Closing the Mg-Cycle by Metal and Salt Distillation from Black Dross

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Abstract

Magnesium recycling processes typically are based on the use of fluxes, mostly containing $MgCl_2$, KCl, NaCl and CaF_2. They have 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 the both metallic and oxidic magnesium as well as salt components. The formation of black dross has been reported to be about 4000 t/a in Europe. Up to now it has not been yet possible to recycle this sludge economically. Such the investigation to recover metallic magnesium as well as part of the salt flux from this sludge is the task of this work. Vacuum distillation was selected - as an already well-known efficient method to produce highly pure materials - to separate volatile components from oxide and ceramics. This selection was made due to the extreme oxidisability of magnesium as well as the high vapour pressure difference between the components in black dross.

Keywords: flux, salt, black dross, magnesium, vacuum distillation

1 Motivation

"Black dross", the bottom salt slag in magnesium scrap melting process, contains salt, suspended magnesium alloy beside ceramic particles (Mg oxide,-Nitrid, etc.). Up to now no economic processing possibility exists for this suspension and i.e. a significant magnesium loss through recycling process has been inevitable. In some initial investigations it has been shown that by centrifugal treatment a separation of these three phases is partially possible. However, it remains always an oxide-salt-residue which still contains magnesium droplets [1]. Therefore, one part of a recently completed PhD-project at IME/RWTH Aachen [2] has been developing a "zero-waste" process to recover metallic magnesium as well as salt components and a useful ceramic fraction from this sludge with the scope of the environmental requirements.

2 Background

"Black dross" formation occurs regularly and especially during recovery of multi-material-mixes like dross together with scrap from die-casting industries. This formation has been reported to be nowadays about 3500-4000 t per year in Europe with increasing tendency. Through all magnesium melt processing like die-casting or scrap melting, even when the surface is covered by salt or protective gases, magnesium oxide is formed. Also, intermetallic particles segregate as a consequence of small changes in the melt temperature (under cooling). All particles accumulate at the bottom of the furnace and the magnesium content of the sludge is high and lost. Screening the literature, the mechanism of its formation including control is not understood yet, but surface phenomena play an important role. The magnesium bearing fraction of black dross consists of intermetallic phases and reacts heavily with water to evaluate hydrogen. Due to the explosion-ability of hydrogen, black dross is not easy to handle or dispose at a normal dumping ground, therefore the transportation, treatment and disposal costs are high. Such the dark sludge, which is remained from the recovery process, consists also of salt, a second valuable material, needed to be treated [3]. An example of a material balance in a Magnesium remelting procedure is shown in table 1 [3]. Black dross as received from magnesium recyclers is very inhomogeneous as it can be seen in figure 1 [1].

Table 1: Exemplary material balance of a remelting process treating different kinds of magnesium residues with salt [3]

Input	Output
90% Rejects and risers 7% Sludge and dross 3% Refining salt	92% Metallic magnesium 8% Black dross

In order to improve magnesium and salt resource efficiency and to avoid the high disposal costs, recycling of black dross is of high interest. Currently there are two different methods to treat black dross; aqueous (leaching) and mechanical beneficiation; however, these techniques are not able to recover metallic magnesium completely. In the former, leaching water hydroxides magnesium to $Mg(OH)_2$ and in the latter the output is still a mixture of Mg, Mg/MgO and MgO/salt.

A vacuum process is proposed in this work as a suitable method to recycle and refine such magnesium residues. It has been already introduced as an innovative recycling method for magnesium, in which highly metalized magnesium scraps especially machining chips were recycled [4]. Vacuum distillation of magnesium is generally not a new process, as it has been developed in 50th in the so-called Pidgeon reduction process [5]. This method accounts for more than half of the world's magnesium production coming out of China and 9,000 tonnes from Canada [6]. In 1996, Lam and Marx [7] invented a vacuum distillation purification method to establish ultra high purity magnesium. Another investigation on vacuum distillation of magnesium was carried out by Tamura to obtain high purity materials [8]. Mg-20% Al electrolytic magnesium base alloy was used as a raw material.

Impurities such as Fe, Mn, Si, commonly contained in commercial magnesium, were substantially eliminated by this process, resulting in purity over 99.99% that was significant increased from that of electrolytic magnesium (99.93%). Zhu et al. adapted in 2001 a vacuum distillation process to magnesium chips with a little bit oil and water [9]. A Pidgeon type furnace was used there and pure magnesium crowns with only Zn as a contaminant, crystallized in the cold end and the other elements remain in the residue.

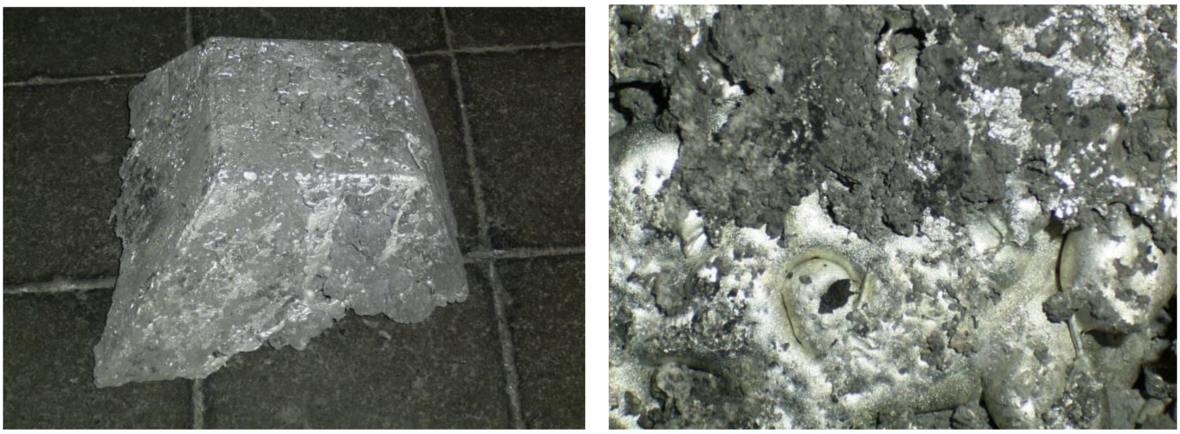


Figure 1: Mg black dross, typical block produced (left) and detail photo (right) [1]

The advantages of vacuum distillation comprise advanced degassing, prevention of oxidation and hence limitation or avoidance of deoxidation agents, no reaction with the atmosphere, gaseous products, higher evaporation and sublimation rate at lower temperatures and the separation of metallic components from a metallic mixture in a relatively pure form. In the case of more than one evaporated component, it is mostly possible to carry out a selective separation of volatile elements, leading to raw materials saving through minor metal loss and minor slagging and environmentally friendly through avoidance of exhaust gas as well as slag [10,11]. It has been shown that recycling magnesium via vacuum distillation is a feasible and plausible method, the composition of scraps recycled has a direct relationship with its recovery ratio and the cost of this method is reasonable but it has to be transferred to complex magnesium residues [9].

3 Vacuum Distillation Experimental Procedure

3.1 Lab-Scale Trials

The schematic picture of the distillation construction including crucible (= evaporator), condenser, refractory rings and etc. is shown in fig. 2. The dimensions (mm) of the graphite crucible, installed in this setup, are approx. 210H, 170D, 120d (mm).

After filling the crucible with black dross (quite 100% of the crucible's volume), a graphite-made lid equipped with an aperture and a thermocouple entry is put over the crucible let the evaporated gas go out directly upward and also to avoid the condensed material to fall back into the crucible.

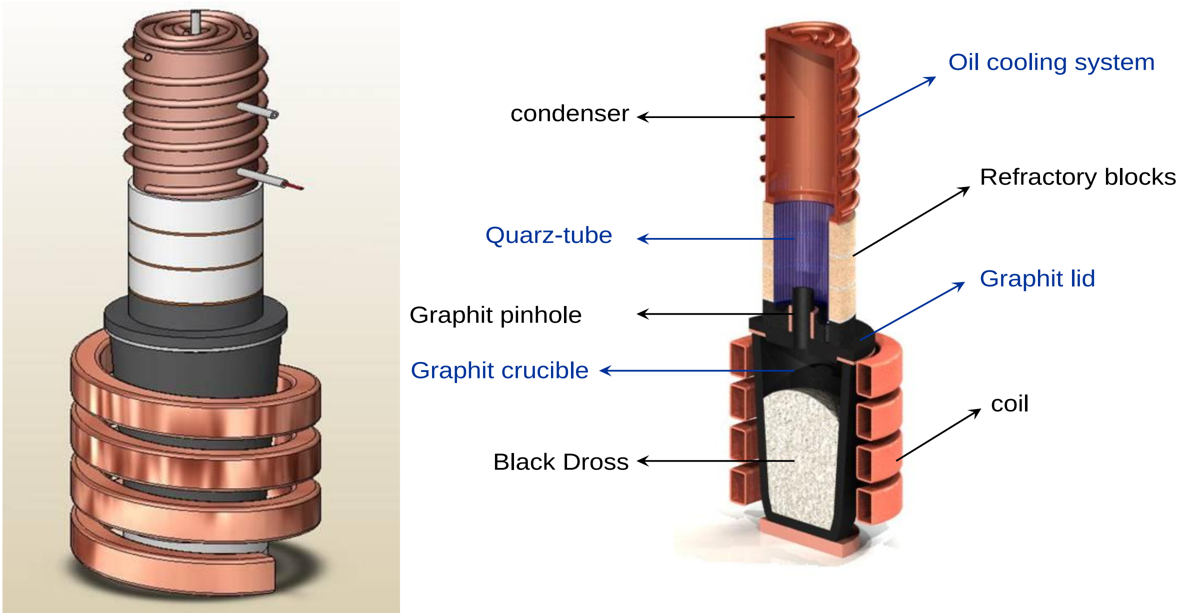


Figure 2: Schematic picture of the entire distillation construction (left) and the detailed description via a cross section (right)

In this construction, three refractory blocks have been placed between crucible and condenser in order to avoid temperature increase in the condenser. These blocks are from a very porous substance, which could absorb condensed material after distillation and that would make it impossible to separate them. To avoid this, a tube from quartz with a 90mm inner diameter and 150mm height and 4-5mm thickness was utilized inside the refractory blocks. If the condensed material flows downward, it could be gathered over this tube and then easily separated with a sharp knife. The Lab-experiments of vacuum distillation are to be divided into two parts:

- Investigation of winning metallic magnesium as well as salt from black dross (feasibility). As black dross is a very heterogeneous material, the distillation feasibility tests have been repeated 11 times in this series of research work to get an accurate result.

- Investigation of selective distillation and subsequent separation of metallic magnesium and salt. The selective distillation of black dross occurred at 600-750, 750, 800, 900, 1050 and 1200°C. The charge applied in each test is the crucible residue of the previous test.

3.2 Pilot-Scale Trials

A charge of approx. 59 kg black dross is treated in pilot-scale experiment. The equipment deployed in pilot scale vacuum distillation is a vacuum induction furnace, able to be powered with max. 350 kW. This power is of course dependant on the type of crucible as well as to be melted material. In this case, where black dross as charge and a graphite crucible including a graphite rod in the middle to help the coupling are used, a power of max. 200 kW is achieved. As the size of the graphite crucible installed for the pilot experiment is huge (480D, 750H, 380d (mm)), the middle of the crucible can’t be heated correctly. To solve this problem, a graphite bar is assembled in the middle of the crucible to form a second coupling field and let the charged material in the middle be heated up. Due to the charge volume in this scale, the positioning of baffle is of great importance. Being too close to the aperture, as seen in fig. 3 (left) would also cause as a barrier for distillation process. Therefore, in an optimizing design the baffle takes much bigger distance to the aperture as illustrated in fig. 3 (right) in the form of a plate fixed to the inner side of the hood. This new design prevents the aperture to become overgrown and impair further distillation. This baffle helps also the evaporated mass, rising directly upwards, not to be sucked via vacuum pump, but to have chance to be distributed over the inner hood/condenser.

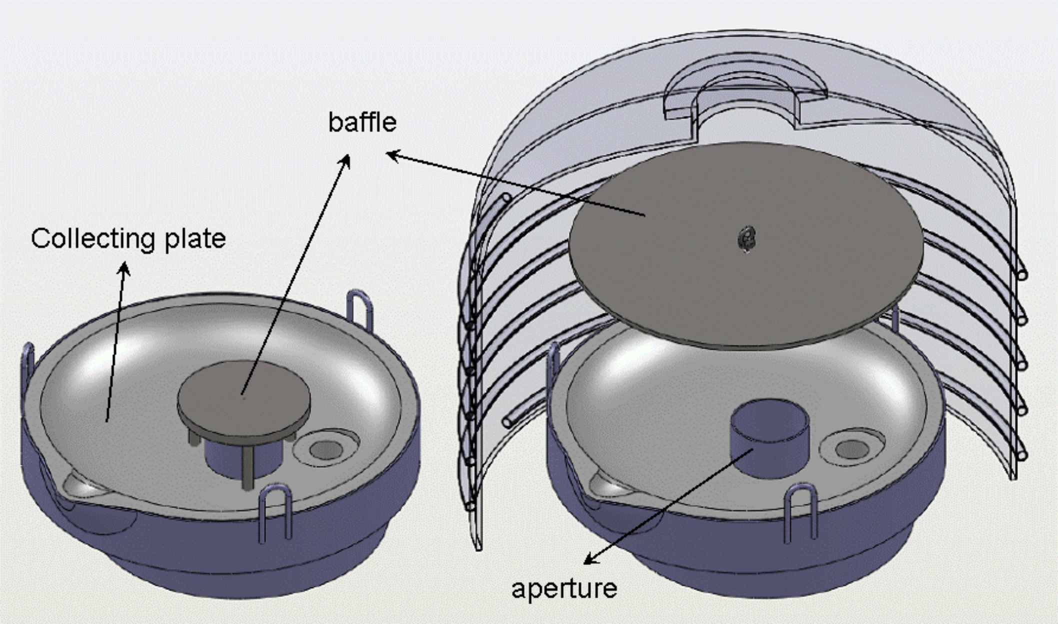


Figure 3: Draft of the position of baffle, aperture and the collecting plate in a pilot-scale vacuum distillation, the initial construction of the baffle (left) and the optimized final option

4 Results and Discussions

4.1 Results of the Lab-Scale Trials

According to fig. 4, two different distillation/ evaporation stages occur during each experiment. The first stage begins when the pressure is decreased to the range of 80-100 mbar. The temperature at the top of the condenser increases to above 600°C dramatically in one minute because of the hot evaporated gas arising from the crucible. After the first stage of evaporation, the condensers temperature decreases slowly, as less “new” hot vapour is produced. With the further vacuum suction, when the vacuum degree deceases to several mbar, the temperature in the top of the crucible increases again. The increasing rate is slowly but the duration time is longer comparing to the first evaporation. The second stage takes place at about one mbar in the furnace and 1150°C in the crucible. After this stage, even with increasing the temperature of the crucible to 1200°C, the temperature in the condenser keeps decreasing and the vacuum in the furnace becomes better. It indicates that the distillation/ evaporation process is already accomplished and the condensation dominates the process.

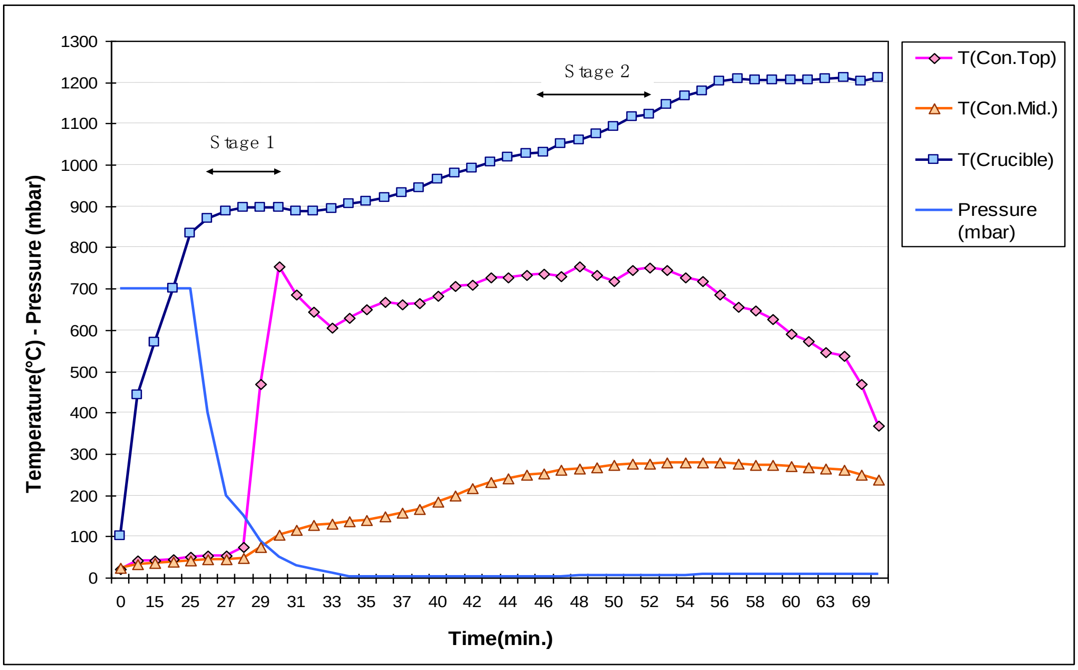
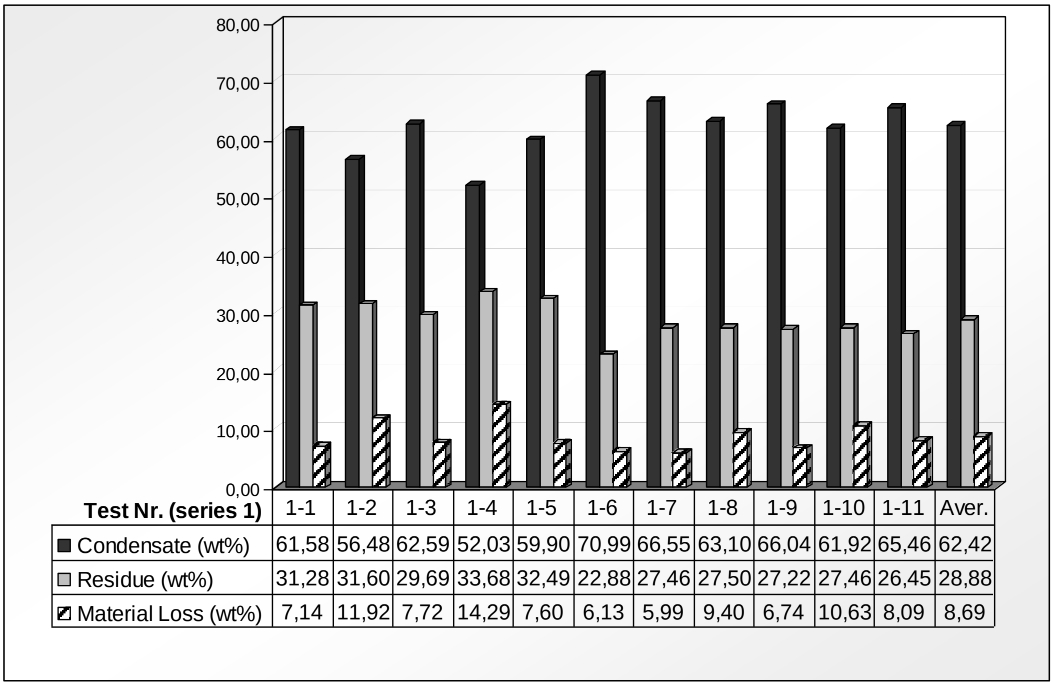


Figure 4: Condenser and crucible temperature and pressure changes during a distillation process

Figure 5 shows the mass balances of eleven vacuum distillation experiments including the obtained amount of condensate and the residue inside the crucible. There is a loss of only 8 wt% during the distillation process, which could be due to the absorption of evaporated material into the refractory rings, into vacuum pump and weighing mistakes. Therefore, if the process condition/ construction is optimized during up-scaling, this will be minimized and this percentage be added most probably to the total amount of condensate (approx. 62%).



Test Nr. (series 1)	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8	1-9	1-10	1-11	Aver.
■ Condensate (wt%)	61,58	56,48	62,59	52,03	59,90	70,99	66,55	63,10	66,04	61,92	65,46	62,42
□ Residue (wt%)	31,28	31,60	29,69	33,68	32,49	22,88	27,46	27,50	27,22	27,46	26,45	28,88
▨ Material Loss (wt%)	7,14	11,92	7,72	14,29	7,60	6,13	5,99	9,40	6,74	10,63	8,09	8,69

Figure 5: Mass balances of the 1st series of black dross vacuum distillation experiments (1200°C, Argon, ~100min.)

In the second part of distillation investigations, the possibility of selective separation of containing components using different temperatures is studied at 600-750, 750, 800, 900, 1050 and 1200°C. it was seen that no distillation occurs at temperatures less than 750°C. Figure 6 shows the mass flow of selective distillation tests, in which the crucible residue of each level of distillation was taken as the charge for the next step. In all experiments the stepwise distillation is proved through observing different layers in figures 7 and 8, the question whether a complete selective separation takes place is still to be answered. The left picture of figure 7 is the condensed material collected in the condenser, showing macroscopically different layers of materials after condensation. A part of this material is then inspected more precisely with highly magnification microscope, represented in the right picture. The digital 3D microscope used in these investigations has a 1000 objective facility, able to recognize quite well up to 1µm. In this picture three different condensed layers with approximately 195µm distance from each other are illustrated. An interesting observation in this inspection is the three-sub-layer formation in each of the above mentioned layers (see the middle layers in fig. 7 right), showing a stepwise behaviour of distillation.

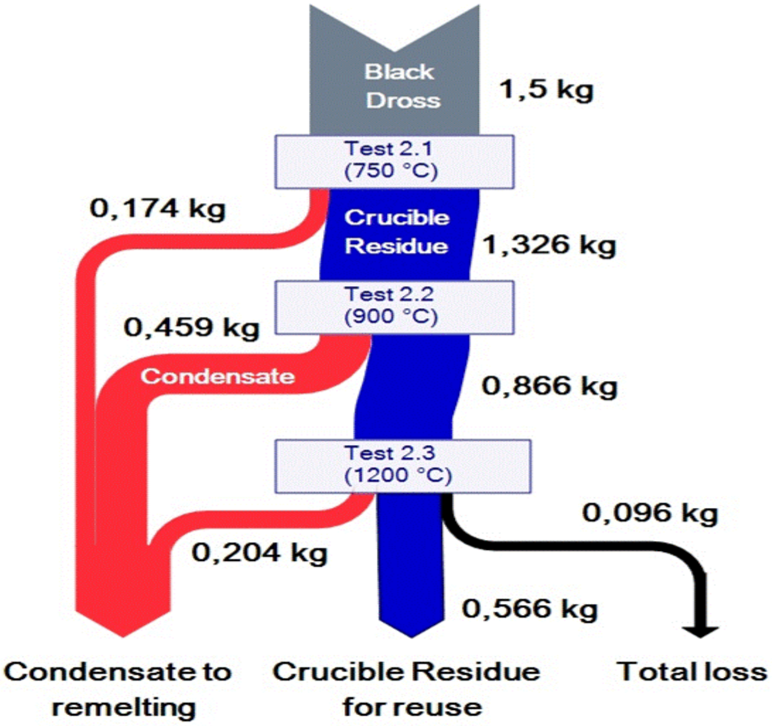


Figure 6: Mass flow diagram of the selective distillation tests

The condensed material in figure 8 collected from the quartz tube at 750°C shows four major layers. The layer Nr. 1 is the closest one to the wall of the quartz tube and layer Nr. 4 is the furthest one. Chemical analyses carried out for them are represented in table 2, showing mostly the same chemical components in these layers. Existing highly amount of magnesium element (> 80%) proves not only metallic fraction in the condensate but also - due to the presence of chlorine - the form of magnesium chloride. Furthermore, other salt components such as potassium chloride, sodium chloride, zinc chloride and/or metallic zinc as well as some traces of manganese metal/chloride, calcium chloride and aluminium chloride are found too. The same situation is dominated for the three other layers. That means a mixture of metallic magnesium and also salt components is distilled stepwise and condensed in layers. It leads to this fact that a 100% separation of high vapour pressure components in black dross is virtually impossible. However, according to the theoretical predictions (via FactSage^{TM}) at 750°C “only” magnesium should evaporate in significant amounts and the > 80% Mg_{met} -content proves this to a good extent.

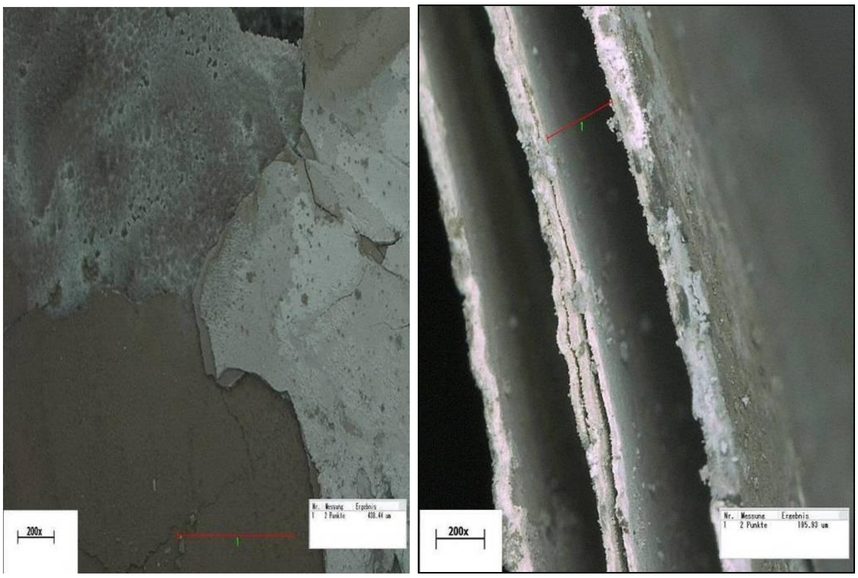


Figure 7: Samples from condensate after distillation test 2-1 at 750°C

Figure 8: Four layers obtained as condensate material in the quartz tube of a selective distillation at 750°C

Figure 9 (left) illustrates a magnification picture of the condensed material after the process at 750°C. It shows obviously the crystallised grains of metallic magnesium, clean and without any kind of contamination and/or co-distilled components. This magnesium has been condensed shortly after evaporation on the inner wall of the quartz tube, installed below the main condenser, maybe because this tube is also “cold enough” to play the role of a condenser for vapour magnesium. It is supposed that the condensation process is carried out very slowly and that’s the reason that condensed magnesium has enough time to grow in the form of crystallised grains. This crystallised magnesium is assumed to be the very first step of distilled material and therefore, it is condensed on quartz tube, because it is almost cold at the beginning. On the contrary, the further steps of distilled materials can not take the quartz tube as a condenser, because it became rather hot due to the high pressure magnesium vapour. Hence, it condensed on the main condenser. On the other hand, this condensate is the rest of metallic magnesium as well as a mixture of different salt components and that's why the magnesium grains did not succeed to grow.

Table 2: Chemical analysis of the condensed layers at 750°C, represented in Fig. 8

Layer Nr. from the quartz tube's wall	Al ppm	Ca ppm	K %	Mn ppm	Na %	Zn %	Cl %	Mg_{total} %	$Mg_{met.}$ % estimated
1	327	190	2.8	< 10	3.2	0.6	5.2	88.2	> 86.44
2	210	175	2.9	< 10	2.8	0.9	7.07	86	> 83.61
3	188	239	2.3	< 10	2.4	0.9	5.83	88	> 86.03
4	142	124	2.0	< 10	2.0	0.9	4.92	90	> 88.34

The interesting observation was then achieved via assessment of the material collected from the quartz tube microscopically (see fig. 9 right). This picture shows the crystallised grains of magnesium are now covered with a layer of salt. It proves from one side that the distillation of metallic magnesium occurs before the other components and from the other side; the condensation of this salt takes place with a considerable time distance with magnesium. That's why the temperature of quartz tube - after condensation and crystallisation of magnesium - again decreases, so that the evaporated salt takes this crystal layer as a new condenser.

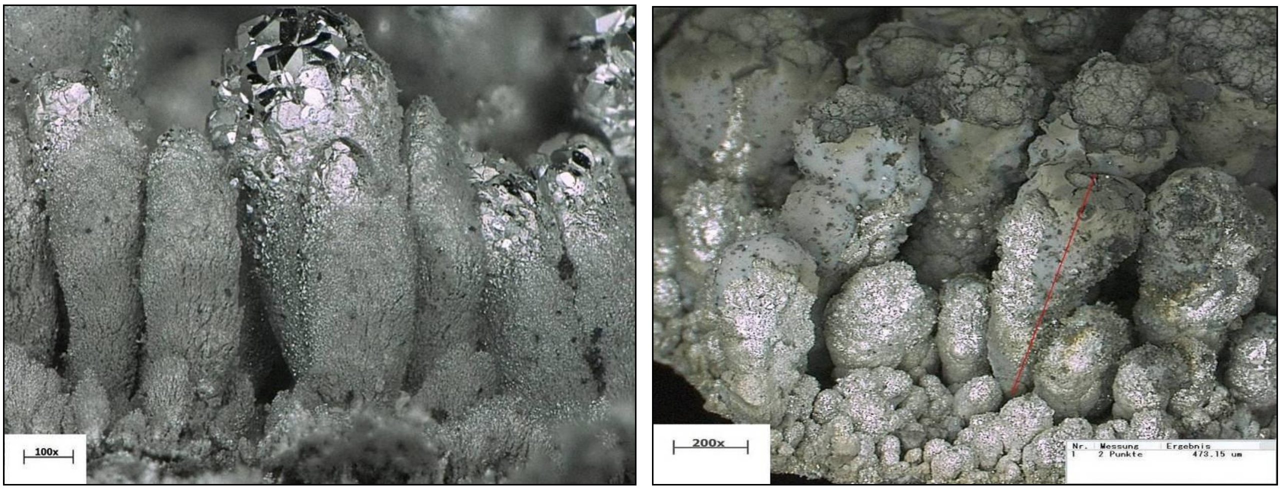


Figure 9: (left) Sample from condensate in the quartz tube after distillation test concluded at 600°C - 750°C and (right) condensed sample obtained in quartz tube after distillation at 900°C covered with a layer of salt

Similar to figure 8 the condensate appears at 1200°C. According to the circles identified in figure 10, four different layers can be observed in the condensed material collected in the condenser at this last distillation step. These layers are then investigated individually through XRD analysis, whose results are represented in figure 11. Beside metallic magnesium, typical chloride components present in Flux 5, including NaCl and KCl are found in these layers, but also some different compounds such as $KCaCl_3$ and K_2ZnCl_4. A new effect seen at 1200°C that is not seen before is related to the fluoride containing salt components. The fluorides have generally much less vapour pressure in comparison with chlorides, but at 1200°C the components such as $KMgF_3$, ZnF_2 and also CaF_2 are detected. On the other hand, still to the last phase of this final heat, magnesium metal can be found in the condensed material. It shows that due to the diffusion resistance or thermal inhomogeneities in the crucible, it needs much longer time (and energy) to recover the Mg-metal at lower temperatures before significant salt fractions will join the distillation gas.

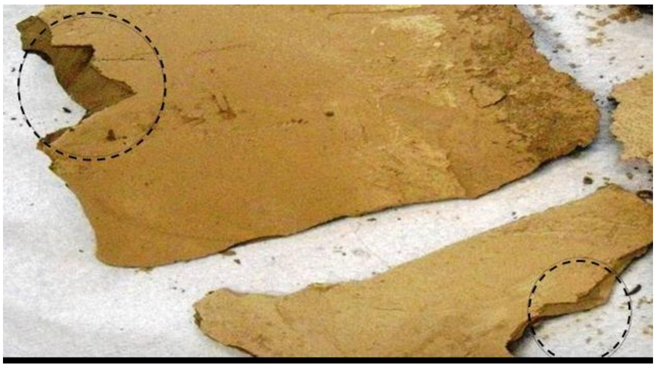


Figure 10: Condensate layers obtained after final distillation at 1200°C

The XRD-pattern of the residue of black dross after accomplishing the vacuum distillation at 1200°C (fig. 12) shows that beside magnesium oxide, salt components ($KCaCl_3$, $KMgCl_3$ and KF) and some intermetallic compounds ($Ca_2Mg_6Zn_3$) as well as metallic aluminium is observed. In the present case, more than one probable phase for each peak can be assumed. Furthermore, the intermetallic compounds of Al-Mg and Al-Mn can not be found here; instead a new intermetallic between Ca-Mg-Zn is identified. Also, the rest of fluorine remains in the residue in the form of Potassium fluoride. This product is very similar to the leaching residue of Al-salt-slag treatment, finding applications e.g in concrete.

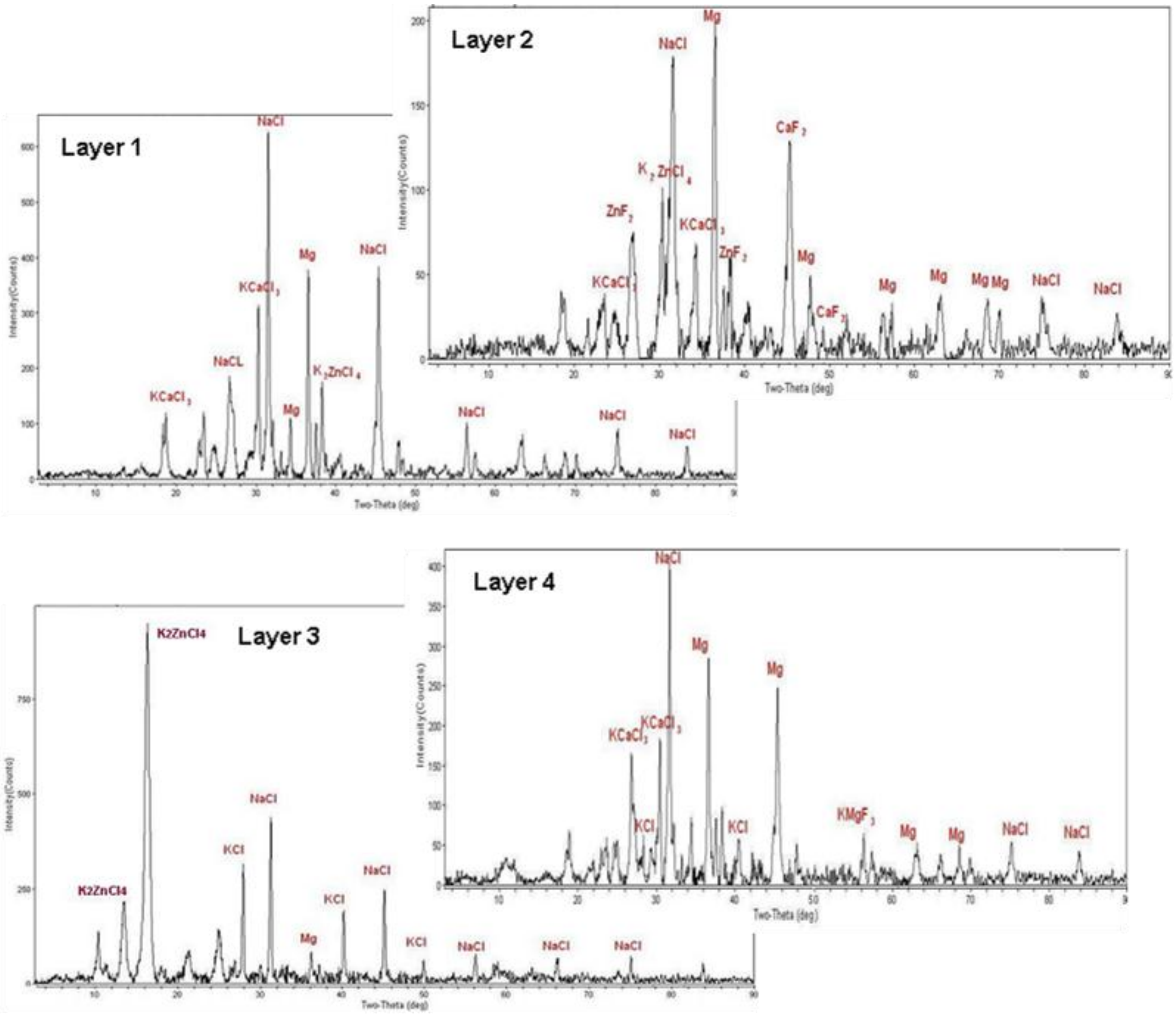


Figure 11: X-Ray diffraction pattern of condensate layers (1.layer is closest to the condenser's wall) at 1200°C

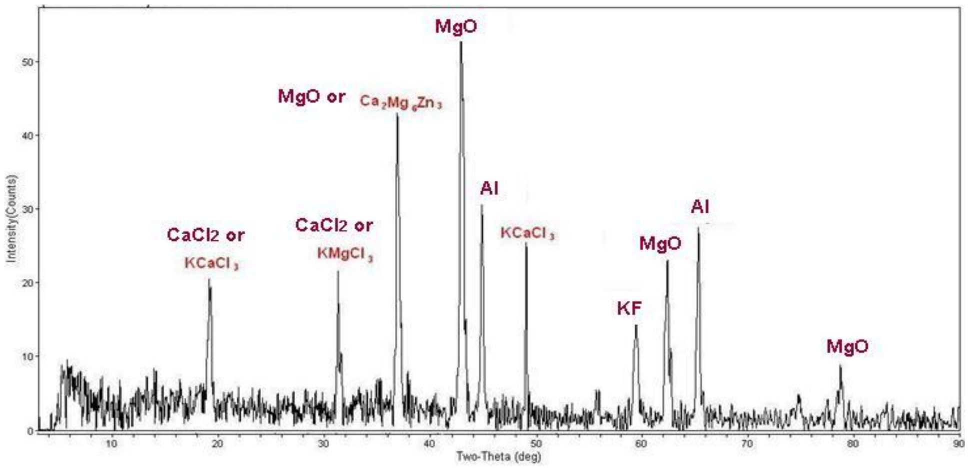


Figure 12: X-Ray diffraction pattern of the crucible residue after final distillation

4.2 Results of the Pilot-Scale Trials

From the pilot-scale trial, totally 22 kg condensed material is collected, from which 14.6 kg were taken from the inner part of the hood, 6.2 kg from the collecting plate as well as 1.4 kg from the aperture. As table 3 shows the condensed material collected in hood is quite different especially from the point of Mg-, Ca- and Cl-wt% from the other samples. In this material the Cl-content is considerably lower than that of aperture and collecting plate, showing the lower amount of salt condensed over the hood in comparison with metallic portions. This fact does well suit to the significant value of magnesium and small amounts of sodium as well as potassium. Also, the Zn-content is obviously higher than other samples. Regarding the fact that Na, K and Al are mostly in the form of chlorides, it is easily to calculate that approx. 3.55% of Cl is in the form of NaCl, 0.82% in the form of KCl and 2.17% in the form of $AlCl_3$. Hence, the amount of Cl attending $MgCl_2$ is about 10.16%, so that the Mg-value in $MgCl_2$ is also to be calculated equal to 3.43%. Therefore, metallic magnesium can be assessed to approx. 70% in the hood. On the other hand, the Cl-content in the collecting plate and aperture is more than twice of that in the hood, pointing out much less metallic magnesium in these samples, which is estimated to be about 40%. A complete different effect in the aperture is the appearance of Mn in its samples, with maximum likelihood not as metallic form, because metallic manganese with a melting point of 1246°C and a boiling temperature of 2061°C is still in the form of solid even at 1 mbar atmosphere and 1100°C and can’t be distilled. Therefore, this Mn should be in the form of chloride, leading to even much less content of metallic magnesium, about 25%.

Table 3: Chemical analysis of the condensed material from three part of the condenser [wt%]

Condensed definition	Na	Mg	K	Ca	Al	Mn	Cl	Zn
Hood (sample 1)	2.3	73.5	0.9	n.a.	0.55	n.a.	17.65	5.1
Hood (sample 2)	2.2	73.1	0.9	n.a.	0.53	n.a.	18.57	4.7
Hood (sample 3)	2.2	72.7	0.9	n.a.	0.58	n.a.	18.72	4.9
Collecting plate (sample 1)	4.1	57.1	1.8	0.18	0.56	n.a.	33.16	3.1
Collecting plate (sample 2)	6.0	54.6	1.7	0.16	0.6	n.a.	34.04	2.9
Collecting plate (sample 3)	4.2	52.7	2.1	0.28	0.57	n.a.	37.15	3.0
Aperture (sample 1)	4.3	29.9	2.1	0.81	4.8	5.2	51.29	1.6
Aperture (sample 2)	4.4	29.2	2.1	0.85	4.8	6.2	50.55	1.9
Aperture (sample 3)	4.6	30.7	2.2	0.82	5.4	6.1	48.18	2.0

In table 4 the chemical analysis of the crucible residue has been represented. That is again to be noticed that neither oxygen nor fluorine is able to be determined via ICP analysing method; however, the Ca-content - more possible to be in the form of calcium fluoride - is too small to have any influence on the total chemical composition. As the very first glance in this table, more than 20% chlorine is still existed in the residue after distillation, showing a non-complete distillation process. The value of chloride components as well as metallic portions can be calculated and approximately 10.7% NaCl, 2.5% KCl, 1.6% $CaCl_2$ and 17.6% $MgCl_2$ can be determined. Aluminium and manganese can be only in metallic form present in the residue; in contrast, magnesium is to be considered as oxidic and/or chloride form. The very surprising effect in this chemical analysis is the relatively high amount of manganese. It is expectable to have manganese inside black dross, due to the usage of e.g. AM50 - the aluminium and manganese containing magnesium alloys - in the recycling process. However, the manganese content is always lower than that of aluminium. The reason of this significant 25% of manganese can be because of the chlorination-ability of aluminium, which leads to produce aluminium chloride and then to evaporate/ condensate this component during distillation process. Hence, the ratio of manganese in the residue increases. On the other hand, considering approx. 32% salt and 35% metallic portion, the value of oxidic magnesium will be about 33%. In the case of leaching of this residue, it is expected to achieve almost 32% salt in the form of salty water.

Table 4: Chemical analysis of the crucible residue after a pilot-scale distillation [wt%]

Crucible residue	Na	Mg	K	Ca	Al	Mn	Cl	Zn
Sample 1	4.0	26.4	1.4	0.56	10.7	25.9	21.8	0.3
Sample 2	4.1	26.3	1.2	0.6	10.7	25.4	22.2	0.3
Sample 3	4.4	27.3	1.4	0.6	9.9	24.5	22	0.3

In formerly published articles of the authors [12,13] it has been shown that an optimum chemical composition of the recycling salt exist. This salt mix achieves the highest coalescence efficiency of molten magnesium droplets and therefore minimizes the metallic loss. It is based on 56 wt% $MgCl_2$, 15 wt% KCl, 24 wt% NaCl and 5 wt% CaF_2. According to the fact that not all salt components (e.g. CaF_2) can be distilled under the operational conditions, the salt composition in the condensate differs from that what was identified for most efficient metal/salt separation and metallic coalescence. Therefore, the missing chloride- and fluoride components were added to the condensate after distillation followed by remelting of the entire mixture at approx. 760°C, pouring the crucible content into a mould and allowing to separate metal from salt (see fig. 13 including the chemical analysis). The presence of approx. 8.2 kg magnesium was determined from 59 kg input black dross, nearly equal to 14%. This ratio suits very well to the investigated value of lab-scale trials. The remaining salt after remelting has the property to be reused in the recycling process, even without preliminary separation from the metal.

Al 0.21 %	**Mn 0.18 %**	**Zn 3.93 %**	**Pb 0.93 %**	**Si 0.06 %**	**Mg 95.08 %**

Figure 13: Casted magnesium after separation from co-distilled and reactivated salt, including its chemical composition

5 Conclusion

The mass flow of an optimized process of black dross vacuum distillation as well as the recovery of metallic magnesium and recycling salt is summarized in fig. 14. The term "optimized" refers to a process, which can be conducted in modified experimental conditions; here, as a mixture of the best results derived from both lab- and pilot-scale trials. In this figure the amount of applied black dross is taken to be 1000 kg, which is then split into approx. 630 kg condensate and approx. 370 kg residue through vacuum distillation. Considering the amount of 1.47 kg (min.) added salt for 22 kg condensate, approx. 40 kg salt addition would be required if the condensate is 630 kg. In this mass flow twice added salt as this value was taken, equal to 89 kg just to ensure the coagulation. By addition of this salt, about 20% of black dross can be recovered in an optimum case as metallic portion. The salt remained after reactivation/remelting process can be then reused as a recycling salt. The crucible residue, mostly containing ceramic/oxidic portions as well as a minor rest of salt, can be leached with fresh water to separate these two parts from each other. The ceramics could maybe used in refractory industry and the salty water remained from the leaching process has to be treated in a vaporizing process or given to the environment, if allowed. It can be seen that almost a zero-waste-process has been developed, which closes the existing gap in the magnesium recycling loop.

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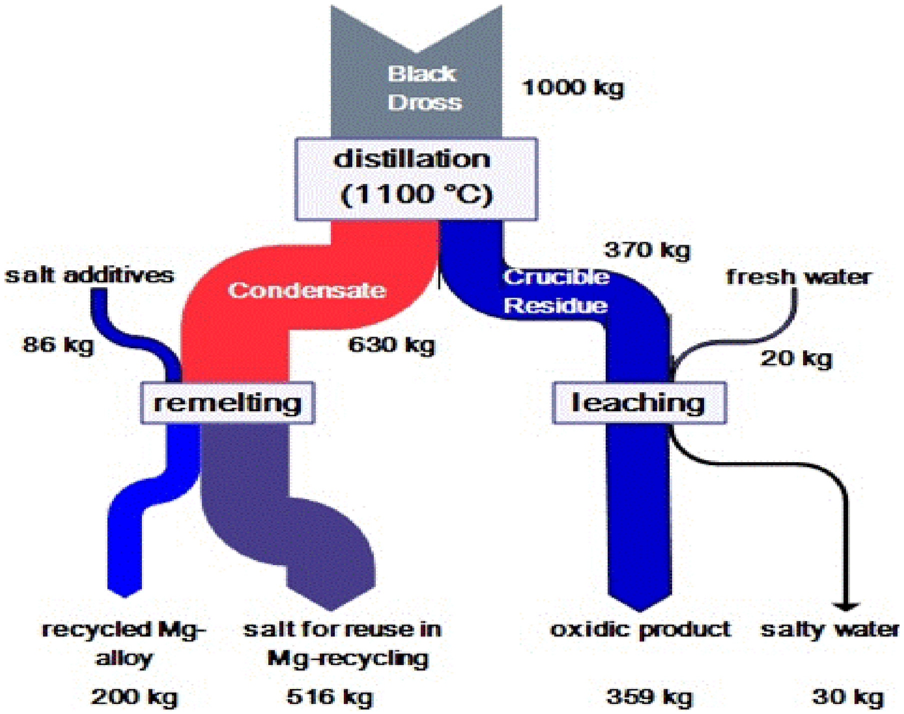

Figure 14: Expected mass flow diagram of vacuum distillation after final process optimization

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