SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

FEhS Institut für Baustoff Forschung

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

D. MUDERSBACH,

P. DRISSEN, H. MOTZ

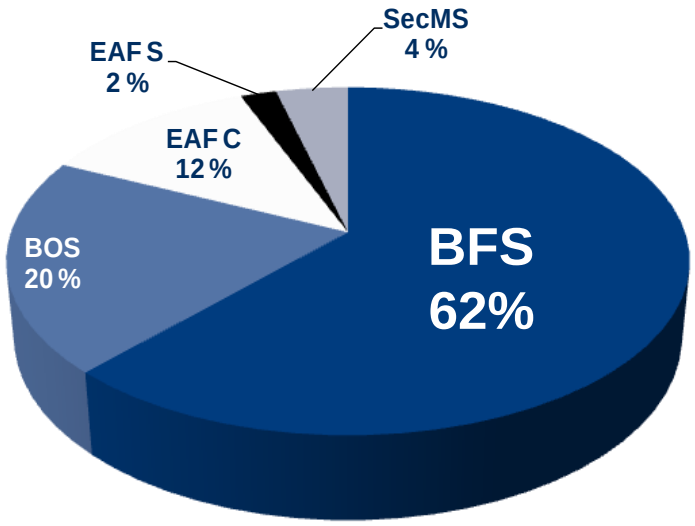
HT centre

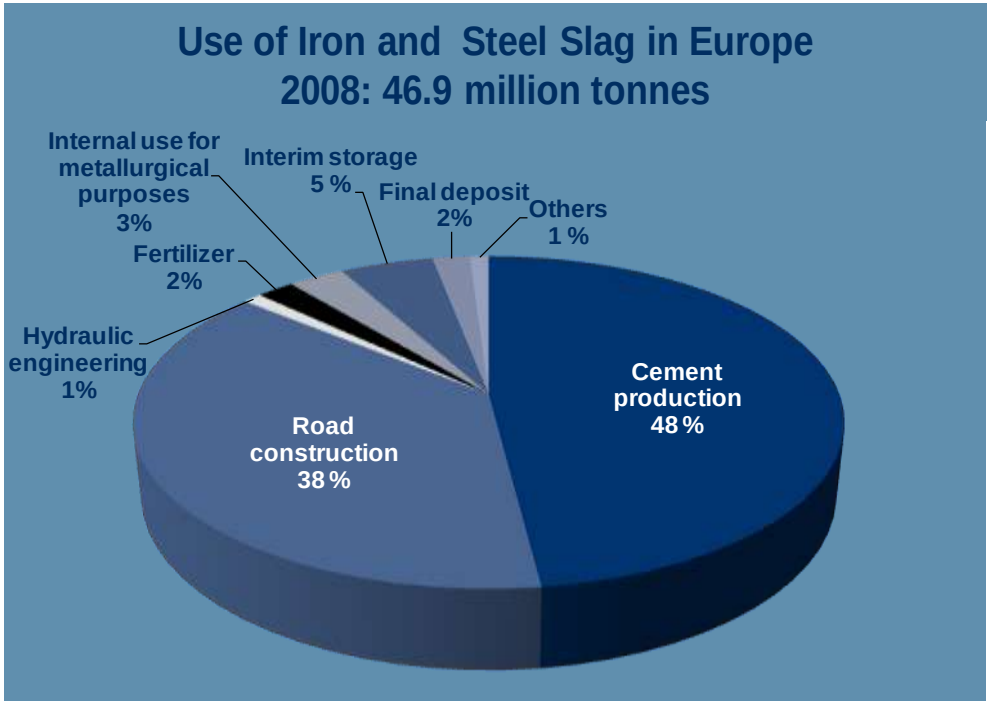
SMART-PRO²

Introduction

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

Production of Iron and Steel Slag in Europe
2008: 45.6 million tonnes





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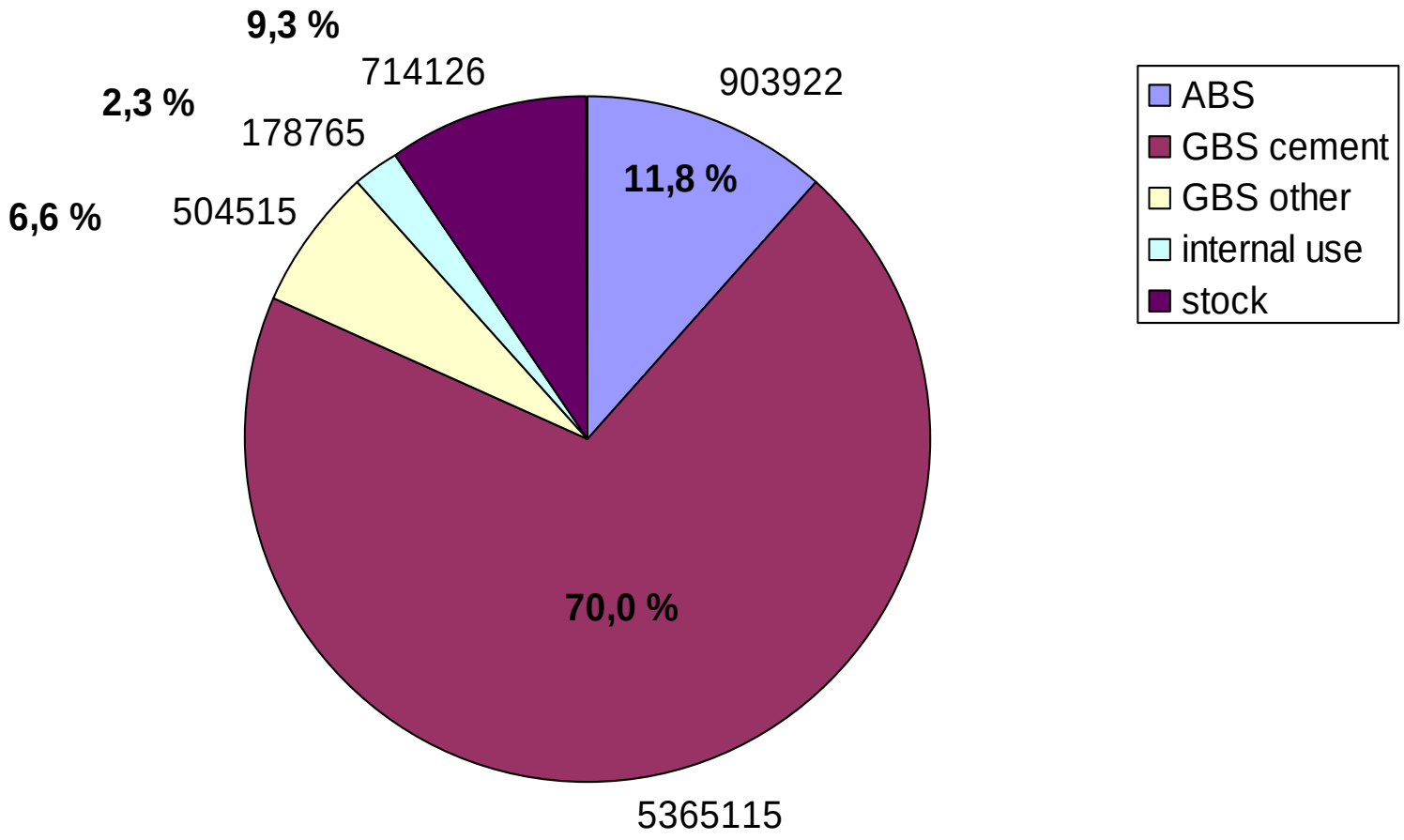
7,7 mio. t Blast Furnace Slags in Germany 2010



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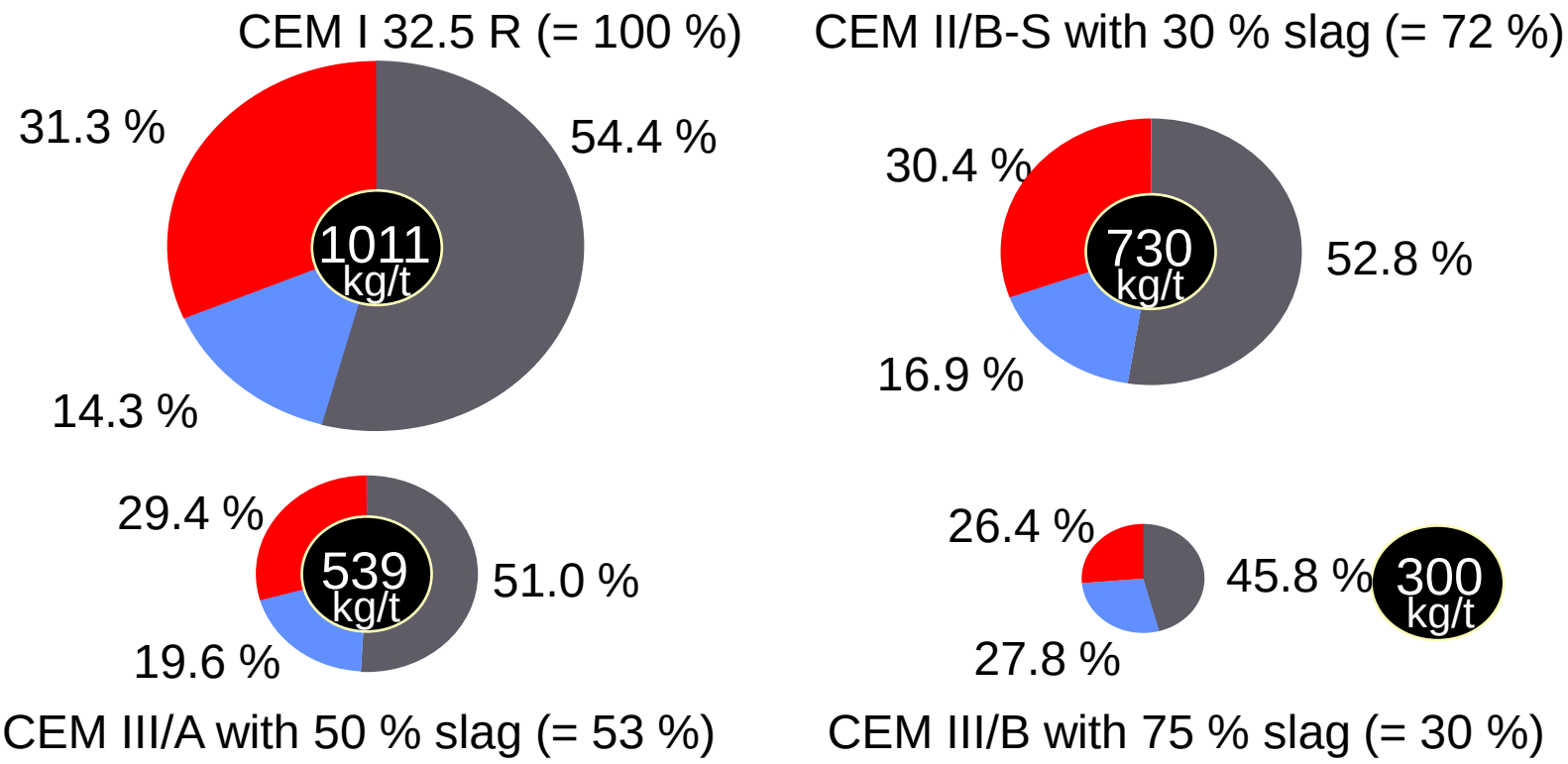
Cement production and CO_2 emissions
- Benefits of slag cements -



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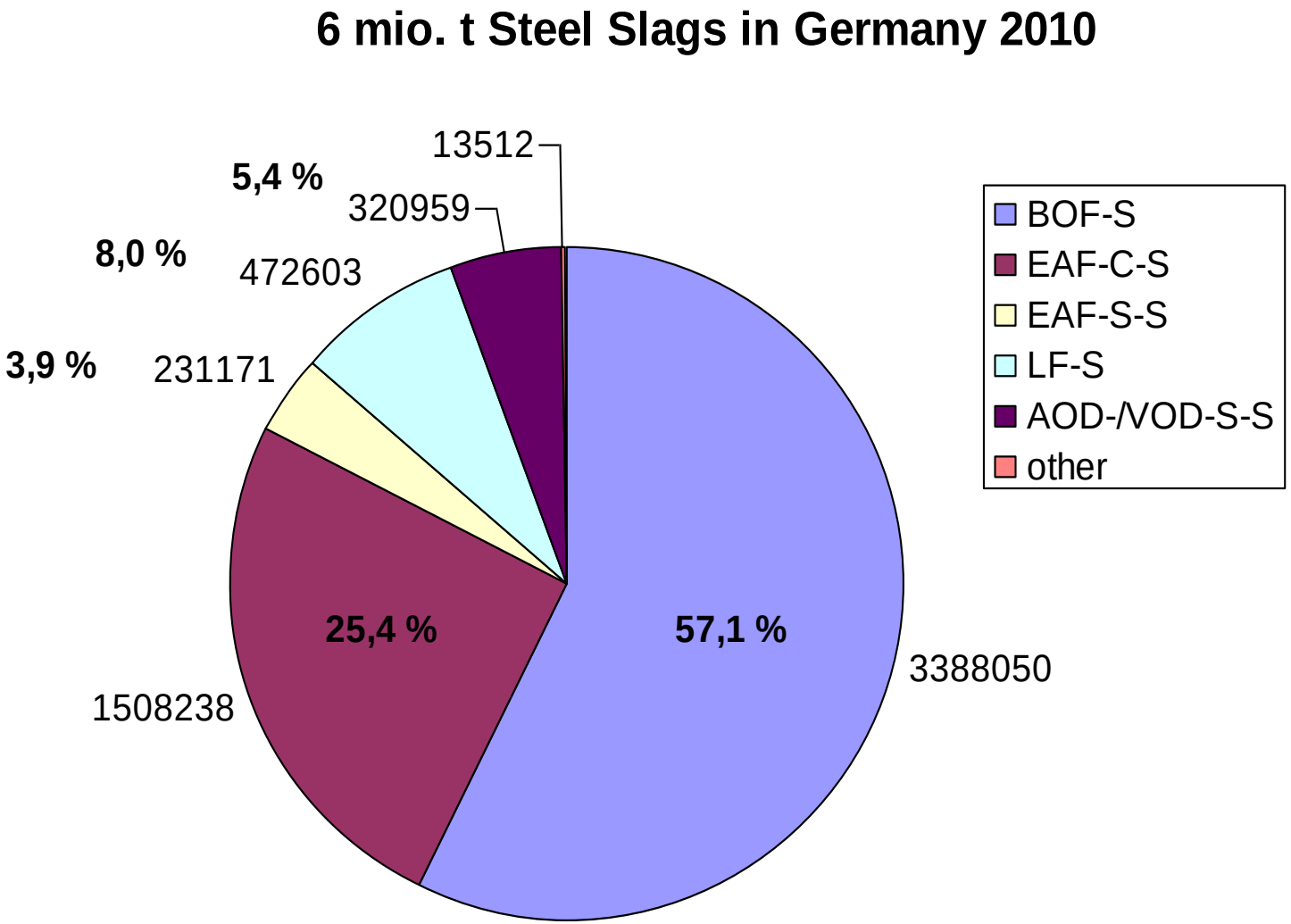

Increasing the quality of water granulated blast furnace slags

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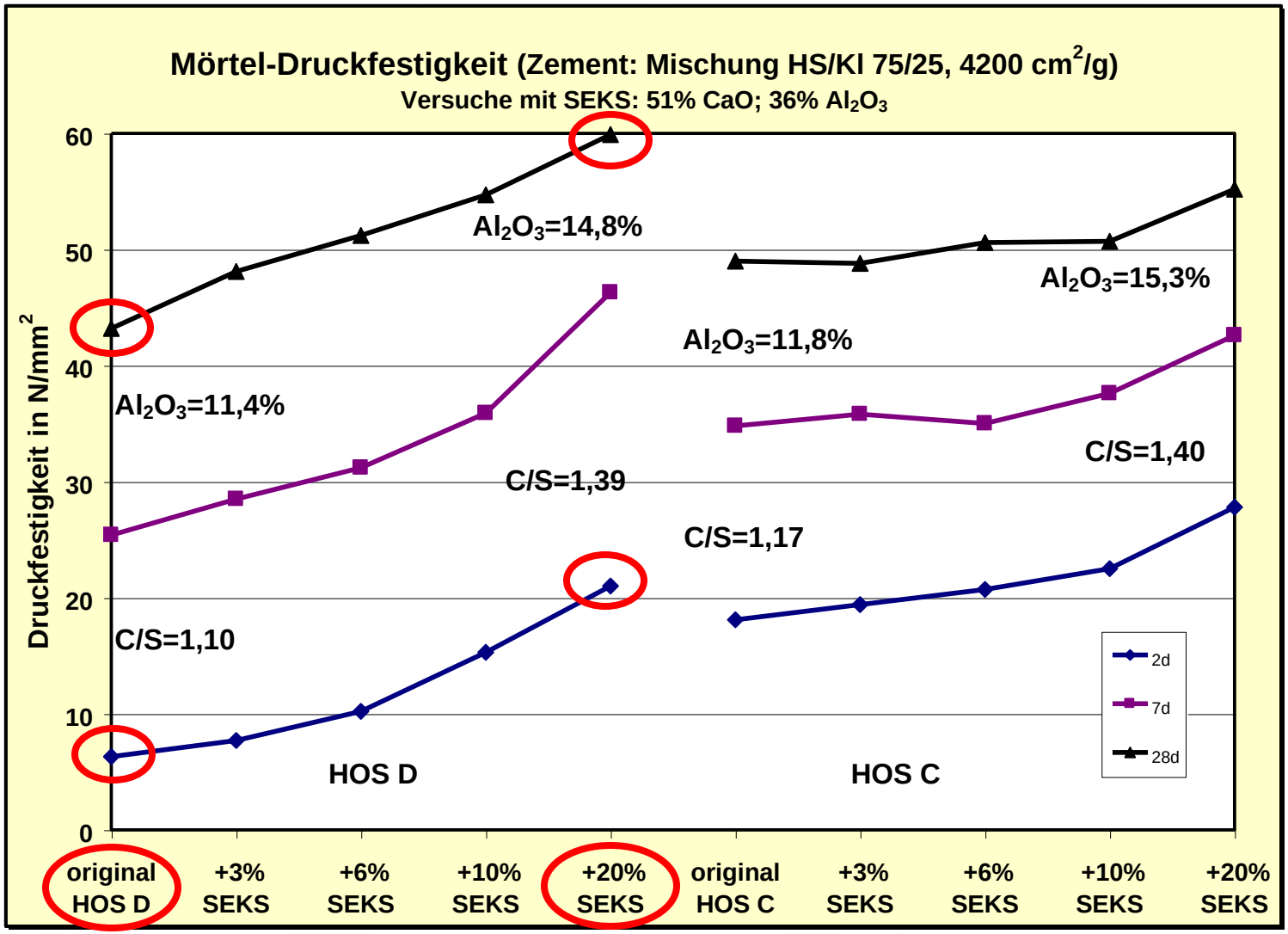

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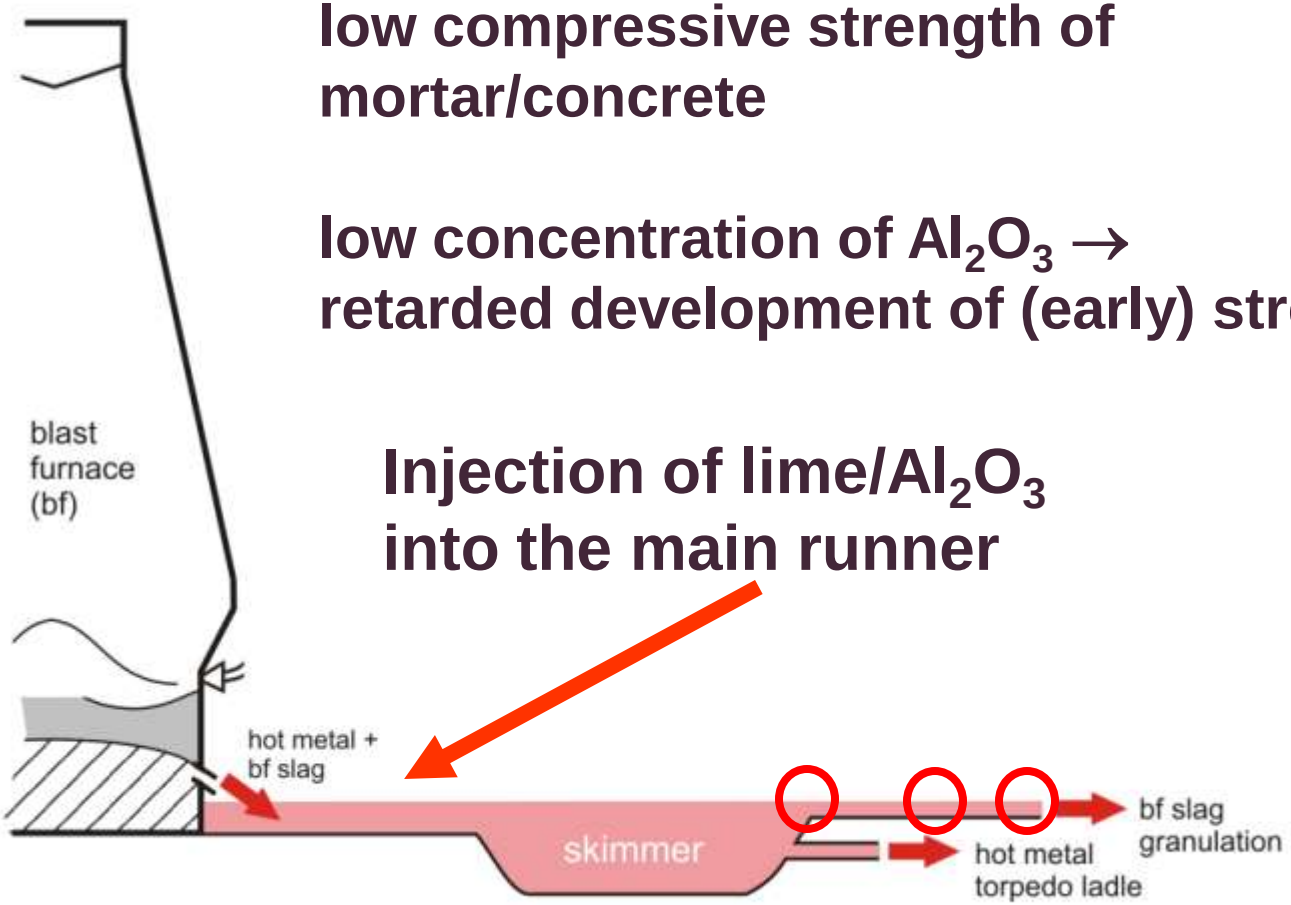
low basicity CaO/SiO_2 →
low compressive strength of mortar/concrete

low concentration of Al_2O_3 →
retarded development of (early) strength

Injection of lime/Al_2O_3 into the main runner



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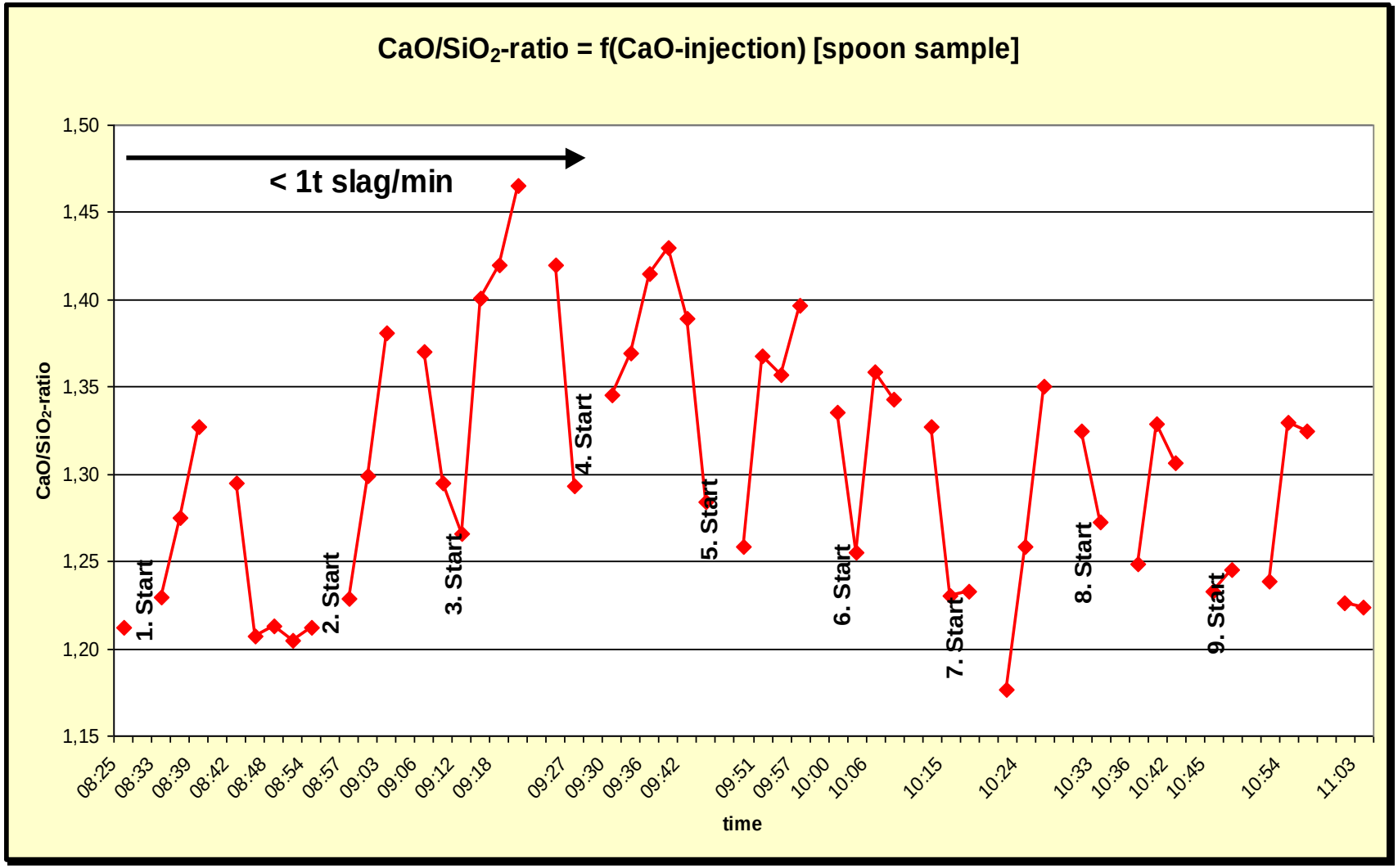

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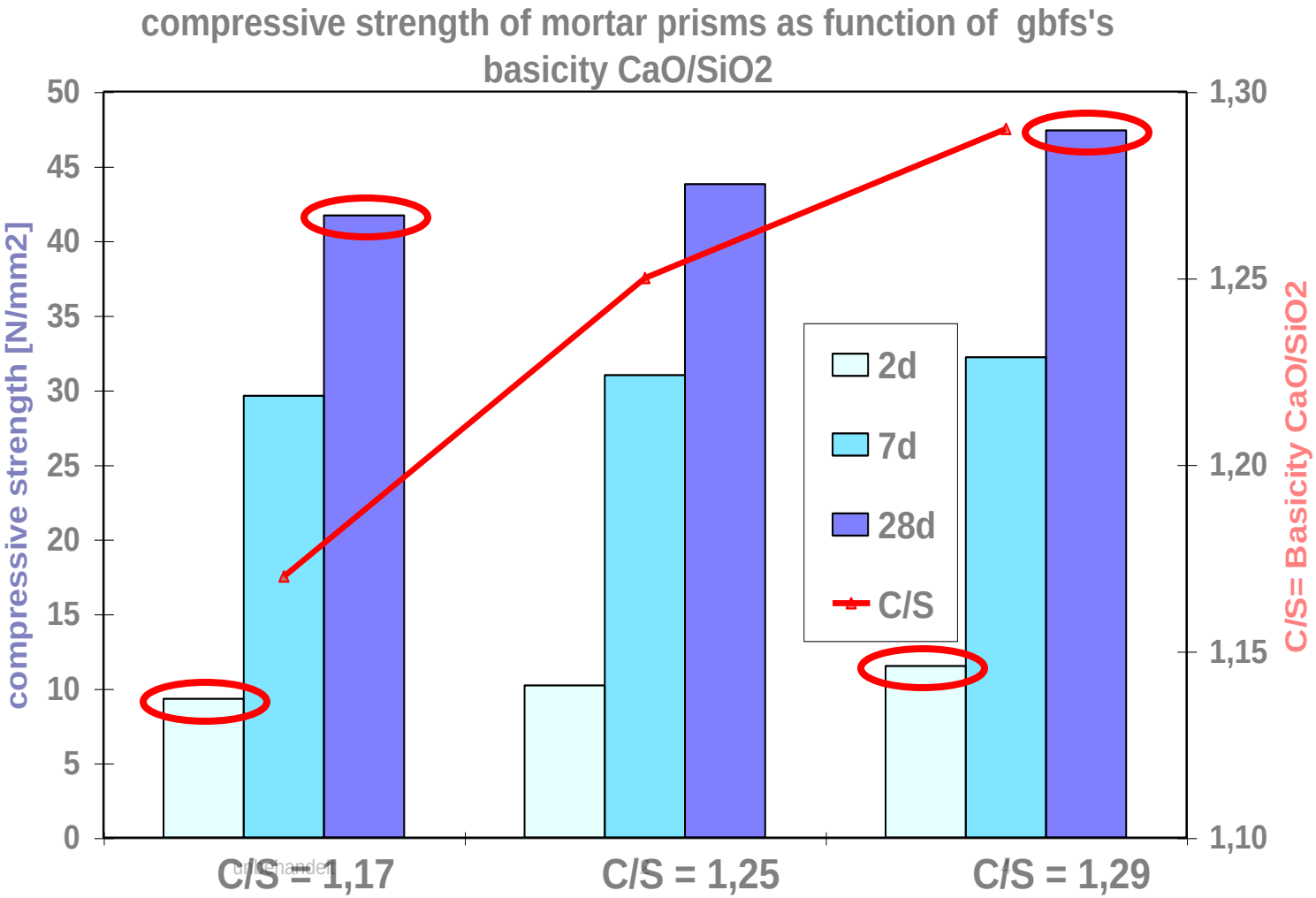
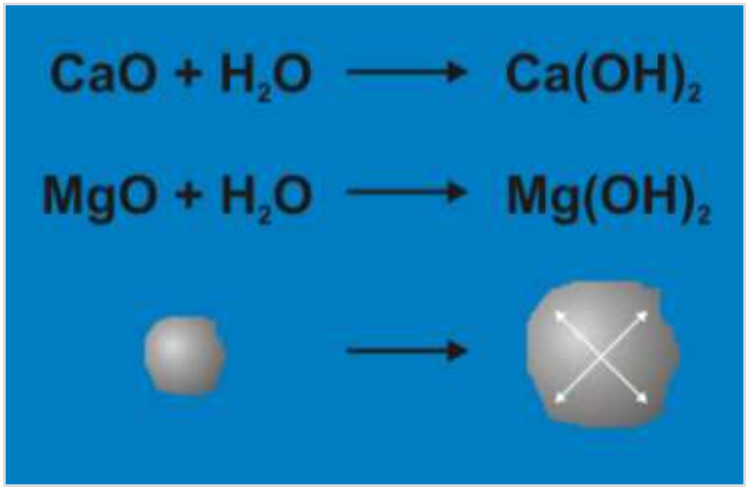


Increasing the quality of basic oxygen furnace slags for the use in road construction

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

BOF/EAF slag might have some free CaO (free lime) & free MgO (periclase). In the presence of humidity the hydration of both minerals causes 100 % increase in volume of the crystals.



The hydration is a serious problem in using steel slag as construction material !

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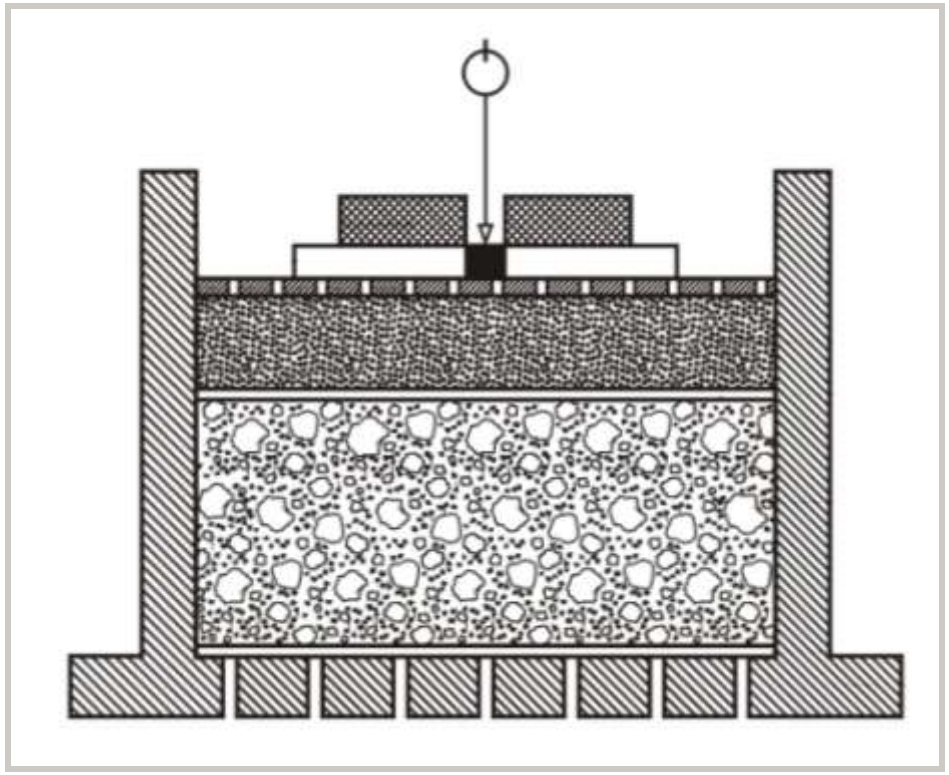

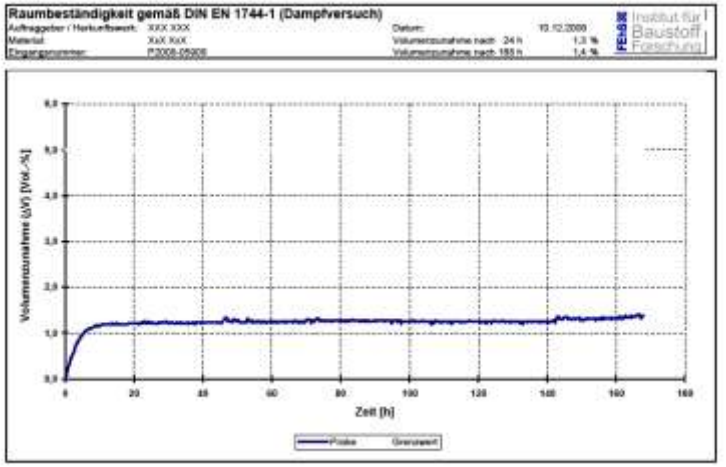

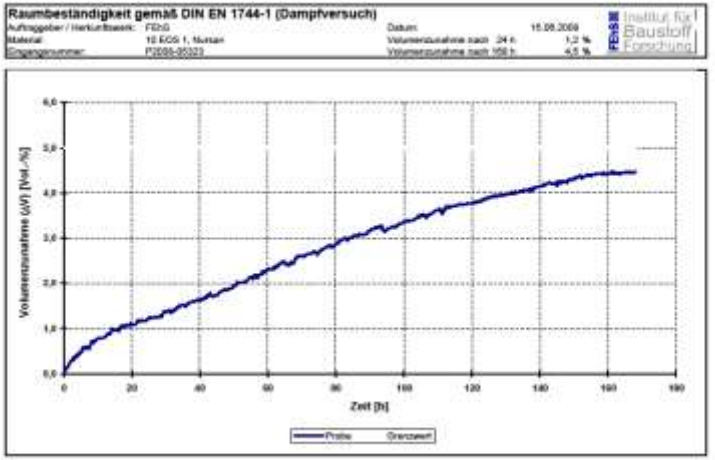

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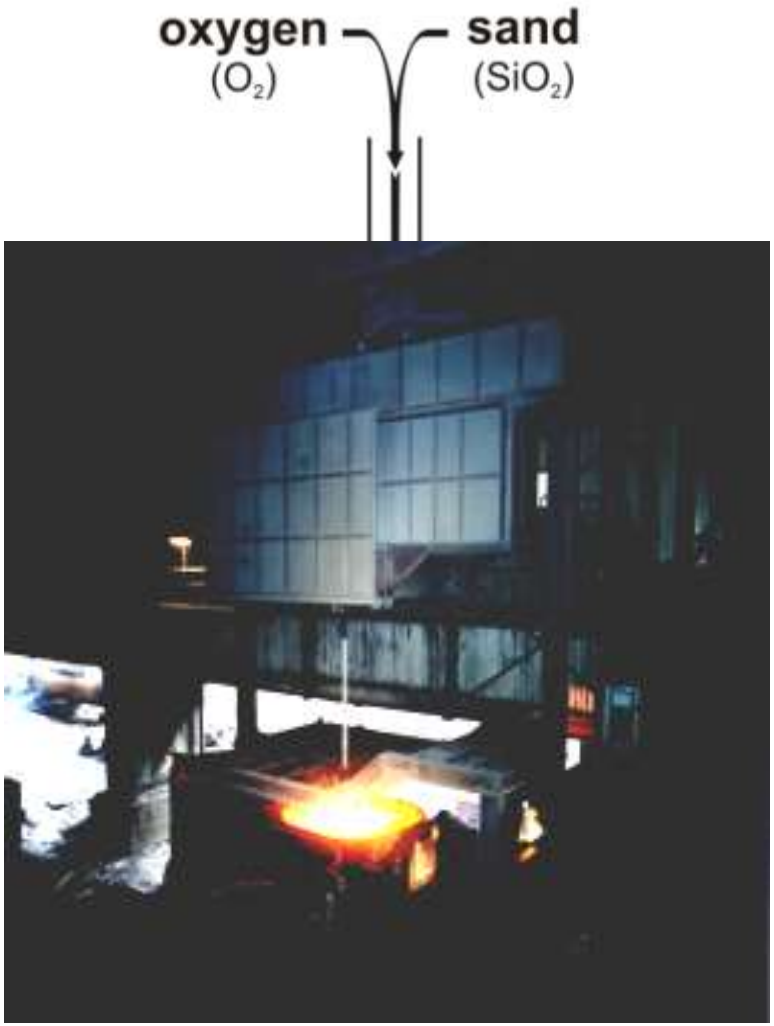


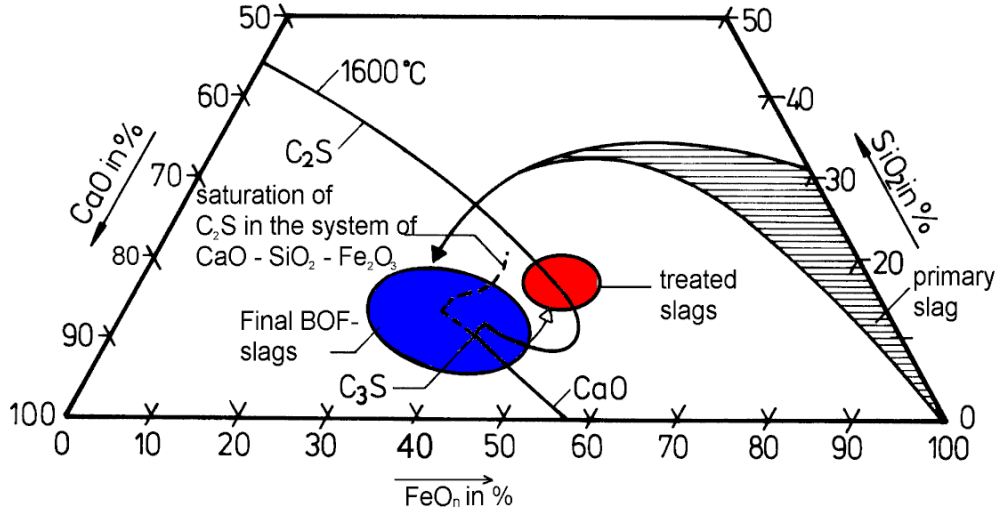
$O_2 + 2\ FeO \longrightarrow Fe_2O_3 + energy$

$2\ CaO_{free} + SiO_2 \longrightarrow 2\ CaOxSiO_2$

$2\ CaO_{free} + Fe_2O_3 \longrightarrow 2\ CaOxFe_2O_3$

by injection of sand and oxygen:

➔ **additional heat is generated**
- **to keep slag liquid**
- **to heat up and dissolve the sand**



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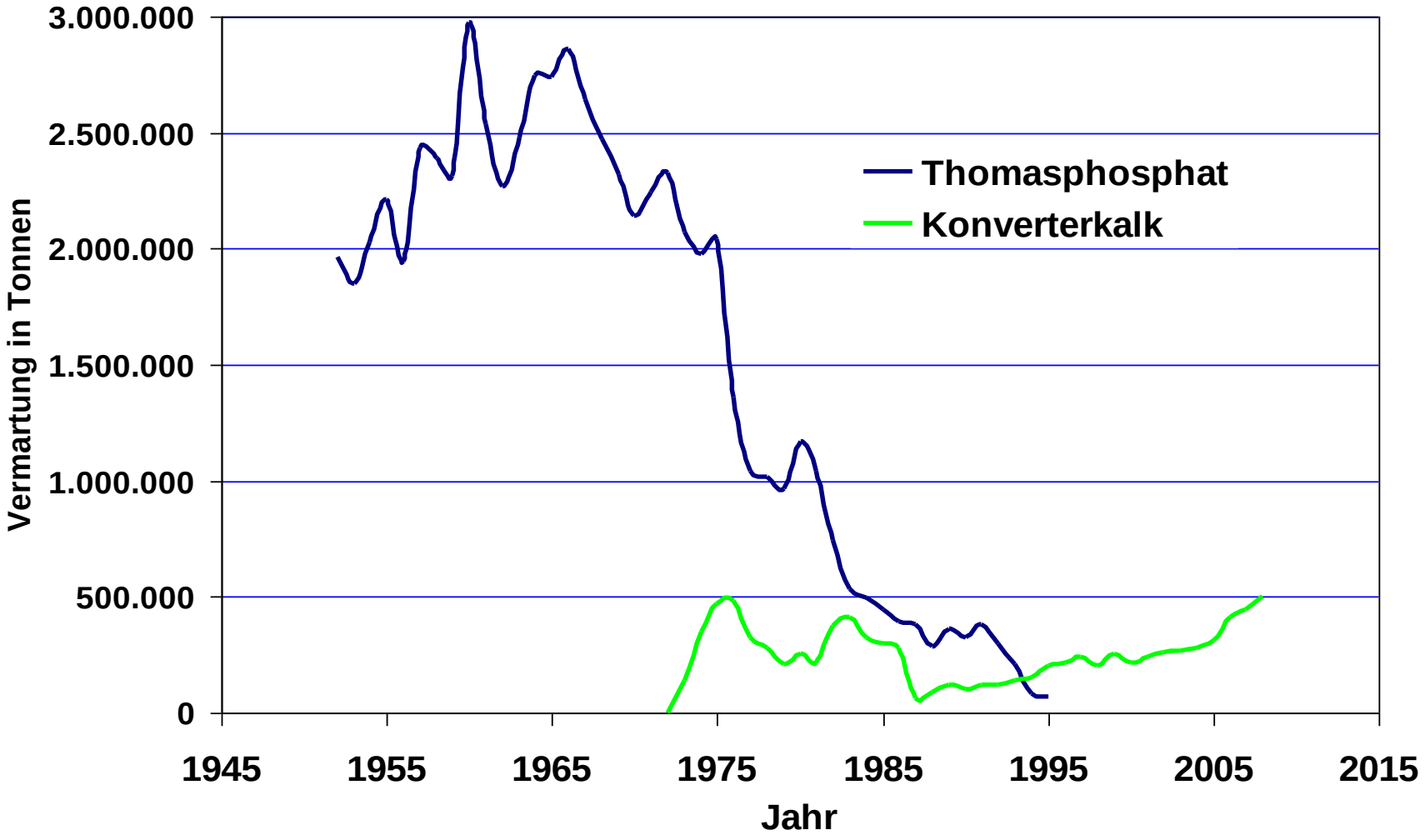
Increasing the quality of basic oxygen furnace slags for the use as fertiliser

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT



IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

Aim:

sewage sludge ash + BOFS → „Thomasphosphate 2nd Generation“

~ 20 % P_2O_5 ~ 1,5 % P_2O_5 ~ 10 % P_2O_5

with ~ 40 % ~ 95 % ~ 99 % available for plants

Whitlockite + Dicalciumsilicate → Calcium-Phosphate-Silicate

$$Ca_3(PO_4)_2 + 6\ Ca_2Si_{1-x}P_xO_4 \rightarrow Ca_{15}(PO_4)_2(SiO_4)_6$$

Approach:

dissolution of the ash in the liquid slag

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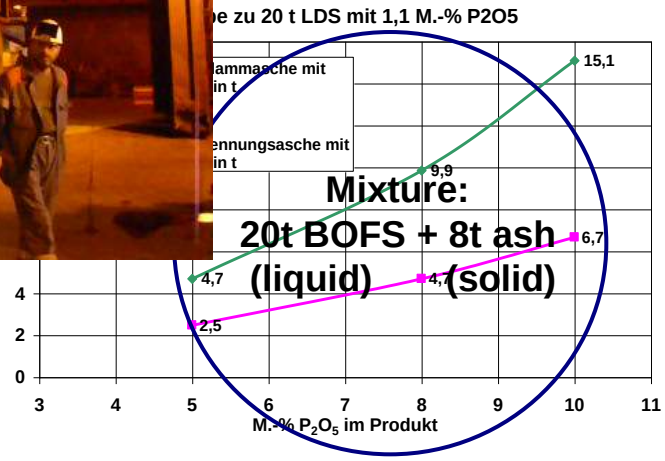

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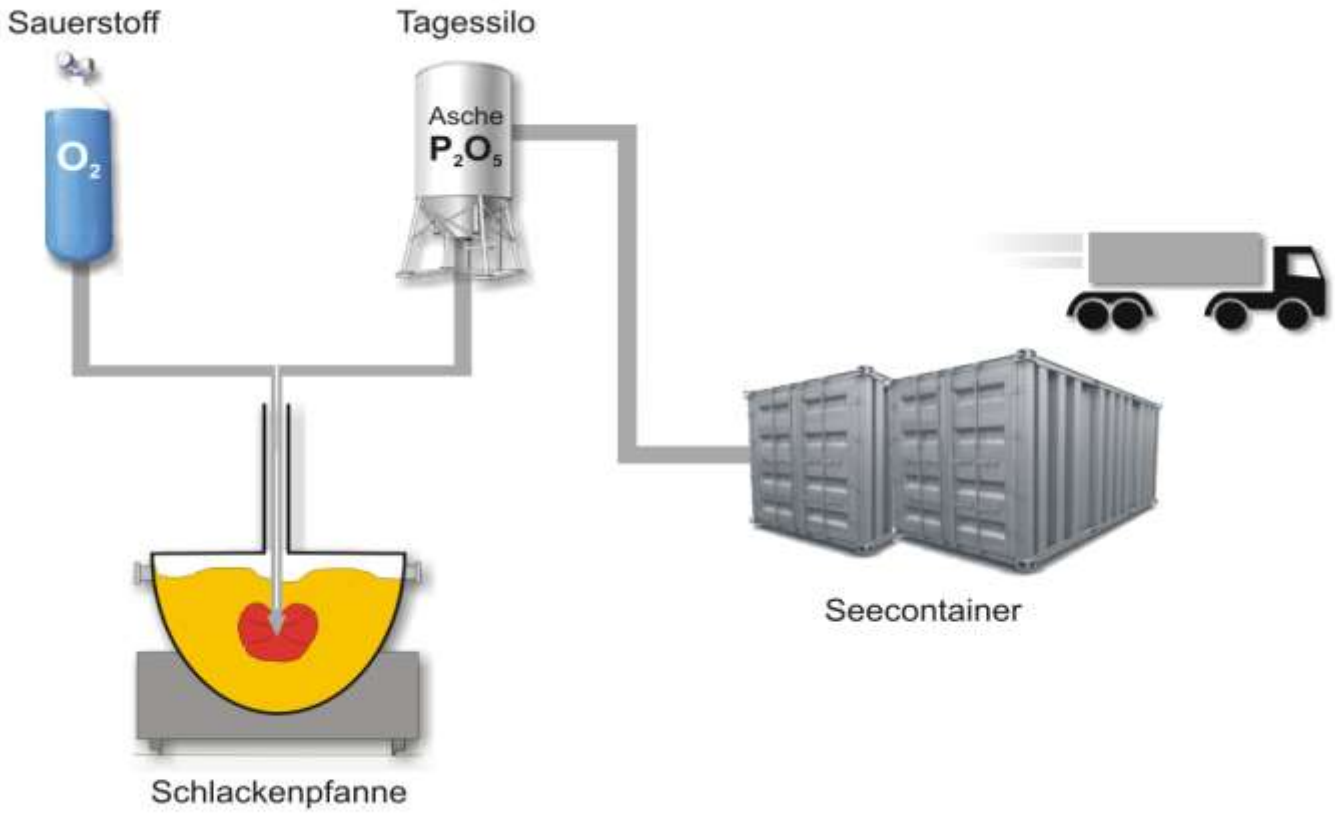


IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

Optimising the metallurgical work of electric furnace slags

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

Gehalt	42 - 52	1 - 3	2 - 3	2 - 4	1,5 - 0,5	32 - 42	1,2 - 0,5
Stahlzusammensetzung							
Stahlver-zehrung	Fe_2O_3	SiO_2	CaO	Cr_2O_3	NiO	ZnO	PbO
Gehalt roh	42 - 48	1 - 3	2 - 3	24 - 42	3 - 1,5	30 - 2	0,5 - 0,1

Recycling/Utilisation:

Scandust/Valera

Internal Recycling

Stope filling

Waelz kiln

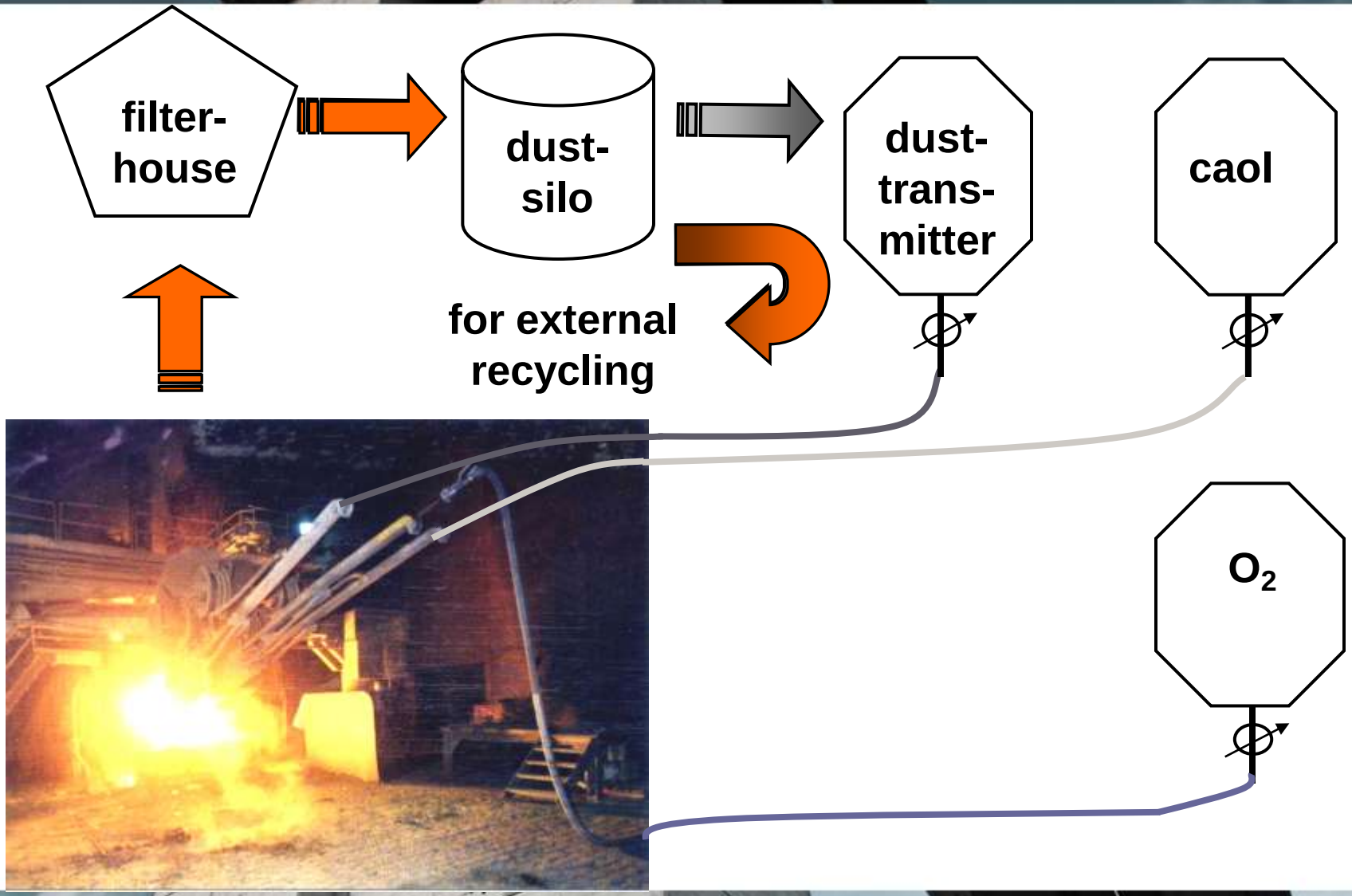
Steel

EAF-Slag

Waelz Oxide

Waelz Slag

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT



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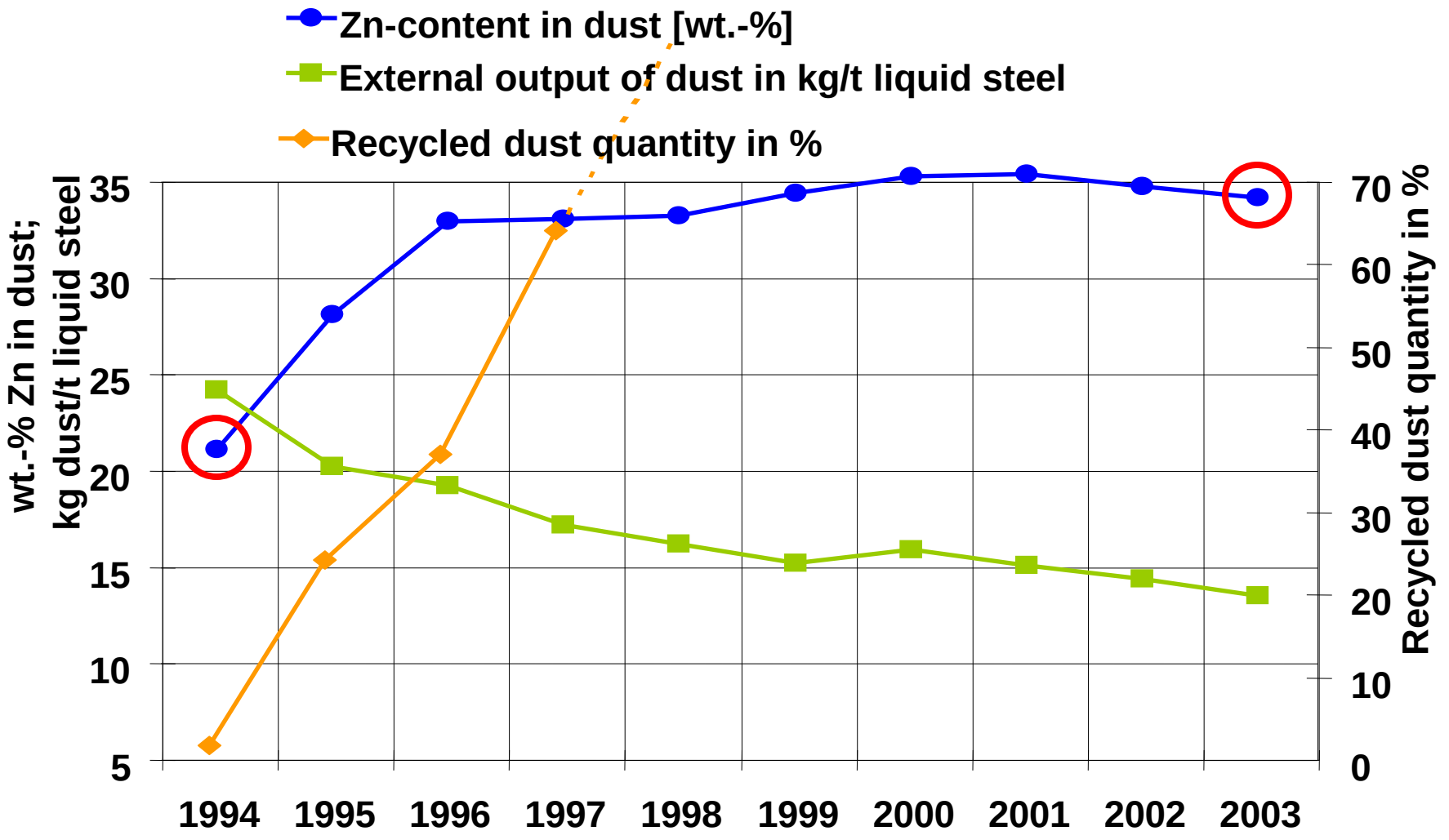

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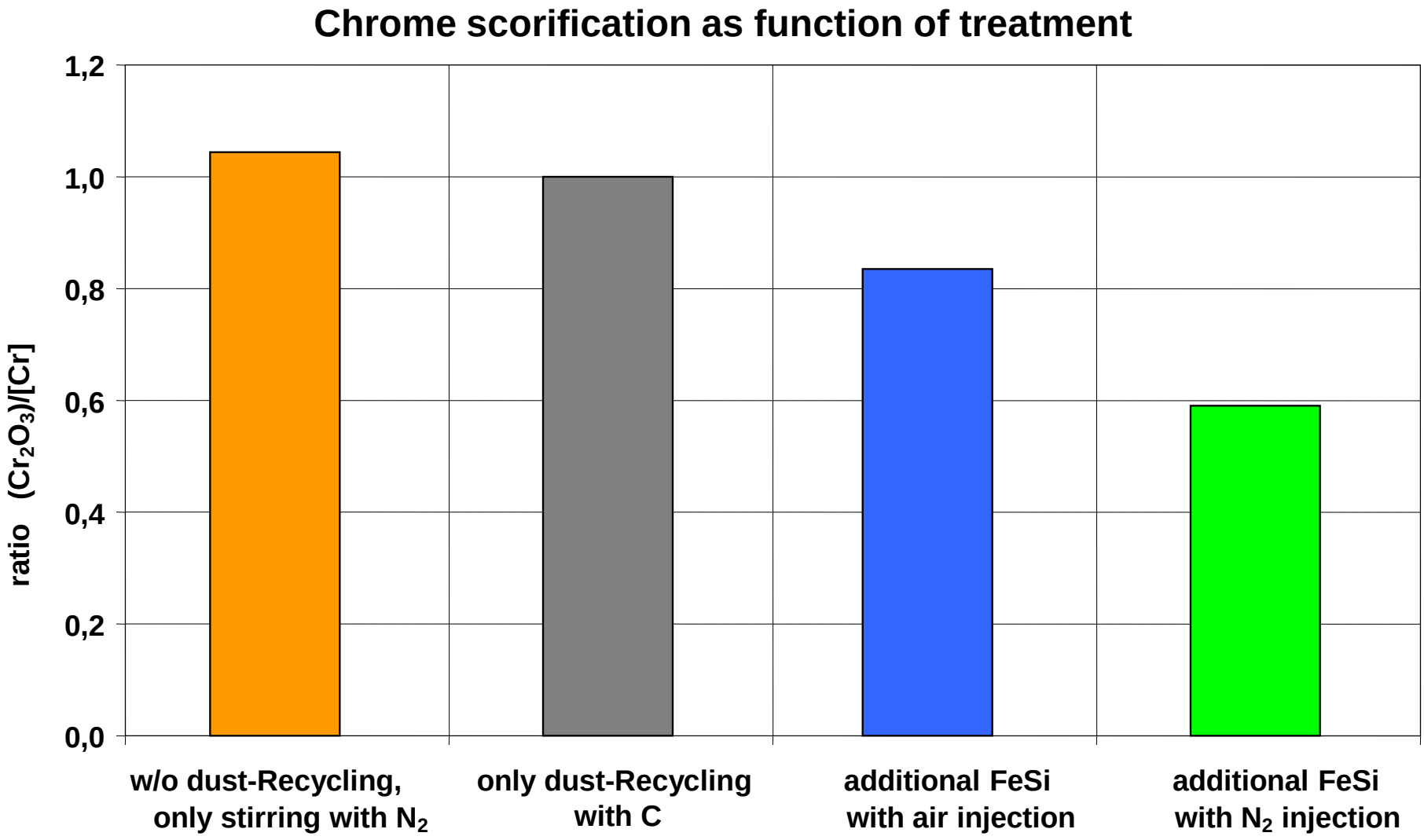
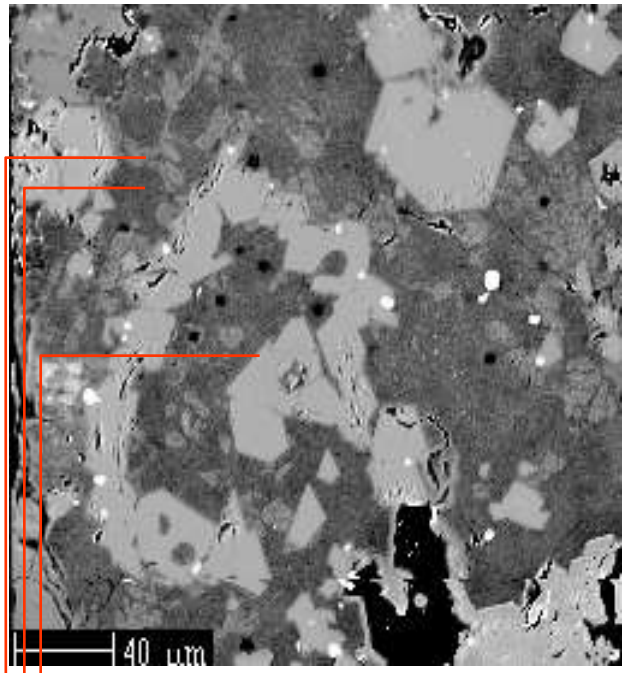


Increasing the quality of stainless steel slags

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT



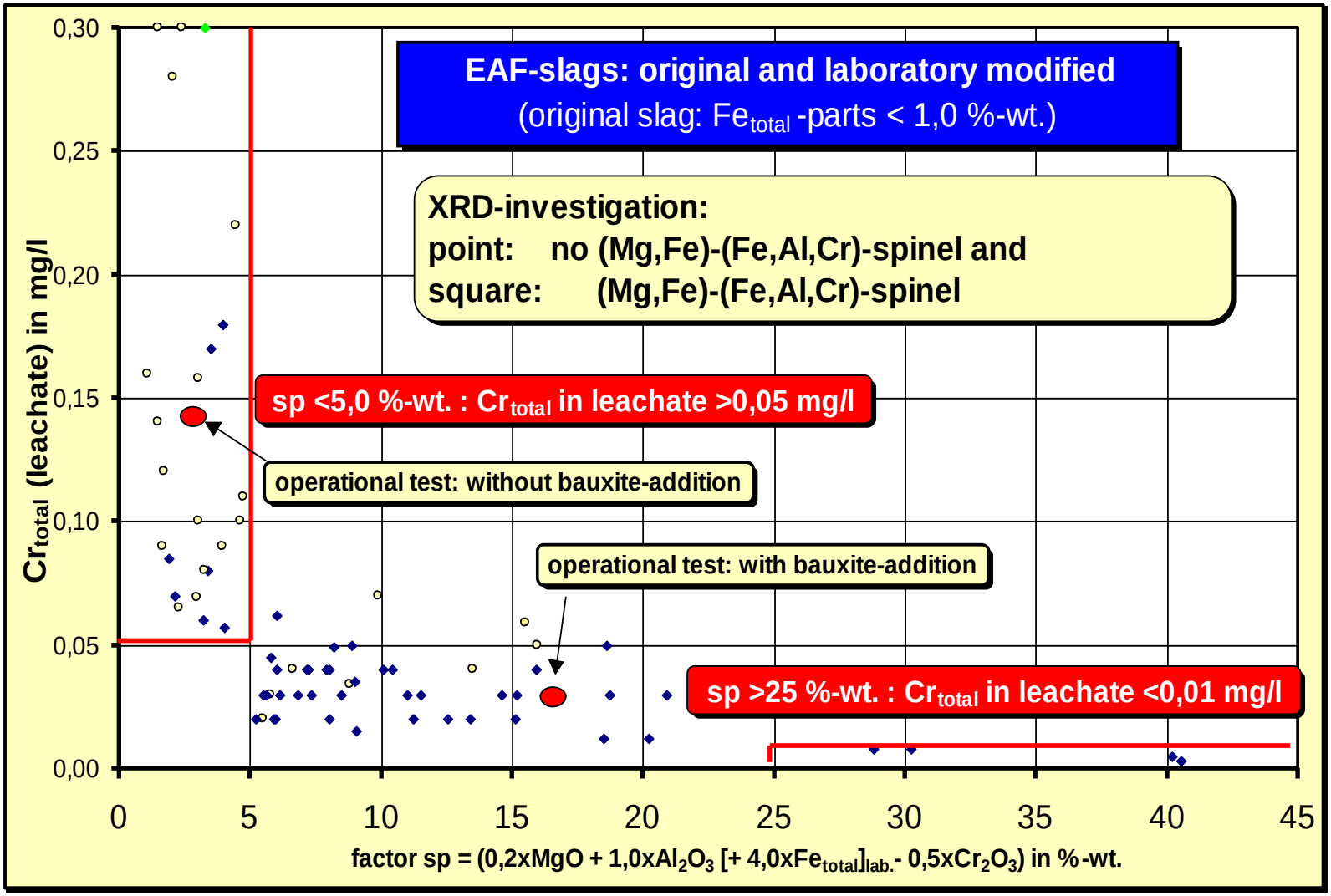
Compared to 19 wt.-% Cr_2O_3 in solid material, the leaching of 0.7 mg Cr/liter slag is surprisingly low.

95 % of the total Cr is fixed as chromite, a Spinel-type mineral. ($Me^{2+}Me_2^{3+}O_4$, with $Me^{2+} = Fe^{2+}, Mg^{2+}, Ni^{2+}$ and $Me^{3+} = Fe^{3+}, Al^{3+}, Cr^{3+}$) are known to be very stable under environmental conditions. Further progress is possible by stimulating the formation of spinels.

Mineral:	Idealisied Formula:	% of Mineral:	Electron Microprobe Analyses of Minerals [wt.-%]										
			SiO_2	Al_2O_3	CaO	MgO	Cr_2O_3	MnO	Fe_2O_3	NiO	MoO_2	P_2O_5	S
Melilithe	$Ca_2Al_2SiO_7$	20	33,3	14,1	37,9	2,2	0,1	10,9	0,1	0,03	0,00	0,10	0,53
Bredigite	$Ca_7MgSi_4O_8$	45	34,3	0,1	46,5	10,4	1,4	2,4	2,5	0,01	0,01	0,08	0,02

Factor SP = 0.2 MgO + 1.0 Al_2O_3 + n Fe_{total} + 0.5 Cr_2O_3

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT



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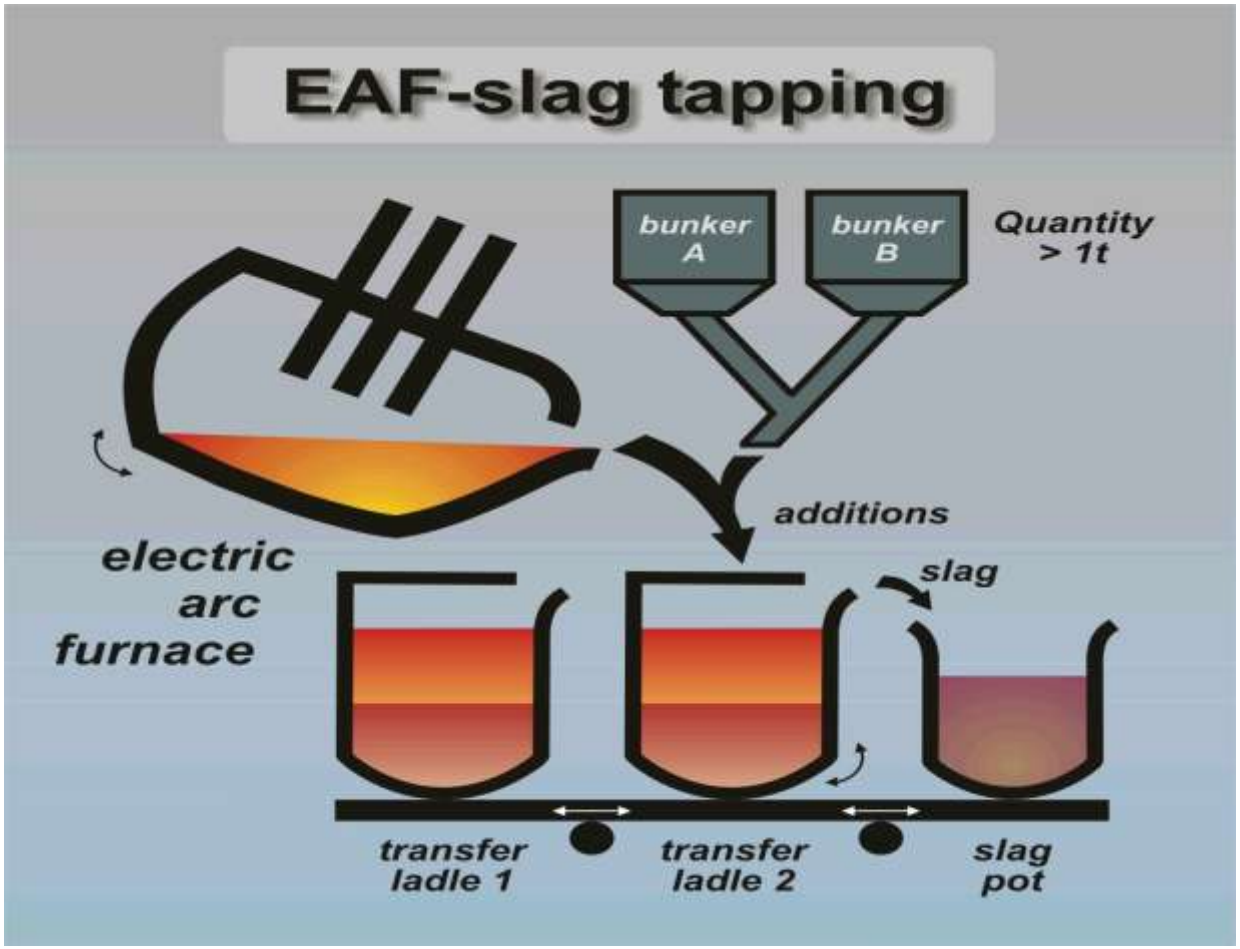
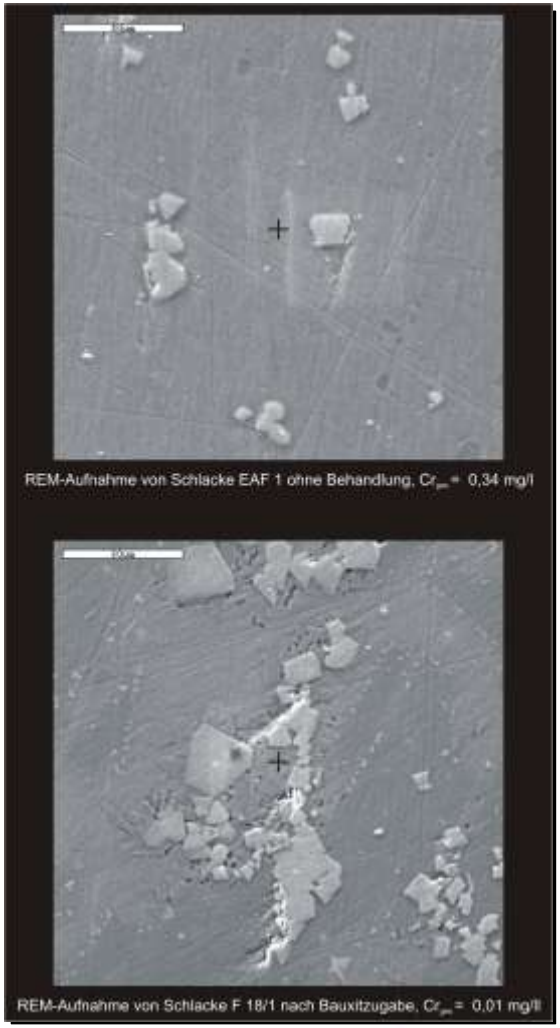


Operational tests



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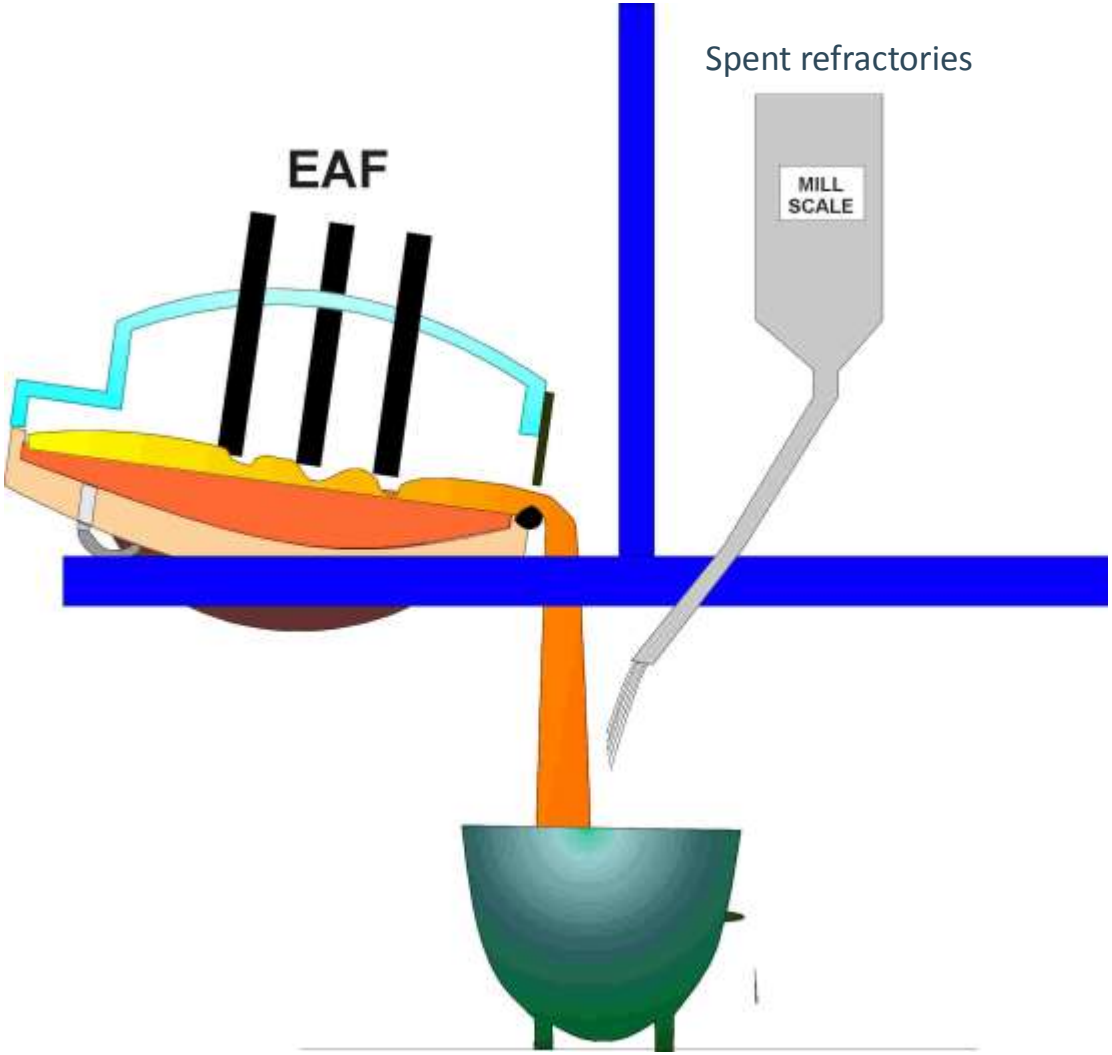


Increasing the quality and optimising the recycling of secondary metallurgy slags

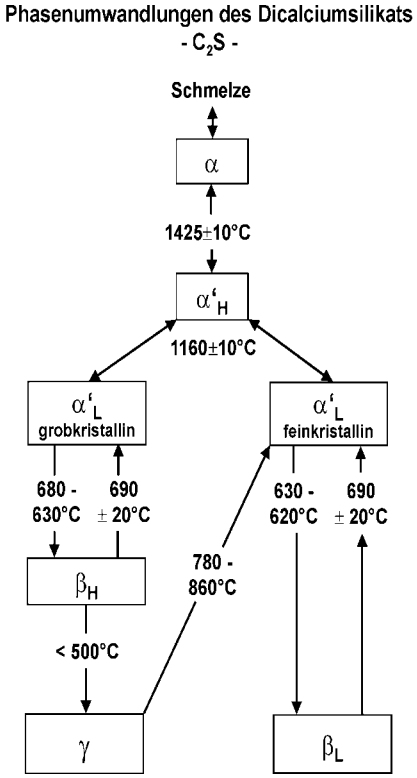
IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

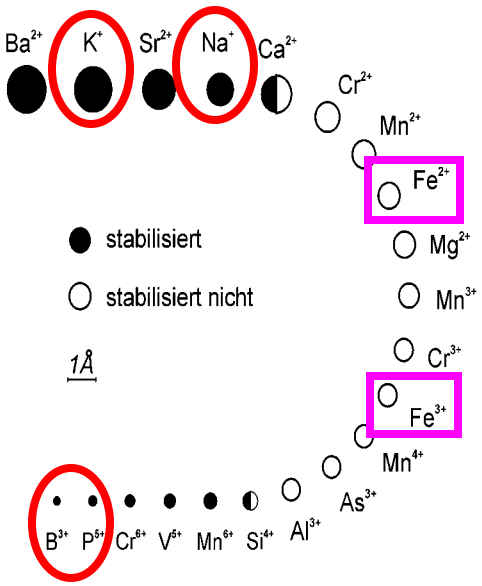
During solidification of secondary steelmaking slag some dicalciumsilicate (C_2S) is built, mostly. By further cooling C_2S transforms from β - to γ - modification. The transformation is accompanied by an increase in volume of 11 % of the crystals. The increase in volume destroys the structure of slag.

The transformation causes several problems:

- ⊗ **formation of dust,**
- ⊗ **fine grained materials are hardly used in civil engineering,**
- ⊗ **progressive leaching according to the high specific surface area.**

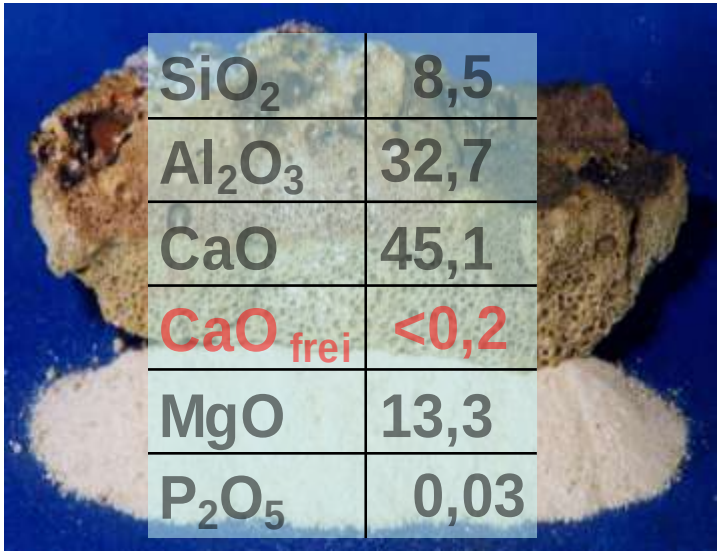
IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT





IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT

- **Solution 1 : rapid cooling of the slag**



cooling-rate (K/min)	amorphous	Periclase (MgO)	beta-C2S (Ca_2SiO_4)	gamma-C2S (Ca_2SiO_4)	Mayenite ($Ca_{12}Al_{14}O_{33}$)
> 1 - 5	X	X	X		X
porous	*	X	X		X
< 1		X	X	X	X

- **Solution 2: Addition of stabilising elements to the liquid slag**

The transformation of C_2S is suppressed by distinct elements like P and B. For example in BOF slag the transformation is suppressed by the already available P_2O_5 (1.3 - 2.1 %). B is more efficient as ≈ 0.5 % B ensures stabilisation of LF-slag.

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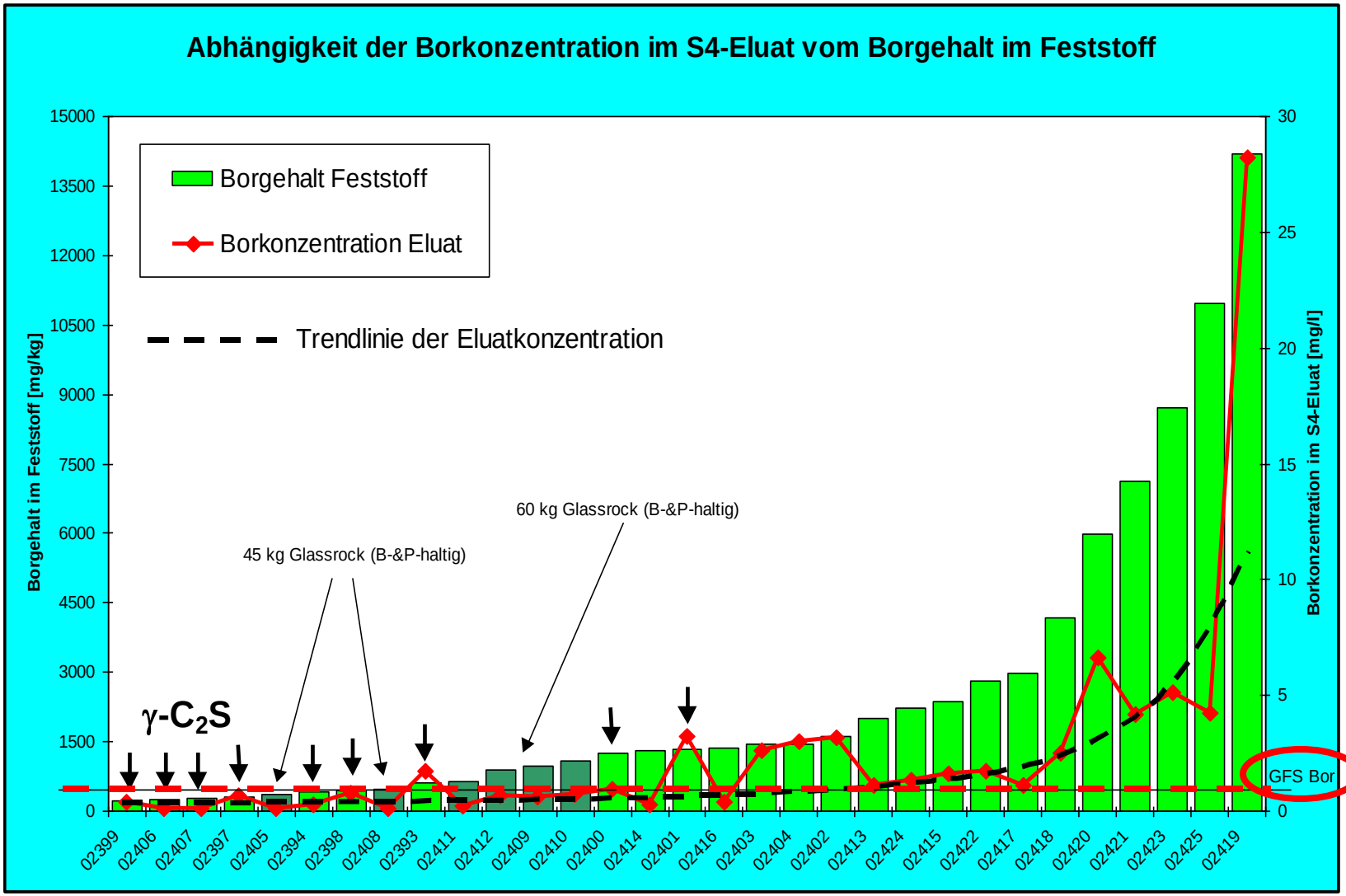

Conclusion

IMPROVED SLAG QUALITIES BY LIQUID SLAG TREATMENT