



Solubility of CaF₂ in NaCl-KCl salt flux for Al-recycling and its effect on Al-loss.

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Abstract

CaF₂ is often used as a fluoride addition to chloride base salt fluxes for the melting of aluminium scrap. The solubility of CaF₂ in the chloride salt system is limited. Dissolved CaF₂ is considered to improve the properties of salt fluxes. Experimental results indicated that the solubility of CaF₂ in 70 wt % NaCl/30 wt % KCl, German salt flux used in aluminium scrap melting, might be lower than published previously. As a consequence the pseudobinary section CaF₂-(70 wt % NaCl - 30 wt % KCl) was investigated in detail by differential thermal analysis (DTA). The determined solubility of CaF₂ appeared to be considerably lower than presented in the literature and is 2.6 % at 750 °C. The pseudo binary section calculated using thermodynamic data confirmed the results to a large extent. DTA allowed also determining the crystallization temperature interval of the two phase area consisting of the solid solution NaCl-KCl and CaF₂. Based on these results semi production scrap melting tests in a salt bath were conducted. A calculating model for metal loss in the salt in dependency of CaF₂-content, temperature and salt/scrap ratio was developed. The F-loss during the scrap melting was quantified. The experimental data confirms the theoretical recommendation for using a 30:70 KCl-NaCl-mixture with 2-3 % CaF₂ and low salt/scrap ratios.

Keywords: aluminum recycling, phase system, salt flux, CaF₂, NaCl, KCl, solubility, coagulation, fluoride consumption.



1. Introduction

Salt fluxes in remelting of aluminum scrap reduce the metal loss by protecting the metal bath from oxidation by the atmosphere and adsorbing of metal surface contaminants. There are many salt flux compositions tested worldwide. Most of them are based on NaCl and KCl. A salt flux widely used in Germany for aluminum scrap remelting is based on a mixture of 70 w. % NaCl and 30 w. % KCl. Fluoride salt additions in salt flux increase the metal yield by decreasing the amount of suspended metal in the salt phase. Without fluoride salts the oxide layer on aluminum is stripped very slowly, which hinders the coalescence of metal droplets in the salt. The mechanism of the influence of CaF_2 and other fluoride salts is still not clear. Most possibly fluoride salts dissociate in the molten salt flux producing free fluoride ions, which act as a surface active component of the salt flux [2]. As fluoride addition calcium fluoride CaF_2 is used very often due to its reasonable price. The concentration of CaF_2 in salt flux varies between 2 and 5 w. % [1].

It can be assumed that fluorides can only produce free fluoride ions, if dissolved in salt. Beside of dissociation reactions, it is important to know the solubility of fluorides in the salt melt. From previous experiments in Aachen [2, 5] the CaF_2 solubility appears to be lower than according to Bukhalova and Bergman, the only available study on the ternary system CaF_2 -NaCl-KCl [3]. In this study the polythermal section of the ternary system NaCl-KCl- CaF_2 related to the salt flux based on 70 w. % NaCl and 30 w. % KCl was studied experimentally by DTA. The solubility of CaF_2 corresponds to the CaF_2 side of the solidus line. A thermodynamical calculation of the polythermal section was added to understand the situation. Using of salt flux in Al-recycling processes causes metallic losses as a result of metal dispersion in the salt. On the one hand the F-ion provides oxide film cracking, on the other hand the interfacial tension between Al and salt decreases with increasing F-content. During scrap melting the salt adsorbs oxides and the melt viscosity increases. This slows down the coalescence rate. Therefore in this work the coagulation of Al-droplets was studied as a complex process under semi industrial conditions and a model for Al-losses under dependency of salt / scrap ratio and CaF_2 -content was developed.



2. Experimental

2.1 DTA measurements - phase diagram

NaCl, KCl and CaF₂ (Table 1) were dried during 24 h at 120 °C. Then samples containing 1, 2, 3, 5 w.% of CaF₂ were prepared and milled to 100 µm. Weight ratio NaCl to KCl in all samples was 70/30. The sample weight for DTA was 100 mg. Al₂O₃ was used as a reference. Argon gas flow (150 cm³/min) was applied to take the salt vapour from the DTA furnace. The temperature measurement absolute error was ±1°C. The weighing error of CaF₂ concentration was about ±0.02 %. Cooling and heating rates were 20°C/min and 5°C/min respectively. The sample with 5 w. % CaF₂ was heated to 850°C and other samples to 770°C.

Table 1: Purity of used sodium resp. potassium chlorides and calcium fluoride.

Chemical (Producer)	NaCl (Fluka)	KCl (Fluka)	CaF ₂ (Riedel-de Haën)
Main compound, %	≥99.5	≥99.0	≥99.5
	K≤0.01%	Na ≤0.05%	Chlorides (Cl): %≤0.1
Sulphate (SO ₄), %	≤0.01	≤0.01	≤0.005
Ca, Cd, Co, Cu, Fe, Ni, Pb, Zn, %	≤0.005	≤0.005	Pb ≤0.1; Fe ≤0.01; As ≤0.0005

2.2 Scrap melting

The lab scale melting of cast alloy Al-turnings was carried out in a short rotary drum furnace (Figure 1) with a length of 0.7 m, a diameter of 0.60 m and a max. capacity of 25 l melt.. The heat source was a gas-air burner with about 100 kW power output. The melting procedure was always conducted in the same manner: at first the whole salt amount was melted and heated to

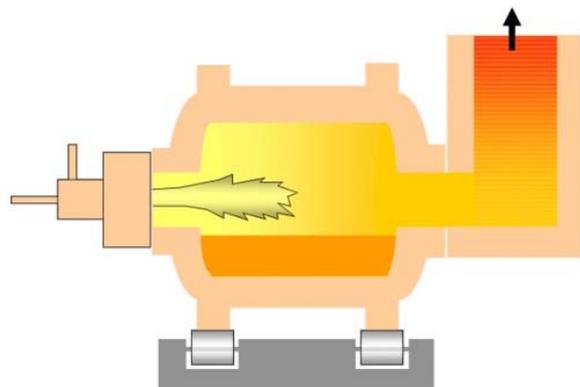


Figure 1: Short drum furnace for Al-melting with 25 l melting capacity.

~. 750 °C, then turnings were charged as long as the salt stayed liquid, after heating up the next portion was fed, this procedure was repeated until all turnings were molten. Finally the



whole melt was tapped in a steel crucible. After cooling the slag and metal were separated manually. The salt slag was leached in water to determine the soluble part as well as oxidic and as good as possible metallic Al-inclusions.

2.3 Thermodynamical calculations

FactSage[®] software by GTT Technologies was employed for the thermodynamic calculations. The program uses data from Barin et al. [4].

3. Results and discussions

3.1 DTA measurements - phase diagram

The binary system NaCl-KCl was studied by many researchers in the past (Figure 2) [3, 7-15]. The minimum liquidus temperature was examined to be between 645 and 665°C and corresponds to the equimolar composition. The phase transformation temperatures were determined by various methods: hot- and cold stage microscope techniques, differential thermal analysis and combined techniques. Some methods allow determining only the liquidus line. That explains that there are more experimental data for liquidus line than for the solidus line.

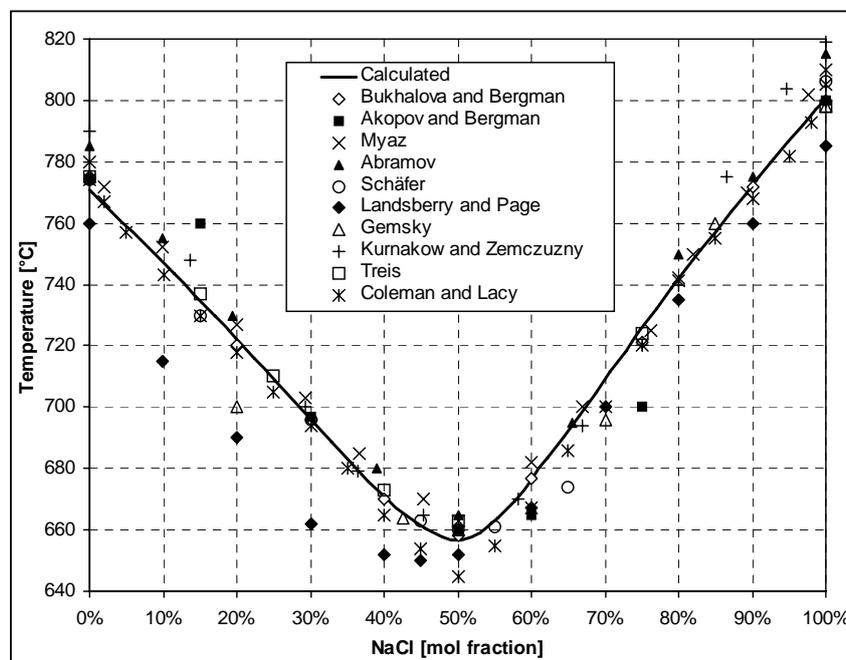


Figure 2: Liquidus line of the binary system NaCl-KCl, data received from various authors [3, 7-15]

The calculated liquidus and solidus lines resulted from own Factsage[®]-computations show good accordance with the experimental points (Figure 3). The measured liquidus temperature



of the German salt composition at 70 w.% NaCl (~75 mol.%) is between 690 and 712°C. The solidus temperature varies between 644 and 670°C. Calculated liquidus and solidus temperatures are respectively 709°C and 663°C.

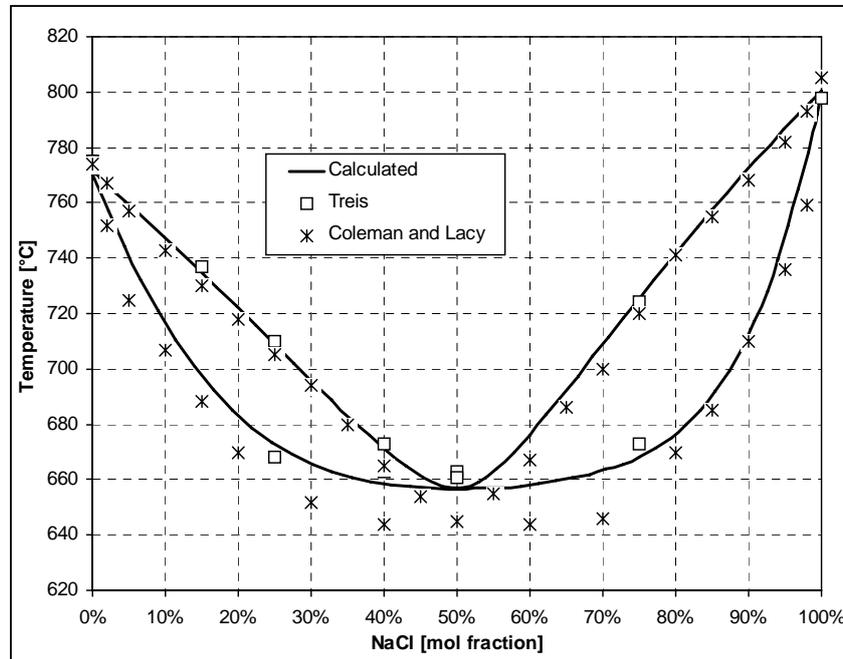


Figure 3: Binary system NaCl-KCl (own Factsage[®]-calculation versus published data)

As the binary systems NaCl-CaF₂ and KCl-CaF₂ show, the liquidus temperature differences between the experimental data of Ichaque [16] (DTA) and Bukhalova and Bergman [3] (visual method) are more than 100°C (Figure 4 and Figure 5). The Factsage[®] calculated equilibrium lines have better agreement with Bukhalova and Bergman than with Ichaque.

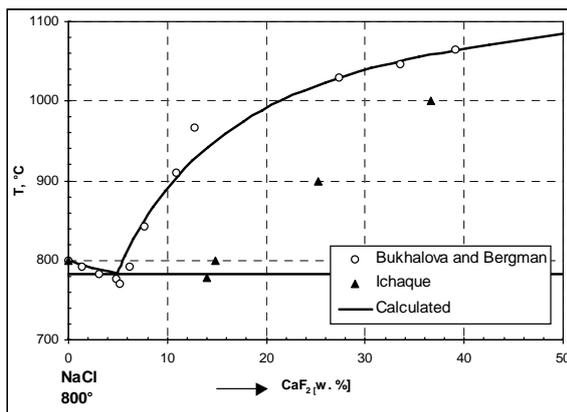


Figure 4: Binary system NaCl-CaF₂ (Factsage[®]-calculation versus published data)

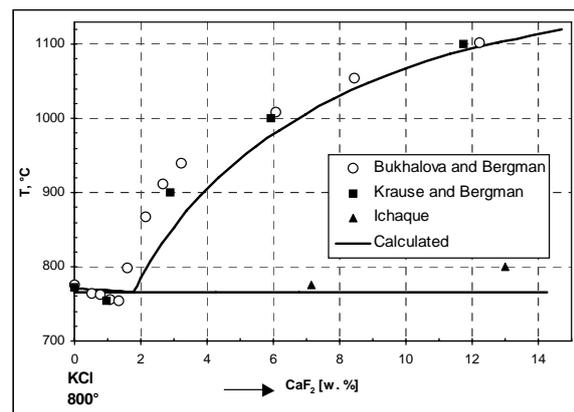


Figure 5: Binary system KCl-CaF₂ (Factsage[®]-calculation versus published data)

The ternary phase diagram NaCl-KCl-CaF₂ has been also investigated by Bukhalova and Bergman [3] (Figure 6). Interesting is that the isothermal lines show a turning point at higher Na₂Cl₂-concentrations. This curvature change is thermochemically unlikely and therefore not seen in the Factsage-calculated phase diagram (Figure 7).

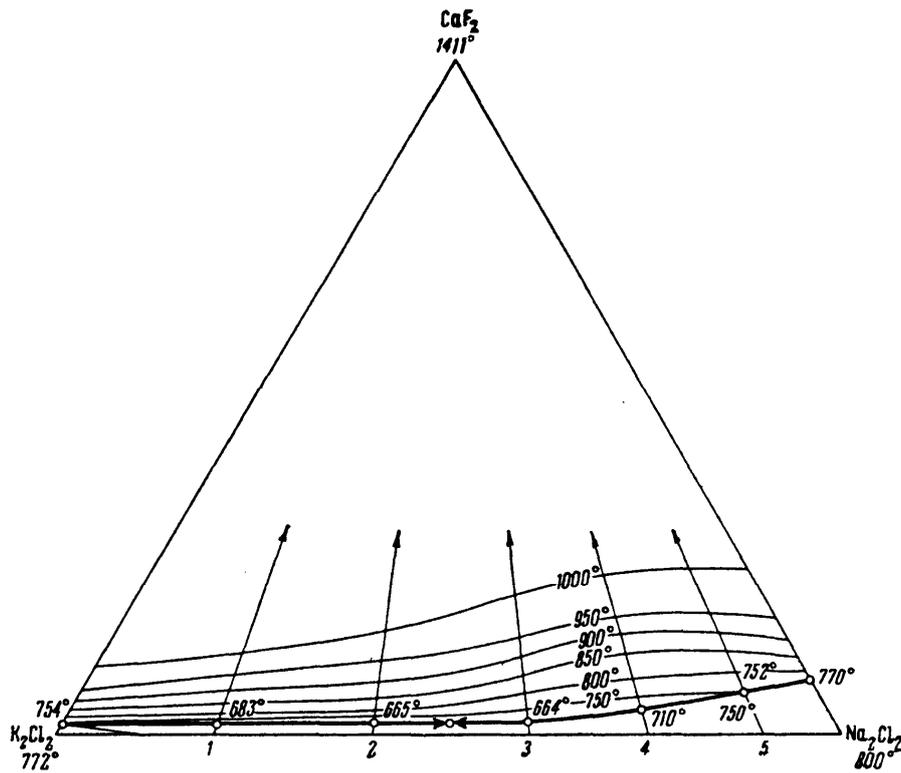


Figure 6: Ternary phase system $\text{Na}_2\text{Cl}_2\text{-K}_2\text{Cl}_2\text{-CaF}_2$ [3]

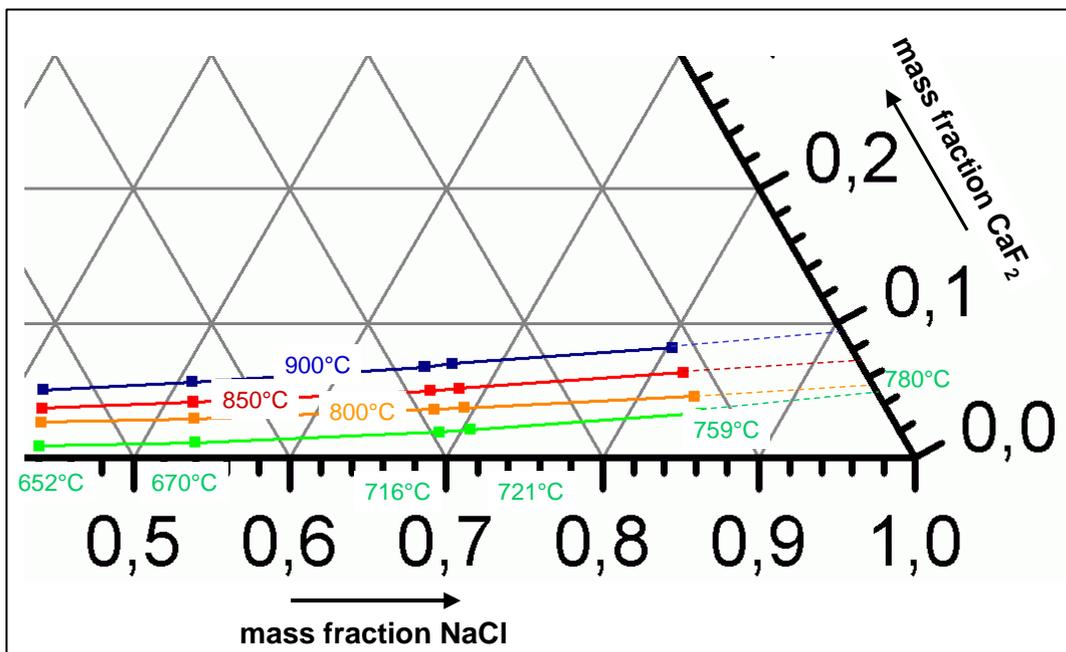


Figure 7: FactSage[®] calculated phase system NaCl-KCl-CaF_2 . Three upper lines are isotherm, the lower line represents the ternary eutecticum.

Investigating the quasi-binary section $70\text{NaCl}/30\text{KCl-CaF}_2$ first DTA results showed that the salt evaporated very fast. Weight losses were above 50 % within 30 min. at 860°C . Employing of an alumina cover lid for the crucibles and reducing of the maximal temperature to 820°C decreased the evaporation to less than 1%. The DTA phase transformation tempera-



tures were plotted on Figure 8. The liquidus line appeared to be higher than presented by Bukhalova and Bergman. The reliability of the experimental liquidus temperatures is very low.

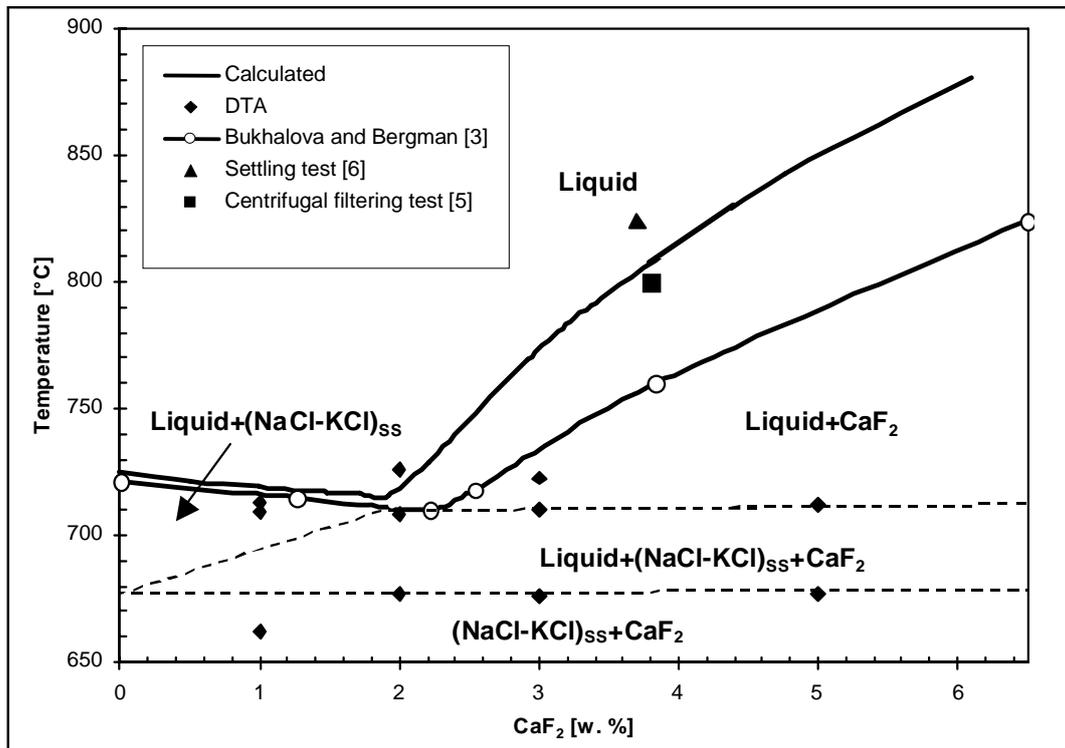


Figure 8: Quasi-binary section CaF₂-[70 %NaCl-30% KCl] of the ternary phase system (own Factsage[®]-calculation versus published and own experimental data)

The calculated liquidus line is even higher than obtained from DTA. In the region of hypoeutectic compositions the liquidus temperature difference between calculated and Bukhalova and Bergman data is between 2 and 4°C. In the hypereutectic compositions the liquidus line is much higher and the difference is more than 100°C. Results from own salt centrifugation [5] and salt settling tests [6] are close to the calculated liquidus line. Molten salt flux samples were filtered by a centrifugal technique at 800°C and filter cakes were analysed. The CaF₂ / (NaCl+KCl) ratio in the filter cake was the same as in the filtered melt if the CaF₂ concentration was lower than 3.8 w. %; at higher CaF₂-contents this ratio increased for the filter cake, which indicates undissolved CaF₂ in the salt flux. In the settling tests molten salt flux was allowed to settle up to 110 min. A clear salt sample from the top of the melt was taken and analysed for CaF₂. In coalescence tests [2] 5 w.% of CaF₂ addition into the 70NaCl-30KCl salt flux at 830°C resulted in undissolved CaF₂ particles in the melt, but with 3 w. % no undissolved CaF₂ was observed. Under the liquidus line in the hypoeutectic range an area of crystallisation exists (NaCl-KCl solid solution). On the hypoeutectic side CaF₂ crystallises precipitate on cooling until 708-709°C. Then the precipitation of a two-phase eutectic begins consisting of NaCl-KCl solid solution and CaF₂. The solidification ends at 676-679°C (Figure 8).

Contrary to the above results the thermodynamically calculated liquidus line in the polythermal section of the equimolar NaCl-KCl system is in good agreement with the data of Bukhalova and Bergman [3] (Figure 9).

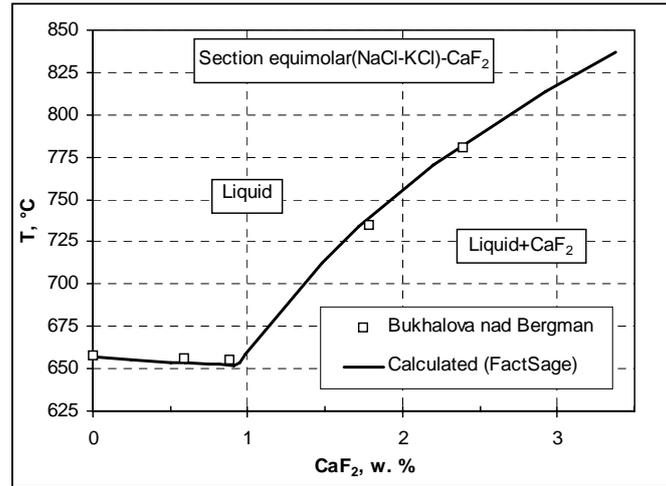


Figure 9: Quasi-binary section (equimolar NaCl-KCl)-CaF₂ of the ternary system NaCl-KCl-CaF₂ (own Factsage[®]-calculation versus published data)

This result leads to the statement that at 750 °C typical melting temperature in Al-recycling only max. 1.9% CaF₂ can be homogeneously dissolved in the American equimolar flux compared to max. 2.6% CaF₂, which can be homogeneously dissolved in the German flux melt, This is a much lower value than 3.6% postulated by Bukhalova and Bergman [3] and believed in the recycling community.

3.3 Scrap melting

After a multifactorial test planning [17] 16 melting trials were carried out. Varied parameters are salt/scrap ratio, CaF₂-content and temperature. As result two linear models for metallic losses in the salt were found for two ranges of the CaF₂-content. Equation 1 is valid for [CaF₂] < 0.5 % and Equation 2 for 0.5 < [CaF₂] < 3.5 %.

$$M_{Al(met)}^{Slag} = (2.205 \pm 0.014) - (3.47 \pm 0.060) \cdot (C_F - 0.25) + (0.014 \pm 0.0050) \cdot (\varphi - 70) - (0.046 \pm 0.0012) \cdot (T - 800) \cdot (C_F - 0.25) - (0.078 \pm 0.0020) \cdot (C_F - 0.25) \cdot (\varphi - 70) \quad (\text{Eq. 1})$$

$$M_{Al(met)}^{Slag} = (1.58 \pm 0.94) - (0.0083 \pm 0.0020) \cdot (T - 800) + (0.18 \pm 0.066) \cdot (C_F - 1.5) + (0.0073 \pm 0.0033) \cdot (\varphi - 70) + (0.0075 \pm 0.0020) \cdot (C_F - 1.5) \cdot (\varphi - 70) \quad (\text{Eq. 2})$$

with C_F – as CaF₂ content in salt in mass. %, T – salt temperature in °C and φ – salt/scrap ratio in %.

Based on those models Figure 10 has been constructed for a constant temperature 800°C. It shows that the combination of salt/scrap ratio and CaF₂-content varies the metallic losses as follows: at CaF₂-contents lower than 0.5 % the Al-concentration in the salt increases with reducing CaF₂-contents for all salt/scrap ratios. At 0.5 % CaF₂ there seems to be a minimum, above that the Al-content in the salt increases slightly again with the CaF₂-content. The switch between the two models gets uneven at extreme low salt ratios.

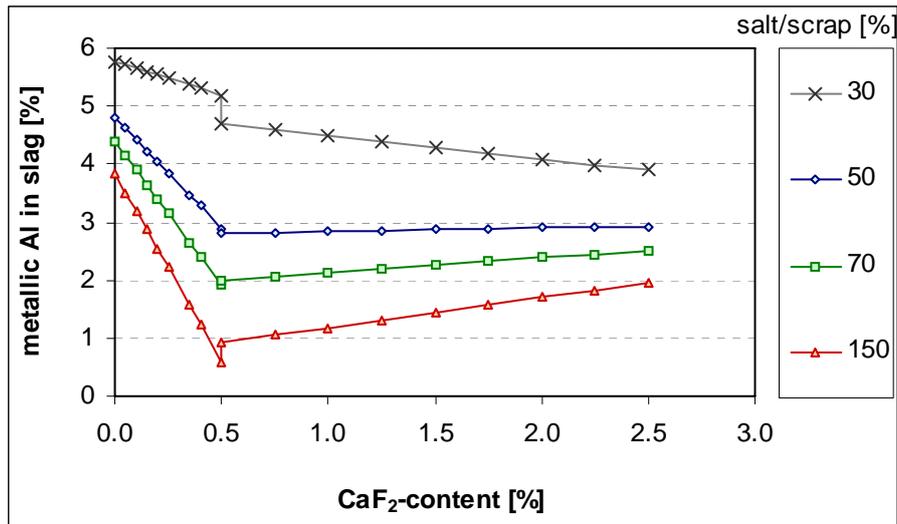


Figure 10: Dispersion model for metallic droplets in salt bath.

A higher salt/scrap ratio generally causes lower Al-dispersion, which means higher Al-concentration in the salt; the absolute loss of Al related to scrap amount by using more salt is nevertheless higher, as shown in Figure 11. This may be explained with following influences: At low CaF_2 -contents the impact of fluorides is not strong enough to strip the oxide layer from the Al-pieces, so they stay in the melt and can not coalesce. With increasing CaF_2 -content the interfacial tension between the salt and Al decreases and lets more Al-droplets disperse in the salt. The stripped oxides increase the viscosity of the salt slag, this additionally hinders the coalescence. In an overall assessment the ratio salt/scrap of 30 % causes the lowest absolute Al-losses in the salt.

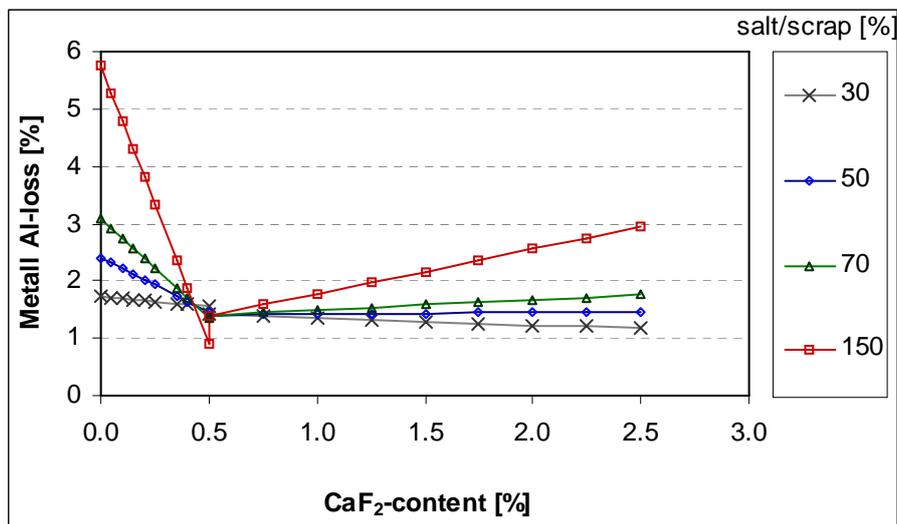


Figure 11: Dispersed metallic losses in the salt as a part of molten scrap.

There was also found, that during the melting and contact of fluid Al and salt the F-content of the salt decreases with time (Figure 12). To assess the interaction between fluoride and furnace liner, the F-content was measured in a holding trial with pure salt bath (without Al-scrap addition). The F-content did not change during 3 hours. So a reaction between Al und fluorides must take place, which is more intensive in the melting period as fig. 12 shows, proba-



bly because of a higher reaction surface. The reaction rate (loss fluoride per hour and m^2) for fluoride on the salt/metal interface was calculated using the bath surface area of 0.49 m^2 , a value of 2.13 % dispersed Al-droplets with a specific surface of $5.2 \text{ m}^2/\text{kg}$ to be about $0.16 \text{ g/m}^2\text{h}$.

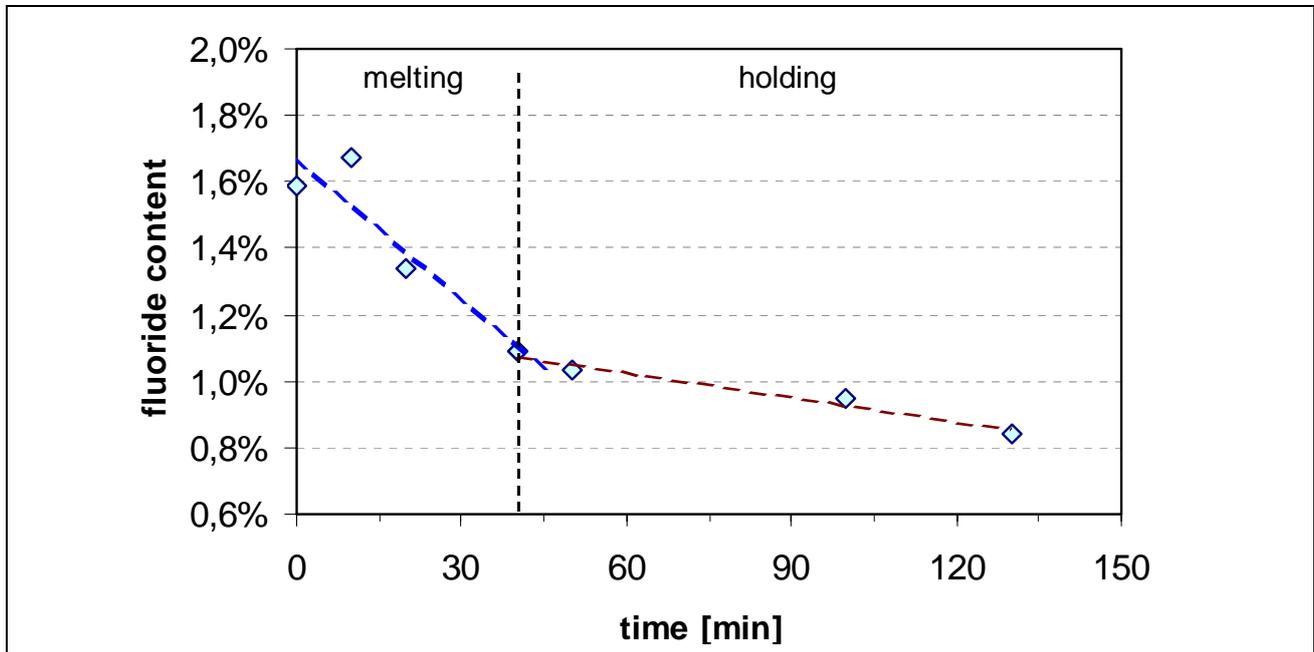


Figure 12: Fluoride consumption during the melting and holding of Aluminium in a salt bath.

Conclusions

Experimental results from DTA-measurements and scrap melting, literature data and the thermodynamical calculations indicate, that the solubility of CaF_2 in the salt flux (70 w. % NaCl -30 w. % KCl), widely used in Germany in aluminium scrap remelting, is 2.6 % at $750 \text{ }^\circ\text{C}$ and significant lower than 3.6 % according the only available ternary phase diagram NaCl-KCl-CaF_2 of Bukhalova nad Bergman [3]. The knowledge of the CaF_2 solubility allows avoiding its unnecessary overconsumption which can increase the metal loss by increasing viscosity of the salt flux and amount of the residue after the water leaching of salt slag. The reaction between Aluminium and in the salt dissolved fluorides with fluoride consumption rate of 0.16 g/h per 1 m^2 Al - salt surface should be considered to hold the finish CaF_2 -content at 0.5 %, greater CaF_2 -content is not necessary for investigated cast alloy and increases metal loss in the salt flux because of lower interfacial tension between salt and metal. The metal loss in the slag is proportional to the salt / scrap ratio. The authors recommend 1.6-2.6 mass. % CaF_2 -content in salt flux and preferably low salt/scrap ratios for melting of Al-scrap.



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