SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

LULEÅ UNIVERSITY OF TECHNOLOGY

KATHOLIEKE UNIVERSITEIT LEUVEN

Hot stage slag engineering as a method to improve slag valorisation options

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centre

SMART-PRO²

Use of iron- and steelmaking slag in Europe and Sweden

Sweden

2008: 1.3 million tonnes slag

External use: ~ 35 %

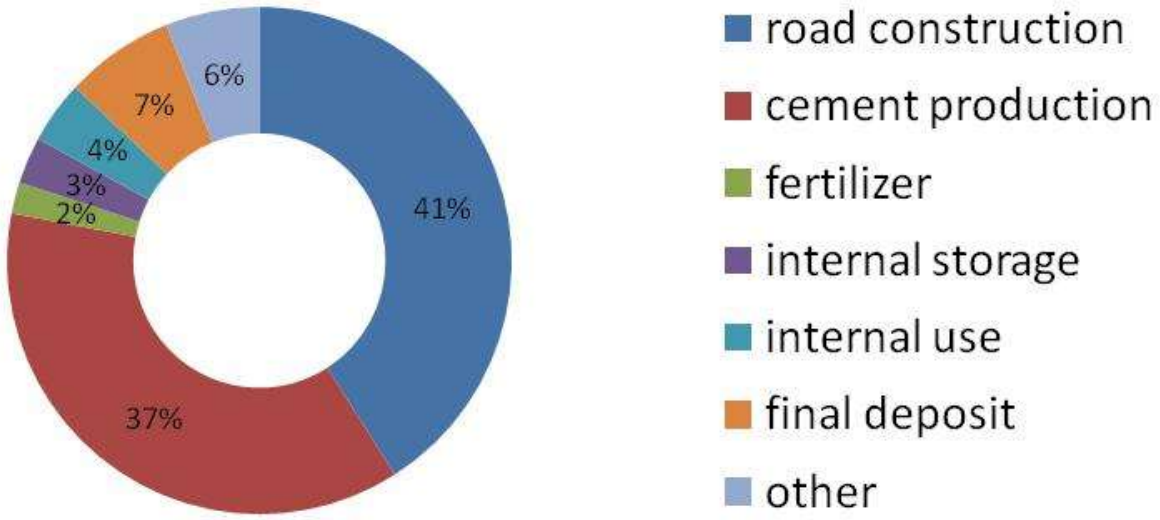
Landfilling: ~ 20 %

Europe

2006: ~ 45 million tonnes slag

External use: ~ 80 %

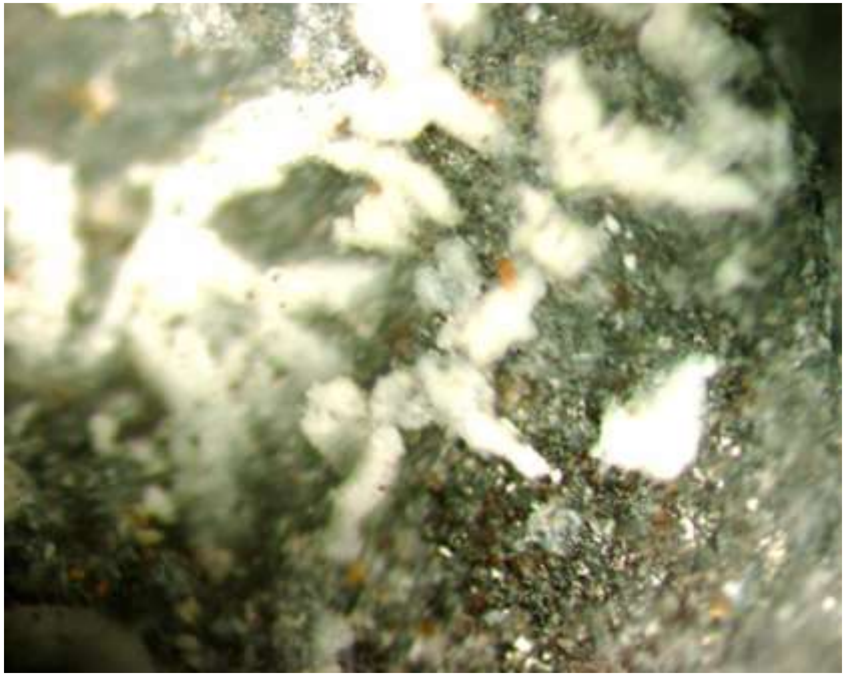
Europe



Obstacles

for use in external applications

- **Leaching of metals**
- **Volume expansion**
- **Disintegration**
- **Low volumes at each site**



Reasons for low utilisation of steelmaking slag in Sweden

- Good access to high quality natural stone material
- High availability of land for land filling
- No criteria for use of slag in construction applications but materials compared with requirements for inert materials

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- 35 million tonne virgin material used in construction annually
- Focus from steel industry has been on use in road construction

Obstacles

for use in external applications

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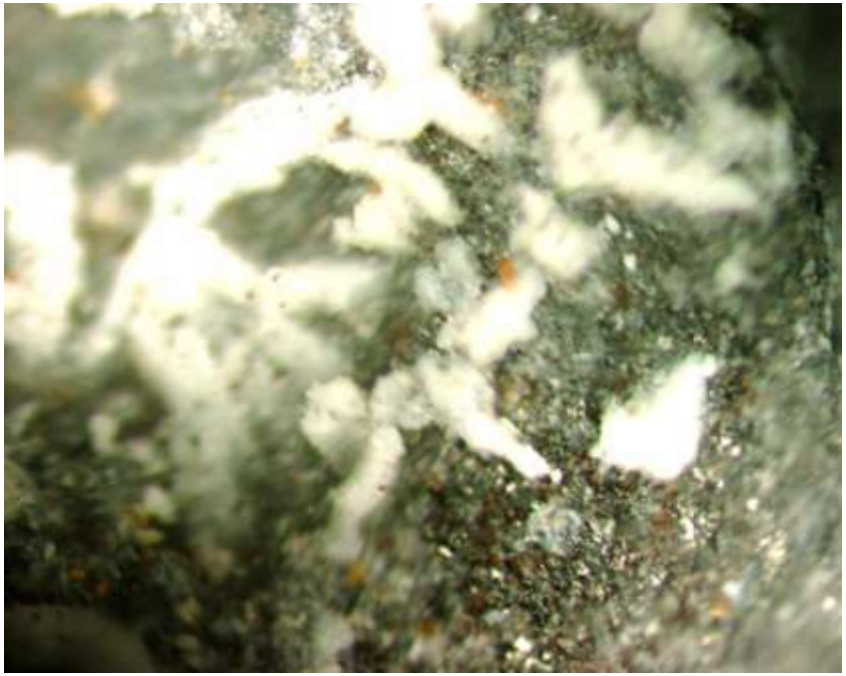

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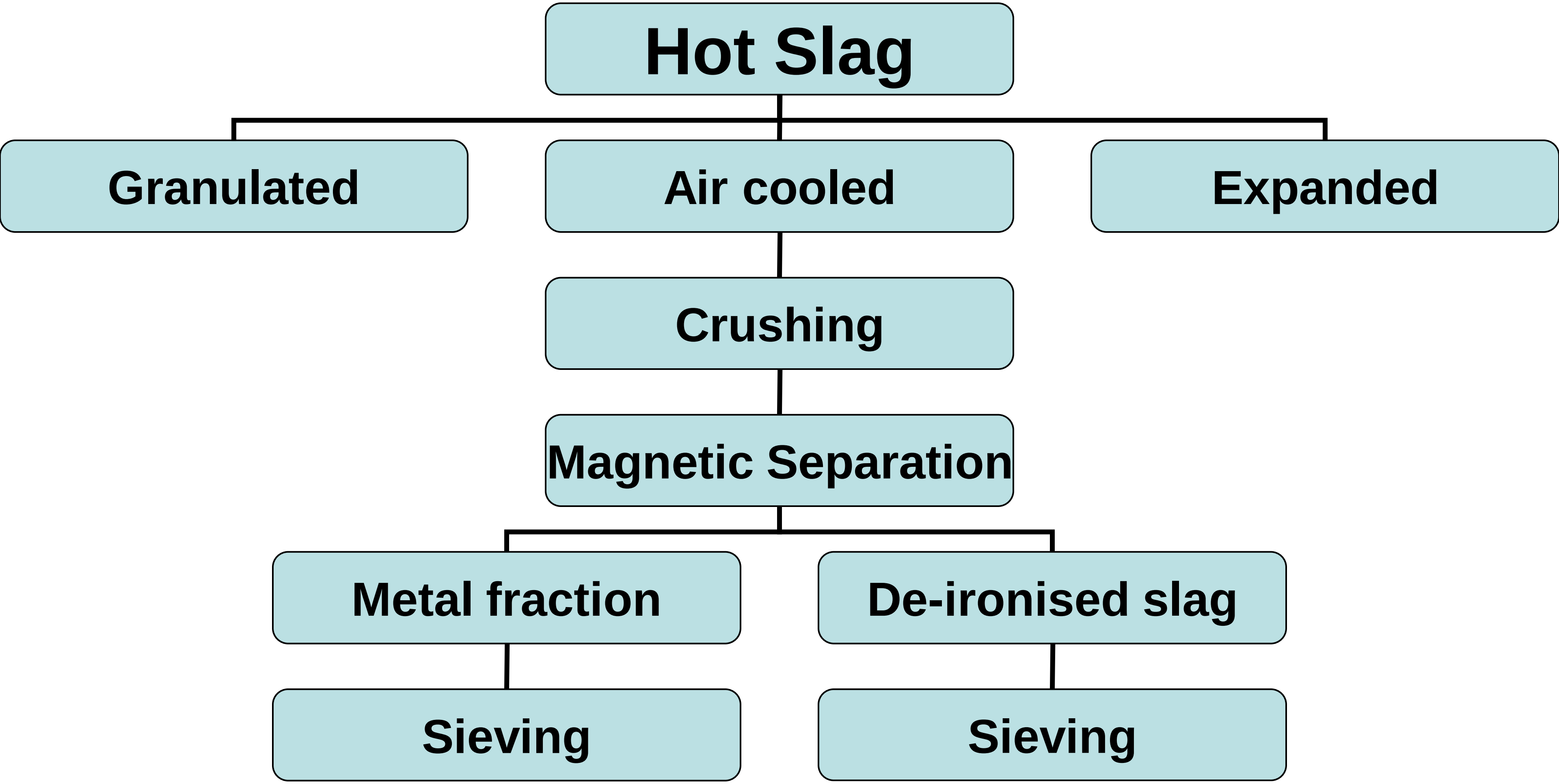
Todays slag practice



Hot stage slag engineering

Additions in the metallurgical process

Additions during tapping

Cooling path

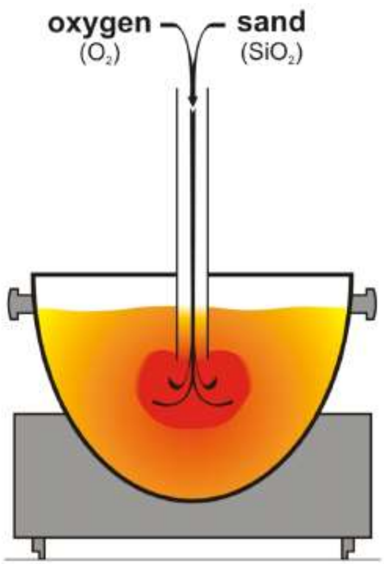
Slag engineered for the product demand

Limited by product demand

Limited by availlable heat and mixing conditions

Ways to eliminate free CaO and MgO

- **Ageing in natural conditions during longer time**
- **Forced ageing through steam treatment**
- **Additions that react with CaO and/or MgO, e.g. additions of silica, waste glass etc.**



$O_2 + 2\,FeO \longrightarrow Fe_2O_3 + \text{energy}$

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

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

by injection of sand and oxygen:

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

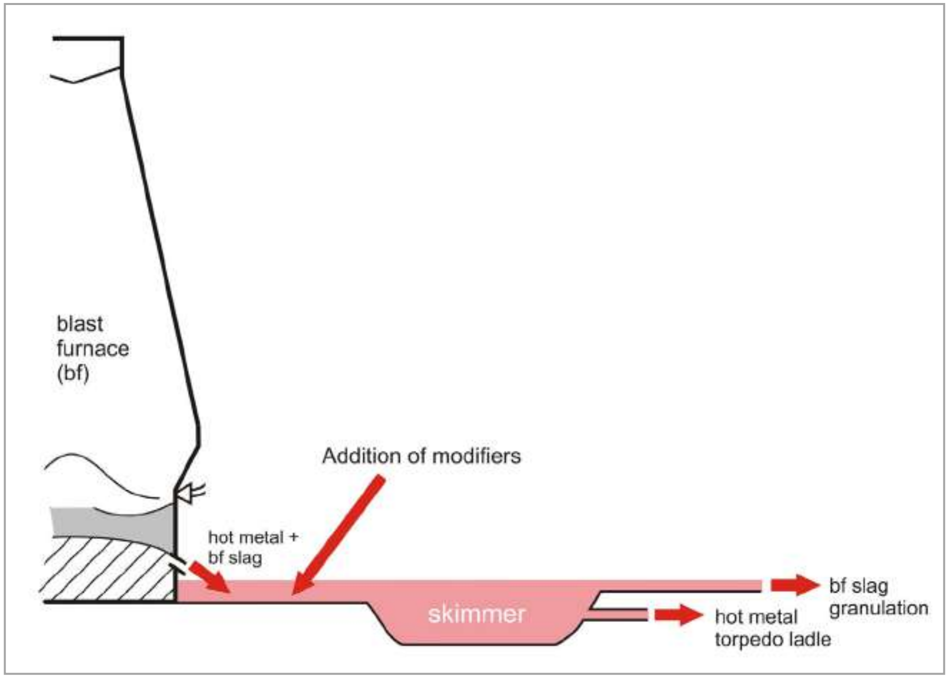
→ CaO/SiO_2 is reduced

→ free lime is dissolved and chemically bound

Kuehn et al and Drissen et al

Modification of Blast Furnace Slag

To increase the hydraulic properties of GGBS lime was injected into the main runner. Increase of basicity from 1.1 to 1.4 gave 25% increase in compressive strength of mortar prisms. (Drissen and Mudersbach)

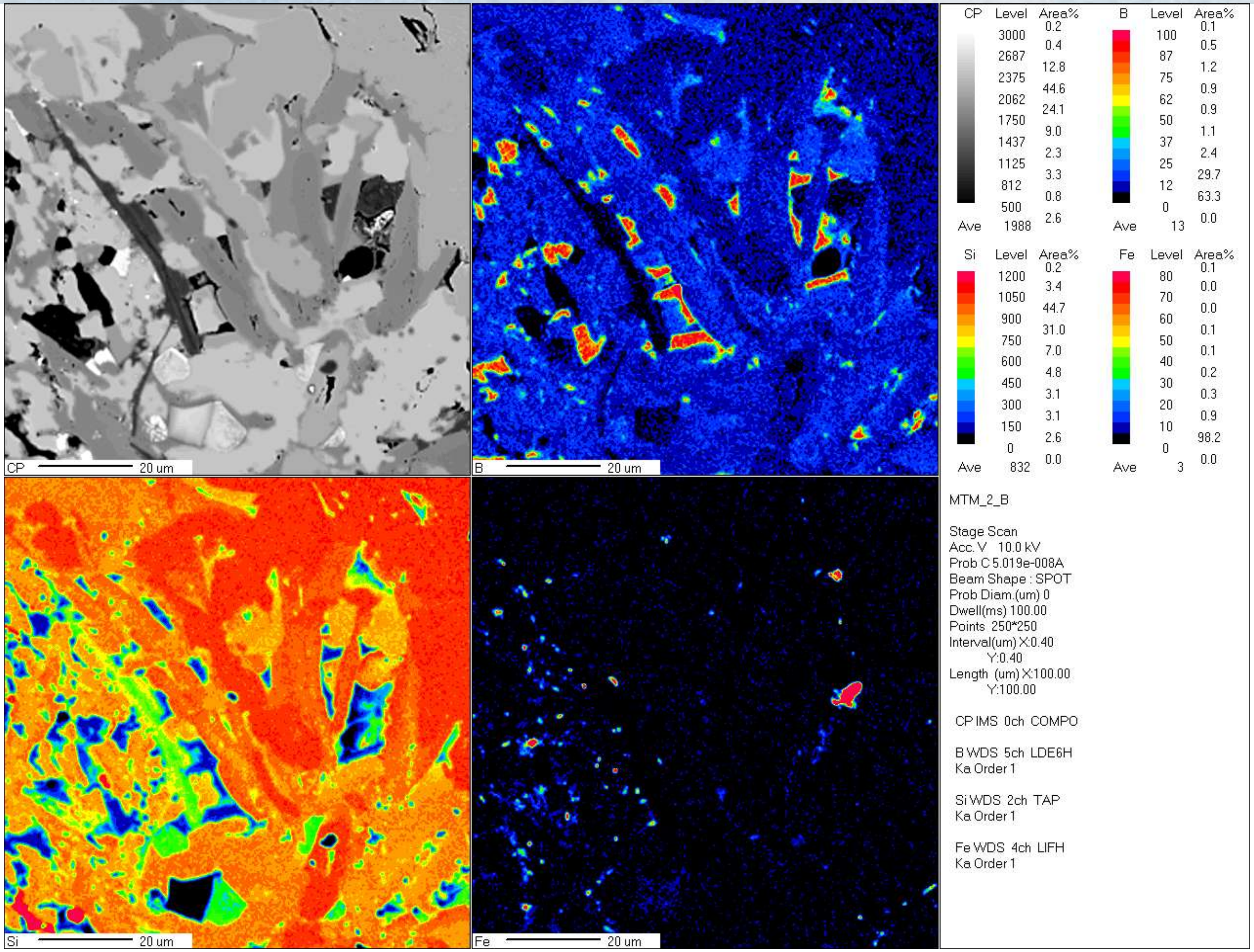


Ways to eliminate disintegration due to β to γ transformation in C2S

Additions to slag in hot stage

- Borates, 1-2 % as B_2O_3, Considerable distribution between phases present in the slag, studied by Durinck and Geysen et al
- The α and α´ polymorphs have been reported to be stabilised by MgO, Al_2O_3, Fe_2O_3, BaO, K_2O, P_2O_5 and Cr_2O_3. The β polymorph by the addition of Na_2O, K_2O, BaO, MnO_2, Cr_2O_3. (Ghosh et al)
- Phosphates, 2% for an industrial slag, 0,3% at lab scale, needed to stabilize α and β C2S according to Yang et al
- Addition of silica (Sakamoto and Yang et al)
- Addition of non-ferrous fayalite slag (Kitamura et al)
- Quick cooling (Yang et al, Kriskova et al, Gautier et al)

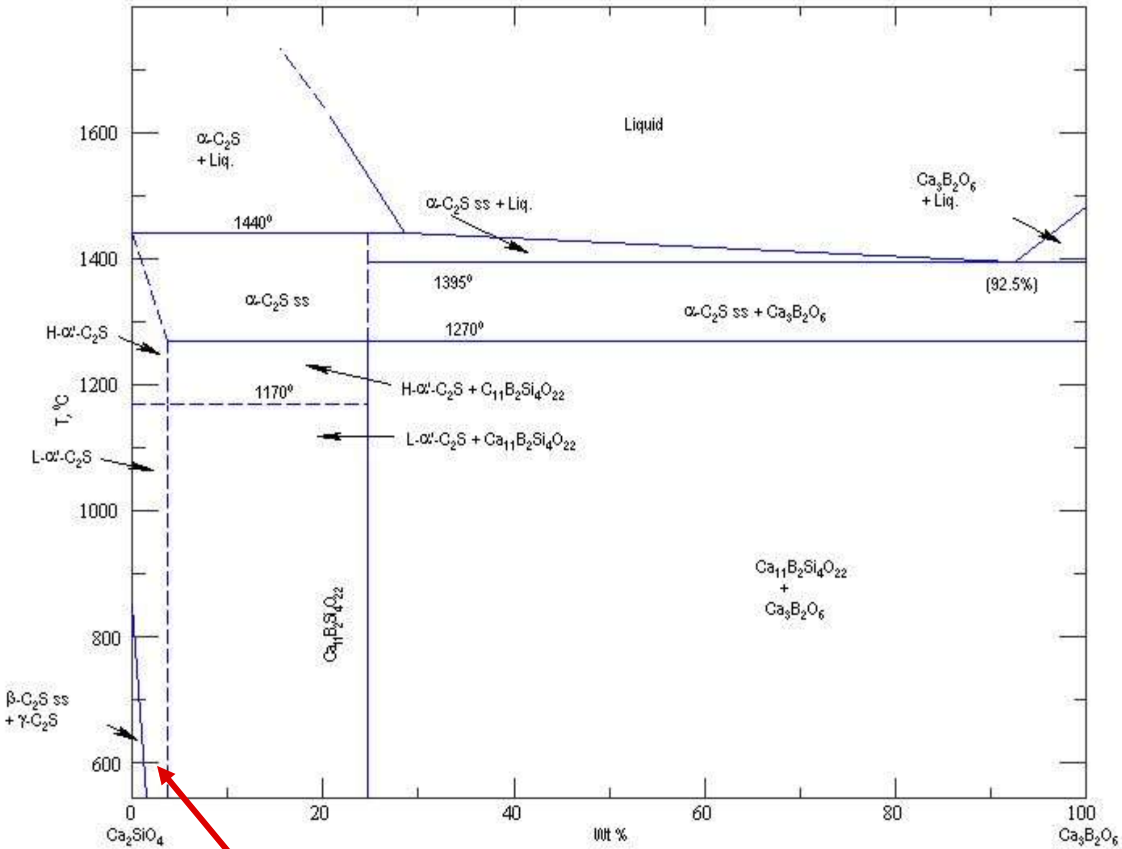
Elemental mapping for B, Si and Fe of an industrial slag sample, performed with a FEG-EPMA. Adapted from Geysen et al.



Phase identification and B_2O_3 content of an industrial slag sample. From Geysen et al

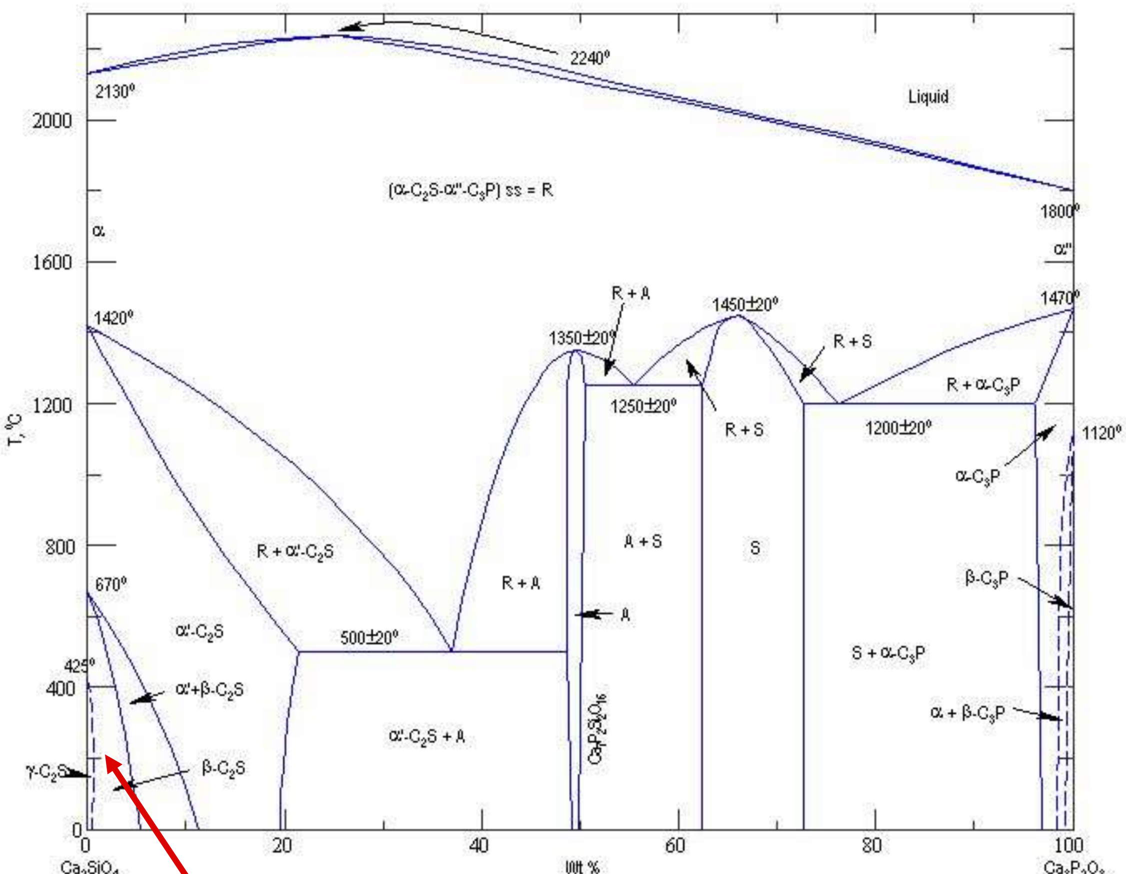
Number	Phase	Total B_2O_3 wt%	Sample	Phase	Total B_2O_3 wt%
1	Merwinite	0.37	6	Spinel	< 0.1
2	$Ca_{11}Si_4B_2O_{22}$	5.2	7	Cuspidine	1.83
3	$Ca_xS_yB_zMg_sO_t$	17.0	8	Cuspidine	1.45
4	MgO	0.35	9	$Ca_xTi_ySi_ZMg_sO_t$	0.44
5	Merwinite	0.31			

System Ca_2SiO_4 – $Ca_2B_2O_6$



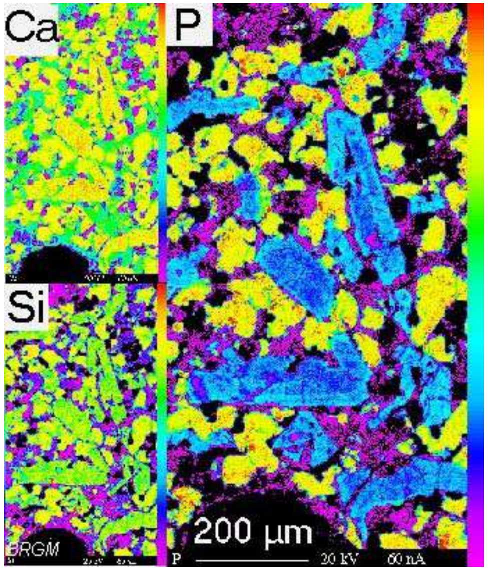
~ 1 wt% $Ca_3B_2O_6$ ↔ 0,6 wt% B_2O_3

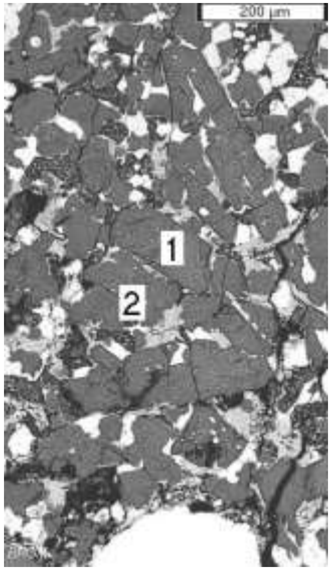
System Ca_2SiO_4 – $Ca_3P_2O_8$

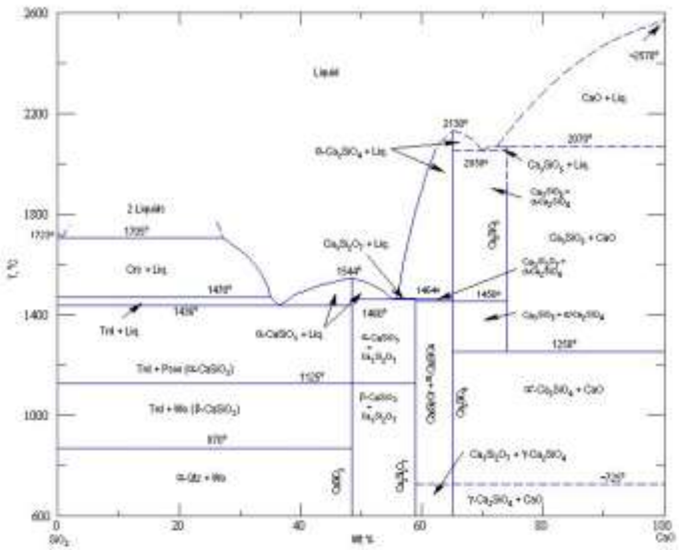


~ 0,5 wt% $Ca_3P_2O_8$ ↔ 0,2 wt% P_2O_5

Phosphorus distribution in BOS slag





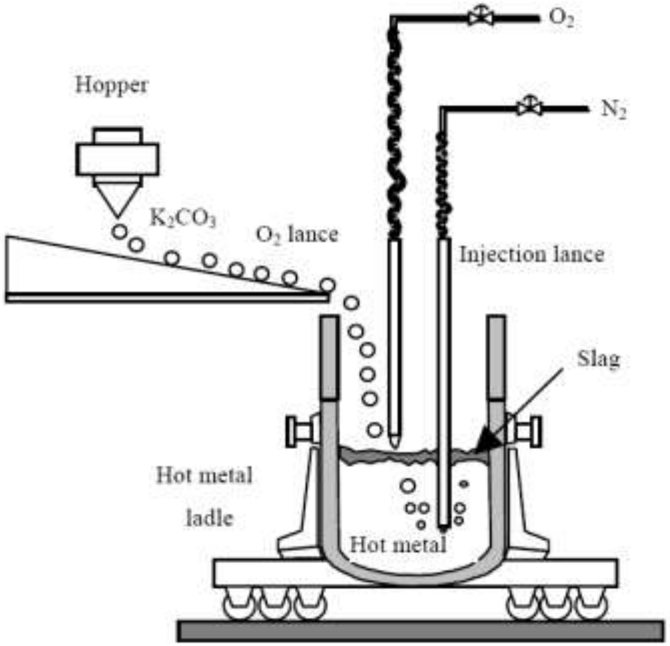


P content in calcium silicates in BOF slag according to Bodénan et al

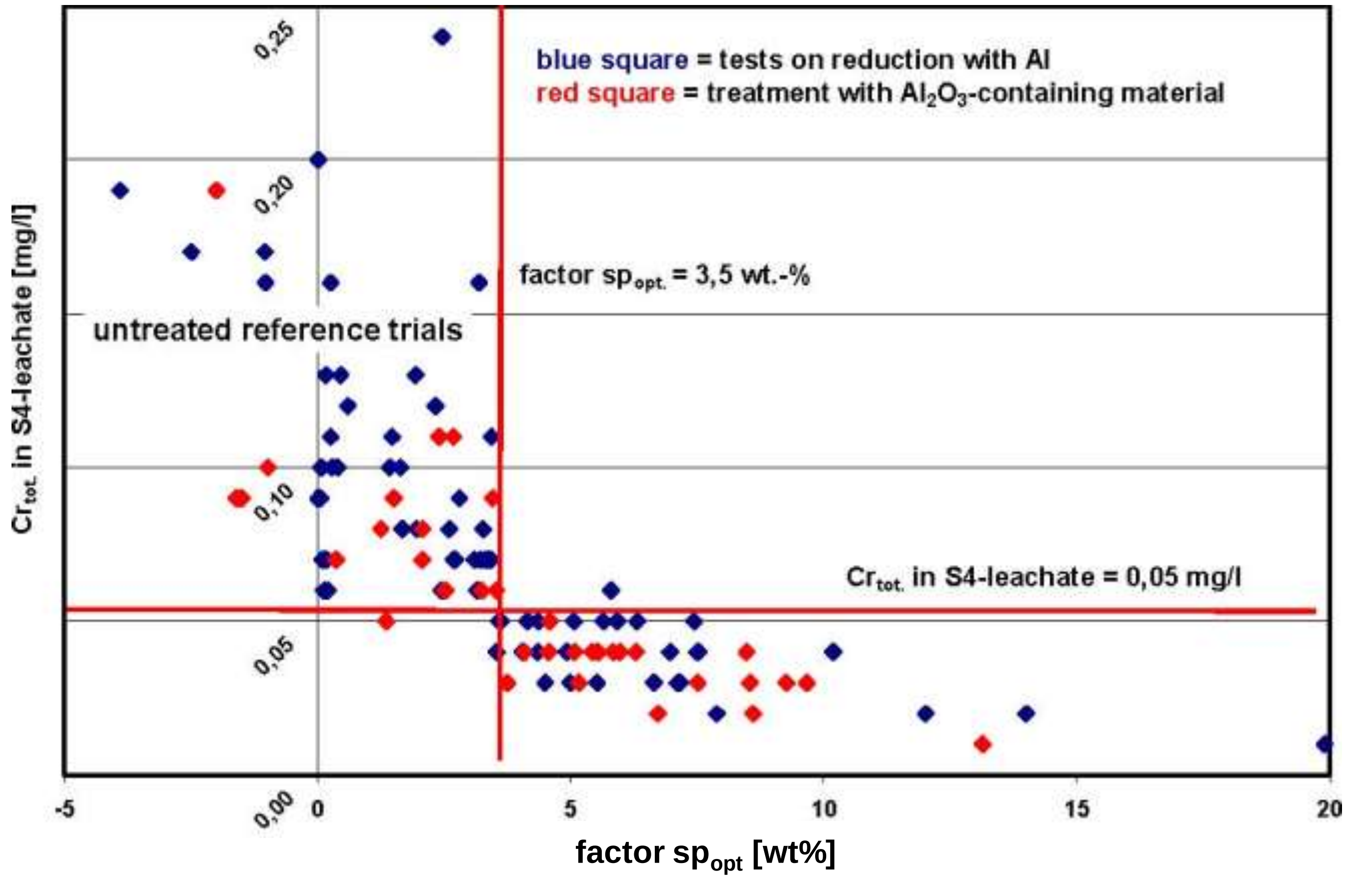
% P_2O_5	Rapid cooling	'Industrial' cooling (quantity)	Slow cooling (quantity)
Ca_2SiO_4 (P+)	4.5	8.0 (+)	5.3 (++)
Decomposed Ca_3SiO_5 (P-)		2.9 (++)	2.4 (+)

Fused K-P-silicate fertilizer

Combined De-Si, De-P of hot metal and addition of Potassium Carbonate, to produce a fused K-P-silicate fertilizer at NKK according to Takahashi et al



Leaching of chrome in terms of factor SP for pilot tests in an EAF when adding Al or Al_2O_3, from Drissen et al



factor SP = 0.2 x MgO + 1.0 x Al_2O_3 + n x Fe_{total} - 0.5 x Cr_2O_3

Al injection practised at BGH Edelstahl Siegen (Stubbe et al)

Ageing investigation (Engström)

Materials included in the investigation

EAF 1 – EAF slag, low alloyed

EAF 2 – EAF slag, stainless steel

EAF 3 - EAF slag, high alloyed

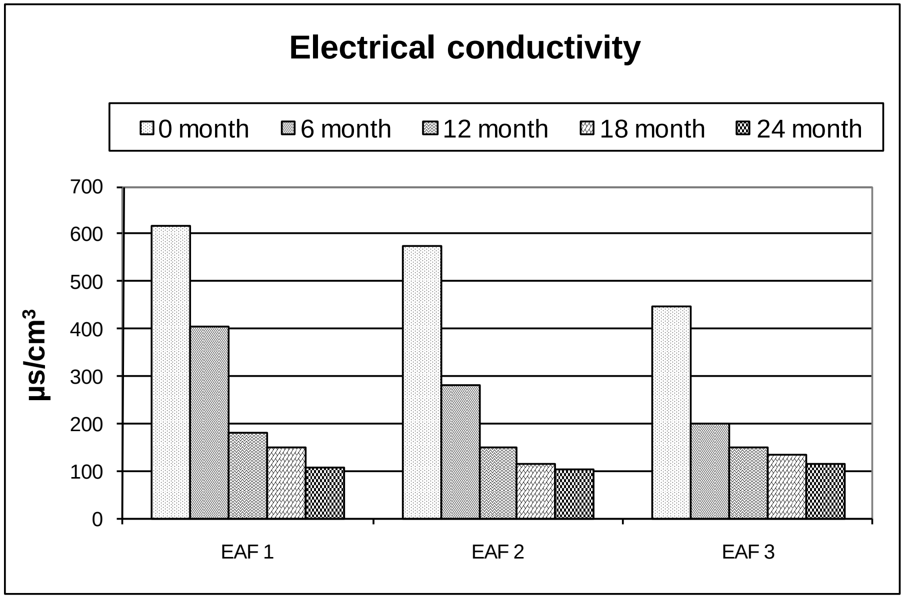
Slag	CaO	SiO2	MgO	Al_2O_3	Cr_2O_3
EAF 1	28.8	14.2	8.5	4.9	2.0
EAF 2	41.0	28.4	4.7	10.1	5.7
EAF 3	26.4	31.0	18.1	9.4	7.0

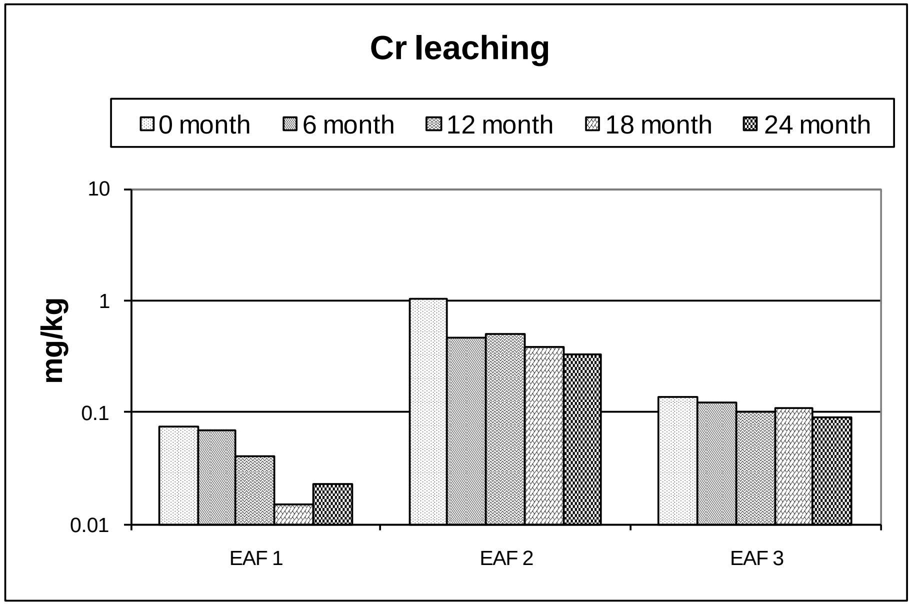
The slag were crushed 100% < 4mm

Fraction < 1 mm was excluded.

The material was well distributed

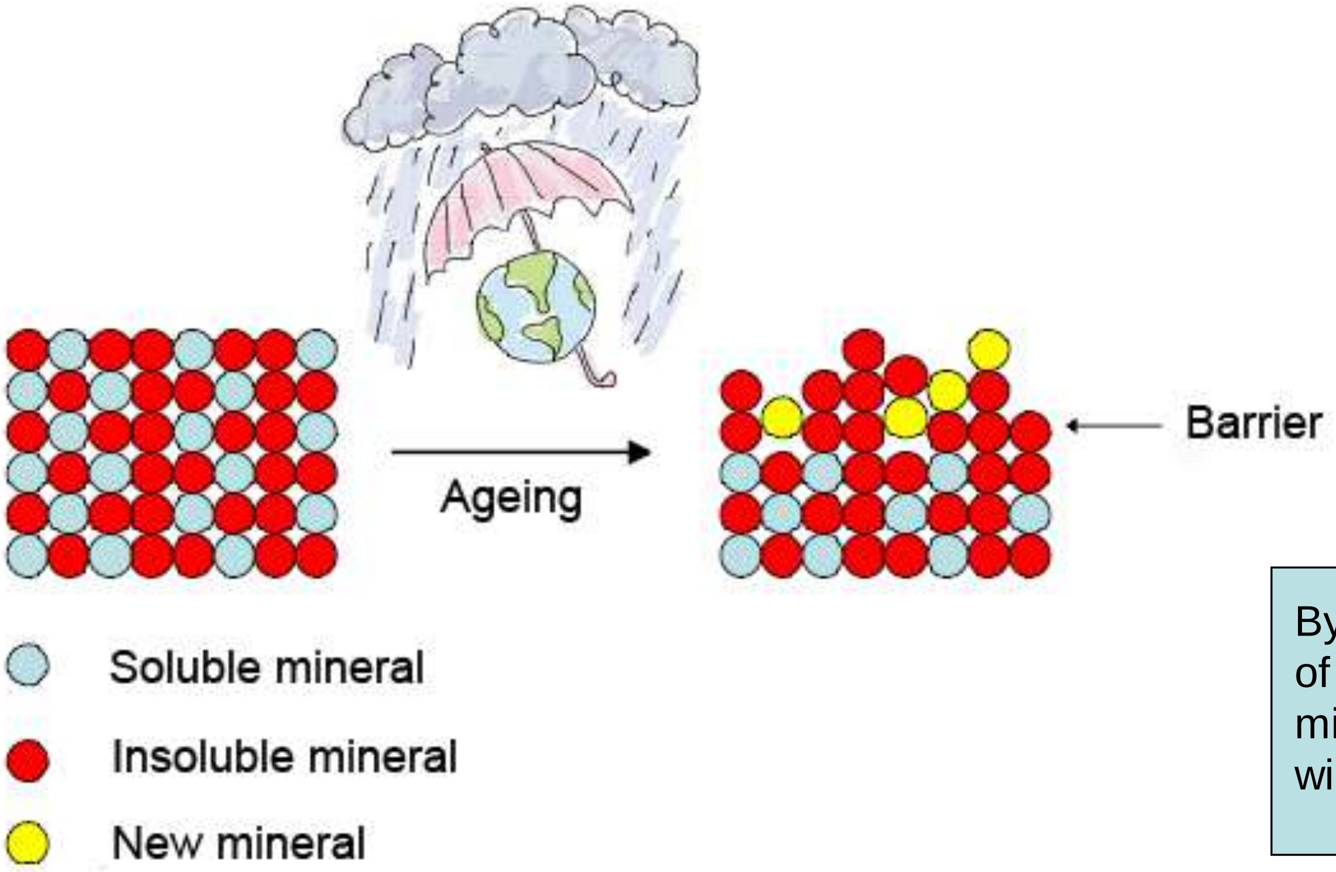
Total leachability and leachability of Cr (Engström)





% Cr_2O_3: 2.0 5.7 7.0

Summarising reactions taking place (Engström)

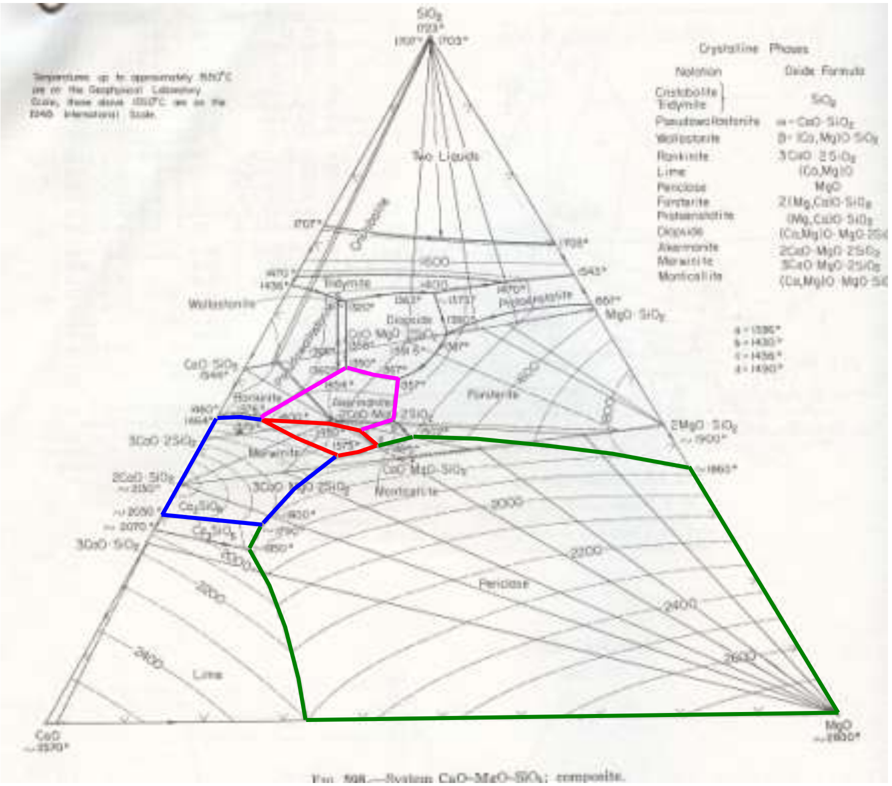


By forming a barrier, of new and insoluble minerals, the leaching will decrease

Individual mineral solubility and distribution of elements on phases important (Durinck, Engström)

If different slag minerals dissolved differently how will that influence the leaching of e.g. Cr?

	Dissolves chromium
Merwinite	Yes
Akermanite	No
γ-Ca_2SiO_4	No
MgO	Yes
Gehlenit	No
$Ca_2Fe_2O_5$	Yes
$3CaO*Al_2O_3$	No



Synthesises of slag minerals (Engström)

BOF

EAF

AOD

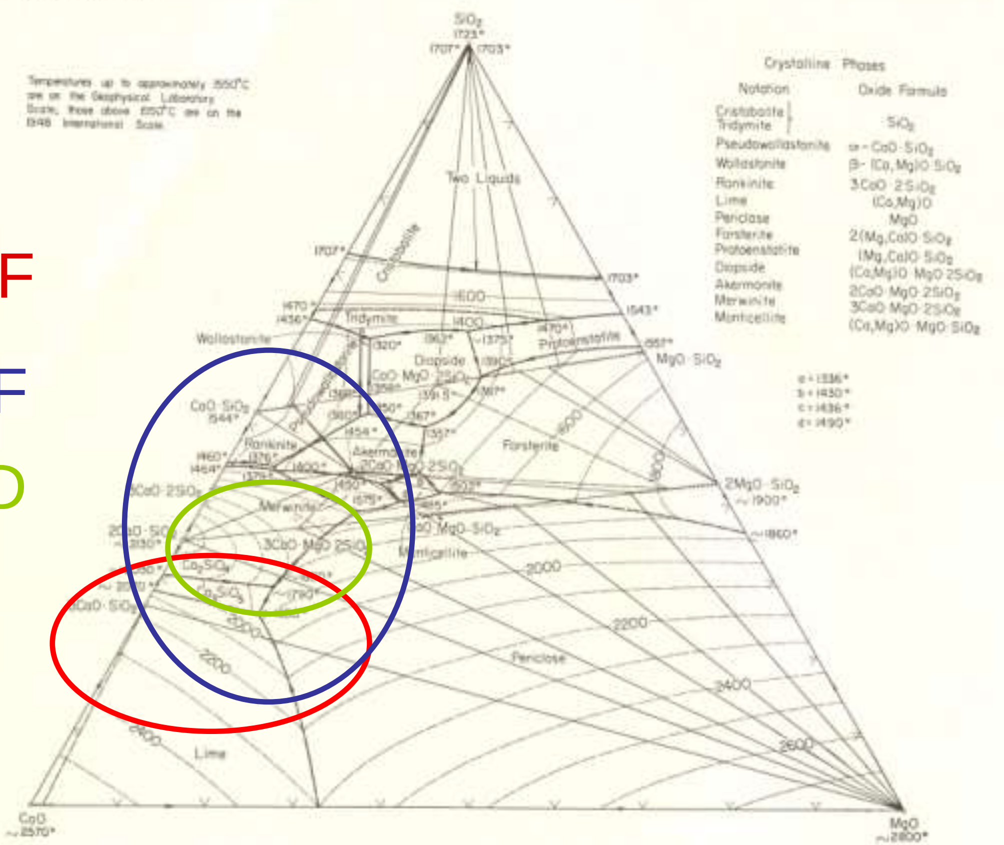


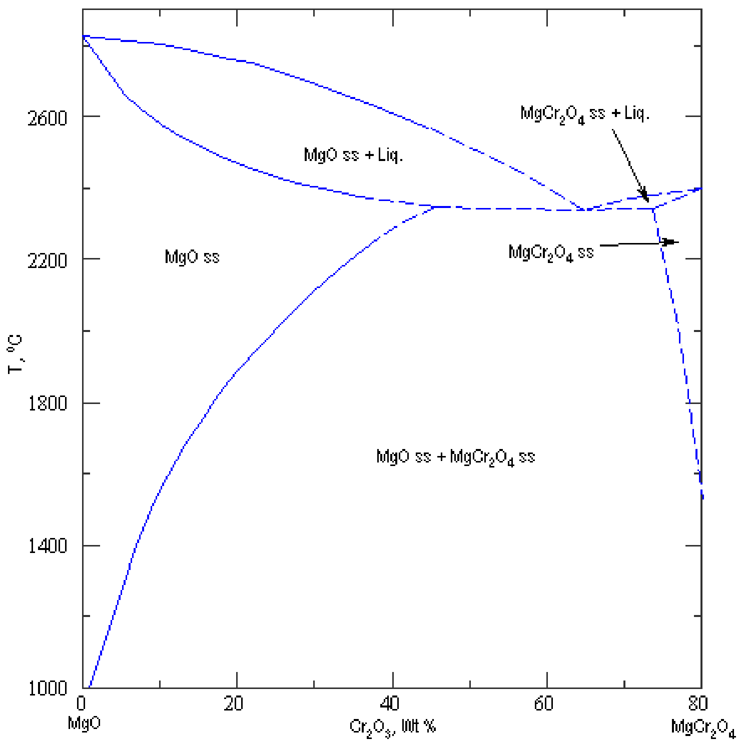
Fig. 598.—System CaO-MgO-SiO₂; composite.

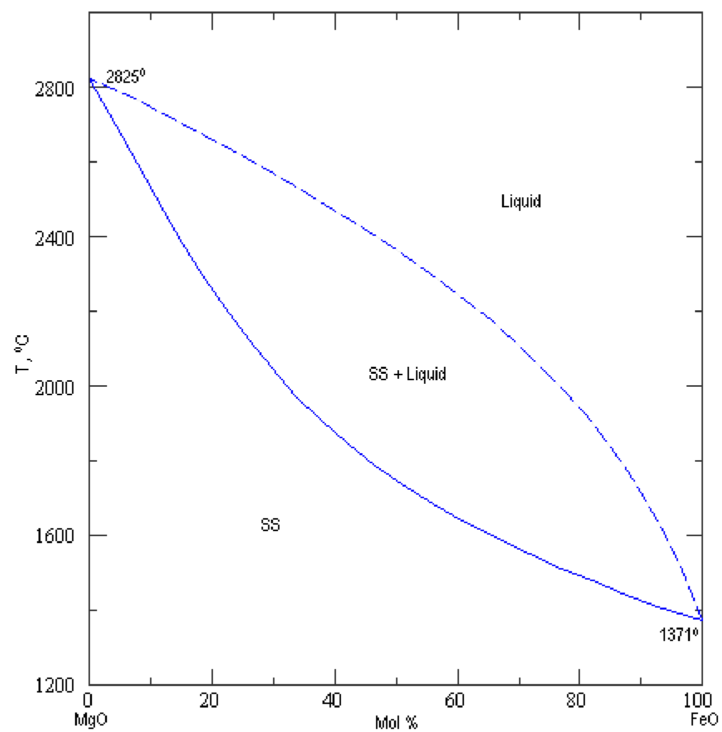
E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 2, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

Six common slag minerals!

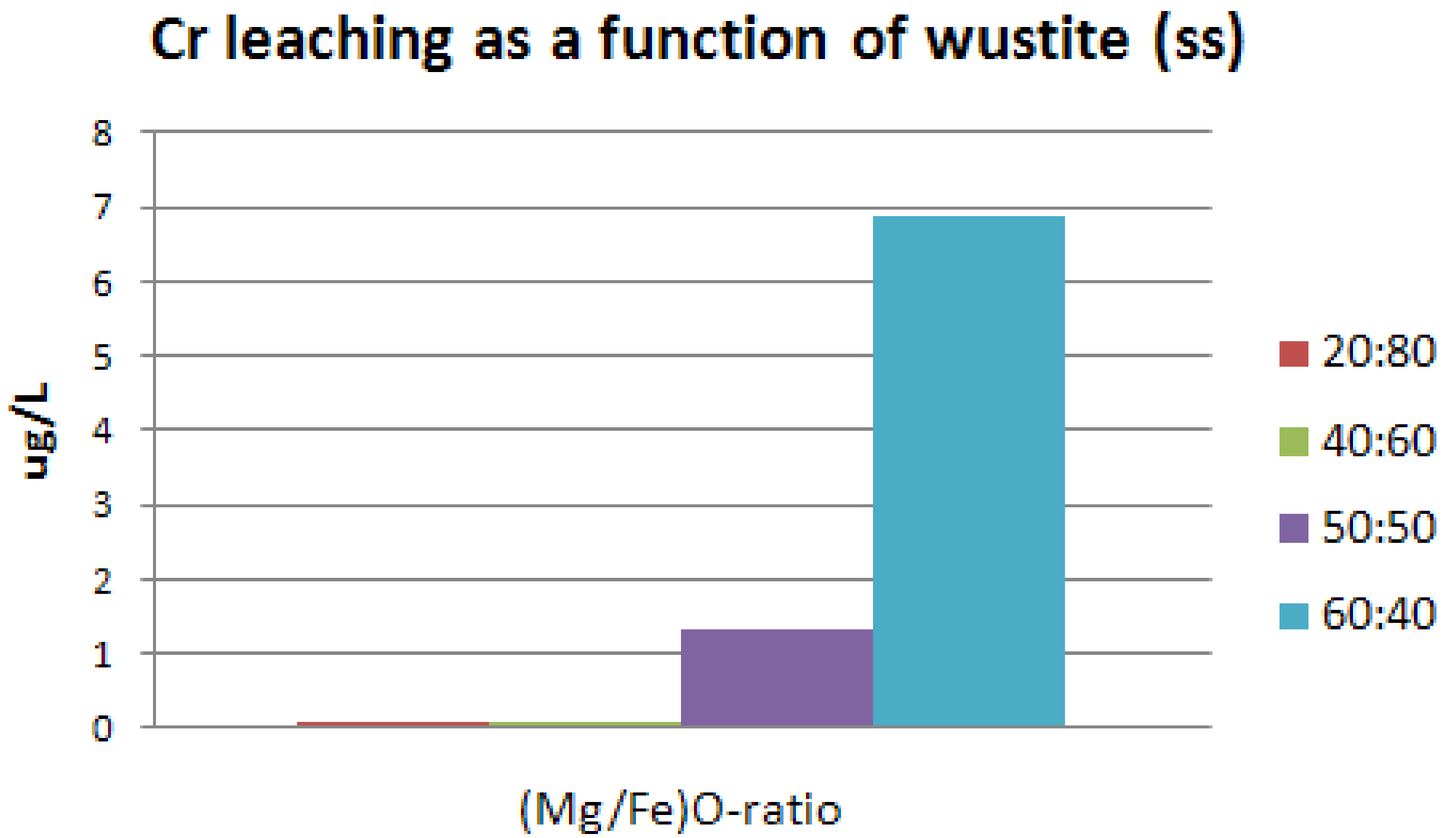
Mayenite	$Ca_{12}Al_{14}O_{33}$
Merwinite	$Ca_3MgSi_2O_8$
Akermanite	$Ca_2MgSi_2O_7$
Gehlenite	$Ca_2Al_2SiO_7$
Ingesonite	γ-Ca_2SiO_4
Tricalcium alum.	$Ca_3Al_2O_6$

The systems $MgO\text{-}Cr_2O_3$ and FeO-MgO



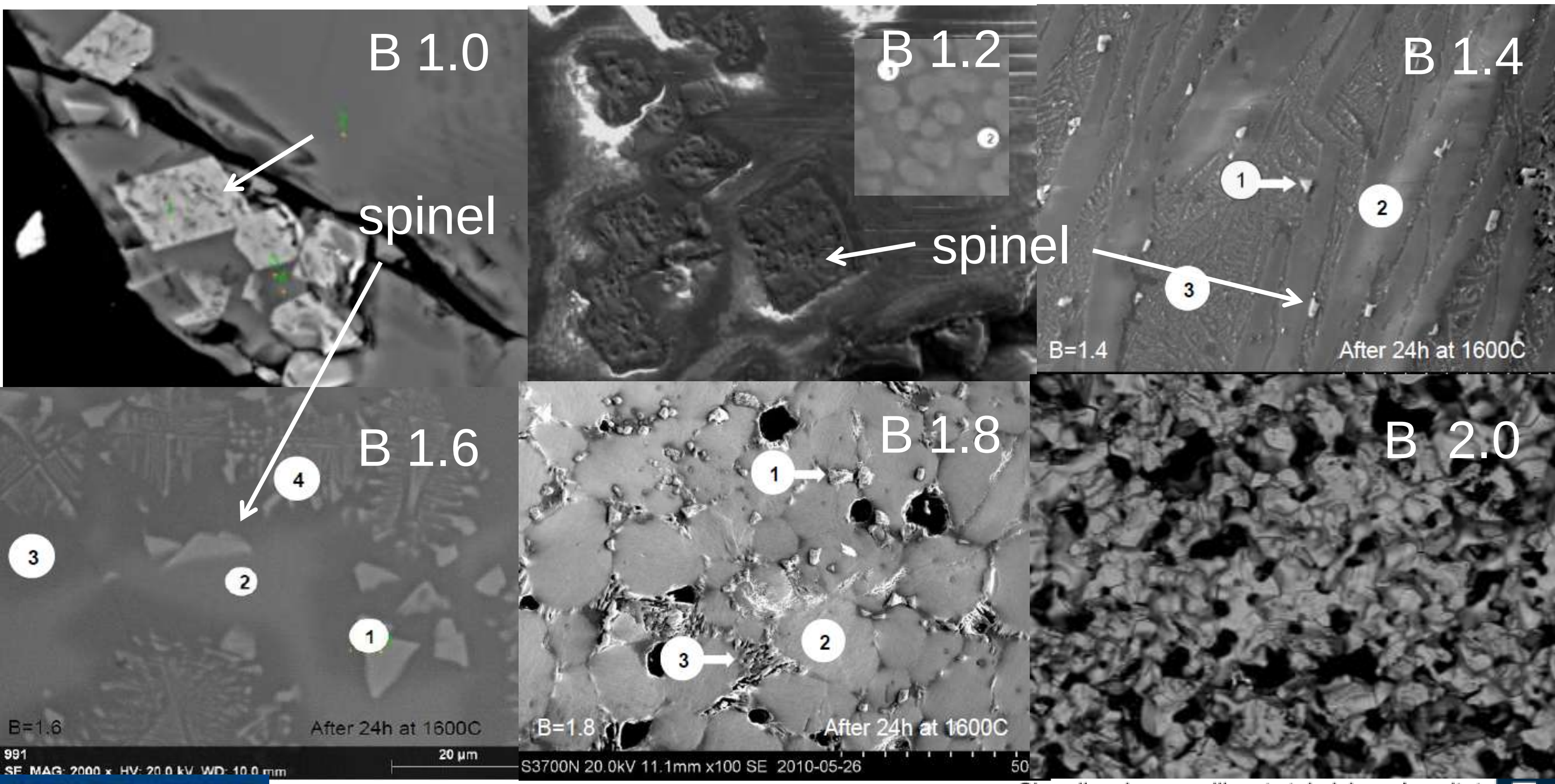


Chromium leaching as a function of (Mg:Fe)O composition (Engström)

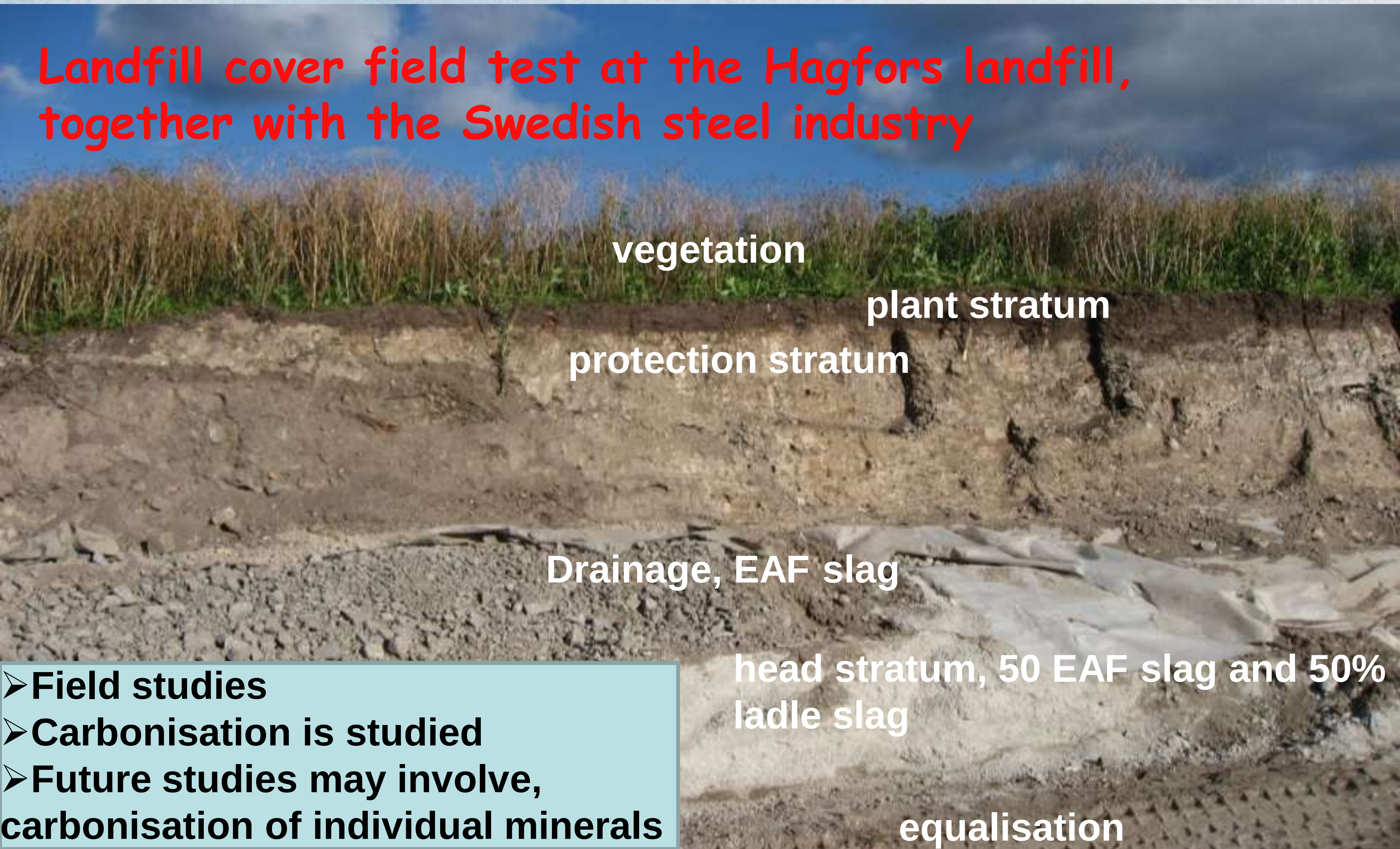


Mineralogical composition at equilibrium conditions for slags in the system CaO-MgO-SiO_2-Cr_2O_3-Al_2O_3 studied at KTH in collaboration with Luleå University of Technology

Effect of the bacisity at 1600 °C



Landfill cover field test at the Hagfors landfill, together with the Swedish steel industry



- Field studies
- Carbonisation is studied
- Future studies may involve, carbonisation of individual minerals

Conclusions

- Hot stage engineering of slag, although limited attention so far, is a subject of increasing interest
- Increased effort to market slag as products will necessitate increased focus on quality control, e.g. involving hot stage engineering of the slag properties
- By hot stage adjustment of slag composition, new more value added products will be achievable
- As both steel and slag become products at a steel plant, it will increase the motivation to optimize the production from the viewpoint of the quality of both products
- At least from our perspective it is still very much left to do regarding utilisation of possible hydraulic or pozzolanic properties of slag

Thanks for your attention

Questions