Process Integrated Thermal Treatment of Black Dross (Sludge) from Magnesium Production

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Abstract

Magnesium has been increasingly used in the recent years as construction material especially because of its good electromagnetic shielding performance and its low density. After the development of high efficient motors for vehicles and the reduction of the car´s air resistance, growing emphasis is put again on weight reduction or stable weight despite more interior (electronic) equipment. Magnesium helps lowering the fuel consumption and lowering emissions, but with the disadvantage of its high energy consumption through primary production. Whereas for the extraction of magnesium from recycled scrap only 10-30 % of this energy is needed.

With the growing use of magnesium alloys the amount of production residues will also increase. Nowadays contaminated consumer scrap, fine metallic material and material of low metal content like turnings, sludges and drosses are not or limited recycled. This loss of magnesium must be economically minimized with a strong view to ecological targets. To close this gap the present work reports about the possibility to treat a complex production waste, a molten sludge ("black dross" of high inhomogeneity with approx. 10-30% Mg, salt and non-metallics like oxides) by centrifuging direct in the process line maximizing the magnesium recovery as well as inhouse-recycling of salt in liquid stage. The idea is to remove the majority of the magnesium-oxide content from the sludge and to reuse the received liquid salt/metal fraction replacing virgin salt and recovering molten metal. This new "IME black dross recycling concept" was tested in a 35 l resistance heated special magnesium furnace (first step: dilution and Mg recovery) and subsequently in a 30 l resistance heated centrifuge-furnace (second step: oxide removal ans salt recovery). After the treatment a significant reduced amount of concentrated magnesiumoxide has to be dumped and the cleaned salt can be used again.

The recovery of magnesium metal and the separation of the magnesiumoxide content from the sludge leads to a reduction of landfilling and therefore to a minimization of the disposal fees. Most of the Magnesium metal relating to the content in the black dross can be recovered directly just by remelting in salt (first step) and the amount of sludge to be dumped is more than 60% reduced after centrifugation.

1 Introduction

During the last 30 years magnesium has obtained growing significance in the transportation industry. This is because its density is 35 % respectively 70 % lower than the one of aluminium and steel – the most commonly used constructional materials in the automotive industry. After the development of more efficient motors for vehicles and the reduction of the air resistance, nowadays growing emphasis is put on weight reduction or stable weight combined with more widespread use of equipment. By lowering the gas consumption it is possible to counteract the growing consumption of ongoing expansion of individual transportation. Higher gas efficiency and lower emissions will help deal with today's environmental problems [1, 2].

As the use of magnesium alloys is growing the amount of production residues will be rising. Because of environmental laws the amount of consumer scrap returning to the industry will be growing short after. The recycling of production residues and consumer scrap is prescribed by the laws of recycling and must be implemented.

Nowadays contaminated consumer scrap, fine metallic material and material of low metal content like turnings, sludges and drosses are not recycled [3]. This take-out of magnesium of its closed loop is economically and ecologically unreasonable while amounts of production residues and consumer scrap are rising. It is also neglecting the laws of recycling for all kinds of material.

A disadvantage for the primary magnesium production is the high energy consumption. In contrast to that, only 10-30 % of the energy consumption of the primary extraction is used for the extraction of magnesium through recycling of magnesium scrap [4]. Due to this fact magnesium recycling is the only way in Germany for producing magnesium. But only massive new scrap can be economically recycled. If, for example, magnesium turnings are remelted under a special salt a sludge is formed. This sludge is on the one hand very expensive to dump on the other hand magnesium (and salt) gets lost out of the magnesium loop [5].

In this 4 years research project at IME, Aachen recycling possibilities of sludge were investigated. The target is to decrease the magnesiumoxide content (minimization of viscosity) and to reuse the salt/metal-fraction as melting salt. The used methods are sedimentation and centrifugation. The investigations are made in a 35 l resistance heated special magnesium furnace and in a 30 l resistance heated centrifuge-furnace. In the beginning five industrial salts were tested with different kinds of scrap, where the best results referred to metal yield and handling are achieved with fluxes produced by Rheinkalk HDW. Furthermore, the high metal content of sludge is negative. Up to 60% of the treated material (metal scrap + salt) formed sludge depending on the charged scrap. The metal contents in this sludge varied between 17 % (clean briquettes) and 24 % (turnings) [6]. The chemical analysis showed that this sludge is always extreme inhomogeneous. When the oxide content rises about more than 35 %, the sludge has such a high viscosity that it looses its function as melting salt.

A main target of the investigation was the separation of an oxide enriched fraction. Prior experiments showed that only by using a centrifuge the separation of oxides is possible [6]. The chemical analysis showed that the solid product of the centrifuge consists of 60 % of oxides. This indicated in lab-scale, that the way of cleaning sludge with a centrifuge is possible. For industrial trials the centrifuge had to be constructive optimized. This paper will present results from a small pilot line in Aachen and from productions trials in industry to refine sludge by the minimization of the oxide content then to reuse the salt/oxide-suspension and of cause the Magnesium metal in it.

2 Refining of Black Dross

2.1 Facilities

For the first process step, melting of scrap and black dross from industrial magnesium production a new resistant heated furnace was developed and built up at IME, Aachen. The furnace which is heated by SiC rods has a crucible capacity of 35 l and is equipped with extra safety features (Figure 1). The hydraulic tilting device allows a controlled tapping of the melt. The hydraulic driven lid contains a ring pipeline for using inert gas to protect the melt surface for oxidation. The lid as well as the tilting device is remote controlled. The heating energy of this furnace is 46 kW.

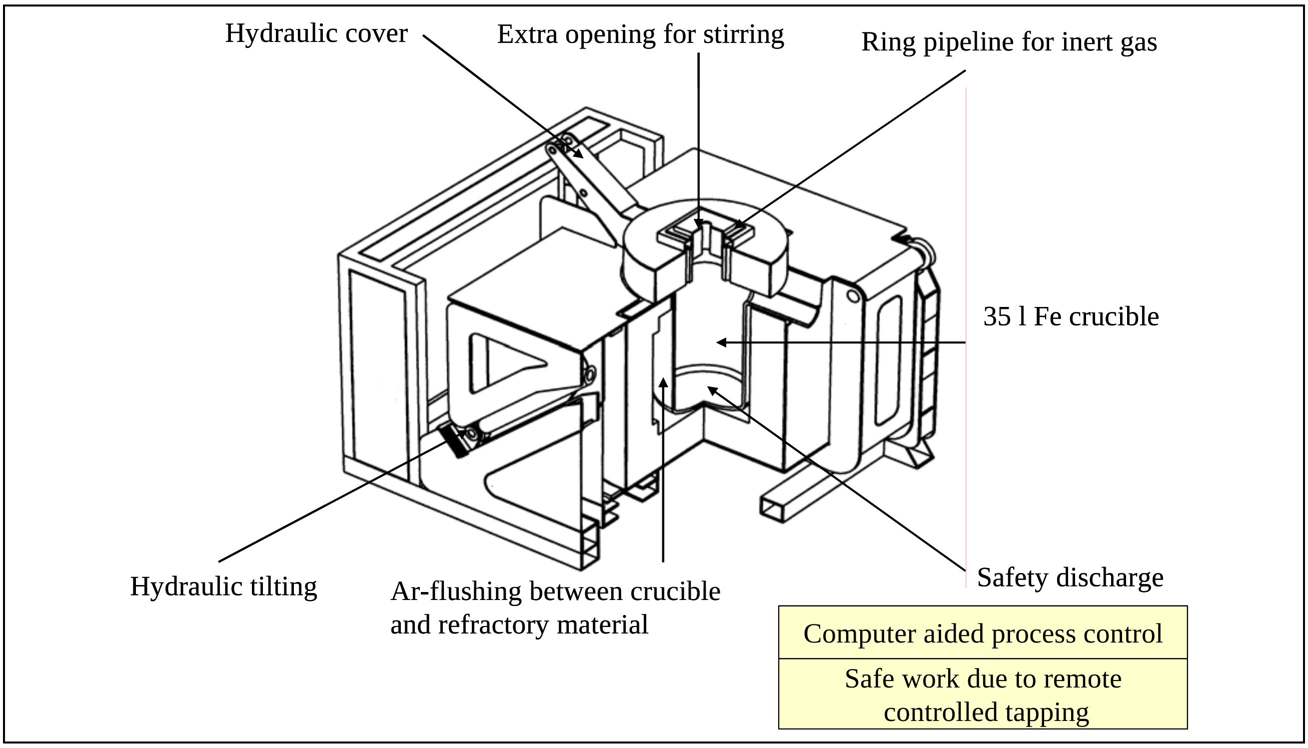


Figure 1: 35 l resistant heated furnace for magnesium recycling and black dross treatment

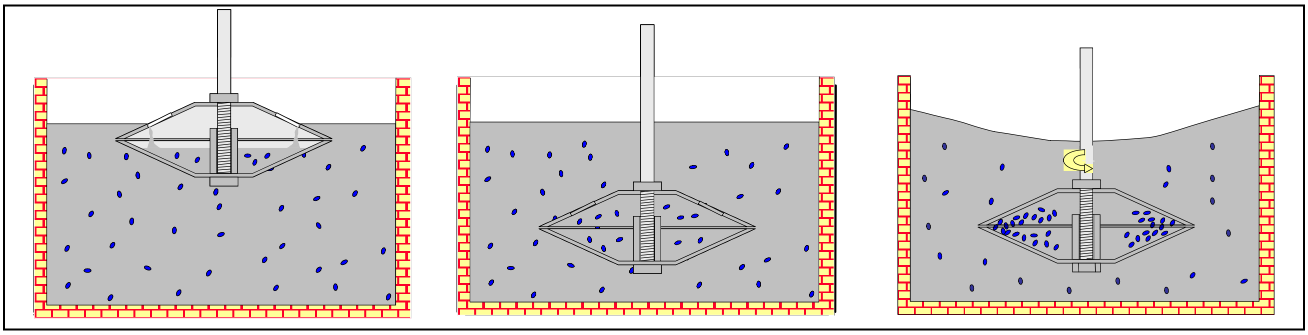
The computer aided process control allows a degree defined rising of the temperature. Temperature variations because of e.g. feeding can be compensated by the high heating energy. In case of a broken crucible during the melting process an extra safety discharge is integrated and the melt can be removed into a high grade steel tub which is located under the furnace. As another security measure the cavity between crucible and refractory material is filled with protective gas during the trials. The entire furnace is adjusted on a high-grade steel metal on the ground to avoid reactions with magnesium and the concrete ground. On top of the furnace an industrial full automatic Foseco impeller for melt treatment is installed (Figure 2).

Figure 2: 35 l furnace, Foseco impeller

The second step is to remove the heterogeneous non-metallic particles (e.g. oxides and intermetallics) out of the melt (suspension). Therefore a second resistant heated furnace with a capacity of 30 l and 20 kW power was erected. Maximum temperatures of around 1000 °C can be reached. On top of this furnace a rotor head for centrifugation can be adapted (Figure 3).

Figure 3: 30 l furnace, centrifuge and control system

The centrifuging process is devided into three steps. First, the rotor which has to be preheated is immersed into the melt. There it starts to rotate and collects melt inside of its two shells for about a minute. In the second step the rotor is lifted above the melt and the centrifuge starts to accelerate up to a rotation velocity of 1700 rpm. In this phase a filtercake of oxides is produced and the salt and metal is hurled out of the plates. In a third phase the centrifuge head totally moves out of the furnace and the two shells got opened to release the filtercake. The following figure 4 describe these sequences of the process in details.



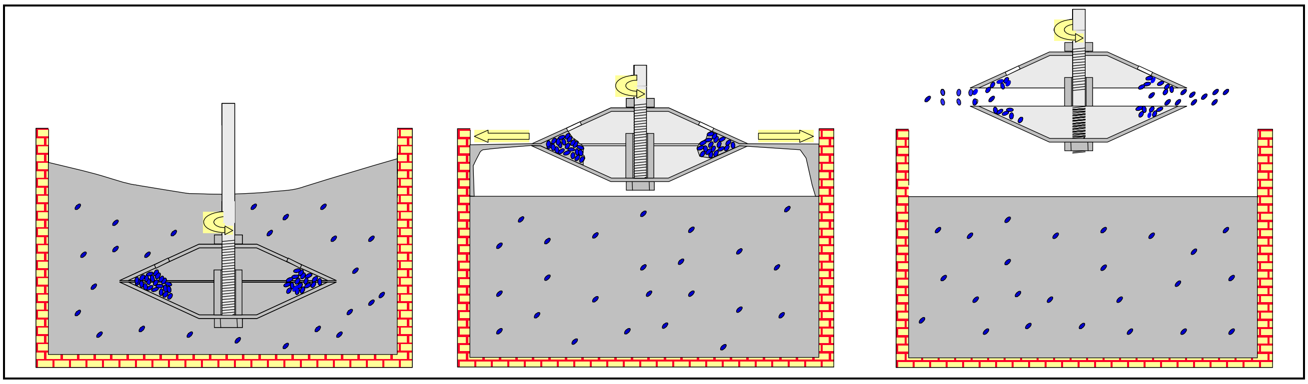


Figure 4: Removal of suspended particles using a immersed centrifuge rotor head; top:collecting particles; bottom: build up of filter cake, hurl out of liquid salt and metal, release of filter cake

2.2 The IME recycling concept for black dross

From previous experiences of the recycling of turnings a procedure concept for the processing of the black dross, consisting of a first **conditioning** step (separation of magnesium metal and preparing a liquid suspension) and the second **separation** step (removal of suspended particles was developed (Figure 5).

Following this concept a significant proportion of metal and salt on the one hand should be led back to the magnesium loop and on the other hand the amount of sludge which has to be dumped should be reduced to more than 60 %. In the following large scale experiments are presented in order to prove this concept.

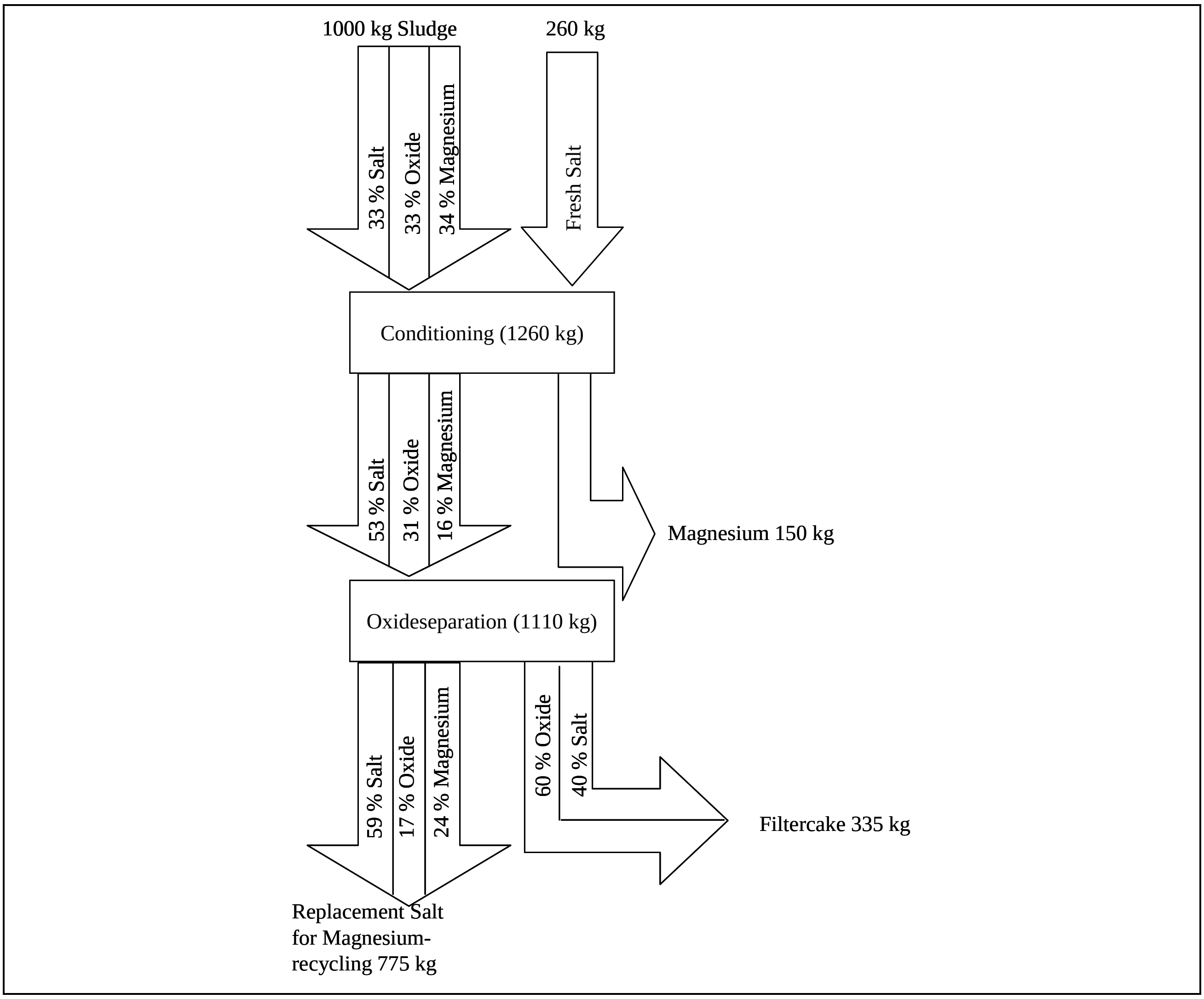


Figure 5: The IME recycling concept for black dross [6]

2.3 Conditioning

Industrial black dross originating from recycling of massive new scrap metal was used. According to Figure 5 the first step is to separate the metal from the sludge by adding fresh salt. Melting tests were done to find out what amount of new salt is necessary to maintain a sufficient low viscosity of the melt and a high metal yield. For these tests flux 5 of HDW was used (Table 1).

Table 1: Composition of Salt (flux 5 from HDW) used for black dross conditioning

Salt	CaF_2	KCl	NaCl	$MgCl_2$
Flux 5	5 %	20 %	25 %	50 %

The process parameters and the results of these tests can be seen in the table 2. In the beginning always 5 kg of fresh salt was added, after a first tap, different amounts of salts were added to investigate if further Mg-separation occurs as well as if the viscosity can be improved further. As can be seen the treated sludge blocks were mainly consisting of salt and were poor in metal. The blocks were selected from 300 kg of black dross in 6 loads with approximately 41 kg each so that they fit of their dimensions into the crucible. Brittle salty pieces could be chopped up roughly and be assigned to a load (Figure 6). Blocks which contain a lot of metal and did not fit in the furnace were rejected under acceptance of unreproducibility or unrepresentativity. So it has to be expected, that the Mg-content was not 1/3 (as the practical experience show in average), but more between 10 and 25%. Also the reaction with fresh salt (moisture) and not coagulated droplets cause lower metal yield than expected.

Table 2: Conditioning of black dross - separation of metal by salt dilution

Trial	Fresh Salt [g]	Black Dross [g]	Mg-Metal [g]	Metal Recovery [%]
1	11.000	40.500	5.420	13
2	12.000	41.300	7.760	19
3	13.000	40.500	4.400	11
4	14.000	40.900	3.009	7
5	15.000	40.600	3.012	7
6	15.800	40.600	4.850	12

Figure 6: black dross block, separation of metal and sludge

The yielded metal recoveries between 7 and 19 % have to be compared to the expected Mg-content of 10-25% (we calculate in the following with 73%). It is obvious that there is no influence in Mg-yield caused by an increased amount of fresh salt. Already after an addition of 11 kg of fresh salt a clear phase separation was done and a lowering of the viscosity was not taking place due to a further addition up to 5 kg of Flux 5. By eye-observation and quick sampling many small Mg-droplets could be detected easily after this treatment. Finally it was decided that an addition of 25 % of fresh salt is sufficient enough for almost complete separating metal from the black dross. Such the weight of removed Mg-metal is replaced by salt, leaving an unchanged oxide concentration behind.

2.4 Separation

In forehand a theoretical calculation was done to define the targets in respect to remaining oxide content in the purified suspension. Tables 3 and 4 summarize the results of this simple calculation. An oxide content of 30 % in the treated (salt conditioned) sludge and of 60 % in the filter cake is assumed. 60 to 70 % of the oxide contained in the sludge must be removed to reach rest oxide content from 14 to 17 %. Besides, the loss of salt and magnesium is around 16 to 18 %. Approx. 70 % of the valuable sludge-components can be returned to the magnesium loop. This is a theoretical calculation which combined the results of all of the pre-trials to get a final refining process with defined parameters.

Table 3: Theoretical calculation of oxide content evolution in the recycle-salt after their removal by centrifugation at different removal degrees with an assumed oxide content in the conditioned sludge of still 30 %

cond. sludge input [g]	Mg + salt content [g]	oxide content [g]	degree of oxide removal [%]	weight of oxides removed [g]	weight of remained oxides in recycle-salt [g]
34.400	24.080	10.320	100	10.320	0
34.400	24.080	10.320	80	8.256	2.064
34.400	24.080	10.320	60	6.192	4.128
34.400	24.080	10.320	40	4.128	6.192

Table 4: Theoretical calculation of salt- and Mg-losses during sludge refining with an assumed oxide content in the filter cake of 60 %, based on table 3

weight of recycle-salt [g]	oxides in recycle-salt [%]	filter cake weight (Mg/salt/oxide) [g]	losses of Mg + salt in filter cake [g]	losses of Mg + salt in filter cake [%]
17.888	0	16.512	6.192	26
21.190	10	13.210	4.954	21
24.493	17	9.907	3.715	15
27.795	22	6.605	2.477	10

Table 5 indicates theoretically the influence of the oxide content in the filter cake on salt and Mg-losses. An oxide content of 17 % in the recycle-salt is assumed for this calculation. It becomes clear that the oxide content in the filter cake should be at least 50% in order to reduce the salt and Mg-losses and to reduce the volumes to be dumped down to ⅓. Therefore it is necessary to build up a filter cake with bigger oxide particles which is permeable for the liquid salt and metal and consists all together to 60% out of oxide. If such a filter cake is possible it is realistic that in future approx. 71% of the salt / magnesium mixture can be recycled.

Table 5: Impact of oxide content in filter cake on recycle volumes and Mg-/salt-losses, calculation based on 17% oxides remained in recycle-salt, based on table 4

Condit. Sludge input [g]	assumed oxide content in filter cake [%]	weight of filter cake [g]	ratio filter cake/ sludge input [%]	weight of recycle-salt (Mg + salt + oxides) [g]
34.400	70	8.914	26	25.486
34.400	60	10.400	30	24.000
34.400	50	12.480	36	21.920
34.400	40	15.600	45	18.800

Validation trials with industrial produced sludge as well as with synthesized MgO-salt-suspensions were conducted in the centrifuge and it turned out that a lot of factors had an influence on the produced oxidic filter cakes. For example the shape of the rotor shells which collect the oxides as well as the rotation speed turn out to be important. So during the experimental campaign those parameters were investigated carefully and a process window was defined.

Until now a first industrial proof of principle for the efficiency of this process is made and some results are given in Figure 5 and 6. The salt content in the suspension is as double high as in the filter cake, whereas the MgO content in the filter cake is almost four times higher than the content in the sludge, although in this case the sludge was already containing a low amount of oxides.

Figure 5: Salt content in sludge (before treatment) and in filter cakes from first up-scale industrial experiments for oxide removal from Mg-black dross with a pilot centrifuge

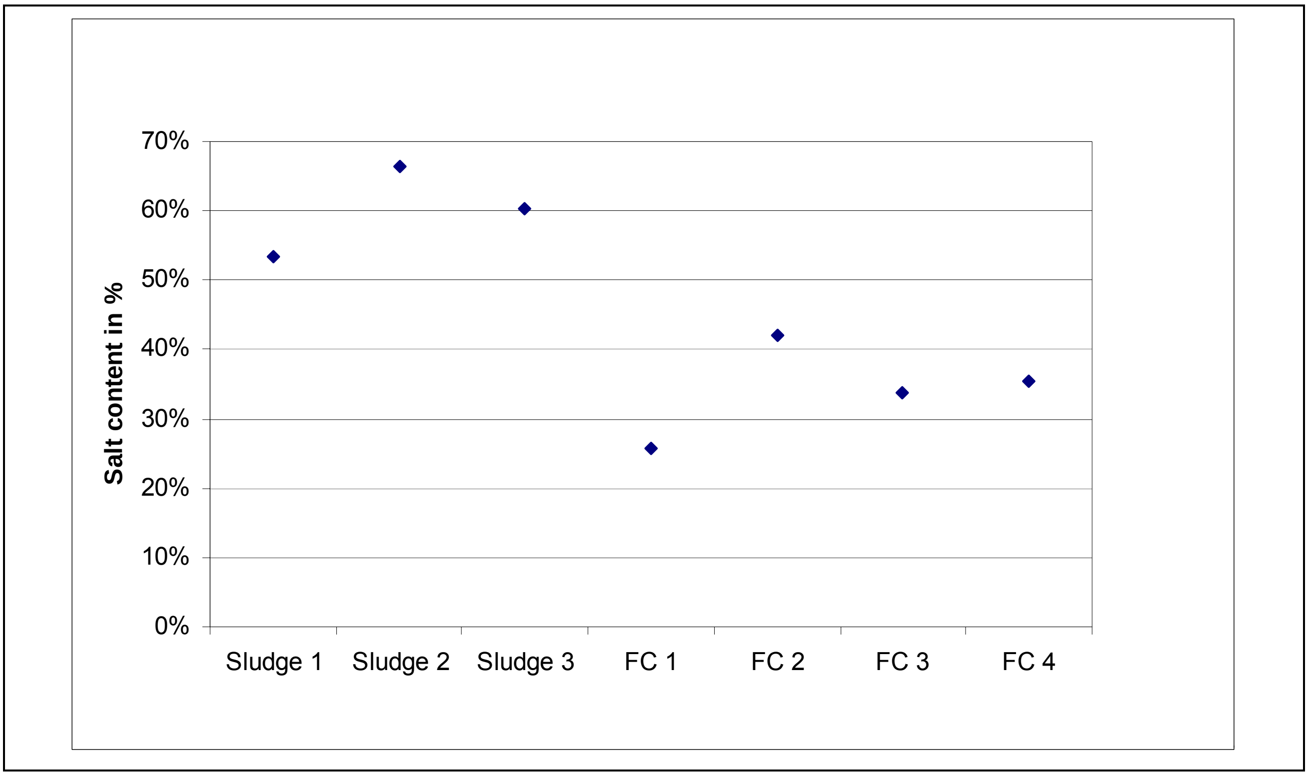
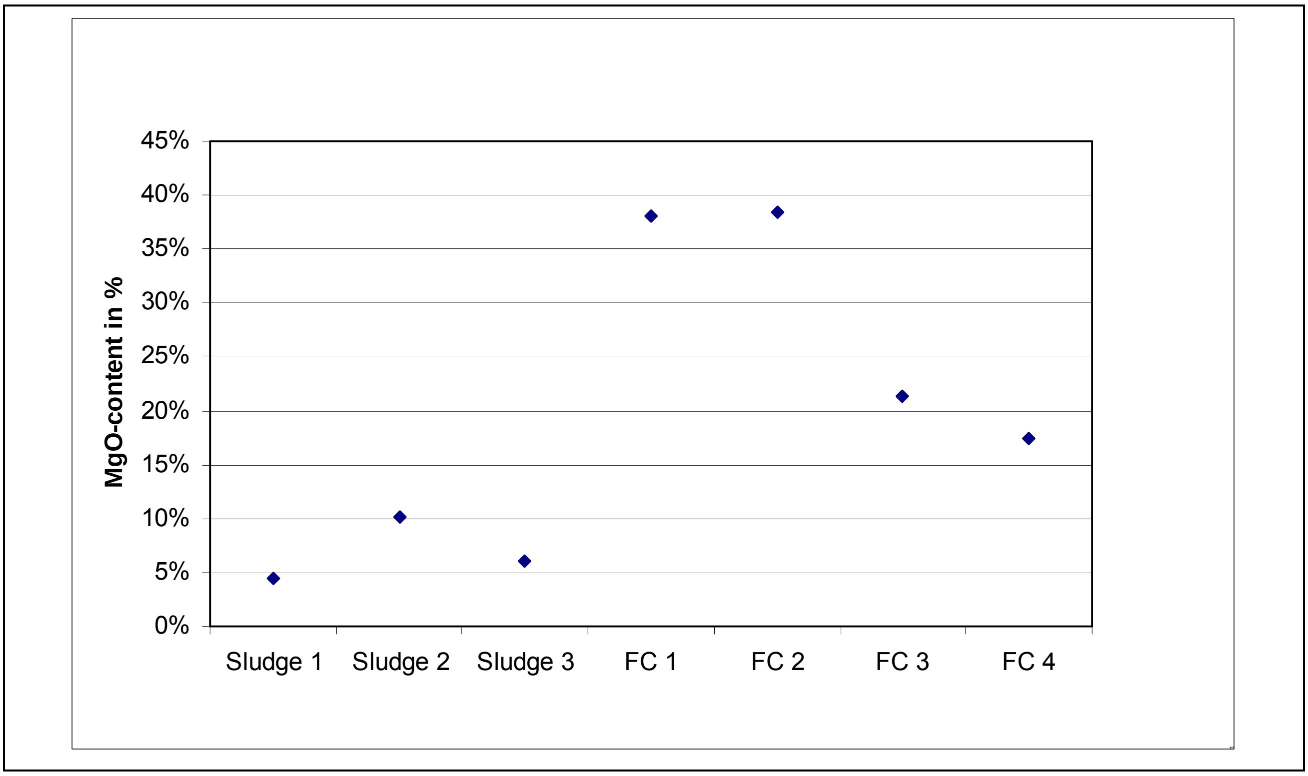


Figure 6: MgO content in sludge (before treatment) and in filter cakes from first up-scale industrial experiments for oxide removal from Mg-black dross with a pilot centrifuge



2.5 Conclusion

After intensive lab-experiments and from first industrial screening trials it seems feasible to follow the IME recycling process for Mg black dross. At first black dross must be conditioned with addition of about 25% fresh salt and a hot separation from the Magnesium metal. A Mg recovery yield up to 73% seems to be achievable. This already causes a lowering of the viscosity and the oxide content of the melt is less than 35 %. This step can easily be made in a simple resistant heated furnace from which the metal phase can be decanted. The temperature in the furnace should be kept between 680 and 700 °C. Subsequently the conditioned sludge is refined in a centrifuge. Here an oxide concentration in the filter cake must be reached of 60% in order to minimize salt and Mg-losses as well as to minimize dumping efforts. The latter is one of the major environmental driving forces of the project. The 60% value could not be reached up to now in industrial tests. Furthermore more than 60% of the oxides have to be removed from the sludge-salt-suspension, to reach significantly lower values than 17% in the recycle-salt. But the principle of the idea had been proved, the recovery of liquid Mg and salt was shown, which again can be used directly for the magnesium recycling.

3. Perspective

Final tests at the IME in which the whole process was run through in a row were done recently. The results of these trials will be presented on the coming emc meeting in june. The following pictures already give a first impression of the process (Figure 7).

Figure 7: charging material, separation of metal, tapping of hot sludge, filter cake, recycled salt

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