THE FUNDAMENTAL KINETIC CHARACTERISTICS OF AQUEOUS DISSOLUTION OF CHLORIDE AND FLUORIDE SALTS FROM SECONDARY ALUMINIUM DROSS

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Abstract

The salt content in the secondary dross obtained beside the recovered aluminium by the hot processing of the primary melting dross hinders further utilization of this material. Secondary dross samples obtained from the industrial hot processing of the primary dross generated by the melting of aluminium alloy scrap were leached with water at room temperature with different Liquid/Solid (L:S) ratios. Vessel filling (the relative volume occupied by the sludge) in the shaking bottles required further consideration in the interpretation of the results. Samples taken regularly within 15 minutes during vigorous shaking showed that NaCl and KCl can be dissolved almost instantly, and completely irrespective of the parameter settings. However, the fluoride additive (CaF_2) has a complex behaviour. The results suggest its relation to some side reactions indicating also the conditions of the hot process producing the examined material. The results suggest that the salt content of the secondary aluminium dross can be lixiviated within a $2 - 4$ minutes virtually completely, but the L:S ratio and the a vessel filling have to be coordinated. At the lowest L:S ratio examined of 1.0, a vessel filling of max. 11% should be observed to achieve this fast salt dissolution. The same dissolution rate can be reached with double the vessel filling (i.e. smaller unit) if the L:S is also increased in this ratio.

1. Introduction

The most significant by-product of melting aluminium (alloy) scrap is dross, resulting from the oxides generated at high temperature and introduced from the dirty surface of the raw material. Primary dross is inevitably produced along the aluminium alloy melt. This material is heterogeneous, containing more metal than the non-metallic matric. Most of its metal content can however be efficiently recovered by applying high temperature and some mechanical pressure in a "thermo-mechanical" treatment combined with salt addition to break the oxide layers insulating the molten droplets [1]. Secondary dross is the residue obtained beside the recovery of the entrapped metal. In the modern secondary aluminium industry - basically applying carefully sorted and physically prepared aluminium (alloy) scarp as the starting material – melting is carried out in large gas fired reverberatory furnaces. The usual amount of the primary dross obtained as a by-product of scrap melting may be as high as 5%.

Primary dross from scrap melting often named as "wet", or "white", contains a high amount (often 70% or even more) of recoverable metallic aluminium (alloy). It usually forms large clumps or blocks in gas fired melting (or holding) furnace operations [2]. The common secondary dross, generated during some aluminium recovery process, on the other hand is often referred to as "dry" or "black" dross. It contains less metal, and it is a mixture of mainly

aluminium oxides and other compounds. The recoverable aluminium content is usually as low as ~ 15%, beside a larger salt content, usually higher than 40%. [3] The term 'salt cake' refers to a specific kind of secondary dross. It arises from a high temperature thermo-mechanical "converting" of dross in gas fired rotary furnaces with the addition of much salt flux. It generally contains only 3–5% residual metallic aluminium. [4]

The use of salt flux promotes the coalescence of suspended metal droplets and helps separate the clean metal from the oxide [5] in at the high temperature "converting" in rotary furnaces. The main components [6] detected in aluminium dross include Al metal; the oxide compounds (Al_2O_3, $MgO \cdot Al_2O_3$, MgO, SiO_2, Fe_2O_3, Na_2O); other simple or complex aluminium compounds (AlN, Al_4C_3, $NaAlCl_4$, $KAlCl_4$), the main salt components ($NaCl$, KCl) and small amounts of fluorides (CaF_2, MgF_2, a K_2NaAlF_6). The final "secondary dross" after metal extraction is considered worthless and even hazardous, a burden to the producer. It may be further processed by grinding and screening the little remaining metal content as coarse granules, which step is not justified economically by the few percent of the remaining metal recovered additionally if it is not supported by other funds offered by the smelter for the disposal of the residue. This material is officially categorized as hazardous according to the European Catalogue for Hazardous Wastes [7]. Therefore, it may entail a severe financial burden for the mandatory handling. Its disposal is prohibited in many countries of the EU. A major problem is reactivity with water and even the humidity in ambient air, leading to the formation of some toxic and even potentially explosive gases, such as NH_3, CH_4, PH_3, H_2 and H_2S [2]. Any utilization [6] of such a residual aluminium dross may help alleviate the costs and the environmental hazards of disposal.

In order to make also this residual dross useful, it is imperative to eliminate the water soluble salt content. The recovered salt can be recycled to the hot thermo-mechanical treatment of the primary dross [8]. The remaining small quantities (a few per cent) of the metallic aluminium may be indifferent or even useful in some applications, especially if covered by a thick and firm oxide layer. The salt-free final residue, containing the oxides with a minor amount of the Al metal, could be utilized in different industrial technologies [8] as additive to:
• asphalt (to increase wear resistance);
• produce glass foams and ceramic foams;
• steel making (also the residual Al metal content would be useful);
• special cements and concrete.

The chloride salts are readily soluble in water also at room temperature. The secondary dross residue of high salt content is usually crushed and ground. It may be followed by the simple physical removal of the malleable metal grains of larger size, and the fine powder can be mixed in water to remove the salts. This seems simple, however it is also important to use as little water as possible for a complete dissolution in a reasonably short time. For the possible alternative application of the residue a practically complete removal of the salt is generally required. However, the effluent also needs further treatment, which can assure the recycling of the removed salt and water. It is only possible by evaporation and subsequent condensation of the water. As it implies energy and time, it has significant consequences on the economy. As it is commonly known, the solubility of the principle salt components ($NaCl$, KCl) is so high (~35g / 100cm^3 water) at room temperature, that it cannot be a practical constraint of leaching. This high concentration would only be reached with a thick sludge of the dross (containing ~ 20 - 30% salt) that would make dispersing the mixture homogeneously difficult. Even though solubility is provided, it is still important to determine the kinetic

characteristics of dissolution, which may determine the practical time sand L:S ratios for optimum leaching conditions. Beside the readily soluble chlorides, there exists the question about the behaviour of the CaF_2 additive in the common fluxing salts used in the hot processing of the dross. These queries are addressed by the following experiments.

2. Experimental procedure

The raw material used for these kinetic leaching experiments was the secondary dross collected from the industrial thermo-mechanical (hot) processing of various batches of primary dross. This is the residue obtained in relatively large amounts at the aluminium smelters using basically scrap as the starting material. It was obtained as the by-product from the hot thermo-mechanical treatment of the primary melting dross, where a significant amount of the standard fluxing salt was added. This type of salt usually contains 60 – 70% NaCl, ~ 30 % KCl and just a few per cent of CaF_2. The raw material for the experiments was primarily crushed and the metallic particles were screened out. The residue was then finely ground to a particle size of < 250 µm. Samples of 10 g mass (and 20 g in one case) were taken from this dross powder and mixed with different volumes (10, 15, 20 or 25 cm^3) of distilled water in bottles of 100 cm^3 capacity. The lowest L:S ratio (water to dross) applied in the experiments was 1.0 and the highest 2.5. Even the lowest relative volume of water, just enough to produce a liquid sludge, could ensure a complete solubility of the total salt content in the dross, as this secondary dross contained ~ 33% salt as determined by complete dissolution and evaporation [8].The speed of horizontal shaking was set to produce a homogeneous mixture. The process was stopped intermittently, for taking 0,5 cm^3 solution samples after letting a few seconds of clarification each time. The samples were directly diluted (10 X) to produce sufficient volume for gravitational filtering with micro-funnels. The last solution sample was obtained from completely filtering – applying vacuum - the material remaining in the shaking bottles. Atomic absorption spectrometry was used for analysing the concentrations of Na, K and Ca. The analytical samples of the alkali metals were further diluted to the required concentration range. The procedure is illustrated in Fig. 1.
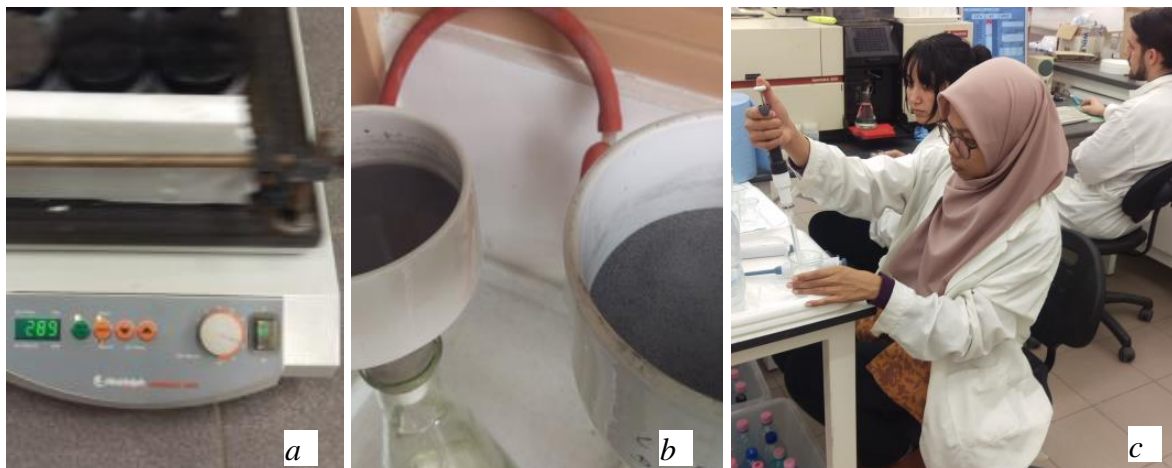

Fig. 1 The main steps of the experimental leaching procedure (*a* – shaking, *b* – final filtering, *c* – sample dilution and analysis).

The analytical results were filtered and corrected in an Excel database devised for correcting the random changes in the conditions of the instrument indicated by the repeated standard and blank samples. The corrected results were plotted as yields of the dissolved metal relative to the mass of the dross sample leached.

3. Experimental results and discussion

Distribution of the components in the particles of the ground dross cannot be considered accurately homogeneous, as well as the particles are naturally different. Therefore, comparing the results of experiments run with different batches of the raw material inherently implies the major cross effect of sample heterogeneity. However, this disturbing effect was mitigated by the mixing effect of ball mill grinding and the subsequent homogenisation by shaking and stirring the whole amount of the ground dross in the container bag. The basic presentation of the kinetic results in Fig. 2 shows the effect of leaching time.
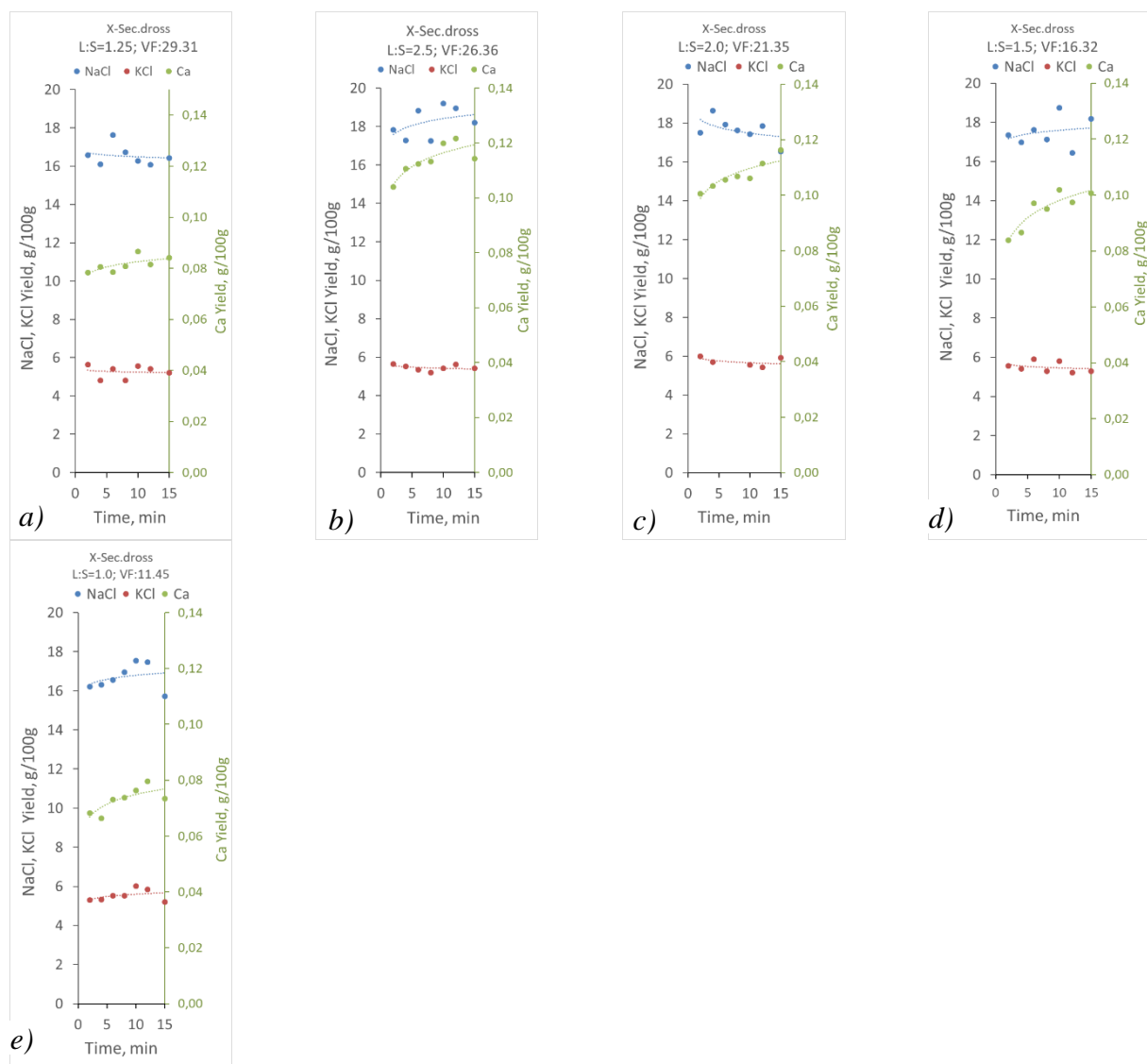

Fig. 2 The process of leaching the average secondary dross with H_2O (a – L:S=1.25 & VF=29.31; b – L:S=2.5 & VF=26.36; c - L:S=2 & VF=21.35; d – L:S=1.5 & VF=16.32; e – L:S=1 & VF=11.45).

The yield of NaCl and KCl (relative to the mass of the leached dross sample) does not show any clear increase after the first 2 minutes of leaching, which was technically the shortest time

to be taken technically into consideration. Thus the main chloride components can be dissolved virtually completely quicker than the first solution sample could be taken from the shortly shaken and partly settled sludge in the bottle. The change and the level of the KCl yield was almost exactly the same independently from the time of leaching and also from the volume settings in the examined range. Dissolution of NaCl showed more response to the examined factors in the applied ranges, but the higher analysed concentrations also implied higher deviation. As dissolution of NaCl was also virtually complete until the first sampling of the solution, mostly the effect of the solution volume to the mass of the solid material and to the volume of the vessel can be further examined. The effect of leaching time is however seen in the results of Ca dissolution. Although the first sample at 2 minutes could already indicate an almost instantaneous dissolution of 85 − 90 % of the total amount of Ca dissolved until the final sampling at 15 minutes, there was a definite increase in the yield during the whole procedure of leaching. The soluble compound however cannot be the original CaF_2, which is hardly soluble in water, as it can be calculated (~ 15 mg/dm^3) from the extremely low solubility product (3.3×10^{-10}) [9] [10]. With the applied direct dilution of the small volumes of the solution samples for filtering, this solubility could represent only 1.5 − 2 mg/dm^3 in the analysed solution samples. This value is negligibly lower than the analysed concentrations (40 − 60 mg/dm^3) in the cases represented by Fig. 2. Therefore, in this case only the dissolved amount of the metal is indicated in the diagram. The CaF_2 component in the salt added to the charge is thus transformed during the hot thermo-mechanical treatment of the primary dross, resulting in some soluble compounds. It may be possible by a reaction with the abundantly available molten metallic Al to a degree allowed by the

$$2/3Al + CaF_2 = Ca + 2/3AlF_3 \tag{1}$$

reaction. The thermodynamic conditions of liberating calcium are further assisted by the volatility of the AlF_3 product at the high (~ 1000 ^oC) temperature of dross "converting". Physical states and the concentrations of the reagent and the product allow the actual value of the Gibbs free energy of reaction (1) to change in the negative direction. Magnesium, if it is also contained in the metallic phase of the primary dross at a higher Mg concentration may enhance the above reaction of CaF_2. The liberated calcium $[Ca]_{Al}$ is oxidised to form calcium aluminate:

$$Ca + 2Al + 2O_2 = CaO \cdot Al_2O_3 \tag{2}$$
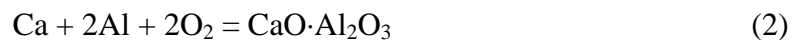
which react with water to form a metastable solution where the CaO/Al_2O_3 mole ratio will increase gradually from 1 to 3 in a few days and 5 after longer periods of standing by a preferential $Al(OH)_3$ precipitation [11]. The initially dissolved $Ca(Al_2O_2)_2$ (or $CaO \cdot Al_2O_3$) calcium aluminates gradually form $Ca(OH)_2$ and Al_2O_3 of various hydration levels. These transient products can further transform resulting in a certain degree of Ca dissolution, accompanied by the increase of alkalinity. The overall aqueous process may be expressed as:

$$Ca(AlO_2)_2 + 4H_2O = Ca(OH)_2 + 2\underline{Al(OH)_3} \tag{3}$$

and $Ca(OH)_2$ can be partly dissociated to result in dissolved calcium:

$$Ca(OH)_2 = Ca^{2+} + 2OH^- \tag{4}$$

As the dissolution of Ca from the thermo-mechanically treated secondary dross is accompanied by the generation of free OH^- ions, any side-reaction also producing alkalinity may suppress the calcium dissolution. If the thermo-mechanical dross converting is carried out with the metallic phase overheated in contact with air, AlN may arise in significant

quantities, which can react with water in the subsequent leaching of the residual (secondary) dross:

$$AlN + 4H_2O = \underline{Al(OH)_3} + NH_4OH \tag{5}$$
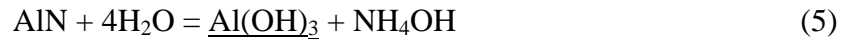
It results in the formation of ammonium hydroxide, which also dissociates and generates free OH⁻ ions beside NH_3 gas. The higher concentration of these OH- ions may depress calcium dissolution through the equilibrium of reaction (4). This additional effect was proved by the lower dissolved yield of Ca in cases of higher finally reached pH. Therefore, as seen in Fig. 2, applying higher L:S ratios for the water leaching of the secondary dross can be efficient in allowing higher Ca concentrations to develop in the solution.

The effect of the L:S ratio had a clear effect on the dissolution of Ca from the secondary dross, however the readily soluble chloride salt components showed a practical indifference toward the relative volume of the applied water, just as well as toward the leaching time in the examined ranges. This response may also be covered by the relatively large scattering of the relevant points especially in the case of NaCl. The disturbance caused by the inaccuracy in the NaCl results may be mitigated by examining just the average amount of the dissolved material referring to the whole duration of the leaching experiment, instead of each analysed result belonging to the micro-samples taken at the regular time intervals. The errors in the sample preparation and analysis are thus partly cancelled. The average yields obtained in the complete 15 min leaching procedures applying different L:S ratios for the solution volumes and sample masses are shown in the two parts of Fig. 3. The first part shows the results of the highly soluble chloride components, and the second stands for calcium with a different scale. As the L:S ratio was changed, vessel filling (VF) also changed in a regular manner, except for a singular point at the L:S value of 1.25, corresponding to an extremely high VF value. As the relevant points of all the yields lie slightly below the tendency determined by the rest of the points, it suggests that vessel filling - originally not considered as a target parameter − had also some role in determining the leaching yields by influencing the kinetic conditions in the shaking bottle.
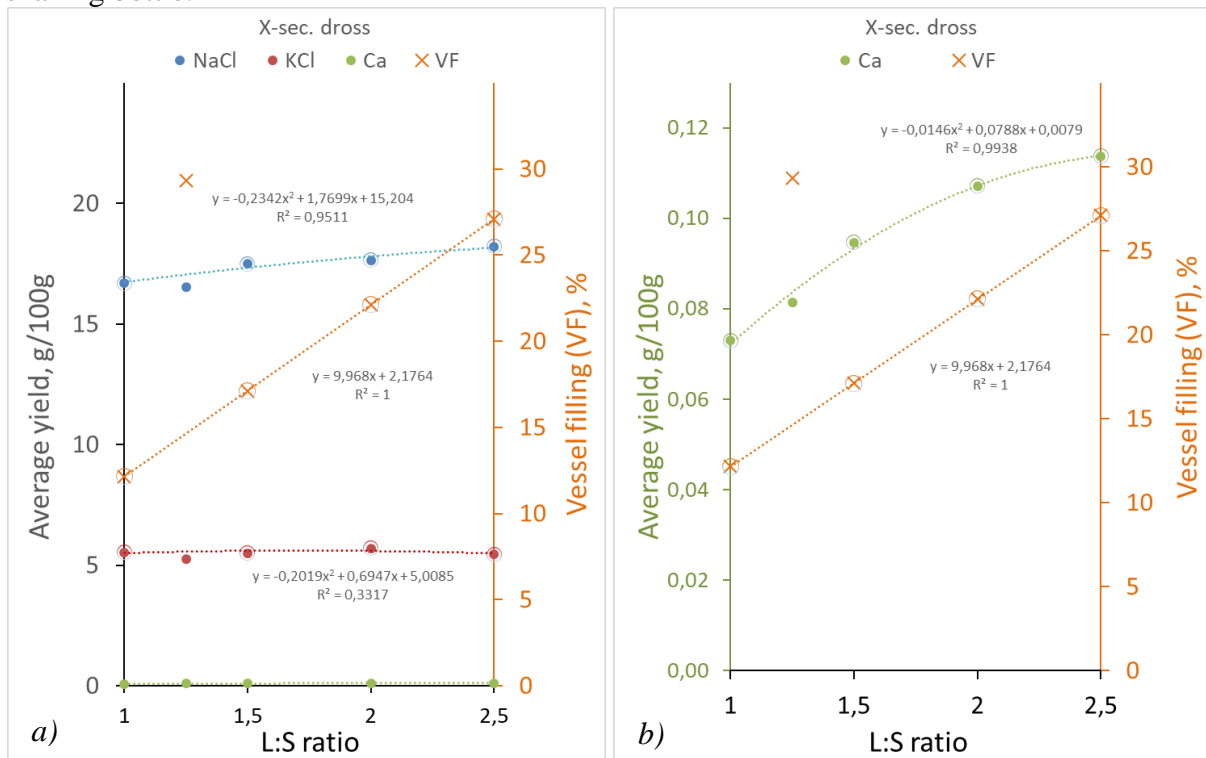

Fig. 3 Average yields of NaCl, KCl (*a*) and Ca (*b*) and the volumetric vessel filling as functions of the L:S ratio (cm³/g) of the leaching water to the sample mass.

The higher L:S ratio enhances the reactions of dissolution but – as in the case of the second point in the diagrams of Fig.3, if it is increased only by 25% and the VF is increased 250% the chloride leaching yield dropped off from the otherwise regular tendency and could not even increase. However, in the case of Ca, the effect of the relative solution volume is so strong, that despite the 10 times higher VF, this slight increase in the L:S ratio resulted in an increased yield. This can be interpreted by the double strong depressing effect of the solution pH which is reduced by the larger volume ratio irrespective of how much the bottle volume is occupied.

In the case of the chloride salt components, dissolution yield was not affected in the case of KCl and it was just slightly increased by increasing the L:S ratio, while the VF ratio was also regularly increasing. This is explained by the conditions where the saturation of the solution was not even reached by the lowest S:L setting. However, due to the effects of the progressively increasing activity coefficient expressed for the dissolved NaCl in Fig. 4 in the actual $2 - 5$ molality range of the ternary $NaCl$-KCl-H_2O system, NaCl solubility increases with dilution.
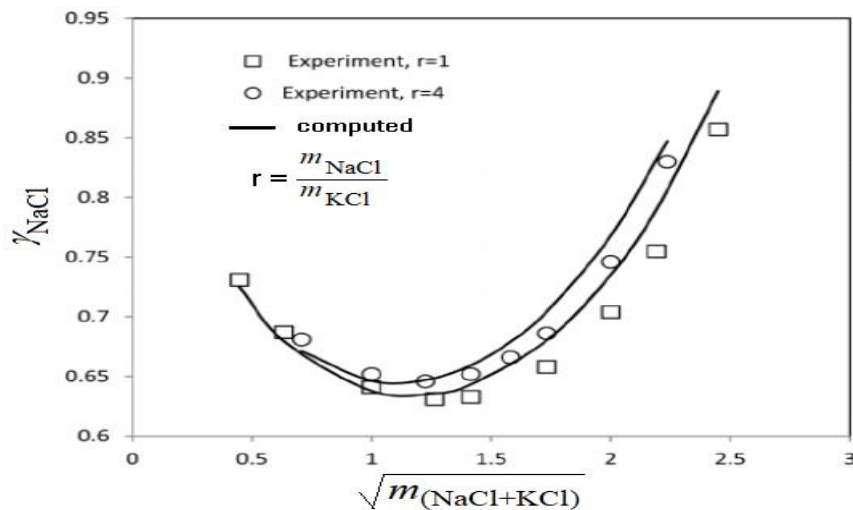

Fig. 4 The predicted and experimental activity coefficients of NaCl in the ternary system $NaCl$-KCl-H_2O at different salt ratios as functions of the square root of total molality [12].

In the case of the NaCl the larger ratio of the solution volume is only slightly favourable to the dissolution yield, while the yield of KCl at the actually lower levels of concentrations in the solution are not affected by it, or the slight effect may be compensated by the other slight but unfavourable effect of the proportionally increased vessel filling.

4. Conclusions

Simple water leaching of the salt containing secondary dross - obtained from the hot thermo-mechanical processing of the primary melting dross for aluminium recovery – can be efficiently carried out in a short time. The preconditions however also imply a fine grinding of the solid raw material. Dissolution of NaCl and KCl, the main salt components, can be completed within a few minutes by applying only the physical minimum volume of water that is still capable of producing a fluid sludge and an agitation intensity to prevent settling during the leaching process. Liquid to solid ratio in the examined range only seems practically to affect the solubility of the compounds of calcium. Although the dissolution of the residual

calcium salt is of minor practical significance, its behaviour could indicate the examined effects of leaching parameters. The results could also suggest the formation of calcium aluminates from the CaF_2 additive during the preliminary hot treatment. The filtered residue – after a proper washing - can be considered practically salt-free to the level required by the alternative applications. The brine solution obtained – with the application of the minimum volume of leaching water - can be evaporated to dryness to recover the NaCl-KCl salt for recycling to the thermo-mechanical treatment of the primary dross.

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