Steel Slags as cementitious materials

Jean-Marie DELBECQ,
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Summary

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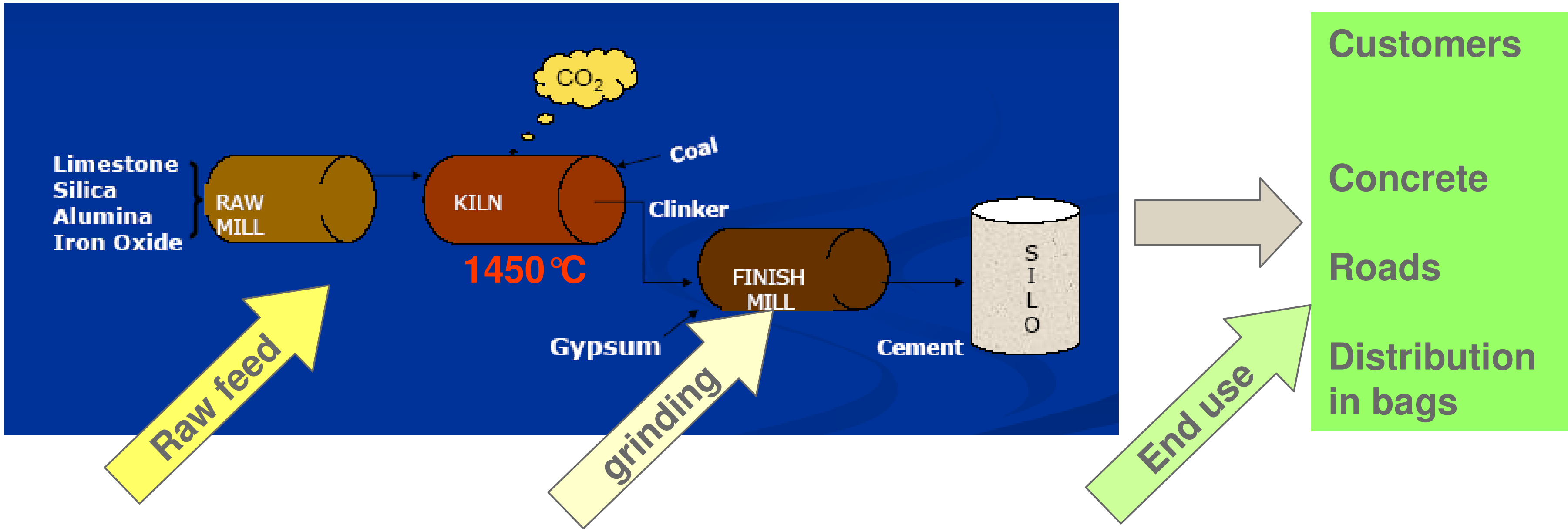
- Different applications
- Diversity of Steel Slags
- Stakes
- Steel Slag as raw feed material
- Steel Slag as cement component
- Processing : sorting, additions to liquid slag, cooling, grinding
- Outlook
- Conclusions

Slags for cement and concrete
Where in the value chain ?



- Note : the use of slags as aggregates in concrete is out of the scope of this presentation. But the use as fillers, with partial substitution to cement, is in the scope.

Steel slags are diverse and variable

Desulfuration slag
(5 kg/t steel)

Fe	15 to 30	%
Al2O3	1 to 3	%
SiO2	10 to 15	%
CaO	30 to 50	%
P2O5	0.5 to 1	%
S	0.5	%
MnO	0.5 to 1	%
C	3 to 8	%
MgO	3 to 4	%

Basic Oxygen Furnace slag
(80-120 kg/t steel)

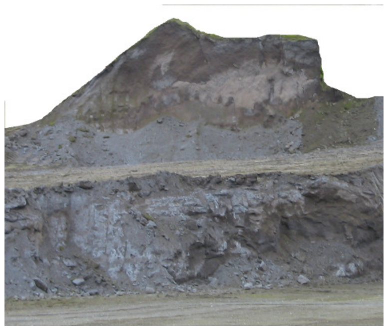
Fe	15 to 25	%
Al	1 to 3	%
SiO2	10 to 15	%
CaO	40 to 55	%
P2O5	1 to 2.5	%
Cr2O3	0.1 to 0.3	%
S	0.05	%
MnO	3 to 5	%
MgO	2 to 7	%

Steel slags are **diverse** and **variable**

Electric Arc Furnace slag
(80-120 kg/t steel)

Fe	20 to 30	%
Al2O3	2 to 6	%
SiO2	10 to 20	%
CaO	32 to 50	%
P2O5	0.5 to 1.5	%
Cr2O3	0.1 to 0.2	%
S	<0.2	%
MnO	2 to 7	%
MgO	2 to 7	%

Secondary metallurgy slag
(10 kg/t steel)



Fe	0 to 15	%
Al2O3	10 to 30	%
SiO2	8 to 16	%
CaO	40 to 55	%
Cr2O3	0 to 1	%
MnO	0 to 1	%
MgO	4 to 9	%

Sorting is the very first action to carry out to maximize valorization

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1) Sorting between tools (typically BOF and Secondary Metallurgy slags) in the Steel shop

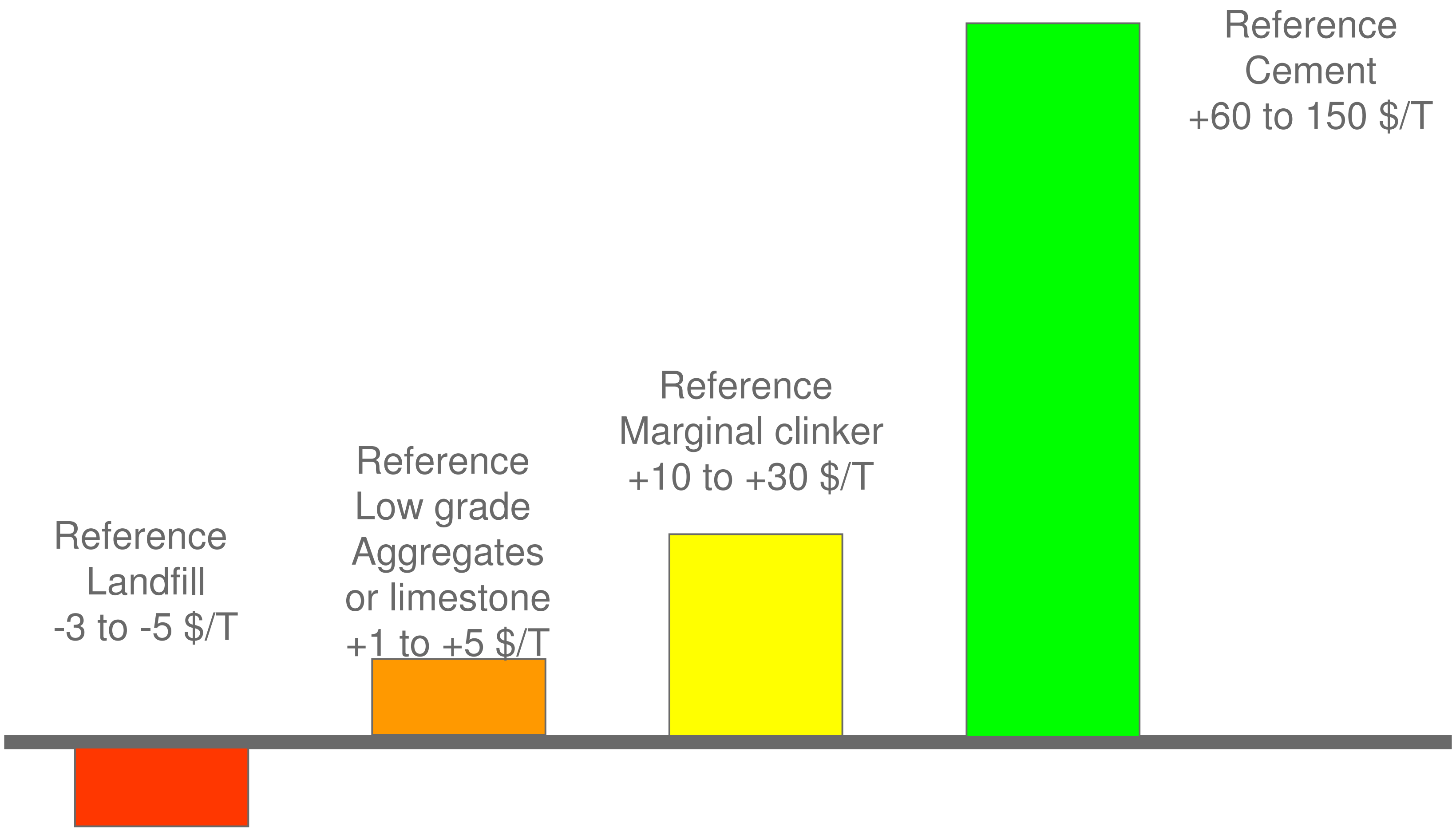
2) Sorting between BOF slags acording to low/high free lime (or P if the goal is internal recycling to the sinter plant)

→ Use of predictive tables or softwares

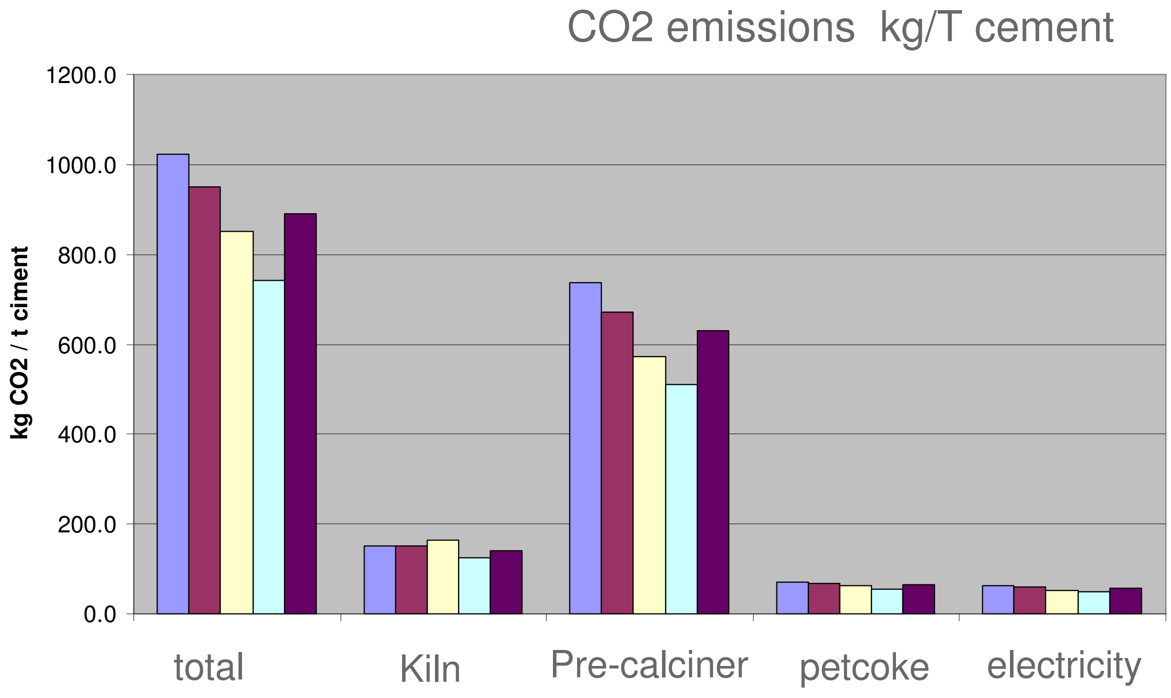
→ Can only be done with post-blowing data (slag final basicity, O2 amount blown, etc.) from the steel shop

→ Refractories maintenance procedures (using mostly dolomitic lime) have also to be taken into account.

Slags value scale



CO2 Stakes :



Reference : Portland cement

Case 1: 15% BOF slag as raw material, mixed with raw feed

Case 2: 15% BOF slag as raw material, directly injected into kiln

Case 3: 15% BOF slag as additive to clinker, k=0,9 (replacement rate)

Case 4: 15% BOF slag as additive to clinker, k=0,4

Steel slags used in cement in the world

- Japan : about 600 KTpa are used as raw feed for kilns, mainly BOF slags, ie 1% of clinker production
- USA : about 400 KTpa are used as raw feed, ie 0,4% of clinker production
- Europe : about 170 KTpa are used as raw feed or cement component , ie less than 0,1% of clinker production
- China : Steel Slags are used in cement , but no statistics are available

See more in appendix

Steel slags
as kiln feed material

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Chemistry

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Constituent	Portland cement	BOF slag
CaO	64 – 65	45 – 55
SiO_2	21 – 22	10 – 12
Al_2O_3	5 – 6.5	1 – 3
Fe_2O_3	2 – 3	7 – 10
MgO	1 – 1.4	1 – 8
MnO	-	2 – 4
SO_3	1 – 2	-
FeO	-	10 – 16
P_2O_5	0.1 – 0.8	0.5 – 3
CaO/SiO2	3	5

- **Major clinker oxides are dominant in BOF slag** : CaO, Fe2O3/FeO, SiO2, Al2O3 amount to 85-90%
- **Minors elements** can have a detrimental influence on clinker hydraulic properties : MgO, MnO, TiO2, P2O5
- **The limiting parameter is the Fe content** : if the need of Fe2O3 addition in the clinker is 1%, the amount of slag cannot exceed about 5% (of the clinker weight)

Secondary Metallurgy Slag could be used instead of BOF Slag : more Al2O3, less Fe, usually less Cr,. But it must be consistent.

Slag as Kiln Feed
Advantages

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- Slag has been completely calcined and does not generate CO_2.
- Slag readily combines with other raw components to produce clinker
- Both of these effects result in fuel savings.

Advantages

- Significant reduction in exhaust fan volume; **potential for increased clinker production by 5-7%**
- **Fuel Savings**: lower energy for decarbonation due to lower carbonate content of kiln feed
- Significant **decrease in CO_2 emissions (less fuel, less decarbonation)**
- Reduced alkali in kiln feed; potential to reduce Clinker Kiln Dust for alkali control

The Chromium VI issue

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- Severe legal limitations have been put in Europe on the CrVI content in cement. Under the EU Directive 2003/53/CE, hydrated cement must not contain more than 2 ppm of soluble CrVI, in the dry cement mass.

→BOF slag cannot be used anymore as an important raw material, as 10% of the total Cr injected in the kiln becames CrVI.

→Example : If 10% of the feed is replaced by BOF slag with 700 ppm total Cr, the final clinker would contain 7 ppm additional Cr VI.

- Cases of CrVI pollutions were detected in the USA, pointing out that clinker raw materials like steel slags and scales were containing Cr.
  (Cemex Davenport, California – TXI Riverside, California)

Industrial practice

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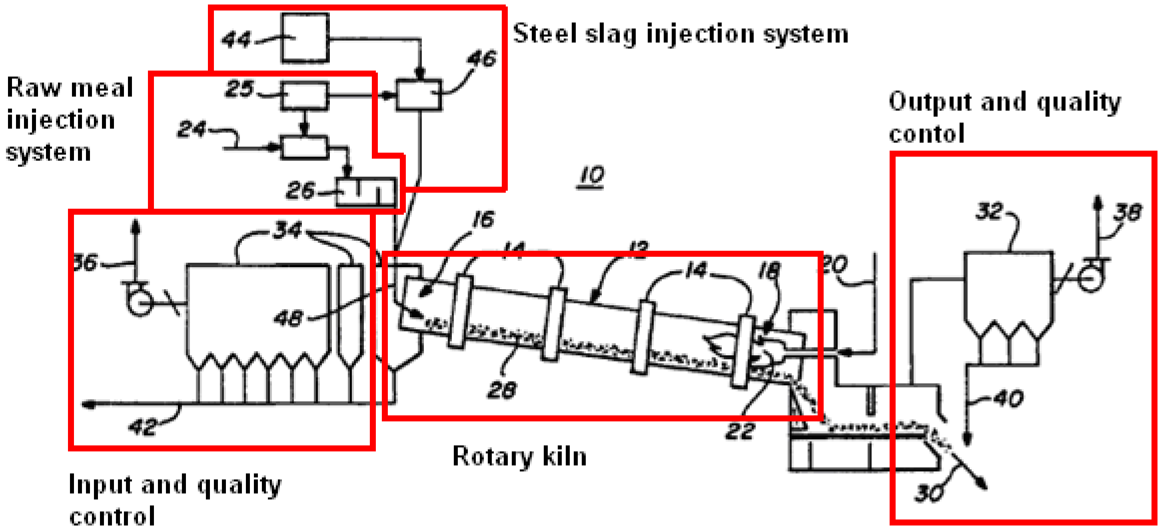
- Well known practice implemented industrially, but with limited tonnages (**typically max 5% of clinker, to cover iron oxides needs**), in Japan, USA, Canada, Indonesia, France and Brazil (not exhaustively)

- Exemple of patent : CEMSTAR technology (TXI)

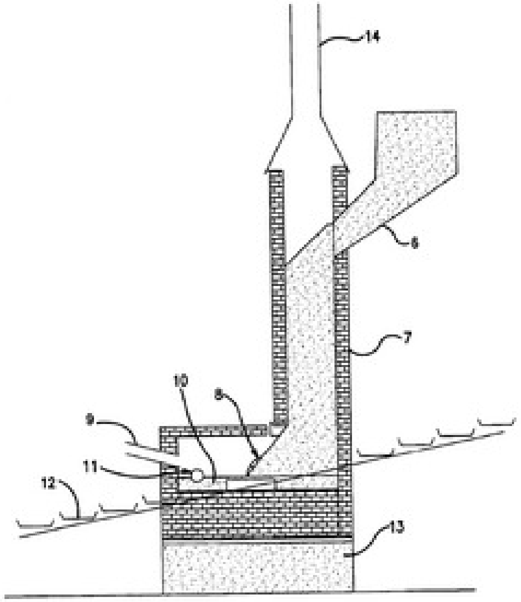


→energy and CO2 savings by avoiding the pre-heating (decarbonation) of the cement raw meal.

Secondary Metallurgy slag as raw material for aluminates binders

- SM slag also contains majors elements for cement, and especially high-alumina cement (30% to 70% of Al_2O_3, in C_3A and C_4AF form
- SM slag is currently sold to cement manufacturer Kerneos in France
- Technical limitation : MgO content of all slags which can combine with CaO, thus lowering the CaO available for Al_2O_3.

→ MgO should be as low as possible.



Reverberatory furnace for high alumina cement

Steel slags as hydraulic component

BOF slag as a reactive (hydraulic) component

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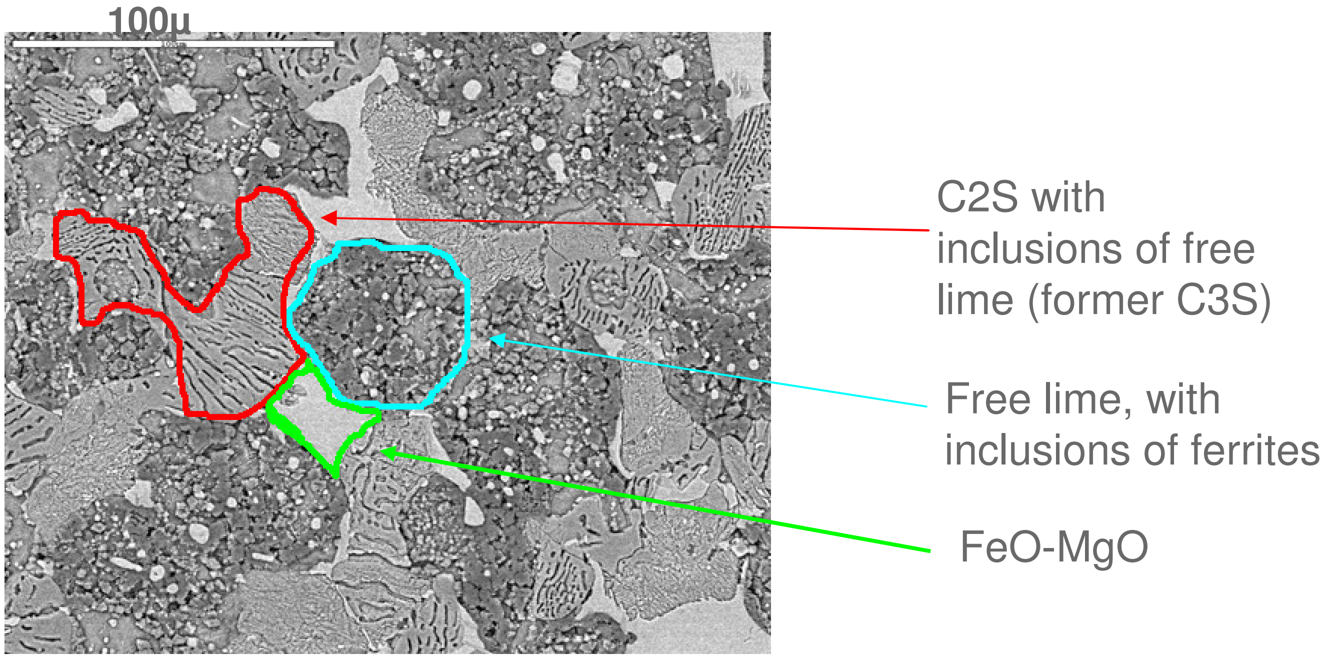
- Minerals distribution in BOF slag



→CaO of BOF slag can be subject to hydration and carbonation, but with limits (access to micronic lime).
→A lot of iron is still present in BOF slag.

Reactive hydraulic minerals in BOF slags

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Mineralogy	Portland cement	BOF slag
C3S	+++	-
C2S	++	+++
C2F	+	++
C4AF	+	-
Free CaO	-	+
Free other oxides	-	+

→

	BELITE
Chemical composition	2CaO - SiO_2 (C_2S)
Hydration speed	Slow (days)
Strength development	Slow (weeks)
Final strength	Important (dozens of MPa)
Hydration heat	Low: ~ 250 J/g
Remarks	Main mineral in steel slag

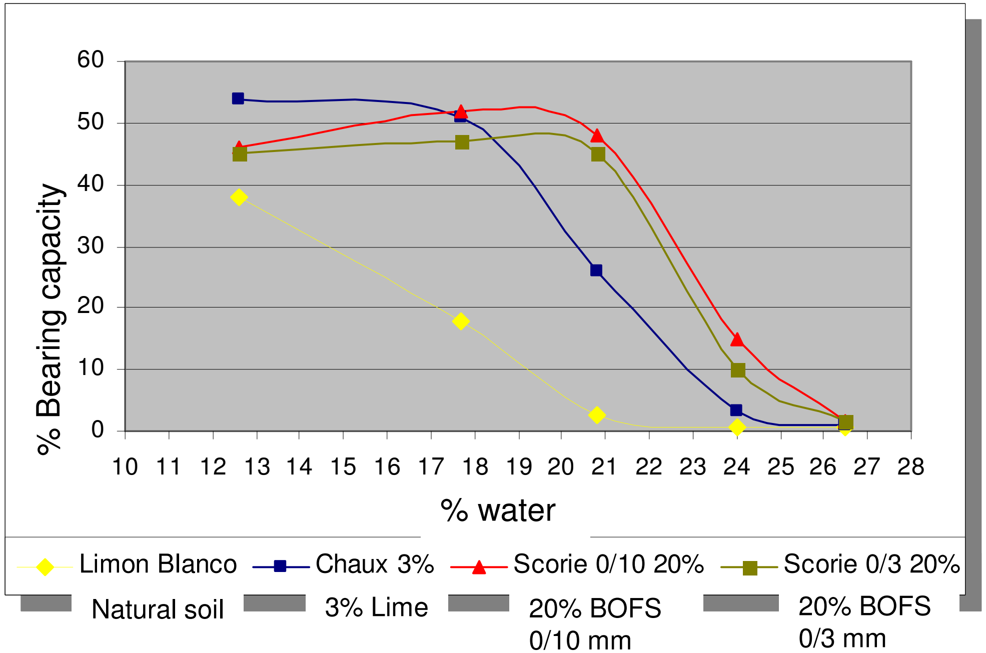
→Stable C2S phase is the most interesting mineral in BOF slag

→Free-lime can be used as activator for other binders (granulated BF slag , pouzzolans, fly-ash)

Soil stabilizer in Belgium

Tested with BOF slag from ArcelorMittal Liège

Practice of soil stabilization, usually with lime, is mandatory in case of clay-rich soils, containing more than 20% of water.



→ Fine BOF slag can replace lime in a ratio lower than 10 to 1. The savings (economical and environmental) justify the increased transportation & handling costs.

Hydraulic Road binder : Sidmix® in France

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- Produced in ArcelorMittal Dunkerque by subcontractor SGA

GGBFS	50 ± 5 %
Ground BOF slag	40 ± 5 %
$CaSO_4$	5 ± 1 %
SS Blaine	3000 ± 500 cm^2/g

Standard specification:
$10 < CS < 30$ MPa at 56 days
compressive strength on mortar

- BF slag and BOF slag are ground separately.
- It can also be used as soil stabilizer, using 4 to 7% of Sidmix, with a lime pre-treatment.
- Sidmix is certified according to EN 14227 standard.
- Ground BOF slag is now accepted in France as a main constituent possible for all road hydraulic binders.

Steel slag cement in China

according to YB/T022-92 standard

Clinker	< 65 %
Ground BOF slag	**> 35 %**
SS Blaine	> 3500 cm^2/g

Standard requirement:
15 MPa at 7 days, 32.5 MPa at 28 days compressive strength of mortar

- Steel slag cement is also praised for its superior resistance to abrasion, in comparison to BF slag cement.
- Resistance to aggressive conditions
  - 100 freeze/thaw cycles at -15℃
  - Exposition to sea water for 1 year
  - Exposition to 1% H_2SO_4 for 1 year
  - Exposition to 20% NaOH for 1 year

European Standards

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- EN 14227-2: Slag bound mixtures
- EN 14227-12: Hydraulic bound mixtures – Specifications – Soil treated by slag
- EN 15167: Ground granulated blastfurnace slag for use in concrete, mortar and grout
- prEN 13282: Hydraulic road binders – Composition, specifications and conformity criteria
- EN 197: Cement
- EN 206: Concrete

Steel Slags not allowed today

The new prEN 13282 (draft) includes BOF Slag as possible main component of Hydraulic Road Binders, up to 40%

Steel slags treatments to boost cementitious applications

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Overview of treatments

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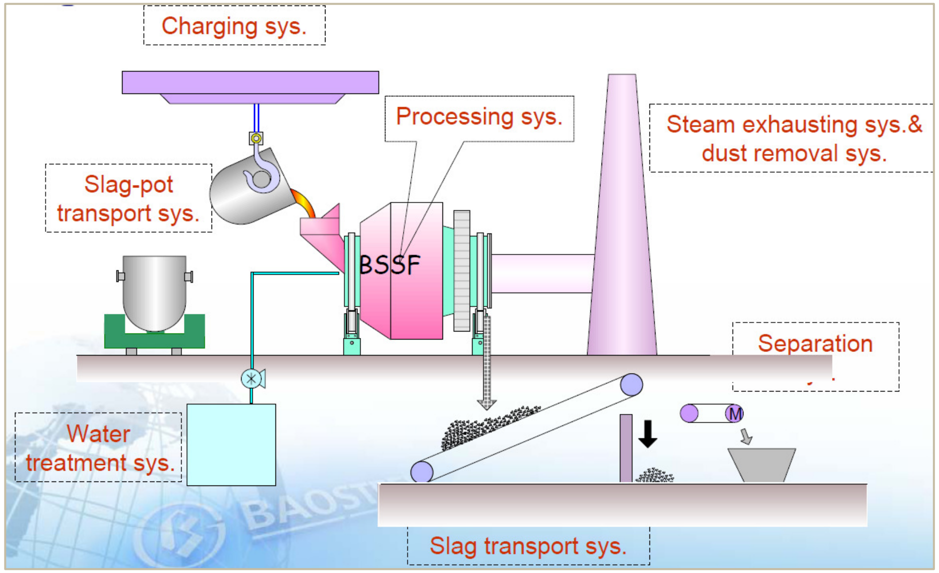
- Objectives
  - Enhance properties → produce more favorable mineral phases, often taking granulated BF slag as mineralogical reference.
  - Allow use of higher quantities → lower content of elements with no reactivity, like iron

- Processes (overview)
  - Sorting → logistics and models development
  - Hot slag treatment → oxidizing and reducing treatments
  - Cooling → granulation of slag

Granulation (quenching)

- BOF slag granulation
  - Objectives : reduce free lime content, stabilize C3S phases and obtain glass phases as in GBFS.
- Technologies :



BaoSteel Short Flow process

Ecomaister air granulation
Producing PS balls
(for shotblasting firstly)

Granulated BOF slag properties Case of Ecomaister, ArcelorMittal , Soutth Africa

- Results : fine product still containing free lime (up to 3%), **no C3S and less than 10% glass.**

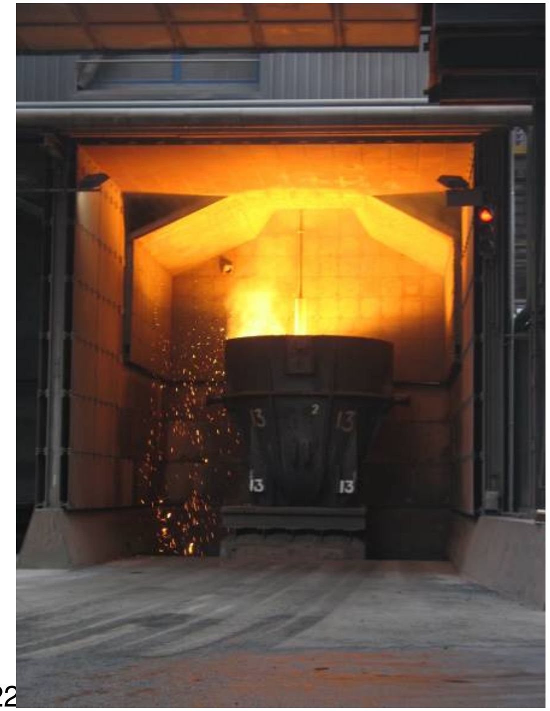
- Technological limitation: granulation of BOF slag is very difficult in case of high viscosity (an important part of the slag produced has a liquid fraction lower than 90%).

- Aesthetic limitation: granulated product is dark-gray, and gives a darker cement, which is less attractive.

Liquid (molten) slag oxidizing treatment

- Injection of oxidizing additives (bauxite,fly ash,sand, etc.)
- The main objective is to combine the excess of free lime with alumina and/or silica to create cement-like phases. O2 is typically the vector gas. Only lab scale tests have been performed in view of cement application.
- Technologies

Addition of Al2O3-rich additives was never performed at industrial scale. The existing installations are used for sand injection and the production of stable aggregates (TKS Duisburg, ArcelorMittal Gent)
This process is also very sensitive to slag viscosity.



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30 t ladles

3-6 t SiO_2 injected

30-60 min per treatment

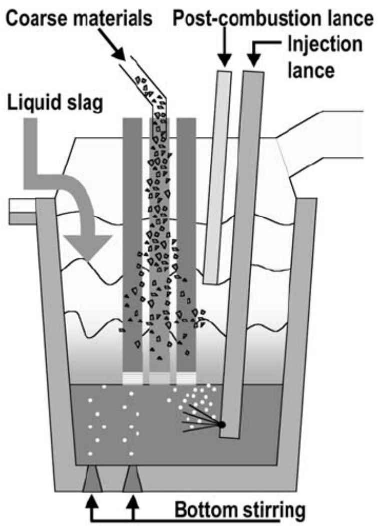
Liquid slag reducing treatment
Costly !

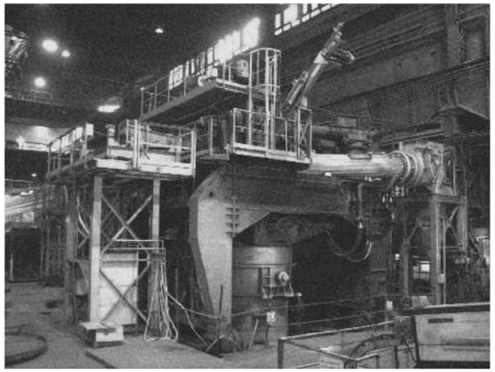
- Second approach: reducing additives (Al, C)

  The main objective is to recover the iron present in BOF slag as hot metal (but P goes mostly to the hot metal). The second objective is to adapt the slag chemistry close to BF slag.
- Several lab scale tests have been performed worldwide, including Brazil (ArcelorMittal Tubarao, using Al as reductant).

  – Technologies

The only industrial pilot scale technology tested was a dedicated EAF, fed with steel slag, bauxite and carbon. The technology was developed in 2005 in a European project. It is owned by VAI.





ZeroWaste pilot plant

Outlook and conclusions

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Outlook for BOF Slag as cementitious component

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- Iron oxide recovery from BOF slag is a significant and growing stake
- BOF slag valorization as cementitious material requires fine grinding (at least Blaine 3000 cm²/g).

→ Is it possible to recover fine iron and iron oxides particles out of ground BOF slag
  - By magnetic extraction ?
  - By other physical processes ?
  - By chemical processes ?

- In this case, process extra-costs would be lower (compared to molten slag treatments), for a combined valorization of slags constituents.
  - Recycling of Fe-rich fraction (metal and oxides) in the steel process
  - Cement for the other fraction

Conclusions

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- **The best way to use Steel slags in cement is as reactive hydraulic component**, rather than raw feed for clinker kilns, as mostly done until now, which has strong limitations, and less value (economic and sustainability value)
- BOF slag is already used for soil stabilization in hydraulic road binders in France , in blend with granulated BF slag, and in cement in China
- **However, we are still at the beginning of the development phase**
- It will take years (even decades) to establish this application in standards and common practice, by common efforts of the steel industry and the cement or concrete industry
- This challenge can be combined too with the aim of recycling as much as possible the iron content of BOF slag in the steel process.

Appendix

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Steel slags used in cement in Japan (as raw feed)

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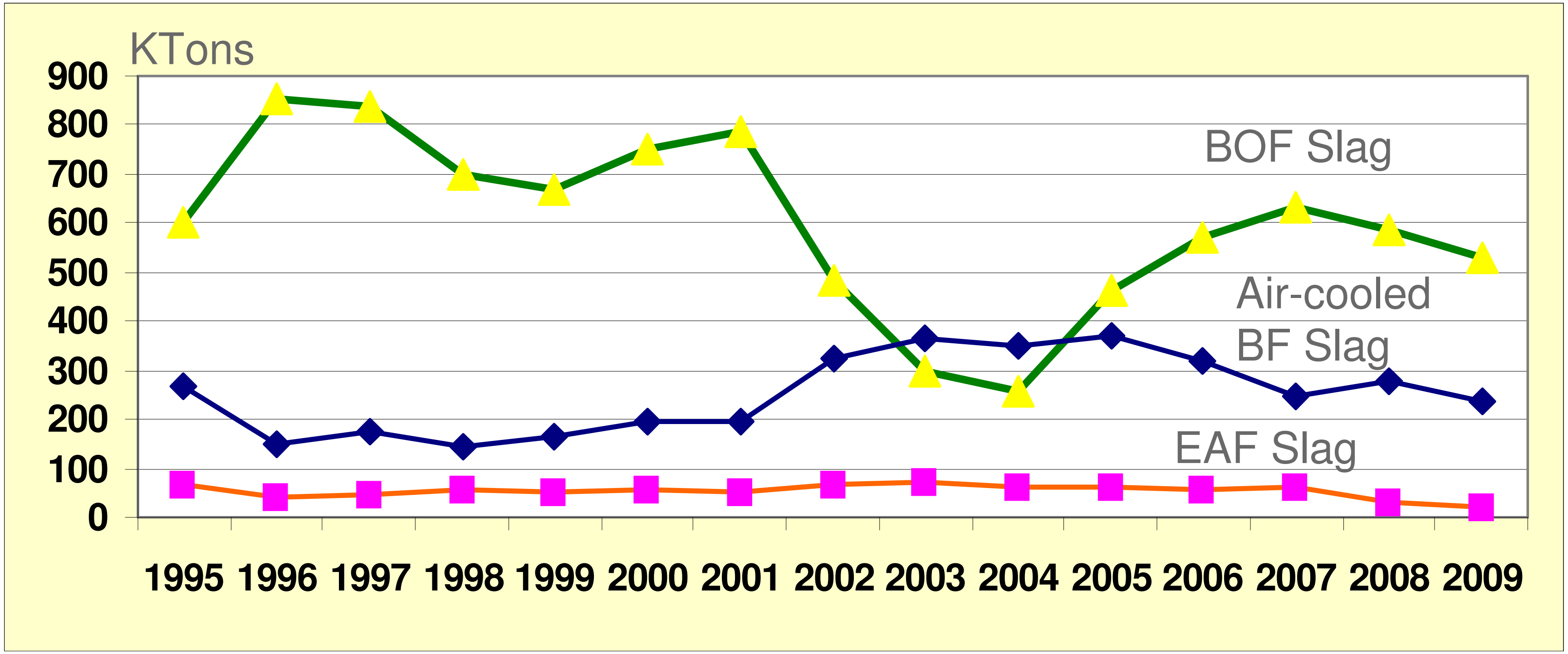
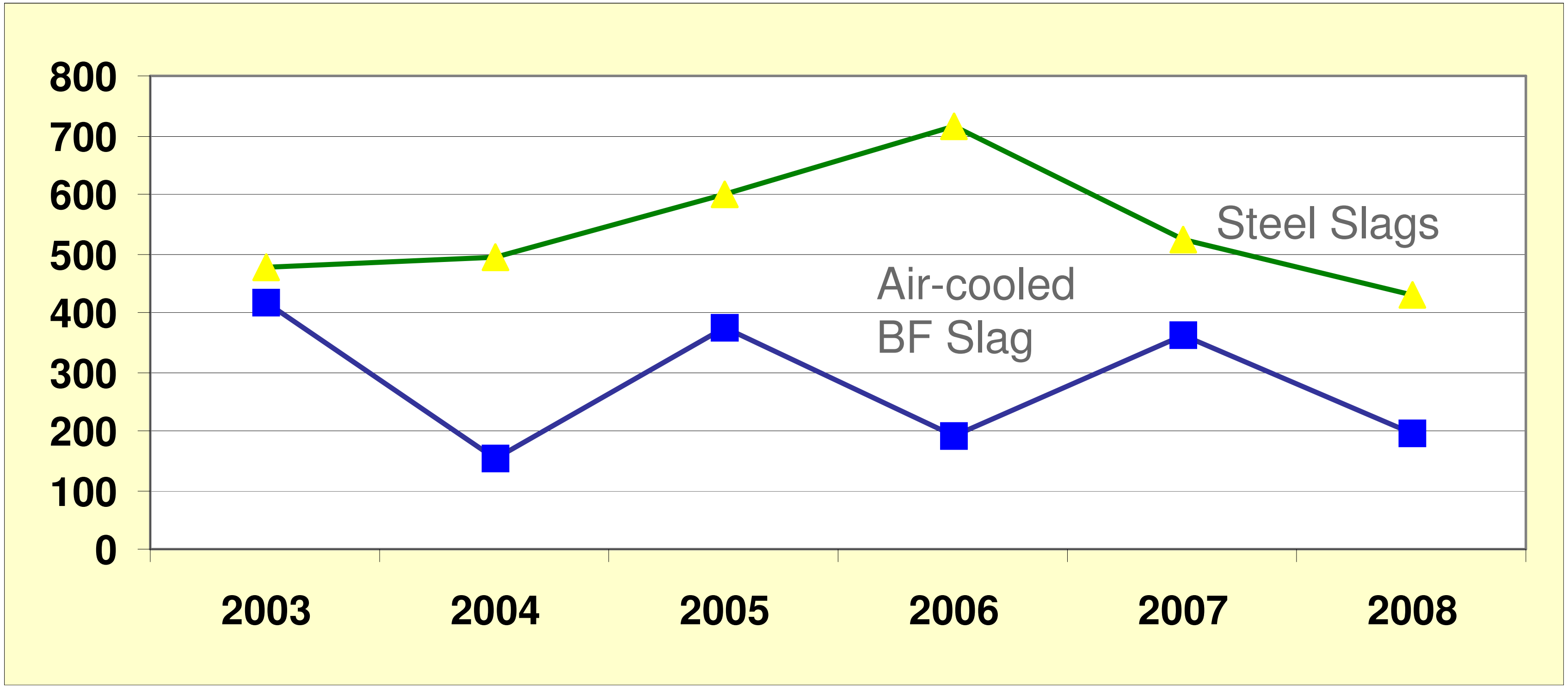


- Source Nippon Slag Association
- Clinker production is around 60 MMTpa. BOF slag use is about 1%.

Steel slags used in cement in the USA (as raw feed)



- Source USGS
- Clinker production is around 100 MMTpa. Steel slag use is about 0,4%.

Steel slags used in cement in Europe
Only 1% or ~ 170 KTpa

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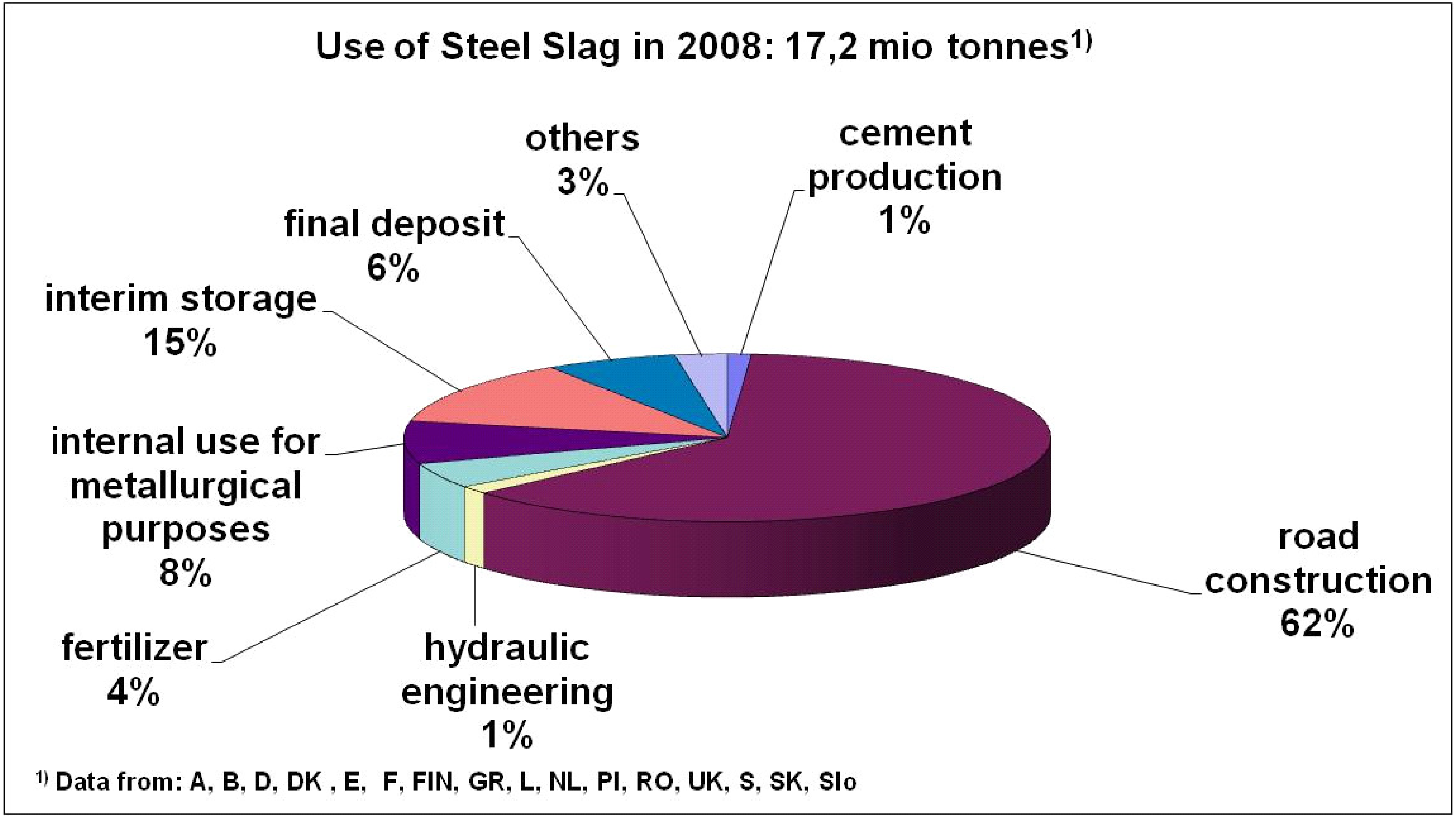

BOF slag as a reactive (hydraulic) component

- Active minerals :

→Probable hydraulic reactivity, but long-term only.

FAMILY	ALITE	BELITE	CELITE	
Chemical composition	$3CaO - SiO_2$ (C_3S)	$2CaO - SiO_2$ (C_2S)	$3CaO - Al_2O_3$ (C_3A)	$4CaO - Fe_2O_3 - Al_2O_3$ (C_4AF)
Hydration speed	Fast (hours)	Slow (days)	Immediate	Very fast (minutes)
Strength development	Fast (days)	Slow (weeks)	Very fast (1 day)	Very fast (1 day)
Final strength	Important (dozens of MPa)	Important (dozens of MPa)	Weak: few MPa	Weak : few MPa
Hydration heat	Average: ~ 500 J/g	Low: ~ 250 J/g	Very high: ~ 850 J/g	Average: ~ 420 J/g
Remarks	Typical of portland cement	Main mineral in steel slag	Sensitive to sulfates	Gives the gray color of cement