THE TREATMENT AND UTILIZATION OF RED MUD: A PRODUCT OF BAYER PROCESS

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Abstract

Metal production generates various forms of by-products. Disposal of these by-products can not only represent a problem of economics (high-cost for disposal and maintenance) but also an ecological problem (possible environment contamination). Therefore, there is now a major effort being made towards by-products treatment and recycling of its valuable components. Red mud and Fe-Ti slag are by-products of alumina and titania production, respectively. The following paper presents a review of red mud treatment patents, and some results of recent research work, the main purpose of which was to find a suitable method for the economical treatment of a mixture of red mud and Fe-Ti slag. Special attention has been given to a method developed for the recovery of valuable red mud components. This process involves the selective leaching of the 'wastes' mixture (red mud + Fe-Ti slag) by direct sulphuric acid contact, followed by hydrometallurgical, thermal or other kinds of processing, to recover valuable species, such as Fe_2O_3, TiO_2, Al_2O_3 and Na_2O. X-ray diffraction, TGA-DTA/DSC, ICP-mass spectroscopy and scanning electron microscopy techniques have also been used to determine physical, chemical and mineralogical characteristics of the red mud and the Fe-Ti slag. Thermodynamic values of the proposed chemical system (red mud + Fe-Ti slag) are also presented. FactSage™ 5.2 software was used to create E-pH diagrams. Finally a process flowsheet for valuable species recovery is proposed.

1 Introduction

Aluminium is now the world's predominant non-ferrous metal in terms of its annual production tonnage. The starting material for the electrolytic smelting of aluminium is pure, anhydrous aluminium oxide, known commonly as alumina. Bauxite ore is the main source of commercial alumina, obtained through use of the chemical process first developed by the Austrian scientist, Karl Bayer (Bayer 1888). The main process step performed in the Bayer process is the 'digestion' of the bauxite by caustic liquor according to the following reaction:

$$2NaOH + Al_2O_3.3H_2O \Leftrightarrow Na_2O.Al_2O_3 + 4H_2O \qquad (1)$$

However, bauxite also contains impurities; these are essentially insoluble in the caustic liquor and create the insoluble residue known as red mud. It consists mainly of such phases as hematite, anatase, rutile, quartz and the desilication product (DSP/sodalite).

The production of one ton of metallic aluminium also yields 0.5 to 2 tons of red mud residues (on a dry basis) for disposal. Overall, the worldwide alumina industry produces about 70 million dry metric tons of red mud residue annually (The Aluminium Association 2000). Disposal of this quantity of red mud represents a considerable environmental problem, mainly because of its fine texture and its high alkalinity (pH 13-13.5) arising from its high content of entrained process liquid. Hence capital and maintenance costs are essentially high, and will be higher in the future because of more strict environmental policy in many countries. On the other hand, it can represent a considerable source of valuable components such as Fe_2O_3, Al_2O_3, TiO_2, Na_2O etc, if they can be recovered economically.

This paper presents a project realized at the Université de Sherbrooke in partnership with Alcan International Ltd, undertaken with the objective of recovering valuable species, mainly from the red mud residue. A short description of the project, its scope and a brief patent overview are now followed by an overview of the theoretical and practical aspects of the undertaken study. Finally some preliminary experimental results are presented.

2 Background – Patent review

2.1 *Possible Red Mud Utilization*

A considerable number of patents and journal papers have been published, outlining possible red mud and its components utilization. The following patent review summarizes relevant patents, issued worldwide over the period from 1957 to 2004. More than 100 have been considered, being divided into several categories according to the mode of red mud utilization:

- Valorization: sodium content recovery
  rare earth metals recovery
  oxides for ceramic industry
  metals, metal oxides, fluorides, chlorides
- Construction, building materials
- Pigment
- Steel production
- Other (PVC, filler, floculant, adsorbent etc.)

As shown in Figure 1, most patents examined are focused on recovery of the useful components contained in red mud (50%) and its use as a construction and building material (26%).
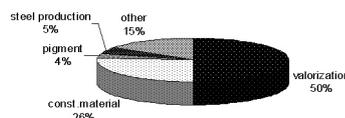

Figure 1: Distribution of patents according to red mud utilization

Recovery of the Fe content for use in iron and steel industry has received the most significant attention in the past because of

the dominant presence of iron oxide in red mud. Thermal extraction methods such as sintering, reduction smelting etc. has been widely considered. The main disadvantages of thermal processes are their major energy consumption levels and poor economics since they would also require low-cost technologies for input red mud dewatering. Mechanical or thermo-mechanical methods have been mainly used for the production of building materials and ceramics. Processes aimed at mud utilization for building materials may significantly ease storage problems, but they are nevertheless only a partial solution. The main disadvantage of these low-cost technological methods is that the final product itself (bricks, construction blocks, other building materials) contains high levels of sodium, which is not very much compatible with cement based products, and in some cases, some radionuclides, which are also unwelcome. The concern about red mud radioactive element content represents unacceptable commercial risks with respect to its use in building products. Hydrometallurgical and thermo-mechanical utilization methods are seen to be preferred in the more recent patents, i.e. those issued between 1990 and 2004. This is probably due to use of more cost effective technologies, with lower energy consumptions, and to complex utilization paths with reduced amounts of inputs. Other methods such as ion–exchange, hydro–mechanical, magnetic separation, fluorination and chlorination, are some kind of alternative methods generally used in combination with some of the methods previously mentioned above.

Most of the discovered patents (~52%) were originally issued between the years 1990 and 2004; some of these were refilled later with upgrades, but the incorporated "improvements" are often not very significant.

2.2 *Red mud treatment – patent examples*

Five patent examples, issued under this broad heading are now described in the following section.

Firstly, a process (Nishimoto 1967) comprising the steps of absorbing SO_2 by a slurry, including red mud of a suitable concentration, to separate and recover the sodium component; adding water to the resulting residue to form an aqueous suspension; reacting the aqueous suspension with SO_2 to dissolve alumina and silica; separating the solution from the insoluble residue (includes Fe_2O_3 and TiO_2); heating the resulting solution to drive off some of the SO_2, supplied in the preceding steps and to deposit silica for the purpose of its recovery; continued heating of the remaining solution to drive off further SO_2 and deposit and separate out the basic aluminium bisulphite later calcined to produce alumina.

Secondly, a process (Zimmer 1978) discloses a treatment for red mud, comprised of heating it to 250°C-350°C, adding concentrated H_2SO_4 or SO_3 gas, water leaching of the formed sulphates, and separating off the solution. This is then heated at ~pH 1 to precipitate titanium oxide hydrate by hydrolysis. The remaining sulphates in solution are then obtained in mixed solids form by evaporation, or by precipitation with acetone, solids then being roasted to convert aluminium and iron species to oxide. After removal of sodium sulphate by water leaching, the Al_2O_3 and Fe_2O_3 components are separated by the Bayer process.

Thirdly, an invention for recovering Al_2O_3, Fe_2O_3, SiO_2 and TiO_2 values from red mud is disclosed (Barnett 2001). Red mud is digested, at between 160-200°C for 15-90 min, in concentrated H_2SO_4, to convert the principal metals to sulphates. Following the steps of digestion and leaching, the resulting liquid is subjected to a hydrolysis step for the purpose of precipitating titanium oxide, this precipitate being separated by filtration. The pH is adjusted with sodium hydroxide and sodium aluminate with iron hydroxide is formed. The solution is then acidified to precipitate alumina trihydrate; this is recovered and calcined at 1100°C.

Fourthly, a process is disclosed that involves contacting red mud slurry with sulphur dioxide to dissolve the soda, alumina and silica present in the treated desilication product (Cresswel 1987). After separation of the insoluble portion, the filtrate is heated to selectively precipitate silica; this is then removed to yield a solution containing the soluble soda and alumina. This liquor extract is then causticized with lime and a caustic aluminate solution is produced that may be utilized

in the Bayer process. Solid calcium sulphite is calcined to recover raw materials used earlier in the process, namely the lime and SO_2 gas.

Finally, another process for separating useful compounds from red mud is described (Tsai 1971). In this example, the red mud is once again digested with SO_2 in the presence of water to selectively dissolve such components as alumina, silica and the soda, leaving Fe_2O_3 and TiO_2 essentially undissolved. Dissolved components are then separated from the solution by precipitation; solution is concentrated to crystallize out Na_2SO_3. Sulphuric acid is added to the separated precipitate forming water-soluble aluminium salts. Silica remains as a residue and is removed from solution. Water and a potassium or ammonium salt is added to the liquor from which the corresponding alumina may be crystallized out.

To the authors' knowledge, some of the methods cited above have been commercially applied but their application is still limited by their poor economics. No patent has seen worthwhile commercial applications for the main purpose of red mud treatment. There is still a great need for a process, which can extract the metal values from red mud in an economic manner.

3   Aim of the Project

Following this patent review, the authors realized that, for an economic process, the treatment of red mud alone will be difficult, so other by-products were considered with the specific objectives listed below:

- to treat at least two by-products with similar chemical composition in the same process
- to decrease the alkalinity of the final discardable waste mixture in comparison with untreated red mud alone, through the use of an acidic residue
- to increase titanium content (interesting in term of its value enhancement)
- to obtain valuable compounds from the treated red mud mixture (Fe_2O_3, TiO_2, Al_2O_3, Na_2O etc.)
- overall to generate a minimum amount of process waste

With these objectives in mind, Fe-Ti slag became the selected ingredient and the following study was performed.

3.1 *Thermodynamics of the chemical system Red Mud + Fe-Ti slag*

A thermodynamic study on red mud residue at a temperature below 100°C was undertaken. FactSage™ 5.2 software was used to create E-pH diagrams. From these diagrams, suitable conditions for component stability in aqueous solution could be estimated. E-pH diagrams of the Na-Al-Si-H_2O and Fe-Ca-Mg-H_2O systems at 90°C were created; these are shown in Figures 2 and 3. Figure 2 shows that the Na+ ion is stable in the solution over the whole of the acidic pH range (pH<7). It corresponds to the Na content that is present in red mud as free Na_2O (leachable soda from entrained liquor) and also from Na_2O that is bound in Bayer sodalite. According to these E-pH diagrams, Si is present in acidic solutions at 90°C in solid form as H_2SiO_3; however it is known that SiO_2 is soluble in acidic environment (Bouallou 1998). Silica also dissolves when aluminium is present in the solution, by releasing monomeric species and soluble polymeric silica appears (Iler 1979). So there is a discrepancy here. $Al_2O3(H_2O)$ is soluble at 90°C and pH value of 3.1 and aluminium passes into solution as the Al^{3+} ion.

As is further shown in Figure 3, iron is at 90°C present in solution as insoluble α-Fe_2O_3, but in the more acidic part of the diagram (pH<5) and at a low chemical potential Fe^{2+} ion appears in solution. The Fe^{2+} ion domain increases with decreasing pH. Titanium is present in the acidic solution as insoluble TiO_2. But, it is well known that TiO_2 is soluble in a strongly acidic environment (pH<1) and that this fact is used in TiO_2 production by the sulphate process (Institut fur Umwelttechnik und Management an der Universitat Witten/Herdecke 2001). E-pH diagram for the Ti-H_2O system shown in Figure 4 (Pourbaix 1966) partly proves the abovementioned fact about TiO_2 solubility in strong acidic environment.

Some discrepancies, existing between E-pH diagrams and practical experiences, can be explained by the limitation of the thermodynamic software used for diagram construction.
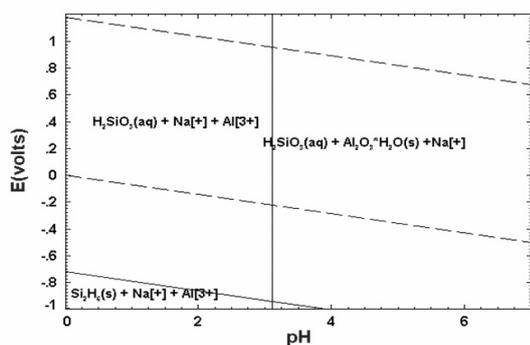
Figure 2: E-pH diagram for the Na-Al-Si-H₂O system at 90°C (molality of species = 10-6)
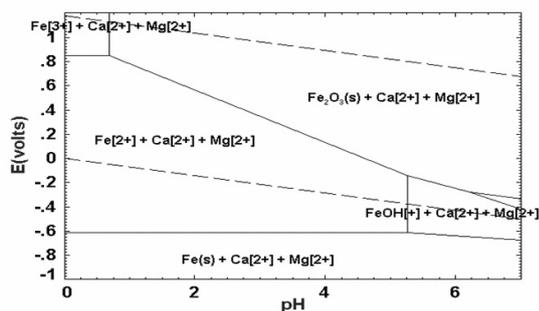

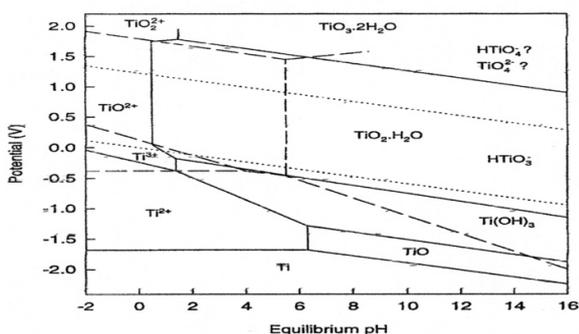Figure 3: E-pH diagram of the Fe-Ca-Mg-H₂O system at 90°C (molality of species 10-6)

Figure 4: E-pH diagram for the Ti-H₂O system at 25°C (adapted from the work of Pourbaix [11])

4 Experimental

4.1 Process diagram

The leaching process was selected for red mud + Fe-Ti slag mixture treatment. Experiments were carried out according to process diagram, which is schematically described in Figure 5. The process diagram was divided into 2 stages. In stage one, the mixture of red mud + Fe-Ti slag is the feed material leached by H_2SO_4 under selected conditions to remove sodium content from the by-product mixture into the solution for further treatment. In the second stage, undissolved residue from the first stage was leached under selected conditions to transfer aluminium and silicon contents to the solution for further treatment. Undissolved residue from the second stage can proceed for further treatment to produce TiO_2 and iron.
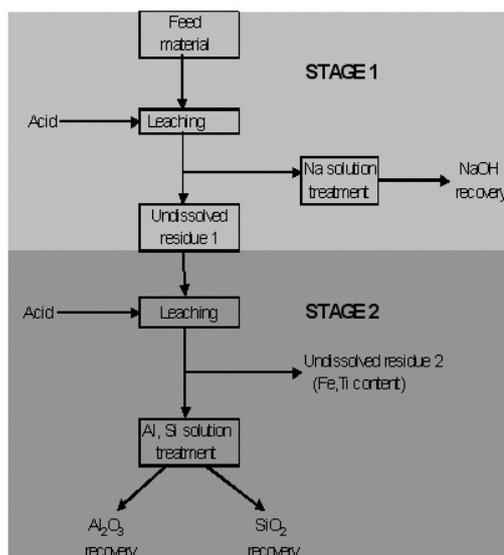

Figure 5: A proposed process flowsheet for the red mud Fe-Ti slag mixture treatment

4.2 Feed Material

The feed material consisted of two by-products (Ratio 1:1): Red mud from the Bayer alumina production process and the Fe-Ti slag, from the ilmenite ore treatment process, used in the production of titania.

Red mud in the unwashed solid form was provided from Alcan's alumina plant in Jonquière (Québec, Canada). Fe-Ti slag sample was obtained from a titania producer. Both materials were dried in an oven at 110°C for 24 hours, milled to 0.1 to 1 μm and characterized by the X-ray diffraction, ICP- AES, SEM-EDAX and TG/DTA techniques.

4.3 Mineralogical composition of the red mud and Fe-Ti slag

Red mud and Fe-Ti slag both have a complex mineralization, depending on chemical and mineralogical composition of the processed ore and on the conditions employed during the ore process treatment. In view of the complex nature of both by-products, it is apparent that more than one method is required for the investigation of the minerals present. The following methods were applied: X-ray powder diffraction spectroscopy and TGA/DTA.

X-ray diffraction analysis was performed on a Philips high-resolution diffractometer (Model X'PERT PRO MPD Pananalytical), equipped with a graphite monochromator for precision measurements with Cu radiation. Crystalline phases were identified using the database of the International Center for Diffraction Data-JCPDS for inorganic substances. The mineralogical components of red mud revealed by this analysis are: hematite (Fe_2O_3), gibbsite ($Al(OH)_3$), boehmite ($AlO(OH)$), anatase (TiO_2), calcite ($CaCO_3$), quartz (SiO_2), goethite ($FeO(OH)$), sodium-aluminium-silicate hydrate (DSP/sodalite) ($3Na_2O.3Al_2O_3.5SiO_2.5H_2O.Na_2CO_3$).

The mineralogical components of Fe-Ti slag are: hematite, ilmenite, rutile, iron, anorthite $(Ca,Na)(Si,Al)_4O_8$, gonyerite $(Mn,Mg,Fe)_6Si_4O_{10}(OH)_8$, clinochlore $(Mg,Fe)_6(SiAl)_4O_{10}(OH)_8$.

4.4 Chemical composition and granulometry of the feed material

Induction coupled plasma – atomic emission spectroscopy (ICP-AES) was used to determine elemental compositions of the two by-products. The average elemental composition of representative samples is set out in Table 1. It is seen that the main components of red mud are Fe_2O_3, Al_2O_3, SiO_2, Na_2O, TiO_2 and CaO. The main components of Fe-Ti slag are Fe_2O_3, TiO_2, SiO_2, Al_2O_3 and MgO. Both by-products also contain "interesting" amounts of ZrO_2 and V_2O_5. No direct, quantitative chemical analysis for elements, other than those indicated in Table 1, was conducted on the examined samples.

Table 1: Chemical composition of representative samples

Sample	Chemical Composition															
	SO_3	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	Cr_2O_3	CaO	P_2O_5	ZrO_2	ZnO	MnO	V_2O_5	K_2O	MgO	Na_2O	LOI
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Red Mud	0.81	20.6	35.4	12.4	6.75	0.11	4.78	0.19	0.24	0.02	0.02	0.2	0.06	0.25	7.53	10.62
Fe-Ti slag	0.05	7.34	35.7	13.3	31.65	0.15	1.92	0.08	0.15	0.12	0.26	0.81	0.46	5.41	1.03	1.67
Mixture (1:1)*	0.9	13.8	35.5	12.8	19.5	0.13	3.32	0.13	0.2	0.07	0.14	0.51	0.26	2.88	4.24	5.58

*Mixture results were calculated

Particle sizes of the materials before undertaking the leaching treatment process was measured by laser particle sizing unit, Malvern Mastersizer (3600 E type). It was found that, after 15 min of milling the particle size of both materials lay between 0.1-1 μm and further milling did not change particle diameter.

4.5 *Leaching technique*

Homogenous mixtures of milled red mud and Fe-Ti slag, having particle sizes of between 0.1- 1 μm, were prepared for the leaching treatment process. 50g of the mixture was used for each experiment. An acid solution of known concentration was transferred to the reactor and heated with constant stirring, to the pre-selected temperature. The 50g of sample was added to the reactor, the pH stabilized at the selected level by further H_2SO_4 addition(s) and reaction commencement time noted. At the end of each test, the contents of the reactor were poured into the filtration system, some 20ml of filtrate being taken for analysis, while the filtration cake was dried in an oven at 110°C over 24 hour period and analyzed.

5   Results and discussion

5.1   *Effect of pH on elements dissolution in the first and second stage*

Figure 6 shows the effect of pH, on the dissolution of sodium, aluminium, iron and silicon species in H_2SO_4 solution, in the first stage of the process. Tests were made at three pH values (3.0, 4.3, 5.0). The amount of sodium species dissolved in the solution increased as the pH decreased. The amount of dissolved aluminium, silicon and iron species at pH = 5.0 and 4.3 was small in comparison to the sodium content; at pH = 3.0 it was slightly increased. To minimize the dissolution of aluminium, iron and silicon, pH = 4.0-4.3 was estimated to be optimal for the selective sodium dissolution.

Figure 7 shows the effect of the H_2SO_4 solution pH on dissolution of the aluminium, silicon, iron and titanium species in the second stage of the process. As an input material for the second stage, the undissolved residue from the first stage of the process was used. It seems that at pH <2.5, the dissolution of aluminium and silicon increases rapidly as the pH decreases. Dissolved iron starts to increase only at pH<2.1. Over the pH range studied, titanium does not appear to dissolve. To minimize iron dissolution, a pH of = 2.1 was selected as that optimal for aluminium and silicon dissolution.

5.2   *Effect of retention time and temperature on sodium dissolution in stage 1*

Figure 8 and 9 show Na content dissolution under different conditions in the first stage of the proposed process. Three different leaching residence times (30, 60 and 90 minutes) and three different leaching temperatures (80, 90 and 100°C) have been considered, all at constant pH. As may be seen from the figures, sodium dissolution increases with leaching time and with leaching temperature up to 90°C, then it drops at 100°C. This effect is possibly due to sodium precipitation in the form of Na_2SO_4. Under optimum conditions, the maximum Na-content dissolution was 91% while the sodium species level remaining in the undissolved residue was less than 0.5%. SiO_2 dissolution decreases with retention time and temperature while Al_2O_3 does not dissolve under the above described conditions.

5.3   *Effect of retention time on Al, Si, Fe, Ti dissolution in stage 2*

Figure 10 shows Al, Si, Fe and Ti solubility in the second stage of the proposed process. Five different leaching residence times (30, 60, 90, 165 and 480 minutes) have been considered at constant pH, leaching temperature and solid-liquid ratio. As may also be seen, aluminium dissolution increased with leaching time until a plateau was reached, then it remained in the solution without significant change. Silicon dissolution increased up to 90 min, then it dropped significantly with longer retention time. Iron content increased with retention time while titanium dissolution was negligible. Figure 11 shows the yield of elements dissolution obtained in this second stage. Maximum yields of dissolved Al_2O_3 and SiO_2 were 54% and 37 % respectively. The yield for dissolved Fe_2O_3 was very small (max.5%) and no TiO_2 was dissolved under described conditions.
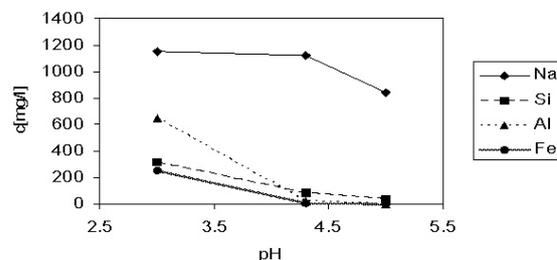
Figure 6: Effect of pH on elements solubility
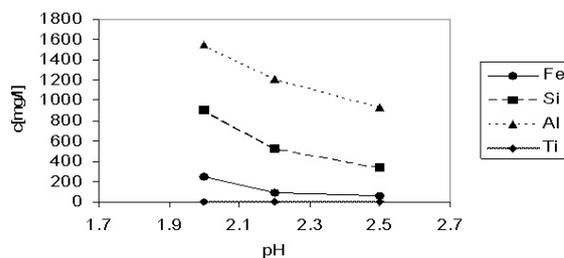(90 min, 90°C, S:L ratio =0.06) (1st stage)

Figure 7: Effect of pH on elements solubility
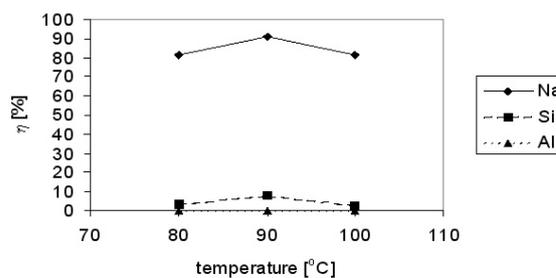(90 min, 90°C, S:L ratio =0.06) (2nd stage)

Figure 8: Yield of the species removal at different temp.
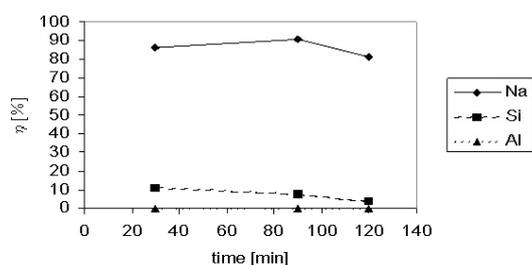(pH=4.3, 90 min) (1st stage)

Figure 9: Yield of the species removal at different retention time (pH=4.3, 90°C) (1st stage)
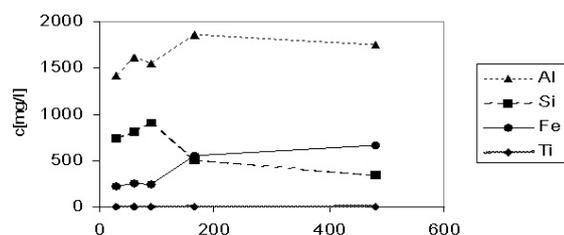

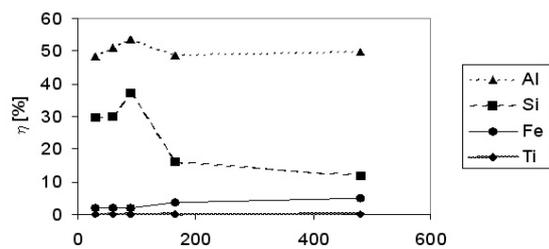Figure 10: Effect of retention time on elements solubility (90°C, S:L ratio 0.06, pH=2) (2nd stage)

Figure 11: Yield of the species removal at different retention time (pH=2, T=90°C) (2nd stage)

6 Conclusions

Many patents related to red mud treatments have been issued by various bureaus since 1990. Only a few of these patents are partially in present application and none are widely used. The situation most likely results from the absence of environmental motivation and an economic solution to this problem. It must be remembered that this problem is not only one related to high disposal cost but also the environmental footprint and legacy. To make red mud treatments more economic, the most probable route is to either combine different methods or treatments of suitable waste mixtures, which would include use of red mud.

Analyses have shown that red mud and Fe-Ti slag are compositionally very similar; it was considered that both materials are suitable for simultaneous hydrometallurgical treatment in the same process and that a useful synergy exists between them, as one is alkaline and the other acidic.

From E-pH diagrams of the red mud material, and the Fe-Ti slag chemical system, a process flowsheet has been proposed, based on achieving suitable conditions for selective species dissolution.

To evaluate the proposed process, several preliminary tests have been conducted to examine the dissolution of sodium, aluminium, silicon, iron and titanium species (from red mud/Fe-Ti slag) in H_2SO_4 solution at different pH values, times and temperatures. Partial results indicate that a maximum in the sodium dissolution occurs at pH 4.0-4.3, with a residence time of 90 minutes and at a temperature of 90°C, while aluminium and silicon dissolution remains minimal. For the second stage of the proposed process, a pH of 2.1 was selected to minimize iron and titanium dissolution and maximize aluminium and silicon dissolution. Further work needs to be performed to determine optimum conditions for aluminium and silicon species recovery from solution without incurring subsequent iron dissolution.

Acknowledgements

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