Salt-Metal Interaction in Magnesium Recycling

Semiramis Akbari, Bernd Friedrich

IME Process Metallurgy and Metal Recycling, RWTH Aachen University

Abstract

Magnesium recycling is typically based on the use of fluxes, mostly containing $MgCl_2$, KCl, NaCl and CaF_2. Salt flux has the role of separation of surface oxides, gases or other contaminations from metal. It is state of the art that application of salt flux in contact with magnesium scrap leads inevitably to the formation of a sludge so called “black dross” containing both metallic and oxidic magnesium as well as salt components. In this paper - based on a newly finished and defenced PhD thesis at IME/ RWTH Aachen [1] - it has been tried to investigate the influence of chemical composition of salt fluxes applied in magnesium recycling on coalescence ability of that salt with the aim of minimization of metallic magnesium loss in black dross. The results represent the general increasing effect of fluorine containing components as well as magnesium chloride inside fluxes. The value of 5 Wt % of fluoride components appeared to have the best effectivity on coalescence and CaF_2 is the best economical/technical choice because of its reasonable price against LiF and MgF_2 as well as its high coagulation effectiveness in comparison with KF and NaF.

Keywords: Flux, Salt, Coalescence, Black Dross, Magnesium

1 Introduction

Use of a salt flux in an Al/Mg recycling furnace helps to strip away and suspend the oxide film so that coalescence of the droplets increases and dross formation decreases. The salt flux wets the oxide film and initiates disintegration of the film, stripping it from the surface of the molten aluminum droplets. Fragments of the oxide film stripped from the aluminum remain suspended in the flux. The flux also prevents further oxide formation by keeping the metal protected from the atmosphere of the furnace.

The coalescence ability of a salt is an important factor to define its suitability as flux in the recycling of aluminum and magnesium. The coalescence of metal drops leads to an increase in the droplets diameter, resulting an increase in the probability of their separation from the salt flux. Therefore, the better the coalescence ability of a salt, a higher yield of recycling process will be achieved [2]. Generally speaking, a salt used for recycling of aluminum and magnesium should possess some common properties. This includes a lower melting temperature than that of Al and/or Mg (although it has not been achieved for Al so far), low densities (that is not easy to be achieved in the case of Mg, due to the extremely low density of Mg), low viscosity, no reaction with or contaminate the molten metal, no attacking against the refractory walls, non-poisonous, inexpensive or easily recycled with low costs and easily separable from the melt. On the other hand, there are still four main requirements for each salt as follows [3,4]:

- cover the metal to prevent oxidation

- dissolve or suspend oxide and other non-metallic contaminations, which adhere to the metal
- strip away the oxide/ ceramic layer from molten metal
- advance and improve the coalescence of molten metal

During the remelting process and recycling, certain metal fraction (aluminum or magnesium) is suspended into the molten salt flux. This phase; containing the rest of salt flux as well as residues floating to the top (in the case of aluminum) or to the bottom (in the case of magnesium) of the bath such as oxides, sulfides, halides and metallic compounds is called “dross”. One of the most important activities in recycling is to reduce metal losses within this layer. Although some fraction of the isolated metal in this dross can be recovered through agitation of the salt, a significant amount of metal remains entrapped [5]. After detaching the oxide films from the metal, they suspend themselves in the flux along with other impurities. That leads to an increase in the viscosity of the salt [4]. Some studies about the effect of oxide concentrations and particle sizes on flux viscosity have been concluded and found out that the oxide even concentrations as low as 10% causes sufficient thickening of the flux to inhibit coalescence [6]. While the remelting process is going to be accomplished, the fluidity of the salt layer decreases significantly and as a result the effectiveness decreases too. That’s the time that further salt should be added and/ or the dross be removed [4].

Ye and Sahai [5] observed that it takes relatively short time that an aluminum piece, put in a cylindrical form into a molten salt bath, to be turned into a spherical-shaped drop. To minimize the total energy of the system, the shape of the metallic piece should tend to change from cylindrical to spherical, which provides the minimum interfacial area. However, this change of shape requires breaking and removing some of the oxide films. It is generally believed that the oxide films are stripped away by the molten salt; however, the mechanism of actual removal is still unclear. It is suggested sometimes that the molten salt involves an attack on the base metal, giving mechanical detachment of the oxide layer. The fluorides attack the oxide film, permitting the rapid penetration of the chloride ions. The detachment of the oxide shall be attributed to the formation of volatile aluminum chloride at the oxide/metal interface. Though, from the thermodynamical aspects, the reaction of aluminum with any alkali chloride to evolve $AlCl_3$ gas is extremely unlikely [5]. This theory is in comparison with another theory related to the effect of interfacial tension forces on the removal of oxides suggested by Van Linden and Stewart [6].

It is known that additions of fluorides to molten chloride in an aluminum recycling flux, affect the recovery ability positively through decreasing the flux/aluminum interfacial tension and thus increasing the capability of flux to free oxides from aluminum droplets [6]. Some researchers investigated interfacial tension of equimolar NaCl-KCl with small additions of Cryolite, Lithium fluoride, Sodium fluoride and potassium fluoride and shows that they can reduce the interfacial tension between flux and aluminum by about 20-50% [7]. Ye and Sahai [5] saw that the addition of NaF to the mixture of NaCl-KCl salt improved its ability to strip the oxide film. However, other forms of fluorides such as KF and Na_3AlF_6 (Cryolite) by other researches showed to have even much better efficiency than NaF (see fig. 1) [8]. Figure 2.19 illustrates the effect of different fluoride additives to the recycling salt in a UBC (used beverage cans) process, showing that 2 wt% of fluorides in the flux is sufficient to increase the recovery yield by at least 5% and also that the fluoride efficiency grows in the following sequence: $CaF_2<NaF<Na_3AlF_6<KF$.

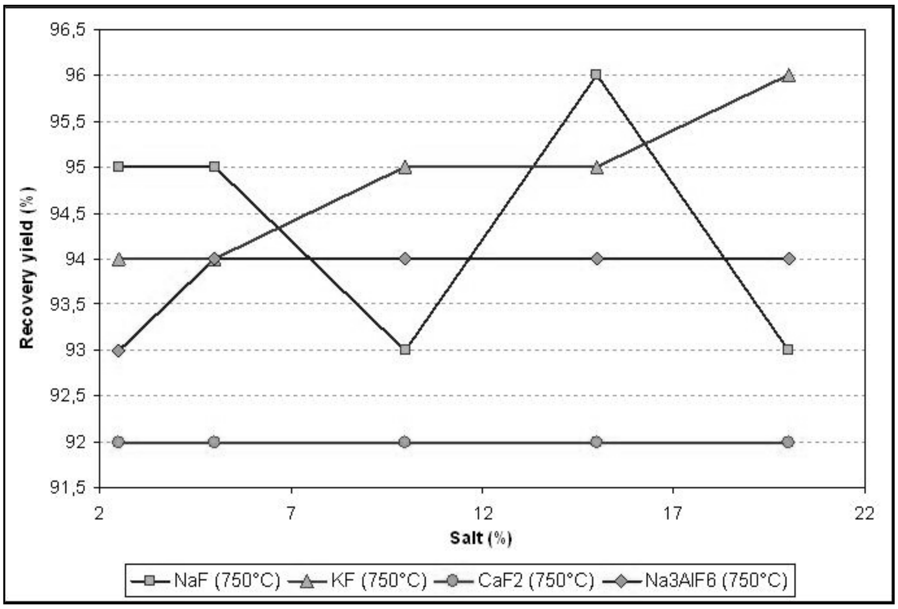


Figure 1: Effect of fluoride addition on the aluminum recovery yield of UBC recycling (NaCl/KCl + XF) [8]

At fluoride concentrations greater than 10 Mol%, the drop in flux-aluminum interfacial tension was roughly the same for NaF and KF and approximately twice the decrease obtained via LiF and Cryolite. But generally, the salts especially those containing fluorides can destroy and remove strong and dense oxide skins from molten aluminum alloys, which can then freely coalesce. Though, that can be provided up to 10% oxide concentrations, at higher concentrations some forms of mechanical agitation are also required because the coalescence is extremely impaired due to the viscosity changes [6].

Similar to the process of magnesium recycling, a considerable loss of metal during the melting processing of Al- UBC is observed too, due to metal entrapment in the dross. This is a heterogeneous system composed of aluminum oxide, solid phase, liquid aluminum and impurities. This system is able to hold the metallic aluminum by interfacial tension effects and hence causes a fall in the recovery yield [8]. According to Stewart [9] other phases such as Al_2O_3, AlN, AlC, MgF_2, $NaAlCl_4$, SiO_2, $MgO.Al_2O_3$ and the salt compounds can be also present in the dross. It has been seen that the existence of magnesium promotes the spinel formation and therefore, the probability of dross formation. So the low yield of UBC recycling process can be affected by Mg-concentration in the alloy or high concentration of the spinel in the dross.

A variety of researches have been already published related to the optimization of salt composition in the recycling process of aluminum. As flux is used to break up the dross structure, releasing the aluminum and promoting the coalescence of Al-drops, the optimized chemical composition is of great importance. Although fluxes are used frequently in dross treatment as well as in UBCs processes, there is little information about salt-dross interactions available in the literature [8]. Tenorio [10] suggested however, that the behavior between molten salt and aluminum dross is similar to the hot corrosion process. Here a metal that develops a protective oxide layer is submitted to an atmosphere containing chlorides and then the concentration of chlorides increases near or at the interface between oxide and metal and causes a weakness in the mechanical stability of the oxide layer. Maason and Taghiei [11] stated that the coalescence of aluminum drops inside the salt layer is affected by the appearance of an intermediate phase. It contains $KMgF_3$ or K_2NaAl_6 on the interface between the salt and the aluminum drops, which remains solid and in the operational conditions this causes an additional complexity for the aluminum coalescence process. Roy and Sahai [2] proved that without any additives, the equimolar NaCl-KCl salt flux required much longer time for the drops to coalesce into one metal droplet. Figure 2 shows the progress of coalescence of UBC drops as a function of time. That can be compared with the results after addition of 5 mass% AlF_3 as well as 5 mass% CaF_2, representing much higher coagulation velocity in fig. 3.

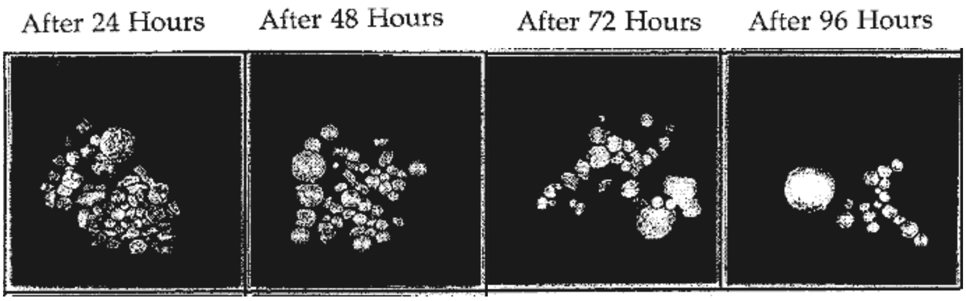


Figure 2: Coalescence of aluminum drops in equimolar NaCl-KCl [2]

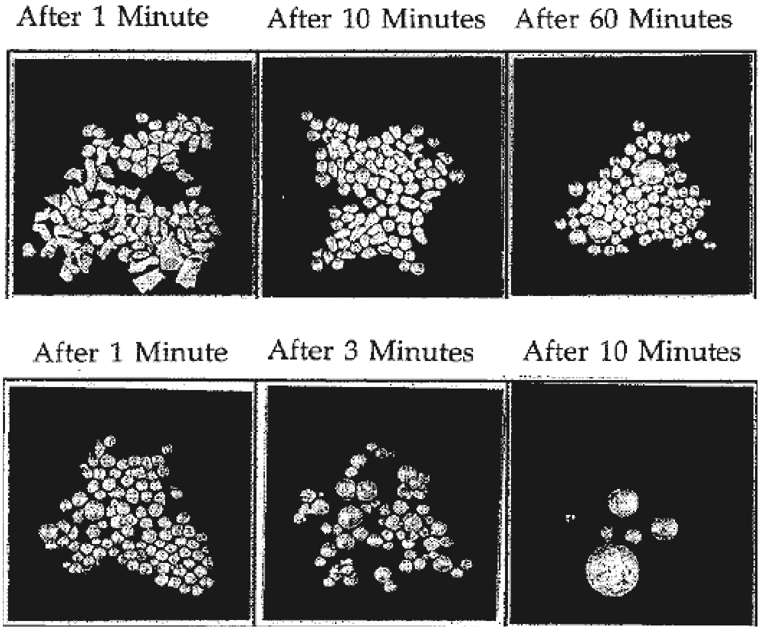


Figure 3: Coalescence of UBC drops in NaCl-KCl-5 mass% AlF_3 (upper) and in NaCl-KCl-5 mass% CaF_2 (lower) [2]

Chloride addition: the chloride salts do not improve the separation of the oxide film from the droplet and promote coalescence. Additions of the chloride salts generally lower the freezing point of the salt flux, which can be a useful property in some circumstances. Unfortunately, some of the chloride salts are hygroscopic such as LiCl and $AlCl_3$. This property can cause problems when the salts are added to molten flux or if the added salts convey dissolved water into the molten salt where it can react with the aluminum or magnesium forming hydrogen gas. More strongly-hydrated salts such as $MgCl_2$ and LiCl may retain their associated water in the melt by simple dissolution or by hydrolyzing through such a reaction as:

$$LiCl + H_2O \rightarrow LiOH + HCl \qquad (1)$$

The hydroxide compound may react further with other salt species or the metal. White precipitates formed with the LiCl addition and may have prevented direct contact between aluminium droplets and salt. By displacing these precipitates using agitation, coalescence occurred [4, 12].

Fluoride addition: in general, all fluoride salts seem to aid coalescence to some extent. Apparently, the presence of the fluoride ion in the molten salt helps to strip away the oxide film on the aluminum and magnesium droplets. Not all of the fluoride salts are readily soluble in the NaCl-KCl system so the extent of their effect can be limited; examples of this would be CaF_2 and MgF_2. The degree to which the fluoride salts promote coalescence, as well as the speed at which they complete the coalescence process, can be subdivided into three categories: Superior, Good, and Moderate. Friesn et al. [4] showed that the "Superior" additives KF, NaF and Na_3AlF_6 all had completed or near completed coalescence in less than 1 second (at 5 wt%), in which the droplet spun violently for 5-50 seconds. As the fluoride dropped into the flux, the reaction occurred and the droplet continued to spin until all of the fluoride dissolved. The next lower level of effectiveness, "Good," consists of LiF and AlF_3. They promote moderate to complete coalescence, but require a longer time interval of up to seven seconds. The "Moderate" group of salts including MgF_2 and CaF_2 has just fair effect on coalescence that takes up to 14 seconds times. It is though important to notice that this classification is related to Aluminum recycling.

On the other hand, Van Linden et al. [6] showed in fig. 4 the results of the fluoride evaluation program. It is clear from this figure that recovery was very high in all cases. It is assumed this is due to the use of the high salt/scrap ratio and the resulting dilute oxide/flux slurry. It is assumed too that the oxide concentration in the molten flux and the effect of oxide concentration on viscosity affect recovery more strongly than fluoride type or concentration.

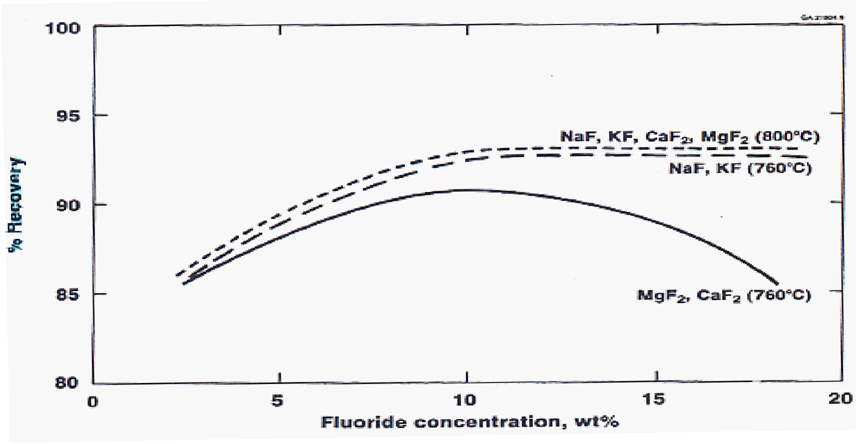


Figure 4: Effect of fluoride concentration and temperature on direct recovery [6]

Fluoride salt additions in salt fluxes increase the metal yield by decreasing suspension of 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 salt. The mechanism of the effect of CaF_2 and other fluoride salts is still not clear and almost not investigated for magnesium. Possibly fluoride salts dissociate in molten salt fluxes and produce free fluoride ions, which act as a surface active component of the salt flux [13]. The NaCl-KCl salt could not remove the thick oxide film formed by the pre-oxidation of metal on any of alloys. The addition of fluoride to the NaCl-KCl salt improved its ability to strip the oxide film. The oxide films on all alloys were easily removed by the salt containing fluoride (see fig. 5) [5]. Also, the fluoride compounds generally are neither hydrated nor hygroscopic so that water entering the salt flux is not a problem. However, the fluoride salts are not as useful as chlorides in lowering the melting point of the salt fluxes [6,14].

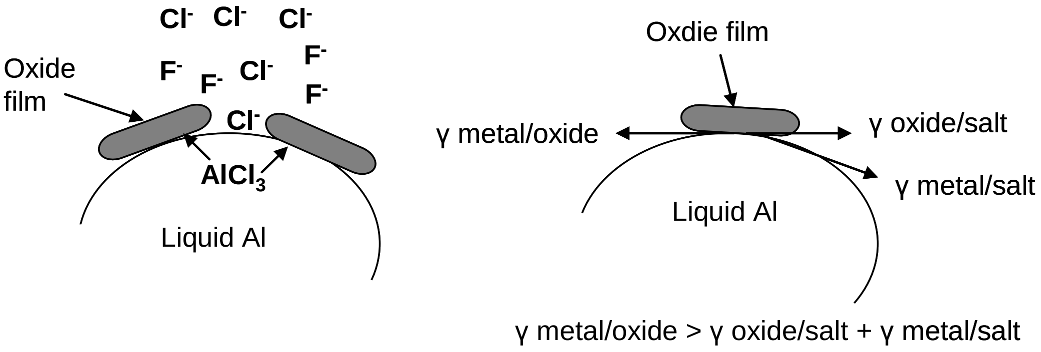


Figure 5: Mechanism of oxide film removal from the metal surface by molten salts [5]

Fluoride addition decreases the interfacial tension between molten salt and aluminum. Ho and Sahai [12] have successfully used the drop weight method to measure the interfacial tension of molten aluminium alloy. Interfacial tension between pure aluminium and equimolar KCl-NaCl salt at 740°C was found to be approx. 710 dyn/cm. From figure 6 it can be seen that all fluorides as well as $MgCl_2$ addition decreased the interfacial tension between aluminium and the equimolar KCl-NaCl salt. The interfacial tensions could be influenced by metal atom adsorption on the metal/salt interface, surface tension of the salt melt as well as mass transport taking place on the metal surface [12].

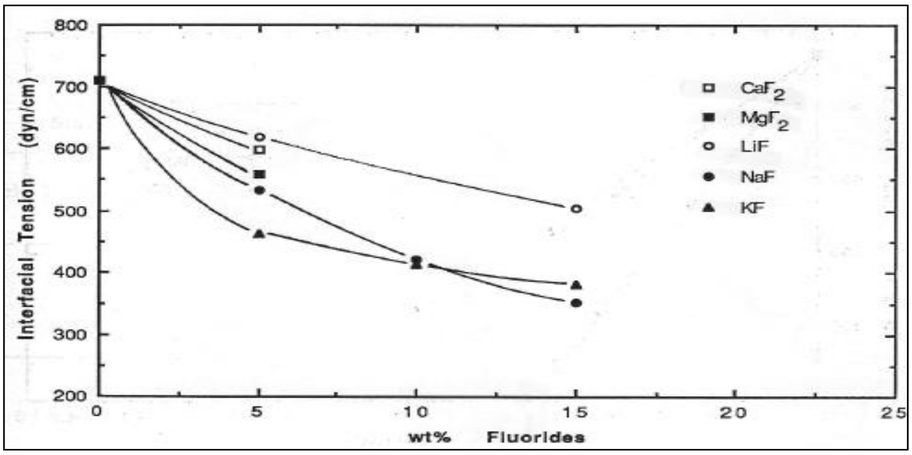


Figure 6: Variation of aluminium/ equimolar KCl-NaCl salt interfacial tension as a function of LiF, NaF, CaF_2, MgF_2 or KF additions at 740°C [12,15]

The effect of metal halide additions on lowering the interfacial tension can be used to evaluate a salt's power in removing the oxide films from the metal drops. Addition of halides, with the exception of $MgCl_2$, decreased the interfacial tension in pure aluminum cases. This decrease of interfacial tension could be caused by adsorption of low surface tension atoms on the aluminum surface. For interfacial tension between pure aluminum and salt, this effect decreases in the following order: $KF > NaF > MgF_2 > CaF_2 > LiF > Na_3AlF_6 > AlF_3$ [12].

Thermochemical calculations showed that all alkali and alkali-earth fluorides additions to the NaCl-KCl mixture recycling salt in aluminum process lead to the formation of NaF in the flux, which causes Al-saturation with sodium. The experimental investigations confirmed this [16]. That means, in spite of the necessity of fluoride additions to the recycling flux to increase the coalescence efficiency as well as decrease the viscosity of the flux, the contamination of Al with sodium - as a negative effect - can not be avoided. In contrast, the addition of AlF_3 reduces effectively the content of sodium in aluminum and has been seen to act (beside to other aluminum fluoride containing salts such as $NaAlF_4$ and Na_3AlF_6) as the best coalescing agents of all the other salts tested as additives in aluminum salt fluxes. The coalescence times have been rapid and the yield high [14]. However, AlF_3 is very expensive [16]. Surprisingly, Sahai [5,2] found the effect of AlF_3 addition just as moderate, in comparison with NaF, KF, LiF and CaF_2 with excellent influences. On the other hand, it has been proved that the sodium contamination may be neutralized by adding $MgCl_2$ through the following reactions [16,17], while the magnesium content in aluminum remains absolutely unchanged. Most interesting is the reaction (4), where cheaper components can produce expensive and effective refining additions.

$$2NaF + MgCl_2 = MgF_2 + 2NaCl \tag{2}$$

$$2Na_3AlF_6 + 3MgCl_2 = 3MgF_2 + 2AlF_3 + 6NaCl \tag{3}$$

$$2NaAlF_4 + MgCl_2 = MgF_2 + 2AlF_3 + 2NaCl \tag{4}$$

In most of articles it is seen that during recycling chlorides and fluorides are used as salt flux mixture. It is also seen that fluorides have a better effect during these remelting processes [5,10,18,19].

The biggest challenge in the investigation of magnesium coalescence is the selection of the most appropriate coagulation methodology, in contrast to the case of aluminum coalescence, where a variety of measuring methods has been already published. Roy and Sahai [2] took a quartz crucible with round bottom for melting of salt flux and to insure that metal chips were in contact inside the molten salt. In figure 7 the schematic design of coalescence experiment based on Roy’s method has been illustrated. They took 100 Al- or UBC-chips weighing approx. 2 g as charge in about 20 g molten salt. In these series of experiments an equimolar NaCl-KCl with 5 mass% different additives was charged as salt flux. The molten salt was then solidified after specific time intervals, varied between some minutes to several hours. Salts were afterwards leached and the numbers of coagulated drops were counted and taken as a factor of coalescence behavior of that salt.

Sydykov [13,20] after reaching the required temperature in the furnace and melting the salt, previously prepared 200 aluminum particles (globules or plates) were introduced into the crucible with 5 g of molten salt flux within 5 seconds by means of a quartz tube (inside diameter 8mm). The number of charged particles was chosen in order to bring all of them in contact at the bottom of the crucible. After a given coalescence time, the crucible was carefully taken out from the furnace and then the crucible content was leached with water (see fig. 8).

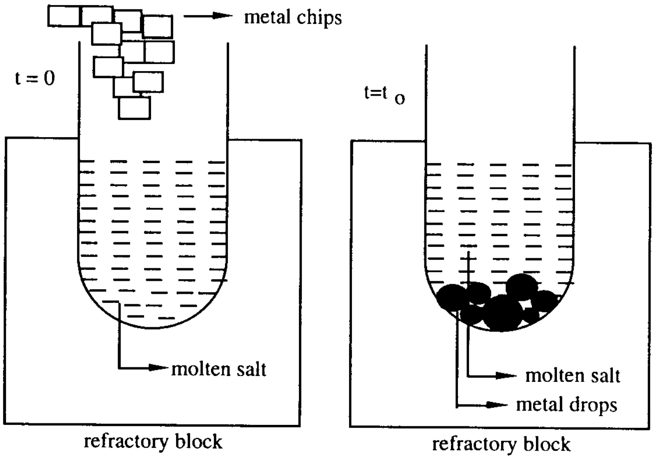


Figure 7: Schematic of coalescence experiment based on Roy's method [2]

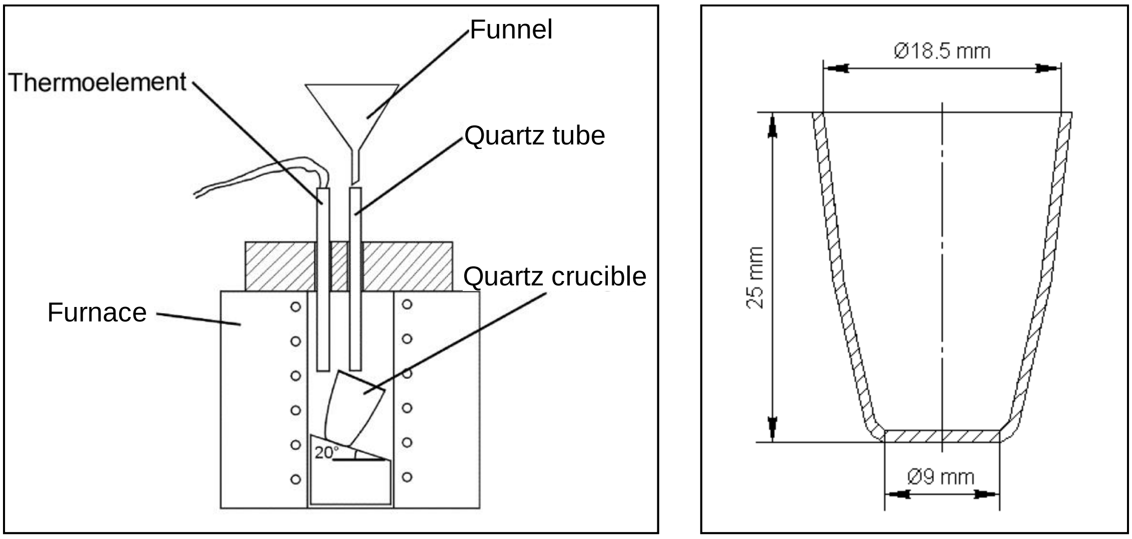


Figure 8: Experimental set-up (left) and quartz crucible (right) for coalescence tests [13,20]

2 Experiments

2.1 Setup

The coalescence experiments took place in a graphite crucible and in a GERO resistance furnace (see fig. 9 and 10). As during the experiments the temperature had to be measured outside of the crucible - in order not to disturb the coagulation effects -the temperature was calibrated to determine the difference equation between the temperature inside and outside of the crucible. Two thermocouples were prepared and they were connected to a computer to measure the temperatures of the thermocouples and all data were saved. The relation between $T_{(Inside)}$ and $T_{(outside)}$ was then calculated; i.e, for keeping the temperature at 750°C, the difference is approx. 5°C.

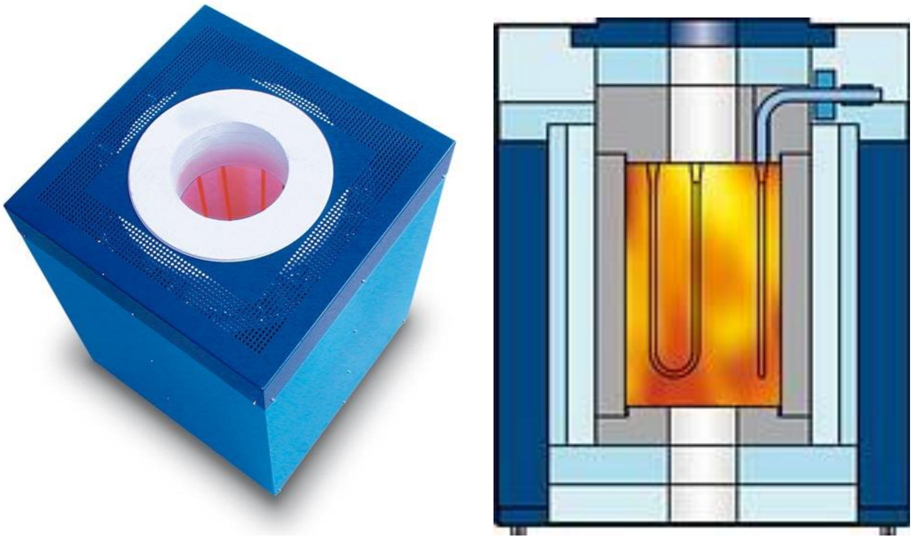


Figure 9: GERO resistance furnace (max. 1700°C) with a vertical tube chamber applied for coalescence experiments

Figure 10: (left) schematic graphite crucible inside the furnace containing Mg-chippings surrounded by two layers of salt mixture and (right) the alumina crucible used for coalescence trials

2.2 Synthesizing of magnesium scrap

As no standard method for magnesium coalescence has ever been published, a new coagulation methodology was developed in this work, based on using magnesium chippings covered with powdery salt flux in a closed crucible. This method avoids the use of magnesium thin sheets as well as their contact with oxygen at operational temperatures.

For these experiments, magnesium chippings were produced through drilling into a block of AZ31 magnesium alloy (see fig. 11 different forms of chippings) and are classified in four sizes. The diagram in figure 12 illustrates the distribution of these different sizes from the point of number and weight percentages. It shows that in approx. 662 pieces of chippings; equal to about seven grams, the two “smaller” types of chippings have the majority.

Figure 11: Different chipping sizes distributed in magnesium chippings

In the experiments best effort was taken to charge identical magnesium scrap with respect to size, morphology and weight for coalescence experiments; therefore, such scraps were fabricated artificially. Before each individual test, magnesium chippings were inserted in boiling water for 10 minutes to be cleaned from the contaminations and to form oxide/hydroxide surface layers, then dried and held in a furnace at 200°C for 16 hours in order to strengthen the surface layers as well as improve and accelerate the aging process. After this procedure, the chippings were used directly in coagulation experiments without using any sample stock. Figure 13 illustrates the SEM/EDX analysis of chippings after the above mentioned scraping process, containing a thin layer of oxide on the surface of those chippings.

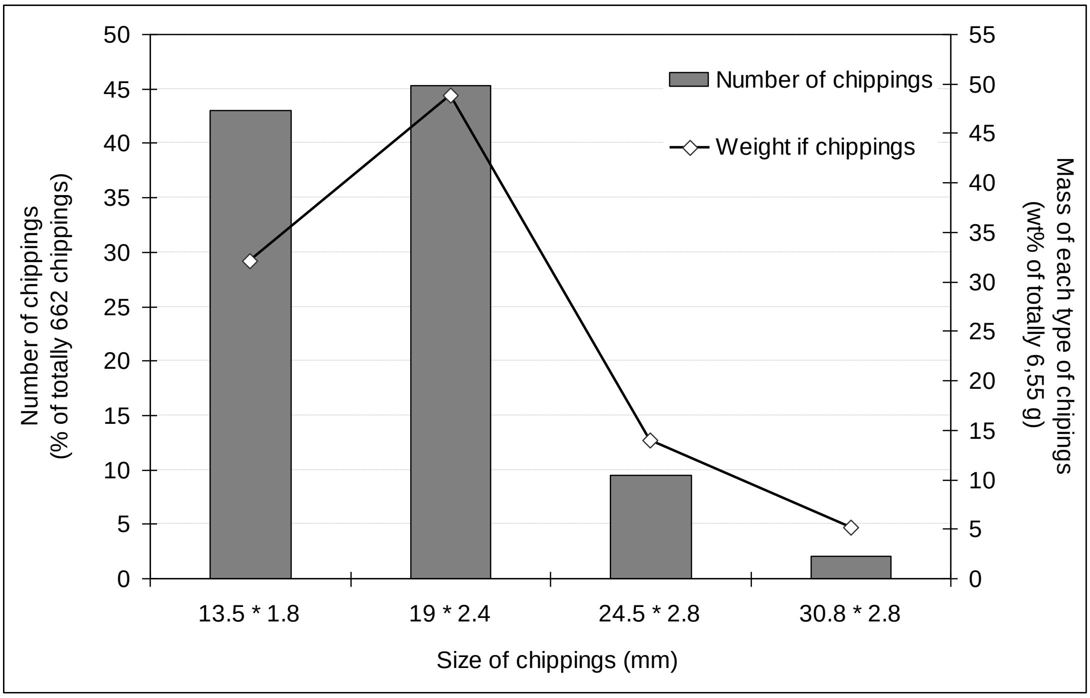


Figure 12: Distribution of chipping sizes, numbers and weight in approx. seven gram of chippings

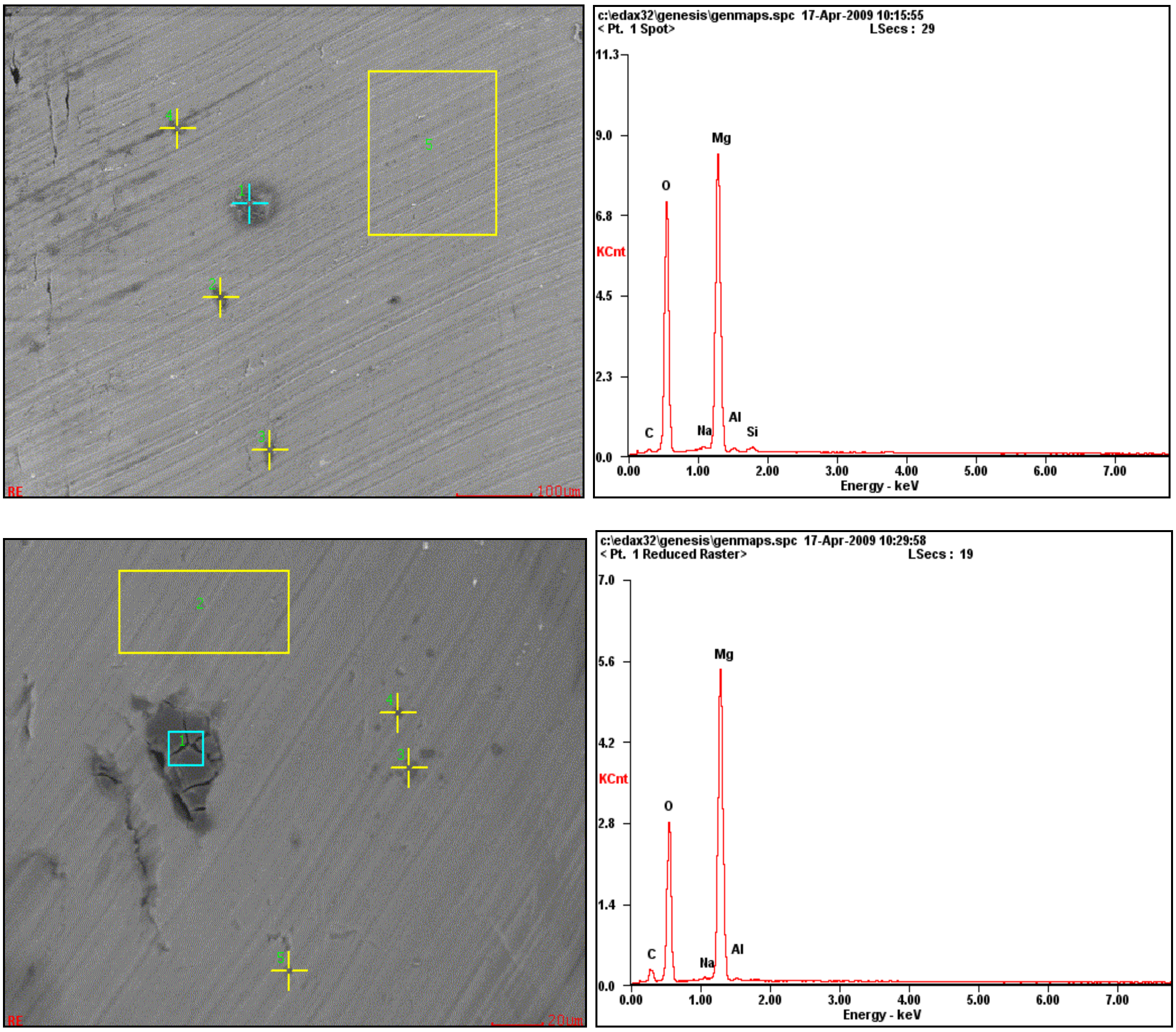


Figure 13: Exemplary SEM pictures as well as EDX-patterns of Mg-chippings after an artificial aging procedure at 200°C for 16 hours

2.3 Preparation metal and salt mixture in the crucible

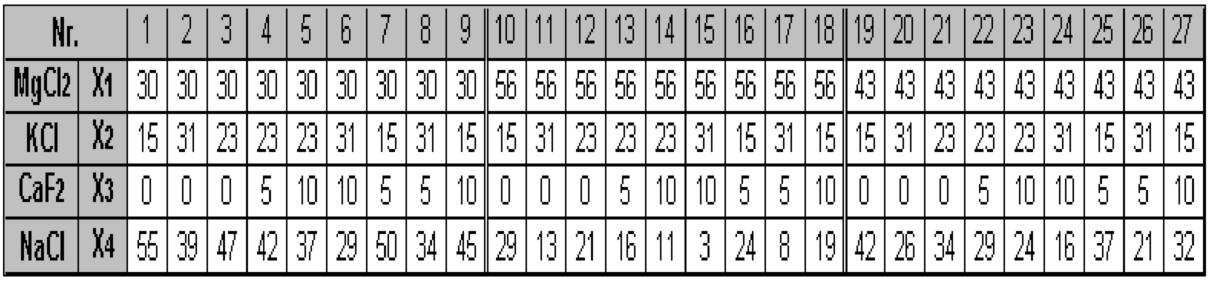
The coagulation experiments took place in a small graphite crucible and in a resistance furnace (see fig. 10) at 750°C. Firstly four times as much salt as the volume of magnesium was prepared according to calculated densities (see later in table 2), assuming that this volume could lead to a complete surrounding of magnesium droplets after melting by molten salt. 20% of the whole salt mixture was placed on the bottom of the crucible, then seven grams of magnesium chippings, being less than 19mm as length were added to the crucible and afterwards the rest (80% of the salt) at the top, over the Mg-chippings to improve the surrounding effect more efficiently as well as to protect magnesium from atmosphere directly after remelting. Additionally refractory is placed on the crucible to avoid the evaporation. Although the coalescence process did not occur in a vacuum system and the existing of oxygen in the furnace/ crucible was inevitable, such preparations lead to a quite similar atmosphere and process conditions for all experiments and make them comparable enough for further considerations.

In this procedure there are three heating stages, heating, holding and cooling. In heating stage, the prepared crucible is placed into the furnace and waited for the crucible to reach 750°C. After holding time of 30 min. finishes, the crucible is taken out and inserted into a bucket of copper chippings for faster cooling. The cooling takes about half an hour long. After cooling, salt and magnesium are taken out from the crucible, crushed a little bit with a pestle in a mortar to separate the solidified salt from magnesium coagulated balls and then classified through sieving. The crushing in the mortar in essential, because magnesium particles can't be washed due to the high oxidation rate. There are three sieves used in this classifying, so the materials are separated in four sizes. These four sizes are >1.6mm, 0.8-1.6mm, 0.4-0.8mm and <0.4mm. The fine fraction represents only salt, >1.6mm and >0.8mm are only magnesium and 0.4-0.8mm particles are half salt and half metal. Magnesium particles can't be washed because of high oxidation rate and that's why the salt is minified with pestle. Then the different sizes are put into evacuated plastic boxes.

2.4 Methodology for optimizing the magnesium salt flux composition

The salt fluxes investigated in this work, are chosen based on the chemical composition of common used fluxes in magnesium recycling processes. They include $MgCl_2$, KCl, NaCl, and CaF_2. A matrix of 27 different salt mixtures is defined through the "statistical design of experiments" and using the "Full-Factorial" method (equation 3^{n-1}, where n is the number of salt combinations). Table 1 shows the matrix of the resulting mixtures, in which the values of $MgCl_2$, CaF_2 and KCl are varied and NaCl represents the difference to 100%. The salt mixtures mentioned in this table are firstly investigated with respect to melting temperature via FactSage^{TM} thermochemical calculations as well as Differential Thermal Analysing method (DTA). These measurements showed that the salt mixtures 1-3, 10-22 and 25-26 (totally 23 mixtures) have acceptable melting points between 374-716°C. The DTA analysis of an exemplary salt Nr. 25 shows in figure 14 a liquidus temperature of about 687°C, a solidus of about 425°C, the evaporated moist mass at 100°C as well as partial deterioration of crystallisation water at approx. 230°C.

Table 1: Matrix of different salt mixtures prepared for the coagulation investigation



Nr.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
$MgCl_2$	X_1	30	30	30	30	30	30	30	30	30	56	56	56	56	56	56	56	56	56	43	43	43	43	43	43	43	43	43
KCl	X_2	15	31	23	23	23	31	15	31	15	15	31	23	23	23	31	15	31	15	15	31	23	23	23	31	15	31	15
CaF_2	X_3	0	0	0	5	10	10	5	5	10	0	0	0	5	10	10	5	5	10	0	0	0	5	10	10	5	5	10
NaCl	X_4	55	39	47	42	37	29	50	34	45	29	13	21	16	11	3	24	8	19	42	26	34	29	24	16	37	21	32

Mixtures with higher liquidus than 716°C can never be used in a magnesium process and are omitted. For the coalescence trials only 18 mixtures are taken to be investigated. The reason of ignoring further 5 salt mixtures (Nr. 2,12,13,15 and 20) was that their chemical compositions could be quite close to other mixtures; therefore, not a significant difference is there to be expected. Such similarities between chemical compositions of salt mixtures developed via SDE method are normally not avoidable. On the other hand, the initially planned three different fluorine contents (zero, five and 10 wt%) are decided not be sufficient for consideration the role of fluorine-containing components during the test work; hence, the steps for CaF_2 is changed to investigate the effect of fluorine more clearly. Finally, thirteen different salt mixtures are remained and tested (Table 2).

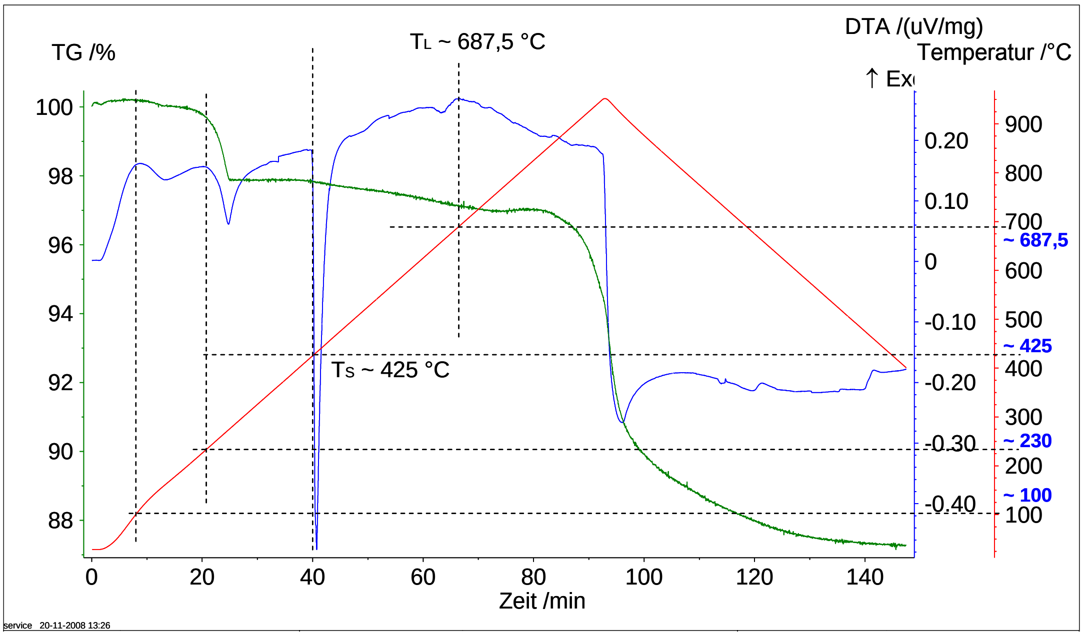


Figure 14: DTA analysis of salt mixture Nr. 25 showing exemplary a liquidus temperature of about 687°C, a solidus of about 425°C, the evaporated moist mass at 100°C as well as partial deterioration of crystallisation water at approx. 230°C

Table 2: Final matrix of salt mixtures applied for experiments, including the density values for each of them and mass of each salt required for coalescence tests

Salt Nr.	$MgCl_2$	KCl	CaF_2	NaCl	Density (g/cm^3) at 750°C	M_{salt} (g)
1	30	15	0	55	1.60	25.776
3	30	23	1	46	1.59	25.702
10	56	15	0	29	1.62	26.13
11	56	31	0	13	1.62	26.018
14	56	23	10	11	1.74	27.9966
16	56	15	5	24	1.70	27.095
17	56	31	5	8	1.68	26.966
18	56	15	10	19	1.74	28.044
19	43	15	2	40	1.64	26.339
20	43	31	3.5	22.5	1.65	26.516
21	43	23	6.5	27.5	1.68	27.143
22	43	23	8	26	1.70	27.433
25	43	15	5	37	1.67	26.918

After this series, in order to investigate the influence of the type of fluorine-bearing components on coalescence efficiency, different fluorides are tested (KF, LiF, NaF, and MgF_2) replacing with 2 wt% fluoride in salt Nr. 19 resp. with 5 wt% fluoride in salt Nr. 16 (see table 3).

Table 3: Salt Nr. 19 and Nr. 16 with alternative fluoride components and the calculated density at 750°C

$MgCl_2$	KCl	Fluoride 2%	NaCl	Density (g/cm^3) at 750°C	M_{salt} (g)
43.0	15.0	CaF_2	40.0	1.64	26.34
43.0	15.0	NaF	40.0	1.62	26.11
43.0	15.0	LiF	40.0	1.62	26.05
43.0	15.0	MgF_2	40.0	1.64	26.31
43.0	15.0	KF	40.0	1.62	26.08
$MgCl_2$	KCl	Fluoride 5%	NaCl	Density (g/cm^3) at 750°C	M_{salt} (g)
56.0	15.0	CaF_2	24.0	1,70	27,40
56.0	15.0	NaF	24.0	1,65	26,60
56.0	15.0	LiF	24.0	1,64	26,44
56.0	15.0	MgF_2	24.0	1,68	27,08

3 Results and discussion

3.1 Effect of contact period between salt and metal

Pre-tests revealed that coagulation occurs mostly with smaller sizes of the chippings, used as artificial scrap in all experiments (fig. 15). That could be due to interfacial tension effects, which need to be much larger for bigger chippings involving the stronger binding between molten salt and magnesium droplets, so they do not coagulate effectively. Hence, two of the smaller types of chippings were applied in the experiments.

In most of the published methodologies for measuring coalescence of aluminium drops [2,13,4], the metal is manufactured in the form of chips and then be immersed into the molten salt. In such cases each chip begins to form a single drop immediately and single drops are coagulated together forming bigger drops/spheres. Therefore, even after one minute a fairly moderate coalescence is observable. That’s why in most of the above mentioned publications, the dwelling time factor is studied from 1-2 minutes to some hours. In opposition to those methods, magnesium chips can not be given directly into a molten salt bath, otherwise they will be oxidized immediately on the surface. In the developed coalescence methodology a period of some minutes is not sufficient for magnesium chippings to be coagulated. Hence, in these series of experiments the dwelling time begins with 30 minutes.

Figure 16 illustrates the effect of contact time between Mg-chippings and salt (in this case Nr. 16) on the coalescence of metallic droplets by weight and diameter of the coagulated droplets. It shows that the fraction of coagulated droplet with a diameter bigger than 15mm is being grown when the contact time rises from 30 to 60 minutes. The ratio of magnesium spheres coagulated to sizes >5.6mm at different retention times is shown in figure 17. The coagulation efficiency is calculated as the weight ratio between the weight of the coagulated droplet and the total “metallic” feedstock in percentage [21]. Furthermore, the total material loss (the sum of both metallic and salt) after coagulation test as well as the individual metal loss is shown in this figure too.

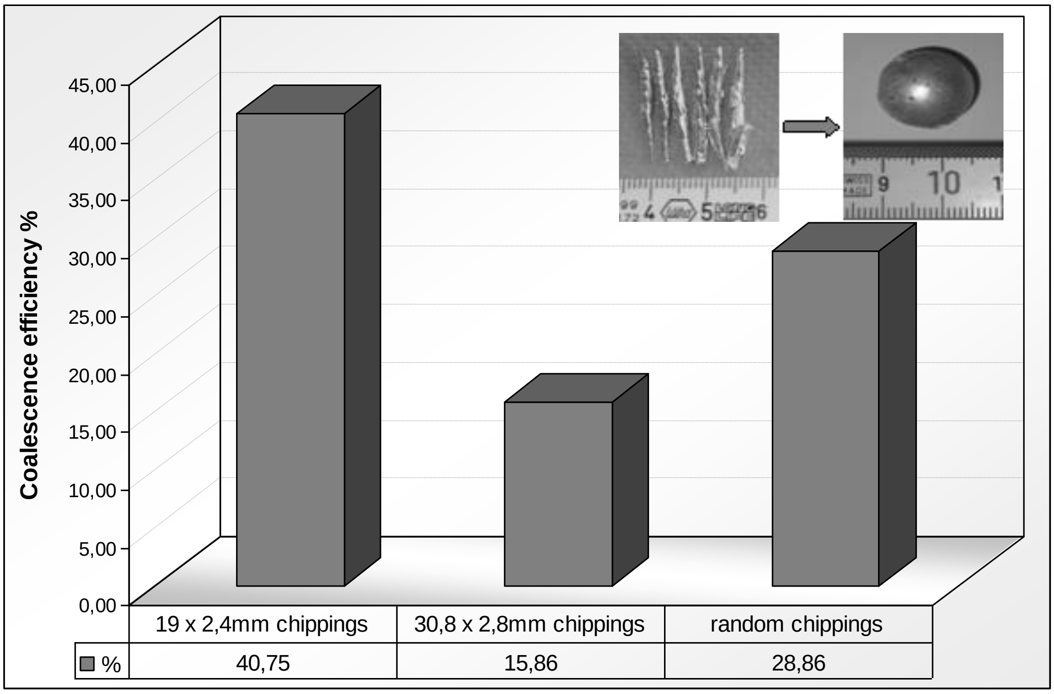


Figure 15: Effect of chipping size on coalescence efficiency

$$\text{Coalescence efficiency } (\%) = \frac{\text{coagulated droplets} > 5{,}6\text{ mm (g)}}{\text{metallic input (g)}} \times 100 \tag{5}$$

The terms of total material mass as well as metal mass can be explained as the following equations:

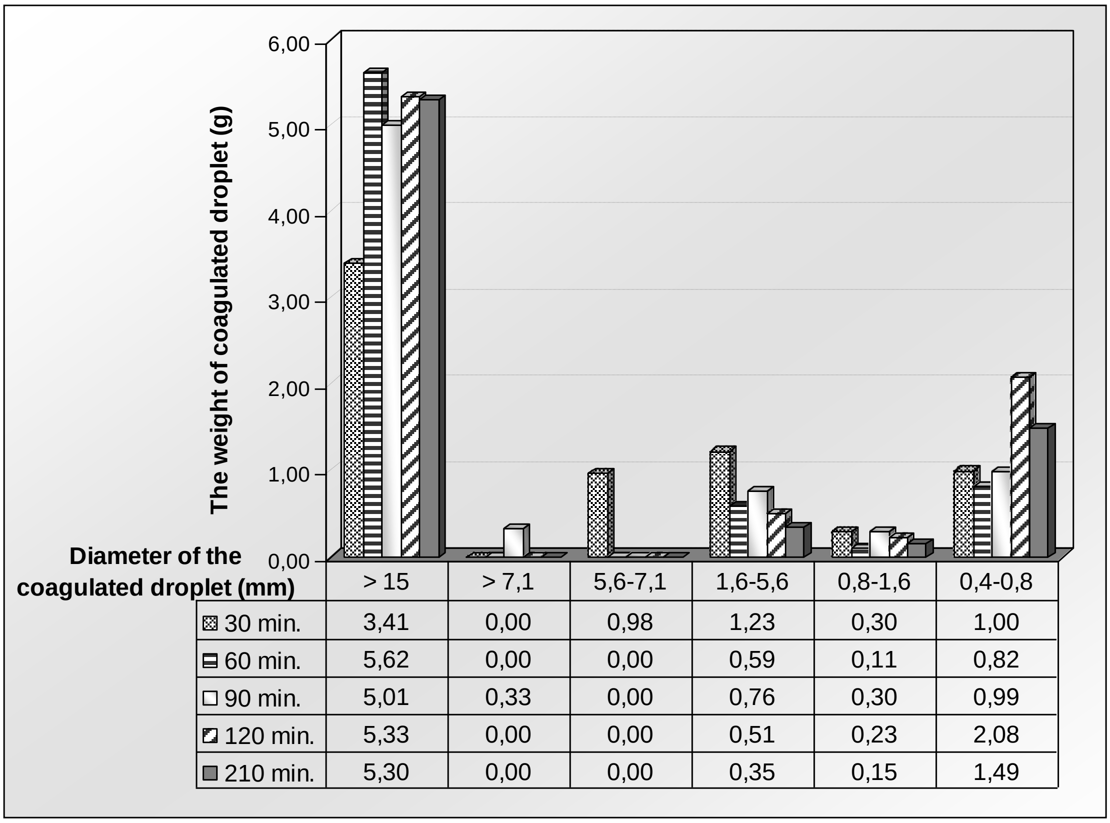
$$\text{Total material loss } (\%) = \frac{\text{input material - } \sum (\text{collected material after exp.})}{\text{input material}} \times 100 \tag{6}$$

$$\Rightarrow$$

$$\text{Total material loss } (\%) = \frac{(7\text{g Mg - chippings} + 27\text{g added salt}) \text{ - } \sum (\text{collected material after exp.})}{34} \times 100$$

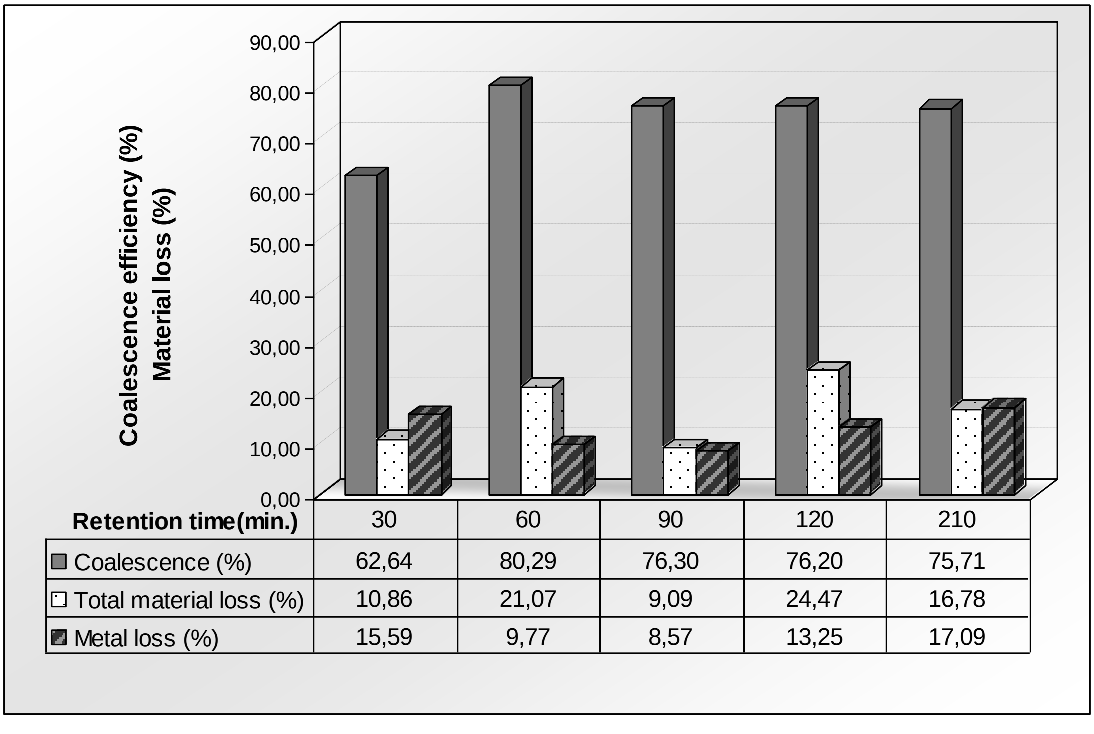
(7)

It is supposed that coalescence efficiency is a function of time depending on various additives present in salt flux. Within an increase of contact time from 30 to 60min., the degradation of oxide film from the surface of metallic magnesium droplets proceeds significantly. However, higher holding time (90min.) increases the risk of re-oxidation of coagulated particles; hence, the coalescence efficiency decreases. The metallic loss is virtually very difficult to be calculated, because the material fraction passed through the sieve with 0.4mm is mostly salt but contains also some amounts of fine magnesium, which can not be separated. Unfortunately and contrary to aluminium coalescence trials, this material can not be water leached and the exact value of metallic loss stays unknown. Though, the coalescence efficiency and the loss obtained in each retention time are as good as possible calculated and presented in figure 17. According to these experiments, 60min. is taken as the most optimum retention time and used for all coalescence investigations.



Diameter of the coagulated droplet (mm)	> 15	> 7,1	5,6-7,1	1,6-5,6	0,8-1,6	0,4-0,8
▩ 30 min.	3,41	0,00	0,98	1,23	0,30	1,00
☰ 60 min.	5,62	0,00	0,00	0,59	0,11	0,82
□ 90 min.	5,01	0,33	0,00	0,76	0,30	0,99
▨ 120 min.	5,33	0,00	0,00	0,51	0,23	2,08
■ 210 min.	5,30	0,00	0,00	0,35	0,15	1,49

Figure 16: Effect of contact time on the weight as well as the size of the coagulated droplet (test conducted with salt mixture Nr. 16)



Retention time(min.)	30	60	90	120	210
■ Coalescence (%)	62,64	80,29	76,30	76,20	75,71
□ Total material loss (%)	10,86	21,07	9,09	24,47	16,78
▨ Metal loss (%)	15,59	9,77	8,57	13,25	17,09

Figure 17: Coalescence efficiency and material loss at different retention times

3.2 The effect of chemical composition of salt flux

Figure 18 illustrates the coagulation results of melting magnesium chippings with different salt mixtures mentioned in table 2. Salt Nr.1 containing no CaF_2 and relatively little $MgCl_2$ shows the worse coagulation efficiency. Through addition of 3.5 wt% CaF_2 into the salt flux the coalescence efficiency is increased dramatically to more than 80%, showing the powerful influence of fluorspar in coagulation procedure. In the absence of CaF_2, the low coagulation efficiency can not be increased by adding $MgCl_2$ (case of salt Nr. 10), and if both $MgCl_2$ and KCl (case of salt Nr. 11 in Fig. 18 below) are added, the efficiency increases only up to 20 %.

It follows that without CaF_2 there is generally not a big chance for magnesium droplets to be coagulated; however, not only fluorspar but also the presence of chloride-containing components such as $MgCl_2$ and KCl is essential for the coagulation procedure. Without CaF_2 it is always seen that metal is mixed with salt and can't be separated, as it is not possible to wash the samples.

Figure 19 represents the influence of different quantities of fluorspar on coalescence efficiency of magnesium droplets. Its value rises significantly by addition of CaF_2 up to 5 wt%. This point, where three salt fluxes (Nr. 16, 17 and 25) with same CaF_2 but various amounts of $MgCl_2$ and KCl show quite similar effectiveness on coagulation, is the peak of this curve. At further addition of fluorspar up to 6.5 wt% an unexpected descent in coagulation is observed, very similar to the situation showed by Tenorio and Delgado [8] in the case of 10 wt% NaF-addition to NaCl-KCl salt flux in aluminium coalescence. Through addition of more fluorspar, the coalescence rises again but still without achieving the maximum peak. In presence of 10 wt% CaF_2 for two salt fluxes Nr. 14 and 18 (both including 56 wt% $MgCl_2$) the coagulation of magnesium droplets is quite similar, which can prove that in presence of highly enough fluorspar and magnesium chloride, the KCl doesn't play probably any big role in coagulation procedure.

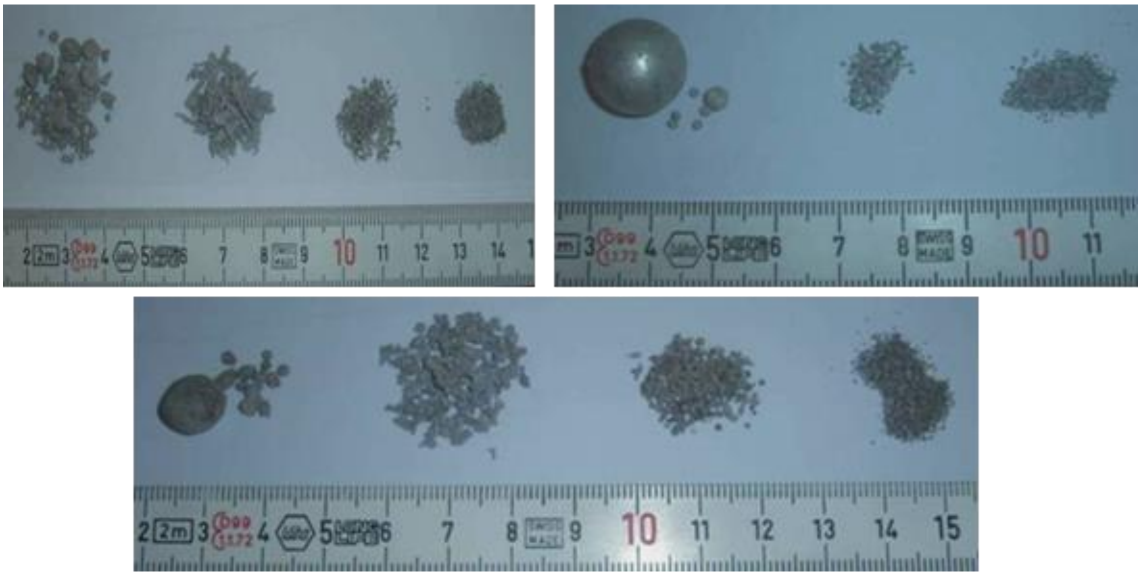


Figure 18: Low-efficiency coagulation of Mg-chippings through salt Nr. 1 (top left), efficiency of about 85 % after adding 3.5 wt% fluorspar by salt Nr. 20 (top right) and only minor yield after addition of $MgCl_2$ and KCl without fluorspar in salt Nr. 11 (below)

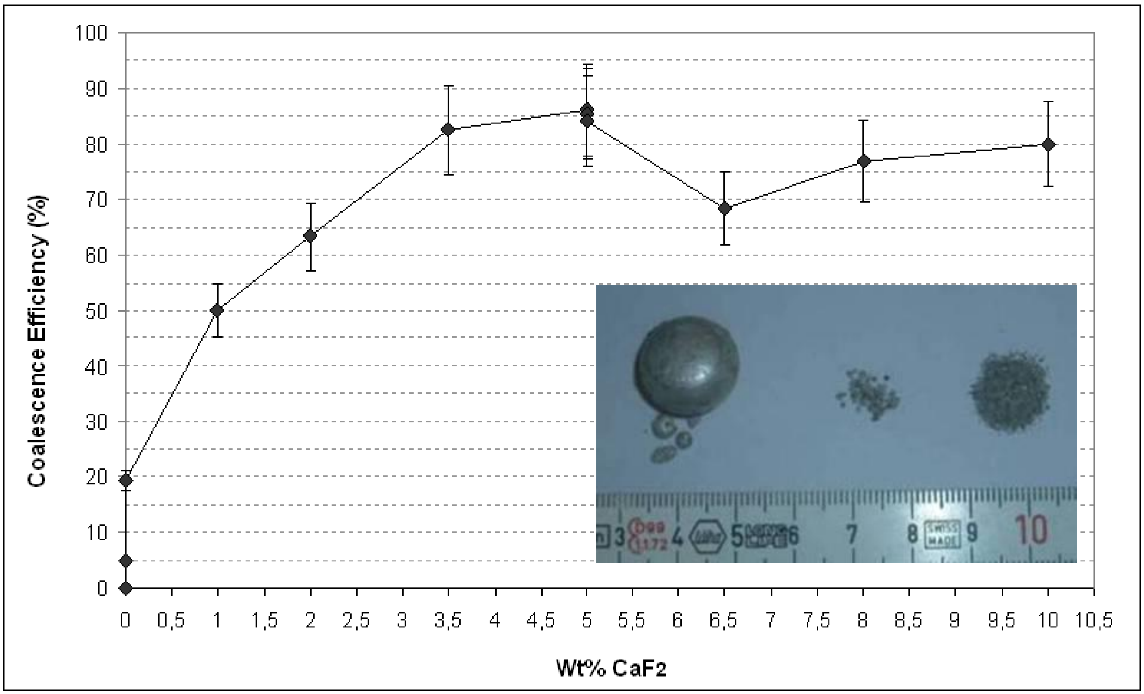


Figure 19: Coalescence efficiency versus the amount of CaF_2 present in the salt fluxes and the droplets achieved through usage of salt Nr. 16 with the best coalescence efficiency of approx. 86%

It is important to notice that dissolved fluoride ions can generally advance the oxide stripping as well as improve the coalescence competence. On the other hand, fluorides additions lead to an increase of surface tension of the chloride melts and decrease the interfacial tension effects between metal and salt, leading to metallic dispersion. As a result, the fluoride content should not be chosen higher than the soluble amount at the maximum processing temperature. Sydykov [22] showed that some fluoride consumptive reactions seem to take place during the melting of aluminium scraps. If this fact is considered and expanded in the case of magnesium too, the fluoride consumption should be also taken into account. That means, the very first interpretation about the results was that maybe the 6.5 wt% of CaF_2 meets exactly the point, in which such consumptive reactions overcome the addition of fluorides, so that the actual value of F-ion is even less than that of 5 wt%. But, this idea would be just true if the operational temperature or retention time for the test with 6.5% was different from the others. Therefore, it can’t be relevant in our case. The other interpretation - probably more close to the reality - is that through increasing the fluoride content to 6.5 wt% the dissolution limit has been exceeded; therefore, some undissolved fluorides has been remained, causing the increase of bath viscosity and deterioration of coalescence process. That means that 5 wt% fluorspar has an effect like “over saturation” and adding more CaF_2 causes some non-dissolved particles on the surface of magnesium droplets, which avoid these droplets to be coagulated together. Hence, the coalescence behaviour of salt fluxes by adding of more than 5 wt% CaF_2 becomes worse. However, the deviation percentage due to the repetition of the tests shows that even the highest efficiency value obtained for 6.5 wt% CaF_2 is still lower than that of 8 and 10 wt%.

To check the above mentioned interpretation, the solubility of CaF_2 in different system mixtures of $MgCl_2$-KCl-NaCl were calculated in FactSage^{TM} and illustrated in figure 20. The calculations proved that at the operational temperature in this work

(750°C) 6wt% CaF_2 in different weight percentages is soluble in chloride systems, with just one exception in the case of 30%$MgCl_2$-15%KCl-55%NaCl. However, the idea about the probability of existence of some insoluble CaF_2 in chloride systems, causing decreased coalescence efficiencies, can indeed be true when the amount of CaF_2 rises to 8-10wt%. In these portions even at higher temperatures some residues of insoluble CaF_2 remain inside the melt, which lead to a drop in coalescence in comparison with 5wt% CaF_2, observing in figure 20 too.

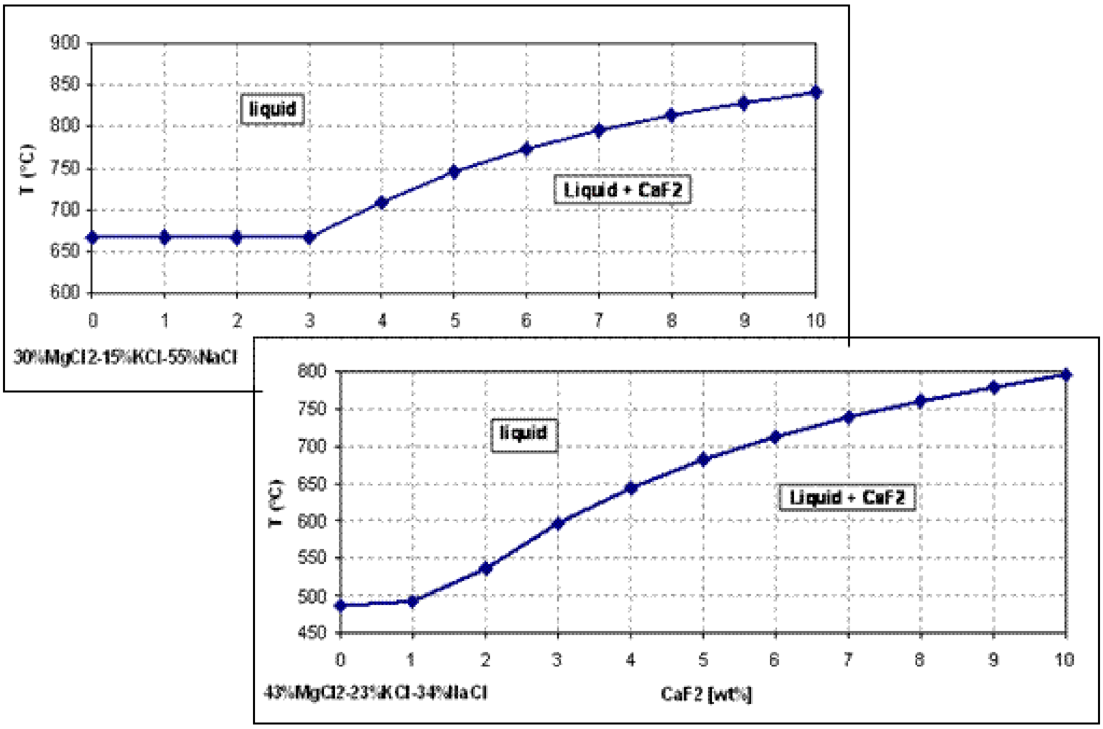


Figure 20: Solubility of CaF_2 in different systems of $MgCl_2$-KCl-NaCl calculated through FactSage^{TM}

In spider diagram (figure 21) the complex relation between KCl and $MgCl_2$ in salt fluxes and coalescence efficiency is illustrated. From the conducted series of experiments it can be supposed that coagulation of Mg droplets is rather independent from the quantity of KCl alone, as the value of KCl changes without any regularity and the coalescence efficiency (CE) does not show any relation with these changes. In the case of $MgCl_2$ a relation can be found for the salt fluxes Nr. 1 and 10, where more coagulation is achieved through higher additions. However, considering the salts Nr. 11 and 3, this relation is - in contrast – downward. Fluxes Nr. 14 and 18 have the same quantity of $MgCl_2$ as fluxes Nr. 16 and 17; though, the last two ones caused more coagulation. As a conclusion, neither $MgCl_2$ nor KCl alone has a significant influence on coalescence in comparison with CaF_2, whose increasing effect has been already discussed. However, it doesn't mean that the chloride-bearing components can not improve the coagulation behaviour of salt fluxes in magnesium processes, but it becomes clear that the presence of fluorspar is definitely essential if an optimum coagulation is desired.

Figure 22 correlates the major component concentrations of all investigated salt fluxes on Mg-coalescence efficiency. In this 3-dimensional diagram the results of figs. 19 and 21 are combined. This map is the distribution of coalescence efficiency as a dependant on the amount of fluorspar as well as chloride factor. It can be seen again that fluxes containing 5 wt% CaF_2 has the highest coagulation effectiveness. Also for fluxes with a high ratio of $MgCl_2/(KCl+NaCl)$ acceptable coagulation values can be reached, which proves again - as discussed before - the increasing effect of $MgCl_2$. From the resulted data it cannot be stated that the other salt components (KCl and NaCl) should be minimized to increase the coalescence, as according to flux 25 results this ratio is quite small, but the coagulation efficiency stayed in the highest level. Therefore, in the presence of 5 wt% fluorspar (as the most effective concentration), the influence of all other salt components seems to be very small; although, their presence is necessary to maintain a low viscous melt, a matrix for non-metallic inclusion collection as well as for avoiding Mg-losses by chemical reaction and air interaction. Such their amount shouldn't be too little.

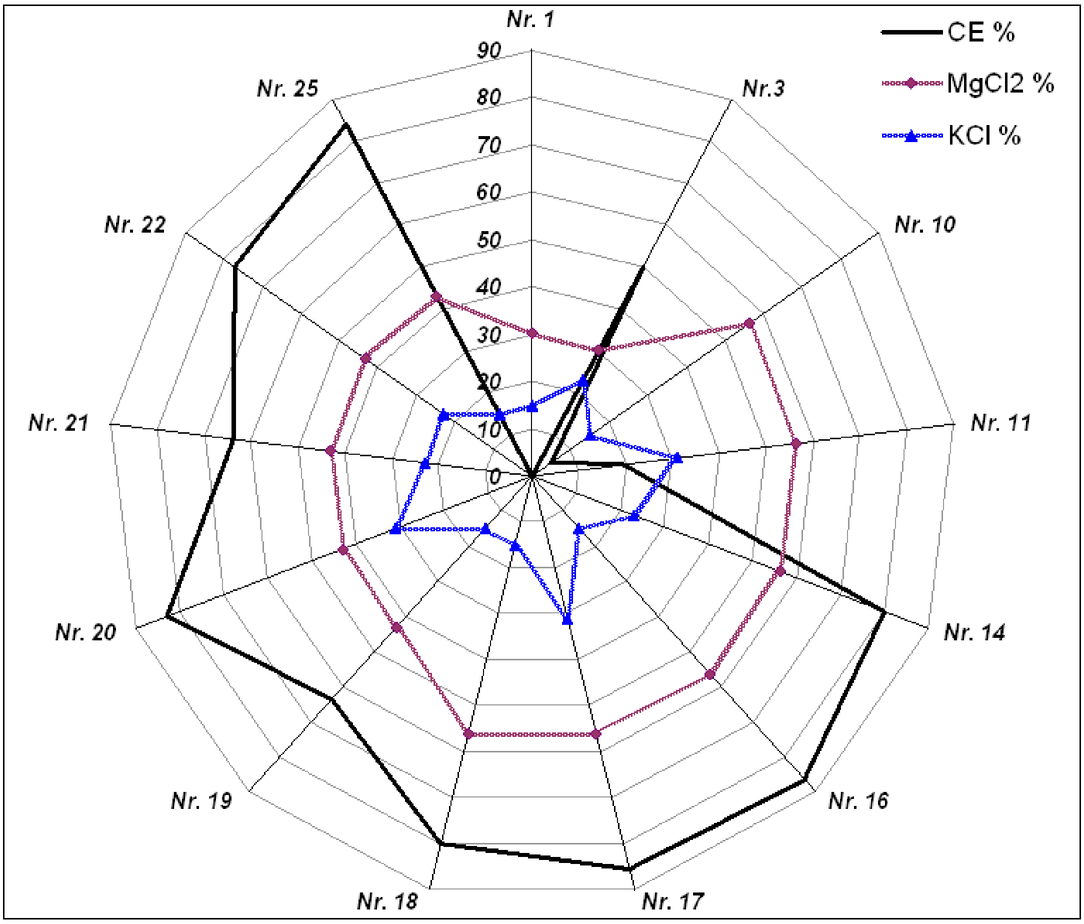


Figure 21: $MgCl_2$- and KCl-content as well as coalescence efficiency in salt mixtures Nr. 1-25 (according to table 3.5)

3.3 The effect of different fluorine compounds

The coagulated droplets achieved through addition of 2 wt% of different fluorides are illustrated in figure 23 and the influence of the used fluorine compound in the flux is represented in diagram 24. Lithium fluoride seems to have the biggest effect on coagulation of magnesium droplets. The coalescence behaviour is also improved if CaF_2 is replaced by KF. In the case of NaF addition less clear changes are observed comparable to CaF_2. The magnesium fluoride has the worse coagulation effectiveness. Nevertheless, taking the error bars into account, all differences are not clearly proven, the statistical maximum value of CaF_2 is for instance above the minimum values of LiF, KF and NaF.

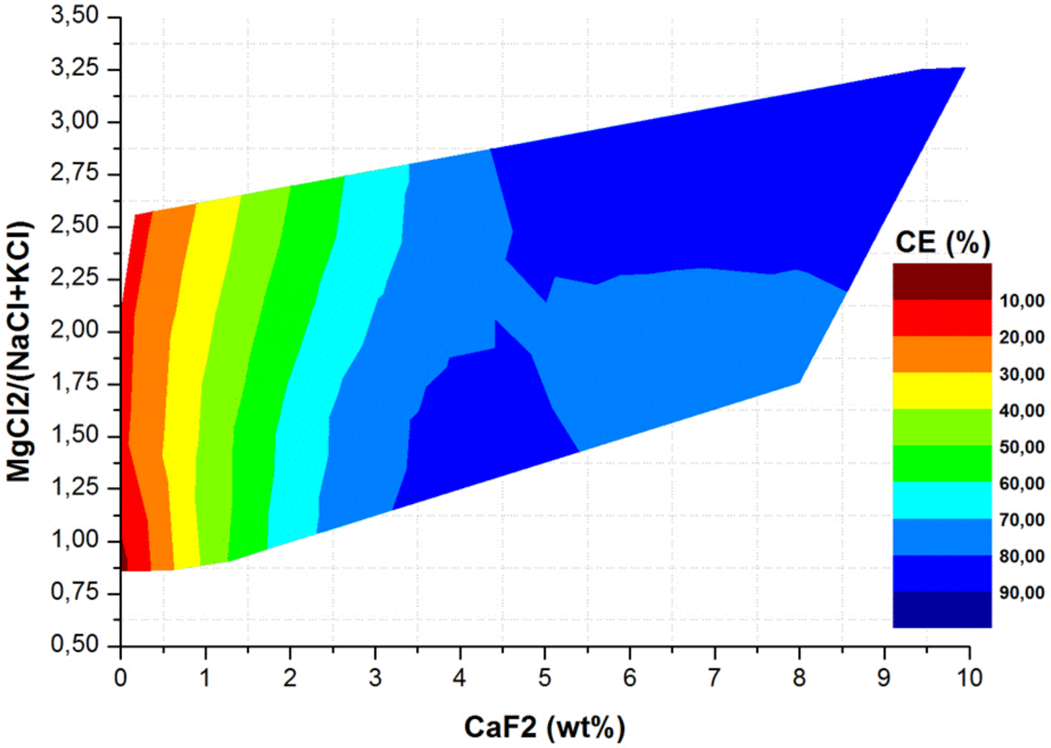


Figure 22: Coalescence efficiency of magnesium chippings in different salt mixtures (according to table 3.5)

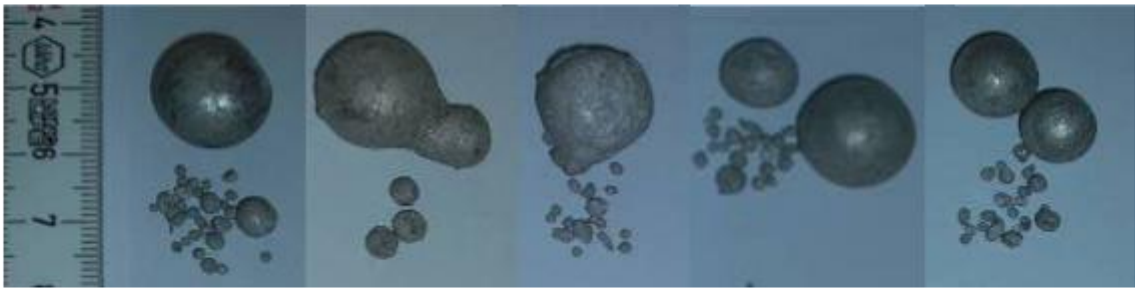


Figure 23: Coagulated droplets using different F-containing components; from left to right LiF, KF, NaF, CaF_2 and MgF_2 based on salt composition 19 (replacing 2 wt% Fluorspar)

If the completed dissociation reported by Sydykov [13] is considered and accepted for this case too, the word “ion” can be hence used for fluorine. It can be easily seen from the following atomic weight series of the above mentioned fluorine components that the ratio of F-ion in each of these components does not follow the order represented in Fig. 24. That means, in spite of bigger amount of F-ion in MgF_2 than Calcium-, Sodium- and Potassium fluoride, the coagulation efficiency of magnesium droplets with this salt component is much less than that of the others.

LiF (73%) > MgF_2 (61.3%) > CaF_2 (48.7%) > NaF (45.2%) > KF (32.7%)

The addition of 2 Wt% LiF leads to almost 1.5 times higher F-concentrations in the flux than 2 Wt% of CaF_2. This suits to the experimental results of Fig. 24. Furthermore, the fact that NaF and CaF_2 have both quite similar contents of F-concentration and should have quite the same coagulation efficiency can be confirmed from experimental procedure too. But, the fact that KF has a less effectiveness on coagulation than NaF, CaF_2 and MgF_2 can not be proven by experimental trials. As a result, it is assumed that for Mg-system not only the quantity of fluorine ion in salt fluxes but also the presence of other elements such as Lithium, Sodium, Calcium or Potassium plays an important role in coalescence efficiency; therefore, it can not be concluded from these experiments that the more fluorine ion the more coagulation.

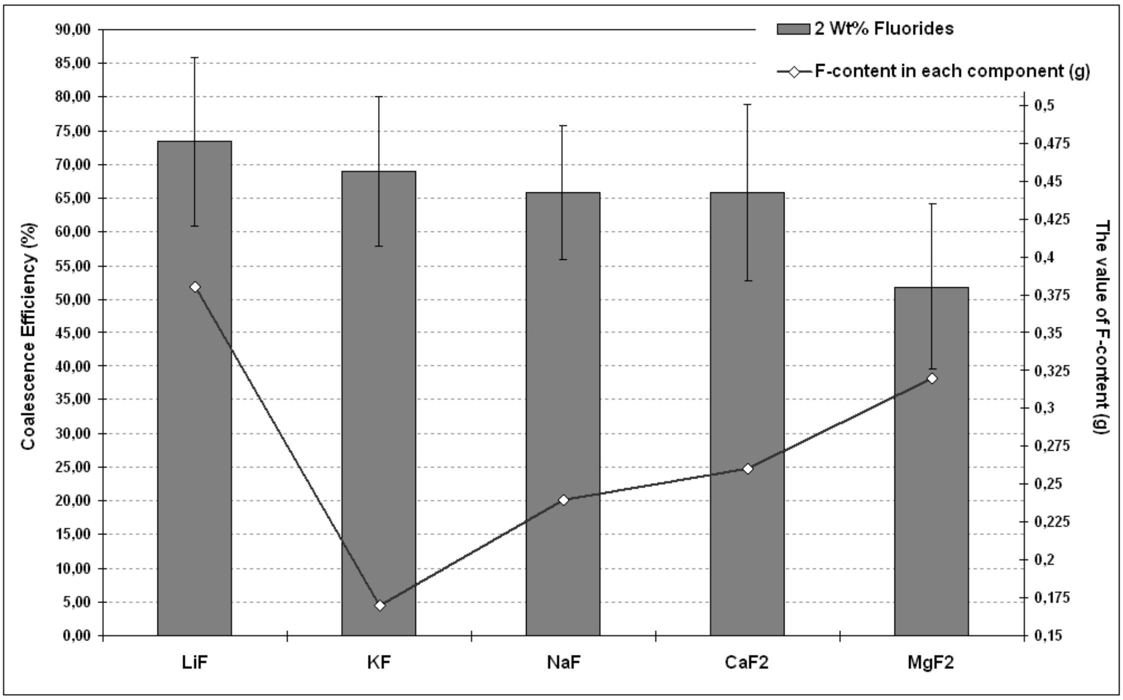


Figure 24: Coalescence efficiency of magnesium chippings using different fluoride-bearing components (all added by 2 wt%) at 750°C

Considering the case of aluminum, different interpretations for the influence of fluorine-containing additives are discussed. From one hand, aluminum oxide has four different forms of structure modifications such as γ, δ, θ and α with different transition temperatures; e.g. the γ to α transition temperature is approx. 1200°C. This temperature can be reduced through addition of fluoride-bearing components even up to 100-200°C and advance the formation of $Al_2O_3(\alpha)$, whose density is much higher than that of γ; therefore, the aluminum oxide layer in the form of α will be cracked much faster and removed much easier from the surface of metallic aluminum [23]. In the case of magnesium oxide, it is not the same; but Fluorine addition seems to increase the potential of two magnesium drops to flow together.

The coalescence trials were repeated for 5 Wt% of the above mentioned fluorides too (see fig. 25). The series of LiF, KF, NaF and MgF_2 is again the same, but CaF_2 moves to the second place with a strong significance, even as high as LiF. All results for both series (fig. 26) allow for an *imaginary trendline*, if an optimum coalescence efficiency of about 85% is assumed. The value of F-ion after a complete dissociation of a fluorine-containing salt (without consideration the type of the salt) should be approx. 3.59 Wt%.

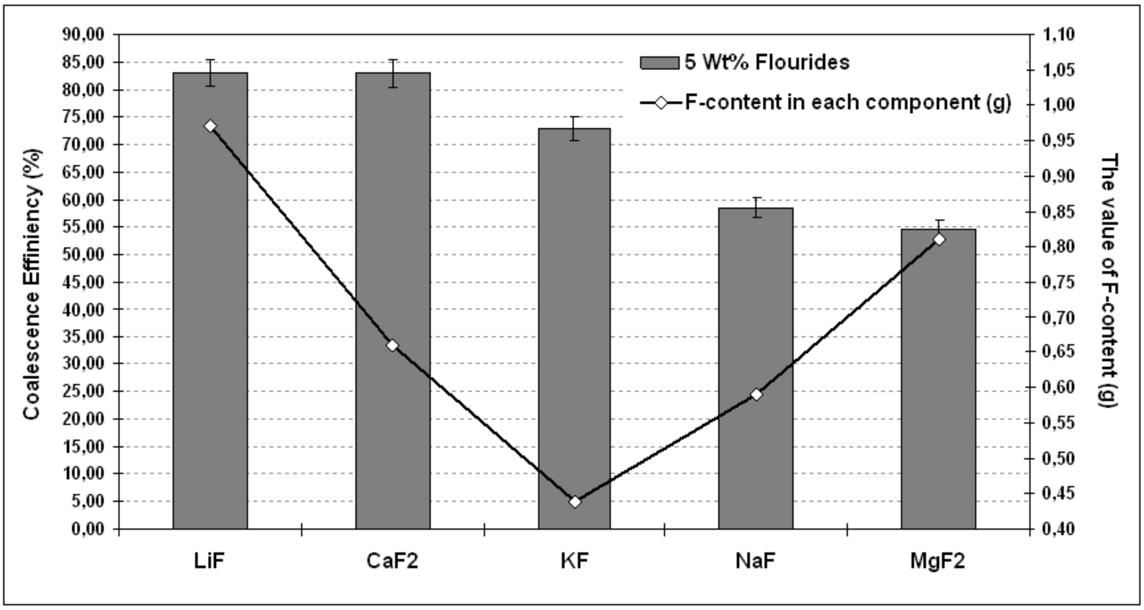


Figure 25: Coalescence efficiency of magnesium chippings using different fluoride-bearing components (all added by 5 wt%) at 750°C

According to actual salts price comparison, LiF and MgF_2 are anyway uneconomic choices to be used in magnesium salt fluxes due to their extremely high prices. But, KF, NaF or CaF_2, whose prices are much less, could be good selections to be applied in magnesium salt fluxes. However, according to figure 26, the point related to 5 Wt% CaF_2 reaches a coalescence efficiency to approx. 85%, despite having just 2.5 Wt% F-ion. This fact intensifies the above mentioned assumption of the importance of other elements such as Lithium, Calcium, Sodium or Potassium.

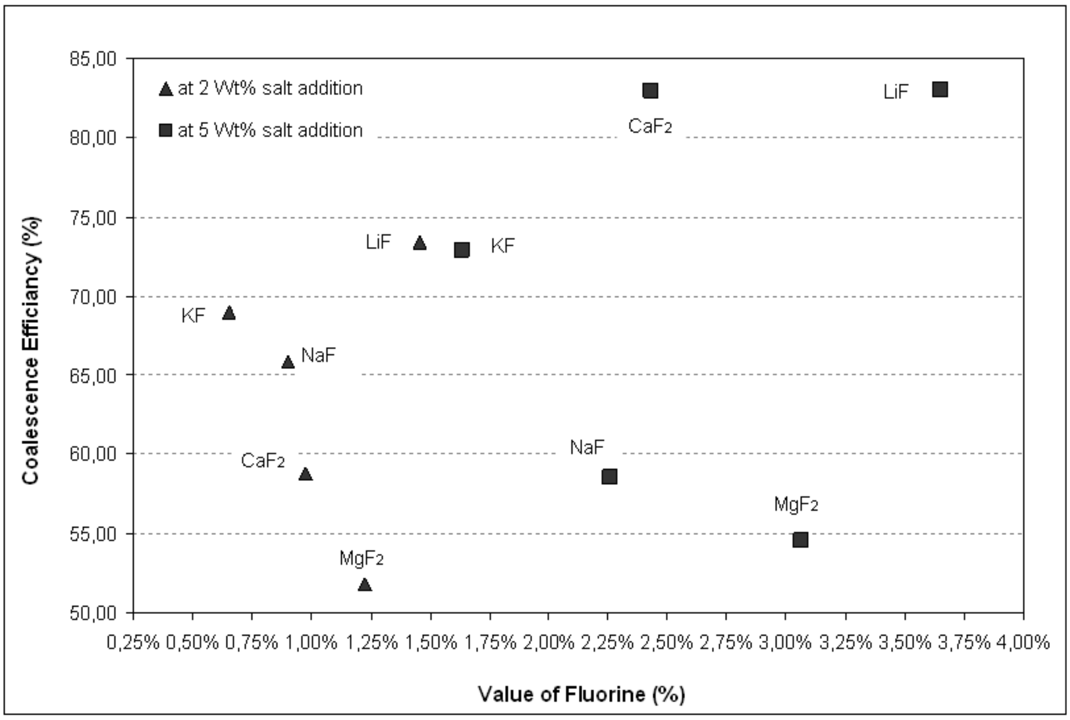


Figure 26: Coalescence efficiency of magnesium chippings versus the amount of fluorine

A fluoride selection can be explained through the stability diagram, shown in figure 27. It can be seen that MgF_2 is one of the most stable salts among the other compounds. That means that adding fluorine-containing components such as KF and NaF would cause a reaction between salt and magnesium to form the stable MgF_2 and arrest some active fluorine ion, which can not be active any more in the coalescence procedure. The only salts more stable than MgF_2 are CaF_2 and LiF, so that these two showed obviously higher efficiencies on coalescence. However, own FactSage^{TM} calculations show conflicts with that statement. Table 4 represents an exemplary salt input including $MgCl_2$, KCl, NaCl and 10 wt% CaF_2 as well as the calculated output via FactSage^{TM}, proving that even CaF_2 has been converted to other forms of fluorine-bearing components such as KF, NaF and MgF_2, despite the high stability of CaF_2.

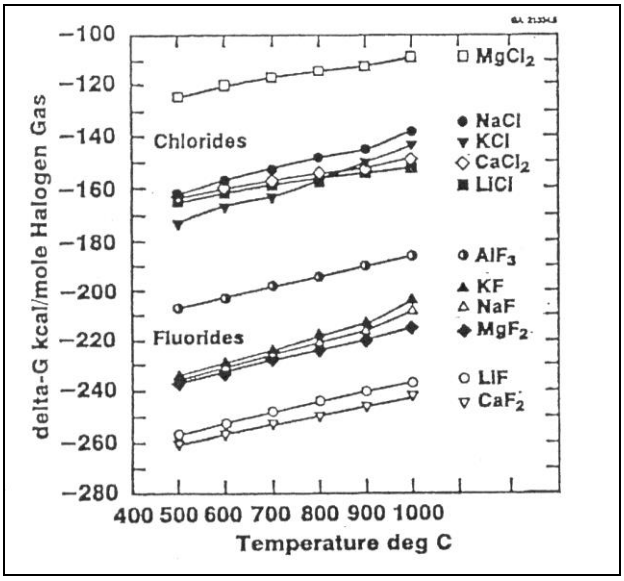


Figure 27: Gibbs free energies of various chlorides and fluorides [6]

Table 4: Chemical composition of an exemplary salt mixture (input and output) calculated in FactSage^{TM}

Input material		Output material			
$MgCl_2$	4.3E+01	NaF	3.1E+00	MgF_2	3.7E+00
KCl	1.5E+01	NaCl	2.7E+01	$MgCl_2$	3.7E+01
CaF_2	1.0E+01	KF	1.5E+00	CaF_2	1.3E+00
NaCl	3.2E+01	KCl	1.3E+01	$CaCl_2$	2E+01

4 Conclusion

In this paper the influence of the chemical composition of salt fluxes on coalescence of magnesium droplets was investigated. The experiments carried out though developing a variety of salt mixtures and investigating their coalescence ability with the selection of the most optimum salt mixture, able to coagulate molten magnesium droplets most efficiently and to avoid its loss. This optimum mixture was then applied to the distillation products in order to improve their separation from each other. The results showed that through increasing the amount of Fluorspar to 5 wt% the coalescence efficiency rises dramatically to 86%, but oversaturated at this fluorspar value, so that at higher CaF_2-contents the coalescence efficiency generally decreases. On the other hand, the investigations with different kinds of fluorine-containing components proved that both calcium- and lithium fluorides have the most influence on the coalescence efficiency; however, LiF is not a strong rival against CaF_2 due to their price difference. As a result, the chemical composition of 56 wt% $MgCl_2$, 15 wt% KCl, 24 wt% NaCl and 5 wt% CaF_2 was selected as the most optimum recycling salt.

5 Acknowledgement

The authors would like to thank DAAD (Deutscher Akademischer Austausch Dienst) as well as DFG (Deusche Forschungsgemeinschaft) for their financial support of this research project.

6 References

1- S. Akbari, Minimizing Salt and Metal Losses in Mg-Recycling through Salt Optimization and Black Dross Distillation, Dissertation, IME/ RWTH Aachen, Shaker Verlag, under publication, 2011

2- R. Roy, Y. Sahai, “Coalescence Behavior of Aluminum Alloy Drops in Molten Salts”, Materials Transactions, JIM, Vol. 38, No. 11, 1997, pp. 995-1003

3- R. D. Peterson, “Effect of Salt Flux Additives on Aluminum Droplet Coalescence”, Proceedings of Second International Symposium -Recycling of Metals and Engineered Materials, 1990, pp. 69-84

4- K. J. Friesen, T. A. Utigard, “Coalescence Behaviour of Aluminum Droplets under a Molten Salt Flux Cover”, Light Meals, 1997, pp. 857-864

5- J. Ye and Y. Sahai, „Interfacial Behaviour and Coalescence of Aluminum Drops in Molten Salts”, Materials Transactions, JIM, Vol. 37, No. 2, 1996, pp. 175-180

6- J. H. L. Van Linden, D. L. Stewart, “Molten Salt Flux Composition Effects in Aluminum Scrap Remelting”, Light Metals, 1988, pp. 391-398

7- L. Martin-Gartin, A. Dinet, J. Hicter, “Liquid-Liquid Interfacial Tension Measurements Applied to Molten Al-Halide Systems”, Journal of Material Science, Vol. 14, 1979, P. 2366

8- J. A. S. Tenorio, F. Delgado, “Optimization of Salt Composition in the Recycling of Aluminum Cans”, Light Metals, 1997, pp. 1105-1108

9- D. L. Stewart, etal., United States Patent, No. 5,057, 1991

10- J. A. S. Tenorio , D. C. R. Espinosa, “Effect of Salt/Oxide Interaction on the Process of Aluminum Recycling”, Journal of Light Metals No. 2, 2002, pp. 89-93

11- D. B. Masson, M. M. Taghiei, “Interfacial Reactions between Aluminum Alloys and Salt Flux during Melting”, Materials Transactions, No. 6, 1989, pp. 411-422

12- F. K. Ho, Y. Sahai, “Interfacial Phenomena in Molten Aluminum and Salt Systems”, Ohio Second International Symposium of Recycling of Metals and Engineered Materials, 1990, pp. 85-103

13- A. Sydykov, B. Friedrich, “Fluoride Salt Dissociation in NaCl-KCl Salt Flux and its Effect on the Coalescence of Aluminium”, ERZMETALL 58, 2005, No. 6, pp. 322-328

14- R. D. Peterson, “Effect of Salt Flux Additives on Aluminum Droplet Coalescence”, Proceedings of Second International Symposium -Recycling of Metals and Engineered Materials, 1990, pp. 69-84

15- F. K. Ho, Y. Sahai, “Interfacial Tension in Molten Aluminum and Salt Systems”, Light Metals, 1990, pp. 717-720

16- A. G. Zholnin, S.E Novichkov, A.G. Stroganov, “Choice of Additions to NaCI-KCI Mixture for Aluminum Refining from Alkali and Alkali-Earth”, Light Metals 2005, pp. 973-976

17- T. A. Utigard, K. J. Friesen, etal., “The Properties and Uses of Fluxes in Molten Aluminum Processing”, JOM, Nov. 1998, pp. 38-43

18- D. T. Ireland, United States Patent No: US 6,206,950, 2001

19- H. A. Mashhadi, A. Moloodi, M. Golestanipour, E.Z.V. Karimi, “Recycling of Aluminium Alloy Turning Scrap via Cold Pressing and Melting with Salt Flux”, Journal of Materials Processing Technology, 2008, pp. 3138-3142

20- A. Sydykov, B. Friedrich, A. Arnold, “Impact of Parameter Changes on the Aluminum Recovery in a Rotary Kiln”, Light Metals, 2002, pp. 1045-1052

21- Y. Xiao, M.A. Reuter, “Recycling of Distributed Aluminium Turning Scrap”, Minerals Engineering, Vol. 15, 2002, pp. 963-970

22- A. Sydykov, Eigenschaften und Ausbeuteeinfluss von NaCl/KCl-basierten Schmelzsalzen des Al-Recyclings, Dissertation, RWTH Aachen, IME, 2004

23- A.V. Kurjumov, etal., Schmelzbehandlung und Filtration der Aluminiumschmelze, Metallurgie, Moskau, 1998, P. 196