

CHARACTERIZATION AND COMPLETE UTILIZATION OF ALUMINIUM MELTING DROSS

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Abstract

Aluminium scrap is a raw material of growing importance in the production of aluminium and its alloys. Due to the thermodynamic properties, melting the recycled metal of high specific surface generates significant amounts of dross consisting of an oxide matrix and a large proportion of entrapped liquid metal. This heterogeneous material is usually processed by a thermo-mechanical treatment with the addition of a large amount of NaCl-KCl based salt to recover the entrapped metal. The residual dross is currently considered as waste, and it is usually disposed of despite of its potentially valuable metallic and non-metallic components. We have examined the structure and composition of different residual dross types applying instrumental techniques and chemical leaching tests. The results pointed out the possibility of utilizing the chloride and the oxide components and removing the still remaining metals. A method of hydrometallurgical processing has been examined for the recycling of the basically NaCl-KCl salt content leaving a residue which may be suitable as an additive to rough ceramic materials used in the construction industry.

Keywords: Aluminium melting, dross, salt recovery, metal content, ceramic material, hydrometallurgy

1. Introduction

The restructuring of the Hungarian aluminium industry in the last decade to cut the primary production and to become based on primarily secondary raw materials was a pioneering change in a country of significant bauxite resources and a long tradition of primary technology development. The change corresponds to a global tendency indicated by the steady increase in the share of the secondary based aluminium production, currently approaching a global 35%. This share in Hungary is well beyond 70%, as primary metal – from import - is only used for technological reasons in the metallurgical production of the required compositions of usually low Fe and Si aluminium alloys. The global share of scrap as a raw material for aluminium production is expected to rise further, as re-melting consumes 95% less energy than primary production and the amount of scrap generated is increasing. Obsolete scrap, recycled from consumption represents a growing share in the charge of melting. It causes an increased dross formation in the usually applied gas fired melting furnaces because the thicker non-metallic surface layers on the usually large specific surface area entails higher degree of oxidation during melting (HAN et al. 2003). The molten drops of the metal are more isolated and the dispersed particles of the metal – implying larger specific surfaces – are faster oxidised. The oxidation of aluminium and – especially – of magnesium, a common

alloying component, is highly exothermic, possibly causing an extreme local superheating which, in turn, results in an increased rate of oxidation. TóTH et al. (2013) have shown the significance of metal losses by dross formation. The highly negative Gibbs free energy change (< –900 kJ/mol O₂) associated with the oxidation of aluminium at the typical temperature (\sim 750 °C) of melting results in an extremely high stability of its native oxide. Magnesium has an even more negative Gibbs free energy (< –1000 kJ/mol O₂) related to its oxidation at this temperature (GILCHRIST 1979). Oxidation is also highly likely by the main furnace gas components, CO₂ and H₂O arising from natural gas combustion. Therefore, oxidation during melting cannot be avoided, and the principal oxide component of the dross is Al₂O₃ and MgO or the spinel compound MgAl₂O₄ when melting of AlMg alloys. The latter compound causes a great structural changes, resulting in higher dross volumes. Due to the great exothermic heat of aluminium oxidation (< 1100 kJ/mol O₂), the surface of the melt can be superheated and such solid phases as AlN and Al₄C₃ can be also formed.

The oxides of aluminium and also of magnesium do not form a protective slag layer as they are solid at the temperature of aluminium melting. Although they have higher densities than that of the molten metal, their fine particular shape and the high surface tension results in the formation of the physically heterogeneous dross layer at the surface of the melt (HO and SAHAI 1990). The oxides represent a direct loss of the metal, but even more molten metal is entrapped physically in the heterogeneous dross layer, usually removed manually from the surface of the metal bath after melting. The structure of the aluminium dross is generally characterised by oxide particles and scales stuck together by the partly frozen metal. The metallic content of the dross may reach as high as 70–80% by weight, which is usually removed by a thermo-mechanical treatment (TÓTH et al. 2013) in a converter-type rotary furnace applying significant addition of NaCl-KCl based salts. Salt addition efficiently serves the separation and disintegration of the oxide coatings and to prevent excessive re-oxidation of the molten metal phase. The metal recovery by the hot processing is shown in *Figure 1*.

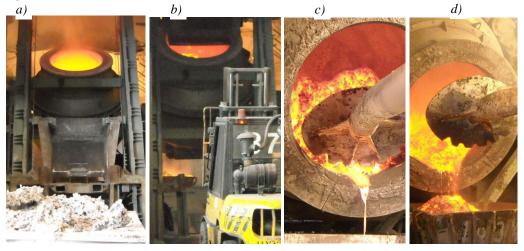


Figure 1

Thermo-mechanical treatment of the aluminium dross to recover the entrapped metal (a - dross charging, b - processing, c - tapping and retaining the residue, d - removing the residual dross)

The heterogeneous material is heated by the jet flame of an oxy-fuel burner mounted in the lid, while the oxide structure is broken by the rotary movement of the furnace drum and the intermittently applied pushing force exerted by the plunging tool used in the tilted position of the furnace.

The tapped metal is aluminium, containing the less reactive alloying components, while Mg is lost by selective oxidation generating extra heat. As most of the entrained metal content can be recovered by this process, the residual dross usually consists of mostly the oxides and the salt components, accompanied by a low (2-10%) concentration of metal. The amount of this residual dross may be $\sim 5\%$ of the produced metal, depending on the Mg content of the grades, reaching levels measured in thousands of tons in Hungary. As no significant metallic value can be recovered from it, and its oxide and chloride components cannot be utilised in this form, the major part of it is disposed of at landfill sites. In order to make the residue also useful it is imperative to separate the salt and the oxide constituents. The recovered salt can be recycled to the thermo-mechanical treatment of the primary aluminium dross. The salt-free final residue, containing mostly the oxides and a minor amount (a few per cent) of the aluminium metal could be utilized in different industrial technologies as:

- slag forming agent in steel making (where the remaining Al content is also of benefit for the reducing effect)
- additive to special cements and concrete (to improve thermal insulating properties)
- additive to asphalt (to increase wear resistance)
- additive to produce glass foams (a novel structural material for heat insulation)
- ceramic production

However, all these novel applications would require an almost complete elimination of the chloride components from the residual dross (XIAO et al. 2005). The remaining aluminium content may be useful (as in steel making slag modification) or harmful (as in ceramic production), or indifferent in small quantities covered by a thick and firm oxide layer (as in the other noted potential applications). In order to meet the requirements of utilization the salt removal is a commonly critical condition, which, at the same time, may also serve the economy of dross processing by recycling.

The basically chloride salt content of the residual dross may be dissolved by pure water at ordinary temperatures. The obtained brine can be evaporated to yield the NaCl-KCl salt for recycling. The minor CaF₂ component - also present originally - may not be recovered, but can be supplied when the proper NaCl/KCl ratio is reset for the repeated application. Thus water leaching should be the fundamental initial step in a hydrometallurgical processing scheme after crushing and fine grinding the residual dross ("salt cake") from the thermo-mechanical treatment of the primary melting dross. The preliminary grinding step may be followed by a physical separation of the larger malleable particles containing a predominant metallic core, or added directly to the leaching step to produce a brine of approx. 25% saturation for efficient dissolution, but also subsequently an energy saving removal of water by evaporation. Side reactions occurring as a result of the high-temperature treatment of the dross may occur, producing some noxious gases too:

$$AlN + 3H_2O = Al(OH)_3 + NH_3$$
 (1)

$$AIN + NaOH + H2O = NaAlO2 + NH3$$
 (2)

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$$
 (3)

If acidic or alkaline solutions are present, the minor metallic aluminium content may also be dissolved:

$$2A1 + 3H_2SO_4 = AI_2(SO_4)_3 + 3H_2 \tag{4}$$

$$Al + NaOH + H_2O = NaAlO_2 + 1.5H_2$$
 (5)

The reactions above – especially the last two – are exothermic, which will beneficially increase the temperature. These effects may also be present if the residual dross is disposed of in the environment.

There are proposed technologies (OLPER and KASPAR 1994) 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 generated heat of dissolution can be utilized for the evaporation of water. Although the proposed hydrometallurgical process may seem straightforward, there remain the questions of dissolution kinetics, efficiency of solid/liquid separation by decantation or filtering, solubility of metals, the application of acid or alkaline media, purity of the solid residue and the efficiency of evaporation. These questions required clarifications by fundamental experiments.

2. EXPERIMENTAL MATERIALS AND PROCEDURE

The raw materials for the experimental examinations were collected from the accumulated residual dross at an industrial site of the thermo-mechanical treatment of aluminium melting dross. There are basically two different extreme types that can be distinguished also by sight. One being light and the other dark in colour. Applying a special method (KULCSÁR and KÉKESI 2017) for determining the metal content (broken down into physically obtainable in the molten form or coarse pieces after granulating the hot treated residue, and the hidden metal content in the separated fine fraction after grinding), it has been pointed out that the lighter material had a metal content of 9.9%, and it was a mere 1.1 per cent in the fine (< 250 µm) fraction obtained after grinding. Whereas these values were 13.6 and 4.5 per cent in the dark material. No metal could be melted out of either samples whereas - after granulating the hot material in water - grinding and classifying resulted in a fine fraction of ~90% from both materials. The characteristic images and the relevant Energy Dispersive X-ray (EDS) and the X-ray Diffraction (XRD) spectra are shown in *Figure 2* and 3.

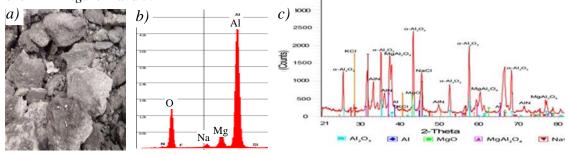


Figure 2
The macro (a), the EDS (b) and the XRD spectra of the light coloured residue from the thermo-mechanical treatment.

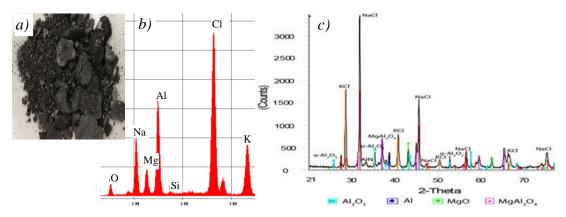


Figure 3

The macro (a), the EDS (b) and the XRD (c) spectra of the dark coloured residue from the thermo-mechanical treatment.

The EDS spectra reveal that the light coloured dross residue mainly consists of aluminium oxide, while the dark residue exhibits a relatively large proportion of the salt components and probably more metallic aluminium. However, the electron beam cannot penetrate below an oxide layer thicker than $\sim 5~\mu m$, thus not all the particles consisting of a metallic core can be detected as metal. The analytical method based on the collected volume of the H_2 evolved from reactions (4-5) could reveal the real metal content hidden under the oxide coatings of the fine particles (Kulcsár and Kékesi 2017). Shown by the XRD spectra, α -Al $_2$ O $_3$ is dominant in the light coloured dross residue. The dominance of the simple oxides in the light coloured dross residue indicates the higher temperature probably reached during the thermo-mechanical treatment, which also enhances the evaporation of especially KCl and Mg and could cause the formation of AlN. However, the remaining NaCl and KCl salt content is significantly higher in the dark dross residue and the MgAl $_2$ O $_4$ -spinel component is also more evident.

Apart from the extreme types of the residual dross, samples were collected from the common grey coloured dross residues obtained from the industrial thermo-mechanical processing of primary dross batches generated in the melting of aluminium alloys of different Mg concentrations. The XRD spectra obtained with the residual dross samples from the thermo-mechanical processing of primary dross batches obtained from the melting of low and medium Mg containing aluminium alloys are compared in *Figure 4*.

The visual appearances of the two residual dross samples are quite similar, but the XRD spectra reveal some differences. The major phases found are marked in either or both diagrams in *Figure 4*. It is obvious that due to the Mg alloying in the metal, the spinel MgAl₂O₄ phase appeared in the residual dross, while the salt and metallic Al content diminished. It can be attributed to the exothermic reaction of Mg oxidation during the hot dross treatment.

Suggested by the observed compositions of the raw materials, it was preferred to use the primarily the dark coloured extreme type dross residue and that related to the treatment of the dross related to the low-Mg aluminium alloy in the hydrometallurgical processing experiments. These cases offered the highest concentrations of the salt and the metal to be recycled or eliminated.

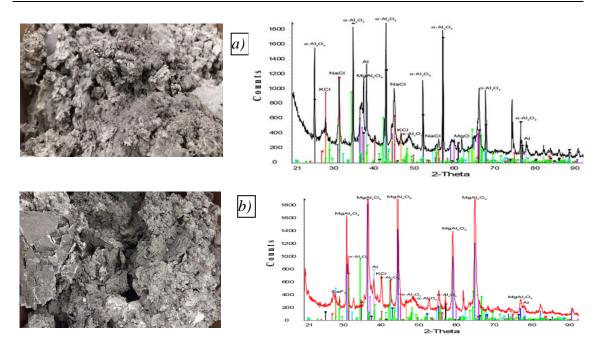


Figure 4
The pictures and XRD spectra of the residue from the hot treatment of primary dross batches obtained from the melting of low (a) and medium high (b) Mg containing aluminium alloys

The fine fraction ($<250~\mu m$) of the ground residual dross samples – obtained from the industrial thermo-mechanical processing of aluminium melting dross – were leached with distilled water and 16.3 m/m % sulphuric acid, respectively, followed by washing and solid/liquid separation steps organised in different procedures. Control tests of high dissolving power for aluminium-oxide were carried out with 6 M NaOH too. Some pieces of equipment and the main steps of the laboratory leaching experiments are shown by *Figure 5*.

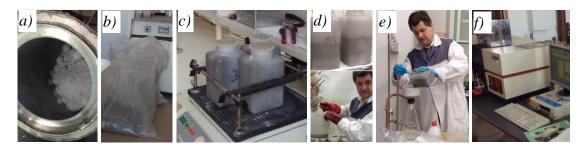


Figure 5
The main steps of the hydrometallurgical procedure (a – grinding, b – raw material, c – leaching, d – settling and washing, e – filtering, f –AAS analysis).

The applied sulphuric acid concentration corresponds to a 10 % by volume ratio, but beyond the convenience of preparation, it is preferred generally in hydrometallurgy (GILCHRIST 1979; BAR and BARKETT 2015). To examine the reaction rate, 10 g or 20 g samples, resp. were contacted with 100 cm³ of the solutions. It was a safe ratio to provide sufficient solubility. A horizontal shaking machine was used to provide a virtually homogeneous dispersion in reactor bottles of 300 cm³ in volume. The kinetic experiments were carried out for various times, but further examinations included set times of leaching (allowing equilibration). The larger scale experiments examining the elimination of the salt content in the various dross samples were carried out usually with 300 g material samples contacted with 500 cm³ of fresh solutions in each step of the complex hydrometallurgical procedure, applying 1000 cm³ reaction vessels (as shown in *Figure 5c*) for set total times allowing equilibrium dissolution at a shaking rate providing homogeneous dispersion. The concentrations of the chloride and the hydrogen ions were determined by classical titration, but the concentrations of the dissolved metals were analysed by Atomic Absorption Spectrometry (AAS). The results are given as yields of the indicated elements (or compounds) relative to the masses of the leached dross samples.

In order to check the analytical results and to demonstrate the possible recycling of the salt content removed by leaching, the brine solutions obtained from the aqueous treatment were evaporated to dryness by the application of a rotary vacuum distilling equipment. The process and the resulted salt products are shown in *Figure 6*.



Figure 6
Salt recovery (a – rotary vacuum evaporation, b – crystallized salt, c – drying in oven, d – products).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Basic studies on the leaching behaviour of the extreme dross types

The kinetic characteristics of the dissolution process are illustrated by the yields of the analysed elements as functions of the time of leaching expressed in terms of the dissolved amount relative to the mass of the raw material. Although the principal aim is to recover the salt content, which can be achieved by applying water, it is of more information and interest to present the results of acid leaching. It is equally efficient in removing the chloride salts, but it may also dissolve the metallic aluminium content. Thus, beside showing the leaching behaviour, it may also reflect the

composition of the treated samples. These fundamental results obtained by water and acid leaching of the extreme types of the residual dross are given by the kinetic curves shown in *Figure 7*.

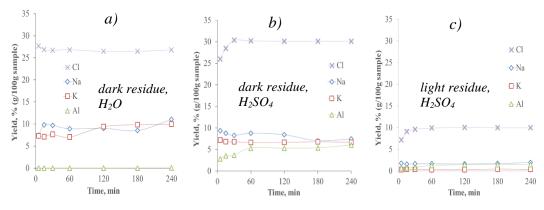


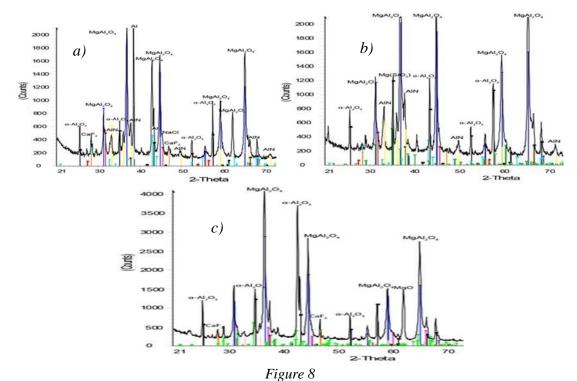
Figure 7
Dissolution rates of Na, K, and Al by distilled water (a) and 16.3% H₂SO₄ (b,c) leaching from the dark (a,b) and the light coloured (c)extreme-type dross samples obtained from the industrial hot treatment.

According to the plotted total metal concentrations, analysed by the AAS technique, the water leaching of the dark residual dross sample yielded an amount of ~ 40 % chloride salt removed, relative to the sample mass, which was ~ 48 % according to the approximate argentometric analysis. The AAS based result is actually ~ 4 % higher than the ~ 36 % value obtained with sulphuric acid. It is not a significant difference, especially considering the heterogeneity of the mass of the powdery raw materials, but it indicates that water is not less efficient in dissolving the chloride salts than dilute sulphuric acid. However, the argentometric analysis of the acid solutions shows a higher chloride salt yield (of ~ 51 %) from the dark residual dross. Beyond the gradual degradation of the AgNO₃ test solution, the argentometric method is more likely to give positive errors in the acidic medium, where the potassium chromate indicator may be converted in a larger proportion to the inert chromic acid form. On the other hand, water leaching of the light coloured dross material yielded only ~ 5 % salt recovery by AAS and 6.4% by the less accurate argentometry. This corroborates the comparison of the two extreme residues by the relevant XRD spectra in *Figures 2* and *3*. The kinetic curves prove that the water leaching of the chloride salt can be completed within a few minutes.

As expected, it is noticeable that applying the sulphuric acid solution, metallic aluminium can be recovered too. This result shows a ~ 6 % recoverable aluminium metal content in the dark sample, which was only 1.5% in the case of the light coloured dross. It corresponds to the results obtained by the special method (KULCSÁR and KÉKESI 2017) determining the metal content in the fine fraction of this dross type. The light coloured dross yielded significantly lower amounts of dissolved salts and aluminium, corroborating expectations based on analytical and instrumental examination results shown above. As the analysed concentrations of the examined metals in the solutions reach their stabilized values, it is indicated that the dissolution of aluminium by the acid

leaching is completed within 60 minutes, while the total salt content is dissolved in less than 15 minutes under the applied technical conditions.

The compositions of the solid residues obtained after the 1 hour leaching treatments were dried at $105\,^{\circ}\text{C}$ and were analysed by the same instrumental techniques as applied for the raw materials. The SEM images revealed wrinkled surfaces of particles consisting of Al and O, indicating the presence of α -Al₂O₃, while the Na, K and Cl peaks disappeared from the EDS spectra of all the treated samples. Although these results already confirmed the successful removal of the salt components, the remaining phases were also examined by XRD analysis. Because of the higher initial concentration of the salt components, the effects of leaching can be even more clearly demonstrated by the solid residues from the hydrometallurgical treatment of the dark coloured residual dross obtained from the industrial thermo-mechanical processing. The phases detected in the solid samples after leaching the dark residual dross with water, sulphuric acid and – for reference – with NaOH are marked on the XRD spectra of *Figure 8*.



The XRD spectra of the solid residues obtained after 1 hour of leaching with water (a), 16.3% H_2SO_4 (b) and 6M NaOH (c) of the dark coloured residual dross samples from the industrial thermo-mechanical treatment.

A comparison of Figures 3 and 8 shows that α -Al₂O₃ and the MgAl₂O₄ spinel are dominating in the solid residue after water leaching, as the previously dominant chloride salts have been removed from the dark coloured residual dross. The XRD spectrum obtained after the sulphuric acid leaching is similar, indicating the high chemical stability of the α -Al₂O₃ and the MgAl₂O₄

compounds. At the same time the intensity of the AlN peaks are slightly higher when the 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 metallic Al phase still detected in the residue after water leaching is clearly removed by the acid treatment. The aggressive 6M NaOH solution – used as a reference - could even more efficiently dissolve the metallic Al, but it also involves a strong evolution of gas and heat, caused by the dissolution of metallic Al, producing H₂ and the dissolution of AlN enhanced by NaOH according to Eq. (2), generating of NH₃. This unfavourable reaction is proved as the AlN peaks are removed after the NaOH leaching. Small amounts of the additive CaF₂, which is not dissolved either in water nor in the alkaline solution, may remain in the residue. However, it may be gradually converted to the sulphate by applying sulphuric acid, but a noticeable, though relatively slight dissolution of Ca may be noticed only during a subsequent water rinsing.

The above results prove that the residual dross – obtained from the thermo-mechanical treatment of the primary dross of aluminium melting – may be successfully prepared for any further applications by a hydrometallurgical treatment. The simplest and cheapest treatment with water can remove the chloride salts. Applying dilute H₂SO₄, which is another inexpensive option, Al and some other metallic components may also be eliminated. The process may consist of single or multiple steps of leaching, washing, solid/liquid separation and a final rinsing filtration. It is important to minimize the necessary process steps and to include the best suitable ones.

3.2. Hydrometallurgical purification of the usually obtained dross type

The technological examinations, carried out with a residual dross from the industrial thermo-mechanical treatment of the primary melting dross containing a metallic phase of low-Mg alloyed aluminium, were carried out with water, sulphuric acid and NaOH reagents in multiple leaching steps followed by repeated washing with distilled water, solid/liquid (S/L) separation by decantation or filtering and the final filtering was continued by rinsing with distilled water. In these experiments the starting material was always 300 g and each step involved 500 cm³ of the fresh solution added. According to Figure 7, the chloride salts are dissolved almost instantaneously from the previously examined extreme-type residual dross samples. However, this had to be confirmed with the average-type of the residual dross examined in the here presented purification experiments. The results, confirming the same behaviour, are shown by the relative kinetic curves of Figure 9a. Here, the deviation from the average concentration in the solutions obtained after various times of leaching are plotted. While NaCl and KCl are dissolved after a few minutes completely, a slowly developing Al dissolution can also be observed, which can be attributed to reaction (1), although the maximum Al concentration was just around 50–100 mg/dm³. It also implies that a very short water leaching can be applied to remove enough chloride salt before a significant volume of NH₃ is evolved. Figure 9b shows that changing the S/L mass/volume ratio (g dross/cm³ water) from 10:100 through 100:100 did not have any appreciable effect. The solubility and the dissolution rate of NaCl and KCl are high. Figures 9c and 9d show the results of repeated leaching steps with water lasting each for 10 minutes. The subsequent washing steps were carried out in a wide vessel agitated by manual shaking and the S/L separation applied was

simple settling and decanting. The final step was vacuum filtration combined with water rinsing (thus doubling the collected volume of the solution in this step).

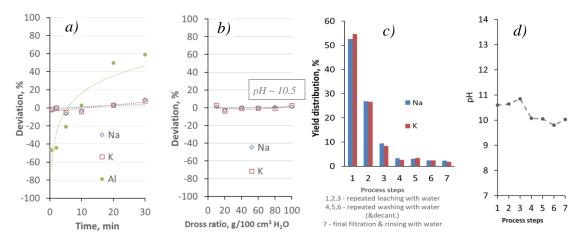
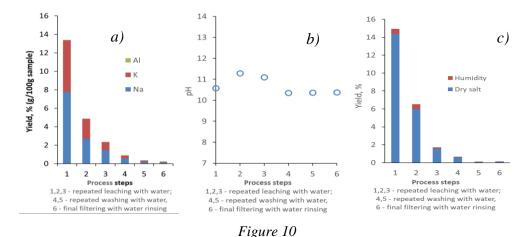


Figure 9
Dissolution of the common type of the residual dross by applying only water (a, b - deviation from the average of all the solutions, <math>c - yield distribution among steps, d - pH of the solutions)

Most of the chloride salt content is dissolved in the first leaching step. However, the imperfect S/L separation by simple settling and decantation left a considerable amount of the liquid phase behind in the settled thick sludge in each step, therefore the salt content in the subsequent solutions could not be reduced efficiently. Even the last rinsing filtration – after six steps - could still remove some significant portion of the salt content. The alkaline pH generated is a result of the dissolution of AlN according to Eq. (1). Still applying the simple settling and decantation for separating the obtained solution in each step, Fig. 10.a shows the yields of the dissolved metals by water leaching and subsequent washing steps, as well as by the final rinsing filtration. As the S/L separation was still very rough, significant portions of the water-soluble NaCl and KCl were carried over among the subsequent steps. As water leaching did not result in any Al dissolution, AlCl₃ was not found to be present at a recognisable level in the common type of the residual dross, however the presence of AlN was confirmed by the alkalinity of the solutions obtained. In order to check the tendencies determined by the AAS analysis of the solution samples, the rest of the solutions were evaporated and the dissolved NaCl-KCl salt was crystallized and weighed. As shown in Fig. 10c, it yielded similar tendencies of salt removal in the multiple step procedure, although due to significant losses, the total yield of the directly crystallized salts (~33%) was less than that calculated from the analysed concentrations (~ 48%) taking the chloride molar mass ratios into account. A further discrepancy is caused – beyond the potential systematic error in the analysis of the concentrated samples – by the settling after the leaching step, leaving the more concentrated portions of the – not perfectly homogeneous - solution in the residue at the bottom of the reaction bottle. Nevertheless, the final elimination and the distribution of the yields of the salt content by the water treatment was confirmed.



Metal yields (a), solution pH (b) and evaporated salt masses (c) obtained by water leaching of the common type residual dross in multiple steps, followed by washing and rinsing filtration

Applying dilute sulphuric acid for the leaching steps had the expected effect of removing aluminium and other impurity metals. In view of the slower dissolution reaction of the metallic phase, the acid leaching was carried out for longer (30 min) periods. However, it was repeated with fresh reagent only once, after decanting off the first solution. For a better separation of the acidic and the subsequent quasi-neutral steps, the last leaching step here was followed by a filtration, applying also water rinsing, instead of the simple decantation. *Figure 11* shows the results of leaching with both the preferred dilute (16.3%) and with a more concentrated (23.5%) H₂SO₄ concentrations.

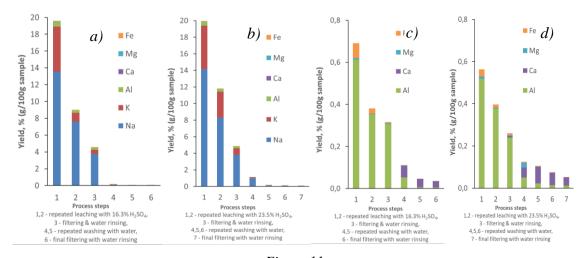


Figure 11 Metal yields obtained with 16.3 % (a,c), and 23.5% (b,d) H_2SO_4 solutions applied for leaching and water for the subsequent rinsing and washing steps to purify the common type residual dross

Despite fine grinding of the examined dross samples, some extent of heterogeneity cannot be excluded, therefore comparing the results of different experiments starting from nominally the same raw material cannot be made accurately. Nevertheless Figure 11a and b reveal that increasing the sulphuric acid concentration may not increase the yields of NaCl and KCl by leaching. In order to examine the effect of H₂SO₄ on the solubilisation of Al and the other impurity metals in it, results from the same experiments are plotted on a different scale in Figure 11c and d. It is seen that increasing the H₂SO₄ concentration did not improve the efficiency of metal dissolution. However, the latter two figures also show that some CaF₂ is solubilized as a result of the sulphuric acid treatment. It may be converted into the CaSO₄ form, which is however not dissolved – due to the solubility product – until the sulphate ions are removed by the water rinsing. Calcium appears significantly only in the neutral solutions of washing after the sulphuric acid leaching. In practice, it may be of reason to apply water leaching first and recover the salt content of the neutral solutions. The desalinated solid residue neutral procedure may be further treated by acid leaching to reach the necessary level of purity if any possible application requires it. This procedure has also been tested on the laboratory scale. A preliminary water leaching in three repeated steps followed by a double water washing was used to remove the chloride salt content from the common type of the residual dross samples. These pre-treated materials were then leached with sulphuric acid reagents of 8.5% (reduced), 16.3% (preferred) and 23.5% (increased) concentrations according to the procedure described above. The results are summarized in *Figure 12*.

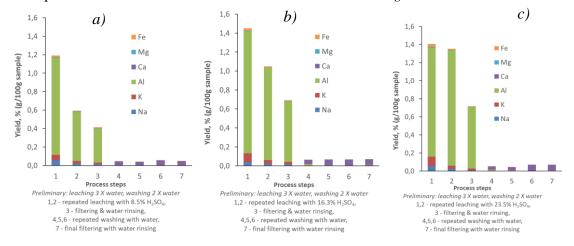
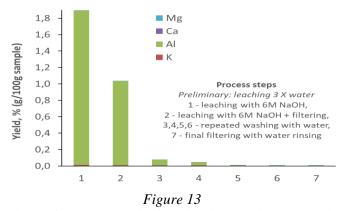


Figure 12
Metal yields obtained with 8.5%, (a), 16.3 % (a,c), and 23.5% (b,d) H₂SO₄ solutions applied for leaching and water for rinsing and washing steps, after preliminary water-leaching, to purify the common type residual dross.

The analysis of the minor components in the leachates was probably more accurate after the preliminary removal of the high salt content. The comparison of *Figures 11* and *12* suggests that the preliminary treatment of the residual dross with water (3 times leaching and twice washing in series) could remove more than 95% of the chloride salts. Especially the recovery of NaCl was

efficient. Some remaining KCl and NaCl were completely removed by the subsequent acid leaching steps. Increasing the sulphuric acid concentration from 8.5~% to 23.5~% could enhance the efficiency of removing the metallic Al, although the preferred dilute $16.3\%~H_2SO_4$ concentration may be just satisfactory.

In order to compare the efficiency of a strong alkaline leaching, where the oxide coatings of the hidden aluminium particles may be more efficiently digested (GASTEIGER et al. 1992), experiments with different NaOH reagents were also carried out. Results are shown in *Figure 13*.



Metal yields obtained with 6M NaOH applied for leaching and water for the subsequent rinsing and washing steps, after preliminary water-leaching, to purify the common type residual dross

After a preliminary triple water-leaching treatment to remove the chloride salt content, the applied 6M NaOH leaching could remove virtually only aluminium, which may have been mostly in the metallic form, but some Al₂O₃ dissolution from the coatings of the particles may also have contributed to the analysed values. The second leaching was combined with filtering where a minute amount of rinsing water was also applied. It was followed by the usual washing and the final filtering steps, applying water to remove the remaining solution. Despite all the expectations, the aggressive alkaline leaching could remove significantly more metallic aluminium than the procedure applying 16.3% or 25.3% sulphuric acid solutions as leachants. Although the decantation steps involved in the preliminary water-leaching treatment may have wasted some of the starting material, which could reduce the overall amount of dissolved metal.

4. CONCLUSIONS

A thorough examination of the residual dross samples collected from the industrial thermo-mechanical processing of aluminium melting dross materials revealed that the salt content can reach as high a level as ~ 40 %, the major constituents being NaCl and KCl. The examinations proved that a multiple-step procedure consisting of leaching, rinsing filtering and washing steps with water at room temperature and applying shaking can remove the chloride components efficiently. The dissolution of chlorides may be completed in a few minutes and a such a high S/L mass to volume ratio as 1 g/1 cm³ can be still efficient. Thereby the cost of recovering the salt by evaporation and crystallization can be reduced. The reaction of AlN, also present in the residual dross from the hot treatment, can react with water, and especially with alkaline solutions, to produce

unpleasant NH₃ emission. It may be suppressed by acid media, but a practical way to diminish its evolution is to apply shorter leaching, which may be efficient to dissolve the salts, but prevent the development of unwanted reactions. Applying repeated leaching steps may not increase the efficiency of salt removal, however washing the residue with water and separating it by vacuum filtration, while rinsing the cake with water can usually guarantee at least a 95% efficiency in removing NaCl and KCl. If the S/L separation is carried out as much as technically possible, the product can be suitable for various new applications, such as cement and glass foams, geopolymer production, or asphalt conditioning, but the conventional use of a purified material in steel making is also advantageous. The residual minor amount of metallic aluminium in the product from the water-leaching procedure is mostly covered by an oxide layer making it virtually inert for applications in the construction materials industry, and it is even useful in steel making. Any practical metallic component content however, can be readily eliminated by applying dilute sulphuric acid leaching followed by the necessary washing and rinsing-filtering steps in a second purification procedure. Sodium hydroxide, although more efficient in digesting the Al₂O₃ layers, was not found significantly more efficient in removing the metallic aluminium from the residue of the water-leaching procedure.

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GLASS FOAM FROM WASTE HOLLOW GLASS

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Abstract

Present paper deals with glass foam development from waste hollow glass. It is focused on the influence of glass particle size on the foaming process and physical characteristic of glass foam pellet. After the determination of the raw materials' properties, green pellets were produced in a pelleting table using optimal pelleting parameters (2.5 w/w% bentonite concentration, 20 w/w% moisture content, heat curing of 850 °C) developed in our previous research. Ground glass with different particle size distribution (<106; 80; 45 and 20 μ m), Na-bentonite (to improve the initial strength of pellet) and dolomite (as foaming agent) were used for the pellet production. The apparent density, and pore size (by optical microscope) of the resulted glass foam pellets were determined. The mechanical stability (abrasion resistance) was investigated by abrasion test in a Deval-drum. The use of finer glass particle size resulted smaller density of glass foam pellets. The lowest density of glass foam was 0.52 g/cm³.Based on the results of mechanical stability, it can be stated the abrasion of coarser size pellets was higher. The pore size of pellets was different, it changed between few micron and 1000 micron.

Keywords: waste glass, particle size, glass foam pellet, foaming agent, dolomite

1. Introduction

In Hungary, the glass waste is generated in approx. 180,000 tons/year, most of which (about 80%) is colored hollow glass. However, utilization of a significant ratio (60%) is not solved. Due to the technical and economic development of recent years, protection against the harmful effects of waste has become one of the most important economic and environmental factors. Waste should be properly collected, handled and disposed, otherwise it may have an adverse environmental impact. Along with recognizing the environmental impact of wastes, the role of wastes in the rational management of natural resources, material and energy management has become more apparent. In the developed countries, the significant part of waste is re-used as raw material, secondary raw material or secondary energy source [1].

According to the EU Waste Directive 2008/98 / EK: "The primary purpose of any waste policy is to minimize the negative effects of waste generation and waste management on human health