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

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Abstract

Global deposits of rich in REEs residues from mineral industry can be exploited as a stable supply route for many Critical Raw Materials (CRM)[1]. It can also shift the interest of the metallurgical industry to the symbiotic processes and their synergies with significant environmental benefits by the diminishing of discarded residues. Bauxite Residue (BR) from the aluminum industry is a globally distributed resource of Sc, with the Greek BR to be a characteristic example of the economically viable cases. Aluminum of Greece produces ~750,000t annually[2-4] of highly alkaline and very fine grained dried BR, consisting mainly of Fe,Ca,Al,Ti and Si compounds, accompanied by numerous trace elements[5], and a REEs-content of ~1kg/t dry BR, with Sc to count >90% of this economic potential[4].

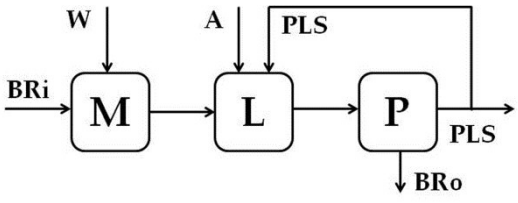
The optimized Leaching with Mineral Acids (LMA) currently appears as the most ready and economically viable method for the first stage of Sc recovery. Sc-hydrometallurgy usually involves Mineral Acids (MA) under strong conditions[6,7], while some alkaline methods also exist[8]. However, alkaline solvents do not favour any subsequent Resin ion eXchange (RX) and/or Solvent liquid eXtraction (SX), for Sc purification. Nanofiltration and leaching with ionic liquids are under development[9,10], but still with high operating cost. Among many different tested acids, nitric acid has showed the best recovery and selectivity for Sc[4,5]. However, a synergy of economic and environmental aspects has given prominence to sulphuric (H_2SO_4) as the most suitable acid[2,3], although restrictive specifications for the Pregnant Leaching Solution (PLS) are arisen by the subsequent advanced-RX (SIR©,II-VI Inc.,PA,USA) and the avoiding of colloidal silica gel formation. This work presents a chemically optimized method of the Sc-oriented leaching, while the specifications of leachate solution required for the subsequent processes are satisfied. The conceptual design for the scaled-up process is depicted in Fig.1a.

The optimized mild conditions for the ambient leaching of the Greek BR are located elsewhere in the vicinity of the experimental data in Fig.8,§3.9.[3]. The specifications of

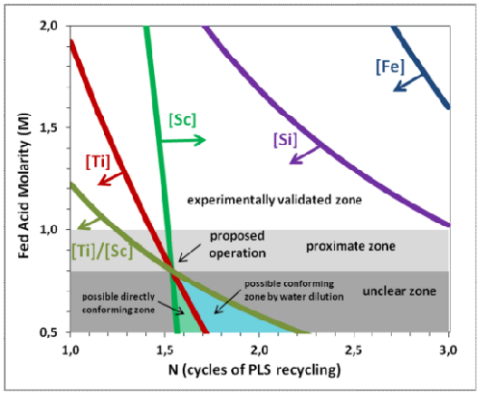
the SIR© method for the PLS are: "(i)[Sc]≥6mg/L, (ii)[Fe(III)]≤3000mg/L, (iii)[Ti]≤1700mg/L, (iv)[Zr]≤100mg/L". Moreover, the unhindered operation of the leaching unit demands: "[Si], pH and Temperature have to be suitable for remaining of: (i) the PLS in thin fluid state after 30 days of resting, and (ii) the leaching pulp in fluid state after 48 hours of resting".

By assuming sufficient level of confidence for linear interpolation between 1M and 2M sulphuric acid experimental values and by having ascertained the linearity between N=1 and N=3 (Fig.8 of ref3), two-variables linear functions derived for [X]'s from new available data, where: X=Sc,Ti,Fe,Si,Al, such as: $[X](C_{FA},N)=a_X+b_XC_{FA}+c_XN+d_XC_{FA}N$, (mg/L), where: C_{FA} is the Fed-Acid (FA) molarity, in M (i.e., molarity of the diluted acid (A) by water (W) and recycled PLS, in Fig.1a), and N is the laboratory cycles of PLS recycling (or, $N\approx R+1$, where: R is the PLS reflux ratio in Fig.1a); a non-integer N means a last laboratory cycle with respectively fractional quantities of PLS and BR.

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 it participates only in: $[Fe]\leq[Fe(III)]_{lim}$. [Si] has a qualitative specification, which is quantitatively indirect and depending on multiple variables[11]. It has not 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 ref12) and tests have shown that samples with [Si]<2500 mg/L and $C_{FA}\approx$1M are conforming, even at ~5°C (ref 9,deliverable D.1.1); the ineq. $[Si]\leq[Si]_{lim}$=2500mg/L is also added. Specifically for Si experimental data showed that no gel formation was 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 amounts extracted in the leachate solution with a viscosity of 250 and 650 cP for S/L 20 and 30% respectively (Fig.2). Regarding gel redissolving the use of different agents such as H_2O_2, NaOH or water dilution with or without heating and stiriing do not affect gel destruction[9]. Gel is not soluble since formed. Finally, the ineq. for [Zr] is omitted, since the involved SL ratio causes always conforming [Zr].



(a)



(b)

Figure 1: (a) 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. **(b)** Investigation of mild optimized conditions. Greek BR ambient leaching for Sc; H_2SO_4, *SL*=10%; BR analysis is presented in details elsewhere[3-5]. Thick lines show boundaries, or ineqs. $a_X+b_XC_{FA}+c_XN+d_XC_{FA}N \leq (\geq) [X]_{lim}$. $[Ti]/[Sc] \leq [Ti]_{lim}/[Sc]_{lim}$ implies a wider conformity zone by water dilution, at RX feed.

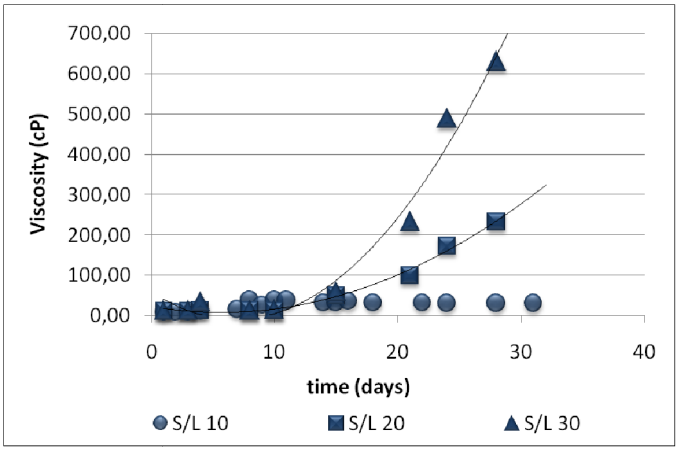


Figure 2: Change in the leachate solution viscosity as a function of time for 2M H_2SO_4.

Given the increasing trend of [X]'s with C_{FA} and N, the optimization target is described as the (C_{FA},N) that gives 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: $\left(\frac{[Si]}{[Si]_{lim}}-1\right)^2 \Big/ \left(\frac{[Sc]}{[Sc]_{lim}}\right)^2$. Conforming of [Si] is pushed to the higher allowable level, since [Si] and [Sc] are parallelly increased, while [Ti] constraints hold the conditions inside, or close to, the experimentally validated zone (Fig. 1b). Two main operation modes, namely *mild* and *strong*, have derived by this chemical optimization. The investigation of an optimized conditions set for the *mild* case is presented in Fig.1b, while a displacement of the sets is possible after a future optimization with economics-terms.

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