ENHANCING THE METAL YIELD OF THE ROTARY CONVERTER MELTING OF ALUMINIUM DROSSES WITH SIMPLE SODIUM-CHLORIDE: THERMODYNAMIC AND KINETIC CONSIDERATIONS

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Abstract: The rotary converter melting of Al-containing drosses with and without NaCl addition was examined. It was found that simple NaCl can enhance the recovery by 9% while decreasing the mass of the secondary dross. It implied a significant decrease in the metallic Al concentration, which indicates a superior coalescence of the molten metal drops when NaCl is present. However, the thermodynamic analysis showed that it might also imply the possibility of a certain degree of aluminothermic and magnesiothermic reduction of NaCl. On the other hand, neither the analysis of the flue dust nor that of the tapped metal showed the presence of the reaction products; thus, no melt contamination occurred.

Keywords: Aluminium dross, rotary furnace, NaCl additive, aluminium recovery

INTRODUCTION

Aluminium is the second most important mass-produced metal – after steel – with a total yearly output of ~70 Mt [1]. It is produced primarily by electrowinning from molten solutions using massive coke-based anodes. Since this process has a ~14 kWh/kg specific electric energy consumption and a ~1.4 kg CO_2 is emitted per one kg produced metal, secondary production is more and more important [2]. Contrarily to the ~170–180 GJ/t total energy requirement of the Bayer-Hall-Héroult route, secondary production only requires ~25–30 GJ/t energy. Currently, ~40% of the yearly aluminium production comes from secondary smelters [3]. Secondary production begins with a scrap remelting process, usually conducted in oxygen-enriched air – fuel-fired reverberatory furnaces [4]. This process entails the production of "metal melting" drosses with large (60–90%) metallic Al content. It is generally accepted that ~1 and ~5% of the total metal input can be lost in the dross during primary and secondary productions, respectively. This yields ~2.1 million tonnes of dross every year worldwide. Metal melting dross can be considered a valuable by-product because of its high metal content [5]. The recovery of most of the metallic Al content from metal melting drosses is most often carried out by an aggressive melting procedure in oxy-fuel rotary "converter-type" furnaces. Larger smelters are usually equipped with such furnaces with 5–20 t capacities. Beside the large smelters, there are a few companies – also in Hungary – specializing in dross melting. This procedure is efficient in recovering ~60–80% of the metallic Al from the metal melting dross, but requires a large amount (20–50%) of additive agents in the form of alkali and alkaline earth chlorides and fluorides. It is generally accepted that salt is required for melting [6], but there

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is no consensus on the optimum salt composition; thus, there are many different mixtures on the market, all of them raising serious costs of processing. Moreover, there is no available literature that examines the exact effects of these salts on Al dross melting. The critical step is the coalescence of the molten Al droplets [7], but is unclear how the added salt enhances recovery. Although it is a common practice to apply a mixture of KCl and NaCl and fluoride additives [8] [9], economical reasons may justify the examination of aplLying only the cheapest and abundantly available NaCl. The following theoretical and experimental investigation may clarify the potential benefits and point out the possible mechanisms to be further examined in the future.

1. EXPERIMENTAL PROCEDURE AND MATERIALS

The theoretical considerations of the possible reactions by thermodynamic calculations were carried out using the HSC Chemistry software. The raw dross from Al scrap melting was obtained from Arconic-Köfém Kft. The large pieces were crushed into a homogeneous mixture in a hammer mill to an average particle size of 1–10 mm. Experiments were carried out in a laboratory rotary furnace of air-fuel firing, designed and built at the Institute of Metallurgy. The discharged residual dross was finely ground and classified with 0.25, 0.5, 1, and 5 mm sieves. In order to examine special effects, stationary melting experiments were also carried out in a vacuum induction furnace (Indutherm MC 20) and a resistance furnace (Nabertherm, LHT 02/16), offering the possibility of determining the metallic content of the secondary dross fractions. The masses of the tapped metal and of the residual dross fractions were used for evaluating efficiency.

2. THERMODYNAMIC AND KINETIC CONSIDERATIONS

In order to evaluate a possible salt additive thermodynamically, the temperatures and the kinetic conditions in the furnace must be understood. *Figure 1* shows a comparison of the 5 kg laboratory and 5 tonne industrial furnaces. It is seen that temperatures above 900 °C were easily reached in the bulk of the charge, as indicated by the bright orange hue.
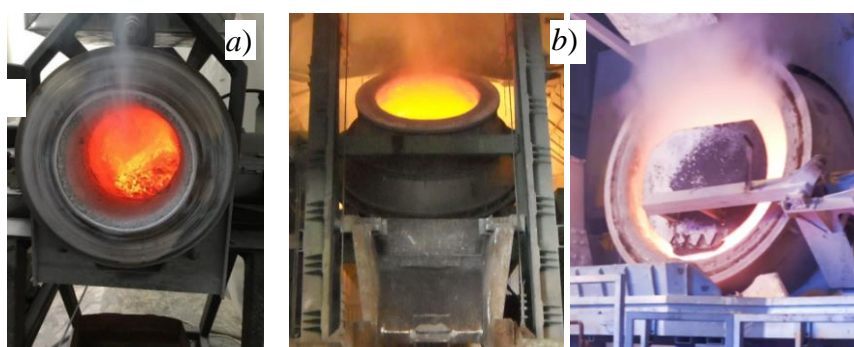

Figure 1
A laboratory (a) and an industrial (b) dross processing furnace during operation

The inside of the laboratory furnace during operation is shown in *Figure 2*, where the measured temperatures often surpassed 1000 °C. It can also be seen that the "salt slag" formed a mushy layer above the molten metal pool by the rotation. This ensures favourable kinetic conditions between the metal and the salt additive. Rotation – by the implied physical

effects – enhances the liberation of the metallic droplets entrapped in the oxide matrix. However, it also encourages the coalescence of individual metal droplets inside the salt slag, eventually leading to their transfer into the molten pool. The atmosphere directly above the salt slag is
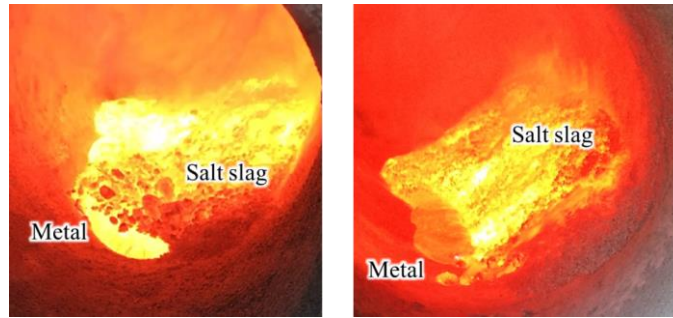

Figure 2
The dross charge inside the furnace during operation

The favoured salt additive is NaCl, as it is widely available and costs only ~15–20 \$/t. However, its ~805 °C melting point is a significant drawback made worse by the relatively high enthalpy of fusion, as seen in *Figure 3*. Thus, it will remain solid inside the furnace for a substantial length of time, allowing the excessive oxidation of the melt.
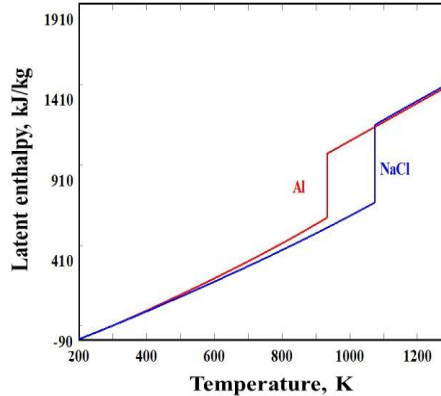

Figure 3
The latent enthalpy of Al and NaCl

Since there are small Al droplets finely dispersed inside the salt slag, there is a large surface where NaCl can react with Al. As seen in *Figure 4*, elemental sodium and aluminium chloride may be formed inside the furnace. This reaction is significantly enhanced by the turbulent gas flow inside the furnace caused by the powerful oxy-fuel jet burner. As such, the gaseous reaction products are rapidly transferred from the surface. The majority of the formed Na may leave in the exhaust vent, while a small portion may dissolve in the Al. This is usually not a critical difficulty in secondary smelters with advanced melt purification systems. On the other hand, the flue dust usually does ntt show elevated amounts of Na_2CO_3, Na_2O or NaOH levels. Thus NaCl can be considered safe to use.
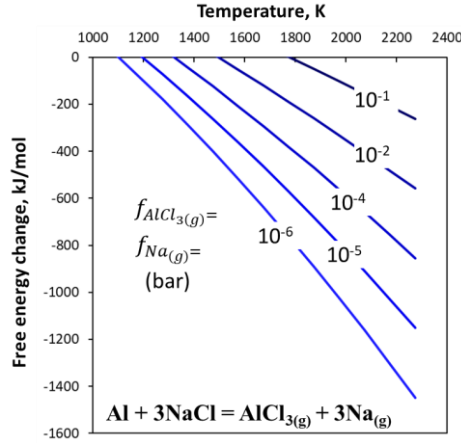
Figure 4
*The calculated Gibbs free energy change of the reaction
of Al with NaCl under different conditions*

However, most Al alloys also contain 0.09–4% Mg, a potent reducing agent. As seen in *Figure 5*, the presence of Mg in the alloy can significantly enhance the reduction of NaCl into elemental Na. Based on the thermodynamic figures, the magnesiothermic reduction seems more likely to occur when the alloy contains higher levels of Mg, and the fugacity of the produced Na vapour is low. Magnesium is especially prone to evaporation and excessive oxidation, which would mitigate the possibility of a reaction with NaCl. Indeed, soluble $MgCl_2$ is usually not detected in the secondary dross; thus, these reactions are of doubtful practical relevance. Therefore, the application of higher proportions of NaCl in a conventional $NaCl$-KCl-CaF_2 salt mixture or even in a pure state is worth the experimental testing. This concept has been followed, urging the research reported here.
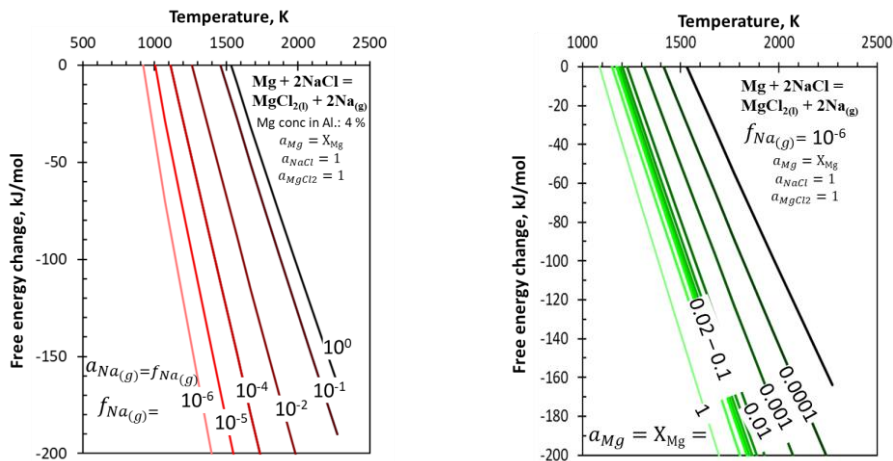

Figure 5
*The calculated Gibbs free energy changes accompanying the magnesiothermic
reduction of NaCl salt at different temperatures*

Indeed, the addition of pure NaCl salt can significantly enhance the metal recovery during the rotary converter melting of Al dross. This is illustrated by *Figure 6*, showing the relative masses of the separated fractions of the hot processing of the melting dross.
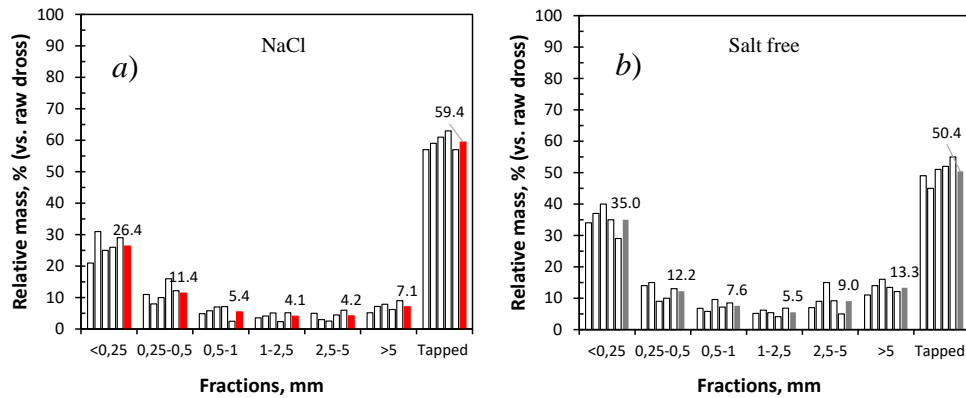

Figure 6
The relative mass of the products obtained by rotary melting with (a) or without (b) the addition of NaCl (applied rate: 20%)

The most notable difference was in the tapped metal yield (the relative mass of molten aluminium tapped from the furnace), which seemed to increase by a relative 17%, as NaCl was added. It also implies the decrease in the masses of the different secondary dross fractions, as compared to the salt-free melting. *Figure 7* shows that the residual dross fractions obtained by melting with NaCl had a lower metallic Al concentration. This – combined with the relative mass of the fractions – indicated less oxidative melt loss and enhanced coalescence of the separated metal droplets. The reason for increased coalescence cannot be the dissolution of the oxide coatings, as Al_2O_3 has no significant (<0.01%) solubility in the NaCl melt at 850–950 °C.
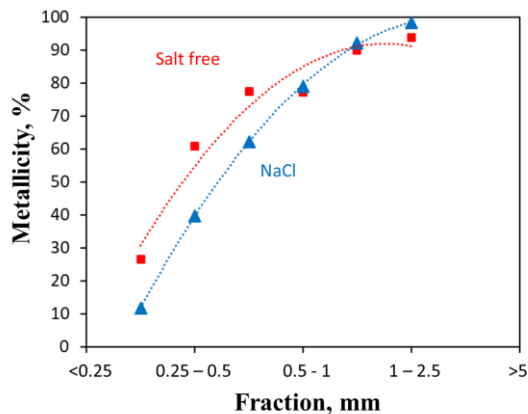

Figure 7
The metallic Al concentration in the different residual dross fractions

The coarsest fraction of the classified residual dross can be considered practically metallic. Actually, the industrial version of the hot dross processing (with large furnaces, where the important physical effects are much stronger) would produce a different distribution of the classified fractions in the product. A few percent higher recovery in the tapped product is significant for any Al smelter, considering that Al costs ~2,500 $/t. While on the other hand, the price of NaCl is only ~20 $/t. A further practical advantage of NaCl is that it can be purchased from various sources, and its storage does not require special circumstances. *Figure 8* shows simple rocksalt – used for melting in an undisclosed Hungarian smelter – stored in large piles in the open under a simple roof.

Figure 8
The rocksalt used for Al dross processing in a Hungarian secondary Al smelter

While the 9% absolute increase in the tapped metal yield obtained with the small experimental furnace is significant compared to the salt-free processing, it still cannot offer as high yields (~75%) as achieved with the 67.5% NaCl + 27.5% KCl + 5% CaF$_2$ salt mixture. The latter additive is prepared by special suppliers for larger industrial smelter companies. However, this complex pre-prepared salt costs ~150–220 $/t. In order to increase the efficiency of the simple NaCl addition, some other inexpensive additives may be applied in combination without greatly increasing the cost. This could be a promising direction for smaller secondary smelters that melt low-quality Al scrap and drosses purchased from different foundries and smelters.

CONCLUSIONS

Simple NaCl salt additive can enhance the tapped metal yield (obtained in liquid form) of the rotary melting of aluminium dross by an absolute ~9%. The mass and the metallicity of the residual dross also decrease, indicating lower melt losses and better coalescence of the metal in the salt slag phase. Thermodynamic calculations indicate that metallic Al and Al-Mg alloys are capable – within narrow limits – of reducing NaCl into elemental Na vapour and AlCl$_3$ or MgCl$_2$ salts. Though these reactions are found to be practically negligible. Nevertheless, pure NaCl addition at a rate of 20% offers ~15% less increment in metal recovery compared to that achievable with the traditional – and expensive – 67.5% NaCl + 27.5% KCl + 5% CaF$_2$ mixture. Thus, further research should be directed at improving the tapped metal yield by enhancing the effect of NaCl by combining it with some other inexpensive additives.

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