Recovery of impurities from secondary alumina by acid leaching

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Abstract

Gas scrubbing in aluminium primary production effectively forms a closed loop leaving the produced metal and the bath as the main sink for impurities. To avoid this negative impact on metal quality and negative influence on current efficiency due to redox reactions in the bath, it is desirable to create another sink for impurities. Several attempts have been made to strip a size fraction of the secondary alumina where the impurity loading is high. Mapping of impurity distribution in secondary alumina has, however, shown that impurities have different distributions, thus complicating the selection of a particle cut-off size setting. A high cut-off value would remove a significant amount of the secondary alumina. Fluorides residing in the finer fractions would also be lost. Another strategy is to remove impurities from the stripped alumina by acid leaching. Different acids have been evaluated with respect to their leaching efficiency for the impurities of highest negative impact. It has been found, using excess acid, that leaching efficiencies as high as 90 % can be obtained. In order to minimize the acid consumption in leaching, a quasi-cascade leaching process has been evaluated. By recycling acid in several steps, a more cost-efficient recovery process is obtainable. The economic potential of the recovered impurities is also discussed.

Keywords: Secondary alumina; impurities; stripping; acid leaching.

1 Introduction

Modern dry scrubbers are very efficient in capturing dust particles in the off-gas; returning the particles to the cell and leaving the impurity bleed to the metal and surplus bath. From previous work it has been shown that the finer fraction of the secondary alumina from the off gas dry scrubber in aluminium plants are enriched in impurities [1, 2, 3]. For some impurities, an accumulation is also observed in the bath causing loss in current efficiency. Hence, removing these impurities may improve both the metal quality and contribute to better current efficiency.

The main sources of impurities are alumina and anode coke. Raising concerns about degrading purity of traditional anode coke qualities and the introduction of non-traditional anode cokes, with higher levels of impurities to cover the anode coke demand, may make impurity removal even more attractive in the future [4].

Based on investigations of the impurity distribution in secondary alumina, it is found that removing the finer fraction of the secondary alumina potentially removes more than 50 % of many of the impurities [1]. Since the impurities represent only part of this fine fraction a significant amount of valuable materials is also lost, especially alumina and fluorides. To reduce loss of valuable materials, stripping may be run in campaigns or stripped alumina can be subject to recovery processes. Some methods have been proposed [5, 6], however, not many methods have been subject to comprehensive studies. In addition to studies on secondary alumina, the composition of dust in the off gas before the scrubber has been investigated [2, 3]. Hence, it may also be possible to reduce the amount of impurities by treating the pot off-gas before the dry scrubber.

Regardless of method, disposal of waste materials should be reduced to a minimum and a strategy for recovering all materials is beneficial from an environmental point of view. Typical impurities in secondary alumina are Fe, Mn, Si, Ti, Zn, Ga, Be, alkali and alkaline earth elements, such as Li and Mg. Some reported effects of impurities are listed in Table 1.

Both iron and phosphorous are reported to negatively impact the current efficiency [7]. Sturm and Wedde [1] found that the distribution between P in the bath and the tapped metal was about 10/1. In their investigation they found that the impurity stripping could reduce P from about 150 ppm down to 40 ppm in the bath. Removing particles below 45 μm would remove more than 70 % of the impurities.

Table 1. Effects of impurities introduced to the electrolytic bath in aluminium production.

Element	Main source	Main effect
Phosphorous	Alumina	Decrease current efficiency (increase metal corrosion and brittleness)
Sulfur	Anode	May affect current efficiency
Gallium	Alumina	Reduce corrosion resistance and lower mechanical properties of metal
Beryllium	Alumina	Health concern in pot rooms
Heavy metals, Ni, Fe, V, Ti, Zn	Anode	Negative effect on metal purity. May effect current efficiency
Silicon	Alumina	Negative effect on some metal grades
Sodium	Alumina	Increase cryolite ratio, causing surplus bath
Calcium	Alumina	Reduce alumina solubility, increases bath density

Characterization and analysis of pot gas dust and secondary alumina from a Norwegian aluminium plant has been reported previously [2]. In addition, some introductory acid leaching tests was reported [8]. The present paper report on the results from more extensive laboratory experiments for recovering materials in the finer fractions of secondary alumina. Since hydrometallurgical processes usually allow separation of a broad range of elements, it may be an attractive route for purification of secondary alumina and recovery of valuables from the impurity stream.

2 Experimental

2.1 Classification of secondary alumina

A pilot scale classifier was used to separate the fines from secondary alumina. The secondary alumina was mixed with air and fed to the classifier through a vertical pipe positioned at the bottom of the classifier,

Figure 1. The classifying takes place by forced vortex action in the classifying chamber. The coarse material is discharged through the bottom outlet at a flow rate of 70 m^3/h. The finer fractions are separated from the air in a cyclone and collected. The filtered air, after passing through the fan, is exhausted to the atmosphere. The secondary air inlet is used to detach fine particles adhered to the surface of coarse particles by impaction. Two fractions with 50 % of the particles finer than D_{50} = 10 μm and D_{50} = 20 μm were aimed at in two separate runs.

The particle distribution in the secondary alumina and the classified fractions was determined using a Malvern Mastersizer 2000 after dispersing the particles in distilled water.

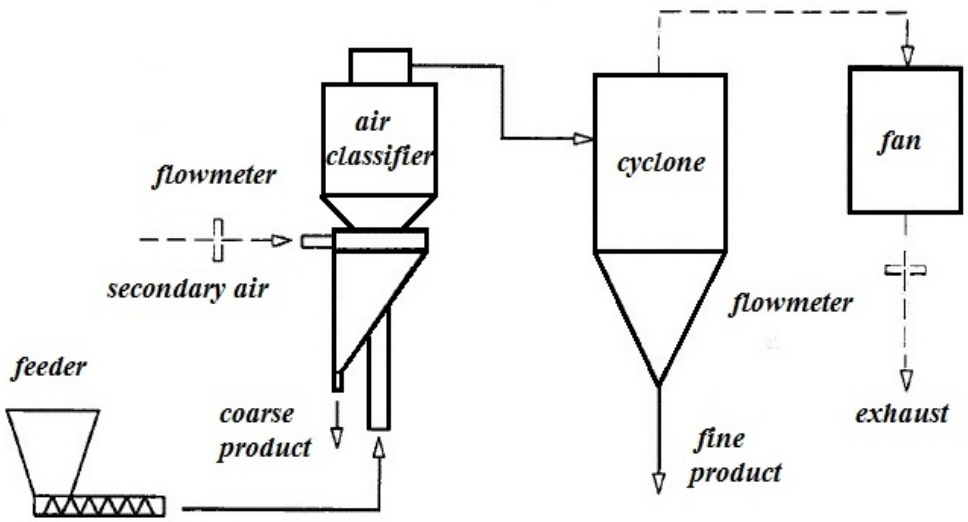

Figure 1. Schematic layout of the classifier used to separate the fines from the secondary alumina.

2.2 Leaching Procedure

In previous work [8], raw gas from the ducts were collected in washing bottles with three different acids at 0.1 M; HNO_3, HCl and H_2SO_4, respectively. Based on these results, which showed little difference in leaching efficiency between the acids, it was decided to focus on one acid in further studies, in this case 1 M HCl. Since an industrial leaching most likely will consist of a countercurrent type of leaching, a simplified experimental leaching procedure was developed to give an indication of what loading may be expected in a fully developed process and as a basis for further studies.

Leaching

1) 20.0 g of secondary alumina sample were added to 100 ml 0.923 M HCl for leaching
2) The leaching sample was heated at 80 °C in an ultrasound bath for 0.5 hour
3) Each sample was transferred to 2 vials of 50 ml and centrifuged for 0.5 hour (15000 rpm) at 20 °C
4) From the centrifuged leach solution, 1 ml was transferred to 15 ml polypropylene vials (PP vials) for ICP-MS analysis
5) The residue was collected and being dried at 160 °C on a Petri dish for 24 hours before being weighed and transferred to glass vials
6) The rest of the centrifuged solution was collected into a new leaching bottle
7) Fresh secondary alumina, calculated based on remaining solution in step 6 (sample weight = $V_{solution}$ (in ml) · 20 g / 100 ml) was added to the new leaching bottle before step 2-5 were repeated
8) A total of 5 leaching steps were performed
9) The leach solutions in the 15 ml PP vials was diluted to 9 ml (to get final conc. of 0.1 M HCl)
10) About 25 - 45 mg of the dried residue samples were digested in a 1.5 ml concentrated HNO_3 + 0.5 ml concentrated HF solution before being diluted and transferred to PTFE vials for ICP-MS analysis

3 Results

3.1 Secondary alumina fractions

Samples of the obtained fines fractions are shown in Figure 2 together with the secondary alumina as received from the plant. About 300 g of the secondary alumina fines was collected for both fractions. The size distribution of the secondary alumina fractions as determined by the Malvern are shown in
Figure **3** and summarized in Table 2.

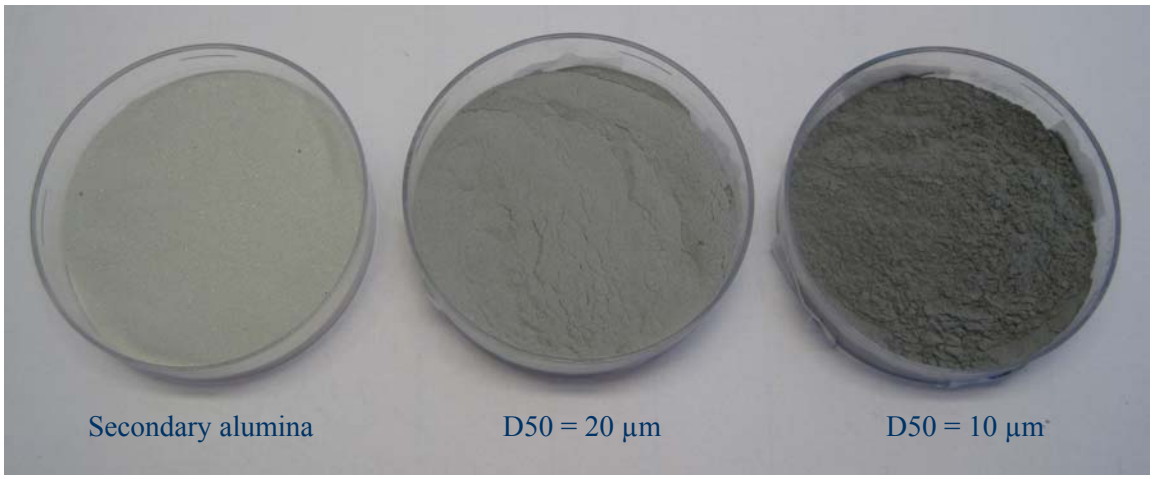

Figure 2. Secondary alumina from the dry scrubber split into the two fractions D_{50} = 20 µm and D_{50} = 10 µm using a pilot scale forced vortex air classifier.

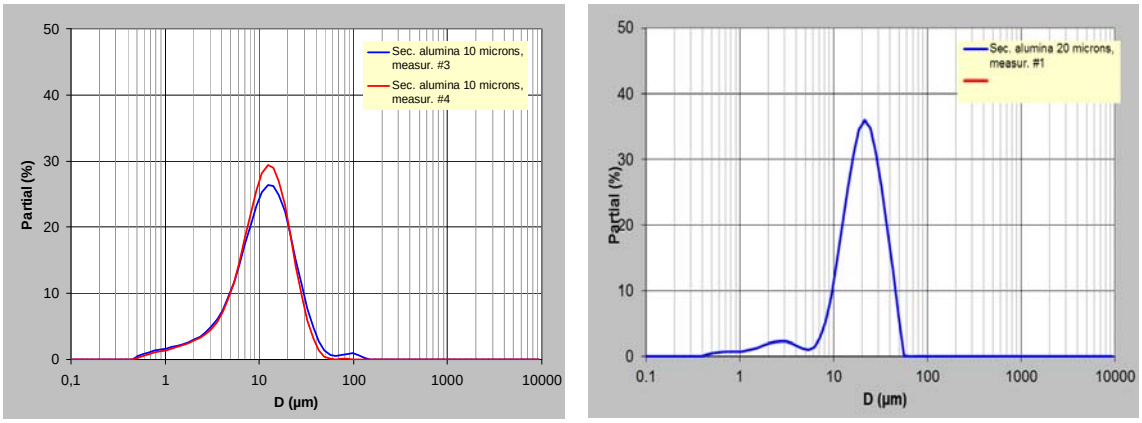

Figure 3. Size distributions of the obtained fine fractions as measured with a Malvern Mastersizer 2000.

Table 2. Samples dispersed in distilled water and analysed using a Malvern Mastersizer 2000 particle size analyser. Particle refractive index set to 1.78 in all fractions.

	1st run D_{50} = 10 µm	2nd run D_{50} = 10 µm	1st run D_{50} = 20 µm
D_{10}	3.469	3.782	8.814
D_{50}	10.730	10.544	19.973
D_{90}	24.404	21.800	35.992

Impurities in the secondary alumina fractions in the studied samples, analysed by ICP-MS, are shown in Table 3. Figure 4 shows the relative distribution of impurities between the different fractions.

Table 3. ICP-MS element analyses of secondary alumina fractions. All values in µg/g.

Fraction	S	Ca	Fe	Ni	K	Si	Pb	P	Ti	V	As	Cu	Zn	Ga	Sr	Sb
D_{50}=10 µm	3232	3758	753	2456	411	1017	78	92	31	70	72	59	18	48	16	44
D_{50}=20 µm	1336	1705	313	853	95	265	29	24	21	30	23	20	12	27	7.6	17
D_{50}=95 µm	1364	321	64	62	13	188	14	3.1	22	6.9	5.0	2.8	3.7	19	1.3	3.3

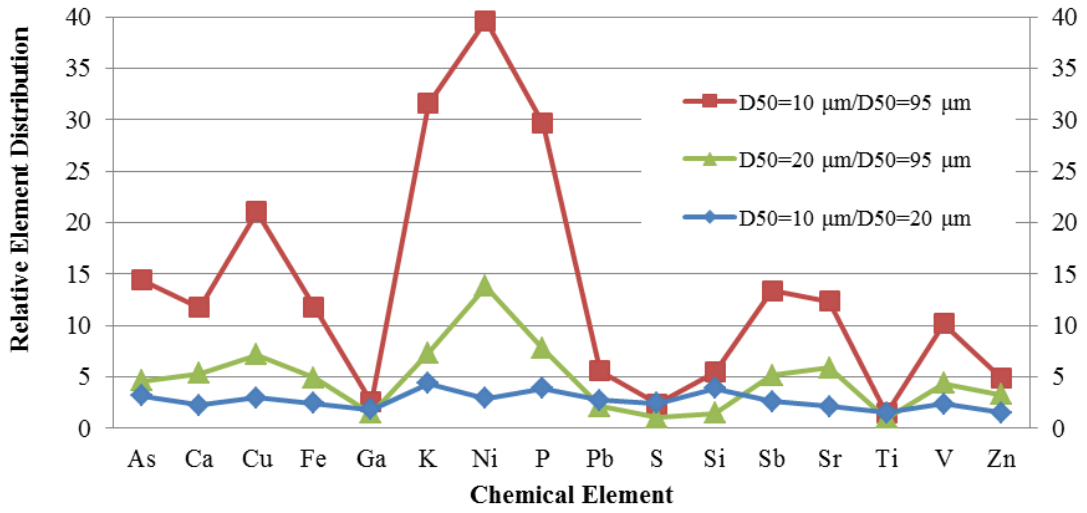

Figure 4. The relative element distribution between the obtained fractions (D_{50} = 95 µm represents secondary alumina from the dry scrubber).

3.2 Leaching

The results of the leaching experiments are shown in Figure 5 and Figure 6 for the leachates and the residues, respectively, for the D_{50} = 10 µm and D_{50} = 20 µm fractions. For better comparison, the most important elements are recalculated to µg/g of secondary alumina added to the leach solution (solution in millilitre 5 times the secondary alumina in grams) in Figure 7, 8, and 9.

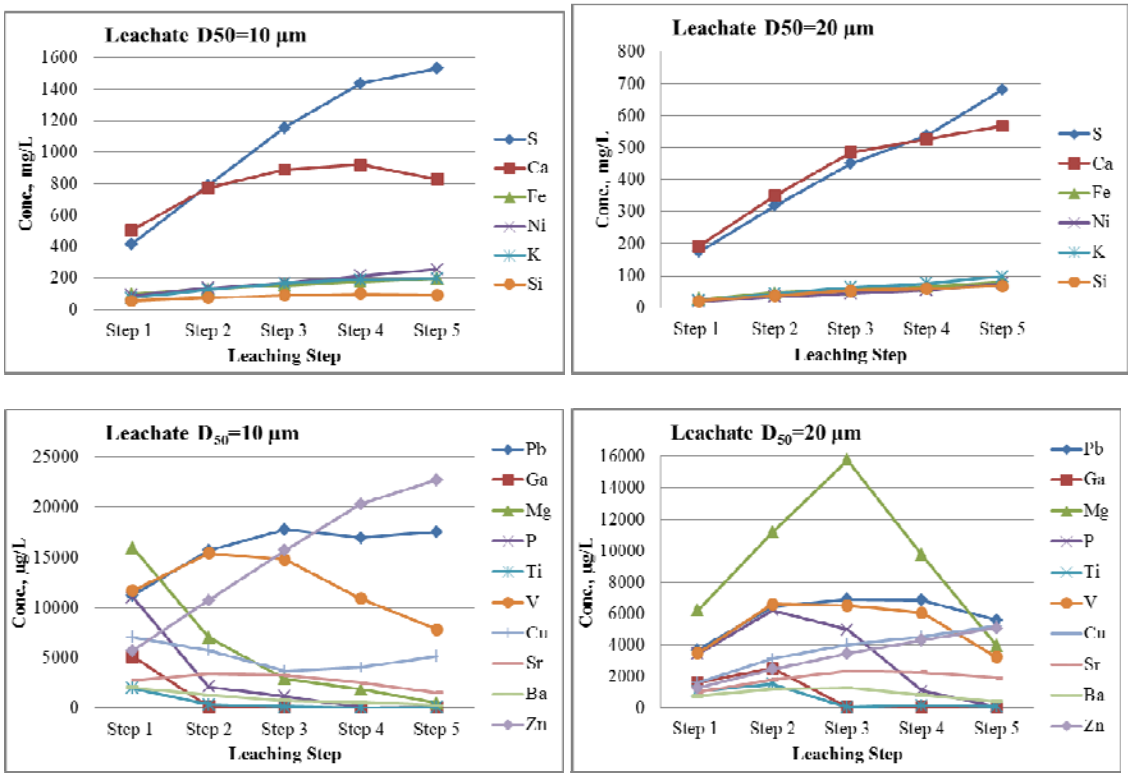

Figure 5. Analysis of leachate after leaching step 1 to 5 for both secondary alumina fractions with D_{50} equal to 10 and 20 µm, respectively.

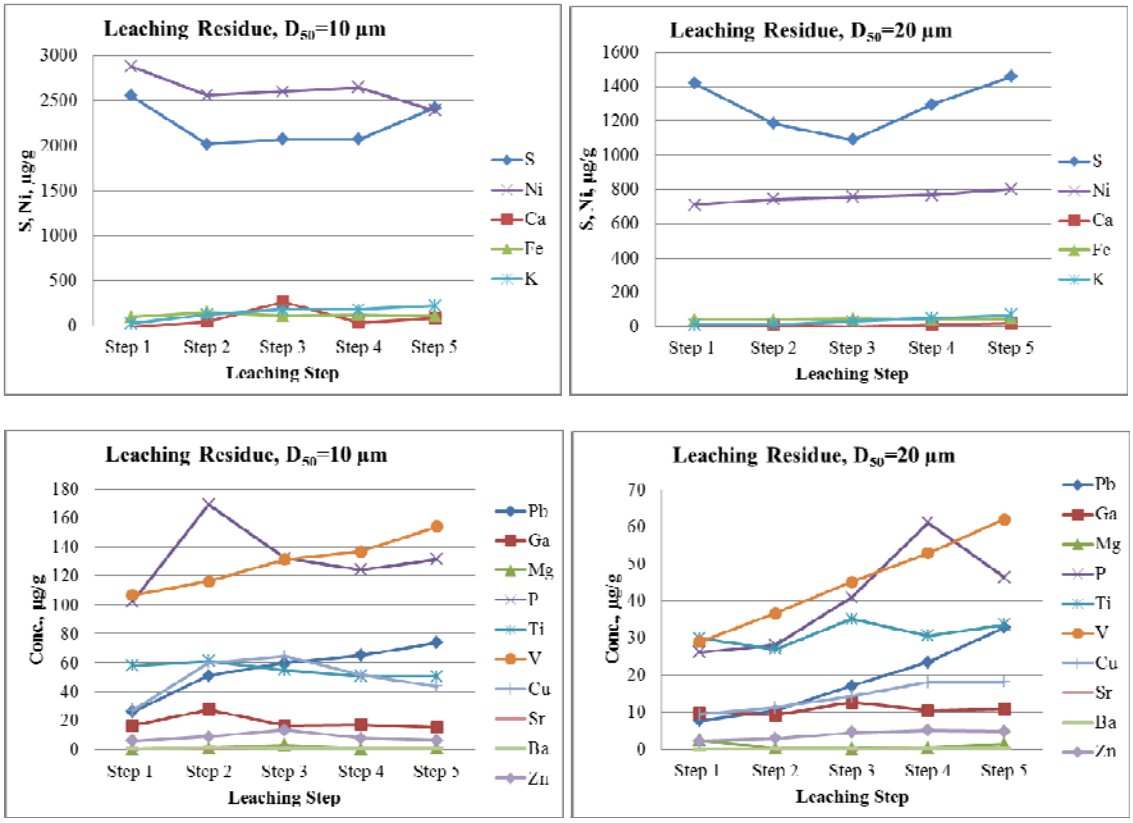

Figure 6. Analysis of leaching residues after the leaching step 1 to 5 for both secondary alumina fractions with D_{50} equal 10 and 20 µm, respectively.

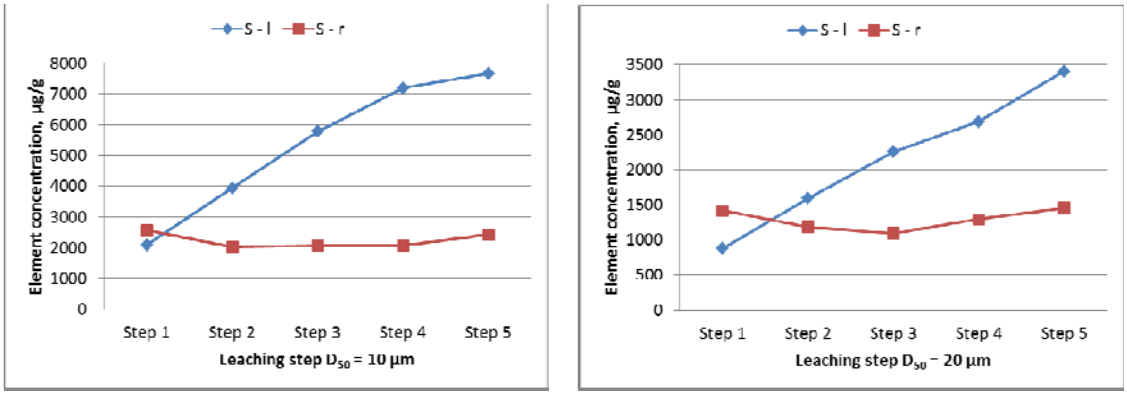

Figure 7. Analysis of sulfur in the leachate (S–l) and residue (S–r) for D_{50} equal 10 and 20 µm, left and right, respectively. The content in the leachate is recalculated to µg/g of secondary alumina fraction added to the leach solution.

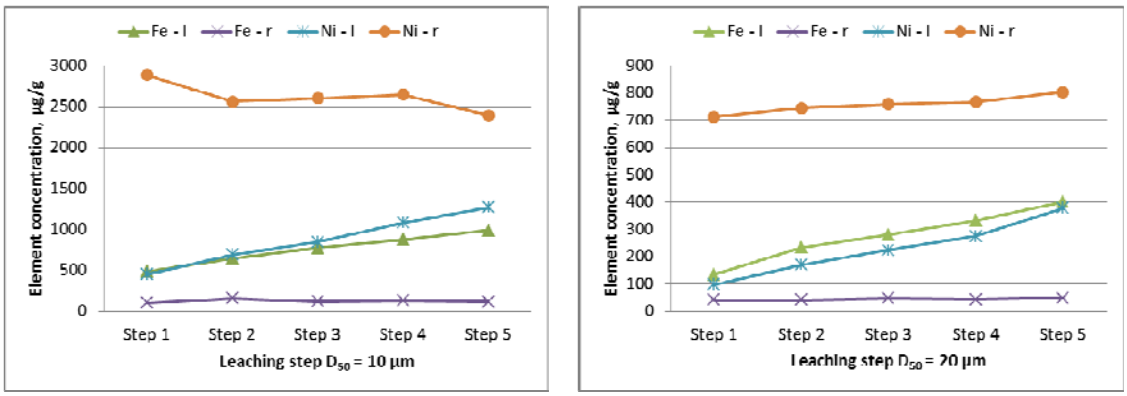

Figure 8. Analysis of iron and nickel in the leachate (Me–l) and residue (Me–r) for D_{50} equal 10 and 20 µm, left and right, respectively. The content in the leachate is recalculated to µg/g of secondary alumina fraction added to the leach solution.

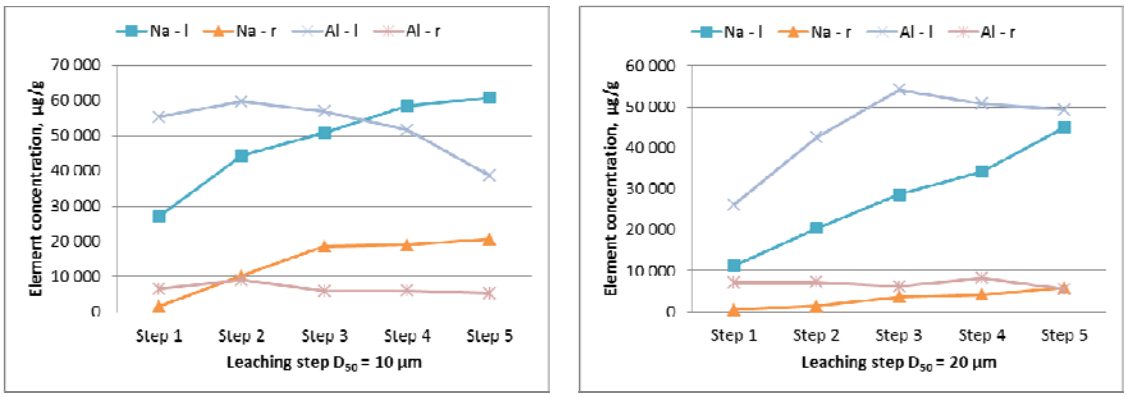

Figure 9. Analysis of sodium and aluminium in the leachate (Me–l) and residue (Me–r) for D_{50} equal 10 and 20 µm, left and right, respectively. The content in the leachate is recalculated to µg/g of secondary alumina fraction added to the leach solution.

4 Discussion

4.1 Element distribution in the fine fractions

Table 4 and Figure 4 show that there are significant variations in how much of the impurities are collected in the finer fractions. For most elements there are a significant increase going from the

D_{50} = 20 µm to the D_{50} = 10 µm. Especially As, Ca, Cu, Fe, K, Ni, P, Sb, Sr, and V are considerably higher in the finest fractions, although many of these impurities are rather low. Elements with high concentrations that seems to be most subject to circulation in the off gas system are the heavy metals as Fe and Ni, besides Ca. Of the less concentrated elements, As, Cu, K, P, Sb, Sr, and V are subject to circulation in the system. Titanium is virtually unchanged, indicating that Ti follows primary alumina and is not evaporating from the bath in significant amounts, although Ti was found in the off gas particulates in previous studies [2]. It is also seen that many of the heavy elements in the anodes, elements that normally will report to the aluminium, are also found in the off gas. This is most likely due to entrainment in the anode gas as these impurities enter the cell through the anodes.

For some elements there are only minor differences between the impurity levels in the different fractions, e.g. Ga, S and Ti. In the case of S, it is known that most of the sulfur is captured in the wet scrubber after the dry scrubber. In spite of that, sulfur is among the elements with the highest concentration in the secondary alumina. Since the difference between the bulk and the D_{50} = 20 µm fraction is virtually nought, it may be speculated that sulfur is due to adsorbed SO_2 in the scrubber, while the enrichment in the finest fraction is due to metal sulphates. This is also in line with previous findings in the particulates in the off gas [2], where sulfur and potassium were found mainly in the submicron range.

4.2 Leaching

The analysis of the acid leach solutions show that the most elements dissolve to some extent in the acid, see Figure 5. The same is the case when fresh secondary alumina is added to the leachate from the previous step, although the results are less conclusive, especially when the results are compared with the analysis of the residues. Since fresh alumina is added in each leaching step, the impurities transferred to the leach solution should increase by a factor of two if the residue from one step to the next report the same impurity content. For instance, Pb and V show a nearly constant increasing content in the residues, while the leachate is less consistent. Some other minor elements are also decreasing rapidly from one step to the next without being reflected in the residues. It is possible that there are some inhomogeneities in the minor elements, e.g. if some of the particulates exists as large particles.

For the elements with a linear increase, it may be anticipated that the liquid is far from saturation and that the solution is in equilibrium with the solid residue. Also, the dissolution rate seems to be fast or, at least, within the timeframe of the experiments for most elements. For instance, sulfur is close to doubling in most of the steps, which should be anticipated since most of the sulfur is believed to be in the form of readily soluble sulphates. The concentrations of most elements are also so low that it is not expected to cause precipitation of sulphates, e.g. Ca which is known to have a low solubility in sulphate solutions. Since we have not analysed fluoride, the total anion concentration is not known. It may, however, be anticipated that the fluoride content is high based on the values for dissolved Na and Al.

As the salt concentration of the solution increases, it is expected that some elements may reach saturation and even start to precipitate in some cases. This may also have affected the analytical values as the solubility at the leaching temperature of 80 °C may be different from the sampling temperature of 20 °C, especially for the most concentrated solutions.

Since the content of sulphate and fluoride anions will increase during leaching it is of interest to find out if this can be seen from the results. For instance, most sulphates are quite soluble, with the exception of lead, barium and calcium. For fluorides, the least soluble ions are magnesium, calcium, strontium, barium and lead. In addition, as the pH increased during each step, some elements may also be subject to hydroxide precipitation. Since Ca is abundant in the secondary

alumina fines, it is also seen that Ca, after an initial increase tends to flatten out or even decrease. This is most likely due to the low solubility of $CaSO_4$. For the other less soluble elements it may be seen that Pb and Mg is the two elements with the most pronounced decrease in the leach solution from step to step. It is anticipated that the increase in fluoride content may be the cause for this observation.

The slow dissolution rate of the nickel is presently not known since the compounds of nickel are not determined. Usually, nickel oxides dissolve quite fast in hydrochloric acid [9], but it may be slowed down due to divalent iron (Fe^{2+}).

As the residue after centrifuging was dried without further washing, some of the impurities in the residue are due to the remaining leaching solution. This has not been corrected for in the present calculations, but on average about 15 % of the solution remained with the residue. The error is of course largest for the elements with highest leaching efficiency.

Currently, the results have not been subject to thermodynamic modelling, however, the present investigation is useful as a base for determining the most significant elements that may affect a leaching process and to determine which elements should be included in a thermodynamic model. A more comprehensive and thermodynamic based approach is a subject to later studies.

5 Conclusion

Acid leaching of secondary alumina fines shows that many of the impurity elements are dissolved, resulting in a residue with much lower impurity content than in the original sample. The results also show that the loading of the solution in most cases has not reached saturation, in spite of the total amount of added secondary alumina fines in kilograms to leach solution in litres reached 1:1. Proper treatment of the leachate will make it possible to recover many of the impurities. Among the most important impurities, nickel seems to behave slightly different from most other elements, probably due to slow dissolution kinetics in the studied system.

6 References

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