Recovery of Magnesium and Salt from Black Dross through Vacuum Distillation

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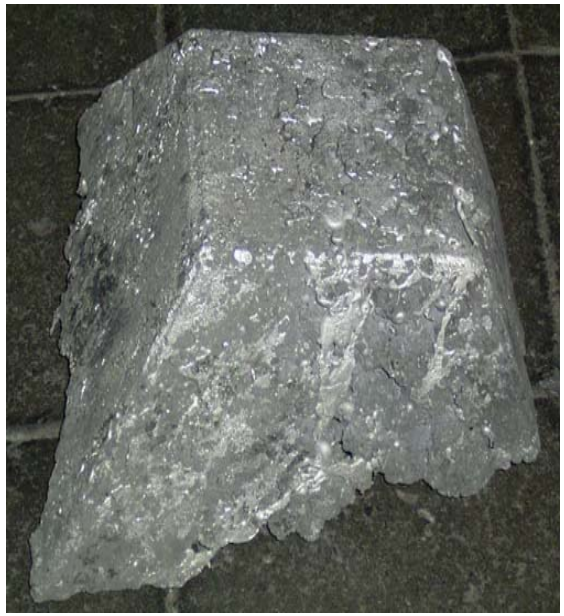
Challenges of Black Dross

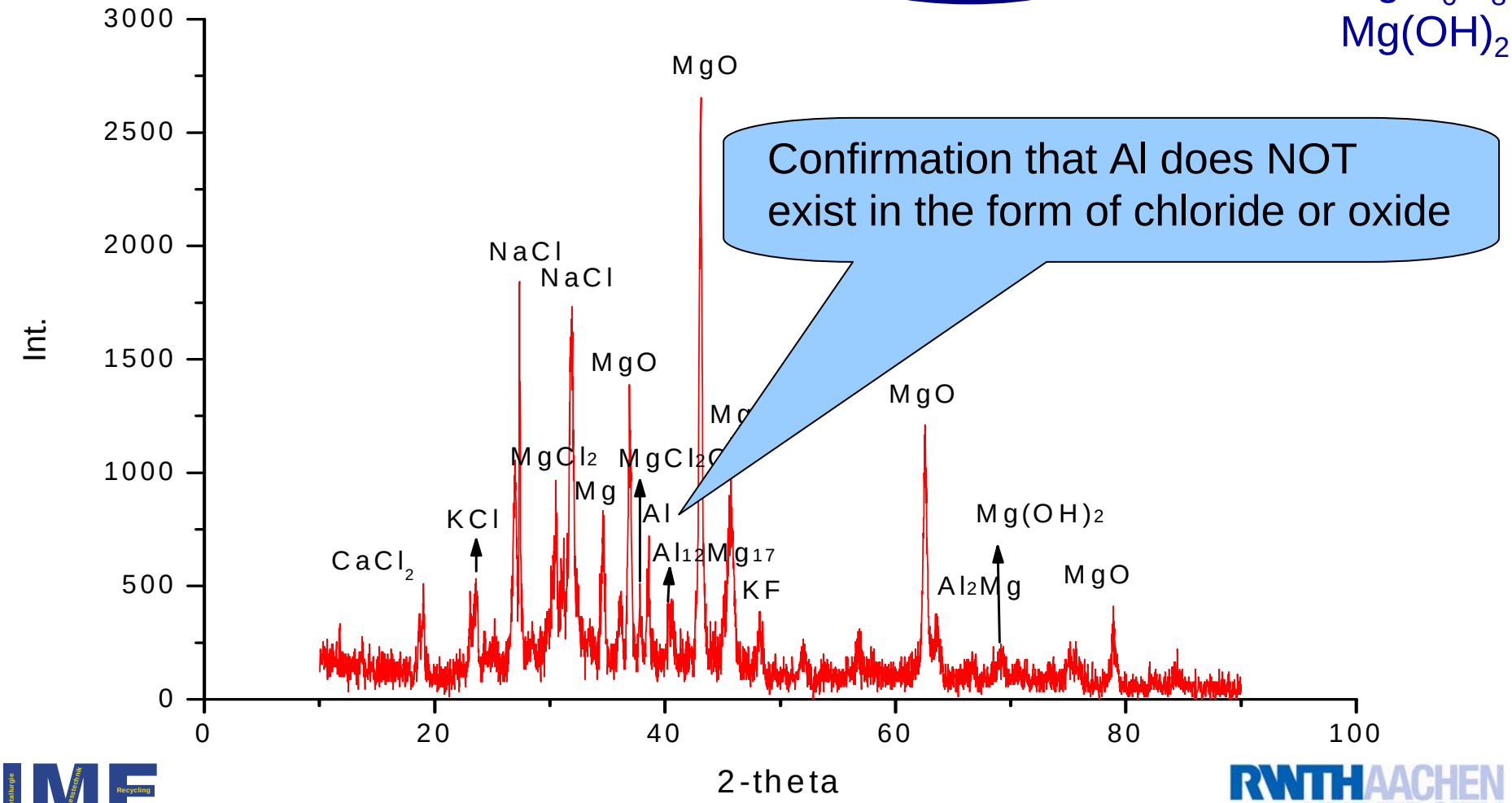
- The formation of sludge (so called Black Dross) in magnesium recycling process can not be avoided
- Black Dross is an extremely heterogeneous material
- Black Dross includes 10-30% metallic magnesium as well as 30-50% salt components
- Currently Black Dross is deposited and has no way to be recycled



Preliminary analysis of metallic Mg in Black Dross (1)

ICP (%)	Cl	Na	K	Ca	Zn(ppm)	Mn	Al	Mg
	26.6	4.0	6.05	1.6	345	0.7	3.25	29.9

Mg
MgO
$MgCl_2$
$MgCl_6O_8$
$Mg(OH)_2$



Preliminary analysis of metallic Mg in Black Dross (2)

x 10

Crushing / mixing

Milling (<1mm)/ sampling

Splitting into 8 identical samples

Dissolution in a leaching system with HCl

H_2 production

Black Dross

Preliminary analysis of metallic Mg in Black Dross (3)

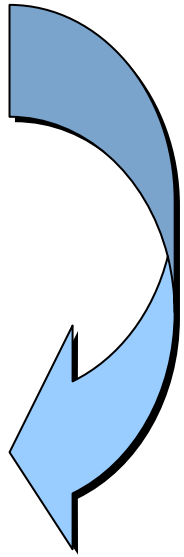
Leaching Exp. Nr.	Black Dross/g	Volume/ml H_2 (total)	H_2/ml by Al	H_2/ml by Mn	H_2/ml by Mg
1	1.00	155	40	2.85	112.2
2	1.02	156	40.8	2.90	112.3
3	1.277	188	51.1	3.64	133.3
4	1.104	158	44.2	3.15	110.7
5	1.119	171	44.8	3.19	123
6	1.222	187	48.9	3.48	134.6
7	1.01	152	40.4	2.88	108.7
8	1.02	160	40.8	2.91	116.3

Min. metallic Mg ~ 12 wt %
(in comparison with industrial announcements of (10-30%)

Economic potential / motivation of research work

- The price of magnesium metal in period between May-June 2008 was about 5000 - 5600 $/MT
- An annual output of Black Dross in Europe between 3500 to 4500 MT that goes to the deposition

If only 10% of Black Dross would be metallic magnesium ...

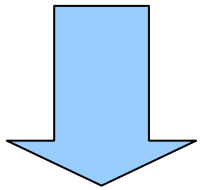


Approximately 1.7-2.5 mio.$ loss annually!

… plus the value of molten salt ...

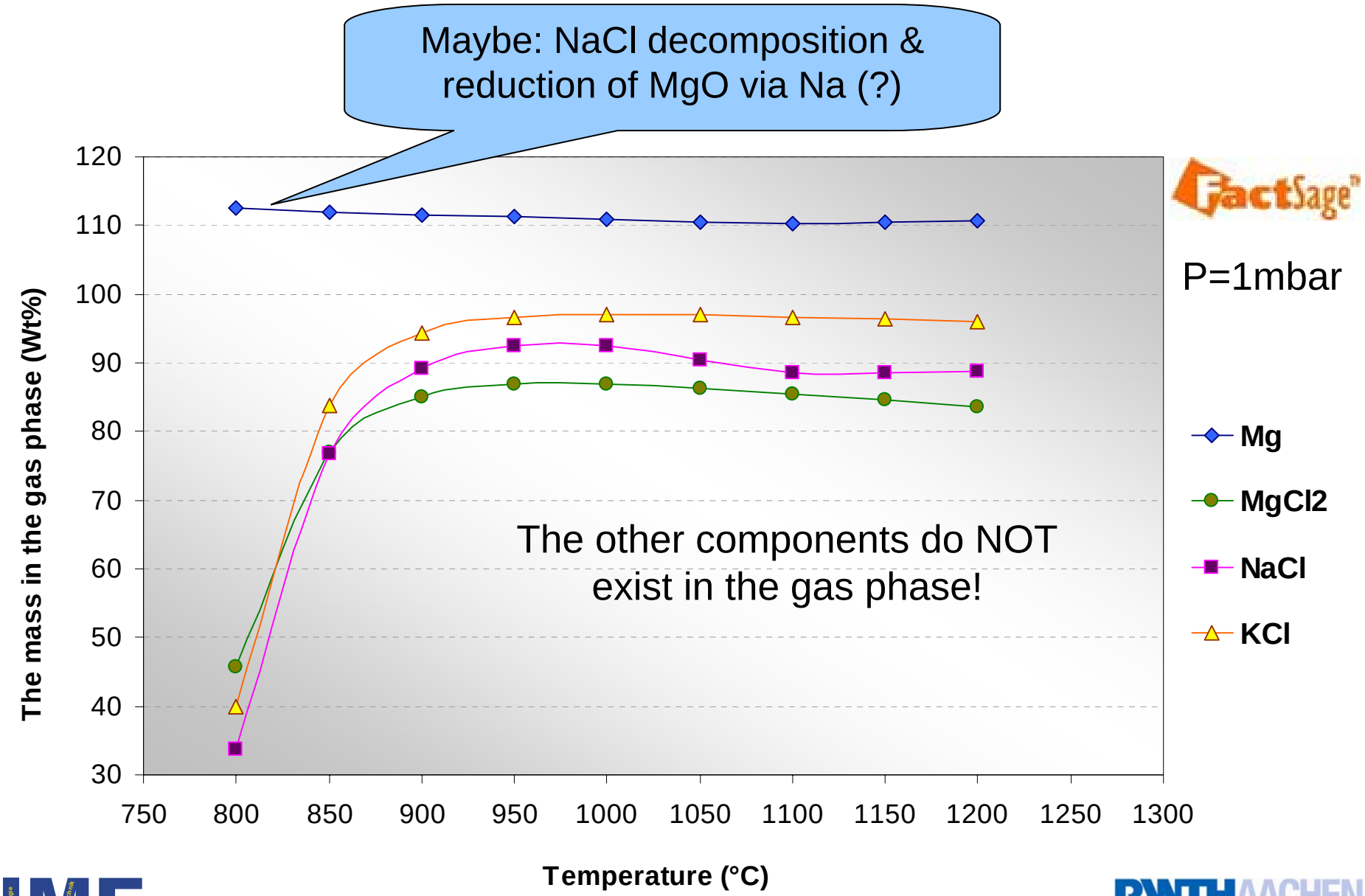
The process idea and concept

- The salt used in Mg-recycling contains mainly $MgCl_2$, KCl, NaCl and CaF_2
- Some new salt components such as NaF, MgF_2, $CaCl_2$ and KF could be also formed during initial recycling process
- Depending on the type of magnesium scrap, some other metallic elements such as Al, Mn and Zn can be also present inside Black Dross



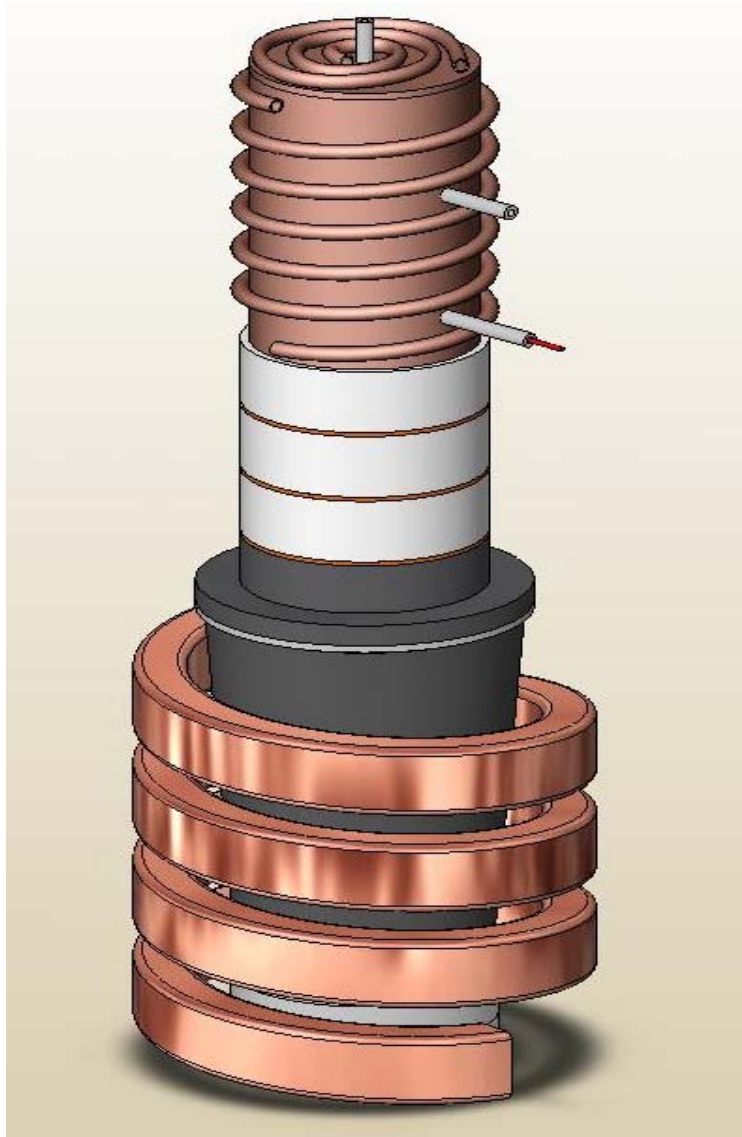
- Due to the different vapor pressures, the separation of valuable components from the oxides should be possible by selective distillation
- The distilled and condensed mixture of metal and salt should be separated through remelting/casting process

Thermochemical modeling of the concept - FactSage

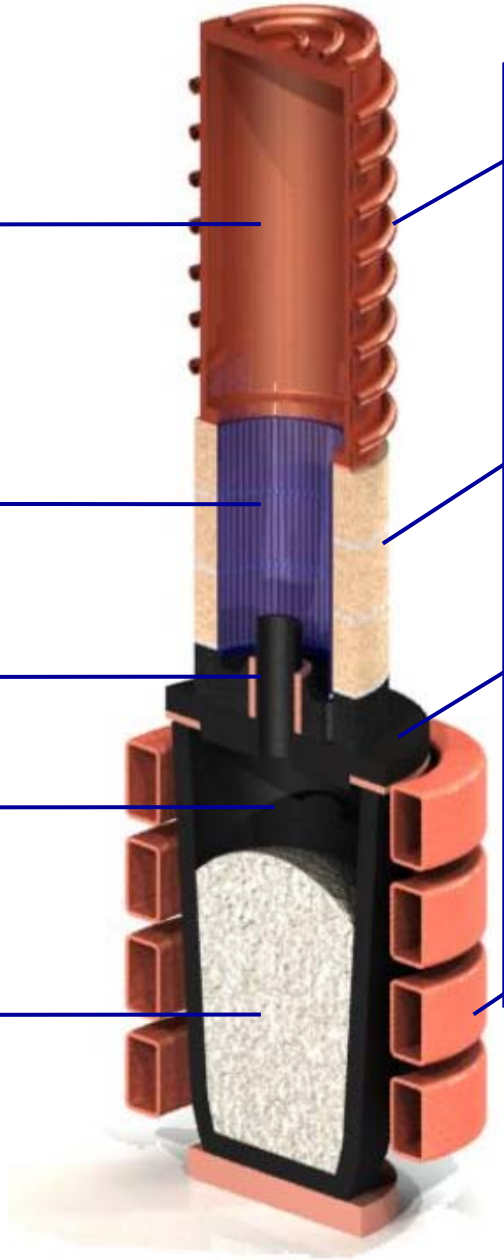


Experimental method: experimental setup

- The distillation attempts were made in a 40 kW vacuum induction furnace with about 0.382 m^3 volume
- Distillation construction design consists of a graphite crucible, a graphite lid with a pinhole, a quartz tube insulated through three refractory rings and a condenser with oil cooling system

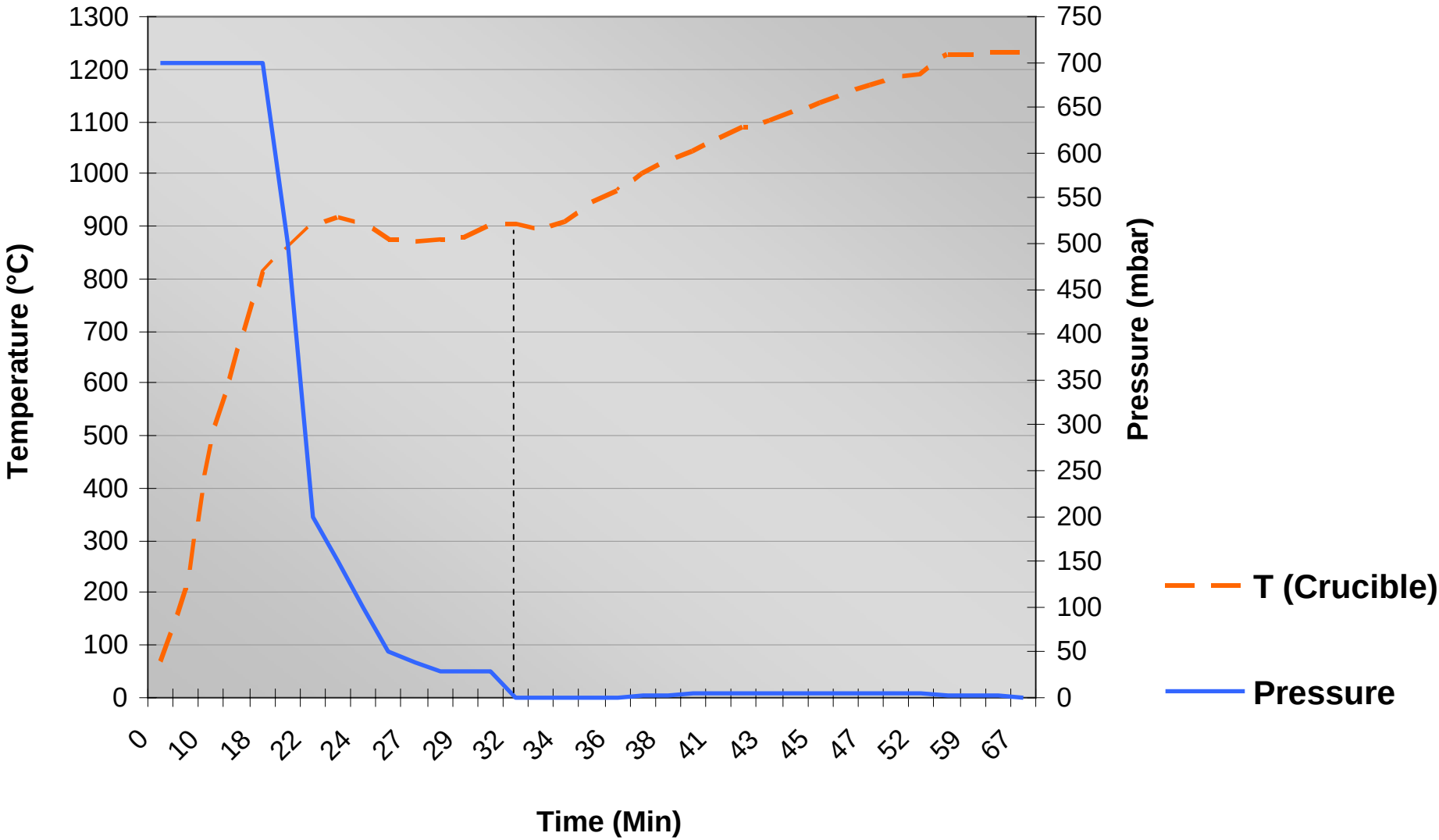


Experimental method: cross-section of the reactor

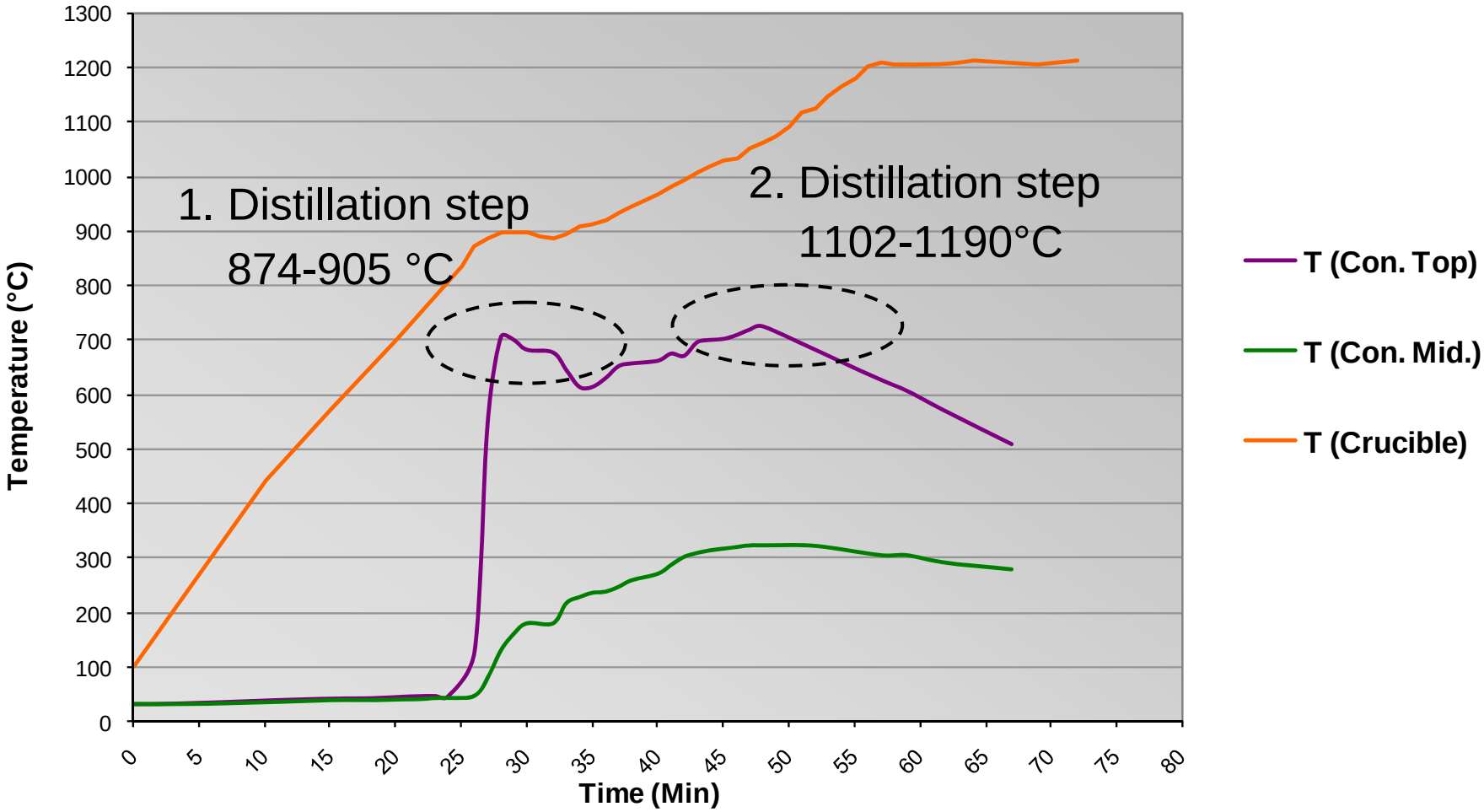


8 experiments
14.4 kg Black Dross

Black Dross vacuum distillation: pressure progress



Black Dross vacuum distillation: temperature progress

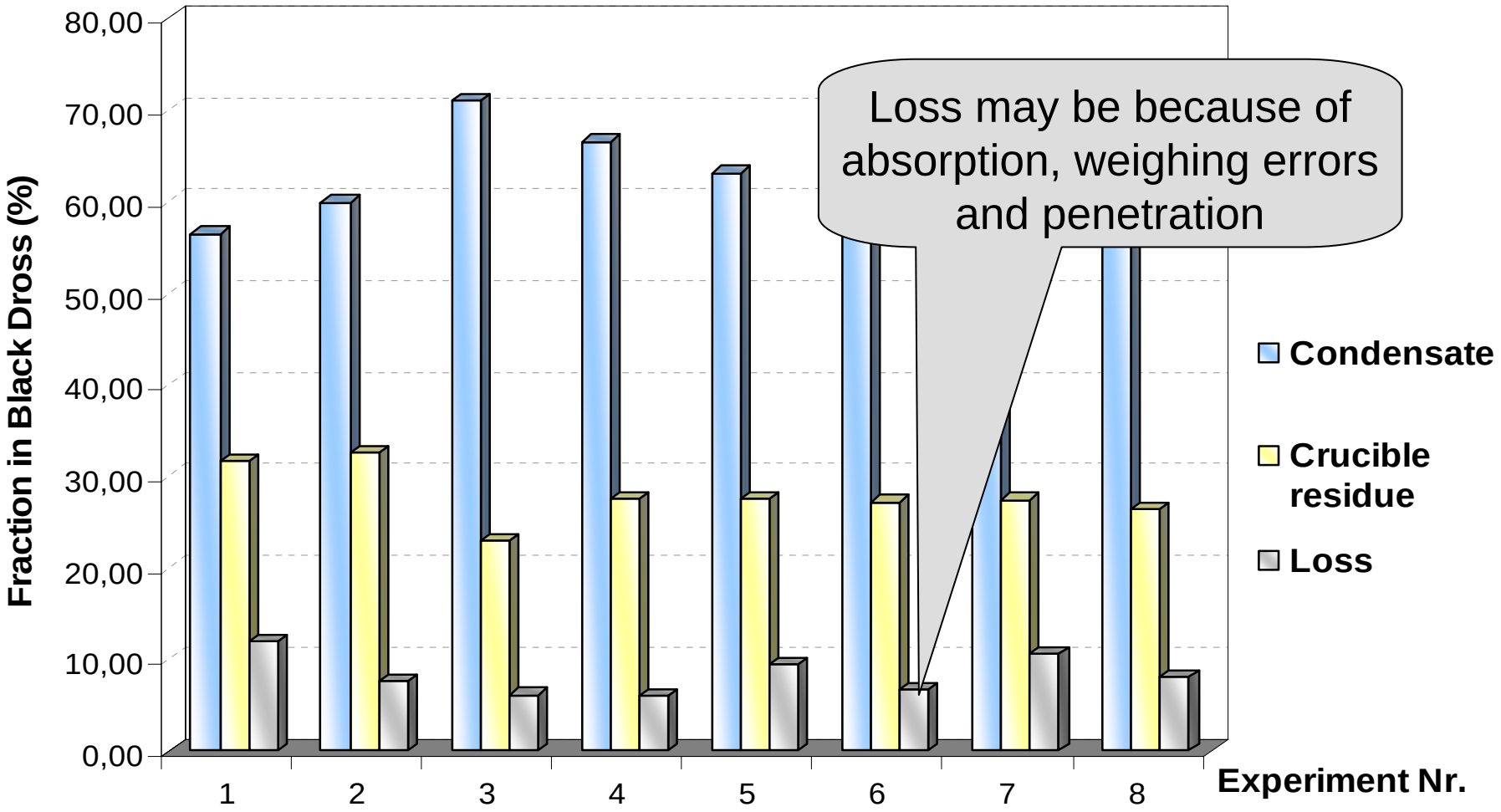


Black Dross vacuum distillation: products

Condensate inside the chamber

Crucible residue

Vacuum distillation: mass balance of products



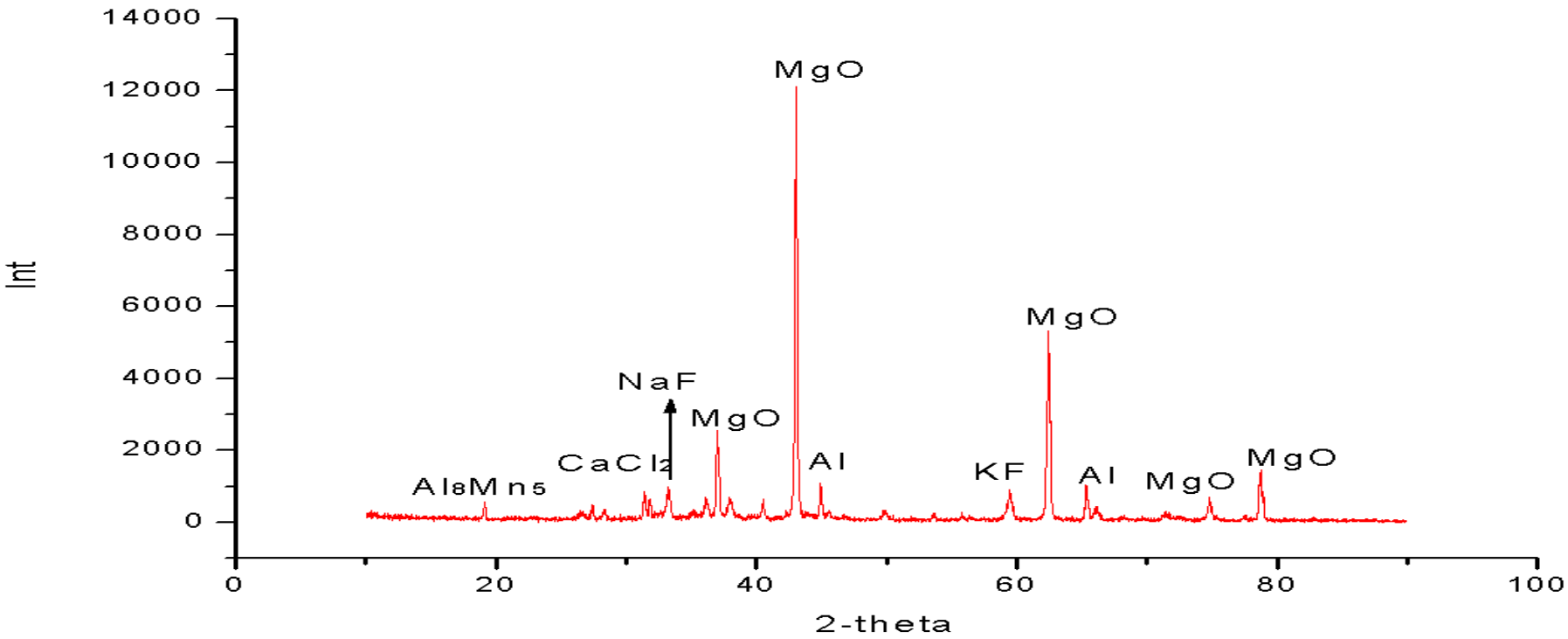
Average:

Condensate (Salt + Metal): app. 64 (+8)%

Residue: app. 28%

Vacuum distillation: analysis of crucible residue (1)

- XRD analysis shows the distillation residue mostly consisting of oxides and a metal phase (Al-alloy)



Vacuum distillation: analysis of crucible residue (2)

- Electron probe micro analyzing (EPMA)

Black dross before distillation

Element	Mass(%)	Atom(%)
O	33.812	48.0026
F	2.419	2.8924
Na	7.233	7.1464
Mg	20.374	19.0371
Al	1.893	1.5935
Si	0.333	0.2694
Cl	26.201	16.7888
K	4.508	2.6189
Ca	2.083	1.1805
Mn	0.722	0.2984
Fe	0.423	0.1720
Total	100.000	100.0000

Residue after distillation

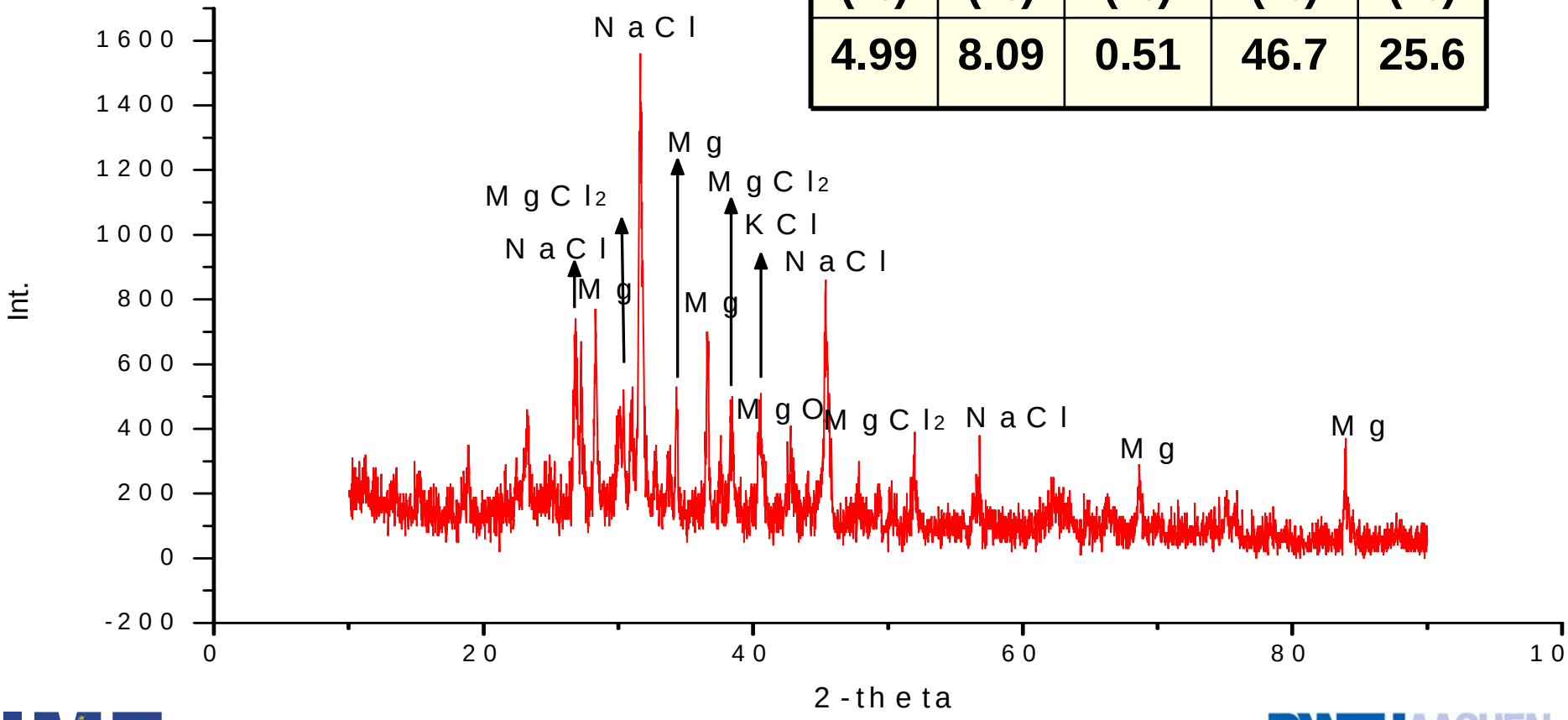
Element	Mass(%)	Atom(%)
O	40.431	52.3123
F	1.983	2.1602
Mg	40.156	34.1955
Al	9.009	6.9126
Si	1.186	0.8737
S	0.244	0.1574
Cl	1.840	1.0745
K	0.147	0.0780
Ca	2.545	1.3146
Mn	1.568	0.5909
Fe	0.891	0.3303
Total	100.000	100.0000

- Chlorine almost all gone, also the most part of K and Na and F, Ca and Mg strongly evaporated. Fe, Al, Si, and a lot of Mn stay in the crucible

Vacuum distillation: characterization of condensate

- X-ray diffraction as well as ICP chemical analysis: showing the condensate consisting of chlorides and metallic Mg

Na (%)	K (%)	Ca (%)	Mg (%)	Cl (%)
4.99	8.09	0.51	46.7	25.6



Recyclability review (1)

Remelting of Condensate

Mg drops could not be coagulated!

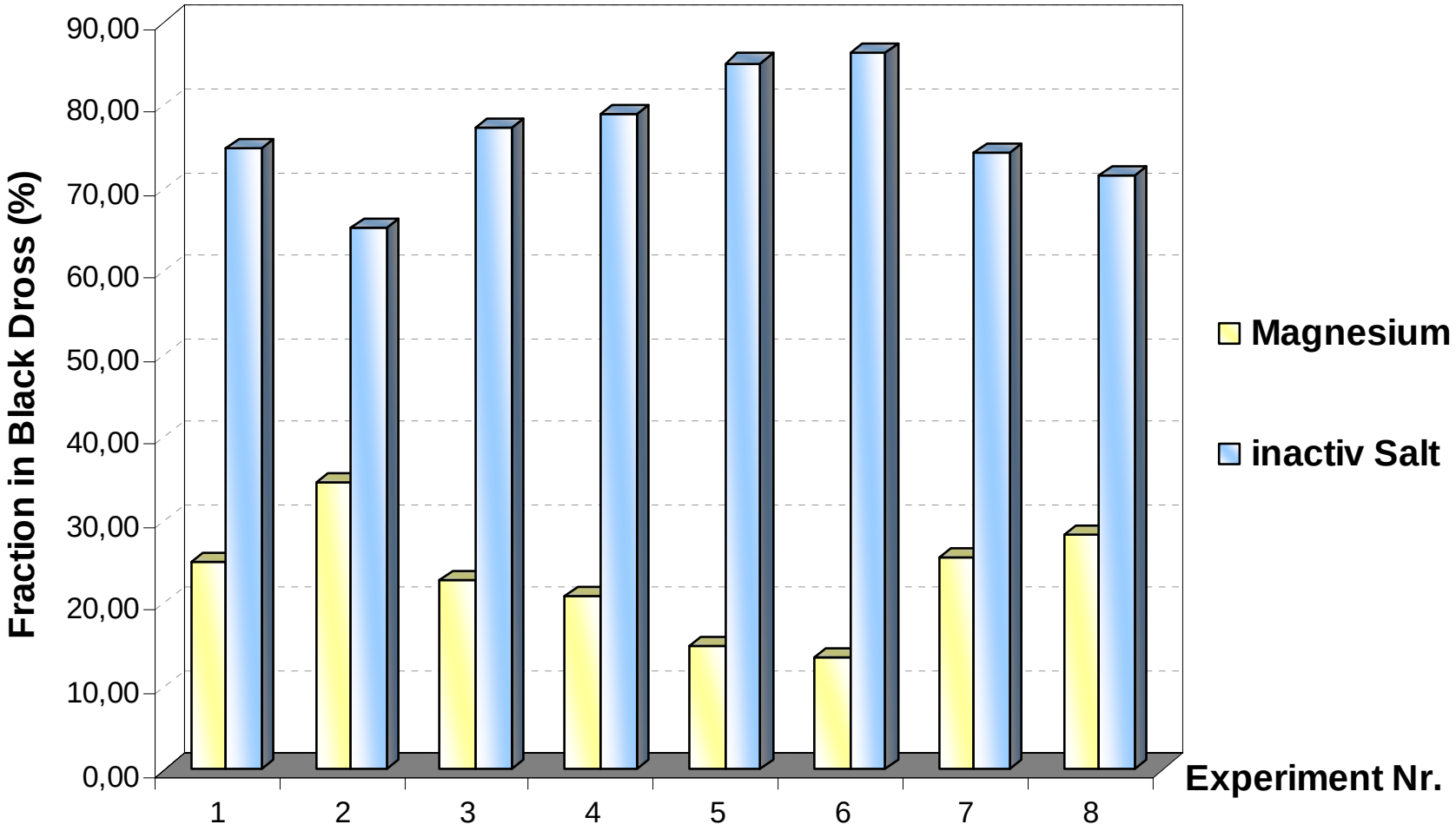
Recycling salt is inactive!

Recyclability review (2)

Addition of fresh salt (Flux 5) including CaF_2

Magnesium drops coagulate

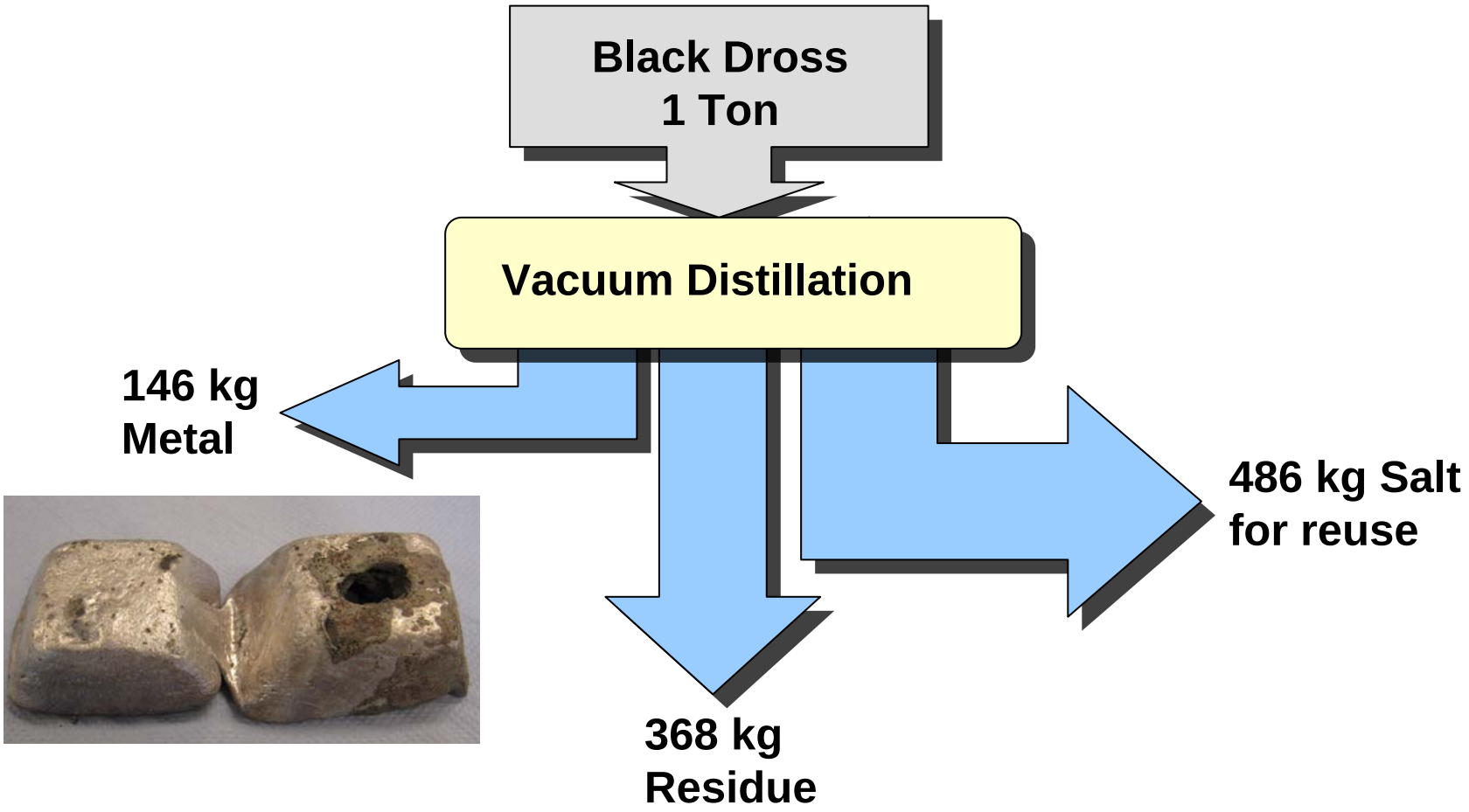
Remelting: mass balance of products



Average (based on the condensate!):

Metal:	app. 25 %
Salt:	app. 75%

The expected material flow of the process



Summary and outlook

- The recovery of magnesium from Black Dross by vacuum distillation has been successfully tested
- The salt from distillation process is not active and must be modified
- The lack of CaF_2 in this recycling salt could be a cause for the inactivity of salt, here some further works are required
- Some fresh salt (Flux 5) was added and a good magnesium/salt separation was achieved
- The thermo-physical properties of the liquid salt (density and surface tension) after distillation as a next step of this work and the influence of the addition of CaF_2 should be investigated

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Thank you for your attention!

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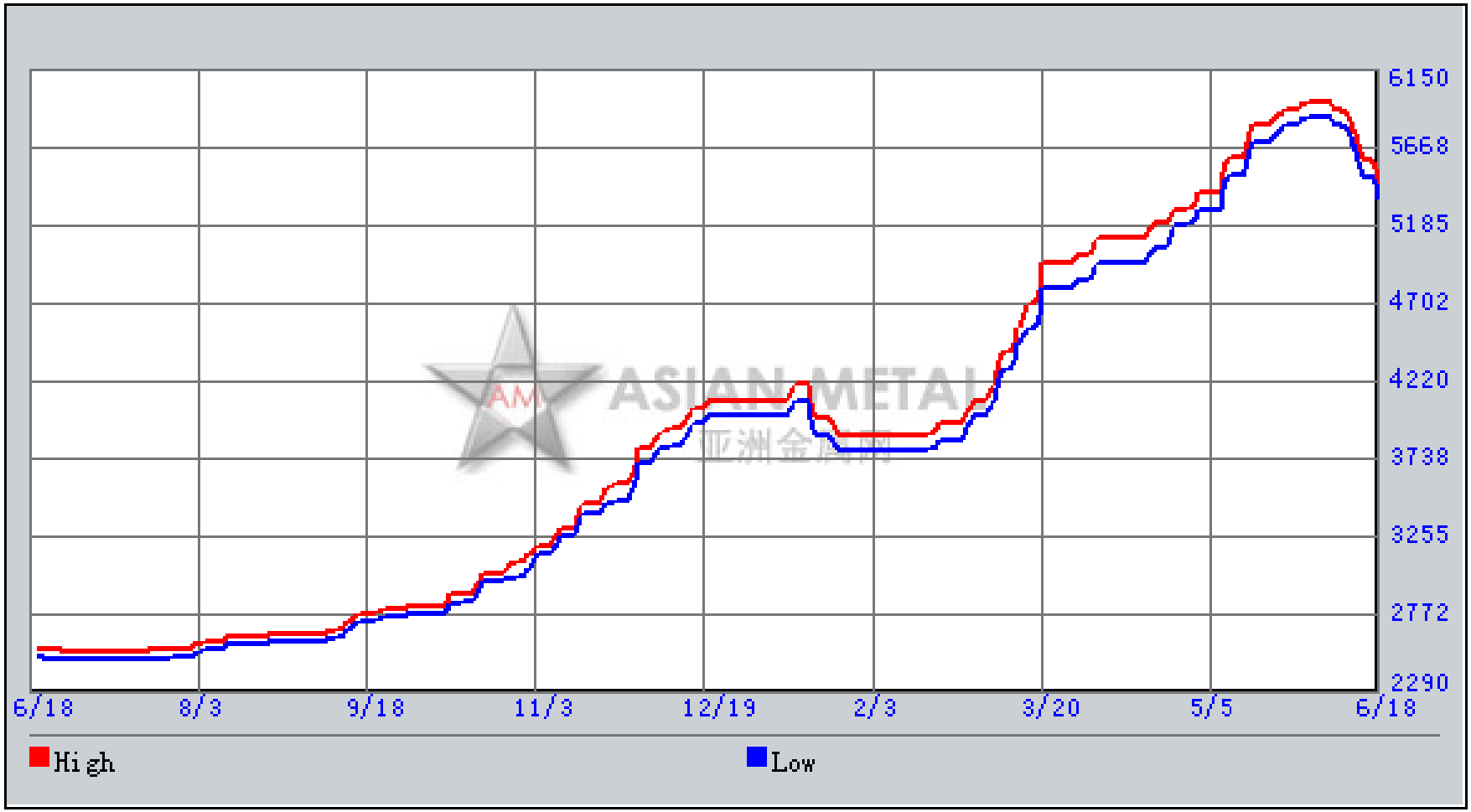

Price curve for past 12 monthsMagnesium
99.9%min FOB China USD/Mt
From 2007-6-18 To 2008-6-18