NEUTRAL, ACID AND ALKALINE LEACHING OF TYPICAL THERMO-MECHANICALLY TREATED ALUMINIUM MELTING DROSS RESIDUES

BALÁZS HEGEDŰS¹–TAMÁS KÉKESI²

A large amount of currently useless – basically oxide – residue is produced by the treatment of dross obtained from the melting of alloyed aluminium scrap. Its negligible residual metallic content does not make it feasible for any further metallurgical processing. On the other hand, it may contain chloride salts, whose removal may not only serve the purpose of recycling but it is required to make this residue suitable for alternative applications, such as construction and road paving materials, or slag forming additive in the steel industry. A hydro-metallurgical treatment with pure water can be efficient in this respect and applying acidic or alkaline media can even reduce the residual metallic content. The composition of the raw residue was examined by instrumental techniques and experiments were carried out to determine the efficiencies of the treatments with water, sulphuric acid and sodium hydroxide. Leaching with water could remove the main salt components of NaCl and KCl in a short time. However, some NH₃ is evolved from the reaction of AlN formed during the preliminary thermo-mechanical treatment. The application of sulphuric acid can be efficient not only in removing the residual metal content but also in suppressing the evolution of NH₃. Although the sodium-hydroxide reagent is capable of aggressively dissolve aluminium not only in the metallic but also in the oxide states, but it also enhances the evolution of NH₃. According to the phase composition and structure of the treated materials, water leaching – perhaps combined with an extra step of sulphuric acid leaching – can be satisfactory for assuring the state of the residual dross to be accepted in different applications.

Keywords: Aluminium dross, salt cake, salt removal, dross utilisation

INTRODUCTION

For economic and environmental reasons, the use of secondary raw materials in aluminium production has been continually increasing. The recycling of obsolete products made of aluminium and aluminium based alloys by melting in reverberatory furnaces results in an increased generation of dross [1], [2]. This inevitable by-product consists of chains formed by the solid oxide particles. As there is no congruent interface, it may entrapt a large amount of liquid metal mechanically [3], [4]. Thus it

¹ Institute of Energy and Quality Management, University of Miskolc
H-3515 Miskolc-Egyetemváros, Hungary
hegedus.balazs@uni-miskolc.hu

² Institute of Energy and Quality Management, University of Miskolc
H-3515 Miskolc-Egyetemváros, Hungary
kekesi@uni-miskolc.hu
may even enhance the heterogeneous oxidation of the aluminium melt. The recovery of the high metallic content can be implemented at the production site by a thermo-mechanical treatment of the hot dross applying heat to melt the entrapped metal and mechanical action combined with salt addition to break the oxide layers insulating the molten droplets. This is usually carried out in an oxygen-gas fired rotary – “converter” – furnace. The relatively large amount of the added – usually NaCl-KCl based – salt [5] serves to help separate the oxide coatings and to prevent excessive re-oxidation of the molten metal phase. After tapping the recovered molten metal, the residual solid waste material (“residual dross”) is discharged, which may contain just a few per cents of the metallic phase [3]. Thus it may not be economically processed by the usual metallurgical processes [6]. In its usual state, it does not constitute any commercially significant value, rather it may mean a burden both from the financial and environmental aspects. Nevertheless, other industries (such as construction and road paving materials production, cement clinkering, chemical industry, steel making with synthetic slags, mineral wool production, agriculture and glass manufacturing) may use the basically oxide containing residue if the unwanted components, mainly the relatively large amounts of salt [7], can be removed efficiently. The almost negligible portion of dispersed aluminium metal particles are covered by thick and refractory oxide layers, therefore they do not cause much trouble even for the applications in the construction materials industry, but it may even be beneficial when steel making or glass foam producing applications are proposed.

The salt content – composed of mainly chlorides – of the residual dross can be readily dissolved by pure water at ordinary temperatures, therefore it may be the fundamental and a suitable initial step in a hydrometallurgical processing scheme. The residual dross of high salt content, often referred to as salt cake, is usually black coloured. It is generally crushed and ground. It may be followed by the simple physical removal of the malleable metal grains of larger size, and the fine powder is mixed with as much water to yield a brine liquor of 20–25% saturation, which offers efficient dissolution and does not imply excessive energy requirement for the subsequent removal of water by evaporation. As a result of the exothermic reactions of dissolution, the temperature may rise to as high as 60 °C during leaching [6]. The subsequent solid/liquid separation can be carried out in multiple steps, including a preliminary centrifuging to remove the coarser particles. The fine slurry is then settled and washed during filtration. The salt-free solid product can be suitable for the aimed alternative ways of utilization and the brine liquor can be evaporated by boiling, followed by the drying of the wet salt crystals before recycling to the thermal process in the rotary furnace. As KCl is more volatile than NaCl, the leaching of the latter by-product is also required, and some KCl may still be added to reset the original composition of the usually equimolar NaCl-KCl mixture used in aluminium melting.

The residual dross obtained from the high temperature treatment of the primary aluminium dross contains nitrides and carbides too. These compounds may also react with water during leaching:

$$\text{AlN} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3 \quad (1)$$

$$\text{AlN} + 4\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3\text{OH} \quad (2)$$
Balázs Hegedűs – Tamás Kékesi

\[ \text{AlN} + \text{NaOH} + \text{H}_2\text{O} = \text{NaAlO}_2 + \text{NH}_3 \]  
\[ \text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 4\text{Al(OH)}_3 + 3\text{CH}_4 \]

The fine metallic particles – after the oxide coating is removed – may react with the alkaline or acidic or even the neutral aqueous medium, like:

\[ \text{Al} + \text{NaOH} + \text{H}_2\text{O} = \text{NaAlO}_2 + 1.5\text{H}_2 \]  
\[ \text{Al} + 3\text{NaOH} = \text{Na}_3\text{AlO}_3 + 1.5\text{H}_2 \]

Some other dangerous gases (phosphine, hydrogen sulphide) may also be evolved. These reactions are all exothermic, and the co-existence of heat and the inflammable gases may even cause danger of fire and explosion besides poisoning. However, these effects may also be present when the residual dross is simply disposed of. There are proposed technologies [7] which are assumed to offer 99% recovery of the salt and a low (<0.2%) chloride content in the final residue, and the harmful gases evolved during the hydrometallurgical treatment are combusted. The heat from the latter step can be utilized for the evaporation of water.

1. EXPERIMENTAL PROCEDURE

As a result of the thermo-mechanical treatment of the aluminium melting dross, solid residues of different colour can be obtained. In the extreme cases they can appear light or dark, as shown in Figure 1. The metallic content of the lighter material is lower. In the obtained sample it was 9.9%, and it was a mere 1.1% in the fine (<250 µm) fraction obtained after grinding. Whereas these values were 13.6% and 4.5% in the dark material representing the opposite extreme quality. The metallic content in the powder fraction was finely dispersed and in particles covered by a thick oxide layer. This part of the metal content in the residual dross could be determined only by the volume of the collected hydrogen gas evolved from the reaction of aluminium with hot and concentrated NaOH solution [3], [4].

![Figure 1](image_url)

*Figure 1*

The macro images of the light (a) and dark (b) coloured residues from the thermal treatment
1.1. The examined material

The major constituent of the two different looking types of the residual dross – serving as the principal raw materials for the experiments – were examined by scanning electron microscopic (SEM), energy dispersive X-ray microprobe (EDS) and X-ray dispersive (XRD) techniques applying the finely ground (<250 µm) fractions. The characteristic micro images and the relevant EDS spectra are shown in Figure 2 and 3.

**Figure 2**
The SEM image (a) and the EDS spectrum (b) of the light coloured residue from the thermo-mechanical treatment

**Figure 3**
The SEM image (a) and the EDS spectrum (b) of the dark coloured residue from the thermo-mechanical treatment
As the electron beam can penetrate into the oxide material to a depth of ~5 µm, the core of the grains may also contribute to the spectra if the oxide coating is thinner. Besides, the X-ray emission of the larger atoms is relatively stronger, thus the Al signal is stronger than those of Na, Mg or O even at practically equal concentrations. On the other hand, the signals of Cl and Ca are relatively stronger. The EDS spectra reveal that the light coloured dross residue mainly consists of aluminium oxide, while the dark coloured residue exhibits a relatively large proportion of the salt components and probably more metallic aluminium. A similar examination of the additive salt pointed out NaCl and KCl as the main components and some added CaF$_2$.

The phase composition of the examined residual dross materials is given by the obtained XRD spectra in Figure 4.

![Figure 4](image)

*Figure 4*

The XRD spectra of the light (a) and dark (b) dross residues

The XRD spectra have proved that the simple and complex oxides ($\alpha$-Al$_2$O$_3$ and MgAl$_2$O$_4$) dominate the light coloured dross residue, whereas the remaining salt content is significantly higher in the dark dross residue. The dominance of the simple oxides in the light coloured dross residue indicates the higher temperature probably
neutral, acidic and alkaline leaching of typical thermo-mechanically treated …

reached during the thermo-mechanical treatment, which also enhances the evaporation of especially KCl and Mg.

1.2. Leaching experiments

The finely ground dross residue samples were leached with either distilled water, 16.3 m/m% (10 V/V %) sulphuric acid or 6 mol/dm³ NaOH solutions. The selected low H₂SO₄ concentration is preferred generally in hydrometallurgy [8], [9], [10], and the high NaOH concentration served as a reference to the strong solubilizing effect for Al₂O₃ [3], [4], [10]. Basically, the light and the dark coloured industrial dross samples were used, but further experiments were also carried out with samples obtained from laboratory thermo-mechanical treatment of different residues obtained from different primary dross samples and mixed with different amounts of salt. The 10 g samples were contacted with 100 cm³ of the lixiviant solutions, providing safe solubility. The suitable kinetic conditions were assured by horizontal shaking to eliminate settling in polyethylene reactor vessels of 300 cm³ volume. The kinetic leaching experiments were carried out each for 5, 15, 30, 60, 120, 180 and 240 minutes. The concentrations of the chloride and the hydrogen ions were obtained by titrimetric methods, but the concentrations of the dissolved metals were determined by atomic absorption spectrometry (AAS). The results were expressed as recoveries relative to the mass of the examined dross samples. The equipment and the steps of laboratory leaching experiments are illustrated by Figure 5.

2. Experimental results and discussion

Instead of common “recoveries”, referring to the original contents of the components, the extraction results are expressed as “yields” referring to the mass of the sample. However, the sequential results indicate that virtually complete recoveries are usually attained.

Figure 5
The fundamental leaching experiments – (a) leaching and sample preparation, (b) vacuum filtering, (c, d) solutions and solid residues from leaching
2.1. Leaching progress

The amounts of dissolved elements yielded by various times of water leaching from the light and dark coloured residual dross samples are given in Figure 6.

**Figure 6**
The yields of components by water leaching from (a) the light and (b) dark coloured dross samples obtained from the industrial hot treatment

Dissolved chlorine was analysed by an instant argentometric method to indicate the soluble salt content of the dross samples directly. As calculated from the more accurate AAS analytical results for Na and K, leaching with water could reach as much dissolved salt as ~40% relative to the sample mass of the dark residual dross. On the other hand, water leaching of the light coloured dross material yielded only slightly over 4% dissolved salt. This is a considerable difference.

It is also remarkable, how quickly the amount of the dissolved chloride salt yielded by water leaching can reach a maximum. It may imply a technically complete recovery. Applying sulphuric acid had a great effect on the removal of the aluminium content, as it is shown by the diagrams in Figure 7.

**Figure 7**
The yields of components by 16.3% H$_2$SO$_4$ leaching from (a) the light and (b) dark coloured dross samples obtained from the industrial hot treatment
Based on the AAS analytical results for Na and K, the acid leaching of the light coloured dross gave similar results to those with water, but the acid could remove only ~34% salt relative to the sample mass. This is ~6% lower than that obtained with pure water. On the other hand, the argentometric analysis of the acid leachates gave seemingly higher dissolved chloride results. However, the K$_2$CrO$_4$ indicator may be partly converted to the inert H$_2$CrO$_4$ form by the acid, causing error. A noticeable change as a result of applying sulphuric acid is the dissolution of ~6% aluminium from the dark dross sample, which was only 1.5% in the case of the light coloured dross. It confirms the assumption that the dross may have received a more aggressive thermal treatment which resulted in a consequently more intensive oxidation, leaving less soluble aluminium in the residual dross. It is shown that the dissolution of the chloride salt content with water is virtually completed in less than 15 minutes, while dissolving Al with the acid may last about four times longer.

### 2.2. Recovered components

The relative recoveries obtained with water and sulphuric acid in leaching experiments lasting uniformly for 60 minutes are compared in Figure 8.

![Figure 8](image)

The yields of components by water and 16.3% H$_2$SO$_4$ leaching from the light (a) and dark (b) coloured finely ground (<250 µm) dross samples obtained from the industrial thermo-mechanical treatment

The one hour leaching tests could show the total amounts of the practically dissolvable components. Confirming the results of the kinetic study presented in Figures 6 and 7, these results also show that the salt content of the dark coloured residual dross
is more than ~5 times higher than that of the light coloured one. However, this ratio is significantly greater for KCl, which is prone to preferential vaporization during high temperatures. It confirms the assumed more aggressive thermal conditions in the case of the preliminary thermo-mechanical treatment producing the light coloured residual dross. The same is the reason for the difference in the dissolved Na/K molar ratios for the two different types of the residual dross (~1.7 in the case of the dark and ~9.3 in the case of the light coloured dross).

Further experiments were carried out to examine the leaching behaviour of residual dross samples obtained by laboratory scale thermo-mechanical treatment [3, 4] of primary melting dross materials originating from the melting of aluminium alloy scrap of negligibly low (<0.1%) and high (~4%) Mg contents, respectively. The results, referring to the 1 hour leaching with either water or 16.3% sulphuric acid, are shown in Figure 9. Again, a great difference is seen in the yielded amounts of the dissolved chloride salts, although they were added at the same rate (~10%) to both charges. It shows that a higher loss by evaporation could happen during the thermo-mechanical treatment of the primary dross containing high-Mg aluminium alloy as the entrained metal. The ratio of the more volatile KCl component to NaCl is lower also in this case, indicating the higher temperatures reached as a result of Mg oxidation. These conditions did not reduce the relative amount of the Al metal dissolved by acid leaching, showing that the thermo-mechanical treatment in the induction-type laboratory furnace did not entail higher degree of re-oxidation even at higher temperatures.

**Figure 9**
The yields of components by water and 16.3% H₂SO₄ leaching from the residual dross related to the production of low-Mg (a) and high-Mg (b) finely ground (<250 µm) dross samples obtained from the laboratory thermo-mechanical treatment.
The compositions of the solid residues obtained from the 1 hour leaching experiments were examined – after drying at 105 °C – by similar instrumental techniques as applied for the raw materials. The SEM images were similar to those of the raw samples in Figure 3, but showed more wrinkled surfaces of particles consisting of Al and O, indicating the presence of α-Al₂O₃. The major difference was the missing Na, K and Cl peaks in the relevant EDS spectra, confirming the removal of the salt content by either examined leaching agents. The phases detected after the leaching of the light coloured dross residue with water, H₂SO₄ and – for reference – with NaOH are marked on the XRD spectra of Figure 10. Because of the higher initial salt concentration, the effects of leaching can be even more clearly demonstrated by the XRD spectra of the solid residues from the hydrometallurgical treatment of the dark coloured dross sample shown in Figure 11. In order to confirm the efficiency of the treatment, these XRD spectra should be compared to those of the starting materials shown in Figure 4.

In the solid residue of the light coloured residual dross, α-Al₂O₃ has become dominant, but the presence of MgAl₂O₄ spinel is also evident as the water leaching removed the chloride salts. The diffractogram obtained after the sulphuric acid leaching is similar, but the spinel seems to be present at a higher proportion, indicating the higher chemical stability of the MgAl₂O₄ compound. The intensity of the AlN peaks are slightly higher when acid was used instead of water for leaching. It shows that the unpleasant evolution of NH₃ may be slightly depressed by the addition of sulphuric acid in the water for leaching the residual dross obtained from the high temperature thermo-mechanical treatment of the primary dross. The remaining – slight – metallic Al content is hidden under a thick oxide cover, which cannot be detected by the X-ray beam of the XRD or the electron beam of the SEM techniques. The leaching with the aggressive 6M NaOH solution could release and dissolve virtually all the metallic Al, but it also involved a strong evolution of gas and heat. Beside the evolution of H₂ from the dissolution of metallic Al, the reaction of AlN with water is enhanced by NaOH according to Equation (3), resulting in a more intensive generation of NH₃. This reaction is evidenced as the AlN peaks are removed after the NaOH leaching.

In the solid residue obtained by leaching the dark coloured dross – of high original salt content with water, the spinel MgAl₂O₄ and the α-Al₂O₃ compounds were predominant and the metallic Al could also remain beside the relatively lower AlN content. The dominance of the spinel component becomes evident, but also the metallic Al is clearly detected. These characteristics are different from the previous case of the residue from the water leaching of the light coloured dross sample. Due to the probably milder thermal conditions during the preliminary thermo-mechanical processing at the industrial plant, the evaporation of Mg metal and the salt components could be less intensive, and the former could extensively form spinel compounds. The greater salt content could enhance the coalescence of aluminium droplets, which resulted in a decrease of secondary oxidation and cleaner surface of the appearing metallic particles. The relatively higher diffraction peaks of AlN can be seen after the sulphuric acid leaching, indicating again the repression of the harmful reaction (2) by the acidic medium. Metallic Al was already missing from the XRD spectrum obtained from the residue after the acid leaching. The only remaining salt component
was the small amounts of the additive CaF$_2$, which is not dissolved neither in water nor in the alkaline solution. Experience has shown, that it may be gradually converted to the sulphate by applying sulphuric acid, but a – relatively slight – dissolution of Ca may be noticed only during a subsequent water rinsing.

*Figure 10*

The XRD spectra of the solid residues of the light coloured finely ground (<250 µm) dross samples obtained from the industrial thermo-mechanical treatment after 1 hour of leaching with water (a), 16.3% H$_2$SO$_4$ (b) and 6M NaOH (c)
Neutral, Acid and Alkaline Leaching of Typical Thermo-mechanically Treated...

2.3. Removal efficiency

The results of the kinetic and the equilibrium studies shown above suggest, that the residue from the thermo-mechanical treatment of the aluminium melting dross may be purified by a suitable hydrometallurgical treatment applying sequential leaching and

Figure 11
The XRD spectra of the solid residues of the dark coloured finely ground (<250 µm) dross samples obtained from the industrial thermo-mechanical treatment after 1 hour of leaching with water (a), 16.3% H₂SO₄ (b) and 6M NaOH (c)
washing steps. The most important criterion for any further application of the residue is the elimination of the salt content, however the removal of the metallic phase remaining in the residual dross after the industrial thermo-mechanical processing was also considered. The chloride salts could be dissolved relatively quickly by applying water, and dilute H₂SO₄ was found suitable to dissolve the minor amounts of the metallic components too. In order to establish a workable process, the efficiency of elimination had to be tested by carrying out multiple steps of leaching and subsequent washing, including solid/liquid separations. The efficiency of elimination is shown by the diminishing concentrations in the subsequent leachate solutions.

In this case, a different experimental set-up had to be applied. The ground residue samples – of 300 g – obtained from the industrial thermo-mechanical processing aluminium melting dross of low-Mg alloy scrap were leached with water for 10 minutes in each step and with 16.3% H₂SO₄ for 30 minutes, respectively. The horizontal shaker was run at a high intensity to prevent settling of the finely ground material. The repeated leaching steps were carried out after decanting the clear solution and replacing it with the fresh leaching solution. After the last leaching in the shaking bottles, decanting was followed by simple washing carried out by adding distilled water to the thick sludge after decanting the solution. Washing was repeated in multiple steps separated by decantation. The final washing step was followed by filtering during which distilled water was used to rinse the filter cake. All the steps of this procedure were carried out by the addition of and 500 cm³ volumes of the leaching solution or washing water. Samples were taken from the decanted solutions for AAS analysis of the dissolved metal concentrations. The yields were calculated to express the amounts of the metals removed by the solution applied at the relevant step relative to the original mass of the treated dross sample. The results of the multi-step leaching with water or dilute H₂SO₄ followed by repeated washing and a final rinsing-filtering are shown in Figure 12. The pH values measured in the solutions of the operation applying water are also given.

The total amounts of the removed salt – calculated from the analysed concentrations of Na and K in the solution samples – are approximately the same by applying water or dilute H₂SO₄. However, the acid leaching was carried out for longer time for dissolving also the metals, which resulted in a more efficient leaching of the salt components in the first step too. The alkaline pH of the solutions in water leaching results from reactions (1), (2), which may also be detected by the smell of ammonia gas. Besides the dissolution of metallic components of the dross, minor amounts of dissolved Ca may also appear especially during the water washing steps after the H₂SO₄ treatment, caused by the partial transformation of the CaF₂ component. Dissolved components appearing in the subsequent steps of leaching and washing may have resulted not only from further dissolution, but also from imperfect liquid/solid separation by decantation, leaving significant portions of the previous solution behind in the sludge.
Neutral, Acid and Alkaline Leaching of Typical Thermo-mechanically Treated ... 37

CONCLUSIONS

A relatively simple hydrometallurgical treatment can significantly change the composition and structure of the residual dross obtained from the thermo-mechanical processing of the primary dross generated by melting alloyed aluminium scrap. Water leaching is efficient and quick in removing the chloride salt content. NaCl and KCl are virtually eliminated within a few minutes. The side-reaction of AlN — generated at the high temperature pre-treatment of the dross — with water may also occur. It causes the evolution of some NH₃ gas. Its absorption or collection and combustion should be coupled with any implementation of the aqueous processing of the dross.

Either H₂SO₄ or NaOH solutions are efficient in dissolving not only the chloride salts, but also the remaining metal content in the treated dross, however this process is slower. The generation of NH₃ is repressed by the acid, but strongly intensified by NaOH in the solution.

Water leaching may be sufficient if only the removal of the easily soluble chloride salts is intended, which can be recycled after evaporating the solution. A low concentration of the remaining metallic phase is dispersed in small particles covered by thick oxide layers. If its removal is also required, a second leaching with dilute sulphuric acid should be included. The leaching operation must be followed by sequential washing steps with water and a final filtering. Less washing steps are required if filtering is used instead of decantation for the solid/liquid separation. The solid resi-
due may be utilized in various industrial technologies. Its minor metal content, covered by an oxide layer, is virtually inert, but it may even be beneficial in some applications (like steel making or glass foaming).

ACKNOWLEDGEMENT

This research was carried out in the Centre of Applied Materials Science and Nanotechnology at the University of Miskolc. The continuation is supported by the GINOP-2.2.1-15-2016-00018 project in the framework of the New Széchenyi Plan of Hungary, co-financed by the European Social Fund. The described study was carried out as part of the EFOP-3.6.1-16-2016-00011 “Younger and Renewing University – Innovative Knowledge City – institutional development of the University of Miskolc aiming at intelligent specialisation” project implemented in the framework of the Széchenyi 2020 program. The project was supported by the European Union, co-financed by the European Social Fund.

REMARK

The content of this paper has been partly presented at the MultiScience XXXII\textsuperscript{nd} MicroCad International Scientific Conference, 5–6 September, 2018, Miskolc, Hungary.

REFERENCES

