



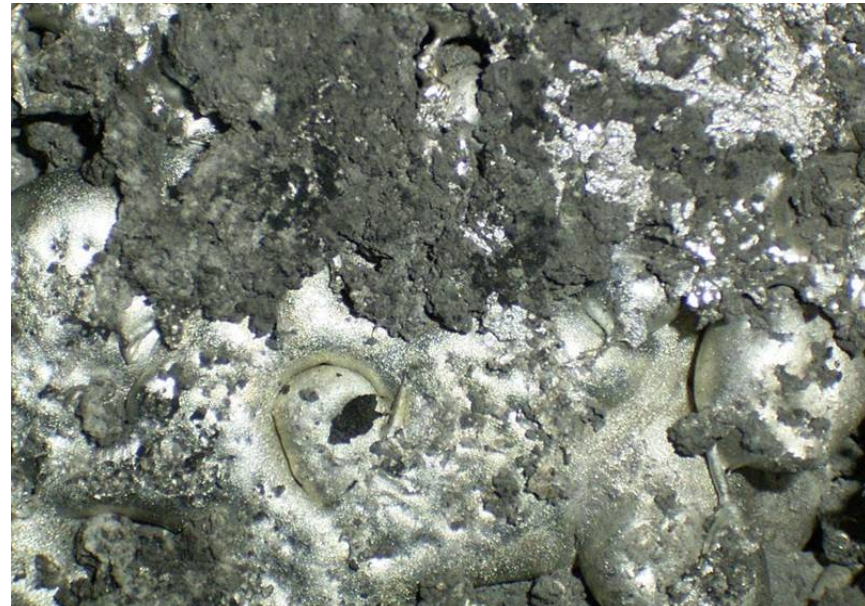
Recovery of Magnesium and Salt from Black Dross through Vacuum Distillation

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Challenges of Black Dross

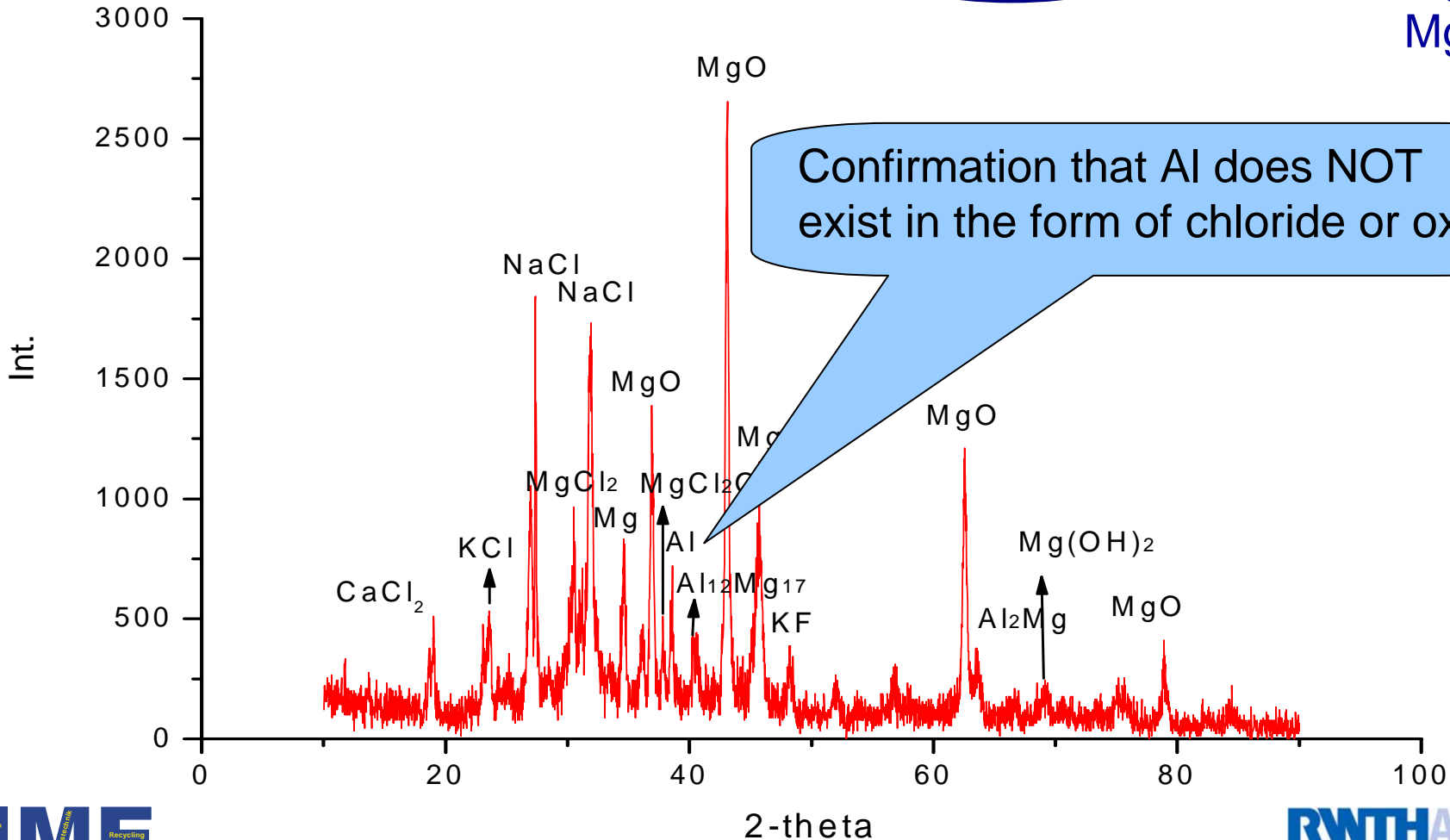
- The formation of sludge (so called Black Dross) in magnesium recycling process can not be avoided
- Black Dross is an extremely heterogeneous material
- Black Dross includes 10-30% metallic magnesium as well as 30-50% salt components
- Currently Black Dross is deposited and has no way to be recycled



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
MgCl₂
MgCl₆O₈
Mg(OH)₂



Preliminary analysis of metallic Mg in Black Dross (2)

x 10



Crushing/mixing

Milling (<1mm)/ sampling



H₂
production

Black
Dross



Splitting into 8
identical samples

Dissolution in a leaching
system with HCl

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 ...**

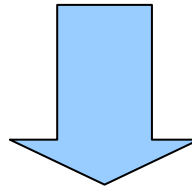
Approximately 1.7-2.5 mio.\$ loss annually!

... plus the value of molten salt ...



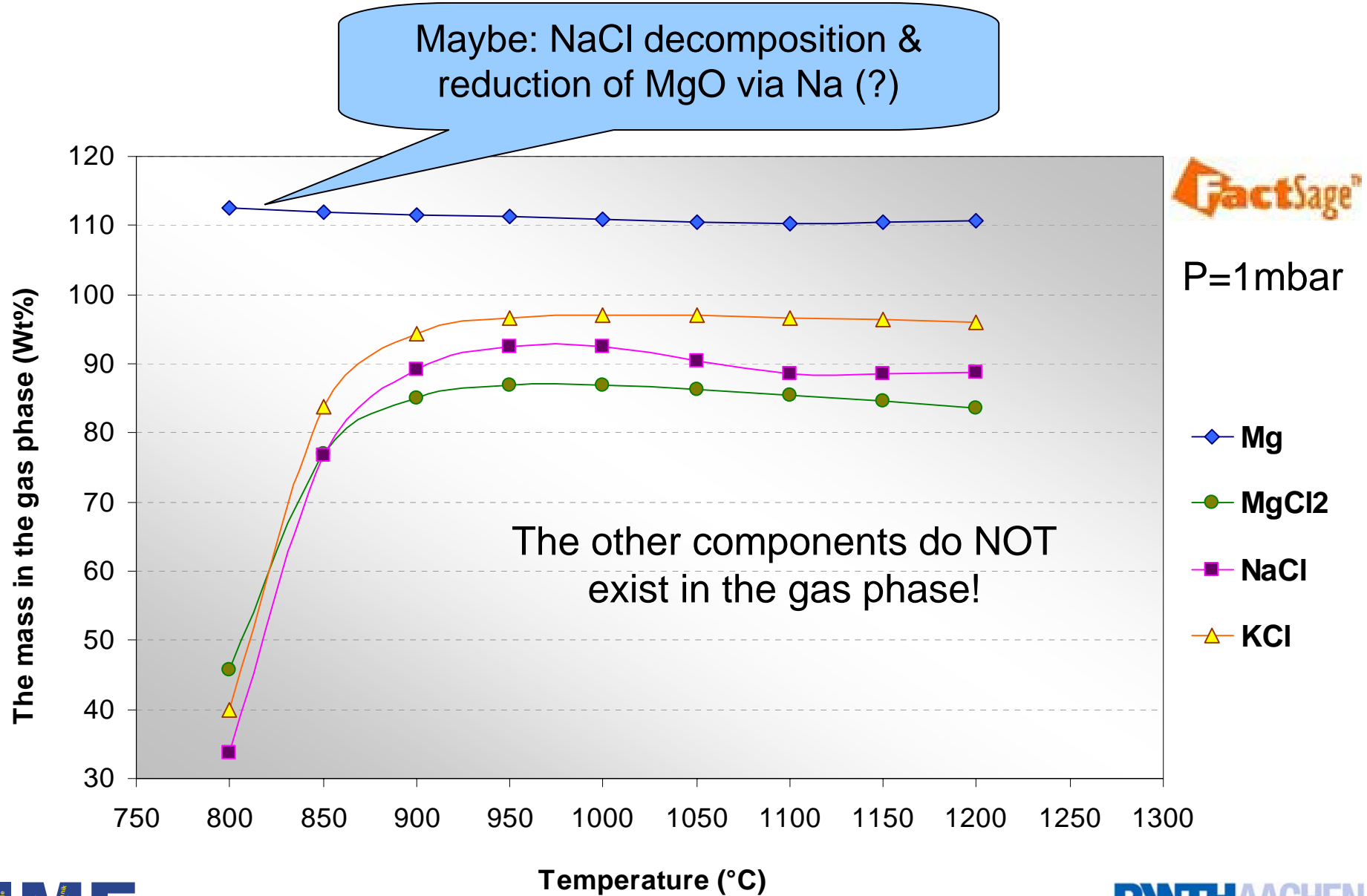
The process idea and concept

- 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



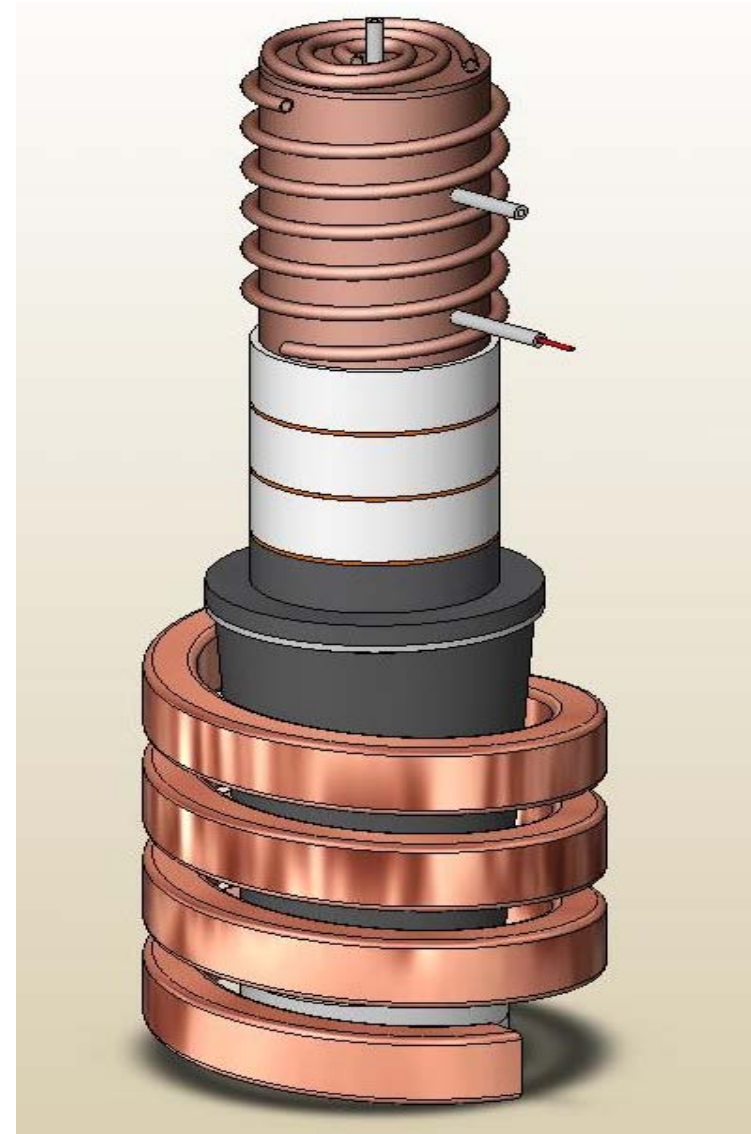
- Due to the different vapor pressures, the separation of valuable components from the oxides should be possible by selective distillation
- The distilled and condensed mixture of metal and salt should be separated through remelting/casting process

Thermochemical modeling of the concept - FactSage

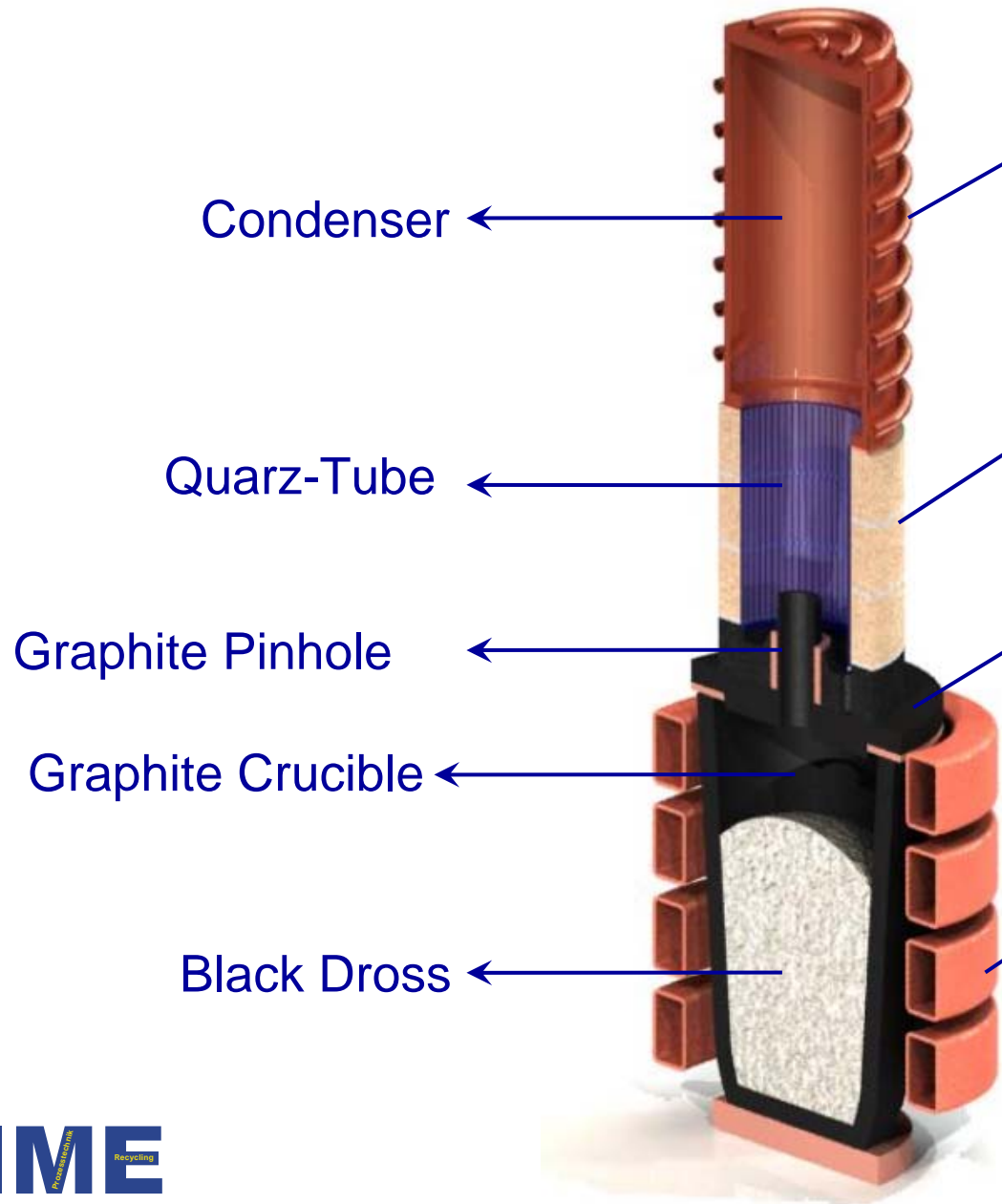


Experimental method: experimental setup

- The distillation attempts were made in a 40 kW vacuum induction furnace with about 0.382 m³ 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

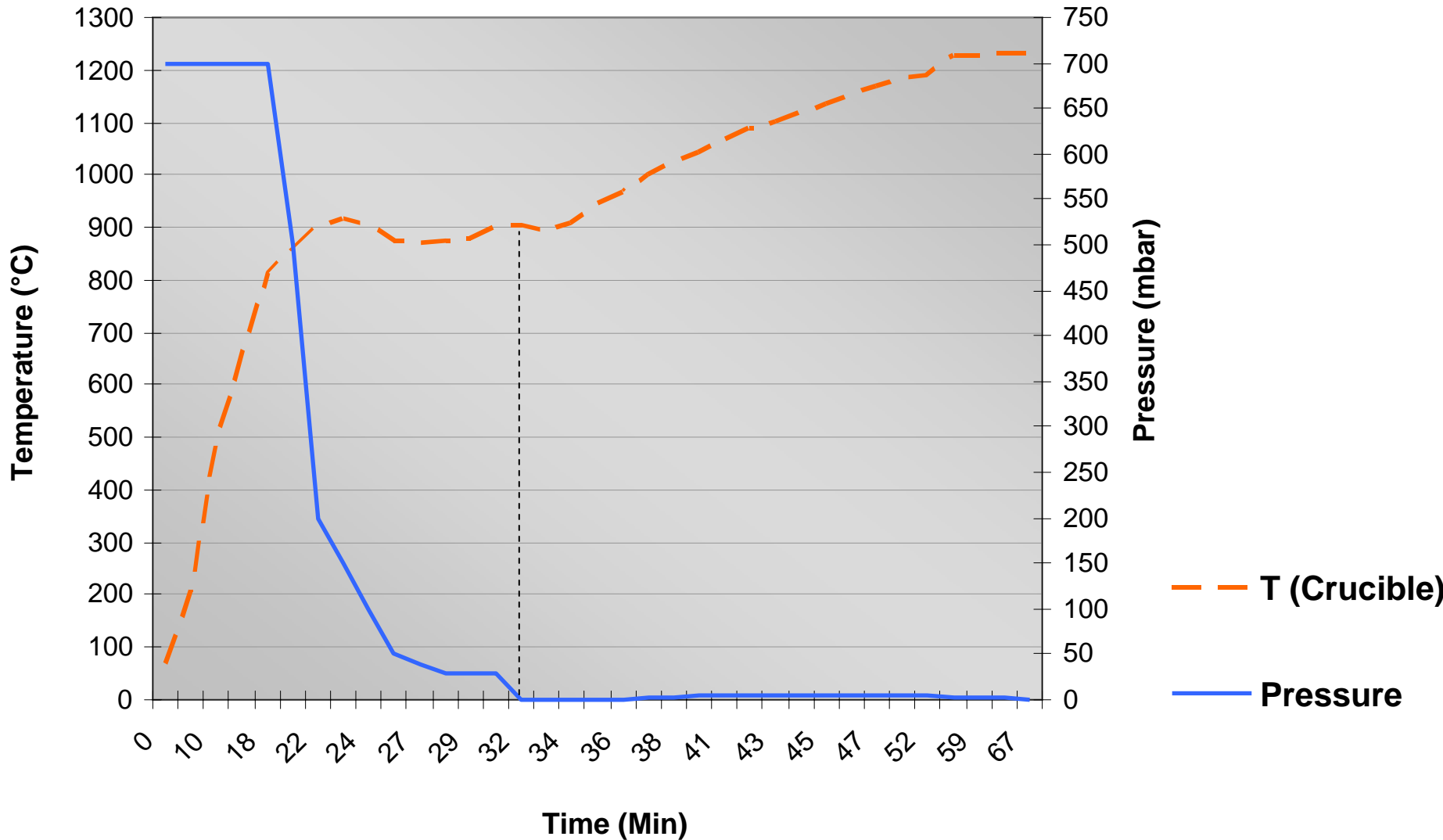


Experimental method: cross-section of the reactor

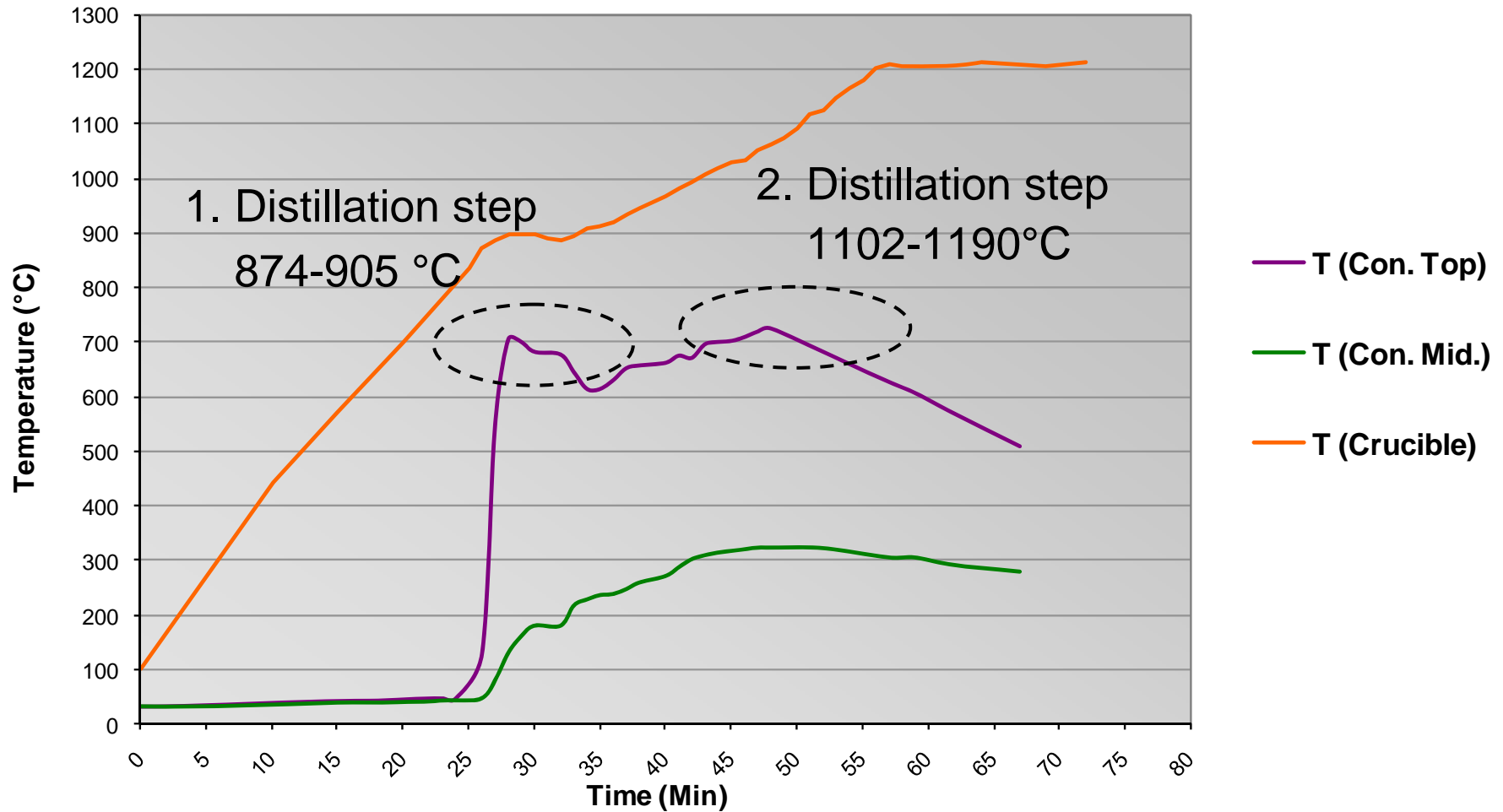


8 experiments
14.4 kg Black Dross

Black Dross vacuum distillation: pressure progress



Black Dross vacuum distillation: temperature progress



Black Dross vacuum distillation: products

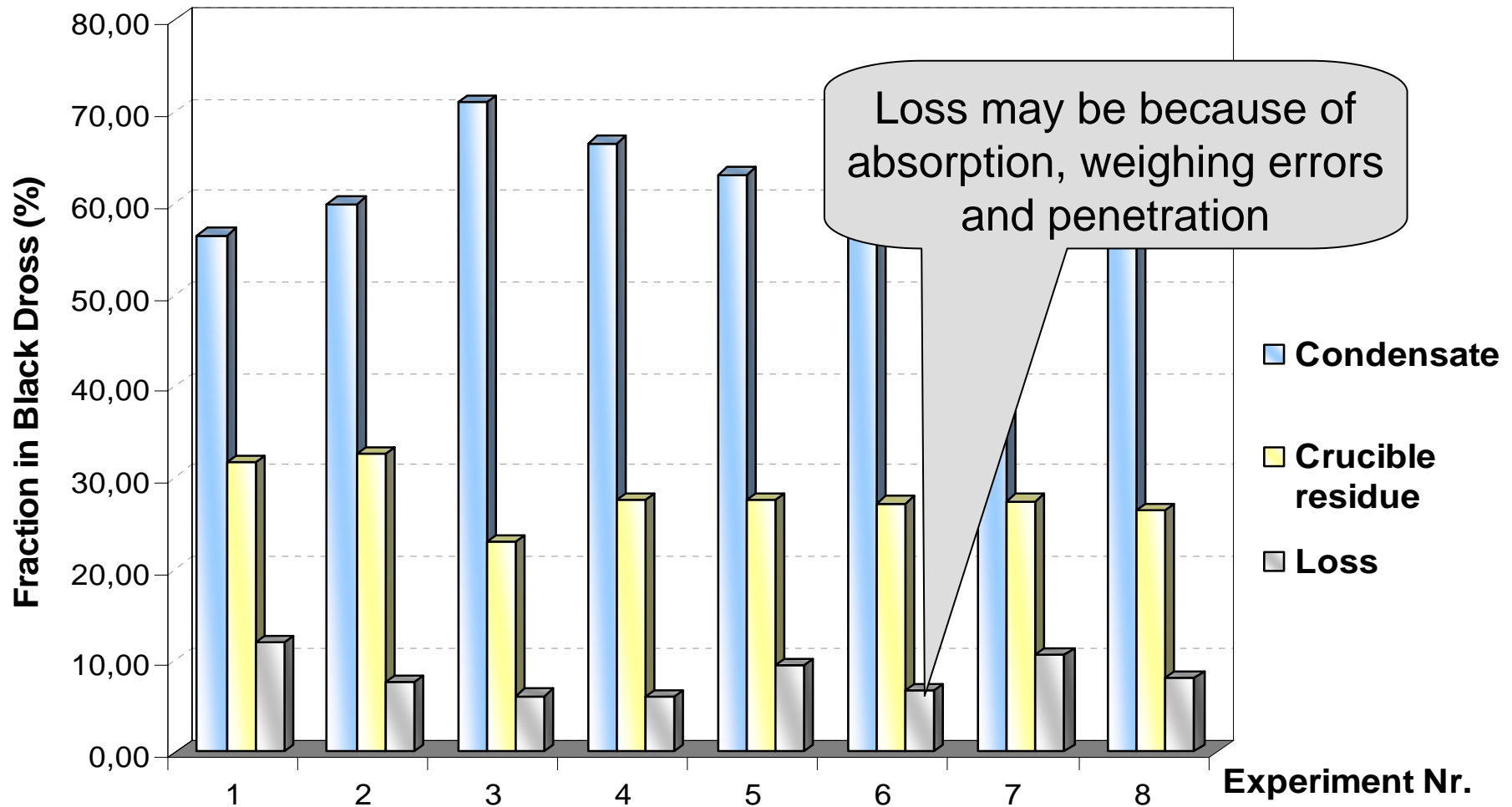
Condensate inside the chamber



Crucible residue



Vacuum distillation: mass balance of products



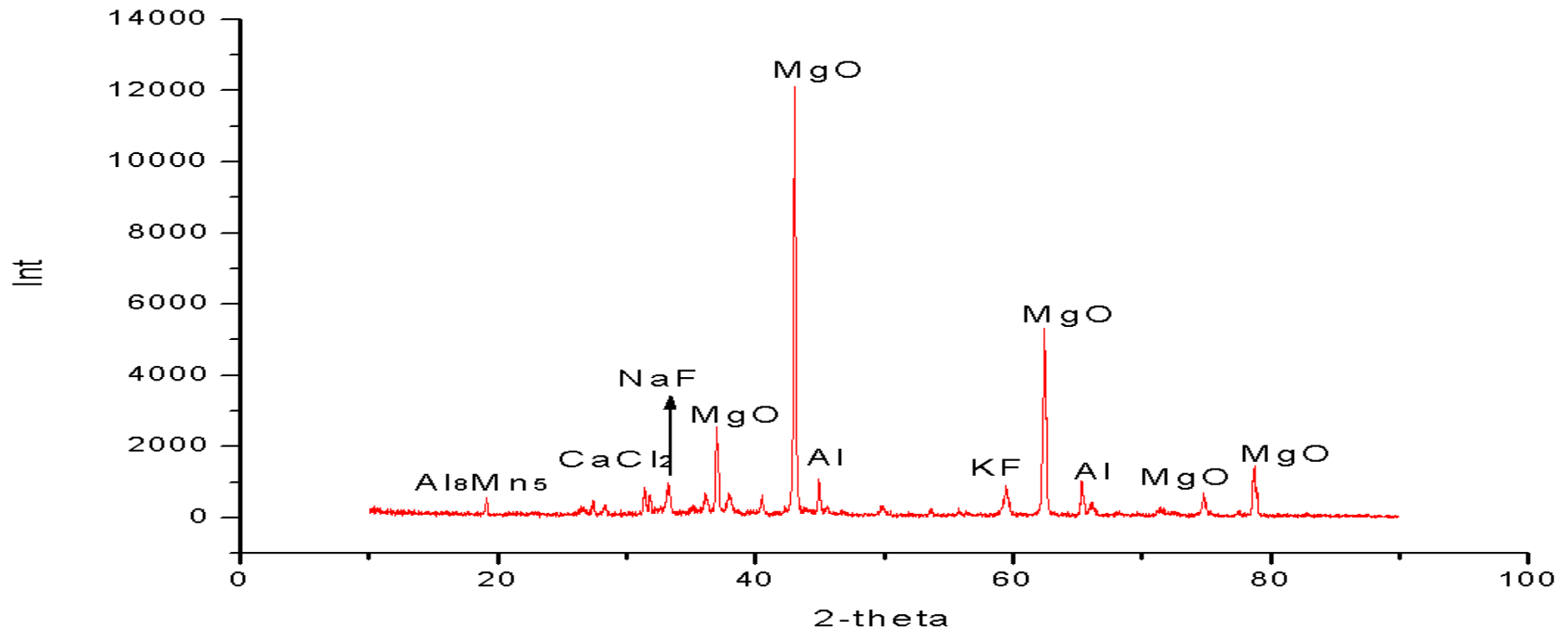
Average:

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

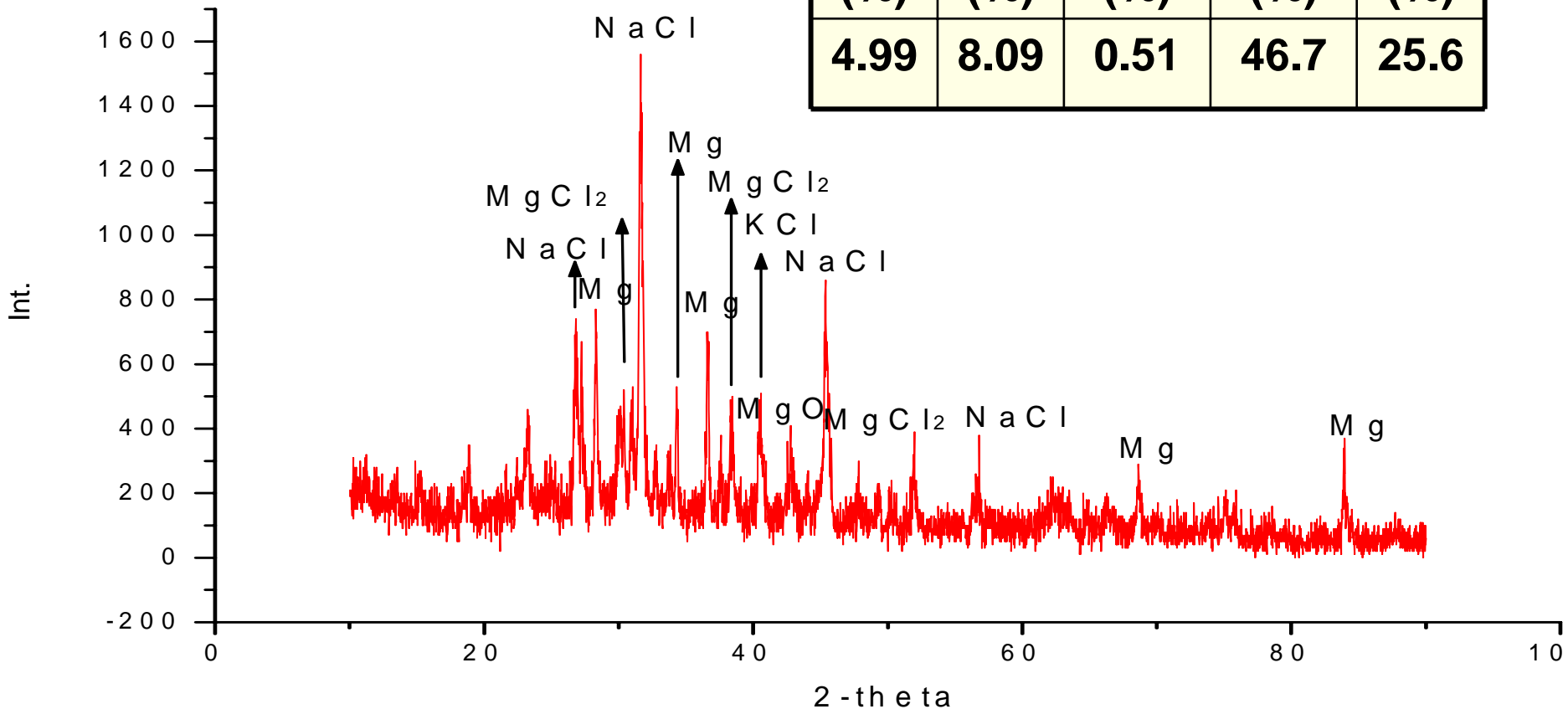
| Element | Mass (%) | Atom (%) |
|---------|----------|----------|
| O | 40.431 | 52.3123 |
| F | 1.983 | 2.1602 |
| Mg | 40.156 | 34.1955 |
| Al | 9.009 | 6.9126 |
| Si | 1.186 | 0.8737 |
| S | 0.244 | 0.1574 |
| Cl | 1.840 | 1.0745 |
| K | 0.147 | 0.0780 |
| Ca | 2.545 | 1.3146 |
| Mn | 1.568 | 0.5909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

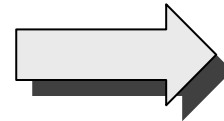
- X-ray diffraction as well as ICP chemical analysis: showing the condensate consisting of chlorides and metallic Mg

| 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)

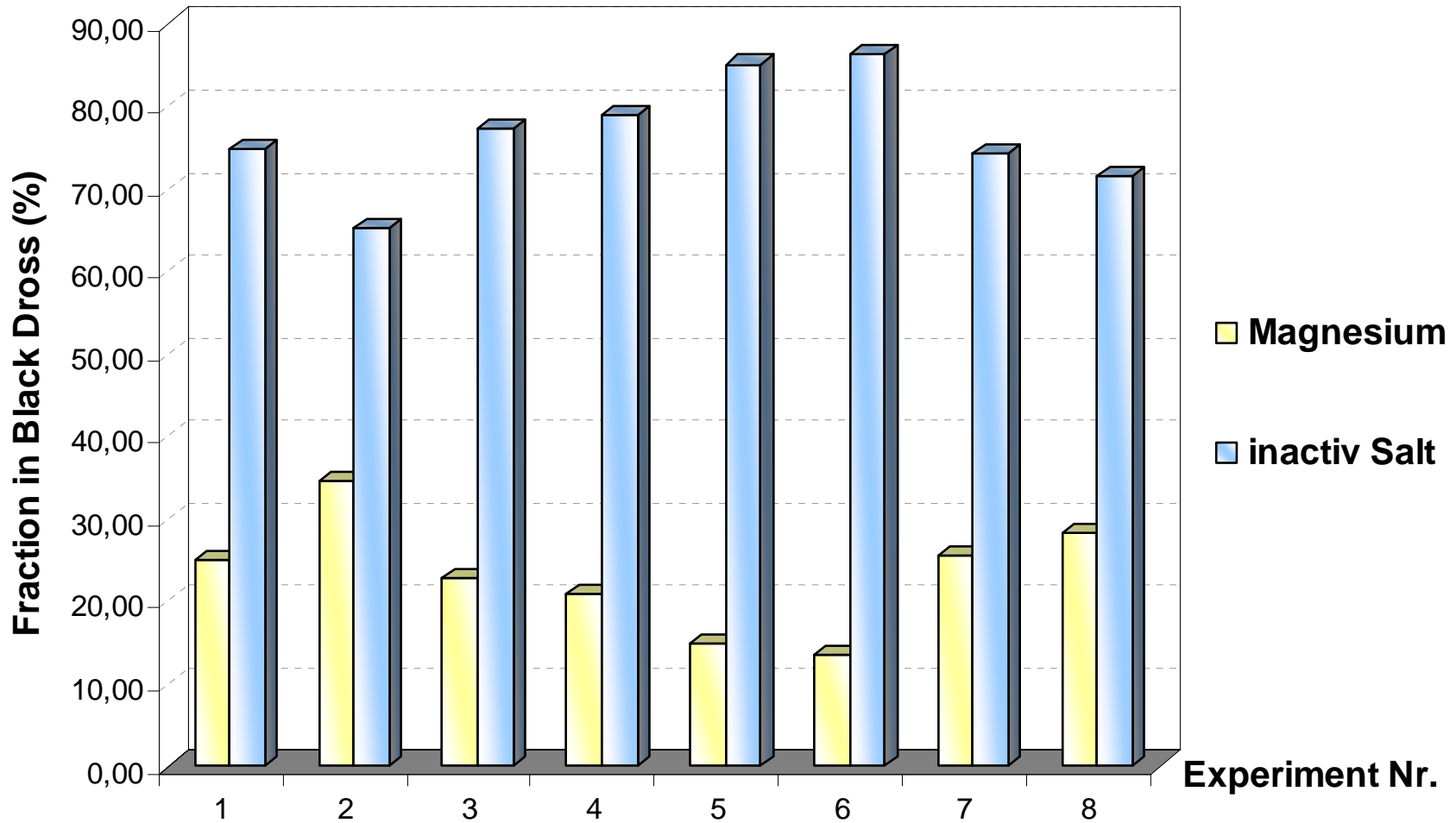


Addition of fresh salt (Flux 5) including CaF_2



Magnesium drops coagulate

Remelting: mass balance of products

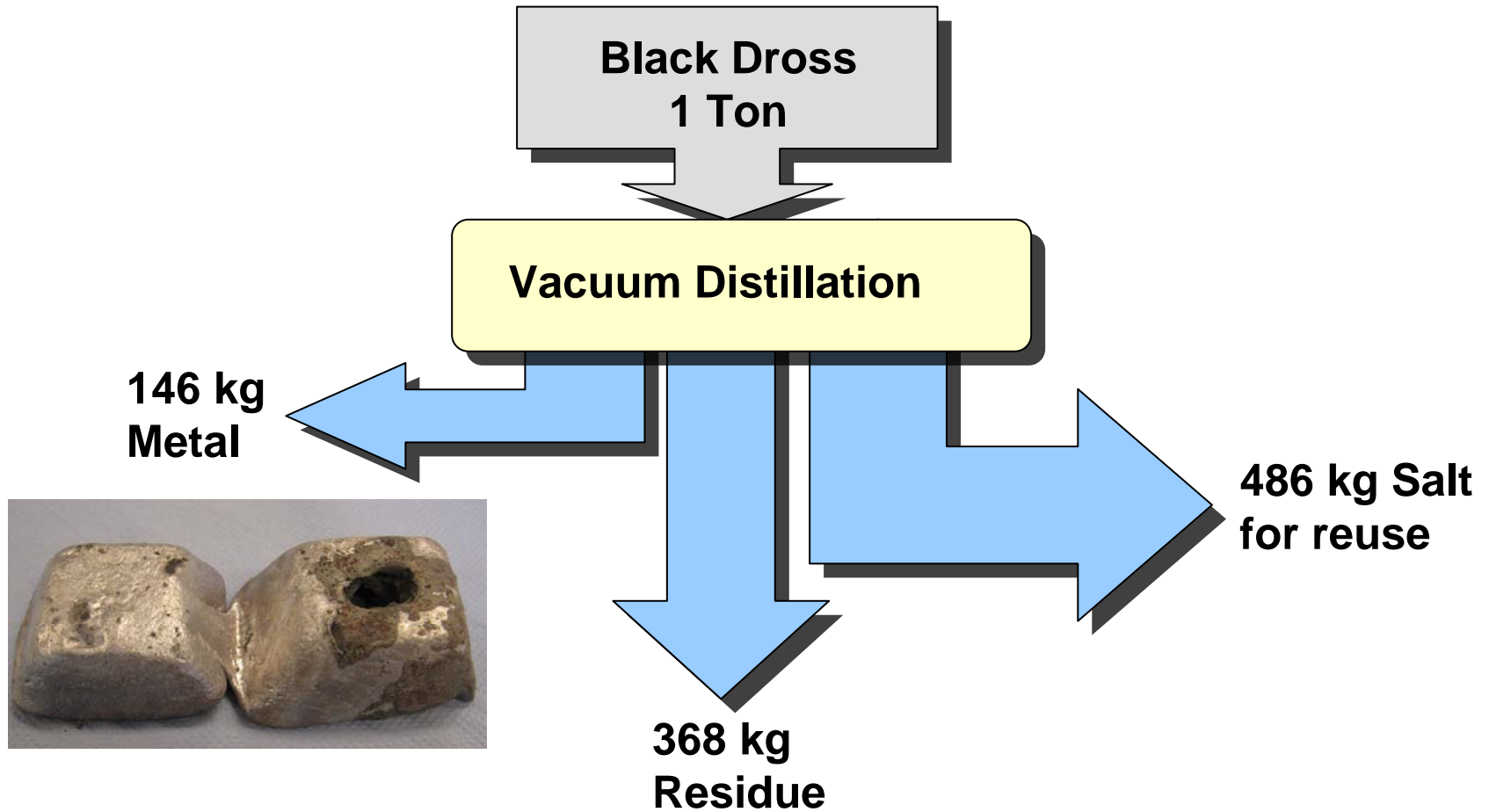


Average (based on the condensate!):

Metal: app. 25 %

Salt: app. 75%

The expected material flow of the process



Summary and outlook

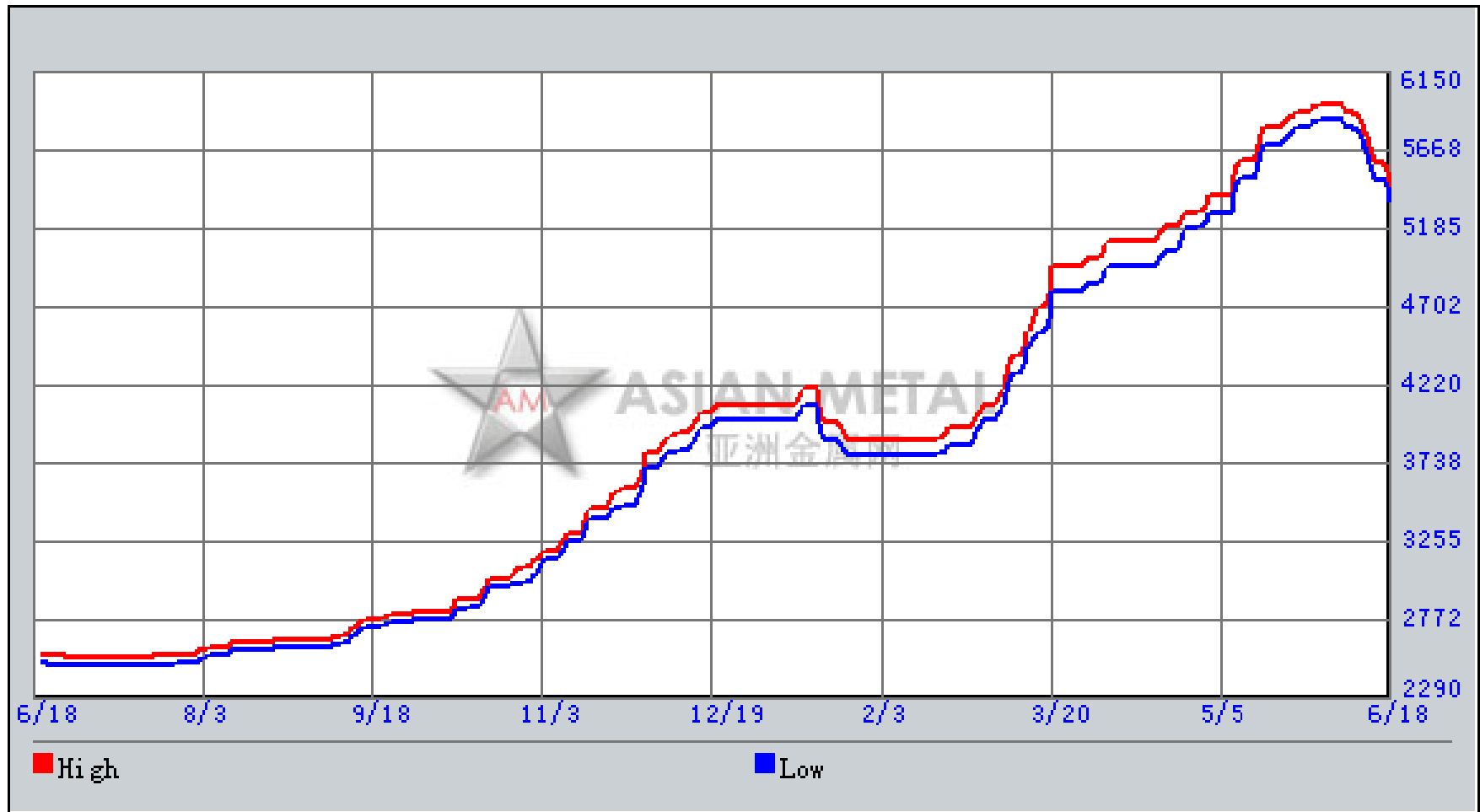
- The recovery of magnesium from Black Dross by vacuum distillation has been successfully tested
- The salt from distillation process is not active and must be modified
- The lack of CaF_2 in this recycling salt could be a cause for the inactivity of salt, here some further works are required
- Some 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



Thank you for your attention!

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