Factors Affecting Solute Analysis of Bauxite Residue Filter Cakes and Resulting Influences on Solute Recovery Calculations

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Abstract

Bauxite residue filter cakes are analyzed regularly at refineries which use filters for the final deliquoring of the solids, relying on the dry cake disposal method. Due to the different raw materials and process conditions, the bauxite residue filter cakes are different as well. Chemical analysis of bauxite residue filter cakes regarding their soluble compounds, especially total caustic, is performed routinely after forming slurry from the cake and pure water by using a certain liquid/solid (L/S) ratio. This paper shows that there is currently no cake analysis procedure which could be used without unexpected variation in the results. This is because several factors affect the analysis result at the filtration and sample preparation stages. The factors discussed in this paper include 1) the filtration and washing conditions, and the sample preparation procedure from filter cakes, encompassing 2) the L/S ratio, 3) the composition of the diluting liquid with respect to its Na_2CO_3 concentration, 4) the temperature, and 5) the cake leaching time. Additionally, examples are provided about particle size measurements and calculation of alkali recovery for the filtration stage. Significant differences in the results are observed when any detail in the sample preparation procedure is changed.

Keywords: Bauxite residue, filter cake, analysis, caustic, dissolution.

1. Introduction

Bauxite residue is the largest waste fraction generated in the alumina industry. According to the recent online statistics of World Aluminium [1], the amount of bauxite residue generated annually has increased mainly in China, and the total amount was approximately 150 million tons in 2015. The total inventory of the residue disposed of during the past decades has been estimated to be over 4 billion tons [2]. The residue is highly caustic [3], has a fine particle size distribution [4,5], and it contains a wide variety of metals, including both environmentally problematic [6] and valuable [7,8] metals. Bauxite residue has a high buffering capacity, which is largely associated with its alkaline solids content, e.g. a variety of hydroxides, carbonates, aluminates and aluminosilicates [9].

The disposal of bauxite residue in the form of filter cakes, i.e. dry cake disposal, is an emerging method, which enables disposal of the residue in landfills, instead of lagooning [10]. The total solids concentration of filtered and washed bauxite residue cakes is typically over 70 wt.% when filter presses or hyperbaric drum filters are used [11,12]. Due to the recovery of the caustic liquor from the cake in the filtration plant, the cakes are prone to a decrease of pH when the samples are prepared for the analysis of solutes by forming slurries with water. The solutes of interest are the total alkali, total caustic, sodium and alumina. All these species may leach out from the suspended solids when the cake samples are mixed with water to form suspensions for analyzing the solute concentrations, for instance by titration, atomic absorption spectrometry (AAS), or inductively coupled plasma mass spectrometry (ICP). However, the influence of the sample preparation conditions on the analysis result has not been summarized in the existing literature.

The objective of this article is to initiate discussion on the factors affecting the analysis results of bauxite residue filter cakes. The paper summarizes the most important findings of the authors, obtained during several years of filtration research with different bauxite residues. The aim is to demonstrate, mainly by using dimensionless values, that the analysis results are highly sensitive to a number of factors in the stage of sample preparation.

2. Materials and Methods

Industrial bauxite residue samples from most continents were used as raw materials in the studies. The cakes were obtained either directly from refineries or as a result of filtration and cake washing experiments performed at Outotec Filters and Lappeenranta University of Technology, both located in Lappeenranta, Finland.

2.1. Effect of Filtration and Washing Conditions

The first part of the study was targeted at investigating the effect of filtration temperature and pressure on the leaching out of solutes from bauxite residue filter cakes. The study was performed by using two different filters, a Nutsche filter ($A \approx 20\ cm^2$) and a Larox PF 0.1 filter press ($A = 0.1\ m^2$). Cake washing was performed in both filters at 65 °C by using moderate wash ratios and water as the washing liquid. Additionally, leaching trials at atmospheric pressure were carried out by using the same bauxite residue slurry that was used in the filtration experiments. The results of the studies on the effect of pressure and temperature applied in the washing and solid-liquid separation stage have been presented earlier in a different form by Kinnarinen et al. [13]. For comparison, dilution of different bauxite residue *slurries* with water has also been investigated by Kinnarinen et al. [14].

2.2. Effect of Sample Preparation Procedure

The effect of the L/S ratio in the sample preparation stage was studied by using a washed, crushed and homogenized filter cake with a total solids content of 78 wt.%. In this case, the cake was obtained directly from an alumina refinery. The cake samples were reslurried and mixed with a VWR orbital shaker at the speed of 250 rpm. A wide range of liquid/solid (L/S) ratios from 1 to 49 was used. The experiments were performed at room temperature, and the samples were let to stabilize for 2 days before performing solute analyses for the clarified supernatant.

The influence of the composition of the dilution liquid was evaluated by using the same cake material as above in the L/S ratio -related investigations. The aim of this series of experiments was to study if it is possible to avoid desorption and dissolution of the suspended solids content of the cake by using a Na_2CO_3 solution with different concentrations in the cake reslurrying procedure, instead of using pure water. The Na_2CO_3 concentrations of the dilution liquids in these experiments were 25.5, 51.0 and 76.9 g/kg, and the temperatures were 20, 50 and 80 °C. Additionally, control experiments were performed for comparison, using pure water and the same temperatures.

When a bauxite residue filter cake is suspended in water, the resulting reactions never take place immediately. To demonstrate the importance of the sample stabilization time in the analysis of the cake, experiments were performed by using short and long stabilization times (75 s and 2 d) and two L/S ratios (1 and 9). For comparison, the effect of the dilution liquid was also studied by using both water and mother liquor, in this case the filtrate, as the dilution liquids. At the end of the stabilization time, the sample was centrifuged at 1700 G with a Jouan GT 422 bucket centrifuge for 2 min. The clear supernatant was separated for analysis immediately after the centrifugation.

The analytical operations were performed with AAS for Na and Al, and with a thermometric titrator capable of measuring e.g. the total caustic and aluminate. The sodium concentrations were measured with AAS by using a Thermo Scientific iCE 3000 atomic absorption spectrometer. The thermometric titrations were carried out with a Metrohm 859 Titrotherm device. The total caustic is defined as follows: the total hydroxyl ion content, which comprises the free hydroxyl ion (OH^-) content and one mol OH^- per mol aluminate. Parallel runs were performed regularly with both devices to ensure reliability of the analyses.

The pH values of the cake sample slurries were measured with a WTW pH 340i pH meter and a WTW SenTix 41 electrode.

Particle size distributions of a washed filter cake sample were measured at different conditions with a Malvern Mastersizer 3000 laser diffraction particle size analyzer and a Hydro EV particle dispersion unit. The particle size analyses were performed both with and without ultrasonication and without dispersing agents by using the stirring rate of 3500 rpm.

3. Calculations and Definitions

The calculation of caustic recovery in the filtration of bauxite residue and washing of the formed filter cakes can be performed by relying on the solute concentrations of the slurry, wash liquid, filtrates, and the cake, as presented in Figure 1.

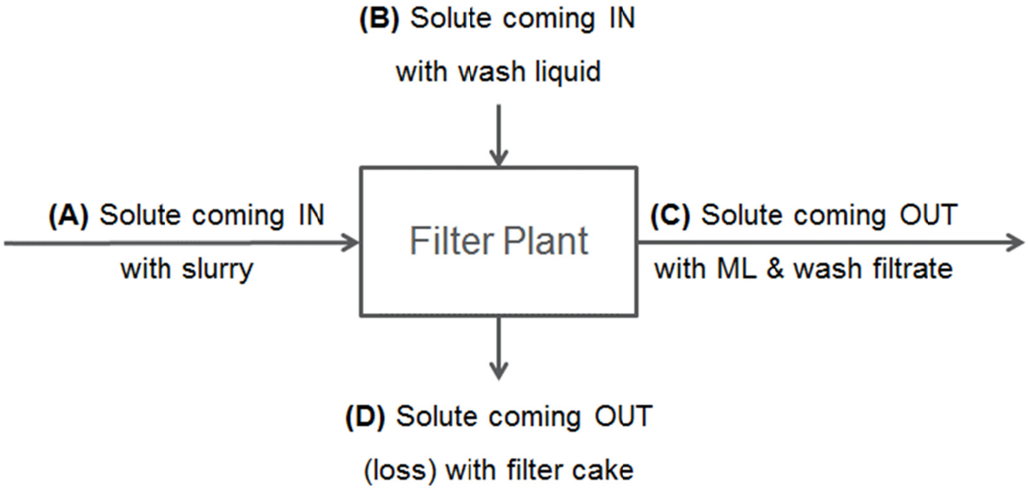

Figure 1. Material streams A - D used in the mass balance and solute recovery calculations.

In this study, the solute recovery is defined in two alternative ways, according to Eqs. (1) and (2) by using the letters A - D introduced in Figure 1.

Recovery R1 (%) is based on slurry (A), wash liquid (B) and filtrate (C):

$$R1 = \frac{C}{A+B} \cdot 100\% \qquad (1)$$

Recovery R2 (%) is based on slurry (A), wash liquid (B) and cake (D):

$$R2 = 1 - \frac{D}{A+B} \cdot 100\% \qquad (2)$$

As can be seen in Equation (2), the solute recovery R2 is increased as a result of a decrease in the measured solute content of the cake (D). What is often not taken into account is the influence of the sample preparation method on the analysis results. The impacts of some variables are considerable, as shown in the Results section of the study. Therefore, the selection of the sample preparation procedure is of crucial importance when the solute recovery is calculated by using the solute contents of the filter cakes.

4. Results

A comparison of the washing of the bauxite residue cakes in pressure filters and the washing/leaching of the same material in the form of slurry with water at atmospheric pressure is presented in Section 4.1. An overview of the factors affecting the solute analyses of filter cakes and the calculated values of solute recovery can be found in Sections 4.2 - 4.4. In addition to the solute contents, some interesting observations regarding particle size measurements are presented in Section 4.5.

4.1. Filtration and Slurry Dilution: Effect of Pressure and Temperature

Figure 2 shows a comparison of the washing conditions of bauxite residue. The filter cakes compacted at pressures of 12 and 6 bar after cake washing at different wash ratios can be observed to release relatively high amounts of sodium from their solid phase. On the other hand, the wash ratios required to reach the same relative surplus of Na dissolution in the slurry leaching tests are much higher. The cake analyses were performed with AAS after reslurrying the cake samples in water (L/S ratio = 9). The slurry analyses were performed after the sample stabilization time of 24 h.

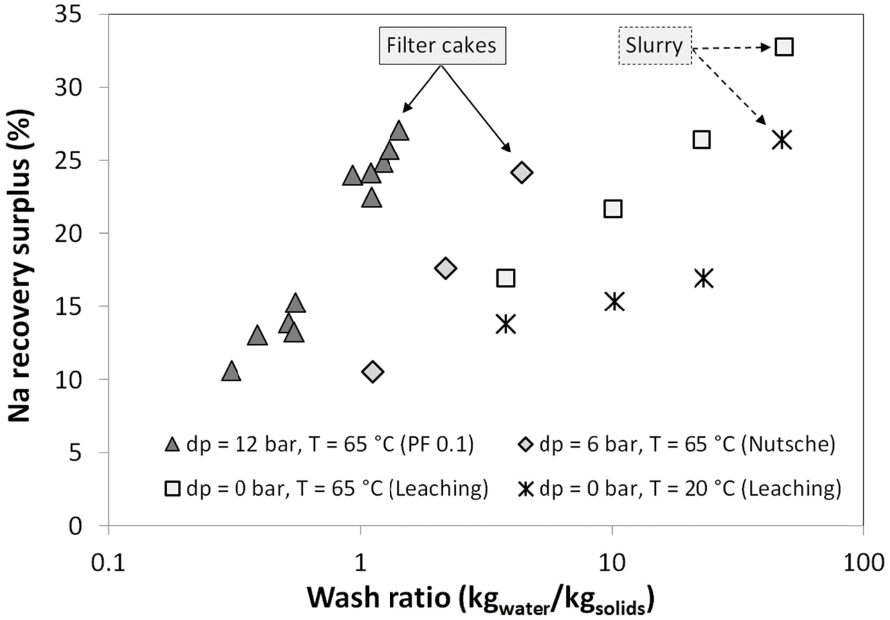

Figure 2. Effect of wash ratio on the dissolution of alkali from the solid phase of bauxite residue filter cakes and diluted bauxite residue slurry samples washed at different temperatures and pressures. Note the logarithmic scale of the x-axis.

The washing of filter cakes in pressure filters is an operation which requires lots of experimental work to be even close to optimal. It is practically impossible to reach a complete removal of solutes from the cake, although displacement washing at high wash ratios may result in excellent washing efficiency. When bauxite residue filter cakes are washed with hot liquid in pressurized conditions, the results often look better than they actually are. There are solids in the cake which are dissolved due to the temperature and a decrease of the pH and ionic strength of the cake liquor. This phenomenon is explained in closer detail the Discussion section of the paper.

4.2. Cake Analyses: Effect of Liquid/Solid (L/S) Ratio

The influence of the applied L/S ratio in the sample preparation step when the filter cake is mixed with water should not be underestimated, as the graphs in Figure 3 clearly illustrate. Dilution of the sample with water causes an inevitable pH decrease, as the ionic strength of the liquid phase decreases, which in turn results in desorption and dissolution of suspended solids from the cake. In this case, the relative quantities of Na and Al originating from the solid phase were calculated on the basis of analysis results obtained by thermometric titration. As shown in Figure 3a, the pH of the cake liquor decreased from 13.5 to 12.1 due to the dilution (L/S ratio = 49), and the decrease of pH was at its steepest at lower L/S ratios. Resulting from the decreasing pH (Figure 3a), the Na_2O and Al_2O_3 surplus (Figure 3b, c) increased steeply at the lower L/S ratios used in the sample preparation step, and more and more Na and Al were liberated from the solids until the highest L/S ratio 49 was reached.

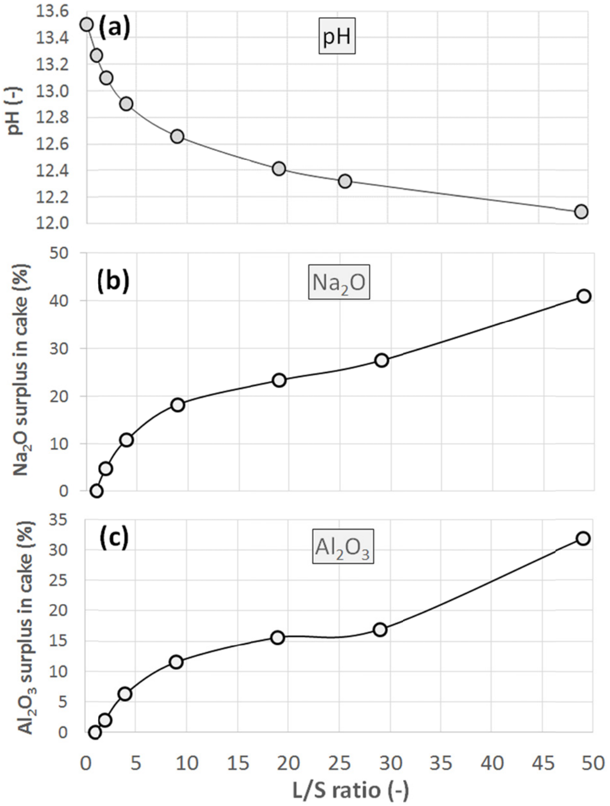

Figure 3. pH curve illustrating the decrease of pH with increasing L/S ratio (a) and the corresponding increase in the dissolution of Na_2O (b) and Al_2O_3 (c) from bauxite residue filter cakes. The sample stabilization time before the analyses and pH measurements was 2 days.

4.3. Cake Analyses: Effect of Dilution Liquid, Temperature and Time

Water and aqueous sodium carbonate solutions were used as dilution liquids in order to study how the solute content and temperature of the dilution liquid would affect the measured total caustic contents of the filter cakes, expressed as Na_2CO_3. Figure 4a illustrates the strong effect of temperature on the analysis results when the Na_2CO_3 concentrations were varied between zero and 77 g/kg liquid. It is easy to see in Figure 4a that the dilution liquids that have the highest concentrations of Na_2CO_3, have also the weakest response to temperature changes, which can be considered a positive feature regarding the avoidance of variation in the results of cake analyses.

Figure 4 b shows the influence of the dilution time, i.e. the leaching time, on the analyzed Na_2CO_3 concentration in the cake liquid for L/S ratios 1 and 9. The long dilution time of 2 days resulted in higher analyzed concentration of Na_2CO_3 in the cake liquid, compared to the short dilution time (75 s mixing + a few minutes for solid-liquid separation). The dilution time had a clear influence on the analysis result when the samples were prepared in water, but when the samples were prepared in a filtrate originating from the same slurry as the cake, the results became even more interesting, as shown in Figure 4b. By comparing the short dilution with water with the dilution with filtrate (45.8 $g_{Na2CO3}/kg_{filtrate}$), it can be observed that the analysis results give about doubled values for the dilution with water.

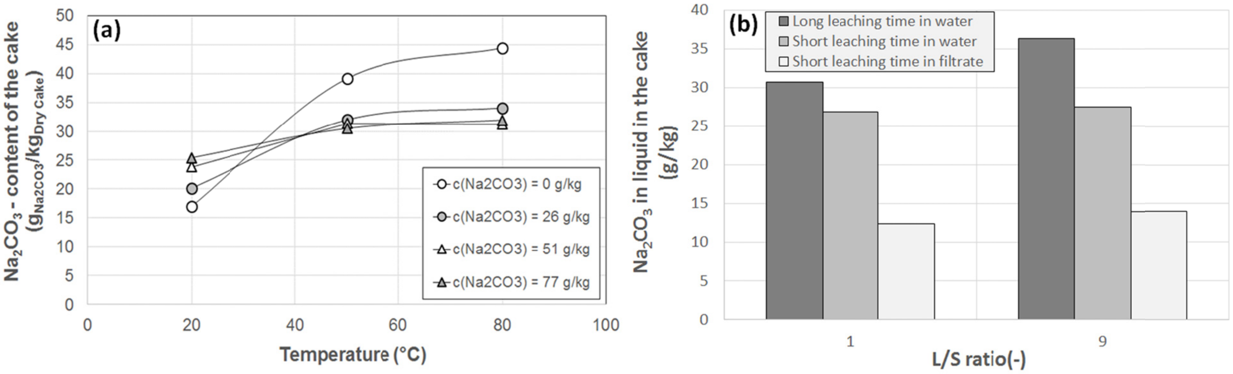

Figure 4. Analysis results of filter cakes with respect to the sodium carbonate contents when the dilution liquid in the sample preparation stage was either pure water or a sodium carbonate solution with different concentrations (a) and when the dilution time was 48 h, and the effect of leaching time at two L/S ratios (1 and 9) when the samples were diluted in water or filtrate by using long and short dilution times (b).

4.4. Calculation of Solute Recovery for Filtration and Cake Washing Operations

The results of filtration and cake washing experiments with respect to the solute recovery depend on the definition of recovery. Solute recovery can be calculated on the basis of the filtrate and the feed (Equation (1)), or on the basis of the mass of solute in the cake after the operation, compared to the mass of solute in the slurry fed into the filter unit (Equation (2)). Figure 5 presents a practical example of solute recovery calculations, showing clearly and consistently that calculation relying on the filtrate and feed concentrations yields a higher recovery, whereas using cake analysis (L/S = 9) in the calculation makes the recovery decrease by 10 - 20 % in most cases.

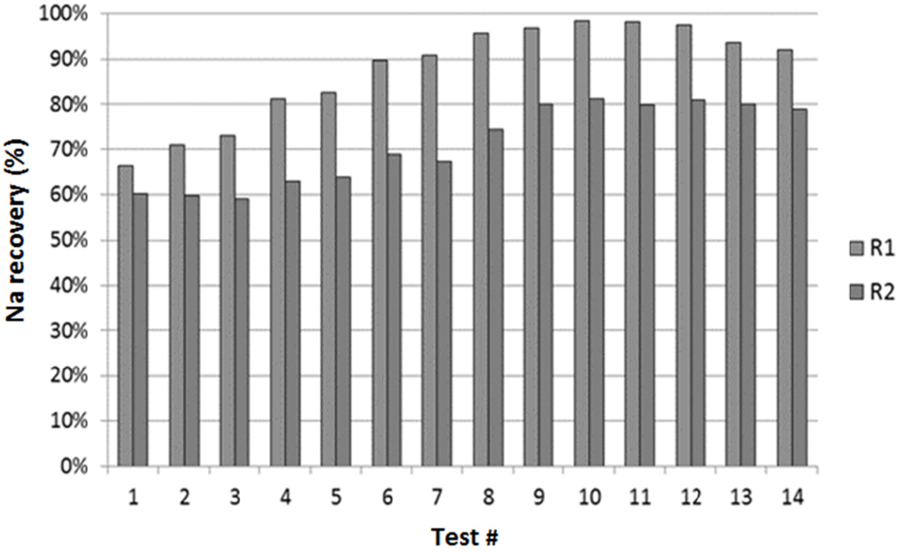

Figure 5. Comparison of calculated solute recoveries R1and R2.

Which definition of solute recovery would then be the most relevant to be used as a new standard of solute recovery calculation? There is no universal answer to this question, due to the influence of the filtration and cake washing conditions (*T*, *Δp,* wash ratio) on the filtrate and the cake. When solute recovery is calculated on the basis of filtrate and slurry, the value R1 becomes higher than it should in fact be, because pressure leaching of suspended solids occurs in the filter. On the other hand, the use of the result of cake analysis in the calculation, the leaching out of suspended solids from the cake results in a decreased recovery R2. The true solute recovery is thus apparently somewhere between R1 and R2.

4.5. Remarks about Particle Size Analyses

Particle size measurement of bauxite residues, in particular bauxite residue filter cakes, is also complicated. Figure 6 describes a situation where cake solids, wetted for a long time prior to analysis, were added into the particle dispersing unit of the analyzer, using water as the dispersing liquid. The solids concentration and the ionic strength of the liquid in the mixing unit were very low as usual, which had an impact on the particle size distribution. As demonstrated in Figure 6a with a washed filter cake, the reduction of the size of large particles is clearly observable when the sample mixing time is increased. Similarly, the application of ultrasound in the sample dispersion system reduces the particle size, which is clearest in the coarse end of the distribution (Figure 6b). The shape of the distribution changes as well, and the fraction of submicron particles increases, unlike in the case when ultrasonication is not used.

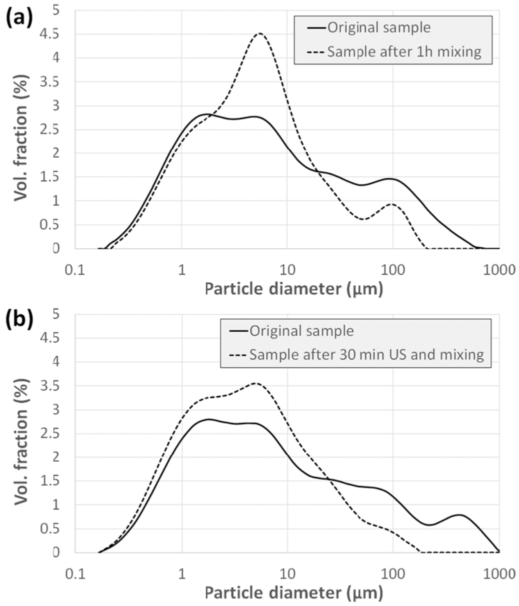

Figure 6. Changes in the particle size distribution of washed bauxite residue filter cake when the sample has been kept under continuous agitation for 1h (a), and under the influence of ultrasonication (US) in the same agitation conditions for 30 min (b).

5. Discussion

The key findings presented in this paper can be summarized in a few bullet points:

- The conditions in pressure filters leach lots of sodium, aluminum and associated caustic out of the suspended solids. Leaching equal amounts of the same components out of the slurry at ambient pressure requires over 10 times higher wash ratios.
- The leaching of caustic and alumina out of filter cakes in the sample preparation stage increases with the L/S ratio. No end to leaching was observed when the L/S ratio was gradually increased to 49.
- The composition of the dilution liquid has also an influence on the leaching of suspended solids from the cake. Water dissolves more material than Na_2CO_3 solutions. On the other hand, sample preparation can be performed more reliably with water when the sample stabilization time is short.
- There seems to be a need for the development of a standard method for cake analysis and solute recovery calculations.
- Additionally, the measurement of particle size distribution should be performed according to the same procedure, because the size distributions vary depending e.g. on the particle dispersing conditions.

According to the existing literature, the main reason for the increased leaching from the solid phase is desorption and/or dissolution of desilication products (DSP). The phenomenon was observed for almost two decades ago by Thornber and Binet [15], who found that desorption of suspended solids increased when bauxite residue was washed with water in four successive stages. Thornber and Binet [15] concluded that the release of sodium, hydroxyl, carbonate and aluminate ions was largely due to the presence of DSP, calcium species, and other minerals having charged species on their surfaces. Chvedov et al. [16] also refer to the importance of silica-containing precipitates which originate from the Bayer process and are deposited on the particle surfaces. They report those silica-containing compounds to be the main source of hydroxyl groups in bauxite residue solids. According to an extensive review by Gräfe et al. [17], the surface charge of such desilication products is negative. The buffering capacities of bauxite residues have been reported to be closely related to the presence of alkaline solids, such as sodalite (present in DSP) and calcite [18].

The pH decrease caused by dilution correlates well with the dissolution of Na, Al and caustic. The solid phase of a well washed and deliquored filter cake has an especially strong tendency to dissolve in the sample preparation stage. This is due to the low residual caustic content of such a cake, which consequently means that the cake does not have the buffering capacity required to persist the pH decrease.

Many metals present in bauxite residues have low solubility, unless acid is used to adjust the pH to the acidic range. Metals such as Na, Ca, Mg, Fe, Cu, Al, Mn, Ti and Cr are increasingly leached out from the material with a decreasing pH [19]. Although Rubinos and Barral [19] report results for pH values below 10, it is apparent from their data as well that the elements present in the desilication products, i.e. Al, Na and Si, are sensitive to pH changes also in the basic conditions.
Khaitan et al. [20] investigated the effect of acid titration time on the acid consumption of the titration procedure. They observed that tens of days may be required to reach the state of a constant pH, and the required time apparently depends on the end pH of the titration.

Additionally, solid reaction products resulting from lime addition in the Bayer process may have an influence on the cake analyses. Kirwan et al. [21] summarize earlier literature on the topic and mention calcium hydroxides, carbonates and aluminates, for instance tricalcium aluminate, as buffering species.

As regards the changes in the particle size distribution when bauxite residue solids are dispersed and kept mixed in water, it is obvious that the breakage of flocs plays a major role, the dissolution of particles being less important.

6. Conclusions

The aim of this paper was to present some selected results of the authors' experimental work performed with various filter cakes during the past years. All bauxite residue filter cakes have been observed to have a more or less similar behavior in the sample preparation stage prior to chemical analyses: dilution with a large amount of water makes the solute content look higher than it actually is, due to partial dissolution of the suspended solids content. When the L/S ratio used in order to re-slurry the cake for analysis has been increased from 1 to about 50, the dissolution of Na has been observed to increase by over 40 % and that of Al by over 30 %. This result depends on the refinery and the fraction of desilication products in the cake. On the other hand, the dissolution of surplus Na and Al can be prevented by diluting the cake samples with a filtrate collected from the same experiment. Increasing the pressure and temperature will inevitably increase the leaching of Na and Al from the solids. The most important factor having an influence on these dissolution phenomena is the decreasing pH of the liquid. However, a short dilution time prior to liquid analysis should not be used, because reaching the equilibrium between the solids and liquid phases may take a long time, which makes the differences between the samples become larger when the cake sample is prepared promptly. Temperature has a strong effect on the dissolution of solutes, especially when water is used as the dilution liquid, but this factor is not likely to cause significant variation in the analysis results in cases where the samples can be prepared at a constant room temperature.

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