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Process Design Aspects for Scandium-Selective Leaching of Bauxite Residue with Mineral Acids

Konstantinos Hatzilyberis [1],*, Theopisti Lymperopoulou [1], Lamprini-Areti Tsakanika [1], Klaus-Michael Ochsenkühn [1], Paraskevas Georgiou [1], Nikolaos Defteraios [1], Fotios Tsopelas [1], Maria Ochsenkühn-Petropoulou [1],*

[1] School of Chemical Engineering (Chem. Eng.), National Technical University of Athens (NTUA); 9, Iroon Polytechniou St., 15780, Athens, Greece; ksh@chemeng.ntua.gr ; oxenki@central.ntua.gr

* Correspondence: ksh@chemeng.ntua.gr ; oxenki@central.ntua.gr ; Tel.: +30-210-772-3296, +30-210-772-3094

Abstract: Aiming at the industrial scale development of a Scandium (Sc)-selective leaching process of Bauxite Residue (BR), a sufficiently numerous set of process design aspects has been investigated, by appropriate exploitation of available experimental data. The interpretation of experimental data for Sc leaching yield, with sulfuric acid as the leaching solvent, has shown significant impact from acid feed concentration, mixing residence time, liquid to solids ratio, and times of leachate re-usage onto fresh BR. The thin film diffusion model, as the fundamental theory for leaching, either with constant particle size for selective leaching, or with shrinking particle size for less-, or non-, selective leaching, interprets sufficiently well the relevant experimental data. In both cases, a concept for an unyielding core supplements the basic model. Especially for the selective leaching mild conditions, the simplest model version keeps step with the experiments, since both prove 1st order kinetics, while especially for the extreme conditions including very low solvent excess, it is proposed a combined conversion rate model with diffusion and chemical reaction inside particles. The maximization of Sc recovery per unit of consumed solvent (i.e., specific recovery) emerged as highly critical for the process economics.

Keywords: Scandium; REEs; bauxite residue; selective leaching; process design aspects; thin film diffusion model; unyielding core; specific recovery

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1. Introduction

The exploitation of BR from the aluminum (Al) industry, as a resource for production of Rare Earth Elements (REEs), with main focus on Sc, emerges as a well promising perspective for a new symbiotic era in the metallurgical processes [1-3]. This concept is fully aligned with the European Union's target for sustainable access to Critical Raw Materials (CRMs) as being of high importance for economy, competitiveness and the environmental protection [3-5].

BR, either as alkaline wet red mud, or as dried ferro-alumina, has to be treated with a leaching process of enhanced selectivity for Sc and of the lower possible yield for the main elements [6-8]. The liquid product of this process (i.e., the Pregnant Leach Solution (PLS)) is led to other advanced extraction methods that could enhance the concentration in Sc from ppm level to higher percentages [3,9,10]. The pertinent REEs-selective leaching process with use of mineral acids was initially developed in laboratory scale [7,8], by NTUA/Chem.Eng./ Lab. of Analytical and Inorganic Chemistry, while it was later scaled-up to a pilot plant [9,10] inside the premises of NTUA/Chem.

Eng., in cooperation with members of the Chemical Process Engineering Lab. of the same School; therefore, an over 20 years experience exists [3, 6-13].

This work presents the investigation of a sufficiently numerous set of design aspects [12], for a selective leaching process with sulfuric acid as solvent and with focus on recovery of Sc, as it is the far most valuable trace element of BR. However, it was emerged that the economic viability of the process depends substantially on the maximization of Sc recovery per unit of consumed acid [11]. Apart from the Sc-selective character of this process, the relevant experimental investigation aimed also at the lower possible iron (Fe) leaching yield, as long as it is the most abundant metal in most of BRs, and especially in the examined Greek BR, in such an extent that could impose complications to the following Sc enrichment stages. Moreover, the process preserves the bulk quantity of BR metallic content in the precipitated solids and therefore it allows its further metallurgical exploitation.

2. Materials and Methods

2.1. The Resource

The raw material and metals resource to be exploited is BR from alumina production with the Bayer process. It is the solid waste industrial stream of the Greek industry Aluminium of Greece (AoG), which is located in the Greek mainland [14].

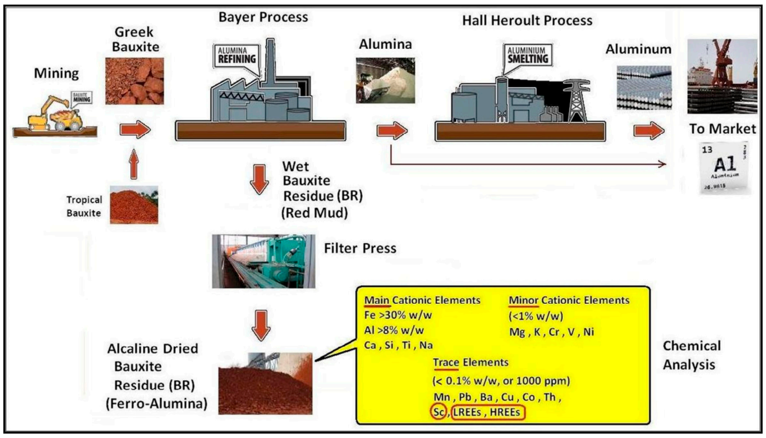

Figure 1. AoG: The production processes, the removal of BR and its coarse cationic analysis [14,15].

Table 1. Concentration [g/dry tn - ppm] of REEs in Greek BR batches (1993-2012) [6,13,16,17]

Year	1993	2001	2007	2012	Mean Value
Element					
Sc	127.9	107.0	130.0	110.0	118.7±11.9
Y	91.2	94.0	94.0	115.0	98.6±11.0
La	149	101.5	132.0	147.6	132.5±22.1
Ce	418	404.0	492.0	498.0	453.0±48.9
Nd	115	86.3	88.5	92.5	95.6±13.2
Sm	28.9	20.5	22.0	24.3	23.9±3.7
Gd	23.3	23.4	20.5	21.3	22.10±1.45
Eu	5.0	3.7	4.0	4.9	4.40±0.65
Er	12.2	12.7	13.1	10.9	12.20±0.96
Yb	15.6	15.0	14.4	15.8	15.20±0.63
Total	986.1	868.0	1010.5	1040.3	976.2±75.5 (±7.7%)

The production line of this industry (horizontal sketches of Fig.1) includes the mining at Parnassus and Ghiona Mountains, the eventual mixing with imported tropical bauxite, the alumina refining unit with the Bayer process, the Al smelting unit with the Hall Heroult electrolytic process and, finally, the transportation out-port. Along the residual solids stream from Bayer Process to the

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disposal landfills (vertical pictures of Fig.1), the wet BR from alumina refining (Red Mud) is separated in a filter press unit to solid BR with about 25% moisture (Ferro-Alumina) and to recovered sodium hydroxide solution that returns to the Bayer process.

It is also presented in Fig.1 (downright yellow frame) a coarse cationic chemical analysis of the Ferro-Alumina, which is divided in Main, Minor and Trace Elements [6,9,15,17]. Fe and Al are the most abundant main elements, while trace elements include significant amounts of Sc, as well as some amounts of other Light and Heavy REEs [16]. Table 1 shows the detailed chemical analysis of Greek BR in Sc and other REEs, with its variation during the last 25 years, where the average concentration for Sc is ~120 ppm and for total REEs ~1000 ppm [6-8,16,17].

2.2. The Target Element

The evaluation of Greek BR as a resource of REEs provides strong evidence for an economically viable recovery, especially for Sc.

The viable exploitation arises from the concentration of Sc in the raw material that, even apparently low, it is comparable to these of the globally exploitable Sc resources. A worthwhile characteristic excerpt, from current investing information [18], mentions: "*Scandium is not particularly rare on the Earth's surface. In fact, it is more abundant than lead, mercury and precious metals. However, the metal also has a low affinity for other minerals. That means it rarely manages to concentrate at higher grades alongside other metals, making commercially usable deposits of this critical material very rare.*" Therefore, Sc is not indeed a rare element in nature, but it is a very rarely concentrated element, particularly over 100 ppm in non-radioactive minerals. Consequently, Greek BR, with the average 120 ppm of Sc, can be considered as a valuable Sc resource.

The exclusive exploitation, among REEs content of BR, derives from Table 2, where it is presented the economic potential of Greek BR in REEs, or otherwise the commercial value of the entire BR content in REEs, if any element was to be fully extracted in its market benchmark oxide. Table 2 estimations, with use of standard prices from the end of 2014 and 2016, show that a percentage well above 95% of the total Greek BR economic potential is coming exclusively from its Sc content. These facts make selection of Sc to be fully justifiable.

Table 2. REEs Economic Potential in Greek BR (Value of REEs in US $ / ton of Greek BR) [6,12,13]

REEs oxides	**Average concentration of REEs oxides (g/tn)**		**2014 (31 Dec.)**		**2016 (31 Dec.)**	
	Bauxite	**BR**	**Price of Benchmark Oxide Grade (US $/kg) [19]**	**Value (US $/ tn BR)**	**Price of Benchmark Oxide Grade (US $/kg) [19]**	**Value (US $/ tn BR)**
Sc	92	195	3800	741.00 [1]	4200	819.00 [2]
Y	71	127	20	2.54	6	0.76
La	102	175	6.5	1.14	2	0.35
Ce	262	490	5.5	2.70	2	0.98
Pr	16	30	134	4.02	52	1.56
Nd	72	134	69	9.25	42	5.63
Eu	3	6	1100	6.60	150	0.90
Gd	15	27	44	1.19	32	0.86
Dy	8	15	525	7.88	230	3.45
Er	9	20	69	1.38	34	0.68
Total	650	1219		777.70		834.17

[1] purity 95.3% [2] purity 98.2%

Furthermore, in the official sector context, European Commission's classification of CRMs [4] ranks Sc as critically high on supply risk, but low on economic importance (2014). Meanwhile, the dwindling of available stockpiles combined with the globally limited production and the evolution of new applications in semiconductors, electronics, and airplane manufacturing, are upraising both the "Supply risk" and the "Economic importance" [2,18,20-22]. Therefore, a future approach of the CRMs chart could elevate Sc in both axes.

2.3. The Investigating Process

A viable Sc exploitation demands an effective design for its recovery processes that will be oriented to the specific requirements of the raw material (here, Greek BR). This work investigates the opener process in the series of the required operations for Sc recovery from BR deposits. It proposes a hydrometallurgical treatment of raw BR with mineral acids being capable to recover the maximum possible Sc content of ferro-alumina per consuming quantity of acid, with the main elements dissolution to remain sufficiently low. Process development has to take into account the following:

- Optimized conditions concerning the selectivity to Sc
- A leachate (i.e., liquid phase of leaching pulp) reflux stream for intensification and especially for enhancement of Sc concentration
- Mild environmental impact from acidic solids residue
- The lower possible operating cost

Greek BR leaching process has been thoroughly investigated in laboratory level, in the context of a long-lasting research [6-11] by NTUA/Chem.Eng/ Lab. of Analytical and Inorganic Chemistry, where nitric acid (HNO_3) was used as leaching solvent. However, the compliance with the latter two targets converged recently to the selection of the sulfuric acid (H_2SO_4) as the most appropriate solvent, since its main rival regarding the selectivity and the Sc concentration targets, the nitric acid (HNO_3), shows inadequate compliance with EU environmental regulations for waste solids disposal and significantly higher operating cost [11] (Phase I).

The focus of this work is on the process design aspects that are the necessary supplies of knowledge for an effective process scaling-up and for its implementation in large scale applications. The design aspects investigation has been based on a preliminary, for the context of [3], experimental data set from Greek BR leaching with H_2SO_4 solutions, which has been presented by the authors, either partially or entirely, in [3,11-13].

3. Results (Design Aspects)

The investigated design aspects are described as follows:

- Selection of process parameters that are considered to affect Sc recovery
- Kinetic investigation for different feed acid concentrations and theoretical conclusions
- Impact of Liquid to Solids (L/S) ratio to the Sc leaching yield and its theoretical interpretation
- The upper limits of Sc specific recovery with recycling of the leachate in the leaching reactor
- Development of a unified mathematical expression for the Sc leaching yield

Seven independent parameters, that are considered to have possible impact on the Sc yield for BR leaching, were experimentally investigated, in preliminary level and mostly for single variation of each parameter. The detailed investigation of parameters and their synergy effect are currently investigated in the context of "Scandium – Aluminum Europe" (SCALE) Research Project of the EU Horizon 2020 Program [3]. The already available laboratory experimental investigation of Sc leaching yield with H_2SO_4 solutions has proven significant impact from:

- Acid feed concentration and the dependent pH value of leachate
- Mixing residence time, especially if it is lower than 1h
- (L/S) ratio, at the leaching reactor feed
- Times of the same leachate re-usage onto fresh BR batches

However, temperature variation (ambient - 90°C) under atmospheric pressure, different agitation modes and selected particle size fractions did not show any significant Sc yield variation, within the investigated range of the preliminary experiments [11] (Phase II).

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Relevant experimental investigations [7,9,16,17,23], that concern a variety of acids and conditions, show a similar set of impacts, either clearly, or as a marginal trend.

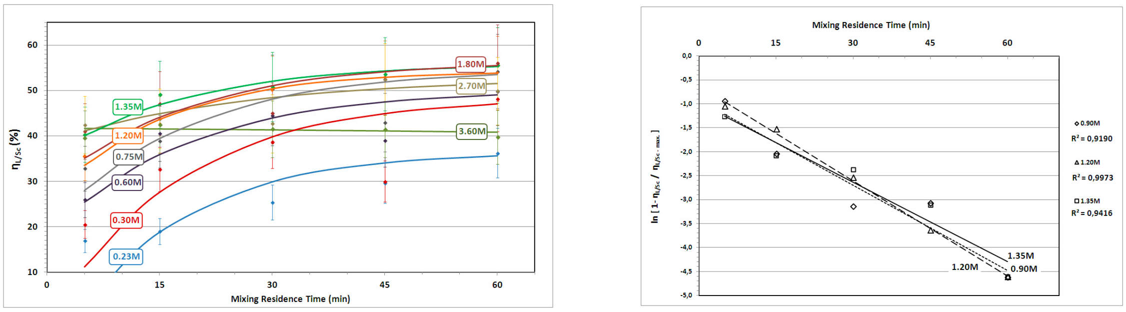
3.1. Kinetics (mixing time impact)

The first investigation concerns the process kinetics, with the feed acid concentration to be a parameter. Fig.2a shows the variation of Sc yield with mixing residence time, when different concentrations of sulfuric acid solutions, constant (L/S) ratio (50:1) and sufficient agitation have been used. The colored curves show fittings of first order kinetics on the different experimental data series.

Fig.2b shows three characteristic examples of Sc-selective leaching conditions, where the logarithmically linearized first order kinetics show sufficiently adaptation on the relevant experimental data. The appended linear fitting coefficient of determination (R^2) can also prove it, since it sufficiently approaches the unit, especially when we take into account that the experiments regard to separate tests of different BR samples, but of the same lot, and that BR is a granular solid material with broadly variable Sc concentration. Accordingly, the kinetic behavior, with acid feed concentration to be a parameter, could be formulated by eq.(1):

$$\eta_{L/Sc}(C_{Af}, t) = \eta_{L/Sc-max.}(C_{Af}) \cdot \left(1 - e^{-m(C_{Af}) \cdot t + k(C_{Af})}\right), \tag{1}$$

where: t is the mixing residence time as a variable, C_{Af} is the acid feed concentration as a variable, $\eta_{L/Sc}$ is the leaching fractional yield for Sc (mg of Sc in the leachate/ mg of Sc in the BR feed), and $\eta_{L/Sc-max.}$ is a theoretical maximum of $\eta_{L/Sc}$ (approximately equal to the experimental yield value for mixing periods exceeding the practical duration of kinetic effects).



(**a**) (**b**)

Figure 2. (a) Variation of Sc leaching yield ($\eta_{L/Sc}$) with mixing residence time, with feed acid (sulfuric) concentration as a parameter, constant (L/S)=50:1, mechanical stirring and ambient conditions. The colored curves show 1st order kinetics fittings to the relevant experimental data [$\eta_{L/Sc} = \eta_{L/Sc-max.}(1-e^{-mt+k})$]. (b) Variation of the logarithmically linearized first order kinetics, in terms of Sc leaching yield, with the mixing residence time, for 3 feed acid (sulfuric) concentrations that lead to Sc-selective leaching results.

This is a typical form of a 1st order kinetics correlation, but it is enhanced with an extra term (k) for correction of Sc yield uncertainty at leaching start (i.e., for t=0). The 1st order kinetic approach is in accordance with a conditional version of the general diffusion mechanism, which describes the transfer of ingredients from solid particles to the bulk liquid volume of a solvent ([24] (§10.2), [10] (eq.(2)), and eq.(6) of this work).

By using multiple least squares regression, the correlation parameters m and k are converted to concentration dependent functions. The mathematical terms for the kinetic data processing are described in Table 3(a). According to the scheme of Table 3(b), for each discrete time value (τ_i, i=1...5), a 4th order polynomial fitting gives a respective polynomial function. Any given value C_{Af}*, for the variable C_{Af} of the 5 polynomials, leads to the calculation of 5 values of yields (η_i, i=1...5), one for each of τ_i, i=1…5. The linearized eq.(1) is fitted on the 5 η_i values, by Least Squares Regression Line (LSRL), to give the best set of (m, k) parameters, or otherwise to give the particular kinetic equation for the specific concentration C_{Af}*. An example of these calculations is included in Table 3(c). The advantage of this data interpretation method is that Sc leaching yield is expressed as an

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explicit function of feed acid concentration and mixing residence time. It is elucidated here that symbol t refers to mixing residence time as a variable, while the Greek symbol τ refers to a discrete time value.

Table 3. (a) Description of kinetic data processing in mathematical terms. (b) Scheme for a comprehensible visual presentation of kinetic data processing. (c) An example of calculations.

(a)

From the 5 experimentally tested mixing residence times (τ_i, i=1…5), i.e., τ_1=5min, τ_2=15min, τ_3=30min, τ_4=45min, τ_5=60min, are derived:

•m(C_{Af})= - Slope of *LSRL* {pairs (τ_i , ln[1- ηpol$_i$ (C_{Af})/$\eta_{L/Sc\text{-}max.}$(C_{Af})])},

•k(C_{Af}) = Interception Point of *LSRL* { pairs (τ_i , ln[1- ηpol$_i$ (C_{Af})/ /$\eta_{L/Sc\text{-}max.}$(C_{Af})]) }, where:

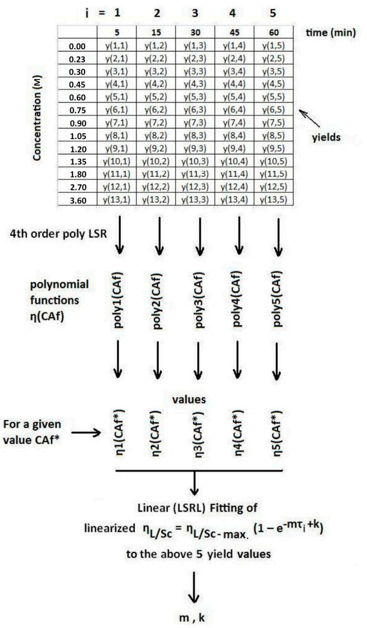
ηpol$_i$ (C_{Af}) = 4th ord. Polynomial LSR {pairs (C_{Afj} , ηexp.|C_{Afj} , τ_i)}, j=1..13 (or C_{Afj} = 0.0 M, 0.23M, 0.30M, … ,3.60M), i=1…5,

where: ηexp. is the experimentally measured Sc yield for concentration C_{Afj} after τ_i mixing residence time,

• $\eta_{L/Sc\text{-}max.}$(C_{Af}) = 1.01 · MAX [ηpol$_i$ (C_{Af})] , for i=1…5.

Note: $\eta_{L/Sc\text{-}max.}$ is taken as 1.01 times (or, 1% more than) the maximum appearing yield in the [0,60]min time interval, as far as any derived logarithmic values from 1st order kinetics linearization to be valid.

(b)



	i = 1	2	3	4	5
	5	15	30	45	60
0.00	y(1,1)	y(1,2)	y(1,3)	y(1,4)	y(1,5)
0.23	y(2,1)	y(2,2)	y(2,3)	y(2,4)	y(2,5)
0.30	y(3,1)	y(3,2)	y(3,3)	y(3,4)	y(3,5)
0.45	y(4,1)	y(4,2)	y(4,3)	y(4,4)	y(4,5)
0.60	y(5,1)	y(5,2)	y(5,3)	y(5,4)	y(5,5)
0.75	y(6,1)	y(6,2)	y(6,3)	y(6,4)	y(6,5)
0.90	y(7,1)	y(7,2)	y(7,3)	y(7,4)	y(7,5)
1.05	y(8,1)	y(8,2)	y(8,3)	y(8,4)	y(8,5)
1.20	y(9,1)	y(9,2)	y(9,3)	y(9,4)	y(9,5)
1.35	y(10,1)	y(10,2)	y(10,3)	y(10,4)	y(10,5)
1.80	y(11,1)	y(11,2)	y(11,3)	y(11,4)	y(11,5)
2.70	y(12,1)	y(12,2)	y(12,3)	y(12,4)	y(12,5)
3.60	y(13,1)	y(13,2)	y(13,3)	y(13,4)	y(13,5)

(c)

Example: From the experimental data of the Concentration vs. Time table of the above scheme (b), with fitting of 4th order polynomials, are produced 5 polynomial functions, one for each experimental mixing residence time value. For example, if C_{Af}*=0.21M (i.e., an intermediate value between experimentally investigated values), these polynomials give: $\eta_{L/Sc}$(5min)=13.92%, $\eta_{L/Sc}$(15min)=19.95%, $\eta_{L/Sc}$(30min)=24.38%, $\eta_{L/Sc}$(45min)=22.13%, $\eta_{L/Sc}$(60min)=30.41%. LSRL fitting of linearized eq.(1) onto these 5 values gives: m=3.5826 and k=0.027, when: $\eta_{L/Sc\text{–}max.}$=1.01 · MAX[$\eta_{L/Sc}$(τ_i), i=1…5] = 1.01 · 30.41% = 30.71%.

Therefore: $\eta_{L/Sc}$ (C_{Af}=0.21M, t) = 30.71% · (1–$e^{-3.5826.t+0.027}$), when (L/S) =50:1 (L of acid/ kg dry BR).

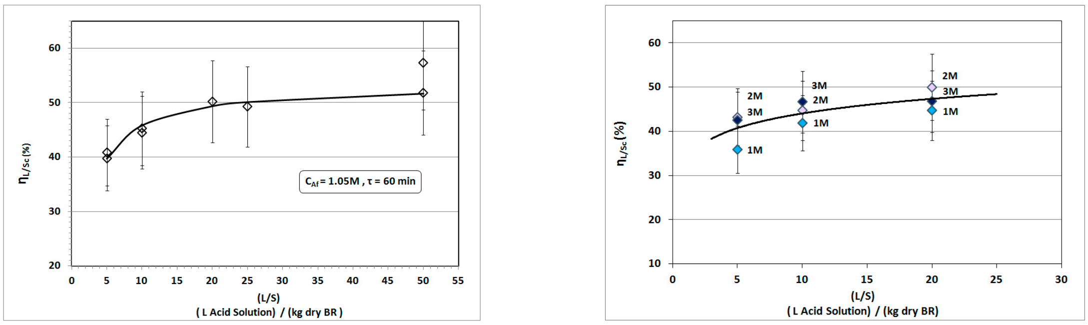
3.2. Solvent Excess (L/S) Impact

Fig.3a shows a typical variation of Sc yield with (L/S) ratio for given feed acid concentration and residence time. A similar Sc yield investigation, but with combined variation of (L/S) ratio and feed acid concentration (C_{Af}), is presented in Fig.3b. This graph offers a visual proof that, for a given (L/S) ratio and for a mixing residence time beyond any substantial kinetic impact, the Sc yield variation with feed acid concentration is limited and comparable to the experimental fluctuations caused by the high variability of Sc content in the raw BR.

For the interpretation of this kind of experiments, it has been used the Fick's second law, in the context of the simple thin film diffusion model with constant product of mass transfer coefficient and particles specific surface area, as it is seen in eq.(2). A similar form of this equation is included in the originally proposed mathematical modeling for Sc recovery from Greek BR with HNO_3 leaching (eq.(5) of [10]), in a published part of authors' work.

$$\eta_{L/Sc} = (L/S)\,\frac{c_S}{(C_{Sc})_{BR}}\left(1 - e^{-\frac{K_L S \tau}{(L/S)}}\right), \tag{2}$$

where: (L/S) is the Liquid to dry Solids ratio (v/w), and with subscript r to mean inside the leaching reactor and subscript f to mean at the leaching reactor feed, it is: $(L/S)_r \approx (L/S)_f$, since the concentrations basis is the liquid volume of the solution; c_s is the concentration (w/v) of the saturated solution in contact with the particles, $(C_{Sc})_{BR}$ is Sc concentration (w/w) in dry BR solids, $K_L(=k'/b)$ is the mass transfer coefficient, k′ is the diffusion coefficient (it is approximately equal to the liquid-phase diffusivity D_L and it could be taken as approximately constant), *b* is the effective thickness of the liquid film surrounding the particles, $S(=A/M_d)$ is the specific surface area of BR particles participating in the leaching process (dry basis), A is the total area of the solid-liquid interface, M_d is the total mass of dry BR particles, and τ is the mixing residence time.



(**a**) (**b**)

Figure 3. (a) Variation of Sc leaching yield ($\eta_{L/Sc}$) with (L/S) ratio, for feed acid (sulfuric) concentration C_{Af}=1.05M, for constant mixing residence time τ=60 min, mechanical stirring and ambient conditions. Solid line shows fitting of eq.(3) to the experimental data. $(C_{Sc})_{BR}$=97ppm. (b) Variation of $\eta_{L/Sc}$ with (L/S) for three different feed acid (sulfuric) concentrations (1M, 2M and 3M), under conditions of (a). Solid line is an automatic logarithmic fitting. Data of (b) have been acquired from a different Greek BR lot, with comparison to the entire data set of this work. Therefore, their use is only qualitative.

A re-arrangement of eq.(2), to make it suitable for non-linear fitting to relevant experimental data where mixing time is beyond the time range of substantial kinetic impact, gives eq.(3):

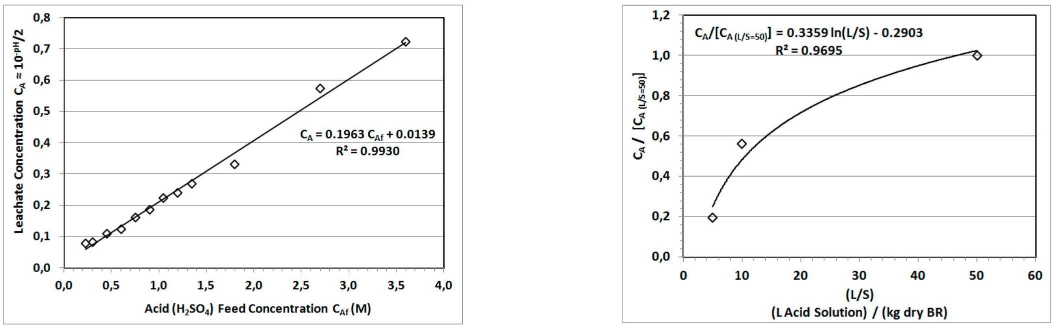
$$\eta_{L/Sc}\big((L/S)\big) = c_s{}^* \cdot \frac{(L/S)}{(C_{Sc})_{BR}} \cdot \left(1 - q^{\frac{1}{(L/S)}}\right) , \qquad (3)$$

where: $c_s{}^*$ and q are both regression parameters; the first is identified as the time average particle surface concentration (w/v), or as a theoretical upper limit for Sc concentration in the leachate, and the second is identified as the term $e^{-K_L S \tau}$ of eq.(2), which can be considered as a constant approaching zero and common for any data set practically standing off the kinetic effects. Also, the Sc yield ($\eta_{L/Sc}$) of eq.(3) is an equivalent of $\eta_{L/Sc-max.}$ in eq.(1), but here independent from feed acid concentration.

The theoretical model for impact of solvent excess (eqs (2) and (3)) does not directly involves the feed acid concentration, which is a fact fully compatible with the experimental behavior presenting in Fig.3b. However, the time range of substantial kinetic effects seems to be essentially dependent on feed acid concentration; for lower acid concentrations (< 0.3M) it is particularly long, for medium acid concentrations (0.3-3M) it seems to be relatively concentration-invariant, and for higher concentrations (> 3M) it is extremely short (Fig.2a). For the medium feed acid concentrations zone, any experimentally observed fluctuations of Sc yield for long mixing time values and given (L/S) are within the experimental error (Fig.2a and Fig.3) and theoretically they are absorbed by the calculation of a common set of regression parameters (c_s*, q) in eq.(3). However, a combination of eqs.(1) and (3) in a unified correlation will introduce a secondary type of variability for $\eta_{L/Sc}$ with C_{Af}, for long mixing times and given (L/S), by the term $\eta_{L/Sc-max.}(C_{Af})$ of eq.(1).

3.3. Chemical Reaction Impact (pH of leachate)

The investigation of chemical reaction impact is presented in Fig.4 (a & b). The acidity of the leachate solution has been found to be dependent on the acid feed characteristics, namely on the acid feed concentration, with the relative variation to be depicted in Fig.4a, and on the $(L/S)_f$ ratio, whose variation is shown in Fig.4b.



(**a**) (**b**)

Figure 4. (a) Variation of leachate acid concentration (M) with feed acid (sulfuric) concentration, for constant (L/S)=50:1 (L/kg), τ=60 min, mechanical stirring and ambient conditions. The eq. of LSRL fitting and the linear fitting coefficient of determination (R^2) are appended. (b) Variation of leachate acid concentration with (L/S), as fraction of the respective concentration at (L/S)=50:1, when feed acid concentration is 1.05M and under conditions of (a). Eq. of ln-LSR fitting and R^2 are appended.

Fig.4a shows that concentration of acidic leachate is varied linearly with concentration of acidic feed, under kinetically neutral conditions (t≥1h). The extent of partial neutralization of acid gives the chemically equivalent consumption of BR alkaline content, which is calculated as concentration difference between acid feed and leachate (C_{Af}-C_A), multiplied by the leachate volume and 2 H^+ per molecule of H_2SO_4. The variation of C_{Af}-C_A, for constant leaching volume and BR quantity among the experiments of Fig.4a, proves that the neutralization of BR is partial and approximately proportional to acid feed concentration (C_{Af}). Fig.4b shows that leachate acid concentration increases with solvent excess (L/S) and the variation mode is either logarithmic, or an increasing exponential decay.

Finally, this investigation is supplemented with average measurements of pH for the ingoing and for the outgoing solids, after long resting and equilibrium with their chemically active moisture. Therefore, the *alkaline BR* (at leaching feed) shows pH≈12, while the *acid BR* (at leaching residue) shows pH≈2 [11].

3.4. Leachate Recycling Impact

3.4.1. Specific Recovery and Process Economics

Studying the economics of leaching process ([11] (Phase II)) showed that the key variable for economic viability is the specific recovery, which is expressed in mg of leached Sc per L of consumed acidic solvent, and it is used for a given acid feed concentration with selective action in leaching process, or the absolute specific recovery in mg of leached Sc per mole of used acid, which is valid for any acid feed concentration (Table 4). Maximization of specific recovery means the maximum possible Sc quantity to be recovered (i.e., turnover maximization), with the minimum possible consumption of acid solvent (i.e., main cost minimization).

In the lower part of Table 4, the specific recovery calculation is extended to case of multiple use of the same quantity of acidic solvent onto fresh BR batches, by leachate recycling, as well as to case of possible re-usage of recovered acidic solvent from the ion exchange (I-X) process, which follows the leaching stage. Conclusively, this crucial for process economics variable is easily shown to be: directly proportional to the leaching yield, the Sc content of BR and the times of same acid re-usage; in inverse proportion to liquid to solvent ratio (and to feed acid concentration for the absolute specific recovery); and finally, it is approximately equal to Sc concentration in the leachate $(C_{Sc})_{Leachate}$.

An experimental finding with significant importance is that the Sc yield divided by (L/S) ratio, or by the modified (L/S)* ratio, is not varied slightly with the (L/S) ratio, but it follows the dramatically intense variation of the exponential decay curve appearing in Fig.5.

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Table 4. Definitions of Specific Recovery

For **single** use of acidic solvent
• **Specific Recovery** (mg Sc / L used acid) = $[\eta_{L/Sc}\,(C_{Sc})_{BR}\,M_{BR}]/V_{acid} = \eta_{L/Sc}\,(C_{Sc})_{BR}\,/(L/S) \approx (C_{Sc})_{Leachate}$ where: $(C_{Sc})_{BR}$ is Sc concentration (w/w) in dry BR solids, (mg Sc/ kg dry BR) and $(C_{Sc})_{Leachate}$ is Sc concentration (w/v) in leachate (mg Sc/ L leachate), M_{BR} is the mass of dry BR fed in the leaching reactor, (kg), and V_{acid} is the volume of acid solution fed in the leaching reactor, (L).
• **Absolute Specific Recovery** (mg Sc / mole used acid) = $\eta_{L/Sc}\,(C_{Sc})_{BR}\,/[(L/S)\,C_{Af}]$ where: C_{Af} is the feed acid concentration, (M).
For **multiple** use of acidic solvent
• For **multiple** use of the same quantity of acidic solvent onto fresh BR batches, by leachate recycling: Specific Recovery = $\eta_{L/Sc}\,(C_{Sc})_{BR}\,/\,(L/S)^* \approx (C_{Sc})_{Leachate}$, where: $(L/S)^* = (L/S)$ / (times of acidic solvent re-usage).
• For **multiple** use of acidic solvent recovered from the, following the leaching, ion exchange (I-X) process: Specific Recovery = $\eta_{L/Sc}\,(C_{Sc})_{BR}\,/\,(L/S)^{**} \approx (C_{Sc})_{Leachate}/k$, where: $(L/S)^{**} = (L/S)^*/k$, and $k = k_1+k_2(1-k_1)$, where: k_1 ($=1-C_A/C_{Af}$) is the fraction of acid molecules consumed on alkaline BR content (from Fig.(4): $k_1 \geq \sim 0.8$), and k_2 is the fraction of the I-X acidic solvent quantity that processes performance does not allow to be re-used.

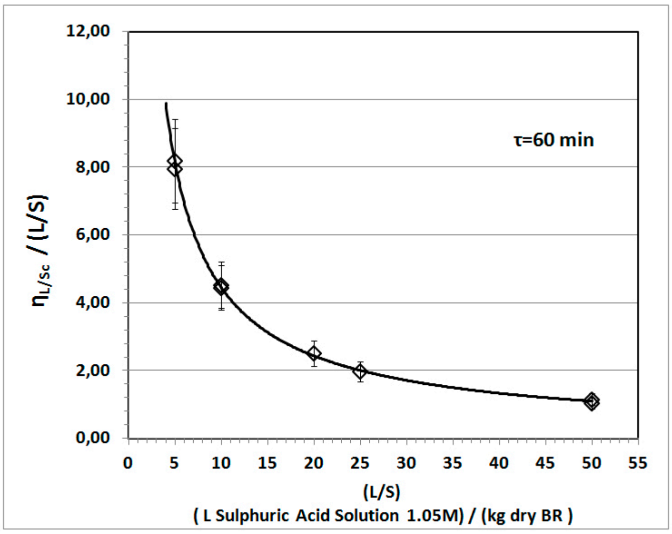

Figure 5. Variation of the $\eta_{L/Sc}/(L/S)$ with (L/S) ratio, for C_{Af}=1.05M, τ=60min, mechanical stirring and ambient conditions. Experimental data and an exponential decay fitting (solid curve). Specific recovery (mg Sc/ L used acid) is proportional to the $\eta_{L/Sc}/(L/S)$ variation.

Therefore, the low (L/S) (or (L/S)*) and the recycling of the acidic solvent both favor significantly the specific recovery and consequently the process economics. Furthermore, a process techno-economic analysis with integrated design aspects [11] (Phase II) showed the following:

- Market competitive operation starts at a minimum plant capacity (kg raw BR / day)
- The process economic viability is particularly sensitive to the cost of the consuming concentrated acid (molecular quantity and price)
- The unit cost depends substantially on the Sc concentration in the PLS, or the specific recovery
- The Sc content in the raw BR and the water price have, also, impact to process economics

3.4.2. A unified mathematical expression for the Sc leaching yield

An attempt to develop a unified correlation for Sc yield of BR leaching process is presented in eq.(4). The formula involves three independent leaching variables, namely: mixing residence time (t), acid feed concentration (C_{Af}) and liquid to solvent ratio (L/S).

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The combination between kinetics and solvent excess correlations is based on, the common for both experimental sets, (L/S)=50 measurements. The kinetic Sc yield predictions, that are valid for (L/S)=50, could be multiplied by the variation of Sc yield with (L/S), when it is expressed as fraction of the (L/S)=50 Sc yield, as long as the assumption of a uniform mode of Sc yield variation with C_{Af} and t for different (L/S) values is approximately valid. Therefore:

$$\eta_{L/Sc}(C_{Af}, t, (L/S)) = \text{Kinetics}(C_{Af}, t, (L/S) = 50) \cdot \frac{\text{Solvent Excess } \eta_{L/Sc} \text{ variation } (C_{Af}{=}1.05\text{M}, \tau{=}60\text{min}, (L/S))}{\eta\text{exp. from Solvent Excess Series} \mid C_{Af}{=}1.05\text{M}, \tau{=}60\text{min}, (L/S){=}50},$$

or, with use of eqs.(1) and (3):

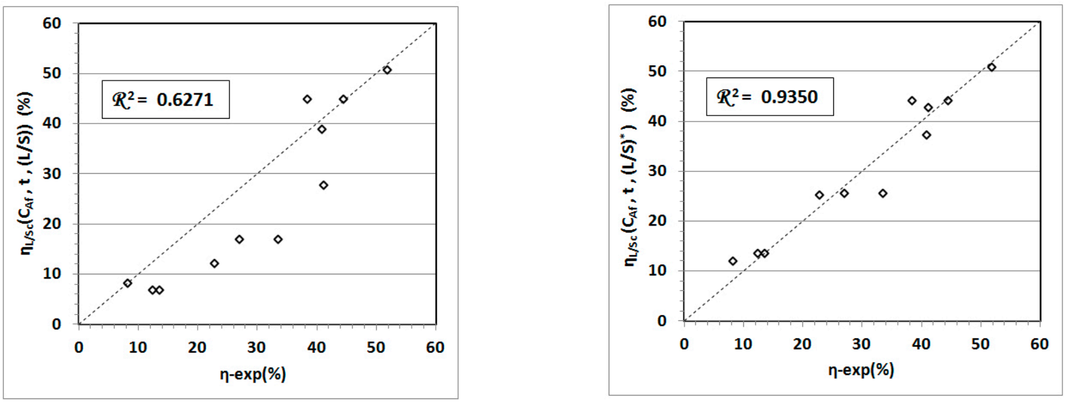
$$\eta_{L/Sc}(C_{Af}, t, (L/S)) = \eta_{L/Sc-max.}(C_{Af}) \cdot \left(1 - e^{-m(C_{Af}) \cdot t + k(C_{Af})}\right) \cdot \frac{(L/S) \cdot c_s^{*}((C_{Sc})_{BR})}{\eta_{max.} \cdot (C_{Sc})_{BR}} \cdot \left(1 - q^{\frac{1}{(L/S)}}\right) \qquad (4)$$

where: $\eta_{max.}$ = (ηexp. from Solvent Excess Series | C_{Af}=1.05M, τ=60min, (L/S)=50), multiplied by 1.01, and c_s*, q are non-linear regression parameters (§3.2).

Investigation of specific recovery limits with recycling of leachate onto fresh BR led to the collection of experimental data that allowed the verification, the generalization and the fine-tuning of the unified correlation (4) for the Sc leaching yield. Therefore, the generalized unified eq.(5) has been derived, which involves the (L/S)* ratio for inclusion of leachate recycling, or of I-X acid by-product re-using. Moreover, a set of deviation correction terms (Δη, C_0, p) has been introduced in the initial mathematical formula to improve its predictability and the result appears in eq.(5):

$$\eta_{L/Sc}(C_{Af}, t, (L/S)^{*}) = \Delta\eta + \left(\frac{C_{Af}}{C_0}\right)^{p} \cdot \eta_{L/Sc-max.}(C_{Af}) \cdot \left(1 - e^{-m(C_{Af}) \cdot t + k(C_{Af})}\right) \cdot \frac{(L/S)^{*} \cdot c_s^{*}((C_{Sc})_{BR})}{\eta_{max.} \cdot (C_{Sc})_{BR}} \cdot \left(1 - q^{\frac{1}{(L/S)^{*}}}\right) \qquad (5)$$

Fig.6 shows comparisons between experimental yields and theoretical predictions, for experiments with up to 3 times of leachate recycling. The fitting performance of the initial unified correlation (4) appears in Fig.6a, while Fig.6b shows the application of the generalized and fine-tuned correlation (5). The general coefficient of determination ($\mathcal{R}^2$), which is a measure of convergence between predicted values and experimental data, is appended in both graphs, so as the superior predictability of the generalized formula to be easily ascertained.



(a) (b)

Figure 6. (a) Comparison between experimental values for Sc yield and respective theoretical predictions of eq.(4), for τ=60 min, $(C_{Sc})_{BR}$=97ppm and data collection from experiments with and without leachate recycling. (b) Comparison between the experimental data of (a) and the respective theoretical predictions of generalized eq.(5). The optimized deviation correction terms are: C_0=1.65M, p=-0.315 and Δη=-7.67%. $\mathcal{R}^2$=1-SS_{res}/SS_{tot}, where: SS_{res} is the statistical residual sum of squares, for predicted values by eqs. (4), or (5), and SS_{tot} is the total sum of squares, for the experimental data set.

The significant improvement of theoretical predictability in eq.(5) was achieved with contribution of the following corrective terms:

- $\left(\frac{C_{Af}}{C_0}\right)^p$: It corrects the minor deviation from the assumption of constant values for parameters c_s*, and especially q, for the entire range of the investigated leaching conditions. This term assigns a particular feed acid concentration (C_0) to the uniform values of c_s* and q, and introduces concentration-dependent deviation from the uniformity. The negative optimum value for the exponent p means higher deviations for lower feed acid concentrations, a fact that is expected from the long-lasting kinetic effects at this concentration zone (Fig.2a and §3.2).
- $\Delta\eta$: It allows correction of the systematic error in prediction of Sc yield. This kind of deviation is mainly explained by possible incompatibilities between the different sets of experimental measurements that were exploited for the unified correlation development.

4. Discussion

4.1. Kinetic Aspects

The kinetic interpretation of Sc yield data - that were acquired with the use of 12 different acid concentrations and of 5 different mixing times (≤1h) - showed that a first order kinetic approach is valid with sufficient accuracy, especially for selective leaching conditions. The 1st order kinetic behavior is in accordance with the general thin film diffusion mechanism. More specifically, it is referred in leaching process fundamentals [24] (§10.2): "*Mass transfer rates within the porous residue are difficult to assess because it is impossible to define the shape of the channels through which transfer must take place. It is possible, however, to obtain an approximate indication of the rate of transfer from the particles to the bulk of the liquid. Using the concept of a thin film as providing the resistance to transfer, the equation for mass transfer may be written as: $dM/dt = k'A(c_s\text{-}c)/b$*". The latter equation is transformed [10] to eq.(6):

$$\frac{dc}{dt} = \frac{K_L A}{V}(c_s - c) \tag{6}$$

where, M is the mass of solute transferred in time t, c is the concentration (w/v) of the solute in the bulk of the solution at time t, c_s denotes the concentration of the saturated solution in contact with the particles (or otherwise the maximum possible concentration under any circumstances in the leachate), A denotes the total area of the solid-liquid interface, or the external surface area of the particles, V is the liquid volume of the solution, and k', *b*, K_L are diffusion parameters that were described below the eq.(2).

Eq.(6) is a typical 1st order kinetics, when the mass transfer parameters are considered to be constant with time. A visual presentation of this theoretical model, which stands as an equivalent to experimental behavior of the real leaching process mechanism, is depicted in Fig.7, where at the left is presented an approach of the real diffusion mode and at the right the thin film concept equivalent.

If 1st order kinetics are valid, with given that k' is considered generally as constant for a certain leaching mixture, then the A/*b* quotient would be considered as constant with time, or otherwise that either the particle size remains intact all over the leaching period, or the thin film layer width (*b*) varies proportionally with the surface area (A) during particles disintegration [24] (§10.2).

Indeed, the experimental deviations from 1st order kinetics, and not the conformity, reveal evidence for the proper application of thin film model to this process mechanism. Fig.8 proves that the best linearity ($R^2 \rightarrow 1$), or equivalently the best fitting to 1st order kinetics, occurs at these acid feed concentrations where the leaching process has experimentally shown the best selective behavior to a trace element as Sc (yields up to 60%), while main elements yields, and especially this of Fe, remain low (<4% for Fe). Therefore, when the bulk quantity of main elements remains approximately intact (i.e., at the most Sc-selective leaching conditions), it is quite possible the experimentally validated 1st order kinetics and the consequently constant A/*b* ratio to mean constant values for both particle size (A) and film width (*b*), all over the leaching period.

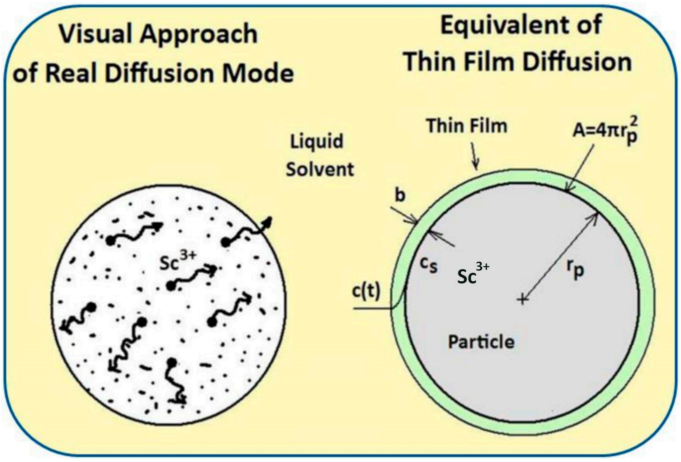


Figure 7. A visual presentation of leaching process mechanism, where at the left appears a visual approach to the real diffusion mode, while at the right appears the equivalent of the thin film diffusion concept [24] (§10.2).

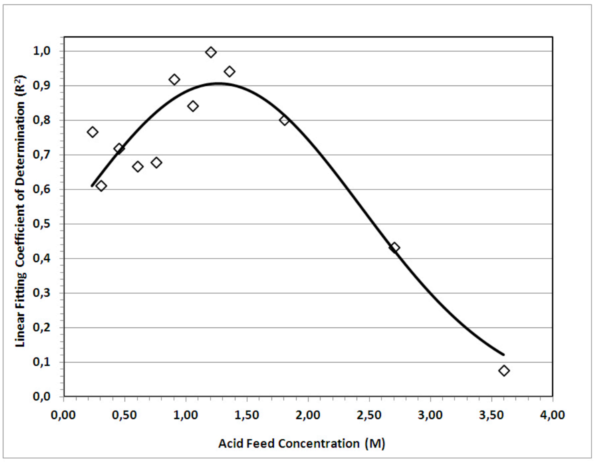


Figure 8. Variation of linear fitting coefficient of determination (R^2) of linearized 1st order kinetics with acid feed concentration (C_{Af}(M)), for the Sc leaching kinetics experiments of §3.1 and Fig.2a (BR leaching with sulfuric acid solution, at (L/S)=50:1). The solid line shows the optimal fitting of a general Gaussian function ($f(x)=a \cdot \exp[-b \cdot (x-\mu)^2]$), where a=0.905, b=0.3673 M^{-2}, and μ=1.267 M.

Under less-, or non-, Sc-selective leaching conditions, the deviations from 1st order kinetics could be explained by the BR particle size decay during leaching, as an effect of enhanced main elements dissolution. In theoretical terms, this fact is interpreted to a varied A/b ratio during leaching period, with the extent of its variation to follow the "distance" from the best Sc-selective conditions. Different modes of A/b variation with the mixing time (t) and the feed acid concentration (C_{Af}) could be tested in a future investigation, where a first evidence is the correction of predicted Sc yields by the factor $(C_{Af}/C_0)^p$ of eq.(5), at t=60 min.

Moreover, apart from the kinetic evidence for the physical phenomena dominance in this process mechanism, the relative invariance of Sc yield with temperature in the investigated range means that, under the prism of an Arrhenius type kinetic equation, the process activation energy is extremely low. In the context of chemical reaction engineering, this fact implies either a well catalyzed chemical reaction, including the case of a spontaneous self-catalyzed reaction, that are phenomena usually irrelevant and rarely secondary to the general leaching process, or quite more appropriately it implies dominance of solids-fluid physical transport phenomena. Therefore, it is additional evidence that the dominant process mechanism, within the investigated range of conditions, is low resistance diffusion [25] (p. 390).

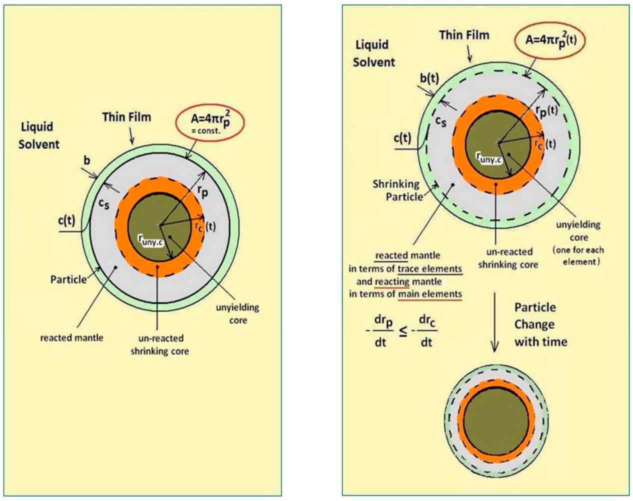
4.2. Theoretical interpretation of solvent excess (L/S) and chemical reactions impact

The impact of solvent excess, or (L/S), to the Sc leaching yield is theoretically interpreted by an already proposed mechanism ([24] (§10.2), [10]), which involves the standard mass transfer rate for diffusion of substances (here, cations) from solid particles to bulk volume of a liquid solvent (i.e., the thin film diffusion pattern).

In case of BR leaching for trace elements recovery (here, Sc) with dilute leaching pulp, the general thin film theory can sufficiently interpret the relevant experimental data, and consequently to emerge the diffusion as the dominant mechanism.

In the contrary, there are indications of significant deviations from single diffusion when a concentrated leaching pulp is involved in this process [3, 26]. For the theoretical interpretation of these cases, it is described here a proposed extension of the diffusion theoretical approach with additional participation of the un-reacted shrinking core model from chemical reactions engineering; either with its typical form for approximately constant external surface area of the particles, or with a modified form of an un-reacted shrinking core inside a shrinking particle.

The chemical reactions of neutralization and complexes formation between acid solvent and alkaline content of BR particles remain, generally, as a secondary rapid stage. But, at very low solvent excess (L/S), the appearance of gel formation [26] indicates that the chemical reaction stage is expected to show non negligible impact to the total rate and the un-reacted shrinking core chemical reaction standard model seems to be the most suitable to equivalently describe the impedance from this additional effect. This concept, for the selective to trace elements conditions, is visually presented in Fig.9a, with the orange colored shrinking core to represent the particle part with trace elements to be extracted, and with the olive colored area to show an unyielding core, where the process is limited. In case of less-, or non-, selective to trace elements conditions and at very low solvent excess (L/S), the diffusion of cations has also to be combined with the chemical reactions effects, but, in opposite to the selective leaching conditions, with time decreasing external surface area of the particle, as Fig.9b shows. A complex model of a surface-reacting shrinking particle for the main elements, and simultaneously of an un-reacted shrinking core inside the shrinking particle for the trace elements, could be in effect. The leaching process extension is also limited to an unyielding core, which, under extreme conditions, could be eliminated.



(**a**) (**b**)

Figure 9. Visual presentation of the proposed leaching model extension: (a) *Selective* to Trace Elements BR Leaching. Standard model: Thin Film Diffusion with constant particle external surface area (A). For very low (L/S) (≤ 5:1): Thin Film Diffusion is combined with the Un-reacted Shrinking Core chemical reaction model. (b) *Less-, or Non-, Selective* to Trace Elements BR Leaching. General case: Thin Film Diffusion with time varying A/*b* ratio. For very low (L/S): A proposed complex model of thin film diffusion with a surface-reacting shrinking particle for the main elements and an un-reacted shrinking core for the trace elements.

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The proposed combination of a physical with a chemical conversion pattern seems to be the most appropriate to interpret experiments of BR leaching that deviate significantly from the predictions of the single diffusion model, especially at conditions where the parallel to diffusion chemical reactions are of comparable rate, while its validity is to be tested in a future work.

Especially for the unyielding core concept, it is clarified that it has been proposed for universal application over any leaching conditions, and as a necessary supplement even of the standalone diffusion pattern for trace elements recovery. Evaluation of the pertinent experimental data shows that the size of this core depends on cationic element and leaching conditions. Apart from the obvious evidence for this concept coming from the partial Sc recovery of BR after long leaching periods, additional strong evidence comes from §3.3., which proves that the alkaline content of a BR particle is only partially neutralized. The residual alkaline content, either entirely or partially, could be considered as an unyielding core inside the BR particle with bound cationic elements.

Furthermore, the solvent excess model of this work involves the average concentration of the saturated solution in contact with the particles (c_s*), or otherwise the theoretical maximum possible concentration of Sc in the leachate, for given Sc concentration in the solid dry BR. This parameter of the model is a significant process limit, which is estimated by an optimization algorithm. More specifically, the non-linear fitting of eq.(3) to the relevant experimental data (e.g., Fig.3a) allows the calculation of c_s* for the BR samples of the examined experimental study; for the data of Fig.3a, where H_2SO_4 is the leaching solvent, and $(C_{Sc})_{BR}$=97 ppm (median value, [11]), the optimized fitting gives: c_s*=12.8 ppm. For the over the years average $(C_{Sc})_{BR}$≈120 ppm (Table 1), the same fitting gives: c_s*= 15.8 ppm. For both cases the optimized fitting of eq.(3) gives: q=0.045.

In a respective Greek BR leaching study with HNO_3 as the leaching solvent, where $(C_{Sc})_{BR}$≈120 ppm, the fitting of the thin film diffusion model to experimental data has given c_s*= 15.0 ppm, as it is already published by the authors in [10]. The comparison of c_s* between sulfuric and nitric acid, for the same Sc concentration in raw BR, indicates that c_s* for Sc is approximately constant, characteristic of BR, and probably independent from the kind of strong mineral acid. Practically, the Sc concentration in the leachate of a selective Greek BR leaching process could not be expected to outreach ~12 ppm, and this prediction is of critical importance for the following I-X process.

4.3. Effects from process intensification (leachate recycling)

The experimental verification of model predictions when Sc specific recovery approaches its limits was implemented by the means of leachate recycling onto fresh BR. These data allowed the further model tuning and led to the development of a unified equation for Sc leaching yield (eq.(5)), which shows a quite sufficient predictability level for processing of a raw material (BR) with broadly variable Sc composition.

The multiple use of the leachate onto fresh BR led to outstanding leaching performance with cases where Sc concentration in the PLS (or, specific recovery (Table 4)) approaches 8 ppm, which is a value exceeding results of previous works with single acid using [10,13,23]. Moreover, a new and still unconfirmed experimental investigation, which is conducted by the authors in the same research context [3], has shown even higher Sc concentrations, but at very low (L/S) ratio where the gel formation effect remains an issue to be confronted [26].

5. Conclusions

Greek BR can be considered as a valuable Sc resource, while Sc is a metal of increasing economic importance and simultaneously of increasing supply risk.

Analysis of the relevant experimental investigation with H_2SO_4 solutions has proven significant impact of Sc leaching yield from: Acid feed concentration, Mixing residence time, (L/S) ratio at the process feed, Times of leachate re-usage onto fresh BR.

The thin film diffusion model, as theoretical standard for the leaching process, either with constant particle size for selective leaching, or with shrinking particle size for less-, or non-, selective leaching, interprets sufficiently well the relevant experimental data. For selective leaching, the standard model keeps step with the experiments, since both prove 1st order kinetics. But, for conditions that include low solvent excess, the thin film diffusion model could perform better if it is to be combined with the un-reacted shrinking core chemical reaction model, or with a more complex model for extreme leaching conditions. Furthermore, a suitable explanation of the relevant experimental data shows that each element (cation) has its own size of an unyielding core inside the particle, which depends on leaching conditions. This core stands as a limit for the leaching yield and for the extension of the parallel chemical reactions.

Specific recovery (mg Sc in PLS / consumed acid quantity) is the key variable for leaching process economics. It is directly proportional to the leaching yield, the Sc content of BR and the re-usage times of the same solvent quantity. It is in inverse proportion to (L/S) ratio (and to feed acid concentration for absolute specific recovery), and finally, it is approximately equal to Sc concentration in the produced solids-free PLS.

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Conflicts of Interest: The authors declare no conflict of any interest among them. Moreover, it is elucidated that a part of the experimental background of this work has been derived in a joint project between NTUA and II-IV Inc. [11], under a funding contract with confidentiality terms, but also with possibility for publication after the approval from the funding sponsor (II-VI Inc.) for the kind of information to be publicly disseminated. II-VI Inc. agrees with the publication of this work and the particular indirect dissemination of its experimental background. Authors declare that the indirect publication of experimental results is limited to the marginally required extent for the scientific integrity of this paper. Also, the results of this work (design aspects) have been derived in the context of the SCALE project [3] and the decision to be published was a matter of collective agreement among the partners of the project consortium; Aluminium of Greece, Member of Mytilineos Group and II-VI Deutschland GmbH, subsidiary of II-IV Inc., are among the members of this consortium. The publication is in accordance with the terms of the SCALE Grant Agreement No. 730105 with the funding authority (EU / EASME). Finally, the funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data, and in the writing of the manuscript.

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