IMPURITIES IN RAW GAS AND SECONDARY ALUMINA

Svetlana Kalyavina[1], Arne Petter Ratvik[1], and Thor Anders Aarhaug[2]

[1]NTNU, Department of Materials Science and Engineering, NO-7491 Trondheim, Norway
[2]SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

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Abstract

It is known that impurities in the secondary alumina tend to accumulate in the finer alumina fractions. Although several treatment methods have been suggested for impurity removal, very few in depth studies are published. In this study, samples of secondary alumina have been split into different fractions using an air classifier. In addition, the secondary alumina has been compared with samples extracted from the raw gas before the dry scrubber. The characterization of the secondary alumina fractions and the raw gas samples are performed by SEM, XRD, EPMA and ICP-MS chemical analysis. Some introductory considerations on acid leaching of the secondary alumina fractions to remove and recover the impurities will also be discussed.

Introduction

The (primary) alumina used in the dry scrubbing of the HF also captures impurities in the off gas. Extensive studies [1, 2, 3, 4, and 5] have been made to remove impurities from the (secondary) alumina after the dry scrubbing. Also impurities in the pot gas before the dry scrubber have been investigated [6, 7]. The overall conclusion is that the impurities are concentrated in the finer fractions of the secondary alumina, and that the pot-gas dust passes nearly unchanged into the secondary alumina [8].

In a modern dry scrubbing system which efficiency is exceeding 99.8 % [9], the system can be regarded as closed loop system between the pots and the dry scrubber. Consequently, the main outlet for impurities is through metal tapping [10], while some elements will also accumulate in the bath, causing reduced current efficiency (CE) and leading to extra additions of AlF_3 and higher frequencies of surplus bath tapping.

The most undesirable impurity according to the aluminium producers is phosphorus. The phosphorus does not directly affect the quality of aluminium metal produced, but does cause the operating temperature of the pot to rise and the current efficiency to decrease. An increase of 100 ppm of phosphorous in the bath will decrease the current efficiency by approximately one percent [11]. Other main impurities are Fe, Mn, Si, Ti, Zn, Ga, Be, alkali and alkaline earth elements, such as Li and Mg. All these impurities may negatively affect metal purity, mechanical properties, bath chemistry, or temperature and affect the wear of the cell lining. Sodium and calcium oxides in alumina dissolve in the bath and change the Cryolite Ratio (CR) and superheat.

It is possible to reduce the amount of impurities by treating the pot gas before entering the dry scrubber. An alternative process is to purify the secondary alumina before sending it back to the cell. It has been tried to carry out the former alternative by using electrostatic precipitators. However, the large gas volumes make it very expensive, and it may be a less favorable alternative.

Previous studies on contaminants removal showed that the impurities are concentrated in the fine fraction of the secondary alumina. Small particles (<10 μm) can be found as deposits on larger alumina particles. Through removal of these fine particles a relatively large fraction of the impurities are removed. In a treatment process, the objective is to remove as much impurities as possible without removing too much of alumina and fluorides. To meet these objectives, a process for efficient removal of impurities from the enriched alumina by using an Impurity Stripper was developed [9]. Impurity stripping is based on impact to detach the smaller particles adhered to the coarser particles and then to separate them from the main stream. The main fraction of the treated alumina is used for metal production while the fine fraction, with a high concentration of the impurities, is removed. Because of the recycling and accumulation of the impurities, removing only a small fraction in the stripper can reduce the concentration of impurities in the cell and in the metal by a much higher value [9].
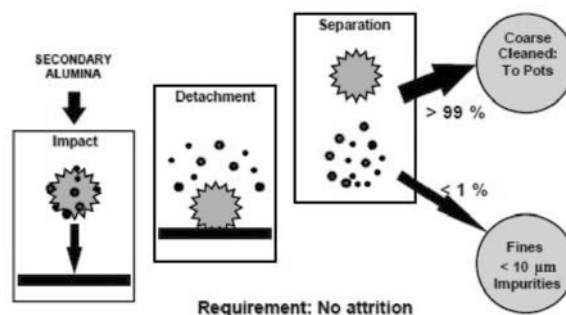

Figure 1. Impurity stripping principle [9].

In the present work, characterization and analysis of the secondary alumina fine fractions and the raw gas samples before the dry scrubber has been performed and compared. In addition, technical feasibility study to perform a treatment for removing impurities within the finer fractions of secondary alumina by acid leaching in a laboratory scale was carried out.

Experimental

Materials and Methods

Secondary alumina was sampled at Hydro Aluminium in Norway in May 2011. After sampling, the secondary alumina was splitted into two fractions using an air classifier. Based on previous studies on removing impurities from secondary alumina, the target was to split the fractions at D_{50} approximately 10 μm and 20 μm.
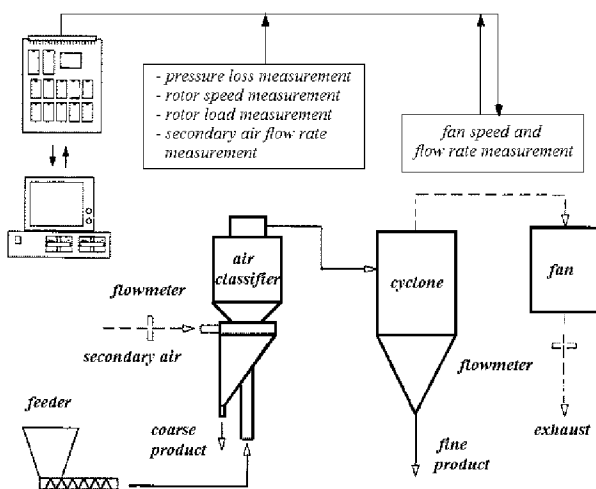
Figure 2. Schematic illustration of the air classifier circuit [12].

Splitting process description

The secondary alumina was fed to the classifier circuit mixed with air through a vertical pipe positioned at the bottom of the classifier (Figure 2). The classifying process takes place in the classifying chamber by forced vortex action. The coarse material was discharged from the air classifier through the bottom outlet at a flow rate of 70 m³/h. The fine fraction was separated from the air in a cyclone and collected. The filtered air, after passing through the fan, was exhausted to the atmosphere. There is a secondary air inlet, supplying the classifier with an additional air jet stream, which is used to separate the coarse fraction from the very fine particles by impaction, as the fine particles tend to adhere to the surface of coarser particles. This provides good classification efficiency [12].
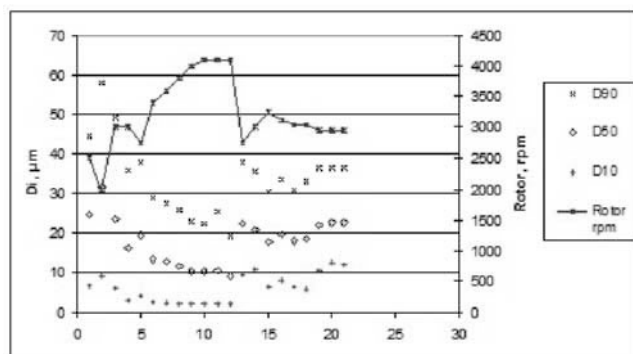

Figure 3. Splitting data from air classifier.

The acid leaching procedure for the secondary alumina was as follows: 20 – 30 mg of samples were leached with 2.16 ml ultra pure HCl (10 M) (2.38 g with density 1.1 g/ml), heated at 80 °C in ultrasonic bath for 1 hour, diluted to 216 ml (216.5 g) and transferred to 15 ml trace metal free vials used for ICP-MS analysis. Blank samples were used to correct for background levels of elements. Acid leaching did not digest the samples completely.

To know the total amount of impurities and to maintain the mass balance, secondary alumina samples were also dissolved in potassium pyrosulfate, 99 % (Sigma Aldrich, Germany). Sample weights close to 0.25 g were dissolved in approximately 5.0 g $K_2S_2O_7$. Exact masses were used in the calculation of the results. Samples were melted in a muffle furnace at 450 °C. Samples were then dissolved by boiling in distilled water and diluted to 500 ml.

The samples were characterized by means of Scanning Electron Microscopy (SEM), Electron Probe Micro-Analysis (EPMA) and analyzed by X-Ray Diffraction (XRD) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses.

To obtain information about the impurity distribution in the raw gas before the dry scrubber, additional leaching experiments were conducted on samples collected in June 2012. Overall 4 samples using sampling times of 50 to 60 minutes were analyzed. The portable sampling system (TPS 4) supplied by Environnement S.A. Deutschland; Bad Homburg, Germany, was used for isokinetic sampling off-gas from pot-room sections consisting of 114 cells. The sample volume is sucked through the entry nozzle (with a filter following downstream) from the gas duct by a frequency controlled gas-tight rotary vane vacuum pump. The sample volume flow rate is measured between the filter and the pump by means of an orifice plate and controlled by a frequency converter. The particle fraction larger than 10 μm was captured by a standard EPA-cyclone [13]. Three washing bottles with impingers were installed after the cyclone. For each run the first two bottles were eached filled with 100 ml acidic solution, 0.1 M HNO_3, 0.1 M HCl and 0.1 M H_2SO_4, respectively, while the third bottle remained empty. The acidic solutions were prepared from the nitric acid, 65 % (Sigma-Aldrich, Germany), sulfuric acid, 95 – 97 %, (Merck KGaA, Darmstadt, Germany) and hydrochloric acid, 37 % (Merck KGaA, Darmstadt, Germany), respectively. The residual fume particles were captured on filters, installed after the washing bottles, as can be seen on Figure 4. The gas flow rate was the same (0.7 m³/h) in all experiments.
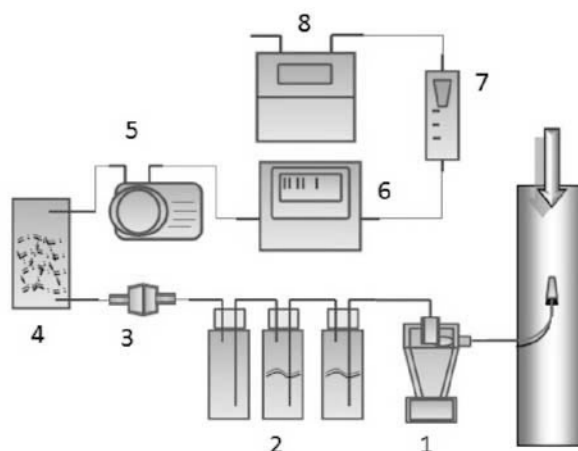

Figure 4. TPS 4 setup: 1 – cyclone; 2 – washing bottles with impingers; 3 – filter; 4 – drying tower; 5 – pump; 6 – flow control unit; 7 – flow meter; 8 – gas meter.

Prior to ICP-MS analysis the samples were heated in ultrasonic bath at 50 °C for 1 hour to remove carbon dust particles from the

plastic bottle wall. Some samples were diluted with distilled water to 15 ml to avoid overload and contamination of ICP-MS equipment. Third bottle was washed with distilled water after every run and these samples were then transferred to 15 ml trace metal free vials. 5 drops of ultra pure nitric acid were added into these samples to provide proper ICP-MS analysis and avoid loss of mass to sample containers.

Results and Discussions

Particle Size Analysis Results

After splitting, the fine samples were dispersed in distilled water and particle size analysis was performed using Malvern Mastersizer 2000 particle size analyzer.

One of the key factors affecting the accuracy of many laser diffraction particle size measurements is the choice of refractive index (RI). Consisting of real and imaginary components the RI describes how light interacts with a material. The real component was listed in the software library. The imaginary component, or *i* term, is a value between 0.0 and 10.0 that correlates to the degree of difference between a transparent and opaque particle. The *i* term is sometimes easy to deduce - for example samples that are transparent and spherical and therefore have an imaginary value of zero. For non-transparent particles the *i* term is a non-trivial selection and directly affects result accuracy. Having considered all the above, RI was chosen to be 1.78 for alumina samples.

Particle size analysis confirmed that two fine fractions with $D_{50} \sim 10 \ \mu m$ and $D_{50} \sim 20 \ \mu m$ were obtained (Figures 5 and 6). The coarse residue after splitting was also analyzed and had $D_{50} \sim 95 \ \mu m$.
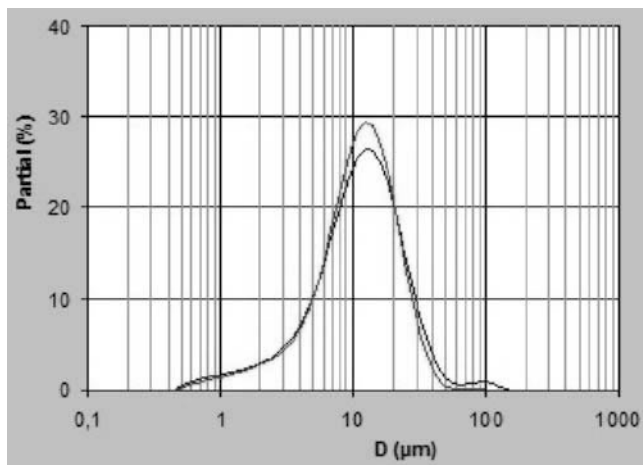

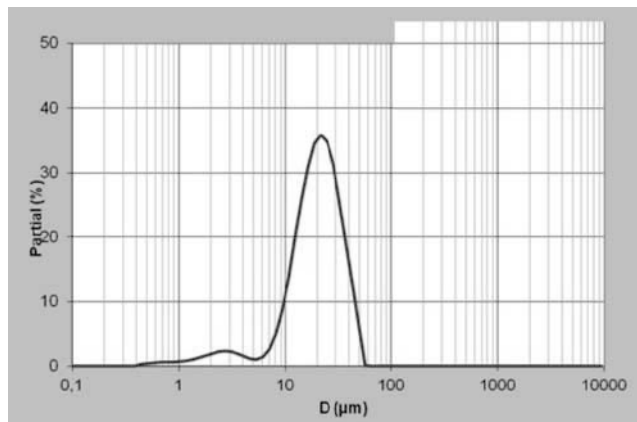Figure 5. PSD graph of the secondary alumina fine sample № 1.

Figure 6. PSD graph of the secondary alumina fine sample № 2.

Samples with D_{50} below 20 μm seem to agglomerate in a range of $1 \leq D_i \leq 5 \ \mu m$ (Figure 6). These agglomerates can be easily destroyed with the help of ultrasound.

SEM Results

First the specimen was sputtered with carbon since secondary alumina is a non-conductor. Thus, carbon particles can be seen on some SEM images. Also, carbon does not interfere with the atomic number contrast.

The contaminants, having higher atomic numbers, are shown by the brightest areas and they are typically found on distinct particles (Figures 7 and 8). This is consistent with previous observations that the secondary alumina contains many small impurity particles adsorbed on the surface of the raw material.
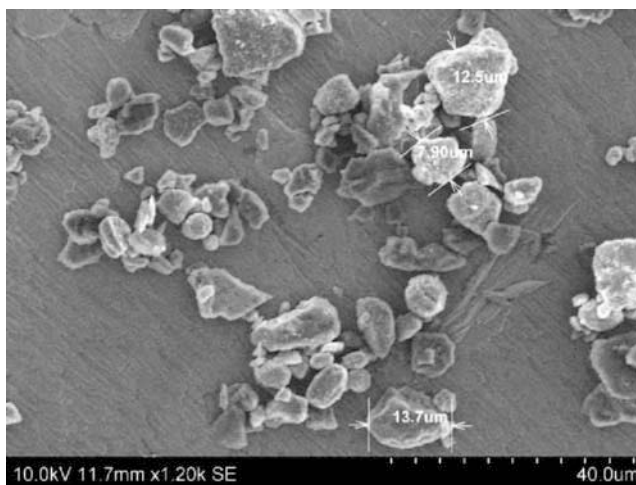

Figure 7. SEM picture of the secondary alumina fine sample № 1 ($D_{50} = 10 \ \mu m$).

Figure 8 SEM picture of the secondary alumina fine sample № 2 (D_{50} = 20 μm).

XRD Results

Besides corundum, cryolite (Na_3AlF_6), chiolite ($Na_5Al_3F_{14}$), and sodium aluminium fluoride ($NaAlF_4$) were identified with XRD analysis of the finer fraction, Figure 9.
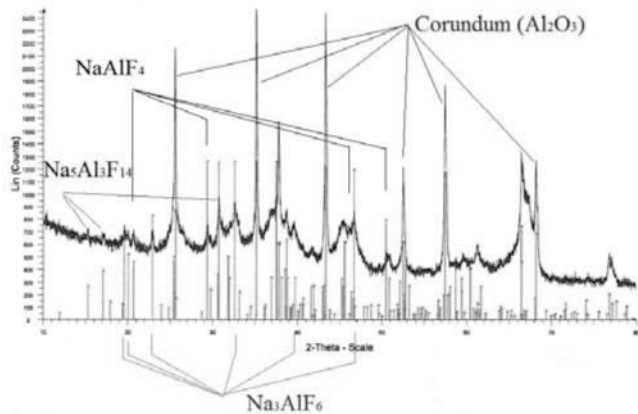

Figure 9. XRD analysis of the secondary alumina fine fraction with D_{50} = 10 μm.

EPMA Results

The secondary alumina fine fraction powder was added to 25 g of EpoFix Resin added 3 g of EpoFix Hardener to prepare the samples for Electron Probe Micro-Analysis. After thorough mixing for 2 min, the samples were poured into special forms with diameter of 25 mm, lubricated on the inside with silicone, and hardened for 24 hours.

It can be observed on Figures 10 and 11 that besides alumina, both samples contain bath particles whose composition mostly consists of fluorine, calcium and sodium. It seems to be impurity particles which come from the electrolyte.
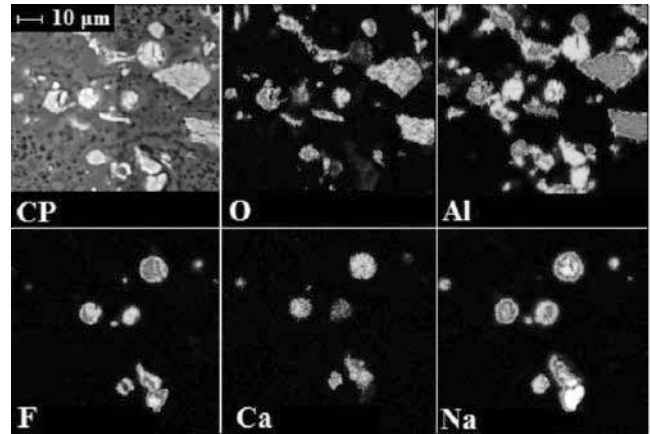
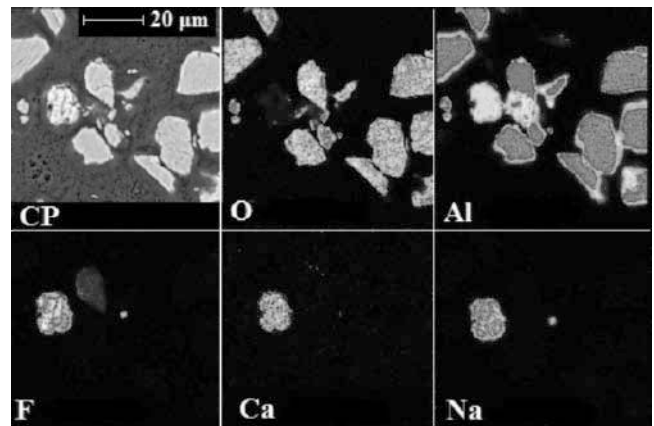Figure 10. EPMA data of the secondary alumina fine fraction with D_{50} below 10 μm.

Figure 11. EPMA data of the secondary alumina fine fraction with D_{50} below 20 μm.

ICP-MS Results

A high resolution ICP-MS, Element 2 from Thermo Electronics was used for analysis. The ICP-MS analysis confirmed the impurities observed in SEM and EPMA analysis. Total impurity content increases with decreasing particle size (Tables 1, 2, and 3).

Table 1. Concentration of the S, Si, Ca, Fe, Ni, and K in μg/g vs. different secondary alumina fractions.

	S(34)	Si(30)	Ca(44)	Fe(56)	Ni(60)	K(39)
D_{50} = 10 μm	3232	1017	3758	753	2456	411
D_{50} = 20 μm	1336	265	1705	313	853	95
D_{50} = 95 μm	1364	188	321	64	62	13

Table 2. Concentration of the Pb, P, Ti, V, and As in μg/g vs. different secondary alumina fractions.

	Pb(208)	P(31)	Ti(49)	V(51)	As(75)
D_{50} = 10 μm	78	92	31	70	72
D_{50} = 20 μm	29	24	21	30	23
D_{50} = 95 μm	14.5	3.1	22	6.9	5.0

Table 3. Concentration of the Cu, Zn, Ga, Sr, and Sb in μg/g vs. different secondary alumina fractions.

	Cu(65)	Zn(66)	Ga(69)	Sr(88)	Sb(121)
$D_{50} = 10$ μm	59	181	48	16	44
$D_{50} = 20$ μm	20	12	27	7.6	17
$D_{50} = 95$ μm	2.8	3.7	19.1	1.3	3.3

Graphs on Figures 12 and 13 represent the trend obtained after leaching with hydrochloric acid of the two fine secondary alumina fractions ($D_{50} = 10$ μm and $D_{50} = 20$ μm) versus the coarse residue with $D_{50} = 95$ μm.
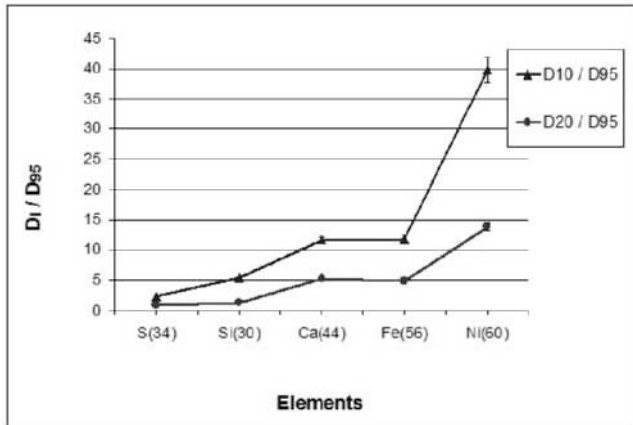
Figure 12. Impurities from Table 1 on the D_i / D_{95} curves.
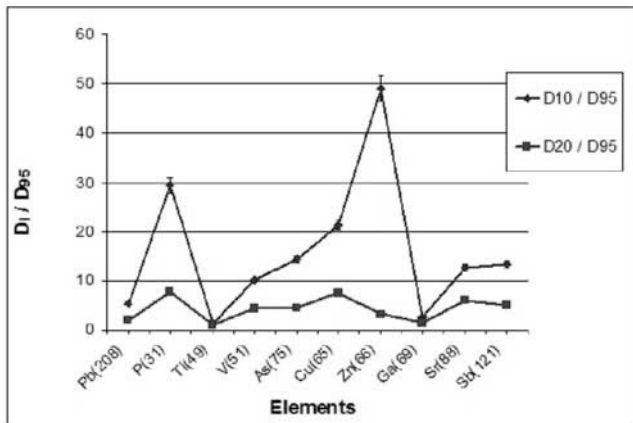
Figure 13. Impurities from Tables 2 and 3 on the D_i / D_{95} curves.

Total digestion in $K_2S_2O_7$.
Sample digestion in potassium pyrosulfate indicated that the acid leaching results are less than 50 % of the results obtained by total digestion. That means that not all impurities were removed by acid leaching. Uncertainties in the digestion results are generally caused by higher number of steps in the sample processing procedure.

Experiment with washing bottles
Sampling the raw gas into washing bottles lasted from 50 to 60 min each run. The temperature of the raw gas reaching the bottles was in 30 ± 1 °C. After sampling, it was observed that the volume of the acidic solutions in the first two bottles decreased by one quarter (from 100 ml to approximately 75 ml). The experimental results are shown in Tables 4 and 5.

Table 4. Total concentration of the S, Si, and Ca in μg/g vs. different acidic solutions.

		S(34)	Si(28)	Ca(44)
		μg/g	μg/g	μg/g
0.1 M HNO$_3$	Run 1 (total in 3 bottles)	10.0	47.3	0.57
	Run 2 (total in 3 bottles)	14.9	58.3	0.80
	Average of 2 runs	12.4	52.8	0.69
0.1 M HCl	Total in 3 bottles	10.3	56.6	0.61
0.1 M H$_2$SO$_4$	Total in 3 bottles	–	43.6	0.45

Table 5. Total concentration of the Fe, Ni, and K in μg/g vs. different acidic solutions.

		Fe(56)	Ni(60)	K(39)
		μg/g	μg/g	μg/g
0.1 M HNO$_3$	Run 1 (total in 3 bottles)	0.42	0.83	0.90
	Run 2 (total in 3 bottles)	0.47	1.06	1.08
	Average of 2 runs	0.44	0.95	0.99
0.1 M HCl	Total in 3 bottles	0.49	0.92	1.00
0.1 M H$_2$SO$_4$	Total in 3 bottles	0.38	0.78	0.77

It has been observed that, in general, the acid type did not give much effect on the leaching efficiency.

Conclusion

The analysis performed confirmed that impurities are accumulated in the finer fractions of secondary alumina. Total sample digestion indicated that not all impurities were leached. Obtained sample digestion results are well correlated with previous work [14].

Experiments with washing bottles indicated that less than 20 % of the raw gas has been leached. For raw gas leaching, acid type had no net effect on leaching efficiency when equal acid concentration was used (0.1 M).

Further work

In order to improve the aluminium metal purity as well as increase the CE and stability of the cells by removing contaminants from secondary alumina, further studies will be conducted. Attention will be focused on two main issues:
1). To remove impurities with minimum loss of alumina and fluoride
2). To optimize the method of impurities recovery to obtain low installation as well as low operation costs.

To achieve these goals leaching efficiency has to be investigated and further experiments with different leaching parameters like acid type, concentration, heating time and temperature have to be performed. The residue after leaching has to be analyzed as well. Cascade leaching as an option to concentrate impurities in the liquid phase has to be studied.

To lower the operation cost alumina can be returned back into the process after the leaching treatment. A high content of fines is harmful due to dusting emissions and mechanical handling problems. Therefore, different methods of growing agglomerates from alumina fines have to be investigated.

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