solid-to-liquid phase in the leaching mixture (w/v), (iii) the acidity of the solution at the end of the leaching process, (iv) the number of stages in the leaching process, and (v) pretreatment of RM with concentrated acids.

(i) Mode of Agitation. Preliminary tests showed that mechanical stirring at high speed caused a waving of the liquid, while lower speed yielded poor mixing between solid and liquid phases. The use of a compressed air upstream caused extensive bubbling inside the mixture, and a homogeneous suspension of solid particles was developed. The simultaneous use of the mechanical stirrer at low speed allowed the dispersion of air bubbles and thus better mixing. The efficiency of the mixing procedure influences greatly the efficiency of the scandium transfer from solid particles to the liquid phase (η_{Sc}). Therefore, most of the pilot-scale leaching runs were performed under the best available conditions of agitation (i.e., combined use of mild mechanical stirring and compressed air upstream). Investigation of the mechanical agitation at an intermediate level of speed (300−500 rpm) showed a sufficiently high process efficiency compared to that of the combined mode. Hence, certain leaching runs of this study were performed under single mechanical stirring. Table 2 shows the process parameters of some representative pilot-scale leaching runs that were performed with leaching acid HNO₃ and various modes of agitation. The quantitative chemical analysis of Fe and REE contained in the filtered bulk leachate solutions produced in runs 4−6, 10−12, and 14 is quoted in Table 3. From the lanthanides, La and Nd were chosen as representative elements for the light rare earths (LREE), while Eu and Yb were chosen as representatives for the medium REE (MREE) and heavy REE (HREE), respectively. As can be seen from the comparison of runs 6 and 14 (runs of the same M_d/V ratio and agitation period but with different modes of agitation), the leaching efficiencies

Table 2. Process Parameters of Representative Pilot-Scale Leaching Tests with Solvent HNO₃ and Combined Agitation [Mechanical Stirring (m), Compressed Air Upstream (a), and Combined Mechanical Stirring with Compressed Air Upstream (m/a)]

run	τ (h)	stages	duration (h) and kind of agitation	leaching volume V (L)	mass of dry RM M_d (kg)	M_d/V (kg/L)
1	0.5	1 of 1	0.5 m	50	5	0.100
2	0.5	1 of 1	0.5 m	51.5	5	0.097
3	0.5	1 of 1	0.5 m	53	5	0.094
4	0.5	1 of 2	0.3 m + 0.15 m/a	25	0.5	0.020
5	1 (=0.5 + 0.5)	1 + 2 of 2	2 × (0.3 m + 0.15 m/a)	50	0.5	0.010
6	0.5	1 of 2	0.5 m/a	25	0.5	0.020
7	1 (=0.5 + 0.5)	1 + 2 of 2	2 × 0.5 m/a	50	0.5	0.010
8	0.5	1 of 2	0.5 m/a	25	0.5	0.020
9	1 (=0.5 + 0.5)	1 + 2 of 2	2 × 0.5 m/a	50	0.5	0.010
10	1	1 of 3	1 m/a	31.8	2.5	0.079
11	2 (=1 + 1)	1 + 2 of 3	2 × 1 m/a	61.8	2.5	0.040
12	3 (=1 + 1 + 1)	1 + 2 + 3 of 3	3 × 1 m/a	111.8	2.5	0.022
13	1 (=0.5 + 0.5)	1 + 2 of 2	2 × (0.3 m + 0.15 m/a)	50	1	0.020
14	0.5	1 of 1	0.5 m	50	1	0.020
15	2	1 of 1	2 m	50	1	0.020

a Example: description of runs 4 and 5. First stage (run 4): 0.3 h agitation with mechanical stirring (m), 0.15 h combined agitation of mechanical stirring plus introduction of compressed air upstream (m/a) and 0.05 h resting (total duration τ = 0.5 h). Second stage: The RM batch of the first stage was leached with fresh 0.6 N HNO₃ of the same quantity as that by the first stage. Duration: 0.3 h agitation with mechanical stirring (m), 0.15 h combined agitation (m/a) and 0.05 h resting (total duration τ = 0.5 h). The leachate of the second stage was mixed with that of the first. This is the product of run 5, which corresponds to the sum of the leaching volumes of both stages and to the leaching duration characterized as 0.5 h + 0.5 h.

Table 3. Quantitative Chemical Analysis of ME and REE Contained in the Filtered Bulk Leachate Solutions Produced in Runs 4−6, 10−12, and 14 of Table 2[a]

	run 4		run 5		run 6		run 10		run 11		run 12		run 14	
element	initial quantity (mg)	% efficiency	initial quantity (mg)	% efficiency	initial quantity (mg)	% efficiency	initial quantity (mg)	% efficiency	initial quantity (mg)	% efficiency	initial quantity (mg)	% efficiency	initial quantity (mg)	% efficiency
Fe	146.0 × 10³	2.7	146.0 × 10³	3.3	146.0 × 10³	3.3	850.2 × 10³	1.9	850.2 × 10³	2.6	850.2 × 10³	3.7	292.0 × 10³	2.4
Sc	60.6	53.6	60.6	68.0	60.6	52.5	313.8	50.7	313.8	67.9	313.8	72.5	121.2	52.0
Y	60.1	39.5	60.1	50.6	60.1	40.7	252.0	52.5	252.0	61.0	252.0	64.9	120.2	42.0
La	59.5	24.6	59.5	36.0	59.5	23.9	311.0	37.3	311.0	40.0	311.0	44.3	119.0	25.4
Nd	49.1	39.3	49.1	53.8	49.1	35.9	260.8	48.8	260.8	43.3	260.8	47.4	98.1	38.8
Eu	2.2	40.5	2.2	60.4	2.2	39.1	12.9	32.5	12.9	39.9	12.9	43.5	4.5	40.3
Yb	7.0	43.2	7.0	62.0	7.0	42.8	38.2	44.3	38.2	69.4	38.2	69.4	13.9	42.1

a The analysis is expressed in terms of the leaching process efficiency regarding the initial element quantity in the RM batch. % efficiency for an element $X = \eta_X \times 100$.

for Sc and lanthanides appear to be similar. This fact shows that single mechanical stirring at an intermediate speed could offer sufficient high efficiency compared to that of the combined agitation, especially for low M_d/V ratios of the leaching process.

(ii) Ratio of Solid-to-Liquid Phase. The variation of the experimentally measured final scandium concentration (w/v) in the bulk leachate solution with the ratio of the mass of the dry RM batch (M_d) to the leaching volume (V) is illustrated in Figure 3. The parameter of this graph is the duration of the leaching runs (h). As can be seen from Figure 3, the concentration of scandium in the bulk leachate solution increases by increasing the ratio M_d/V. These experimental measurements could be interpreted through eq 2 by substitution of time t with the full leaching period τ of each leaching test (Table 2). Also the volume of the leaching mixture could be approximated with the solvent volume V because only low M_d/V ratios were involved in the accomplished leaching tests. The area A of the solid−liquid interface is proportional to the number of solid particles participating in the process and, consequently, to the amount of RM (M_d). The ratio between A and M_d is the fraction of the total specific surface area of RM particles that participates in the leaching process ($S = A/M_d$). The RM particles are mainly comprised of compounds of ME that show a low dissolution in the leaching process under consideration. Therefore, the removal of rare earths
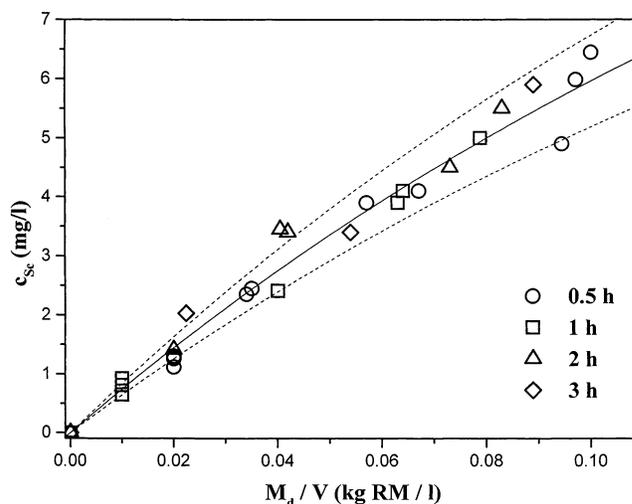
Figure 3. Sc concentration (c_{Sc}) in the bulk solution at the end of each leaching run versus the ratio (M_d/V) of dry RM weight (kg) to leachate solution volume (L). Symbols are indicative for the duration of mixture agitation as follows: (◯) 0.5 h, (□) 1 h, (△) 2 h, (◇) 3 h. The solid curve represents the theoretical fitting of eq 4. The dashed curves define graphically the margin of the average prediction error (13%).

from the solid particles is expected to cause minor changes to their physical structure, avoiding substantial particle shrinkage and conserving their approximately

constant external surface areas. This fact matches the well-known unreacted-core model, valid for the fluid−particle chemical reactions[28] referring mainly to the iron, which is the most abundant element in the RM.[19,21,22] According to this model, the reaction occurs first at the outer surface of the particle, and then the reaction zone moves into the solid, leaving behind completely converted material and inert solid. The rate-controlling step in general can be either a diffusion step or a chemical reaction one. In the case of the leaching process, the rate-controlling step is usually the diffusion through the fluid film surrounding the particle.[23] This rate is strongly dependent on the external surface area of the particles. Although the unreacted-core model can be supposed for the dissolution of rare earths (reactant) and ME (inert) during the leaching process, the model cannot be directly applied to this process because of existing deviations of uncertain influence. Such deviations are the partial, but relatively low, dissolution of RM ME and the mechanical particle size reduction due to the applied agitation. Nevertheless, the assumption of a constant A/M_d ratio during leaching tests ($A = SM_d$, where $S =$ constant) provides the necessary theoretical simplicity for the interpretation of the experimental data. The uncertainty for the validity of this assumption can be surpassed if the meaning of the S parameter changes from that of an instant magnitude to that of a time-weighted average.

Taking into account the above considerations, the form of eq 2 that interprets the experimental results of Table 3 is

$$c_{Sc} = c_s(1 - e^{-K_L S\tau(M_d/V)}) \qquad (3)$$

It is depicted in Figure 3 that leaching tests of the same M_d/V ratios but of different leaching periods show slight variation of the final Sc concentration compared to the experimental error margin. This fact indicates that the leaching periods used in this work were long enough to allow one to approach the state of equilibrium between the participating ions in the leaching solution. Therefore, the time-dependent part of eq 3 is considered to remain constant for the full set of experimental tests, i.e., $e^{-K_L S\tau/w} \approx$ constant, where w is the unary operator for dimension correction. Additionally, the effect of the agitation period in the process efficiency could be indicative of the role of mass transfer as the controlling step of this process evolution. The neutralization reaction and the cation dissolution in the saturated solution in contact with the solid particles are generally rapid steps, a fact consistent with the previous assumption.

For the M_d/V ratios used in this work, the general expression of eq 3, which is described by eq 4, can be fitted to the respective experimental data of Figure 3 through nonlinear least-squares regression, where $p_1 =$

$$c_{Sc}(M_d/V) = p_1(1 - p_2^{w(M_d/V)}) \qquad (4)$$

$c_s^* \approx$ constant (mg/L), $p_2 = e^{-K_L S\tau/w} \approx$ constant, and $w = 1$ L/kg.

Thus, the regression on the experimental data of c_{Sc}-(M_d/V) with use of the Marquardt−Levenberg optimization method was found to be $p_1 = c_s^* = 15.03$ mg/L and $p_2 = e^{-K_L S\tau/w} = 0.006\ 35$, with an average prediction error of 13%, which does not exceed 20%. The solid curve illustrated in Figure 3 is the graphical presentation of the determined function. The dashed curves define

graphically the margin of the average prediction error. It is mentioned that, in general, the prediction error is not exclusively related with the experimental error, but it includes possible deviations between the assumptions of the theoretical model and the real experimental conditions. Such assumptions valid for eq 4 could be the independence from the leaching duration and the constant ratio between A and M_d during a full leaching test. Also, eq 3 shows that the Sc concentration in the saturated solution in contact with the RM particles (c_s) is approximately constant during the evolution of each individual leaching test (i.e., with a given M_d/V ratio). Nevertheless, this concentration seems to increase with increasing M_d/V ratio and to approach a maximum value (c_s^*) in the case of extremely high M_d/V (≈ 1). It should be noted though that, in this case, other parameters such as poor mixing between solid and liquid phases because of the high M_d/V ratio or a very high ionic strength of the resulting leaching liquid because of the dissolution of ME, parameters that are not taken into account in the range of the M_d/V ratios used in this work, may lower the experimental yields for the Sc concentration, from the predicted maximum (c_s^*) value. The calculated parameter p_1 of eq 4 represents this maximum value of the saturated solution (c_s^*) and shows that the accomplished pilot-scale leaching runs yielded a Sc concentration in the bulk leachate solution of up to 3 times less than c_s^*.

Furthermore, using eq 4 and the necessary process parameters (Table 2) can produce theoretical predictions of the Sc efficiency (η_{Sc}) for leaching periods exceeding 0.5 h. Substituting in eq 4 c_{Sc} with m_{Sc}/V and using the relationships $\eta_{Sc} = m_{Sc}/m_{Sc,RM}$ and $C_{Sc,RM} = m_{Sc,RM}/M_d$,

$$\eta_{Sc} = \frac{15.03}{(M_d/V)C_{Sc,RM}}[1 - 0.00635^{(M_d/V)(1\ L/kg)}] \qquad (5)$$

where $C_{Sc,RM}$ is the w/w concentration of Sc in the dry RM (mg of Sc/kg of dry RM), M_d is expressed in kg of dry RM, and V is in L.

(iii) Acidity of the Solution at the End of the Leaching Process. The effect of the acidity in the efficiency of the leaching procedure was studied by slightly varying the amount and concentration of HNO_3 and RM pulp, keeping the ratio M_d/V constant. The results are presented in Figure 4. Thus, for $M_d/V = 0.1 \pm 0.05$, a one-stage leaching procedure with agitation time $\tau = 0.5$ h, and a final pH between 0 and 0.5, which is the range of the optimum recovery of Sc according to laboratory-scale experiments,[19] it is depicted that η_{Sc} and η_Y decrease by increasing the pH from 0.15 to 0.44, while η_{Fe} remains practically unaffected.

(iv) Number of Stages in the Leaching Process. Several experimental runs were performed, varying the number of stages of the leaching process, by adding successive amounts of appropriate concentrations of acid to various amounts of RM pulp, maintaining the pH constant during the whole procedure. Representative results of these experiments are shown in Figure 5, where it is depicted that, for a pH = 0.35 ± 0.01 and three successive stages of treatment of the same amount of RM pulp, η_Y and especially η_{Sc} show a substantial increase compared to a slight increase of η_{Fe}.

(v) Pretreatment of RM with Concentrated Acids. Additionally, other pilot-scale leaching runs were performed, including initial pretreatment of the RM pulp. A representative case included 1 kg of RM in a
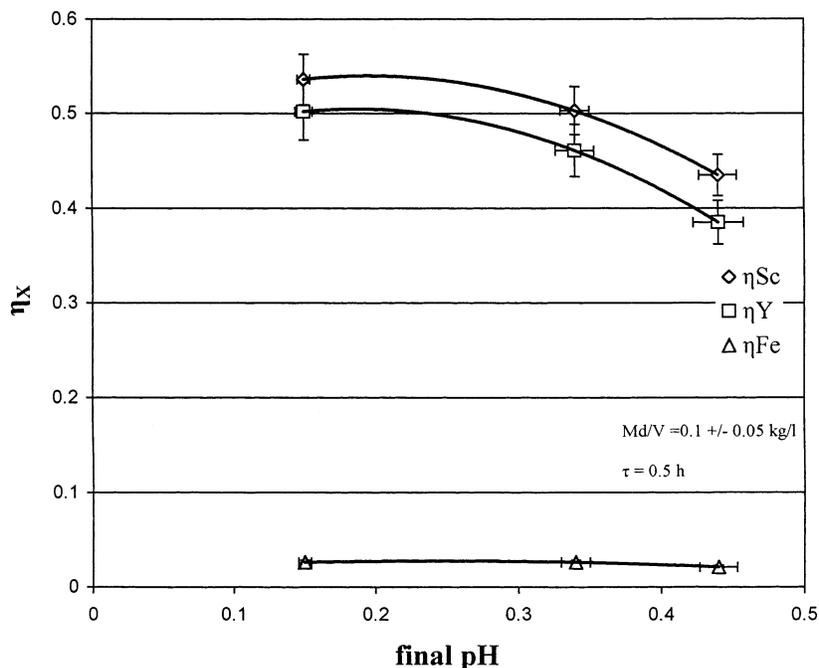
Figure 4. Efficiency of the leaching process for Sc, Y, and Fe versus the final pH of the leaching solution for $M_d/V = 0.1 \pm 0.05$ kg of dry RM/L and $\tau = 0.5$ h.
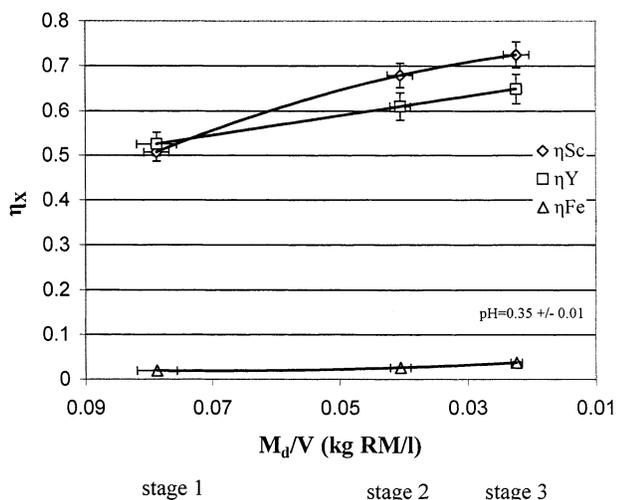
Figure 5. Efficiency of the leaching process for Sc, Y, and Fe versus the number of the used stages and the respective total M_d/V ratio.

dry basis and pretreatment with concentrated acids, i.e., 5 L of 6 N HNO$_3$ and 2.2 L of 12 N HCl. The resulting solution was agitated for 30 min, and then it was diluted with 0.6 N HNO$_3$ until a M_d/V ratio equal to 0.02 was achieved. The diluted solution was further agitated for 0.5 h more. Chemical analysis of the filtered bulk solution did not show a significant change of the process efficiency compared to that of the simple leaching procedure ($\eta_{Sc} = 0.495$, $\eta_Y = 0.370$, $\eta_{Fe} = 0.028$, and $c_{Sc} = 1.20$ mg/L).

Conclusions

The highest Sc concentrations in the pilot-scale leaching tests were achieved using proper agitation and increased M_d/V ratios [dry RM weight (kg) to leaching acid volume (L)], as well as by increasing the number of stages of the leaching process and keeping the acidity of the bulk leachate solution at pH nearly zero. Taking into account that process economics for the whole separation method demand a high Sc concentration in the leachate solution,[22] a high M_d/V ratio (equal or more than 1:10) combined with a sufficient agitation period in one stage and with a pH range between 0 and 0.2 in order to obtain the highest ratio of c_{Sc}/c_{Fe}, yields the most favorable results. The process economics demand for a high Sc concentration has arisen from a combination of the following reasons: (i) RM has only marginal transportation cost as being a waste, (ii) the chemical reagents needed for the full separation method have cost, and their consumption is proportional to the leachate solution volume, and so (iii) a large RM batch with a low leachate volume produces a high amount of Sc (high profit) with a low reagent consumption (low cost).

The possible industrial application of the method would include leaching equipment of continuous flow by using countercurrent RM washing in a series of appropriately designed thickeners. The operation of each industrial thickener is simulated with the operation of the pilot-scale batch leaching equipment under different initial conditions and for leaching and agitation periods equal to the possible residence time of solids for each thickener. The proposed, in this work, leaching model provides the necessary predictions of the Sc concentration and process efficiency for the design of RM leaching equipment. Furthermore, a theoretical mechanism (unreacted-core model with external diffusion control) for the explanation of this leaching process is proposed. This model approaches the separation results between scandium and iron, by taking into account the fact that these elements are released with extremely different rates from the RM particles where they were initially bound in the form of solid chemical substances. Nevertheless, the confirmation of the validity of the model for this process is a subject of further laboratory-scale kinetic testing. Also, future further experimentation in pilot-scale leaching that will be adapted on the data required from the operation model

of a continuous-flow leaching system will allow the final design of the respective industrial equipment.

Nomenclature

DEHPA = diethylhexylphosphoric acid or bis(2-ethylexyl) phosphate [with up to 40% mono(2-ethylexyl) phosphate]

c_{Sc} = concentration (w/v) of scandium in the bulk of the solution at the end of a leaching test (mg/L)

$C_{Sc,RM}$ = concentration (w/w) of scandium in the dry red mud, expressed as a weight fraction (mg/kg)

m_{Sc} = total mass of scandium transferred from the solid particles to the liquid solution in one full leaching test (mg)

$m_{Sc,RM}$ = mass of scandium contained in a red mud batch (mg)

ME = main elements of red mud (i.e., Fe, Al, Ca, Si, Ti, and Na)

p_1, p_2 = parameters defined by nonlinear least-squares regression

REE = rare-earth elements

RM = red mud

M_d/V = ratio of dry red mud weight (kg) to leachate solution volume (L)

η_X = efficiency of the leaching process regarding an element X of the red mud

τ = leaching period (h)

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