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Challenges related to solute analysis of bauxite residue filter cakes

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ABSTRACT

Solute analysis of bauxite residue filter cakes is an important but not very well understood operation carried out at refineries and in scientific research. As more and more refineries rely currently on dry cake disposal after filtration, washing and deliquoring of the cakes, the importance of correctly performed cake analysis will increase. Chemical analysis of bauxite residue filter cakes regarding their soluble compounds, such as the total caustic, soda and aluminate, is performed after forming a slurry from the cake and pure water by using a selected 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 are divided into two groups, including the filtration and washing conditions and the sample preparation procedures. In the filtration stage, the filtration temperature and pressure were found to have a considerable effect on the solute recovery. On the other hand, the sample preparation procedure was observed to be affected by factors like the L/S ratio, the composition of the diluting liquid (with respect to its Na_2CO_3 concentration), the temperature, and the cake leaching time. In addition to the cake solute analysis, particle size measurements and calculation of alkali recovery for the solid-liquid separation stage are discussed as well. To summarize the main findings, it can be stated that significant differences in the results can be seen when any detail in the sample preparation procedure is changed.

1. Introduction

Bauxite residue is the largest waste fraction generated in the alumina industry. According to the recent online statistics of World Aluminium, 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 (Kong et al., 2017) The residue is highly caustic (Clark et al., 2015), has a fine particle size distribution (Johnston et al., 2010; Luo et al., 2016), and it contains a wide variety of metals, including both environmentally problematic metals, such as Cd, Cu, Ni and Zn (Ghosh et al., 2011) and valuable metals, e.g. Ti, V and rare earths (Liu and Li, 2015; Deng et al., 2017). 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 (Gräfe et al., 2011).

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 (Power et al., 2011). 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 (Kinnarinen et al., 2015c; Bott and Langeloh, 2015). As the environmental regulations are becoming stricter in most countries, the need for better understanding of cake analysis procedures is increasing. 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-MS). 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. One of the most important long-term objectives of the paper is to disclose the need for developing a universal, reliable and comparable procedure for the solute analysis of bauxite residue cakes. The paper summarizes the most important findings of the authors, obtained during several years of

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filtration research with a large number of 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 each 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 illustrating the effect of process 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 (at 20 and 65 °C) 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. (2015b). For comparison, dilution of different bauxite residue *slurries* with water has also been investigated by Kinnarinen et al. (2015a).

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 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 weight-based liquid/solid (L/S) ratios from 1 to 49 was used. The L/S ratios can be converted to wt.% according to Eq. (4). 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, according to Metrohm Application Bulletin 313 e (Determination of total caustic, total soda and alumina in Bayer process liquors with 859 Titrotherm). 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. The Fraunhofer optical model was utilized, and each measurement was performed at least three times. Averaged particle size distributions were then calculated from the data.

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 Fig. 1.

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 Fig. 1.

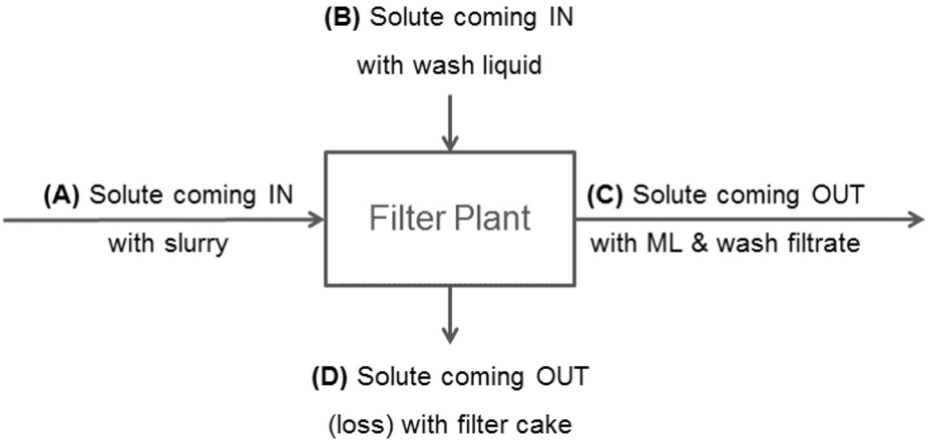

Fig. 1. Material streams A-D used in the mass balance and solute recovery calculations (ML stands for mother liquor).