"The influence of increased NaCl:KCl ratios on Metal Yield in salt bath smelting processes for aluminium recycling"

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"Der Einfluss des erhöhten NaCl:KCl Verhältnisses auf die Metallausbeute in Salzbadschmelzen beim Aluminiumrecycling"

"Influencia del incremento de la relación NaCl:KCl sobre el rendimiento metálico del proceso de fusión de baño de sales para el reciclaje de aluminio"

Abstract

Strongly increased KCl prices force to modify the current salts mixture in the currently used salt treatment processes for aluminium recycling. This study presents lab-scale results about the influence on metal yield varying both the NaCl:KCl ratio from 70% to 100% NaCl and the CaF_2-content from 0% to 3%. The metal yields showed no significant difference at higher NaCl:KCl ratios and as commonly known for standard mixtures a slight increase was observed with rising CaF_2 values in the salt mixture, also when the NaCl content exceeded 70% wt.

Keywords: aluminium, recycling, salt mixture, NaCl/KCL-ratio

Stark gestiegene KCl Preise zwingen die Anwender von Salzschmelzprozessen im Aluminiumrecycling zu einer Veränderung der derzeitigen Salzmischungen. Die vorliegende Arbeit beschreibt die Versuchsergebnisse im Labormaßstab, in denen der Einfluss auf die Metallausbeute bei wechselnden NaCl:KCl Verhältnissen zwischen 70 und 100 % und wechselnden CaF2 Verhältnissen zwischen 0 und 3 % untersucht wird. Die Metallausbeute zeigt keine wesentlichen Unterschiede bei höheren NaCl:KCl Verhältnissen, aber, wie bereits allgemein bekannt, konnte ein leichter Anstieg der Ausbeute bei steigenden CaF2 Werten in der Salzmischung sowie bei einem NaCl-Gehalt über 70 Gew.-% beobachtet werden.

Schlagworte: Aluminium, Recycling, Salzmischung, NaCl/KCl Verhältnis

Introduction

Aluminium scrap recyclers use well known salt treatment to strip the oxide skin from molten metal droplets, to protect the bath from oxidation, to dissolve or suspend other materials attached to the metal and to promote the coalescence of aluminum drops [1]. The influence of different salts on the metal yield has been widely investigated but mostly used NaCl:KCl ratios of 50:50 mol or 70:30 wt. American recyclers typically use the equimolar mixture due to its low melting point (645°C). European recycler uses mostly 70:30 ratios because of historical experiences to provide acceptable coagulation [1] as well as due to its natural appearence. No research has been found in relation to the influence of higher NaCl:KCl ratios on metal yield (MY).

Recently the price of KCl has increased around 2.5 times compared with the price in 2005 (Figure 1). Reasons for this are increased consumption in agriculture especially by China (around 70% is now being imported), the constant increase of freight rates and monopolistic domestic distributors and curtail sales. On the other hand, according to statistics by IFA (International Fertilizer Industry Association) in 2007, the newly production capacity of potassium to be added from 2008 to 2011 worldwide will be 18.0 million t/a. The new capacity in 2008 will however be only 2.0 million t/a. Compared with a demand of 53.8 million tons a year in the world, the new capacity of this year will be far from sufficient [2]. Eventually the increase of potash price will not stop in the next year, and the salts for aluminium recycling treatment will become more expensive. Therefore it is important to investigate alternatives to reduce the process cost. This study presents a result of lab scale experiments as an attempt to determine the influence of increased NaCl:KCl ratios on the metal yield.

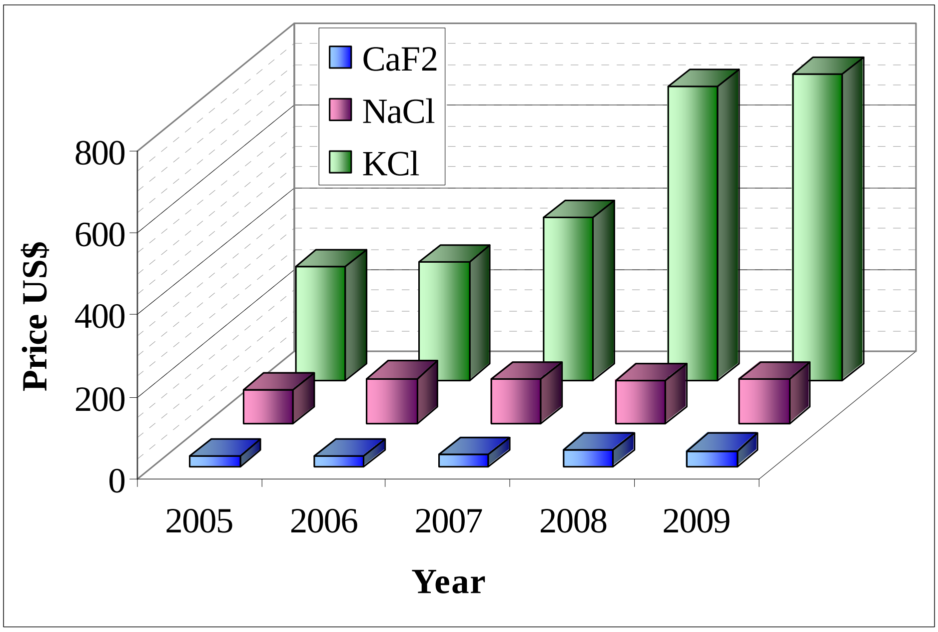

Figure 1: Price increase of KCl, NaCl and CaF_2 in the period of 2005-2009 [3],[4]

1 Theorical background

1.1 Stripping of oxide and triggering of metal coagulation

When immerging Al-scrap in a molten salt bath the metallic core, which is surrounded by an oxide shell, expands strongly and the different thermal expansion coefficients of both materials cause cracks inside the oxide skin, allowing the flux to pass to the metal surface and to initiate chemical reactions like gas formation. Some components of the flux, especially the fluorine containing ones, act as surface active elements and are easily adsorbed at the metal surface. As fluoride ions cause also aluminiumoxide phase modifications leading to oxide shrinkages, additional cracks are formed. Since the distribution of these surface active elements is not uniform along the contact surface, the concentration gradient forces the metal drop to spin in an interfacial movement. This together with the reduce surface tensions salt-metal and salt-oxide compared to metal-oxide creates a stripping force that removes the oxide skin. When metal droplets are are freed from the oxide skin, they are able to coalesce in order to form a metal bath. This is supported by the movement of the rotary drum furnace [1].

1.2 Salts mixture

Currently the aluminium recyclers use NaCl:KCl mixtures of 70:30 wt or 50:50 mol in Europe or American Industry respectively, all with fluorine additions e.g. using CaF_2 between 2 to 5% wt or even cryolite. Some literature is present on the fluorine effect, for example SYDYKOV found that the influence of CaF_2 on the metal yield exhibits an exponential behaviour. The metal yield increases initially sharply and then stays constant, the inflexion point is about 0.5% wt (Figure 2).

The metal fraction of the resulting salt slag decreased to 2% wt CaF_2 and then remains almost constant [5].

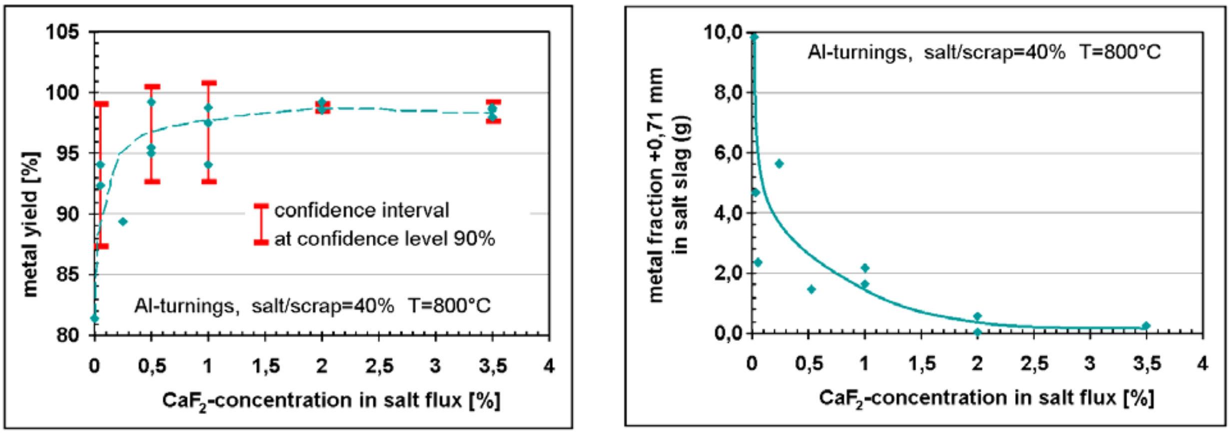

Figure 2: Effect of CaF_2 concentration on metal yield (left) and on metal losses (right) [5].

A variation of NaCl:KCl ratio showed no influence on the metal yield, as the Cl^- concentration remains constant and only the ratio of Na^+ and K^+ is changed. These cations have only minor effect on the surface tensions and do not take part on the main reaction on the metal surface. Changes of NaCl ratios for mixtures > 50% mol NaCl required an increase of the process temperature (melting point of salt mixture) and this increase had some minor influence on the coagulation efficiency.

1.2.1 System NaCl-KCl

The equilibrium diagram of NaCl:KCl (Figure 3) calculated using the thermochemical software FactSage 5.5® using the FACT53 and FTsalt databases shows the lowest melting temperature (eutectic point) at 44 %wt NaCl and 645°C. A composition variation increases the temperature in both directions. The melting point of pure NaCl is 801°C, only 36°C above the melting point (725°C) of salt mixtures currently used by European recyclers. On the diagram the increasing melting points are presented for NaCl additions.

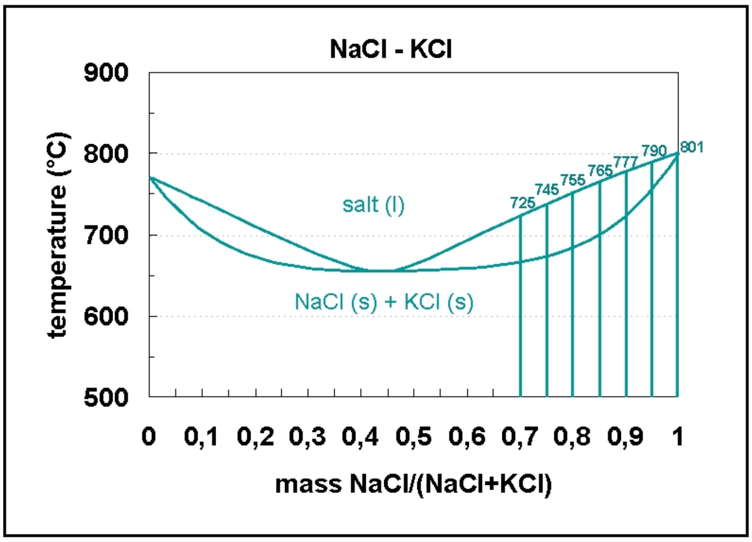

Figure 3: Equilibrium binary diagram of NaCl-KCl by FactSage 5.5®

1.3 System NaCl-KCl-CaF_2

Also the NaCl-KCl-CaF_2 ternary diagram was modelled by FactSage 5.5® using FTsalt-SALTA base-Phase (Figure 4). At temperatures higher than 802°, two areas are present: a small monophasic area of a liquid salt and a bigger biphasic area of liquid salt and solid CaF_2. At lower temperatures there four areas exist (see red line of 770°C). Two of these areas are similar to the above mentioned ones and the other two are represented by a second liquid salt and solid NaCl. The maximal solubility of CaF_2 was determined at different temperatures, e.g. at 802°C it reaches 5% wt in a mixture of only CaF_2 and NaCl, but it reduced to 3.3% wt at the compositions of both European and American salts. At 770°C the solubility of CaF_2 is 2.9% wt in the European salts composition. The gray line (3% wt CaF_2, different NaCl:KCl ratio) indicates that only one liquid phase at 802°C exists, but at 770°C this liquid phase is only found up to a 89:11 NaCl:KCl ratio.

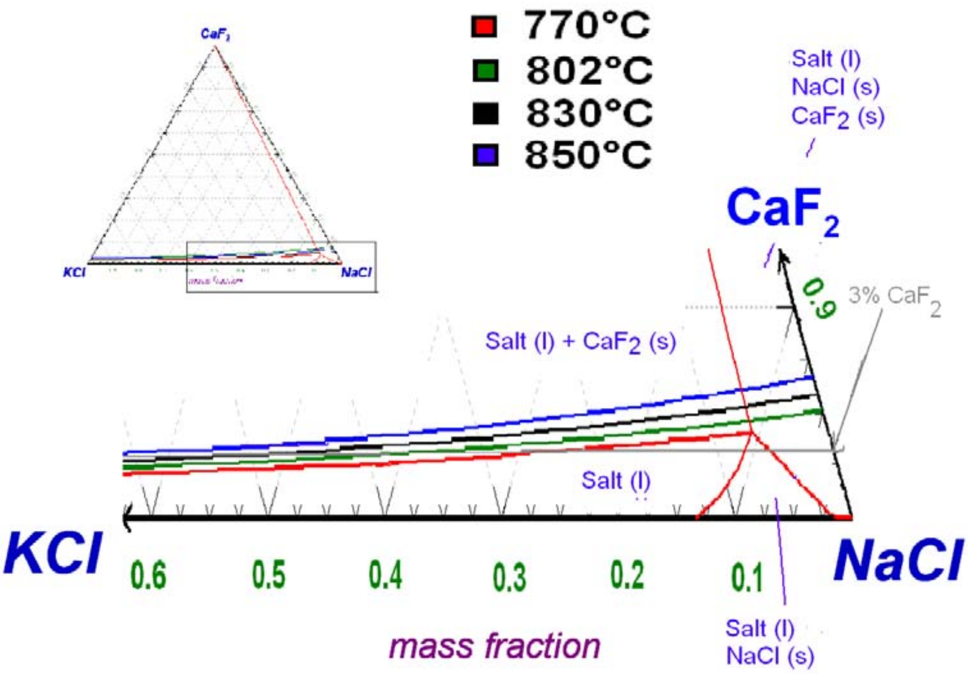

Figure 4: Equilibrium ternary diagram of CaF_2-NaCl-KCl by FactSage 5.5®

2 Experimental set up

Three series of experiments were carried out to evaluate the influence of a variation of the NaCl:KCl ratio from 70% wt to 100% wt NaCl, while varying CaF_2 from 0% wt to 3% wt. Each metal/salt-mixture was heated up to 50°C above the melting point of the specific mixture taken from a NaCl-KCl phase diagram (Figure 3). According to Figure 4 at this temperature only a liquid phase is present. Granulated aluminium scrap (+1.5mm -4mm) and salts of analytic grade were used in all the experiments. No cover gas was used.

The first series was performed with an Aluminium/Salt ratio of 2 changed the NaCl:KCl ratio. The high ratio Aluminium/Salts is frequently used on experimental assay:

- 40 g of Aluminium
- 19.6 g of salt mixture (NaCl:KCl ratio from 70% to 100% wt NaCl)
- 0.4 g of KCl (2% of total weight of salt).

The second one was carried out with the same ratio of the first one, changed the CaF_2 quantity:

- 40 g of Aluminium
- 20 g of salt mixture (NaCl:KCl ratio from 70% to 100% wt NaCl and CaF_2 from 0 to 3% wt)

And the third one was designed with a salt factor of 1.5 (this value is the commonly used on the industry). Salt Factor was calculated with about 90% of metal yield, value close to the obtained on first and second test series.

- 80 g of Aluminium
- 11.76 g of salts mixture (NaCl:KCl ratio from 70% wt to 100% wt NaCl)
- 0.24 g of CaF_2 (2% of total weight of salt)

Each experiment was repeated two times, but when the obtained metal yields resulted in high variations, tests were repeated. The salt mixture was loaded into a clay-graphite crucible and placed in the resistance furnace. A Ni-Ni/Cr thermocouple inside a protective alumina tube was used to measure the temperature. The crucible and the alumina tube were coated with boron nitride paint and fired with a blowtorch to protect them against the reaction of the aggressive molten salt. When the desired temperature was reached one third of the metal weight was added through a funnel. The mixture was manually stirred. Once the temperature returned to the set temperature the loading procedure was repeated until all the aluminium scrap was added. Finally the set temperature was held for 5 minutes and the crucible was taken out of the furnace and cooled down quickly in a bed of copper turnings. The received aluminium button and slag were removed from the cold crucible and weighted to calculate the metal yield (MY) of the test. The salt slag was leached in water and the sludge was filtered. The filter cake was dried at 150°C for 24 hours and screened at 1.5mm, 1.0mm and 0.355 mm. Angular particles of the screened part <1.0mm were taken out to assure that only spherical particles remained inside the sample which were considered to be aluminium. This amount was used to estimate the amount of metal losses into the salt.

3 Results and discussion

The parameters and results of all experiments can be seen on tables 1-3.

Table 1: Experiment Parameter and results of the first experiment series (no fluorides)

Experiment Parameter				**Metal Yield %**			**Metal loss %**		
NaCl:KCl Ratio	**NaCl (g)**	**KCl (g)**	**Temp °C**	**1-1**	**1-2**	**1-3**	**1-1**	**1-2**	**1-3**
70-30	13.72	5.88	775	89.5	89.4	88.7	0.64	1.26	0.33
75-25	14.70	4.90	795	90.1	90.5		1.01	0.34	
80-20	15.68	3.92	805	90.5	87.8		0.54	1.68	
85-15	16.66	2.94	815	88.9	91.1	88.8	0.81	1.22	
90-10	17.64	1.96	827	89.5	90.2		0.75	0.38	0.21
95-5	18.62	0.98	840	90.1	87.8		0.51	2.27	
100-0	19.6	0	850	89.1	87.0	87.7	0.96	3.21	0.64

Table 2: Experiment parameters and result of the second series ("standard")

Experiment parameter						Metal Yield %			Metal loss %		
NaCl:KCl Ratio	**% CaF_2**	**NaCl (g)**	**KCl (g)**	**CaF_2 (g)**	**Temp °C**	**1-1**	**1-2**	**1-3**	**1-1**	**1-2**	**1-3**
70-30	0	14.00	6.00	0.0	775	76.9	79.0	77.7	10.8	2.9	6.3
70-30	1	13.86	5.94	0.2	775	91.0	88.8		0.6	2.5	
70-30	3	13.58	5.82	0.6	775	90.5	88.6		0.2	2.2	
85-15	0	17.00	3.00	0.0	815	86.0	85.8		2.2	1	
85-15	1	16.83	2.97	0.2	815	90.0	87.8		0.1	2.4	
85-15	3	16.49	2.91	0.6	815	90.7	91.4		0.2	1.0	
100-0	0	20.00	0.00	0.0	850	87.0	85.6		2.1	1.8	
100-0	1	19.80	0.00	0.2	850	87.9	87.7		1.0	1.7	
100-0	3	19.40	0.00	0.6	850	89.9	89.2		0.9	1.0	

Table 3: Experiment parameters and result of the third experiment series (less salt)

Experiment Parameter				Metal Yield %			Metal loss %		
NaCl:KCl Ratio	**NaCl (g)**	**KCl (g)**	**Temp °C**	1-1	1-2	1-3	1-1	1-2	1-3
70-30	8.23	3.52	775	78.5	80.9	86.3	9.41	6.28	1.61
75-25	8.82	2.94	795	79.9	81.5		7.35	8.13	
80-20	9.41	2.35	805	83.7	84.1		2.58	2.44	
85-15	9.99	1.76	815	86.7	83.3		1.95	0.78	
90-10	10.58	1.17	827	85.6	87.0		3.66	1.33	
95-5	11.17	0.58	840	81.9	79.5		5.16	8.12	
100-0	11.76	0	850	83.8	80.0	82.7	2.38	7.98	4.10

Variance analyse (ANOVA) was made on each experiment series to evaluate if the change of NaCl or CaF_2 amount has a significant influence on the metal yield. The following figures will show that the change between 70-100% NaCl has no influence on the metal yield. The statistical significance of NaCl was 0.65, 0.22 and 0.22 for the first, second and third experiment series respectively. A significance of 0.65 means there is a 35% probability that NaCl influences the metal yield, but this value is negligible. Only significances < 0.05 ($> 95\%$ probability) assure the influence of independent variables on the dependent variable. The 0% statistical significance of CaF_2 suggests a strong influence of CaF_2 variation. The influence of variation of % NaCl on "metal losses" was negligible too, its significance was 0.67, 0.17 and 0.24 for the first, second and third series respectively.

3.1 Results of the first experiment series (no fluoride addition)

The metal yield average observed (Figure 5) was 89.2 ± 1.2%. The best result appeared at 85% NaCl (MY 91.1%), the worst one at 100% NaCl (MY 87%) The average metal losses of all trials was only 1 ± 0.6 % suggesting a high coalescence. Although there is no statistical influence of NaCl on MY, the data shows a slight maximum at 85%.

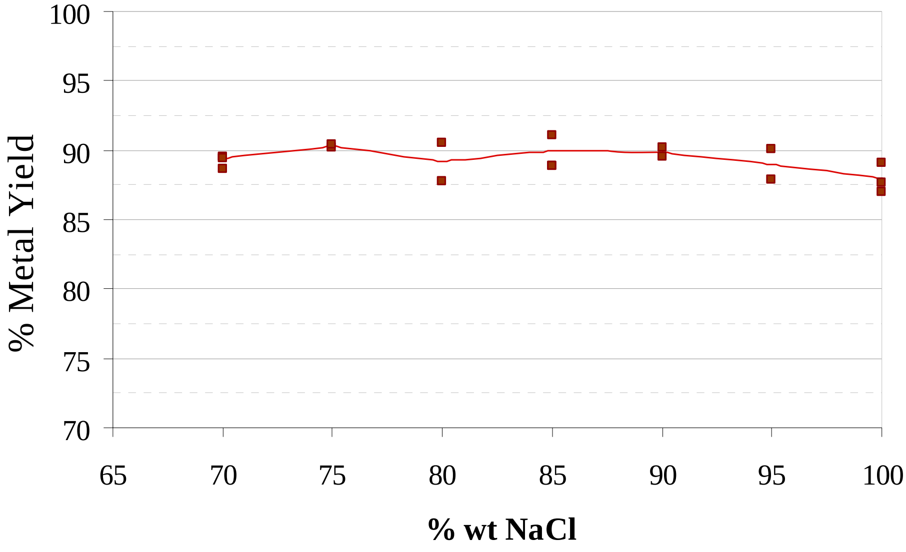

Figure 5: Metal yield to the first experiment series (metal/salt ratio of 2)

3.2 Second experiment series

A second experiment series was carried out to determine the influence of CaF_2 at different KCl/NaCl-ratios on the metal yield. When using the European composition (Fig. 6, blue points) a first addition of CaF_2 promotes a significant increase of about 11%, but when the CaF_2-content exceeds 1%, the metal yield stayed constant, which is in agreement with SYDYKOV [5]. But this is not the case for the higher NaCl:KCl ratios, where CaF_2-additions always lead to a slightly increase of MY. The maximum of 91.4% was reached at 3% CaF_2 at 85% NaCl content.

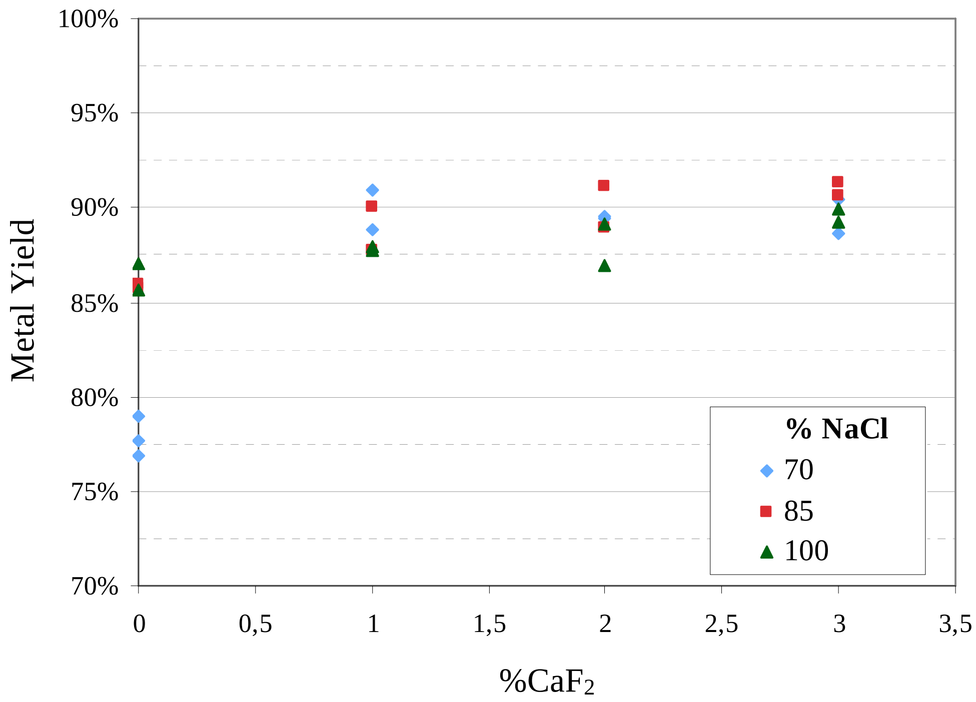

Figure 6: Metal yield versus concentration of CaF_2 (second experiment series)

Figure 7 presents the same data as metal yield versus NaCl-content. Again the maximum of 85% NaCl can be clearly seen, when 3% of CaF_2 was added. Chemically the concentration of Cl^- is almost the same at the different NaCl:KCl ratios between 18.3% and 20.2% wt to the lower and higher value respectively. So as "only" this ratio varies, its influence on the stripping efficiency of the alumina can be assessed. It has to be considered that an increase of the NaCl content leads inevitably to a higher melting point. This effect itself has an impact on the treatment procedure, as it changes the physical properties of the salts like viscosity, density, surface tension etc. and also increases the risk of oxidation when charging scrap. Such the metal yield can change in all directions. Nevertheless as can be seen from figures 6 and 7, increasing NaCl-shares seem slightly to reduce the aluminium recovery, if salts with CaF_2-contents are considered.

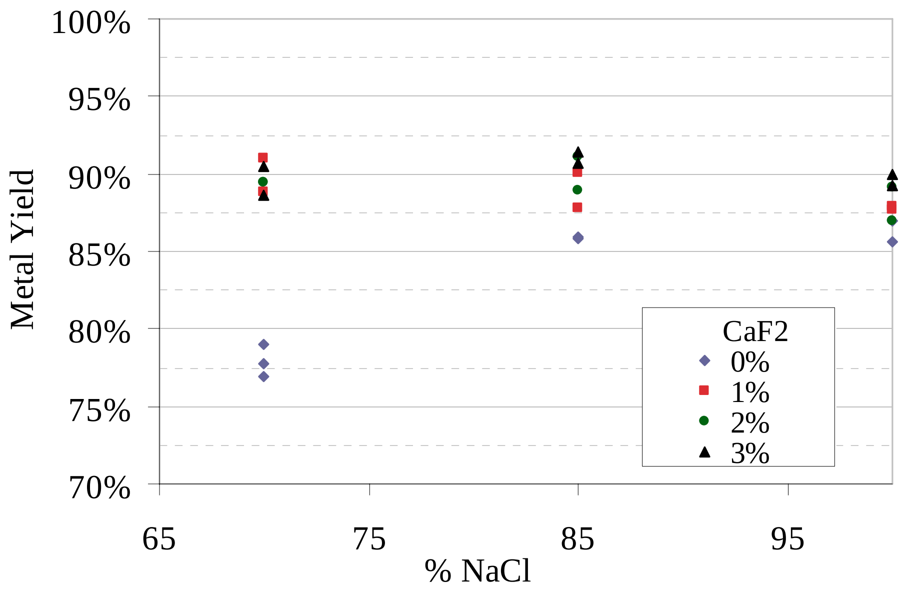

Figure 7: Metal yield versus NaCl:KCl ratio.(second experiment series)

3.3 Third experiment series

The aim of this series was to verify the impact of higher NaCl-contents in the salt on metal yield at increased Aluminium/Salt-ratios (ca. 6,7 versus 2) or Salts Factor (ca. 5 versus 1.5). Generally the efficiency obtained was about 6.4 % in average lower than those of series 1 (see figure 5) and exhibits more dispersion, about 82.8 ± 6.8%. The difference between the best trial (87%) and the worst (78.5%) was 8.6%. The morphology of the small metallic and non-coagulated particles in the resulting slag was generally irregular, only few of them exhibited a spherical form. Metal losses of about 4.6% proof the reduced coalescence on the droplets. Although the higher dispersion of the MY values, the tendency of the curve show again, that the influence of the KCl:NaCl is marginal and a "maximum" may be identified at 85% NaCl.

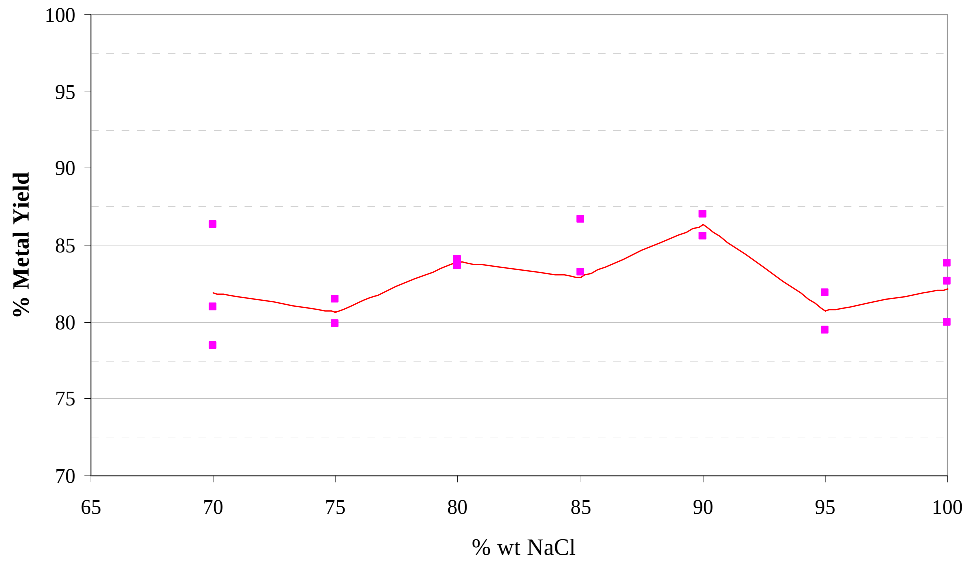

Figure 8: Metal yield versus NaCl-content from third experiment series (high metal/salt ratio of 6.7)

3.4 Savings with respect to salt costs

Table 4 shows the price of the salts at different NaCl:KCl ratios calculated with the currently price of each salt [4] (April 2009) and the possible saving for different salt compositions in comparison to the one used by the European recycler. If KCl is replaced totally on the salt an 83% can be save from the total salt cost.

Table 4.: Currently price and comparison of salts mixture at different composition

NaCl:KCl:CaF_2 ratio	Salt Price [US$/t]	Savings [%]
68,5:28,5:3	243	----
83,5:13,5:3	136	43
97:0,3	40	83

4 Conclusion and Outlook

On laboratory experimental level, a total replacement of KCl by NaCl in the aluminium salt mixture leads to similar values of the metal yield respectively the metal losses. Although there is not statistical influence on the metal yield at different NaCl:KCl ratios, a slight optimum at 85% NaCl can be seen, but experimental research should continue to elucidate its truth and cause. The total replacement of KCl might save up to 80% of the actual salt costs and should not be technologically problematic to the European recyclers as they all ready use temperatures close to the NaCl melting point for much aluminium recycling process, especially when aluminium is delivered in liquid form. An increment of CaF_2 at levels $\geq$ 1% increases further the metal yield if the NaCl:KCl ratio is 85% or higher. These small scale experiments demonstrated for the used Al-scrap type that it was not necessary to use amounts of CaF_2 higher than 1% wt in European flux composition (see also figure 2, [5]). Reproducibility test and scale up experiments with the proposed salt compositions must be carried out to confirm its technical feasibility.

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