

CHEMICALLY OPTIMIZED LEACHING WITH MINERAL ACIDS OF BAUXITE RESIDUE FOR Sc RECOVERY

Konstantinos HATZILYBERIS, Theopisti LYMPEROPOULOU, Lamprini-Areti TSAKANIKI, Kyriaki KISKIRA, Klaus-Michael OCHSENKUEHN, Paraskevas GEORGIU, Fotis TSOPELAS, Maria OCHSENKUEHN-PETROPOULOU

School of Chemical Engineering, National Technical University of Athens, 9, Iroon Polytechniou St., 15780, Athens, Greece

Emails: ksh@chemeng.ntua.gr, veralyb@chemeng.ntua.gr, oxenki@central.ntua.gr

Abstract

Bauxite Residue (BR) is a globally distributed waste and a potential resource of Scandium (Sc). The optimized Leaching with Mineral Acids (LMA) currently appears as the most ready and economically feasible method for the first stage of Sc recovery. In both economic and environmental terms, the sulphuric acid is proven to be the most suitable acid, despite the restrictive specifications for the Pregnant Leach Solution (PLS), as coming from the subsequent advanced Resin ion eXchange (RX) process and the avoiding of colloidal silica gel formation. This work presents the chemically optimized method of the Sc-oriented leaching process, satisfying the relevant imposed limitations. Two main operation modes and respective conditions sets have been derived, which are to be investigated for their economic impact.

Introduction

The exploitation of mineral industry's residues arises as a great contemporary challenge for both scientific and business community. In recent years, global deposits of rich in REEs residues have attracted the international interest since they can be exploited as a stable supply route for many Critical Raw Materials¹. This trend has many significant advantages such as shifting the metallurgical industry's interest to the symbiotic processes and favouring resulting valuable synergies, while also there are important environmental benefits through the diminution and neutralization of the discarded residue volumes.

This is the case for Bauxite Residue (BR), a by-product of aluminium industry, which is a globally distributed resource of Sc with a potential of economic viable processing and exploitation. The Greek BR, which is exclusively produced by the Metallurgy Business Unit of Mytilineos SA (Aluminium of Greece), is such an option. There is an annual production of about 750,000 t²⁻⁴ of highly alkaline and very fine grained dried BR,

consisting mainly of Fe, Ca, Al, Ti and Si compounds, and accompanied by numerous trace elements⁵. The REEs content is about 1kg/t dry BR, and Sc counts >90% of this economic potential⁴.

The optimized Leaching with Mineral Acids (LMA) currently appears as the most ready and economically viable method for the first stage of Sc recovery. In contrast, Sc-hydrometallurgy usually involves Mineral Acids (MA) under strong conditions^{6,7}, while alkaline solvents⁸ do not favour some of the most advanced methods of Resin ion eXchange (RX) and Solvent liquid eXtraction (SX) for Sc purification, after the leaching process. Nano-filtration and leaching with ionic liquids are under development^{9,10}, but still of high operating cost.

Among many different tested acids, nitric acid has showed the best recovery and selectivity for Sc^{4,5}. However, in economical and environmental terms, sulphuric acid seems to be the most suitable acid^{2,3}, despite the restrictive specifications for the Pregnant Leach Solution (PLS) coming from two different sources: the subsequent advanced-RX process (SIR[®], II-VI Inc., PA, USA) in order to maintain high efficiency levels, and the leaching plant itself in order to maintain a steady and safe operation by avoiding the formation of colloidal silica gel. This work presents a chemically optimized method of the Sc-oriented leaching process, as conceptually depicted in Fig.1, which satisfies the contiguously imposed limitations.

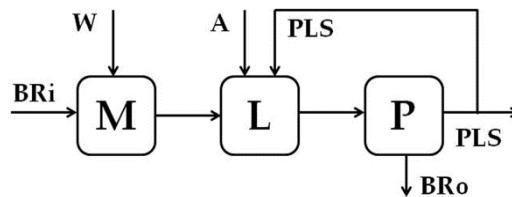


Figure 1: Conceptual design of the scaled-up LMA of BR for Sc. M: Makeup, L: Leaching, P: Purification, i: input, o: output, A: conc. Acid, W: Water.

Results and Discussion

The optimized mild conditions for the ambient leaching of the Greek BR have been reported in previous work and found to be in the vicinity of the experimental data of Fig.8,§3.9³. The specifications of the SIR[®] method for the PLS are: “(i) [Sc]≥6mg/L, (ii) [Fe(III)]≤3000mg/L, (iii) [Ti]≤1700mg/L, (iv) [Zr]≤100mg/L”. Moreover, the unhindered operation of the leaching unit demands: “[Si], pH and Temperature have to be suitable for remaining of: (i) the PLS in thin fluid state after 30 days of resting, and (ii) the leaching pulp in fluid state after 48 hours of resting”.

Assuming sufficient level of confidence for linear interpolation between 1M and 2M experimental values and having ascertained the linearity between N=1 and N=3, two-variables linear functions derived for [X]’s (X=Sc,Ti,Fe,Si,Al) such as:

$$[X](C_{FA}, N) = a_X + b_X C_{FA} + c_X N + d_X C_{FA} N, \text{ (mg/L).}$$

Data and coefficients are extracted from Fig.2, where: C_{FA} is the Fed-Acid (FA) molarity, in M (i.e., molarity of the diluted Acid by Water and recycled PLS, in Fig.1), and N is the laboratory cycles of PLS recycling (or, $N \approx R+1$, R : the PLS reflux ratio in Fig.1). A non-integer N means a last laboratory cycle with respectively fractional quantities of PLS and BR.

Regarding to the N interval [1 cycle, 3 cycles], the kinetic leaching model of the generalized eq.(5) in ref.2 shows a first order increasing variation of $[Sc]$ with N , i.e., $[Sc] = c_s^* \times (1 - e^{-(const.) \times N})$, when the value of any other leaching parameter remains constant. Thus, the model interprets the presented linearity of Fig.2 as an approximation to the starting range ($N=1-3$) of the 1st order variation. Since the kinetics of ref.2 for Sc is based on theory, the same interpretation seems to be valid for the Main Elements (MEs) of the BR. Moreover, the effects of leaching Temperature and Pressure have been presented in previous work³ (§3.6 and Fig.5). The use of high temperature and pressure constrains method's selectivity for Sc compared to the MEs thus deteriorating or even eliminating the possibility for Fe, Ti and Si conformity with the specifications. In contrast, for temperature lower than the standard ambient, the SiO_2 presents lower solubility and the polysilicic acid gelatinization becomes faster. Conclusively, the technically convenient choice of *Standard Ambient Temperature and Pressure leaching conditions* seems ideal.

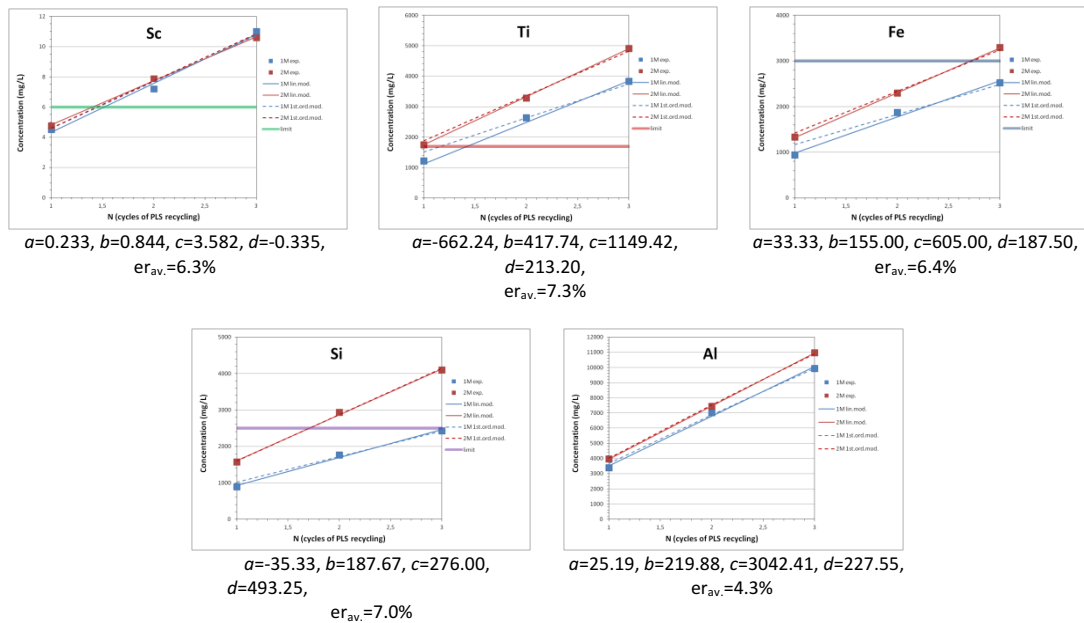


Figure 2: Concentration (in mg/L) of included Sc, Ti, Fe, Si and Al in the PLS. $SL=10\%$, $t=60\text{min}$, $c_{SC/BR}=98 \text{ mg/kg}$, ambient conditions, and magnetic stirring (original experimental data). The respective limits are depicted with thick horizontal lines. The

two variables linear functions for [X]'s are drawn with solid lines. The model of ref.2, for time exceeding the substantial kinetic effects, corresponds to dashed lines.

For a given pulp density (Solids to Liquid ratio, $SL=10\%$, i.e., 10 kg dry BR/100L FA), the problem of the best (C_{FA}, N) pair requires an appropriate objective function. [Fe(III)] appears in, or near to, conformity; consequently participating only in: $[Fe] \leq [Fe(III)]_{lim}$. [Si] has a qualitative specification, which is quantitatively indirect and depending on multiple variables¹¹, not having a given arithmetic limit, but the lower the [Si] value the better the PLS fluidity. However, theoretical evidence (*The Stumm- Morgan diagram*, Fig.3 in ref.12) and tests have shown that samples with $[Si] < 2500$ mg/L and $C_{FA} \approx 1M$ conform, even at $\sim 5^\circ C$ (ref.9, deliverable D.1.1); the ineq. $[Si] \leq [Si]_{lim} = 2500$ mg/L is also added. More specifically, Si experimental data showed that no gel formation observed up to 30 days when using acid molarities up to 1M even for SL up to 30%. Acid molarity of 2M resulted to gel formation after the 10th day, due to high Si extracted amounts in the PLS, with a viscosity of 250 and 650 cP, for $SL=20\%$ and $SL=30\%$, respectively (Fig.3). Regarding gel re-dissolving, the use of different agents such as H_2O_2 , NaOH, or water, with or without heating and stirring, did not result to gel destruction⁹; gel is not soluble since formed. Finally, the ineq. for [Zr] is omitted, since the involved SL ratio causes always conforming [Zr].

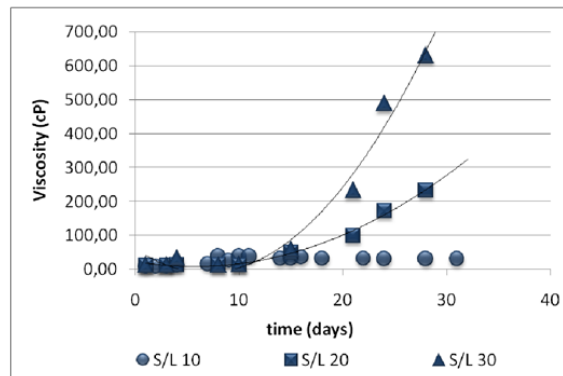


Figure 3: Change in the PLS viscosity as a function of time for 2M H_2SO_4 (ref.9, deliverable D.1.1)

Given the increasing trend of [X]'s with C_{FA} and N , the optimization target is described as the (C_{FA}, N) giving the max. possible [Sc], with either [Si], or [Ti], to approach the respective limit. This optimization is achieved through the constrained minimization of the dimensionless number: $\left(\frac{[Si]}{[Si]_{lim}} - 1\right)^2 / \left(\frac{[Sc]}{[Sc]_{lim}}\right)^2$. Conforming of [Si] is pushed to the higher allowable level, since [Si] and [Sc] show parallel increase, while [Ti] constraint holds the conditions within, or close to, the experimentally validated zone

(Fig. 4). The minimization of this objective function defines the *mild conditions case* of: $C_{FA}=0.8M$ and $N=1.54$, resulting to: $[Sc]=6.0$ mg/L, $[Ti]=1700$ mg/L, $[Fe]=1317$ mg/L, $[Si]=1145$ mg/L, $[Al]=3077$ mg/L, with efficiency of Sc recovery about 40%. A 20% deviation from the C_{FA} interpolation range is considered as acceptable for extrapolation.

Another option for the leaching unit's operation is the *strong conditions case*, where the raw BR is attacked with high molarity sulfuric acid (4-5M), at elevated temperature and ambient pressure. The result of these extreme leaching conditions is an extensive dissolution of Sc, but also of the MEs, and especially of Fe⁹ (internally presented results). On the other hand, an extremely low [Si] appears in the PLS, viz. a strong advantage for the safe unit operation. At 60°C, there is an optimally low [Ti]/[Sc] ratio, while Sc recovery can approach 80%. This extensive dissolution of Fe makes necessary the existence of an intermediate process, between leaching and filtering, where the PLS will be partially neutralized with an alkaline solution and thus, a significant part of the dissolved MEs will precipitate and be mixed with the BR residue. The final pH of this neutralization is a crucial parameter for the precipitation selectivity. An experimental investigation with NaOH 2M⁹ has shown a significant precipitation of Fe(III) for pH=2.5-3.0, and a narrow range round pH=3.0 where the precipitation of the leached Ti is not accompanied by significant losses for the leached Sc; a fact that imposes further investigation of suitable pH values for different additives (e.g., the inexpensive limestone slurry). Conclusively, the ambient pressure and the moderately elevated temperature at ~60°C are ideal for the *strong conditions case*, while the PLS recycling has no economic significance at such a low concentration of remaining free acid.

The investigated area of conditions for the economically advantageous *mild case* and the results for the possibly conforming zones are presented in Fig.4. However, a displacement of the optimized set is possible either after a future optimization with economics-terms, or by investigation of particularly low FA molarity cases. The latter, although counter-productive for Sc, can cause in-situ precipitation effects and possibly an advanced separation.

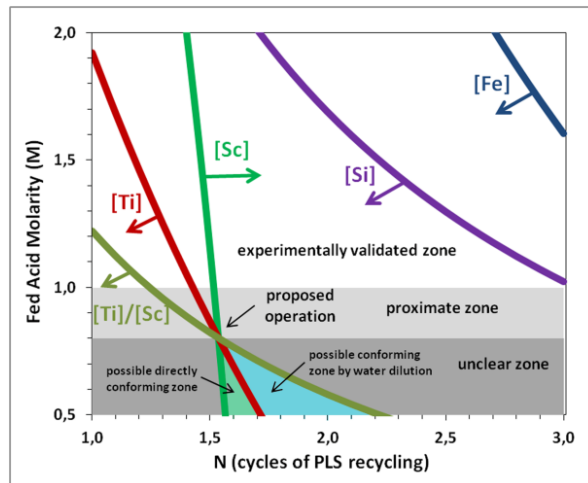


Figure 4: Investigation of mild optimized conditions. Greek BR ambient leaching for Sc; H_2SO_4 , $SL=10\%$; BR analysis has been presented elsewhere³⁻⁵. Thick lines show boundaries, or ineqs. $a_X + b_X C_{FA} + c_X N + d_X C_{FA} N \leq (\geq) [X]_{lim}$. $[Ti]/[Sc] \leq [Ti]_{lim}/[Sc]_{lim}$ implies a wider conformity zone by water dilution, at RX feed.

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