

6th CEWEP Congress 2012

Waste-to-Energy

▶ **Energy & Resource Efficiency**

6-7 September 2012, in Würzburg



Metal Recycling from bottom ash

Prof. Dr.-Ing. R.Deike*; D.Ebert, B.Sc.
Institute of Metallurgy and Metal Forming
University Duisburg-Essen



info@cewep.eu ▶ www.cewep.eu

Table of contents



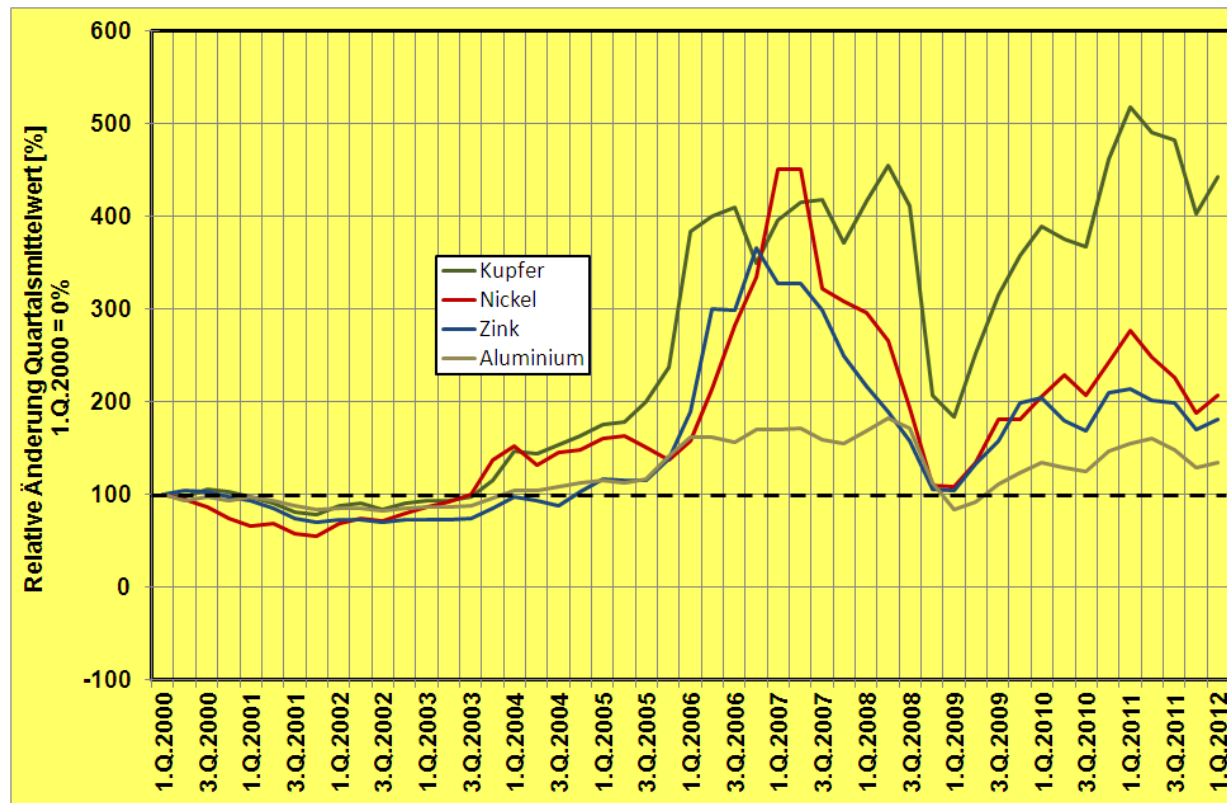
- 1. Changes on global raw material markets**
- 2. Composition changes depending on the bottom ash grain size**
- 3. Phase analysis of certain bottom ash particles**
- 4. Determination and analysis of magnetic fractions in bottom ash**
- 5. Determination of the metal content of bottom ash with a slag remelting process**
- 6. Summary**



Deike, R.: ITAD Messekongress, IFAT, München, 10.05.2012

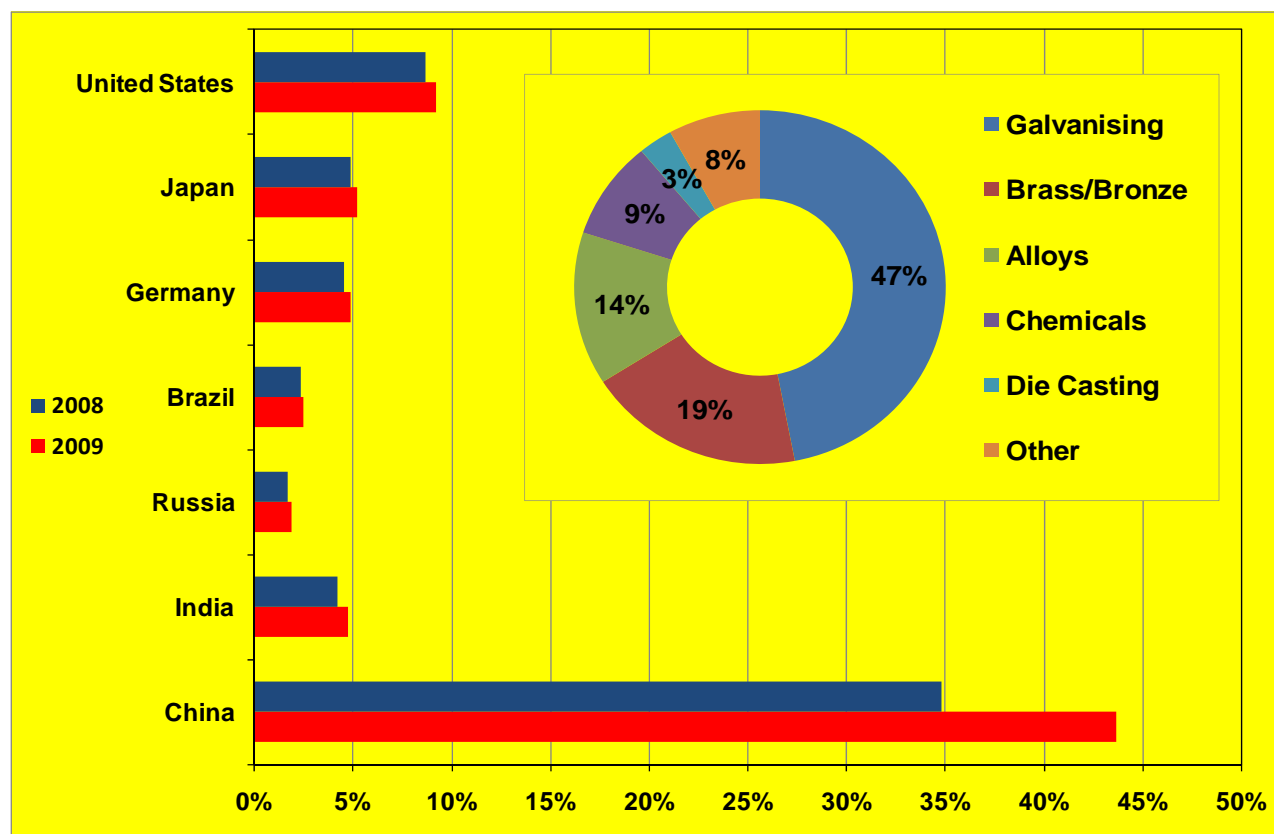
info@cewep.eu ▶ www.cewep.eu

Development of various metals prices quarterly averages (1. Q. 2000 = 100%)



Deike, R, Ebert, D., Warnecke, R.; Vogell, M.: 11. VDI Fachkonferenz Feuerung und Kessel, Bremen, 13.06.2012

World zinc consumption in 2008/2009 (11.5 / 10.8 million tons) divided by regions and major consumers

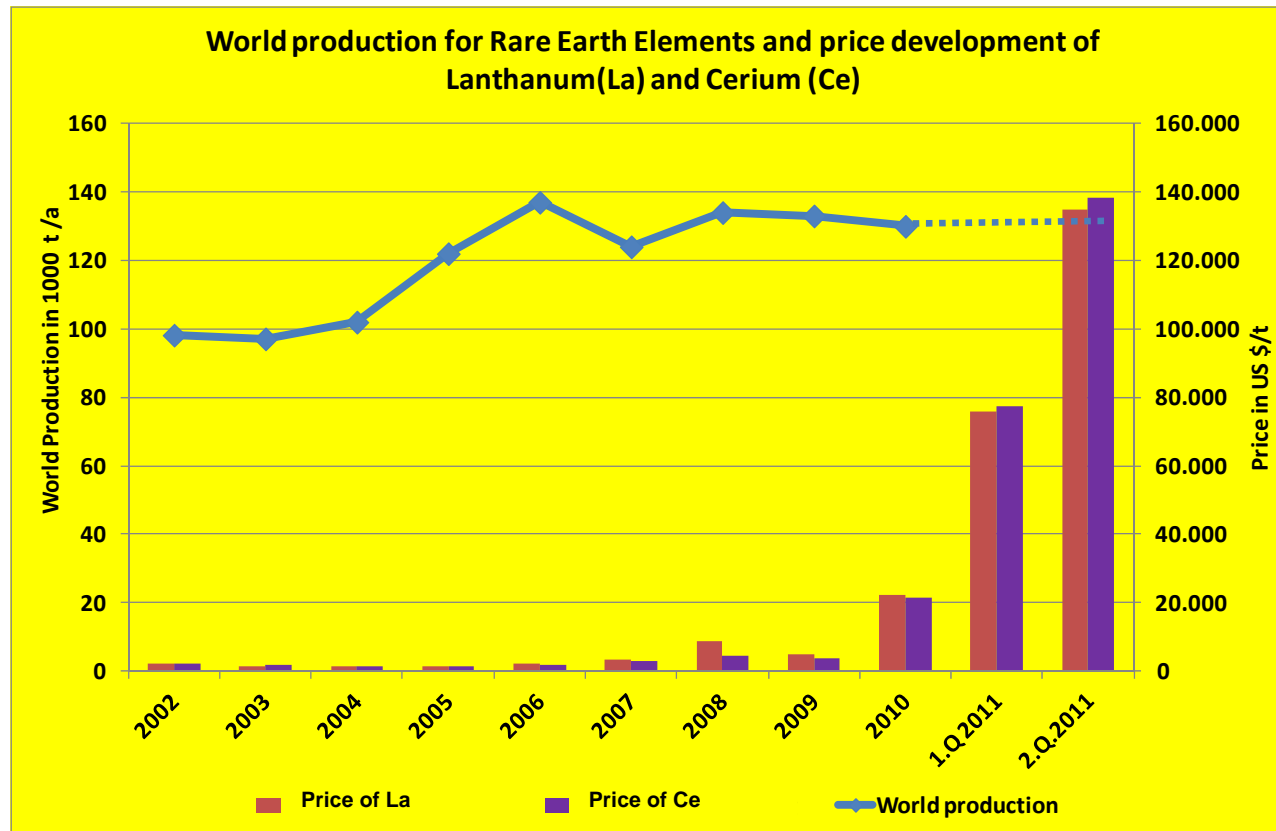


Data of LME and Bundesanstalt für Geowissenschaften und Rohstoffe
Deike, R. : 51st International Foundry conference, Portorož, 15.09.2011

info@cewep.eu ▶ www.cewep.eu



World production of rare earths and the development of prices for lanthanum and cerium in 2011



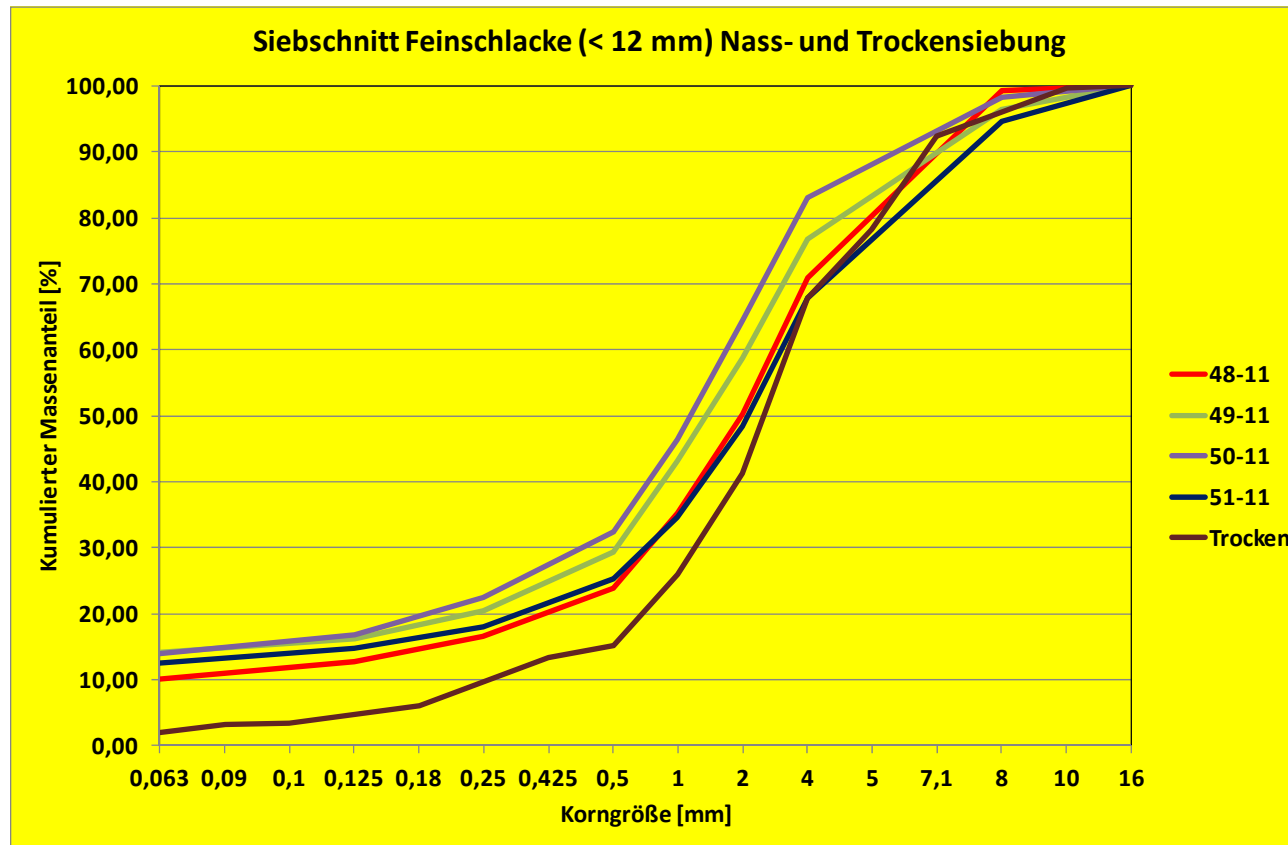
Data of United States Geological Survey, www.usgs.gov; British Geological Survey, www.bgs.ac.uk

Deike, R., Ebert, D.: ITAD Messekongress, IFAT, München, 10.05.2012

info@cewep.eu ▶ www.cewep.eu



Grain size distribution curves of prepared fine bottom ash (< 12mm) under wet and dry sieving conditions

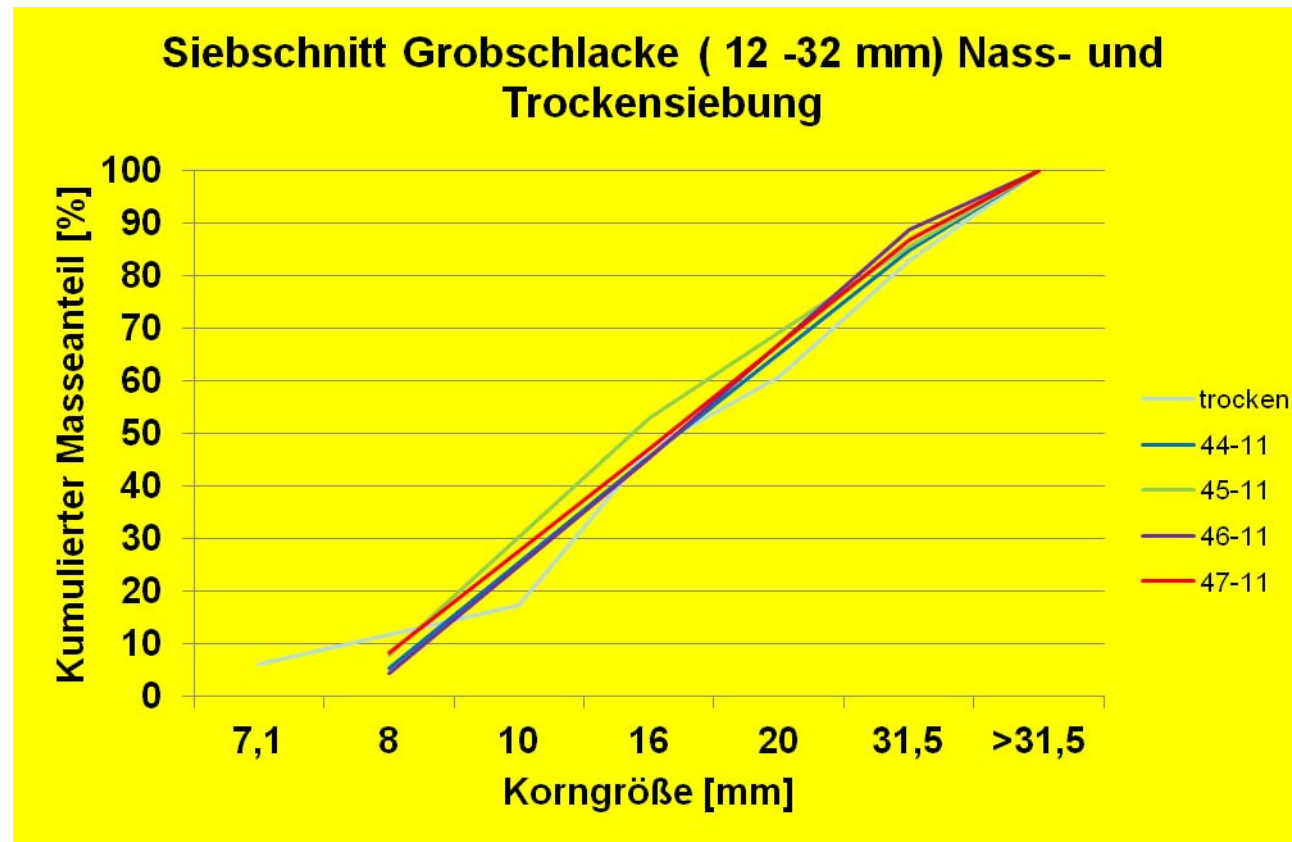


Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

info@cewep.eu ▶ www.cewep.eu



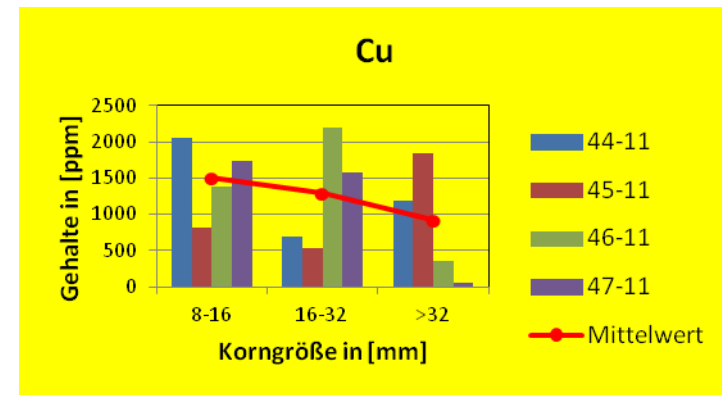
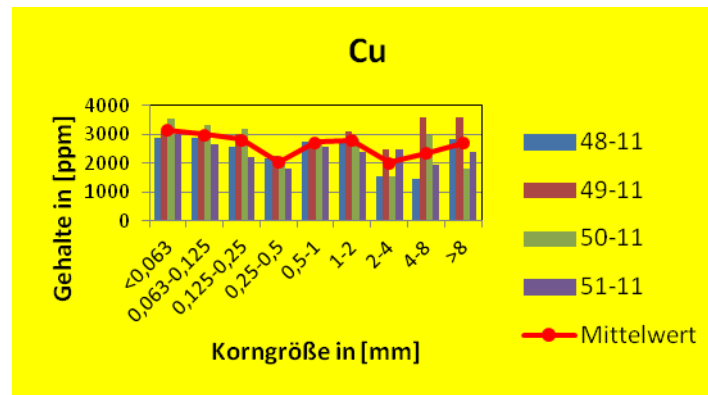
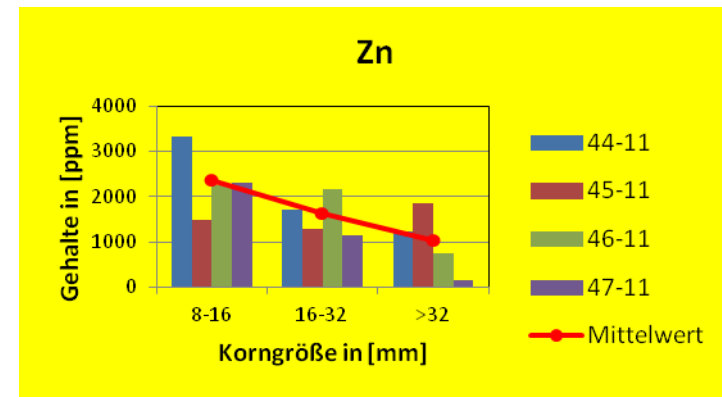
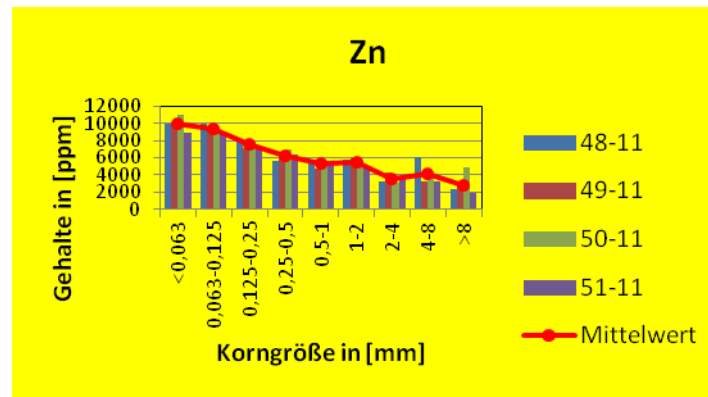
Grain size distribution curves of prepared coarse bottom ash (12-32 mm) under wet and dry sieving conditions



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

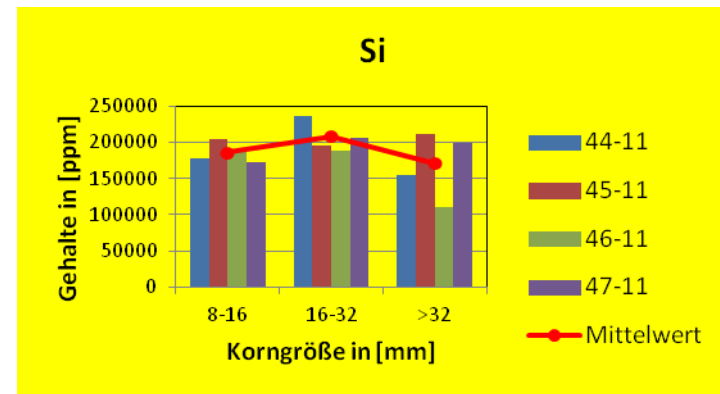
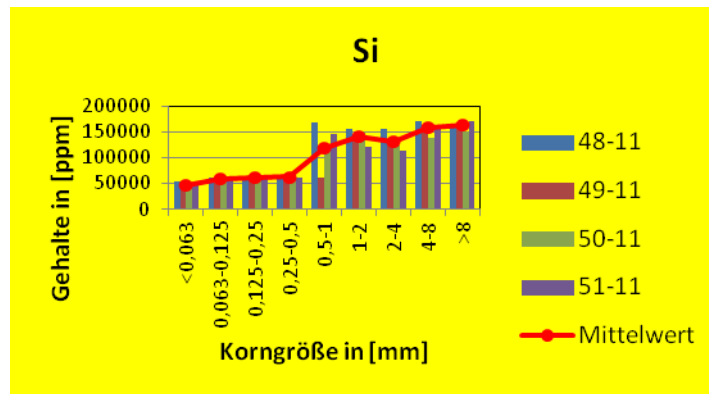
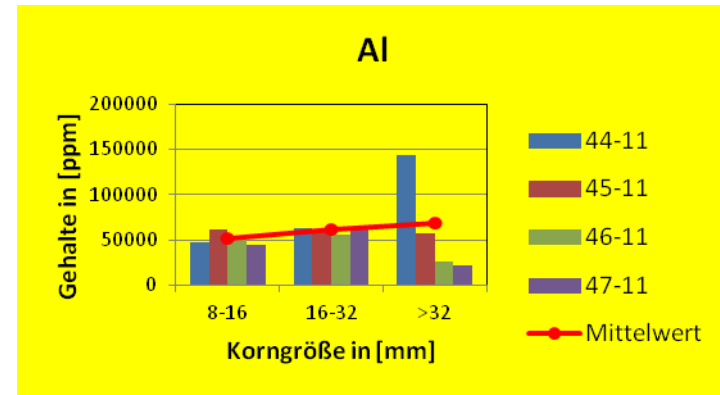
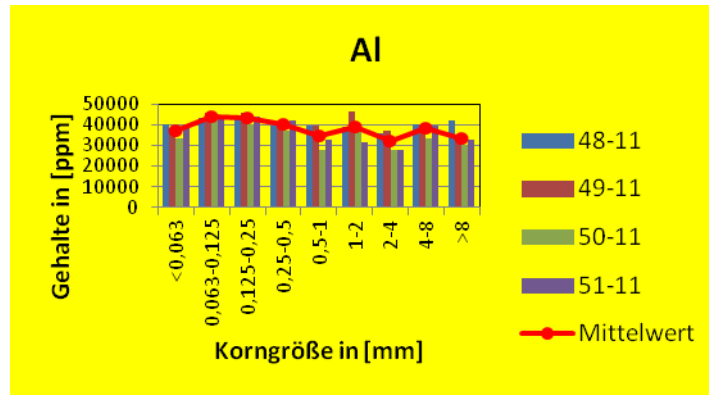
info@cewep.eu ▶ www.cewep.eu

Zn and Cu contents in dependence on the grain size



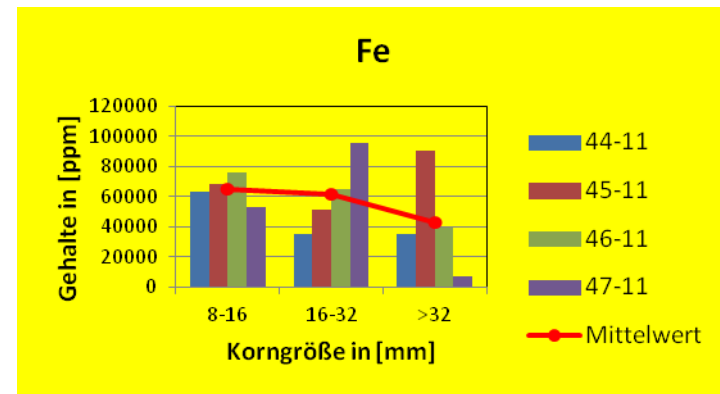
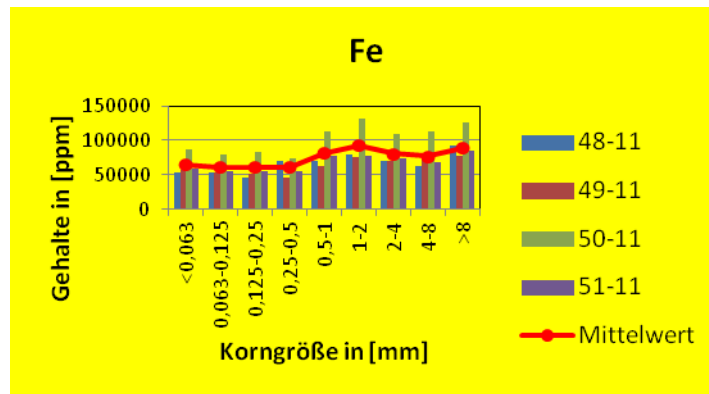
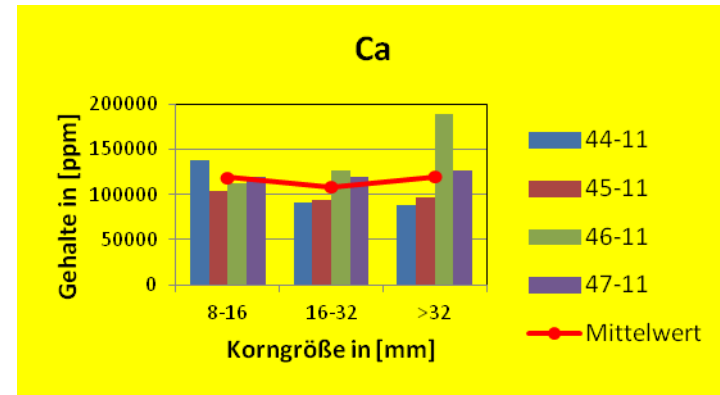
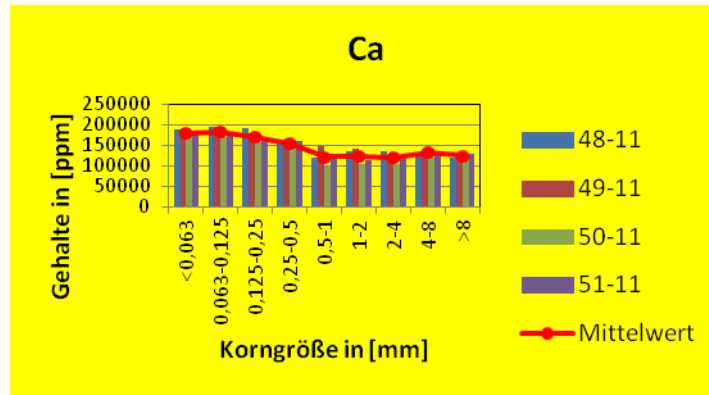
Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

Al and Si contents in dependence on the grain size



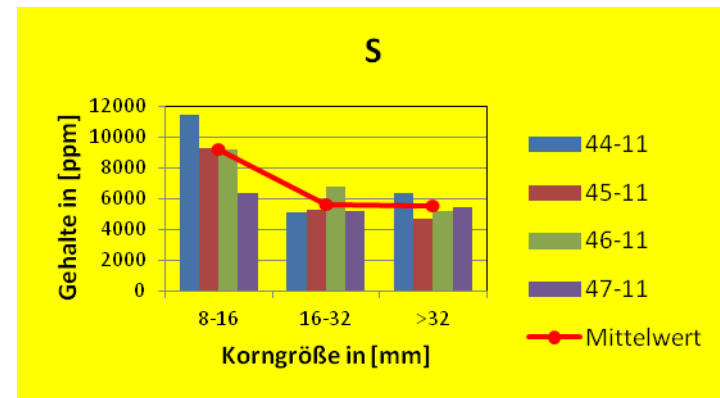
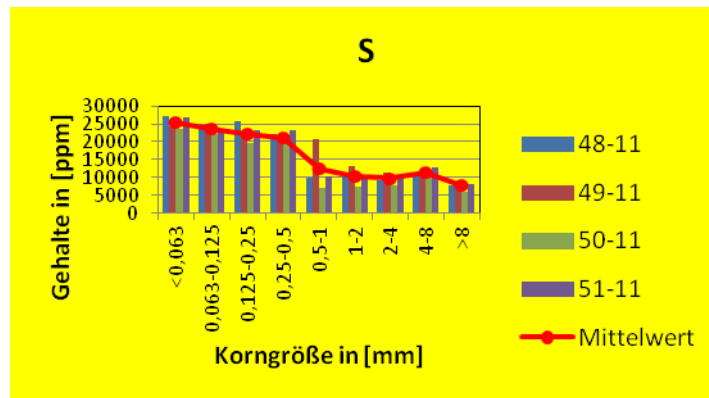
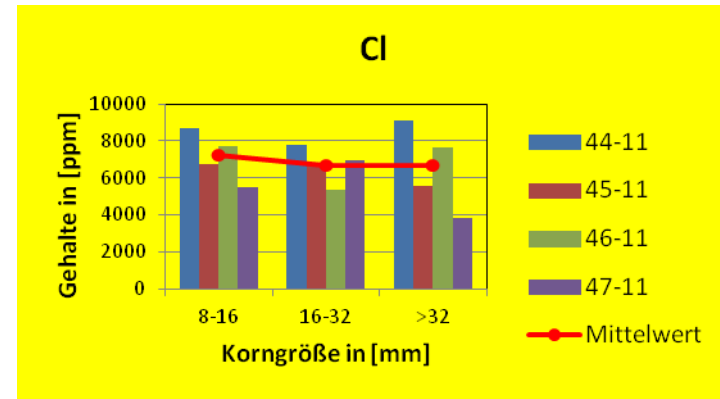
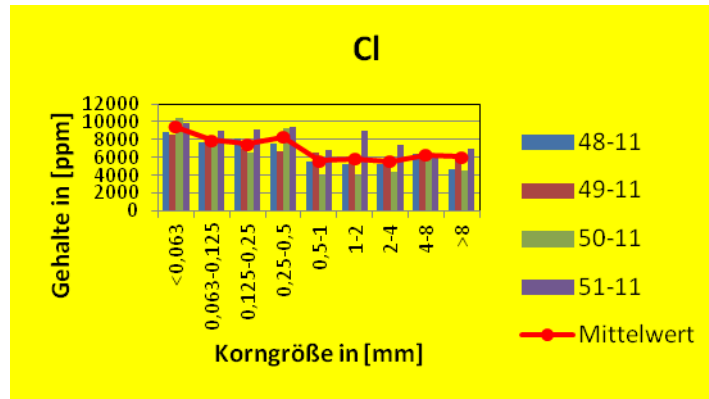
Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

Ca and Fe contents in dependence on the grain size



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

Cl and S contents in dependence on the grain size

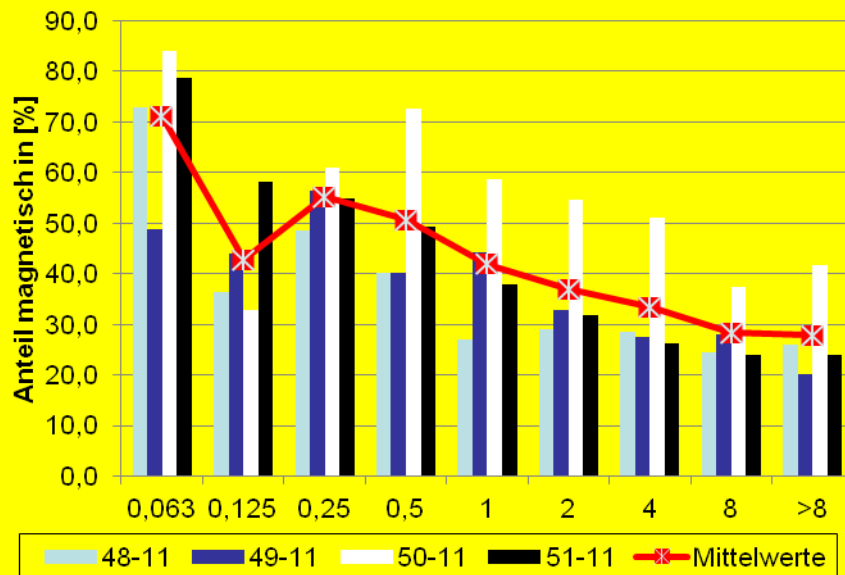


Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

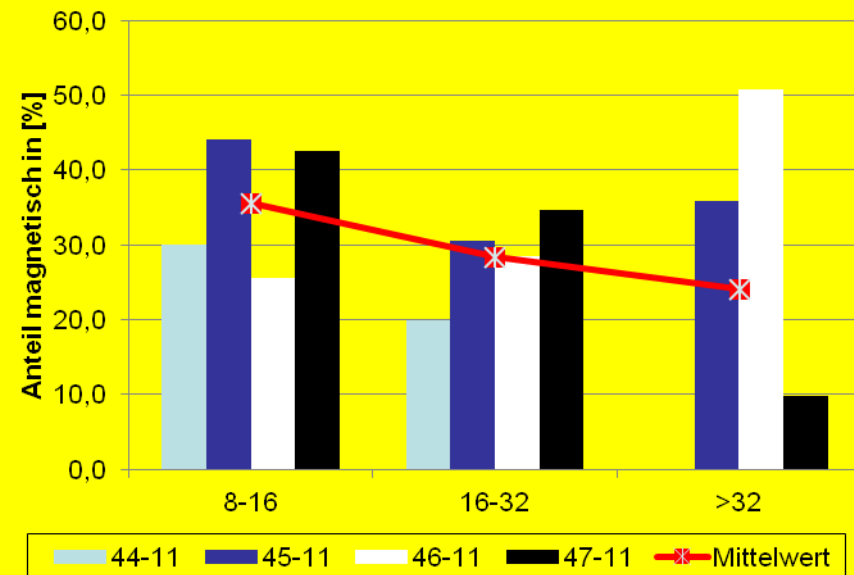
Percentage of magnetic compounds in the various grain fractions of prepared bottom ash



Percentage of magnetic particles depending on the grain size of fine wet sieved slags

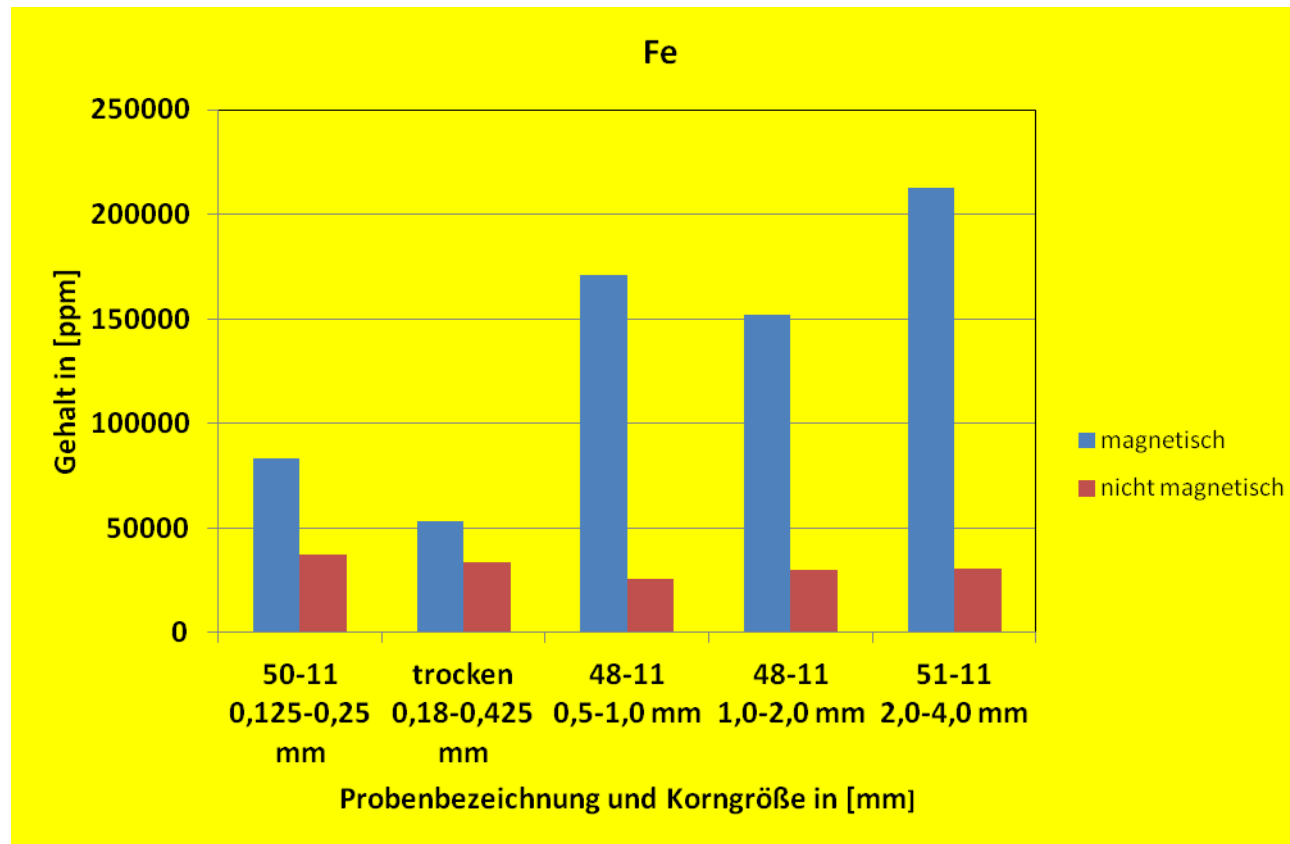


Percentage of magnetic particles depending on the grain size of coarse wet sieved slags



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

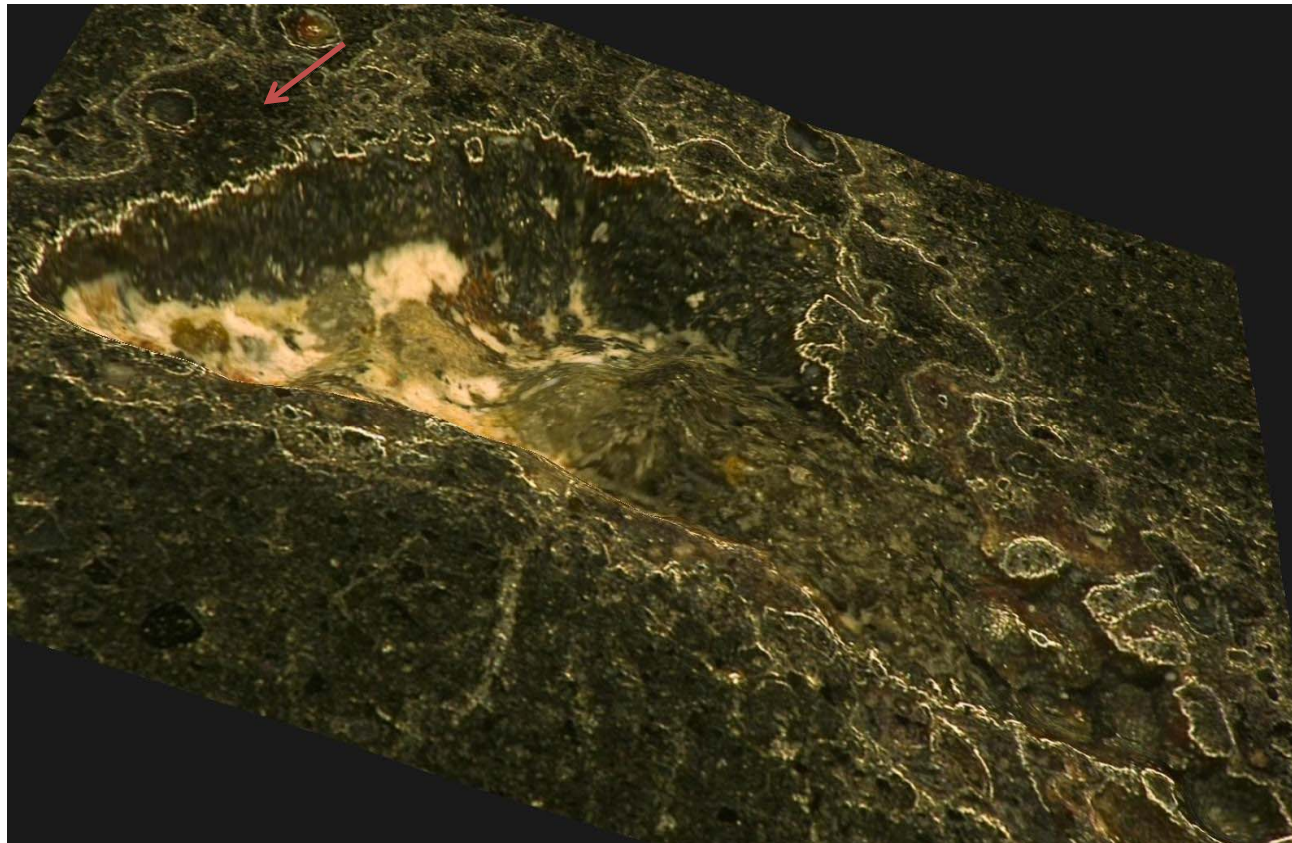
The iron content in the separated magnetic and nonmagnetic parts of fine bottom ash



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

info@cewep.eu ▶ www.cewep.eu

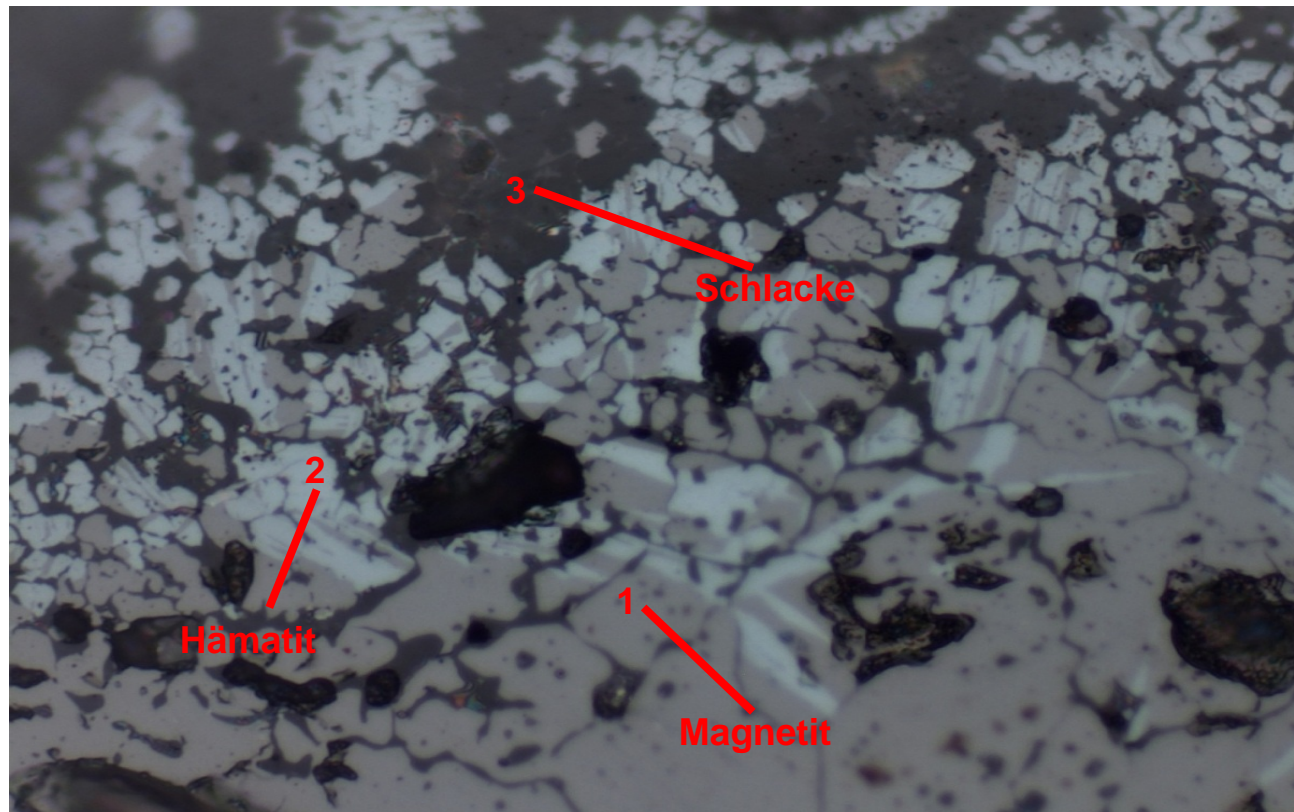
Macroscopic 3D image of bottom ash particles surrounded by a magnetite layer



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

info@cewep.eu ▶ www.cewep.eu

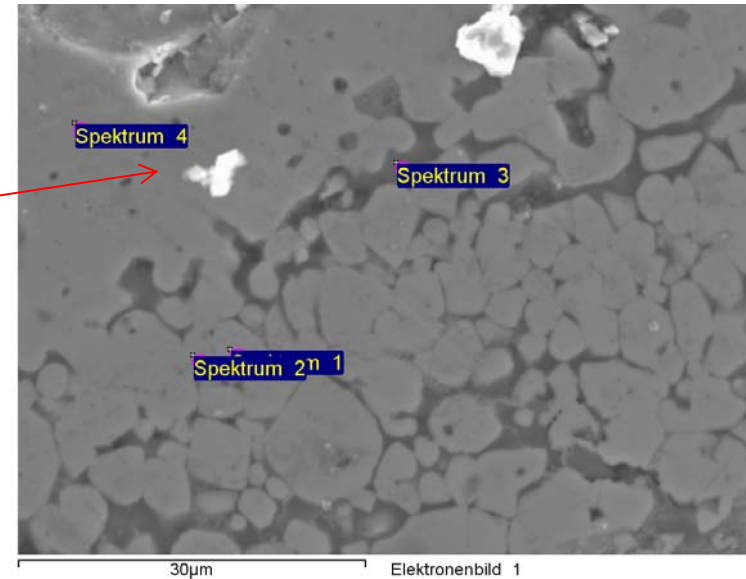
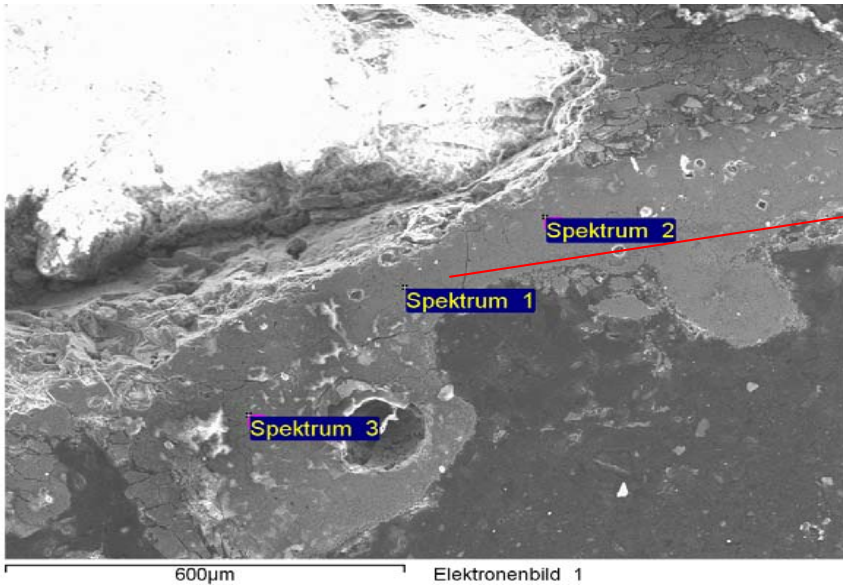
Metallographic analysis of magnetite, hematite and slag in the iron oxide layer in the surrounding of the bottom ash particles



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012



SEM image and EDX analysis of the oxide layer



Spektrum	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Ba
Spektrum 1	8	35	0,5		4,2	9,7	0,3	0,4	0,3	0,5	7,4		0,6	30,8	2,4
Spektrum 2	2,6	35,4		0,4	1,3	7,1					4,8	0,2		48,1	
Spektrum 3	8,8	34,3		0,3	1,3	6,1					4,5			44,8	

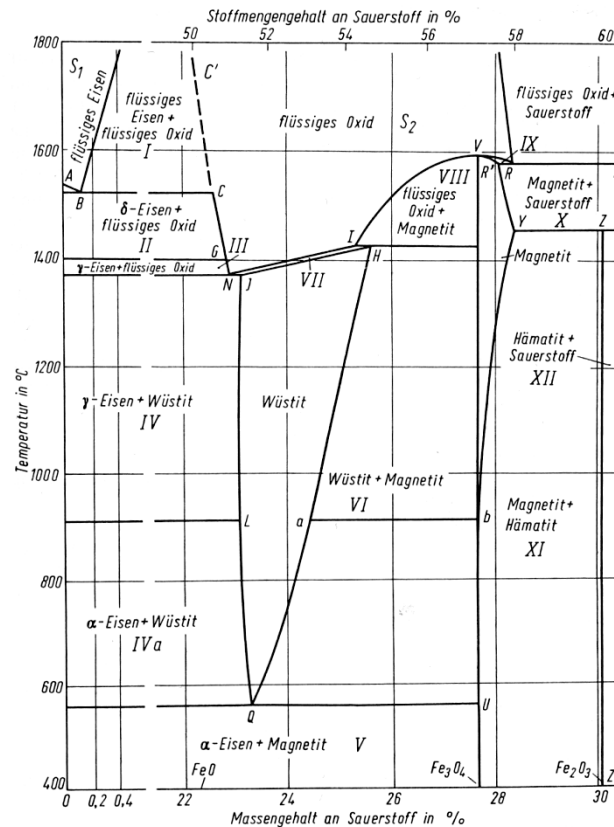
Spektrum	C	O	Mg	Al	Si	Ca	Mn	Fe	Ba
Spektrum 1	3	31,1		0,3				66	
Spektrum 2	2,9	31,5				0,3		65	
Spektrum 3	3,1	34,6	0,6	0,4	18	14	0,5	28	1,2
Spektrum 4	2,7	30,9		0,3				66	



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

info@cewep.eu ▶ www.cewep.eu

Iron-oxygen phase diagram



Oeters, F. : Metallurgie der Stahlherstellung, Verlag Stahleisen, Düsseldorf 1989

info@cewep.eu ▶ www.cewep.eu



First hypothesis to explain the mechanism of magnetite formation. Nice but not correct !

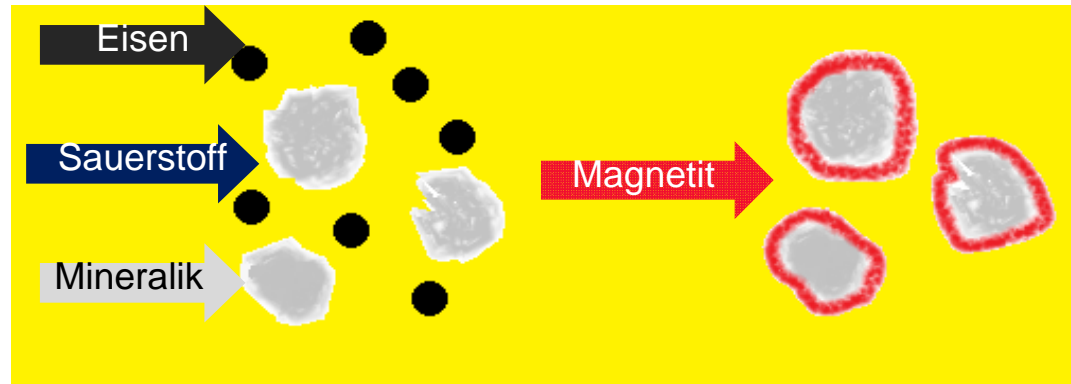


$$2Fe^{2+} + O_2 = Fe_3O_4$$

$$\Delta \bar{G}_{Fe_3O_4} (T, P) = - \frac{\Delta H_{Fe_3O_4}^\circ}{T} \left[\frac{P}{P^\circ} \right]$$

$$\bar{G}_{Fe_3O_4} (T, P) - \bar{G}_{Fe_3O_4}^\circ (T, P) = \int_{P^\circ}^P \frac{\Delta V_{Fe_3O_4}}{T} dP = \Delta V_{Fe_3O_4} \left[\frac{P}{P^\circ} \right]$$

$$\bar{G}_{Fe_3O_4} = \bar{G}_{Fe_3O_4}^\circ \left[\frac{P}{P^\circ} \right] \quad \bar{G}_{Fe_3O_4}^\circ = \bar{G}_{Fe_3O_4}^\circ \left[\frac{P}{P^\circ} \right]$$



Deike, R., Ebert, D.: VGB Workshop Produkte aus der thermischen Abfallverwertung, Bleicherode, 18.04.2012

Experimental procedure to prove the mechanism of magnetite layer growth

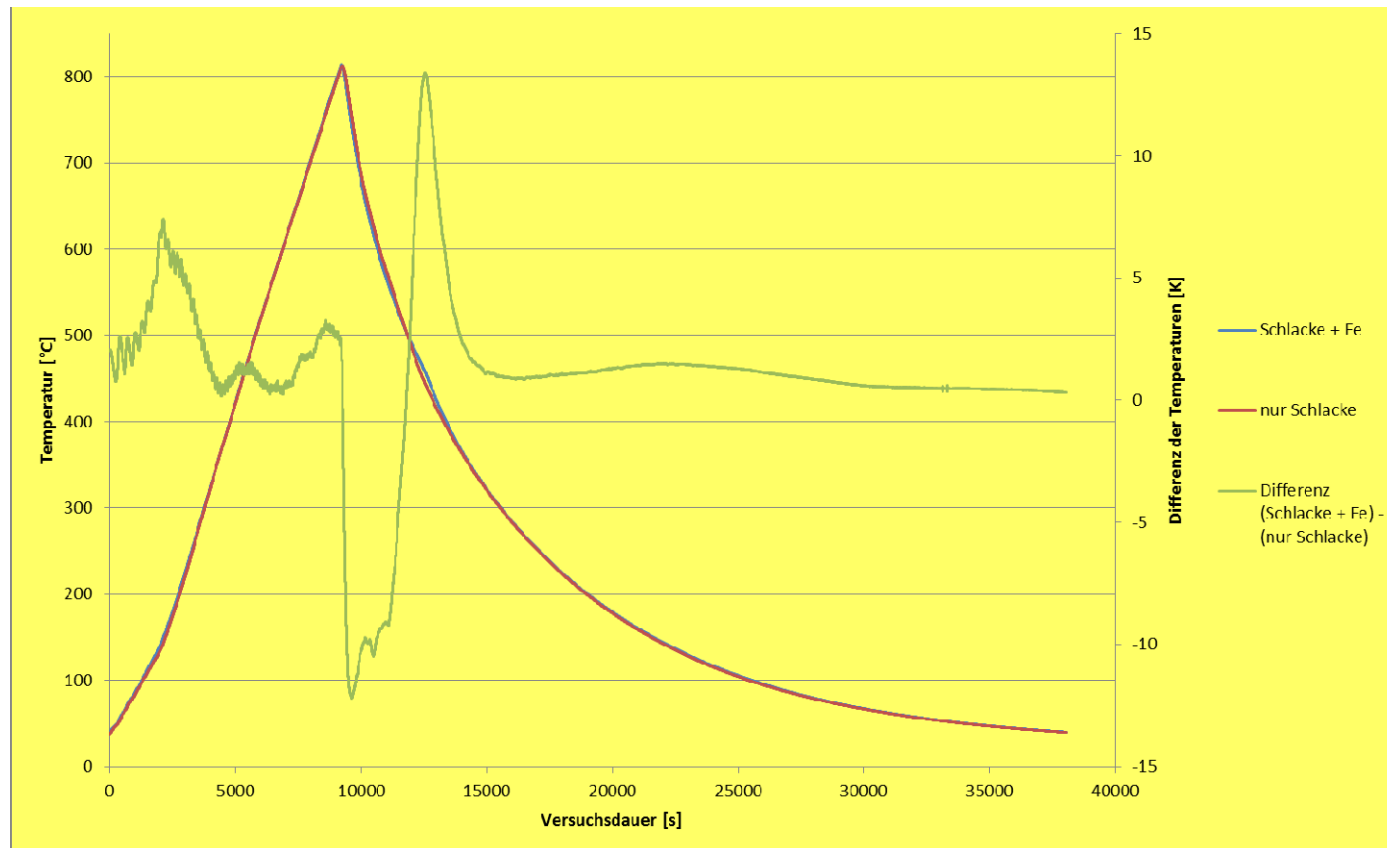


Experiments to produce magnetite layers in bottom ash

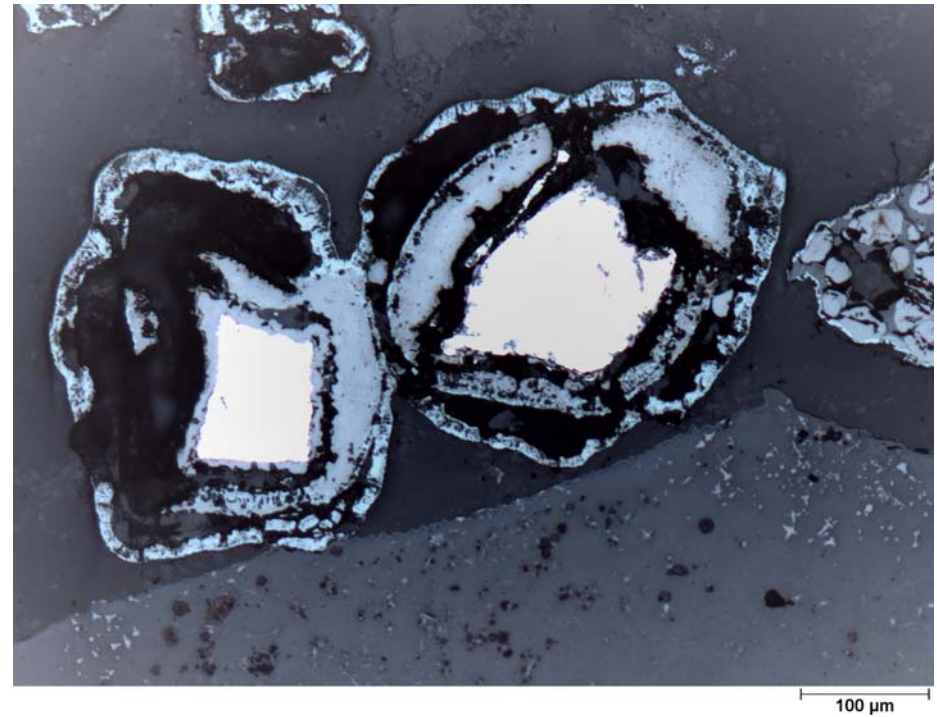
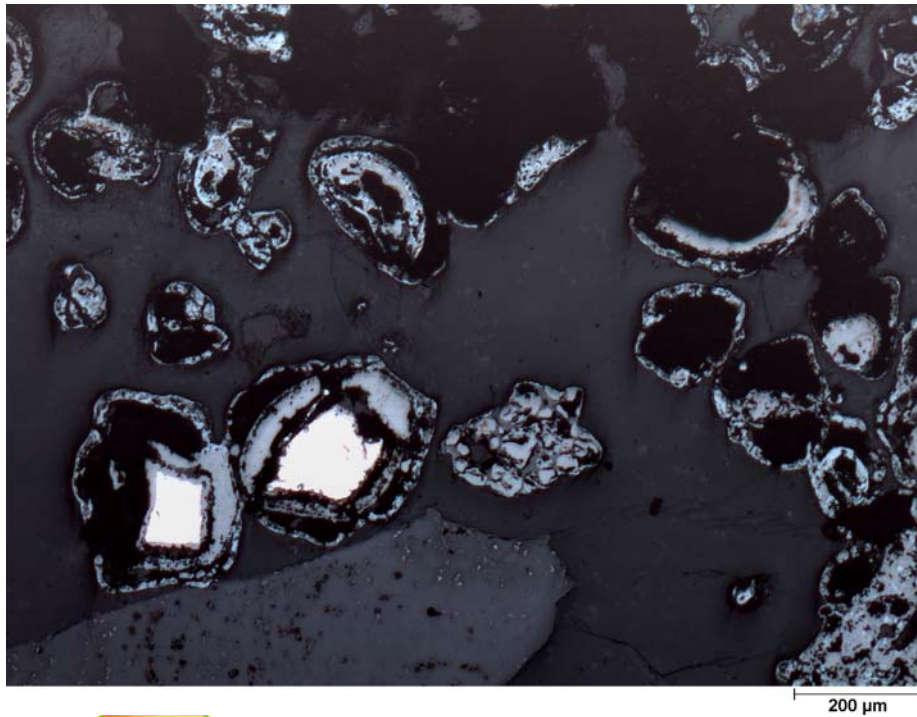
- Parameter:
- Heating rate: 5 K/s
- Holding time: 0 min
- Final temperature:
 - Experiment 1: 850 °C
 - Experiment 2: 1000°C
- Amount of bottom ash and iron chips:
 - 1. Experiment: 50g non magnetic fine bottom ash (1-2mm) + 10g iron chips
 - 2. Experiment: 50g fine non magnetic bottom ash (1-2mm) + 10g iron chips



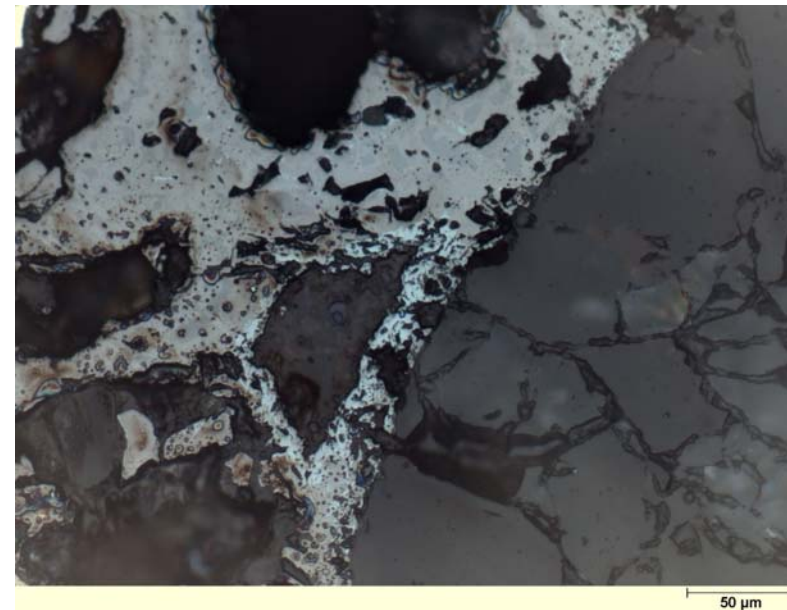
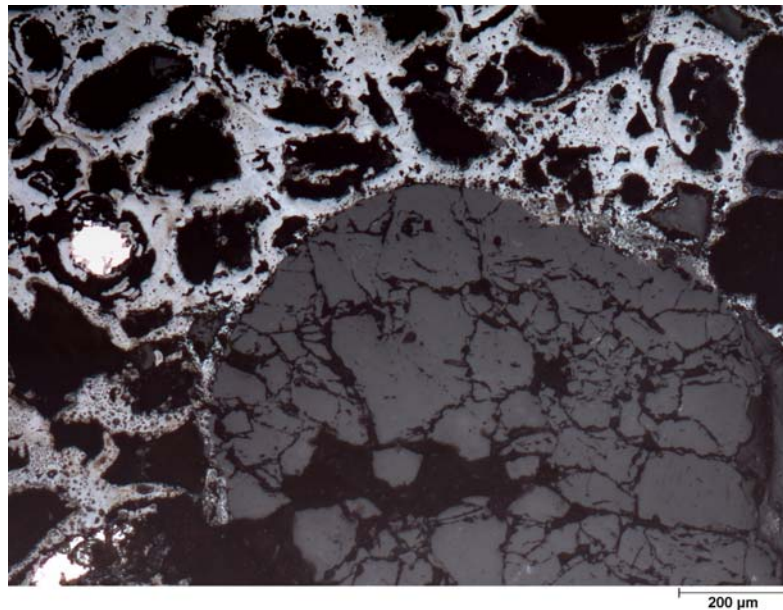
Heating process (temperature vs. time) and temperature difference between bottom ash samples with and without iron.



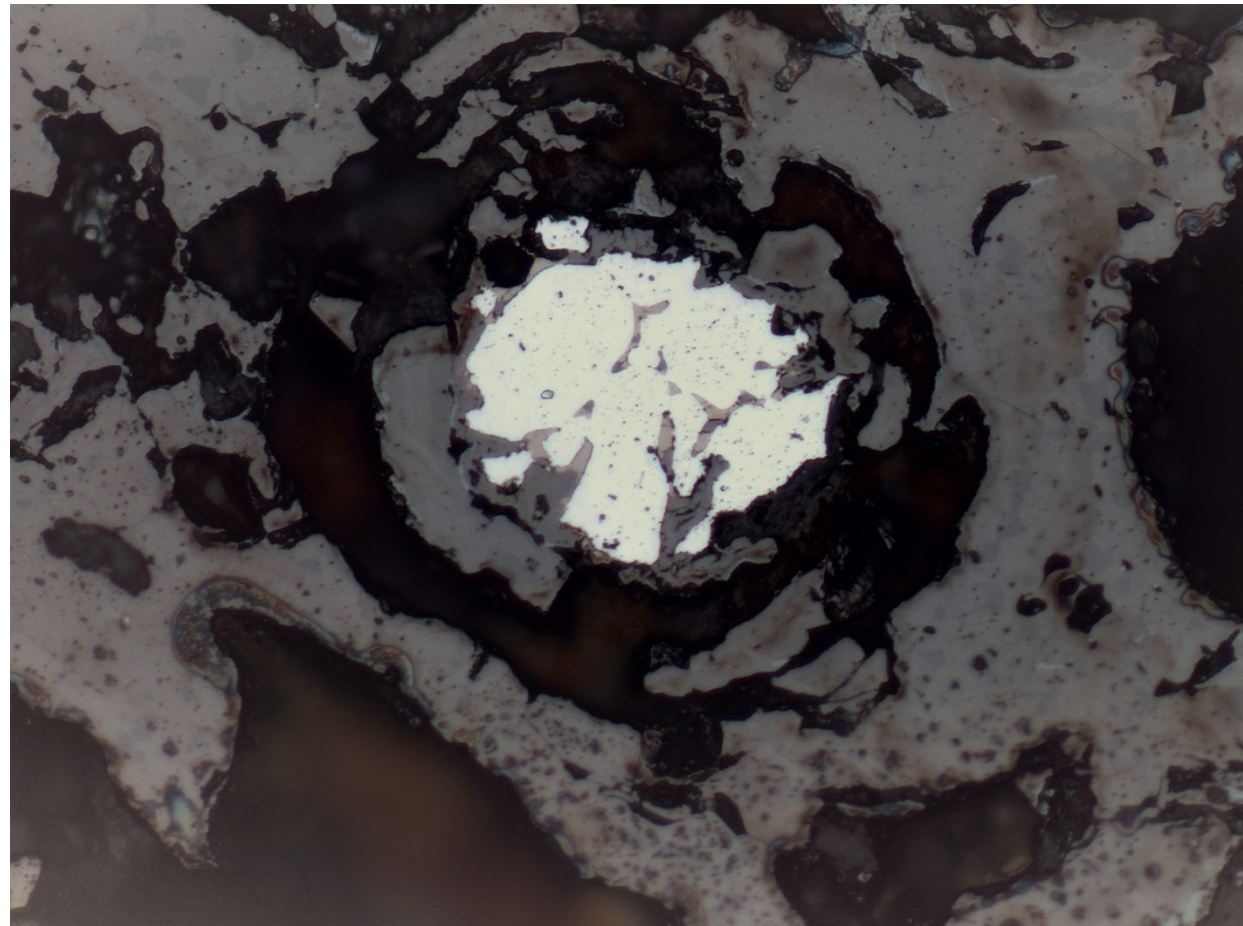
The formation of iron oxide layers at 850°C maximum temperature



Sintering of iron oxides particles and reacting with bottom ash particles at 1000°C



The continuous oxidation process of iron at 1000 °C

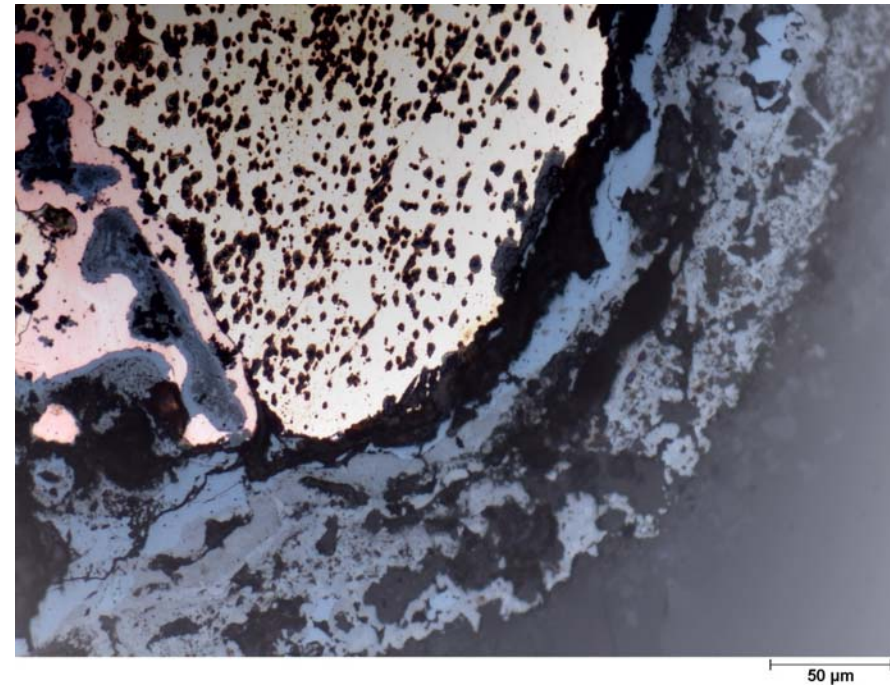


50 μm

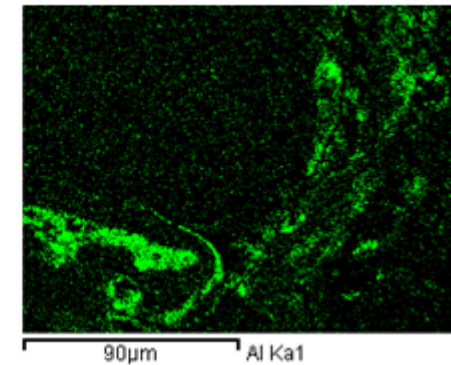
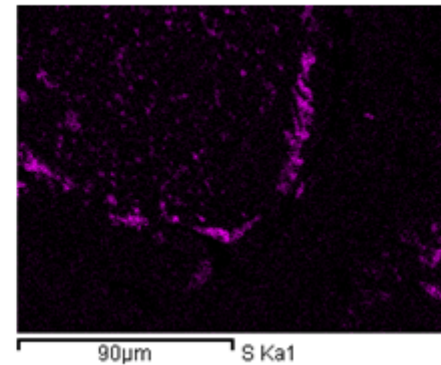
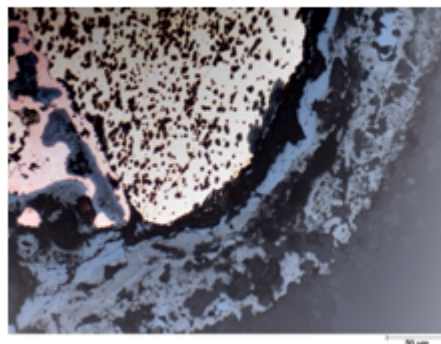
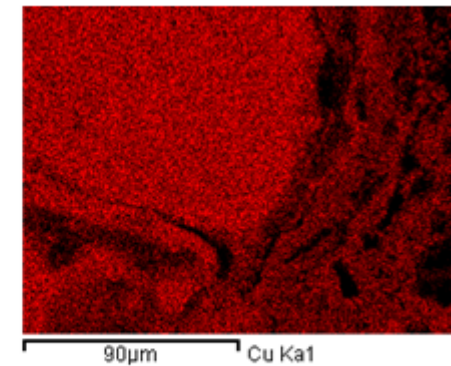
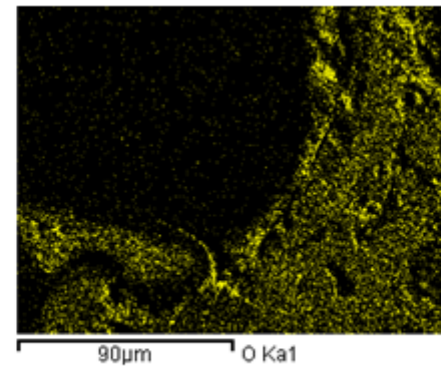
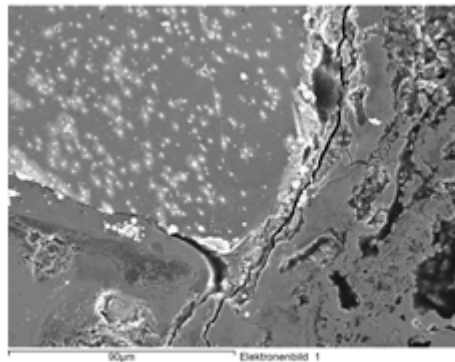


info@cewep.eu ▶ www.cewep.eu

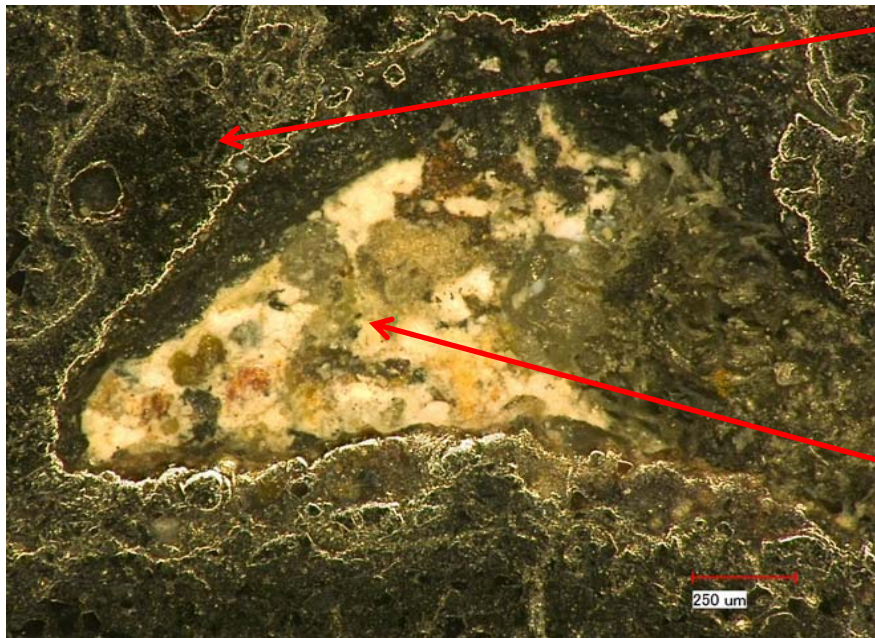
The oxidation of copper rich alloys as constituents of bottom ash



EDX element mapping of the oxidised copper particle and the adherent oxide layer



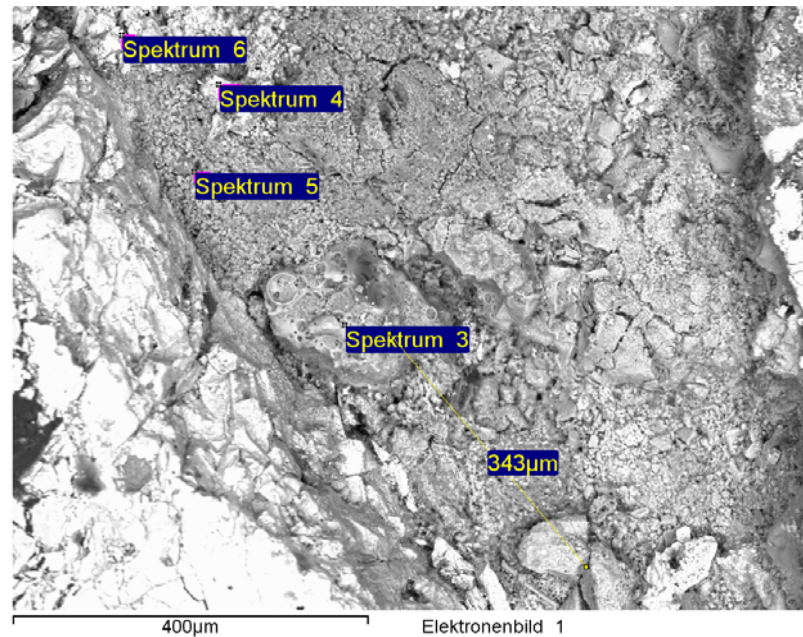
Second hypothesis to explain the mechanism of magnetite formation.



1. The oxide shell is the result of the oxidation of an iron particle.
2. The oxidation stopped when the total iron has been consumed.
3. That seems the main reason for the hole but some breakout during the preparation of the sample is also possible.
4. The bottom ash particles at the ground were at the beginning beneath the iron particle, which is now totally oxidised.
5. The oxide layers sinter together even with bottom ash particles.



SEM image and EDX analysis of single dots of the bottom ash particles at the ground



Spektrum	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Fe	Cu	Zn	Re
Spektrum 3	9,2	49	1,2	1,3	2,4	11	1,1	3,2	0,7	0,7	16	0,5	0,3	2,19		0,66	0,11
Spektrum 5	5,3	56,1		9,1	3,1	1,1		1,6	2,2	0,2	15	2,8		2	0,7	1,72	-0,33
Spektrum 4	5,6	45,5	1,3	1,2	5,5	14		1,1	0,3	2,3	4,4	0,2		13,7		5,18	
Spektrum 6	4,1	42,6		0,5	3,5	5,1		0,5	0,2	1	2,5			27,4		12,55	



Determination of the metal content in bottom ash by a slag remelting process



Deike, R, Ebert, D., Warnecke, R.; Vogell, M.: 11. VDI Fachkonferenz Feuerung und Kessel, Bremen, 13.06.2012

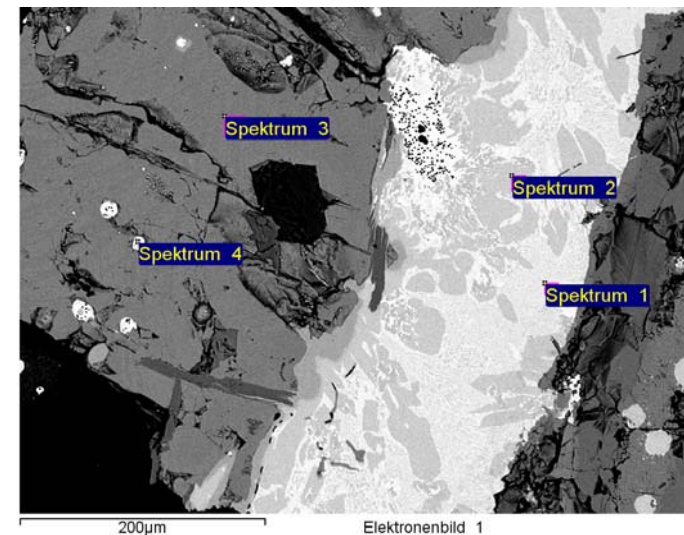
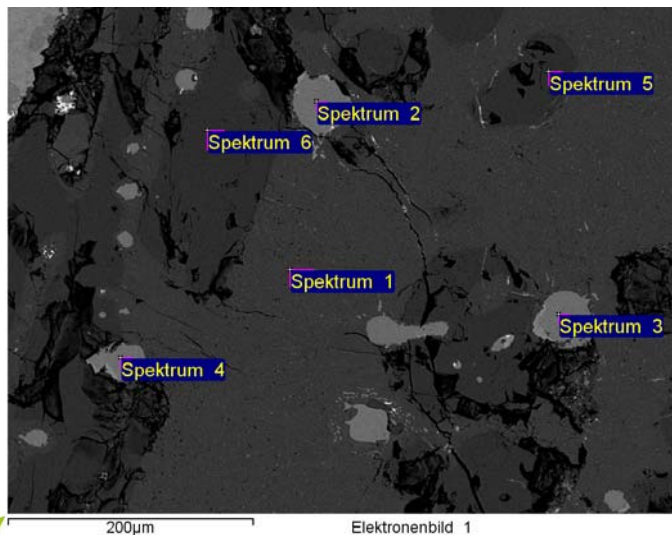
info@cewep.eu ▶ www.cewep.eu

EDX analysis of the metallic fraction after remelting the slag



	C	O	F	P	S	Cr	Fe	Ni	Cu	Sn	Sb
Spek.1	4,68		2,16	10,62	0,4		78,12	0,69	3,32		
Spek.2	3,87						1,8		80,7	10,4	3,2
Spek.3	4,75	3,18					1,34		77,8	9,94	3
Spek.4	2,92						2,04		81,5	10,2	3,4
Spek.5	5,54			21,54	0,32	0,6	72				
Spek.6	6,32		3,24	20,59		0,74	69,11				

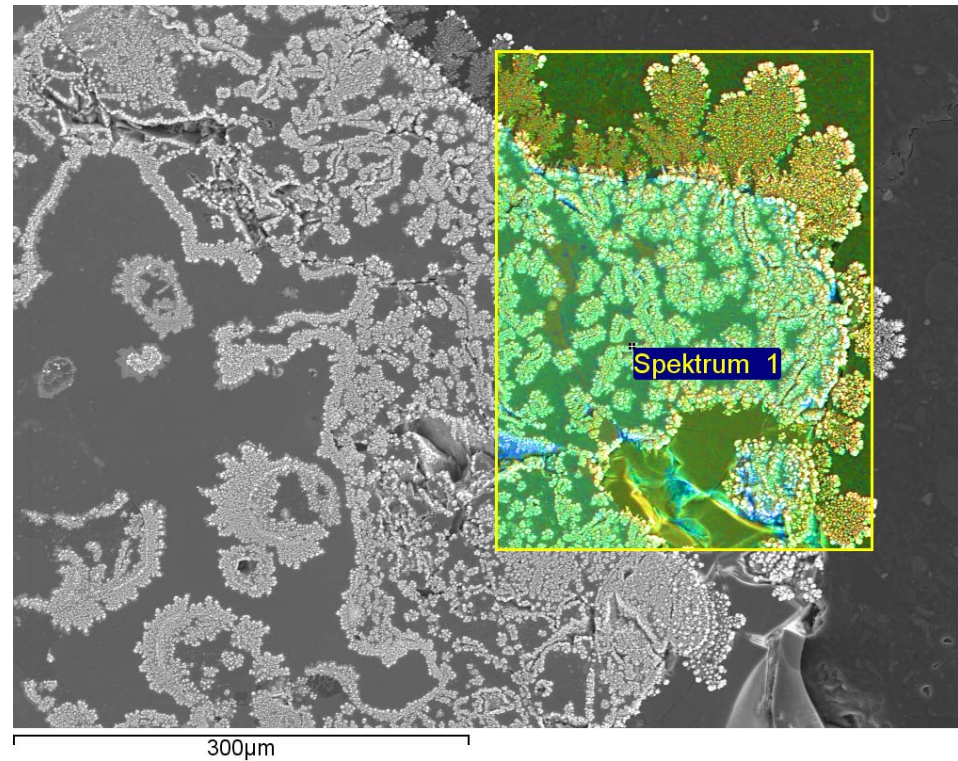
Spektrum	C	O	S	Mn	Fe	Cu	Sn	Sb	Pb
Spek. 1	2,55	1,5				66,8	19,98	9,18	
Spek. 2	3,91					82,03	10,53	3,52	
Spek. 3	6,69		24,09	0,78	10,9	57,54			
Spek. 4	6,58				1,42	72,54	11,15	4,65	3,66



Deike, R, Ebert, D., Warnecke, R.; Vogell, M.: 11. VDI Fachkonferenz Feuerung und Kessel, Bremen, 13.06.2012

info@cewep.eu ▶ www.cewep.eu

Element mapping of a particle after slag remelting



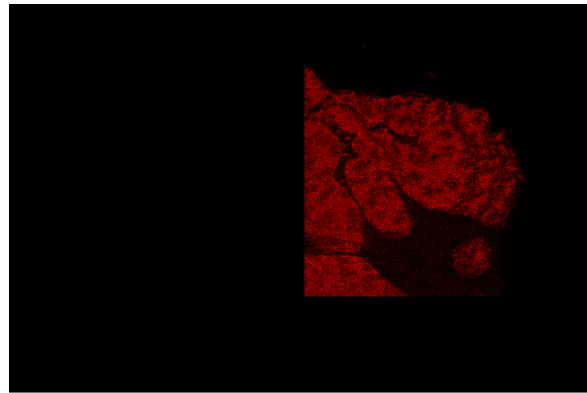
O	Al	Si	S	Ca	Fe	Cu	Pb
5,8500	0,0200	0,1300	24,2100	0,2700	38,0100	31,2500	0,2600

info@cewep.eu ▶ www.cewep.eu

Element mapping of a particle after slag remelting

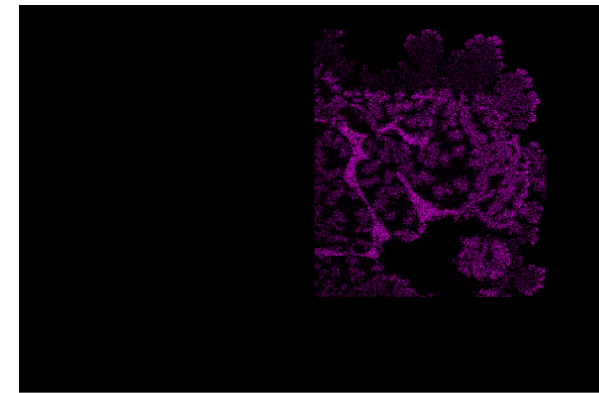


Eisen



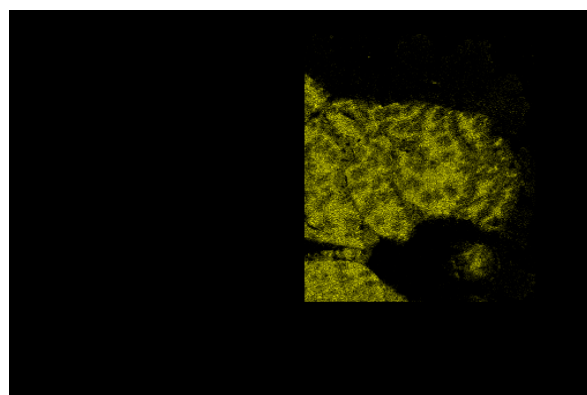
300µm

Kupfer



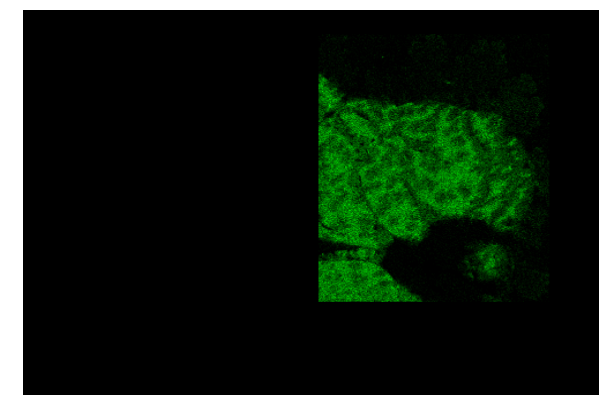
300µm

Schwefel



300µm

Blei



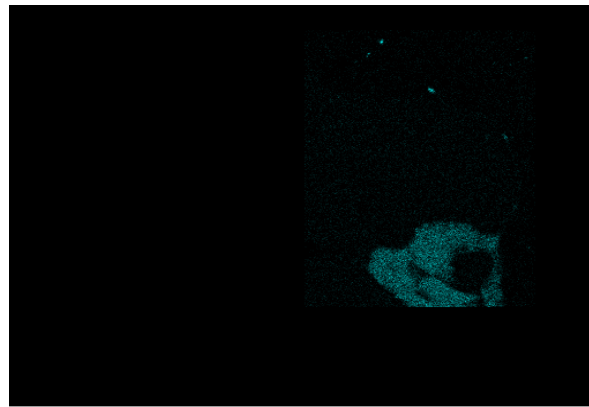
300µm



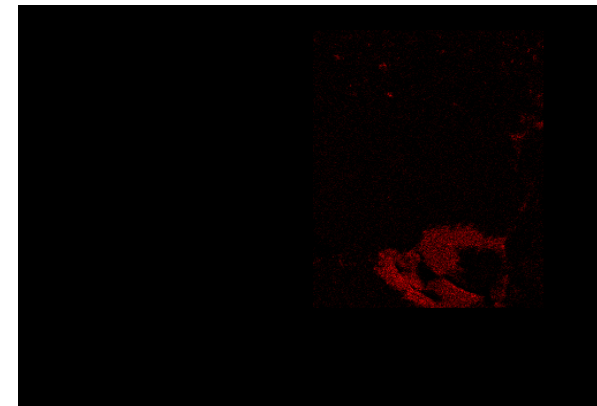
Element mapping of a particle after slag remelting



Calcium



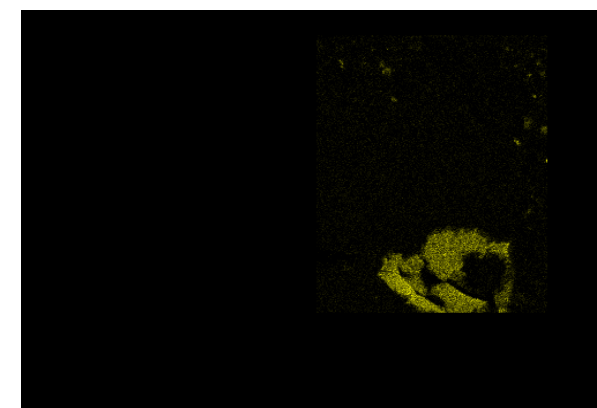
Aluminium



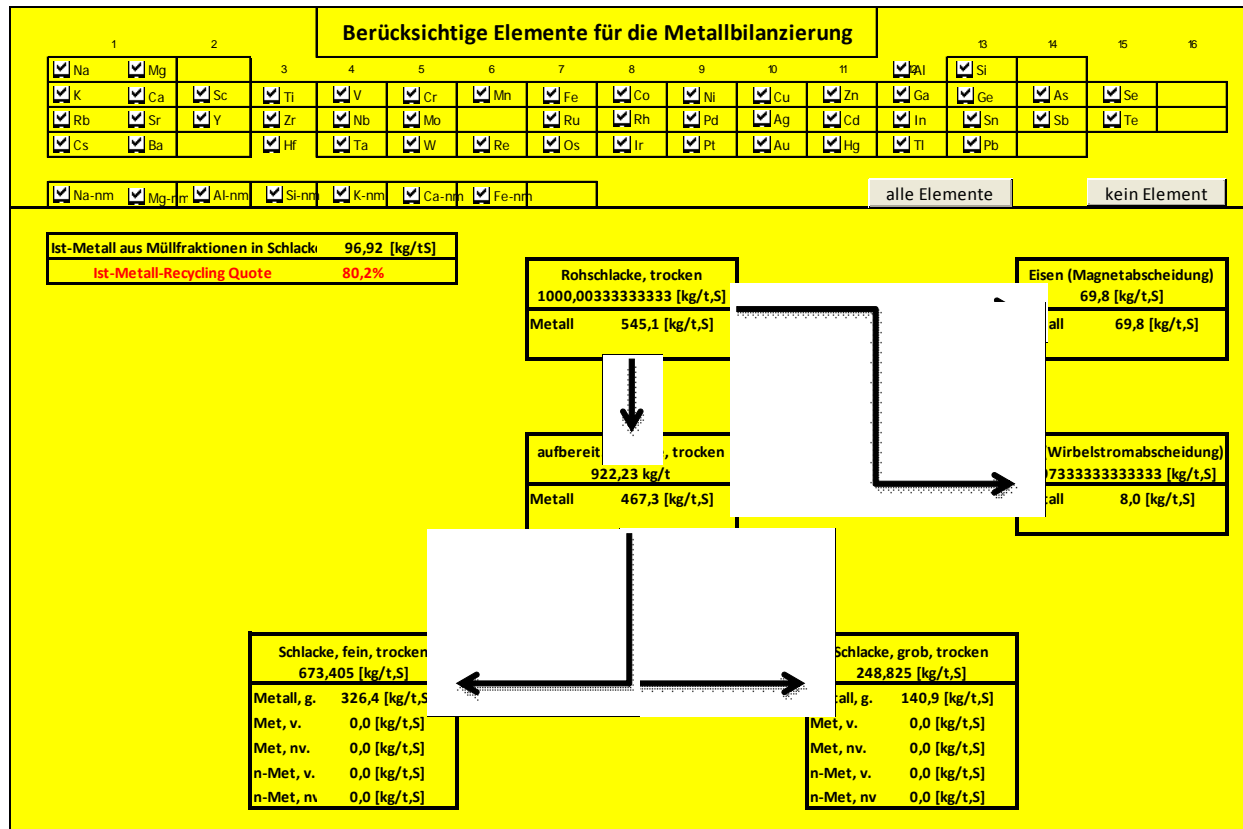
Sauerstoff



Silicium



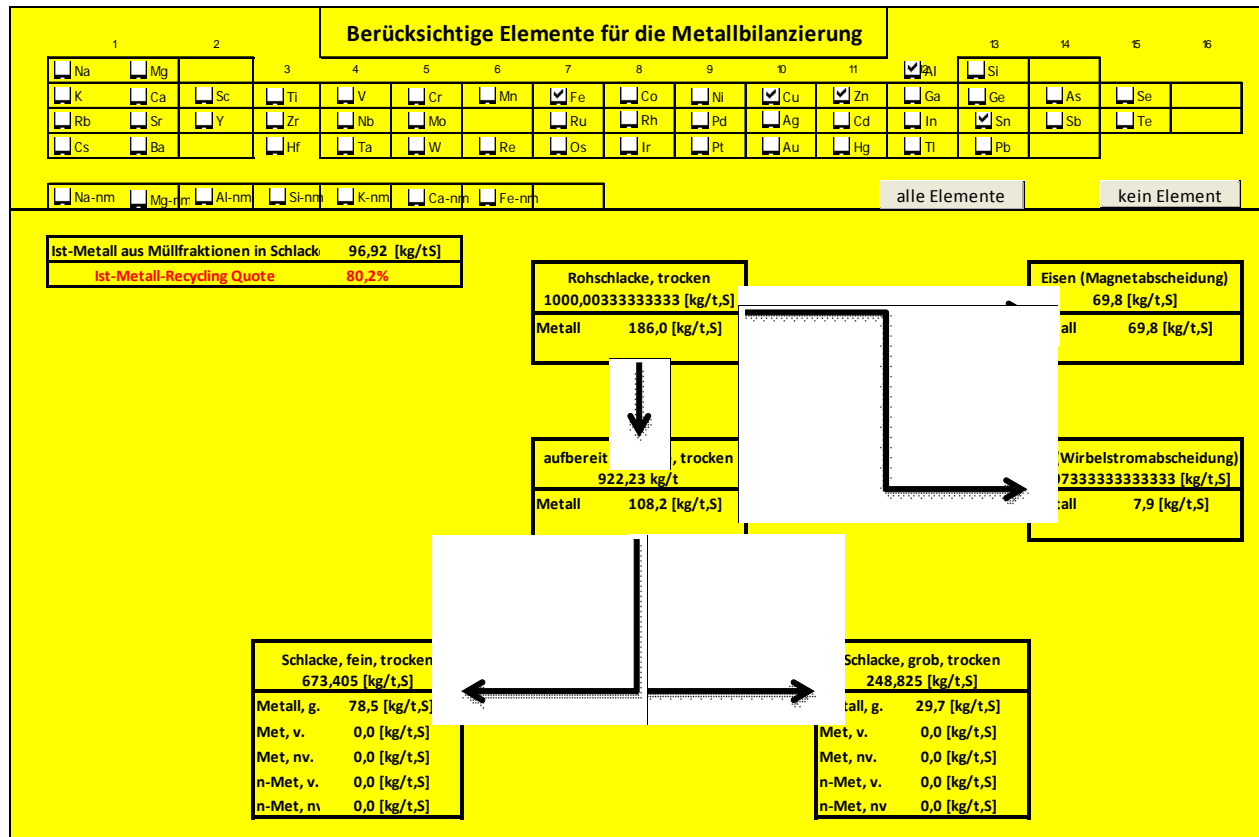
Metal content of bottom ash, current recycling rate and future recycling potential



Deike, R, Ebert, D., Warnecke, R.; Vogell, M.: 11. VDI Fachkonferenz Feuerung und Kessel, Bremen, 13.06.2012

info@cewep.eu ▶ www.cewep.eu

Metal content of bottom ash, current recycling rate and future recycling potential



Deike, R, Ebert, D., Warnecke, R.; Vogell, M.: 11. VDI Fachkonferenz Feuerung und Kessel, Bremen, 13.06.2012

info@cewep.eu ▶ www.cewep.eu

Metal Recycling from bottom ash



Thank for your attention!



info@cewep.eu ▶ www.cewep.eu