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Leaching of Aluminium Dross in Alkaline Solution

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Abstract

The aim of the experimental work was to study the leachability of Al from aluminium dross fines after mechanical pre-treatment in alkaline solution at atmospheric conditions. The next step was oriented to study of recovery of leachable Al in the form of aluminium hydroxide and alumina suitable for utilization as a catalysts carrier or a sorbent in water treatment industry. Based on achieved results it was shown that maximum Al extraction of about 42 % of total content of Al (and around 98 % of leachable Al from dross) by leaching of dross fines at 60 °C in 10 % NaOH solution at 96 °C and S:L ratio 1:100 after 120 min. was achieved. Rising S:L ratio has a negative effect on Al extraction but there were also proposed conditions for obtaining of comparable Al extraction even at higher S:L ratios. Leaching residue contained still non-reacted AlN and chlorides. By precipitation from leaching liquor (by use of various agent) and calcination (600 °C) the alumina with surface area of 55 m².g⁻¹ was obtained and compared with those obtained by precipitation of pure model Al solution.

1 Introduction

Aluminium dross represents from environmental point of view a potential risk, due to the content of leachable chloride salts and due to releasing of dangerous gases like as ammonia, methane and hydrogen in contact with moisture. On the other hand dross can be valuable source of secondary aluminium and other materials. At present in a practice the part of Al is recovered mostly from coarse dross fractions by melting. Fine aluminium dross fractions with low content of aluminium in elemental form (according to [1] 2-5% Al, but often it is more than 12 % and sometimes even about 30 %) are very problematic for producers and processors and of low interest from processing point of view and they are mainly landfilled. The main reason is that fine dross contains a small amount of utilizable (but often only apparently “small” amount) metal and a higher amount of salts, oxides, nitrides and other impurities. On the other hand, due to progressive increase of fees for hazardous materials dumping, permanent legislative pressure on more effective material valorization of wastes and energy saving causes that more and more it is demanding to find solutions for utilization of problematic fine frac-



tion of aluminium dross. At present the hydrometallurgical method represents probably the most convenient way for fine dross fractions. This method can enable the complex recovery of valuable substances from dross. Moreover it was also shown in work [2-3] that there are still possibilities for recovery of small $\text{Al}_{\text{element}}$ particles from fine dross by using of grinding and/or ECS. Therefore, the application of pre-treatment by ECS before hydrometallurgical processing of fine dross fraction seems to offer a promising direction for effective fine dross (white/black dross or salt cake) processing.

2 Theoretical

One of the potential hydrometallurgical methods represents the alkaline leaching of aluminium dross followed by precipitation of aluminium hydroxide $\text{Al}(\text{OH})_3$ [4]. This method of fine aluminium dross processing is economically and environmentally convenient, because by application of industrially known process it enables to change dangerous waste to non-dangerous (inert) and utilizable material. However, dross is very heterogeneous material and applicability and efficiency of proposed method for individual dross samples should be experimentally investigated. Pure aluminium hydroxide can be obtained by dross leaching followed by precipitation. The leaching residue can be then utilized for example in production of refractory/ceramic materials. Moreover, there is also possibility to recover chloride salts to produce fluxing agent. Obtained aluminium hydroxide can be used as a precursor for adsorbents production or for production of abrasives and other materials (flocculants, etc.). In the paper [5] authors prepared active Al_2O_3 with high specific surface by alkaline leaching and subsequent precipitation of aluminium hydroxide by different precipitating agents (H_2O_2 , CO_2 , NH_4HCO_3 , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$, fresh aluminium hydroxide jelly). The highest surface area of $252 \text{ m}^2 \cdot \text{g}^{-1}$ exhibited γ -aluminium oxide after calcination of obtained aluminium hydroxide by precipitating agent H_2O_2 at the temperature of 600°C for 3. In work [6] authors described process - similar to Bayer's method - for recovery of $\text{Al}(\text{OH})_3$ from black aluminium dross and they proposed a non-waste technology of dross processing. After leaching in 10% NaOH solution at ambient temperature for 2 hours and precipitation by CO_2 the obtained $\text{Al}(\text{OH})_3$ was used as additive material for coagulant $\text{Al}_2(\text{OH})_5\text{Cl}$ production (waste water cleaning). According to authors non-metallic residue can be applied in refractory material production. The interesting fact in these results is that recovery of aluminium was not affected by mixing and heating of the solution. Other source [7] interprets methods how to recover hydroxides and oxides with high purity (Al_2O_3 and MgO or MgAl_2O_4) from aluminium dross exactly from non-metallic residue (NMP). Prior to application of these processing methods removal of salts from dross and salt slags by leaching in water is required. Decomposition of NMP (composition: 56% Al_2O_3 and 2.5% Mg in NaOH leaching occurred at temperature 98.8°C during 8 hours. Precipitation of aluminium hydroxide was achieved by adjusting of pH (7) with sulphuric acid. Product on the base of aluminium oxide with Al_2O_3 content 99.75 % was recovered after drying. Experimental results showed that only 20% of aluminium dross can be dissolved and not all amount of aluminium oxide reacts with NaOH . Leaching residue finally consists of spinel (MgAl_2O_4) and non-leached aluminium oxide. In general, it is possible to state, that there is a lack of detailed information and experimental work dealing with alkaline leaching of aluminium dross. But the alkaline treatment process seems to be promising and effective, if we consider that no exploitation of raw material is required to produce pure alumina-based materials. This direction seems to be suitable, but it is necessary to find optimal conditions and make the process more effective for application for heterogeneous Al dross. Thus, the aim of this work was first to show the practicability and restrictions of alkaline leaching of fine white dross



fraction $-1+0$ mm without foregoing salt removal and in the second stage of this work to verify the possibility of pure aluminium oxide recovery by precipitation with different agent and calcination.

3 Experimental

3.1 Materials

For experimental work the sample of white aluminium dross from primary Al industry after pressing was used. Dross sample was autogenously ground for 15 minutes and sieved for 4 grain fractions. The amount of fraction $-1+0$ mm represented more than 31.37 %. The most problematic fraction $-1+0$ mm was used for leaching experiments. The input sample and experimental sample (after grinding) used for leaching and the grain size distribution of this sample is shown in Fig.2 a) and Fig2 b). The chemical analysis of experimental sample $-1+0$ mm was realized by AAS Varian AA-240. In the Table 1 the chemical composition of input dross sample is listed.

Table 1: The chemical composition of Al dross ($-1+0$ mm)

| Element | Fe | Al _{element} | Al _{total} | Si | Mg | K | Na | Mn | Cl- |
|---------|------|-----------------------|---------------------|------|------|------|------|------|-------|
| [w. %] | 0.16 | 12.6 | 53.49 | 0.59 | 0.16 | 3.50 | 5.50 | 0.03 | 17.59 |

The density of aluminium dross $-1+0$ mm represented 2.89 g.cm⁻³ was measured by AccuPyc 1330. Surface area (Quantasorb) was 4.03 m².g⁻¹. The qualitative X-ray diffraction phase analysis was realized by the using of X-ray powder diffractometer Philips PW1710 (Bragg – Brentano) with radiation CuK α . The results showed that white dross contain mainly these components: Al_{element}, Al₂O₃, Si, AlN, NaCl, MgAl₂O₄, KCl, CaF₂, Na₃AlF₆, but there are probable also others minor phases like MgF₂, calcium oxide compounds (CaO.Al₂O₃, 3CaO.Al₂O₃), sulphur (sulphides), carbon (carbides) and other oxides, chlorides and fluorides and some content of amorphous phase. The estimative semiquantitative phase analysis of fine Al dross (based on main most probable phases) has been realized by use of XRD data and software PAN analytical X' Pert PRO + High Score Plus. The semiquantity calculations were done by use of seven identified phases like Al₂O₃ (39 hm%), NaCl (14%), KCl (10%), AlN (16%), Al (7 %), MgAl₂O₄ (6%) and (H₃O)₂Al₂₂O₃₄ (6%). The amount of leachable aluminium supposed to be in this case about 21 % and served only for orientation due to heterogeneity and high complexity of sample.

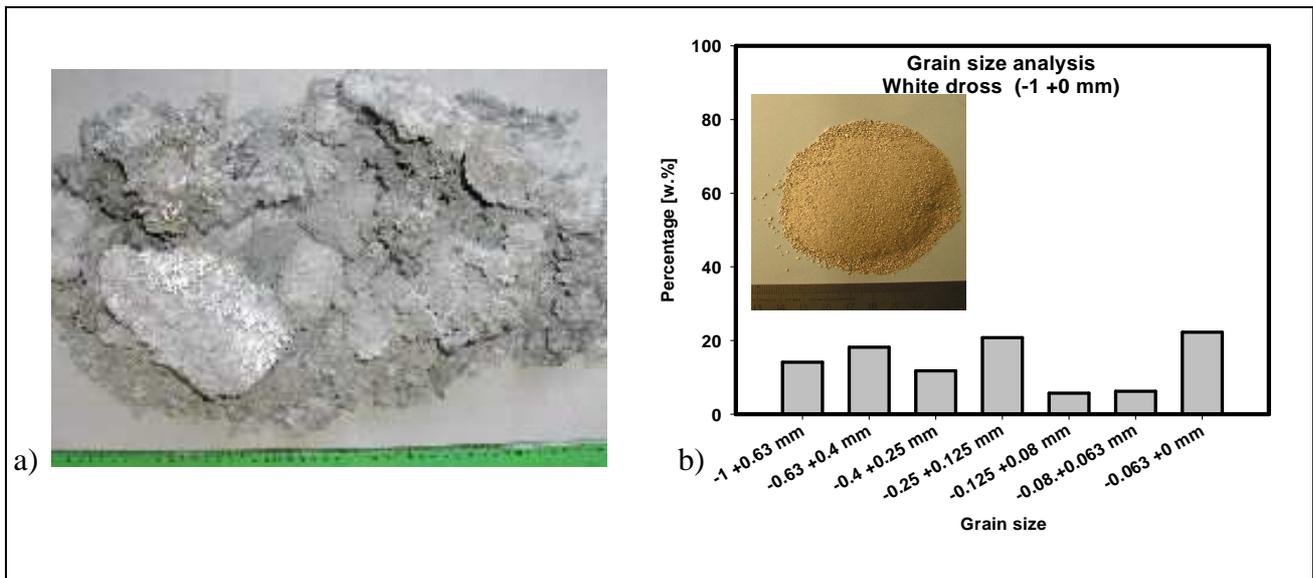
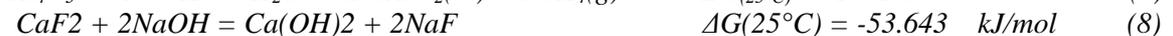
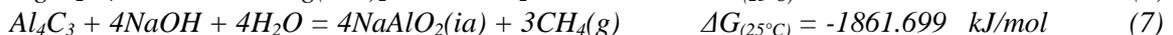
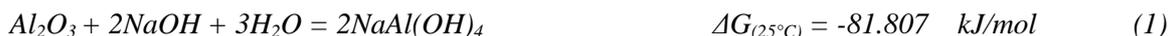


Figure 1: a) Input dross sample before grinding, b) Histogram of fine dross sample granularity

3.2 Alkaline leaching of fine dross

The aim of first part of experiments was first to achieve information about the leachability of Al from dross fines (-1+0 mm) in alkaline medium. In these experiments the influence of NaOH concentration, leaching temperature, leaching time and solid to liquid ratio (S:L) at chosen concentration of sodium hydroxide. The leaching experiments were carried out in apparatus, which consisted of thermostatically controlled water bath, glass reaction vessel with volume of 800 ml, electrical stirrer, glass propeller, cover of reaction vessel with openings for sample off-take and thermometer. The charges of dried dross for experiment were 5 g, 20, 30 and 50g (S:L ratio 1:100, 1:25 1:17, 1:10) and volume of leaching medium was 500 ml. The agitation speed was adjusted to 800 rpm. The used concentrations of NaOH were 1, 5, 10 and 20 % (15%). In the beginning of experiment the sample was introduced into the reactor through the opening in the lid and the time was measured. In the chosen time intervals 5, 15, 30, 45, 60, 90, 120 minutes the samples of volume 10 ml were taken, filtrated and analysed for aluminium. Al content was analyzed by atomic absorption spectrometry (Varian AA-240). After finishing of experiment the pulp was filtrated and filtration cake was washed with water. The volume of leaching solution after filtration was measured in order to execute calculation corrections due to decreasing volume by evaporation and sample off-take.

For better understanding of alkaline leaching process the reaction of individual substances from dross with sodium hydroxide solution were proposed by using of software HSC Chemistry 5.1.





From thermodynamic point of view all proposed reactions (1-8) have the tendency to proceed spontaneously in direction of product formation. It was suggested that cryolite will not react with sodium hydroxide. It is obvious that silicon and silicon compounds will react with sodium hydroxide and consequently contaminate aluminate solution. However, during process the formation of calcium hydroxide is predicted and by subsequent desilication reaction of calcium hydroxide with sodium silicate the silicon should be removed into solid phase.

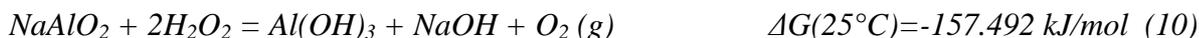
3.3 Precipitation and calcination of Al hydroxide

The aim of these experiments was to test possibility of recovery of pure $\text{Al}(\text{OH})_3$ by precipitation using hydrogen peroxide (H_2O_2), ammonium hydrogen carbonate (NH_4HCO_3), ammonium aluminium sulphate $\text{NH}_4\text{Al}(\text{SO}_4)_2$ (used $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). For experiments the model pure solution (3.46 g/L Al (purity of used Al 99.5%)) and achieved more concentrated leaching liquors (20g, 50 g of dross) were used. Based on Pourbaix diagram (Al- H_2O , 25 °C) pH of solution for precipitation to value 10 was adjusted by use of precipitation agent or by HCl solution. According to proposed precipitation reactions (9-11) the stoichiometric amounts of precipitation agents were calculated:

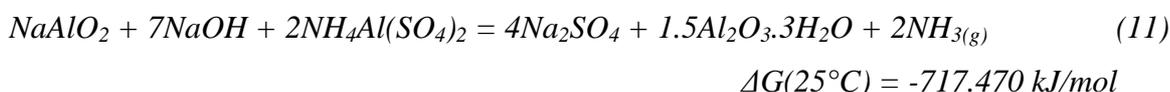
Precipitation by use of NH_4HCO_3



Precipitation by use of 30% H_2O_2



Precipitation by use of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$



Precipitation was realized at the temperature around 20 °C under continuous agitation (500 rpm). After precipitation the samples were filtrated, dried and weighted. The precipitation efficiency was calculated from differences of aluminium content in solution before and after precipitation. The chosen sample were subjected to phase analysis (X-ray diffraction analysis, Diffractometer Dron 2.0) and differential thermal analysis (DTA) (Derivatograph C, MOM Budapest, heating rate: 10 °C/min). Dried samples were then calcined in laboratory electric resistance furnace at the temperature 600 °C for 3 hrs. Selected calcined samples were finally subjected to surface area measurement (Gemini 2360, Micrometrics, USA).

4 Results and Discussion

4.1 Leaching results

The kinetic curves and leaching results from leaching of dross in NaOH solution of concentrations 1, 5, 10, 15, 20 % at used temperatures 20, 40, 60°C are shown in Fig.3-4. The influence of charge 5, 20, 30, 50 g and time in 10 % NaOH on Al extraction is shown in Fig.4b-6. The dependence of charge was studied only at temperatures 20 and 40°C due to vigorous reaction and foaming (tem-



perature increases about 10/20°C) during leaching at higher temperatures and higher charges. From practical point of view for this kind of treatment process it seems to be more convenient to use ambient temperature of leaching in order to avoid mentioned problem. In this case the problematic treatment occurred at S:L ratio 1:10 at 40°C and 60°C and 1:25 at 60°C. As it follows from leaching curves and temperature dependences, the leaching process is more efficient at higher temperatures. The use of concentration of NaOH solution 1% and 5 % is not sufficient for these conditions. The influence of concentration of NaOH and temperature is interesting (Fig.3 and Fig.4a) because as the influence of NaOH concentration above 5 % at 20°C is not significant, at 40°C the use of 20 % NaOH gives the best extraction results, but at 60°C the best results by using of 10 % NaOH solution were obtained. It means that by increasing of temperature the lower concentration of leaching media is needed. The similar behaviour was also observed in work [8] where fine dross was leached in diluted sulfuric acid. At the temperature 20°C the leaching process is very slow and maximum extraction 23 % (at 10, 15, 20 % NaOH) was obtained after 2 hours, but the tendency of curves (10 % NaOH) suggests further increase in Al extraction with increasing time. At the temperature 40°C the leaching rate of aluminium is evidently higher and at these conditions 40 % of Al was extracted to the solution after 2 hours.

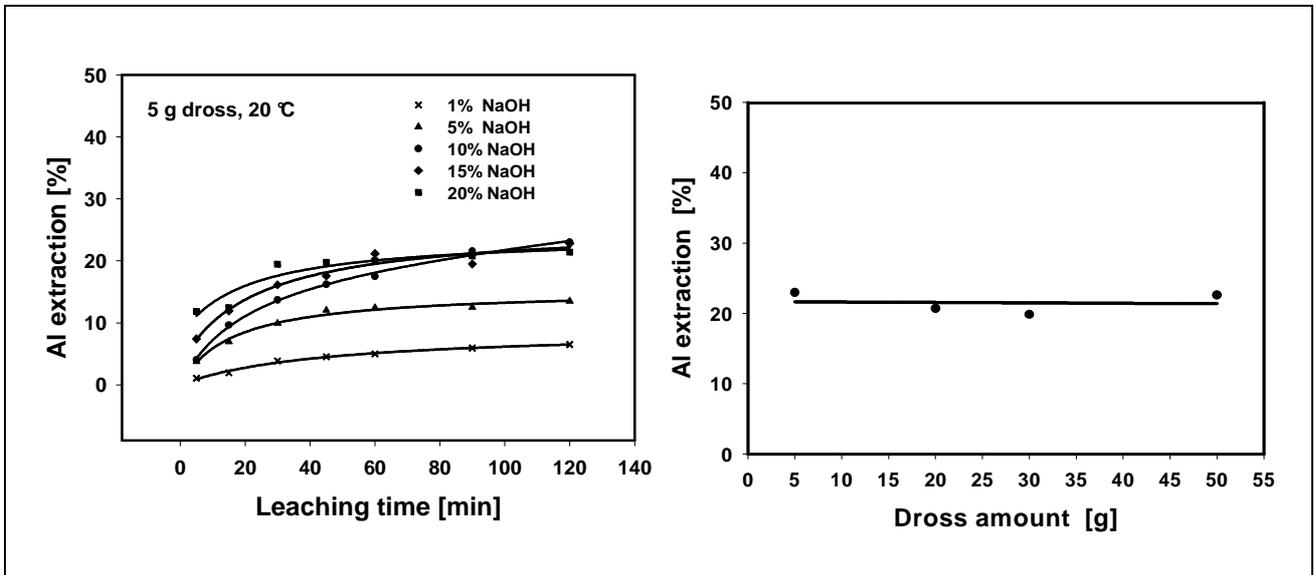


Figure 3: The influence of c_{NaOH} and time on Al extraction at °a) 20°C and b) 40°C

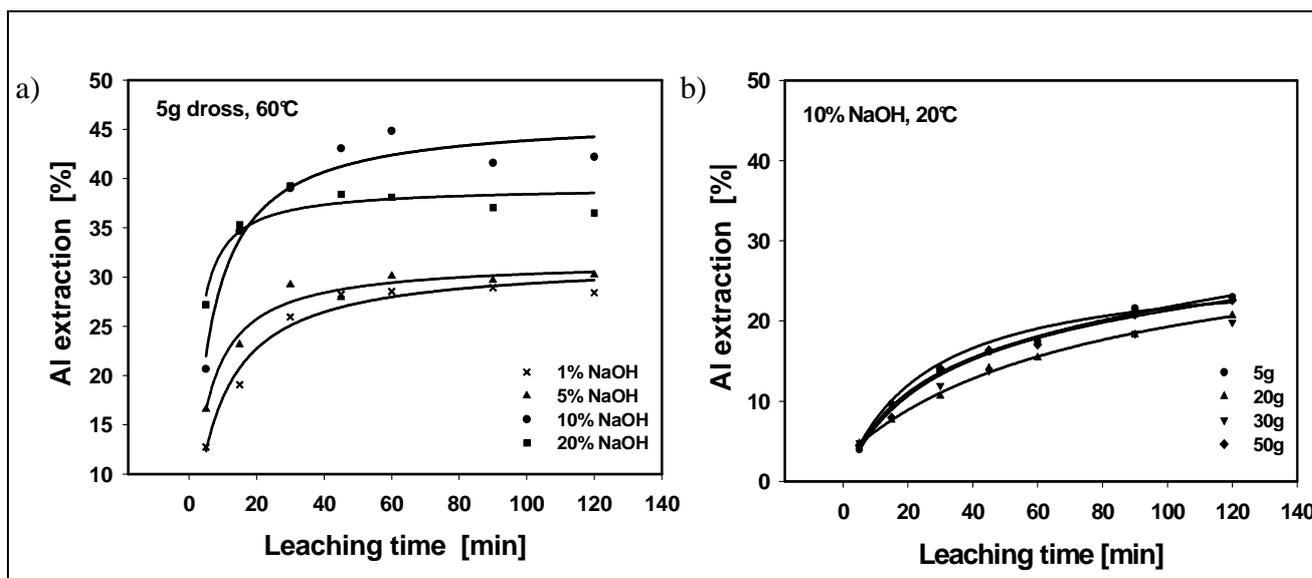


Figure 4: a) The influence of c_{NaOH} and time on Al extraction at 60 °C ; b) The influence of dross charge (5, 20, 30, 50 g) and time on Al extraction at 20 °C in 10% NaOH

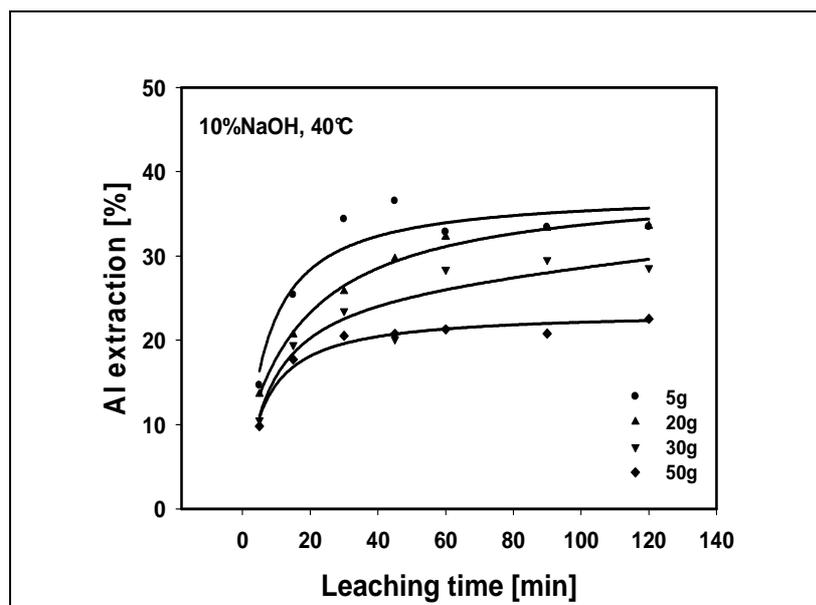


Figure 5: The influence of dross charge and time on Al extraction at 40 °C in 10% NaOH

By further increasing of temperature to 60°C the extraction was not increased markedly but anyway at these conditions (500 ml, 10% NaOH, 5 g of dross, 2 hours) the maximum extraction value was obtained (42.2 %). At the higher temperature the process is faster but after 1 hour the extraction efficiency does not increase significantly.

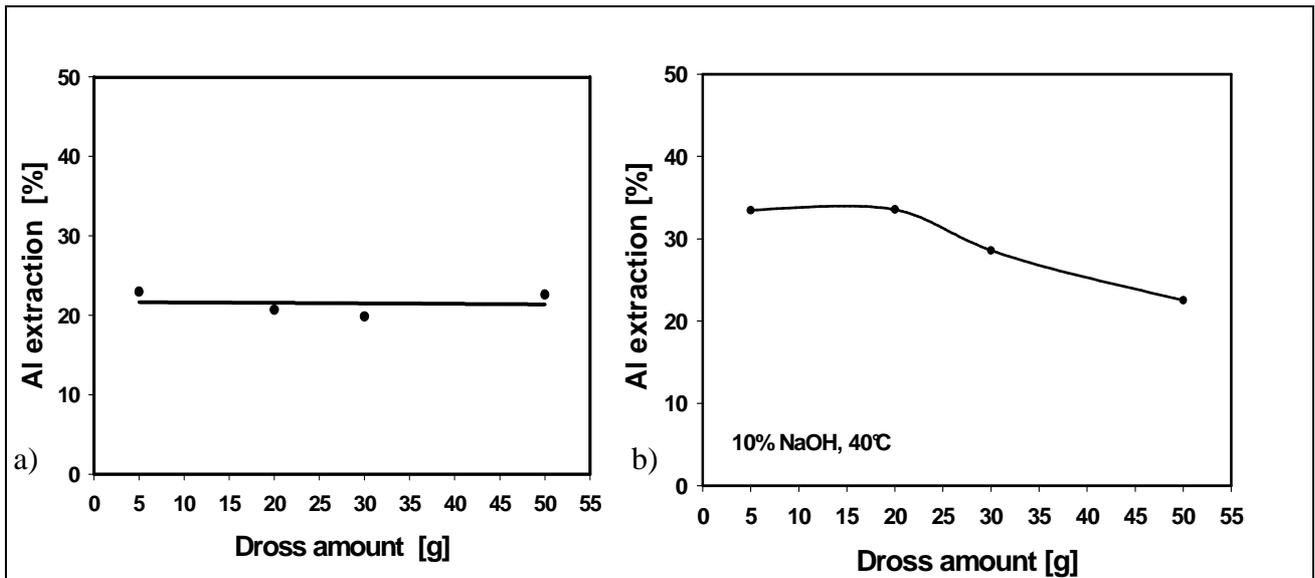


Figure 6: The influence of dross amount on Al extraction at a) 20 °C and b) 40 °C in 10% NaOH

From Fig. 4b- Fig.6 follows that at the temperature 20°C the amount of charge play no role in extraction efficiency, but at higher temperature (40°C) the lower charge is used for leaching the higher Al extraction is obtained. By using of charge 50 g of dross (S:L ratio 1:10) for leaching the maximum extraction reaches about 20 % and does not depend on temperature (20, 40°C) at given conditions. The optimum leaching conditions from practical (charge) point of view and extraction efficiency represents in this case: S:L ratio 1:25, 40°C, 10 % NaOH, minimum 2 hours. On the other hand the positive fact is also that kinetic curves for various charges at 20°C (Fig.4b) promise further rising of Al extraction value with time for all charges. Of coarse it would be suitable to investigate in the future the correlation and the influence of charge of dross together with NaOH concentration on extraction efficiency in order to get further optimization of process. According to chemical analysis (Tab.2) of leaching residue at the best leaching conditions (5 g, 10 % NaOH, 60°C 2 hrs) it is obvious that it is possible to leached out almost whole metallic aluminium from dross and Al from other leachable substances. If we take into account the content of suggested leachable aluminium (calculated from phase semiquantitative analysis) the extraction efficiency reaches about 98 %. The other thing is that leaching residue still contains chlorides. According to content of chlorides in solution after leaching and calculation of content of chlorides in leaching residue it was leached out about 57 % of chlorides. Due to this, the leaching residue is necessary to subject to additional washing in water in order to get inert material or consider foregoing washing of dross before leaching. Based on analysis of X-ray diffraction pattern of studied leaching residue it was obvious that the main phases after leaching are spinel and aluminium oxide and at the same time AlN phase is rather resistant and was not completely leached out as well as chlorides.

Table 2: Chemical composition of leaching residue (10% NaOH, 5g, 60 °C, 2hrs.)

| Element | Mg | Al _{element} | Al _{total} | Si | Cl- |
|---------|------|-----------------------|---------------------|------|-------|
| [w. %] | 1.49 | 1.16 | 31.20 | 0.77 | 24.82 |



4.2 Precipitation results

In table 3 are given pilot results from precipitation experiments of leaching liquor and model pure Al solution.

Table 3: Description and results of precipitation experiments

| Precipitation experiments | Precipitation efficiency [%] | Surface area [m ² .g ⁻¹] |
|---|------------------------------|---|
| Precipitation from model solution by NH₄HCO₃ (100 ml) addition: 35ml 10% HCl, stoichiometric amount NH ₄ HCO ₃ (dissolved in 50ml d.H ₂ O); pH _{final} 9.5 | 99.94 | 54.02 |
| Precipitation from leaching liquor by NH₄HCO₃ leaching liquor: 10% NaOH, 20g dross, 60°C addition: 200ml 10% HCl; 1.9g NH ₄ HCO ₃ (dissolved in 30 ml d.H ₂ O); pH _{final} 10 | 98.87 | 54.69 |
| Precipitation from model solution by 30% H₂O₂ addition: 12-times stoichiometric amount (62.8 ml); pH _{final} 10 | 100 | 33.77 |
| Precipitation from leaching liquor by 30% H₂O₂ leaching liquor: 10% NaOH, 20g dross, 60°C addition: 25-times stoichiometric 30% H ₂ O ₂ (144ml) | 98.34 | 28.48 |
| Precipitation from model solution by NH₄Al(SO₄)₂.12H₂O addition: stoichiometric (12.11g) NH ₄ Al(SO ₄) ₂ (dissolved in 50ml d.H ₂ O); pH _{final} 10.5 | 100 | 58.99 |

It was shown that the efficiency of precipitation almost 100 % in all cases was achieved. Based on XRD analysis all studied precipitates were amorphous and DTA analysis (H₂O₂ and NH₄HCO₃ precipitated sample) assigned the presence of Al(OH)₃ with much lower temperatures of decomposition as it is usual for crystalline Al(OH)₃ sample. In the case of “H₂O₂ precipitated sample” the decomposition temperatures (endothermic peaks) were 170°C and 290°C and for “NH₄HCO₃ precipitated sample” 230°C and 300°C at the same DTA measurement conditions. The surface area of oxide samples indicates that at given conditions the similar surface area values for alumina are obtained by use of pure model solution and leaching liquor. Despite of expectation (literature sources) the values were quite low and use of H₂O₂ does not bring the highest surface area values for calcined alumina. The highest surface area (about 60 m².g⁻¹) by use of agent NH₄Al(SO₄)₂.12H₂O for model solution was obtained and comparable values were achieved with NH₄HCO₃. Prepared aluminas were then subjected to study of heavy metals sorption efficiency from water and results will be published. The next research will be dedicated also to finding of optimum conditions for precipitation and calcination in order to achieve pure alumina with higher surface area.

5 Conclusions

The aim of this work was to investigate the behavior of aluminium during alkaline leaching of fine white dross fraction -1+ 0 mm without foregoing salt removal and by pilot experiments show possibility for recovery of pure aluminium oxide by precipitation with different agent and calcination. Results showed following:



- maximum Al extraction of about 42 % of total content of Al (around 98 % of leachable Al from dross) by leaching of dross fines at 60°C in 10 % NaOH solution at 96°C and S:L ratio 1:100 after 120 min. was achieved
- Rising S:L ratio has a negative effect on Al extraction but there were also proposed conditions for obtaining of comparable Al extraction even at higher S:L ratios
- Leaching residue contained still non-reacted AlN and chlorides
- By precipitation from leaching liquor and calcination (at 600°C) the alumina with surface area of 55 m².g⁻¹ was obtained (by use of NH₄HCO₃) and comparable with those obtained by precipitation of pure model Al solution
- Next research is oriented to find optimum condition for extraction of chlorides from dross, optimum conditions for precipitation of pure Al(OH)₃ (use of ammonium alum) and calcination in order to obtain alumina with higher surface area

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