



Recycling of Mg-sludge: an Investigation to realise a Closed Loop Recycling of Magnesium

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Abstract

Magnesium and magnesium alloys belong to the lightest engineering metals with densities about 1.8 g/cm^3 . Further properties like good heat conductivity, high specific strength and excellent damping behaviour explain the increasing use of magnesium as a basic material for light weight constructions like in planes or automobiles. Parallel to the increase of Mg production and use of Mg products the quantity of Mg scrap rises. Throughout all melting processes (primary magnesium production as well as remelting of magnesium scrap) the formation of dross or sludge cannot be avoided. Dumping or disposal of the dross or sludge in the ocean is not a final solution in matters of saving the resources and our environment.

IME, Process Metallurgy and Metal Recycling, Department of RWTH-Aachen started a three years government funded BMBF collaboration research project in April 2002 to develop recycling concepts. The main target is the recycling of magnesium scrap with a low amount of Mg-metal, e.g. dross and sludge. The intention of this project is to separate the waste into three parts: Mg-metal, oxides and a cleaned reusable salt.

This paper gives an overview of the experimental part in this project. It starts with the calibration of the gas fired crucible furnace and shows the results of the tests in which different salt volumes were used. Subsequently sludge is characterised, which has been used once, twice or three times as melting salt. Furthermore a new resistance heated Mg furnace with a 35 l crucible is presented, especially designed and constructed for this project. Finally the perspective of further work is given.

1 Motivation

Increasing research and development activities in magnesium technology during the last decade open new applications for magnesium and its alloys. But in comparison to aluminium the development has just started. Parallel to the optimisation and the rising application possibilities in automotive and aeronautics, a significant rise in the consumer area is forecasted. During the production and with the end of use of the consumer goods, scrap occurs which has to be recycled to save resources and the environment. Figure 1 gives an overview of the mass flow in magnesium production and recycling.

The main target of IME, RWTH-Aachen and the BMBF is to close the loop of magnesium production scrap without downgrading the magnesium quality. During magnesium processing and magnesium production scrap emerges. Actually this magnesium containing waste is used for alloying, desulphurisation of iron, metallurgy or it is dumped [1, 2], especially when highly oxidised or with a high surface. In the future dumping must be avoided. Through recycling of scrap like dross, sludge or turnings contaminated with oil, emulsion or water, the loop of magnesium production scrap can be closed.

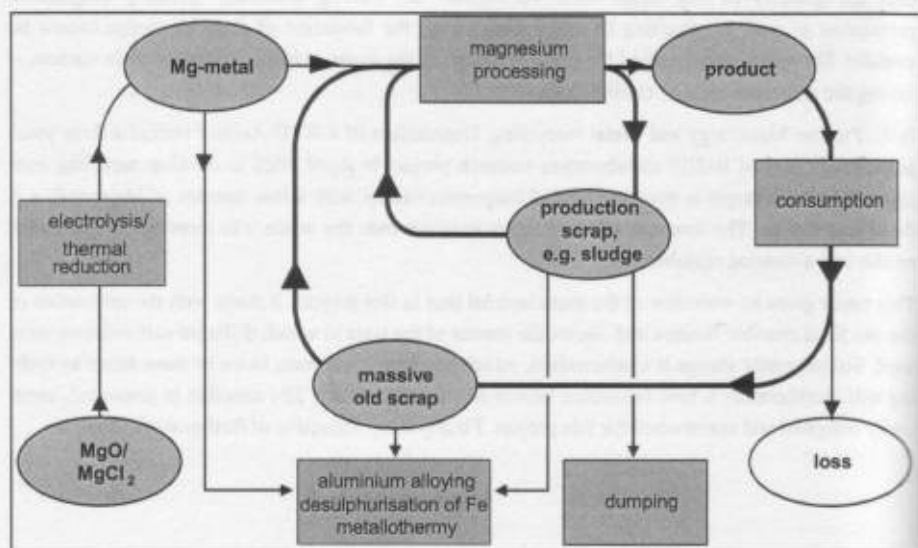
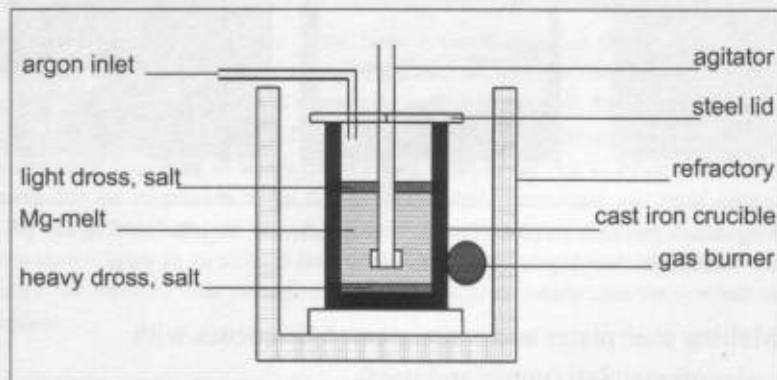


Figure 1: Mass flow in magnesium production and recycling

2 Experimental Set Up and Process Parameters

In bench scale tests industry melting conditions were to be simulated. At the beginning a gas fired iron crucible furnace with a 5 l iron crucible (Figure 2) was used for calibration tests with compact Mg plates allowed to fix parameters like composition and amount of flux and temperature. The influence of the liquid phase during charging, the use of a mechanical stirrer (60 mm ϕ ; 400 rpm) and the charging sequence of materials were tested. The best results were achieved with flux 12, a salt from Rheinkalk HDW, Germany in a range of 5 tested industrial salts [3]. Flux 12 consists of Carnallit with components of magnesium-, sodium- and potassium chloride. Number 12 stands for the amount of 12 % calcium fluoride. The salt has a melting point of 424 °C and a density of 2.28 g/cm³. Some further parameters of the melting process are shown in Figure 2.



fixed parameters:

temperature: approx. 700 °C
atmosphere: argon, 5 -10 l/min

crucible volume: 5 l
Mg content, e.g. briquettes: 3 kg

Figure 2: gas fired crucible furnace [4]

3 Results

3.1 Pre-trials using different salt volumes

An average metal yield of 95 % regarding to the weight of charged compact Mg plates can be reached. If the amount of salt used is between 20 and 50 % of the charged metal mass a good separation of metal and salt or sludge resulted. Only one mix phase is formed of salt appear if less than 20 % of salt is charged. If the salt amount is more than 50 %, magnesium is finely dispersed in the flux (Figure 3). The best results are achieved if magnesium is charged into liquid salt at 660 °C. The

possibility of an overflow of the melting salt had to be observed. Regarding the average metal yield of 95 % of the calibration tests with magnesium plates, the process in a gas fired furnace with optimised parameters is one possibility for melting magnesium. During melting of compact magnesium plates the flux used prevents magnesium from burning and leads to a good separation of magnesium and salt if the amount of salt lies in the above mentioned boundaries [5]. Contrary to these results, the industry uses only 3 % salt. This could be explained by the crucible size. The industry used bigger furnaces e.g. 500 l crucibles, so the ratio of surface to volume is different.

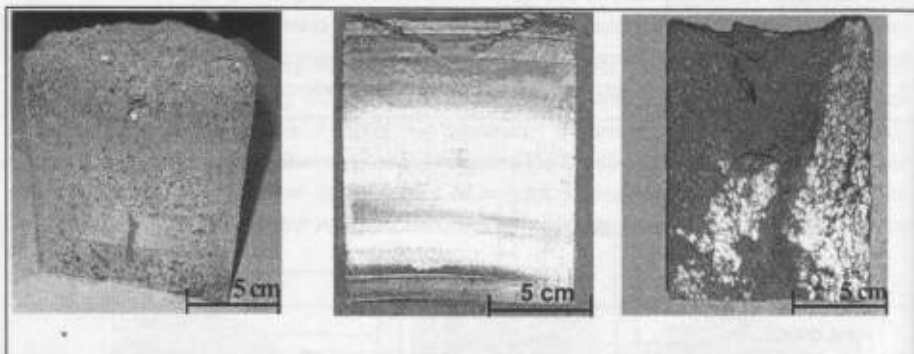


Figure 3: Magnesium castings; molten with 12 % salt (left), 25 % salt (middle) and 60 % salt (right) [5]

3.2 Melting pure plates and contaminated Briquettes with conventional Salt (virgin and used)

While using flux 12 twice or three times its viscosity raised slowly when pure and massive compact magnesium plates were molten. In contrast to this the viscosity increased significantly when melting oil contaminated Mg briquettes until a crumbly sludge appeared. This sludge seemed to be more solid than liquid due to increasing content of impurities. Because of the higher viscosity of the salt, more magnesium metal was dispersed in the sludge, so the metal yield decreased. Also the separation between metal and salt was worse. Significantly more inclusions were in the taped metal. Furthermore it was noticed that the amount of sludge depended strongly on the type of charged material (Figure 4). Contaminated material produced more sludge than e.g. pure Mg plates [5].

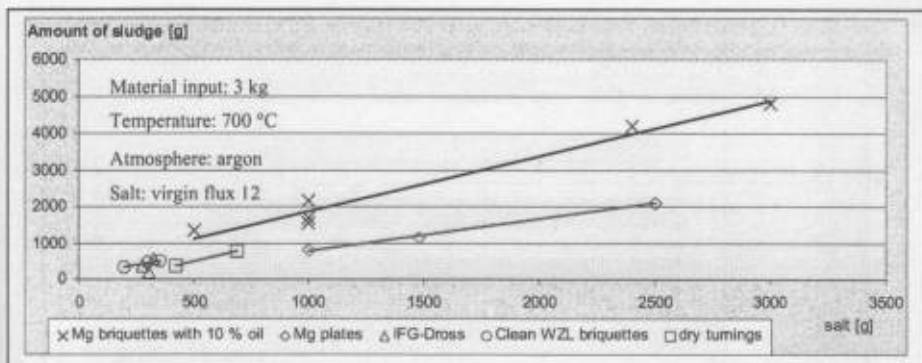


Figure 4: Amount of sludge formed depending on the type of charged material and salt added[5]

The protection against oxidation of the metal is nearly the same like in case of using fresh flux. Only small amounts of fresh salt on top of the melt are necessary to stop small burnings. The melting salt foamed very quickly and covered the surface of the melt. For good isolation salt quantities between 20 and 50 % of the metal were needed and could also be used sludge. Even though viscosity and metal dispersion of sludge rise it makes sense to use flux 12 twice or three times. It can be shown that the magnesium losses during melting due to saturation and metal dispersion is better using sludge than new salt. Also no hydrate water is present so the oxidation of magnesium is minimised (Figure 5). In addition lost metal droplets are brought back into the process when using sludge two times[5]. This procedure opens a potential to reduce costs for new salt and for sludge disposal.

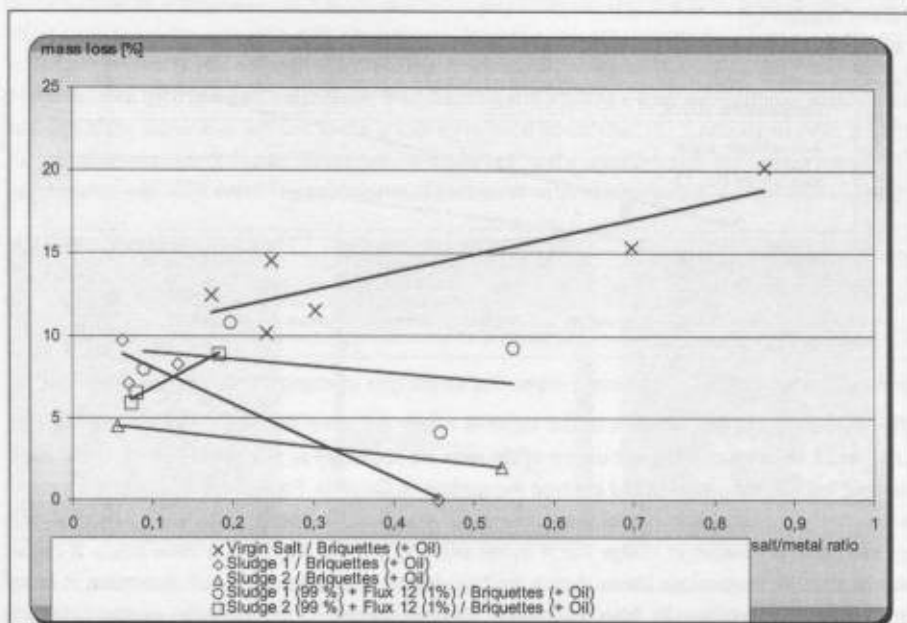


Figure 5: Magnesium losses depending on the on the type of "salt" used [5]

One advantage of the process substituting salt by sludge is that the metal yield rises, especially if related to the charged magnesium briquettes or plates. The second is that sludge which had normally to be dumped can be reused. The metal yield, calculated by the following formula is also depending on the charged material.

Metal yield (%) = [tapped magnesium metal (g) / charged metal (g) (e.g. Mg briquettes)] * 100

With a mix of sludge used once and oil contaminated briquettes a metal yield of 85 % is possible. Further results are shown in Figure 6.

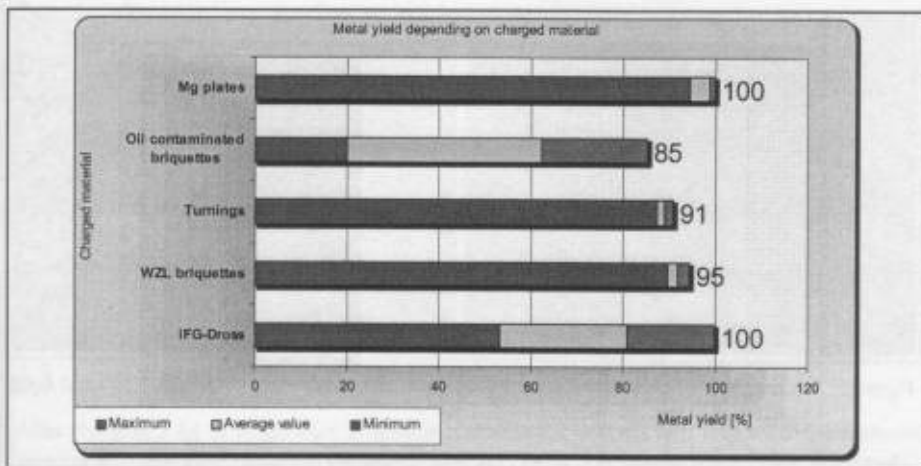


Figure 6: Metal yield subjected to the charged material [5]

4 Characterisation of non metallic input/ output Materials

In order to investigate the change of salt composition during the melting process new salt as well as salt used once, twice or three times (called sludge) were analysed.

4.1 Characterisation of commercial Salt (virgin Material)

Flux 12 powder with a grain size of 5 mm resulted to the following composition (Table 1).

Table 1: ICP Analysis of Flux 12

Mg [%]	Al [%]	Na [%]	K [%]	Ca [%]	Cl [%]	F [%]	Balance [%]
9.8	0.2	10.3	10.4	4.4	50.4	3.8	10.7

Figure 7 shows a micro-graph picture of Flux 12 made by scanning electron microscopy. Noticeable are 4 marked points. The results of their EDX-analysis are given in Table 3. Most of the balance can be assumed to be water or OH-groups.

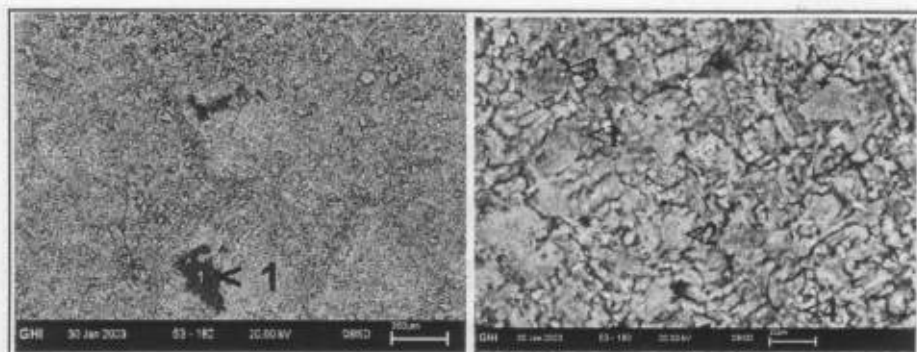


Figure 7: micrograph of flux 12 by scanning electron microscopy left (enlarged 1:50) and right (enlarged 1:500)

Aluminium, fluoride and oxygen rich zones (Table 2) are located in Figure 7 left.

Table 2: EDX – Analysis of Flux 12 (Figure 7 left)

	Al [%]	K [%]	Ca [%]	Cl [%]	F [%]	Si [%]	O [%]
Point 1	23.9	1.2	0.9	5.6	27.8	1.6	38.7

Figure 7 (right) and the chemical analysis (Table 3) prove different phases existing in flux 12. Fluoride and chloride rich zones with different amounts of magnesium, sodium, potassium and calcium are present as are areas with an enriched content of barium, sulphur and oxygen are.

Table 3: Chemical Analysis of different micrograph areas with EDX (Flux 12, refer to Fig. 7 (right))

Sample	Mg [%]	Al [%]	Na [%]	K [%]	Ca [%]	Cl [%]	F [%]	Ba [%]	S [%]	O [%]
Point 1	18.3		6.0	7.4	2.7	32.0	4.2			29.3
Point 2	4.0		0.8	15.3	16.6	44.7				18.2
Point 3	16.8	0.3	1.4	2.3	0.8	9.4	1.2	24.9	6.0	36.9
Point 4	7.1	0.7	25.2	4.7	1.6	52.0				8.4

4.2 Characterisation of molten commercial Salt (without additions)

Virgin flux 12 is molten at 660 °C and samples are taken after each 10 minutes. The results of the samples analysed by inductively coupled plasma spectrometry (ICP) are shown in Table 4.



Table 4: Mean analyses of molten salt based on 16 samples.

Flux 12	Mg _{non ox.}	Mg _{ox.}	Al _{non ox.}	Al _{ox.}	Zn _{non ox.}	Na	K	Ca	Cl	F	Balance
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0 min.	9.8		0.2			10.27	10.44	4.39	50.39	3.76	10.75
10 min.	8.12	2.37	0.08	0.04	0.01	9.21	9.44	4.76	47.58	3.08	15.26
20 min.	8.12	2.49	0.12	0.05	0.01	9.50	9.79	5.17	48.78	3.16	12.83
30 min.	8.01	3.01	0.08	0.05	0.01	9.47	9.83	5.29	48.75	3.79	11.71
40 min.	7.98	3.12	0.10	0.05	0.01	9.31	9.65	5.21	48.40	3.58	13.59

The results of the tests show that flux 12 basically does not change consistence during heating diving the first 40 minutes without contact with molten magnesium.

4.3 Characterisation of Sludge

After charging 3 kg of magnesium briquettes contaminated with oil into 1 kg molten salt several samples of sludge were taken and analysed (Table 5).

Table 5: sludge sample composition after charging magnesium (based on 7 samples)

	Mg _{non ox.} [%]	Mg _{ox.} [%]	Al _{non ox.} [%]	Al _{ox.} [%]	Zn _{non ox.} [%]	Zn _{ox.} [%]	Na [%]	K [%]	Ca [%]	Cl [%]	F [%]	Balance [%]
Minimum	20.2	2.2	2.1	0.12	0.18	< 0.01	1.9	2.0	1.5	10.7	0.96	11.9
Maximum	45.2	4.0	4.5	0.75	0.38	0.011	5.2	5.2	3.0	26.5	1.8	38.0
Average Value	35.4	2.9	3.8	0.40	0.29	< 0.01	4.0	4.2	2.4	20.7	1.3	24.6

The metal content is finely dispersed. Regarding the weight of salt components it is evident that the salt content is nearly constant.

Figure 8 (left) shows a sludge probe after salt contact with magnesium plates (AZ91). In the centre a magnesium droplet with a diameter of nearly 0.4 mm is shown. Remarkable are the bright areas inside and at the edge of the drop, showing different phases. A detailed picture of the inside brighter phases is shown in Figure 8 (right).

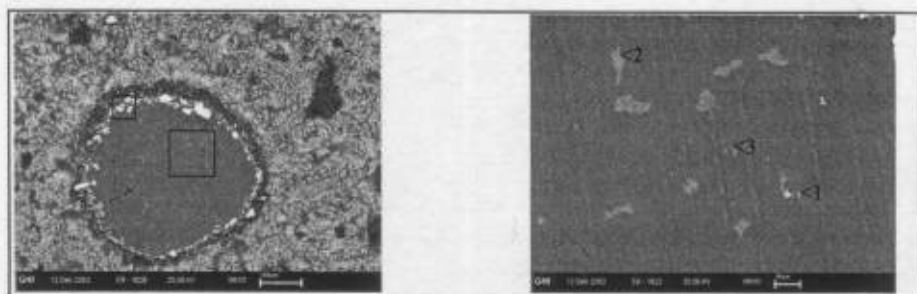


Figure 8: SEM; metallographic investigation of sludge with magnesium drop (charged material: Flux 12 and magnesium plates (AZ91); left: enlargement 1: 100; right: drop center enlargement 1:100

The analysis of the marked points in Figure 8 (right) is shown in Table 6

Table 6: EDX-analysis of metallic phases in the Mg droplet marked in Figure 8 (right)

Point	Mg[%]	Al[%]	Zn[%]	Cu[%]	Ni[%]	O[%]
1	63,0	25,2	2,3	7,4	0,7	1,5
2	64,9	29,2	2,4	1,5		2,0
3	95,5	1,8				2,7

The detail picture of the edge area shown in Figure 8 and the chemical EDX-analysis of the phase interface between magnesium metal and sludge is shown in Figure 9.

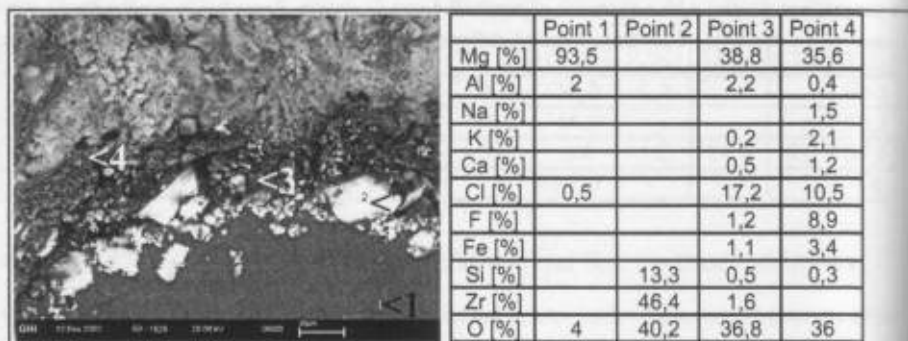


Figure 9: SEM and EDX analysis; enlargement 1: 500; sludge with magnesium drop; charged material: flux 12 and magnesium plates (AZ91); interface between magnesium metal and sludge

The magnesium metal (marker 1) is surrounded by three phases. The white phase (marker 2) consists of silicon, zirconium and oxygen. This may be a drag in from the crucible smoothing. Marker three and four consists mostly of magnesium, chloride, fluoride and oxygen. Differences between marker three and four are mainly the content of chloride and fluoride.

4.4 Characterisation of used Slag

A large scale micrograph of three times used salt/slag after melting magnesium plates (AZ91) is shown in Figure 10. Beside the magnesium and the salt phase some dark and white areas can be seen. An bulk analysis of the surface shows that it consists of 45 % Mg, 20.6 % O and 15.6 % Cl. Further 2.6 % Al, 2.4 % Na, 3.4 % K, 2.8 % Ca and 3.8 % F are detected.

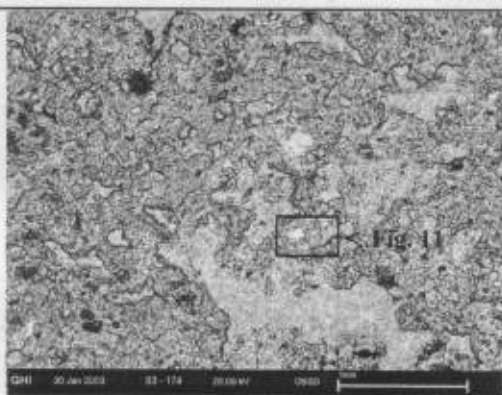


Figure 10: SEM; enlargement 1: 20; general micrograph of flux 12 used three times.

Figure 11 shows the phases in detail. The dark phase (point 1) consists mostly of magnesium, aluminium, chloride, fluoride and oxygen (see Table 7). Potassium and calcium, together with titanium, exist also in this sample, but only in smaller amounts. The main components of phase three in Figure 11 are magnesium, chloride, iron and oxygen. The white phase near the centre (Fe/Point 2) of the picture is pure iron that possibly originates from the crucible.

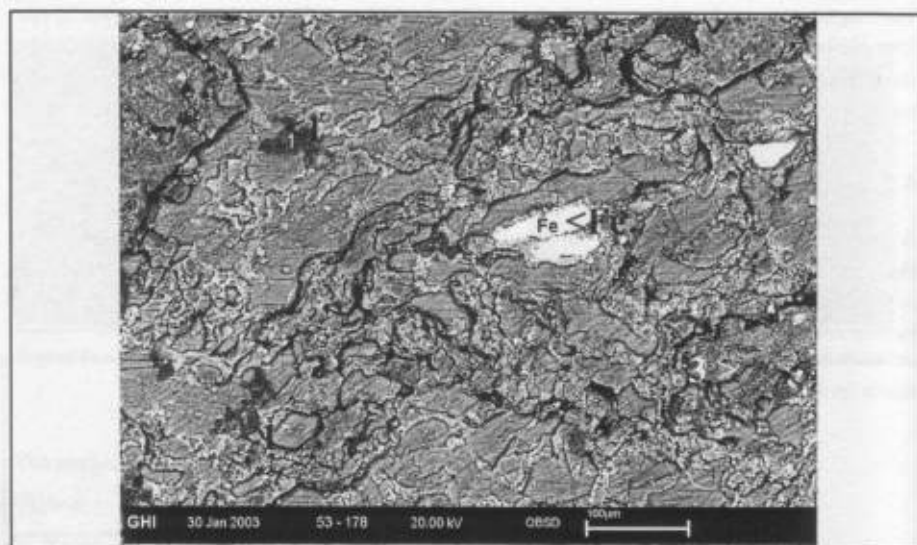


Figure 11: SEM; enlargement 1: 200; detail picture of Figure 10

Table 7: EDX-analysis of phases shown in Figure 11

Sample	Mg [%]	Al [%]	K [%]	Ca [%]	Cl [%]	F [%]	Ti [%]	O [%]
Point 1	33,8	7,6	2,9	1,6	9,3	36,8	0,6	7,4
Point 3	31,4	1,4	0,4	1,3	17,9	6,0		41,6

A more detailed picture is shown in Figure 12 where the transition between salt (sludge) on the left side and magnesium on the right side is mapped. Eye-catching are five phases. Some phases contain nearly 50 % manganese or iron. A summary of the EDX analyses is also given.

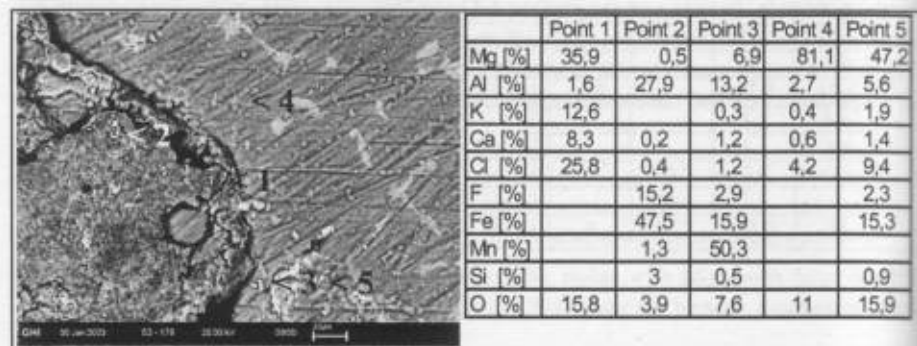


Figure 12: SEM; detailed picture of the boundary between magnesium metal and salt

5 Development of a new resistive heated Mg furnace at the IME

After finishing the pre-trials and comparing the results of the gas fired 5 l furnace with industry processes (800 l) the amount of salt needed in a small furnace rises above the amount used in real production. A bigger furnace with meeting the necessary process parameters, e.g. temperature, salt factors, stirring conditions, was developed in order to simulate industry conditions.

Figure 13 shows a scheme and a picture of the new magnesium furnace developed by IME and constructed by ThermoStar, Aachen.

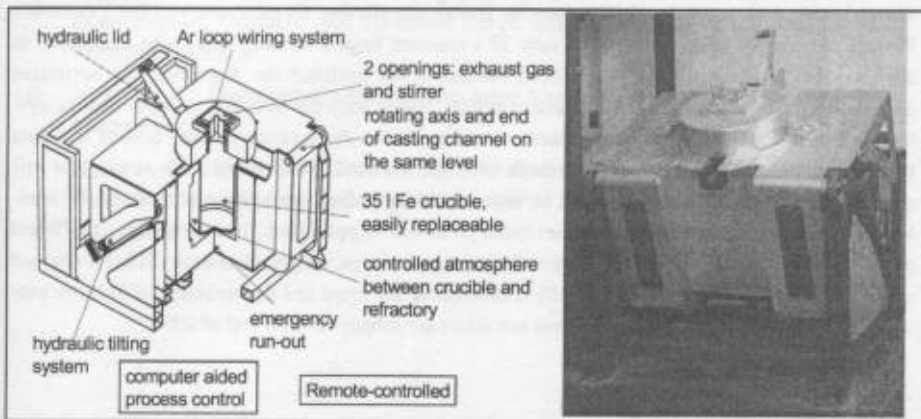


Figure 13: Project developed Argon-shielded and resistive heated Mg furnace (35 l)

The 35 l prototype furnace, heated resistively with SiC bars, serves a high number of special features, e.g. a remote-controlled hydraulic tilting system. The furnace is constructed in a way, that the end of the casting channel is placed in the rotating axis. This allows an easy and secure tapping. Furthermore, the safety is enhanced through an also remote-controlled lid. The characteristic of the top is an argon loop duct system to protect the melt and two openings for a mechanical stirrer and a defined off gas duct. Additional the atmosphere between refractory and iron crucible can be flooded with cover gas. It is easy to control the surface of the crucible (safety!) because of the simple dismantling of the crucible. If, contrary to expectations, the crucible cracks during melting a emergency run out is maintained at the bottom using melt fuse. Instead of iron, also a ceramic crucible can be used. With a power of 45 kW, it is possible to heat the system up to 1500 °C. The excess electrical power is also needed to minimise the first melting phase to minimize the possibility of oxidation. The computer-aided process control carries out special heating programs. This is necessary, e.g., for deoiling of Mg turning briquettes.

Auxiliary equipment, like a mechanical argon injecting stirrer, a continuous material feed or an afterburner, can be used on request.

6 Perspectives

The results achieved in the gas fired furnace are promising. Instead of direct dumping sludge will be reused up to two times. Parallel to saving costs for dumping and new flux, the metal yield rises because the magnesium content of sludge is recovered and the metal oxidation is minimised due to not existing hydrate water.

Important to know is that the results of the gas fired furnace are different to industry practise. Magnesium recycler use 3 % salt referring to charged clean scrap and only up to 20 % salt referring to charged scrap with a high level of impurities. Before transferring the parameters of the 5 l crucible furnace to industry scale, tests in the new 35 l resistive heated furnace have to be conducted to simulate real conditions where a gas fired furnace is not qualified for. Especially the optimised cover gas equipment promises new effective results. Along with the powerful resistive heating system and computer controlled temperature, new possibilities for a better process control and data logging can be reached. This way, methods of removing cooling lubricants from turnings or briquettes like water, emulsion or oil will be tested by using definite preheating parameters. By combination of these methods the magnesium metal yield will be optimised. Because sludge of different processes never has the same composition the produced sludge, subjected to each different charged material, has to be characterised carefully. Furthermore the reuse and the recycling of industry production sludge will be investigated. These test series are scheduled until end of 2004.

7 Acknowledgments:

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- Norsk Hydro Bottrop, Magnesium Producer: providing material (Mg/sludge) and scale up tests
- Rheinkalk HDW, Salt Producer: providing salt
- IFG Düsseldorf, Foundry Institute: tests with recycled magnesium
- WZL-RWTH Aachen, Machine Tools and Production Engineering: safety metal cutting of Mg, producer of dry turning-briquettes or briquettes with oil, water or emulsion as lubricants.
- GHI-RWTH Aachen for the EDX-analyses.

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