Mould fluxes for steelmaking - composition design and characterisation of properties

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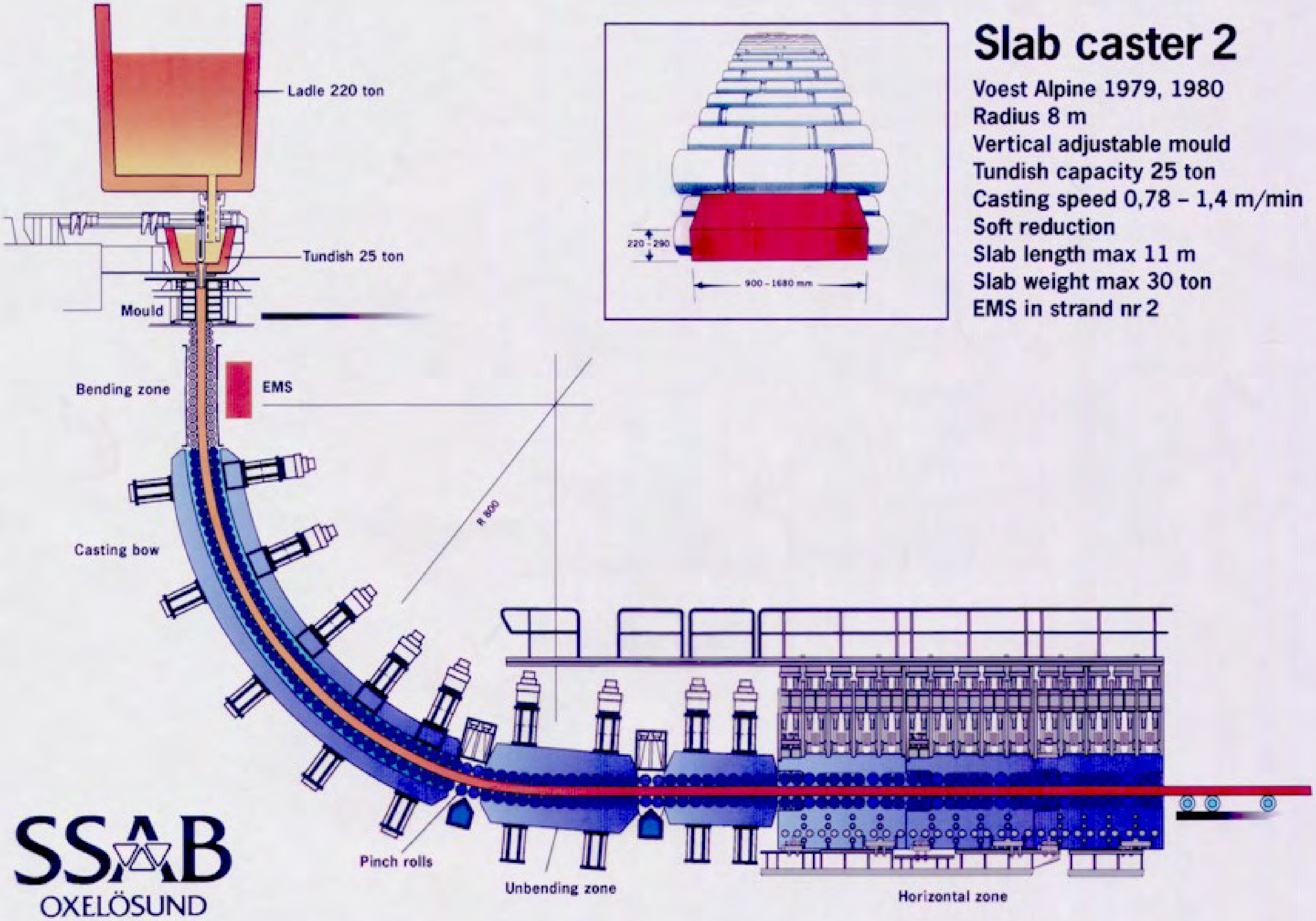
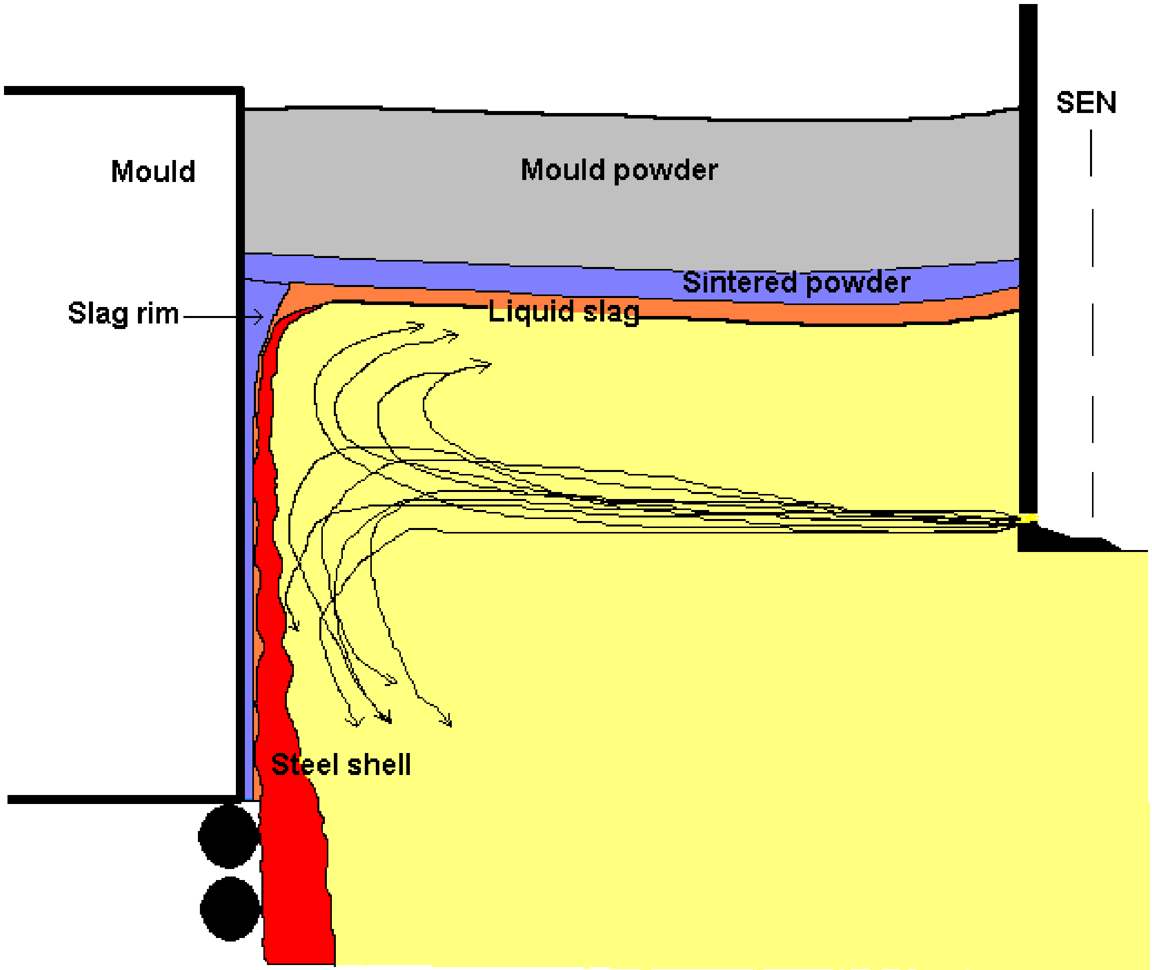
kimab

Slab caster 2

Voest Alpine 1979, 1980
Radius 8 m
Vertical adjustable mould
Tundish capacity 25 ton
Casting speed 0,78 – 1,4 m/min
Soft reduction
Slab length max 11 m
Slab weight max 30 ton
EMS in strand nr 2



The main functions for mould powder - and mould slag



- Isolate the steel surface - prevent freezing
- Protect the steel surface from oxidation
- Absorb inclusions that is transported to the surface
- Maintain a low friction between steel shell and mould by lubrication
- Create an optimum heat transfer from steel to mould

Example of a typical mould powder composition

SiO_2,	wt-%	32.1
CaO,	“	27.3
MgO,	“	1.9
Al_2O_3,	“	5.0
TiO_2,	“	ca. 0.1
Fe_2O_3,	“	ca. 1.2
MnO,	“	< 0.10
Na_2O,	“	11.5
K_2O,	“	ca. 0.3
F,	“	9.3
C-free,	“	4.5
CO_2,	“	7.9
Loss of ignition,	”	ca. 14

A wide variety of raw materials is used for the manufacturing of mould powder which is delivered as fine grained powder or as micro granules.

Composition for some mould slags and insulation fibers

Composition wt-%	**Mould slag – high basicity**	**Mould slag – low basicity**	**Rockwool**	**Glass fiber - insulation**
SiO_2	32,9	41,5	45,5	65
Al_2O_3	7,4	13,8	14,5	2,5
B_2O_3	0	0	0	5,5
Na_2O	7,9	4,8	1,5	14
K_2O	0,2	1,9	0,5	0,5
CaO	32,7	22,4	17	10
MgO	1,9	3,5	11,5	2
TiO_2	0,4	-	1,5	0,3
Fe_2O_3	0,1	0,3	0,5	0,2
FeO	0,7	2,7	7,5	0
CaF_2	11,9	9,3	0	0
Bas. CaO/SiO_2	0,99	0,54	0,37	0,15
NBO/T	2,1	1,0	1,1	0,71

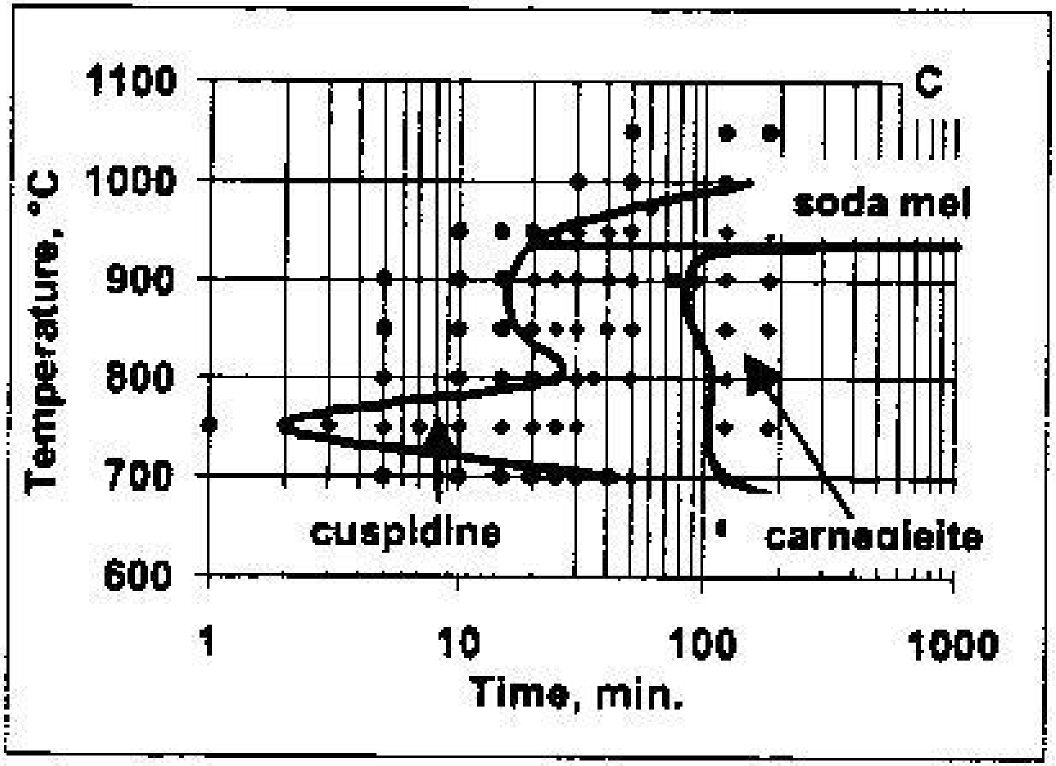
Definition of a glass

A glass can be defined as an amorphous solid completely lacking in long range, periodic atomic arrangement with a time dependent ability to transform to a crystalline phase. Any material, inorganic, organic, or metallic formed by any technique, which exhibits glass transformation behaviour is a glass.

James E. Shelby, *Introduction to glass science and technology*, The Royal Society of Chemistry, 1997

Sample from a high basicity mould slag

Example of a TTT –diagram (Time-Temperature-Transformation)



Composition: 28.7 % SiO_2, 28.1 % CaO, 16.9 % Al_2O_3, 11.1 % Na_2O, 12.8 % CaF_2

P. Rocabois, J.N. Pontoire, J. Lehmann, H. Gaye, *Crystallisation Kinetics of Al_2O_3-CaO-SiO_2 Based Oxide Inclusions*, Sixth International conference on molten Slags, Fluxes and Salts, Conference Proceedings, Stockholm-Helsinki 2000.

Most important properties for mould powder - mould slags

- Viscosity
- Melting rate
- Heat flux

Viscosity

• Very important property regarding both lubrication and heat flux from steel shell to mould.

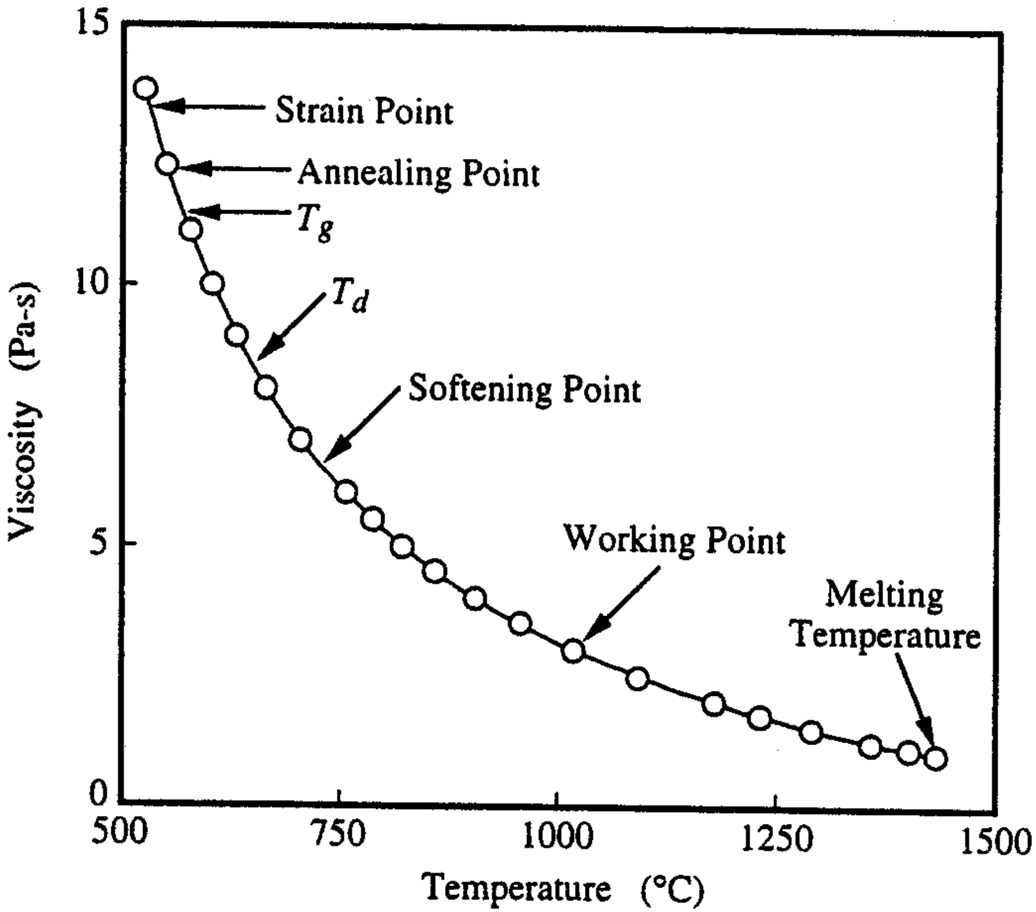
• The viscosity also has an effect on mould powder consumption

Viscosity

- For slab casting normally Visk. At 1300 mutiplied with casting speed = 1.5
- For billet casting normally around 15 Poise at 1300 centigrades.

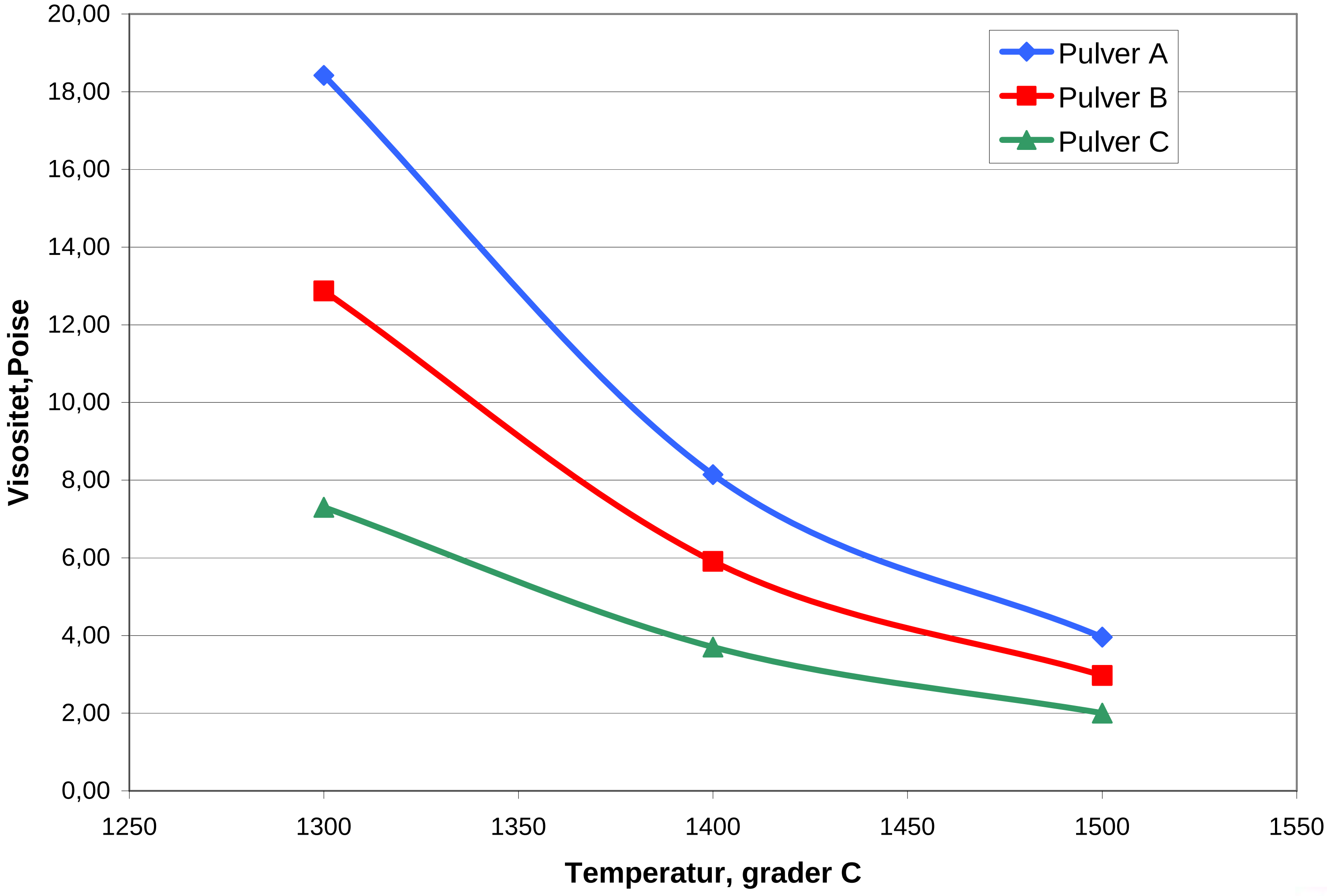
Viscosity

Typical viscosity curve for a soda-lime-silicate glass



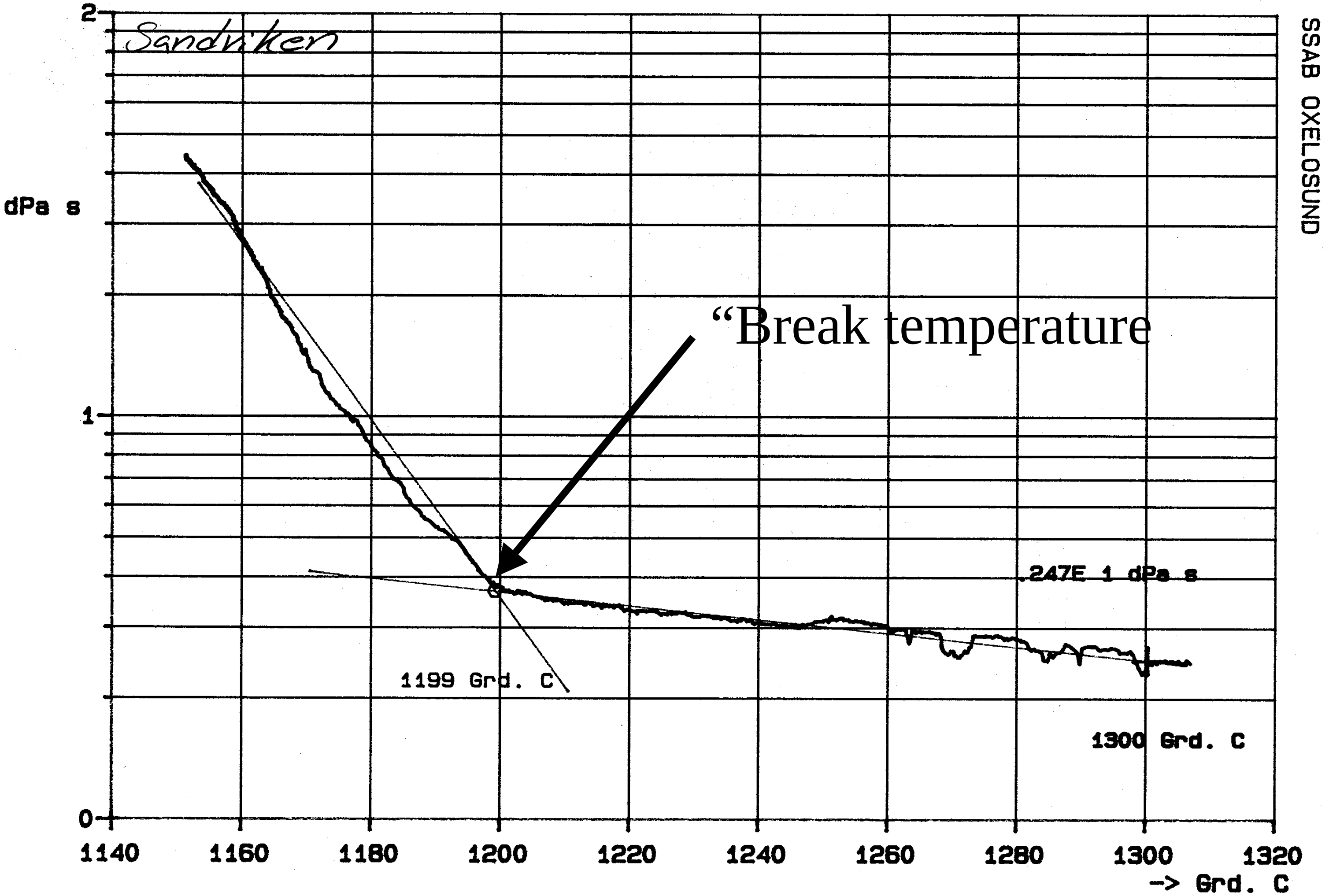
Viscosity

Typical viscosity curves for low basicity mould slags at different basicities



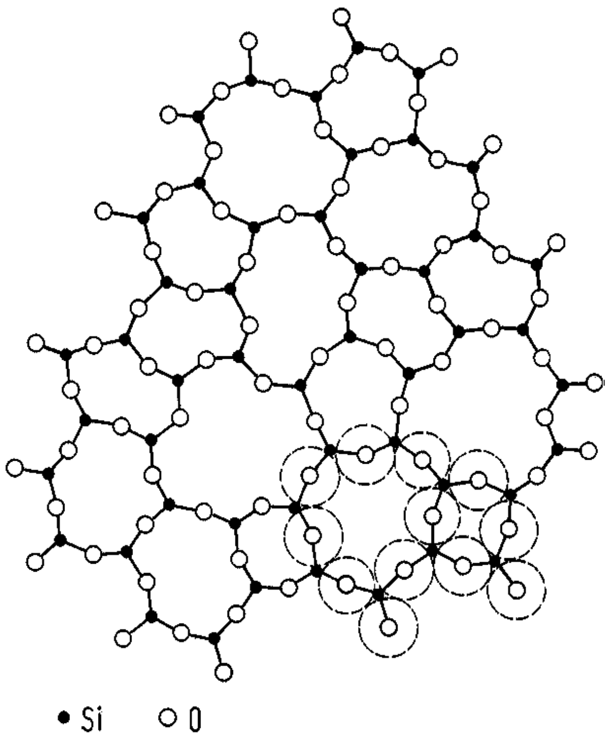
Viscosity

Typical viscosity curve for a high basicity mould slag

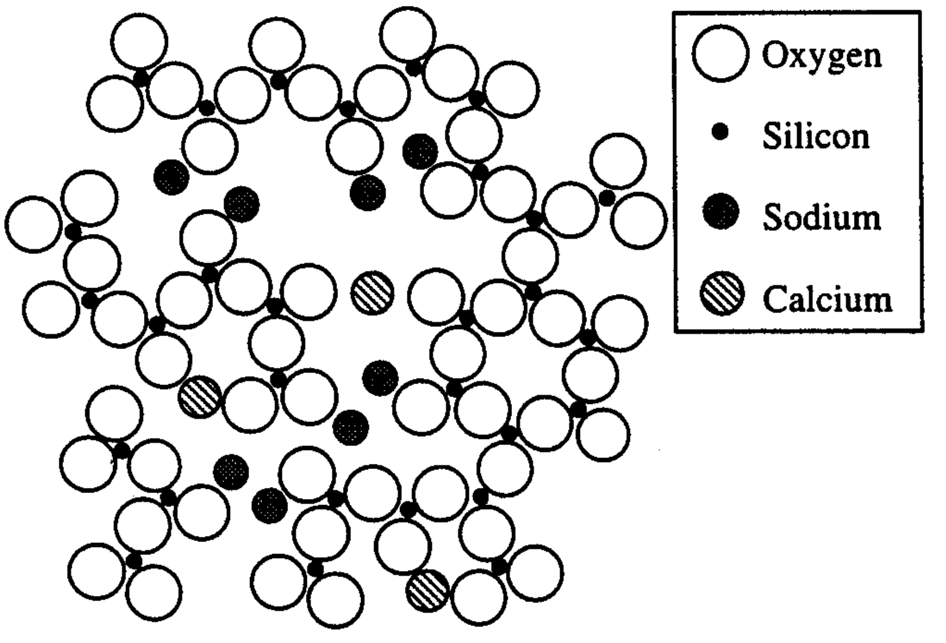


Viscosity

Alkali and alkaline earth oxides are network breakers



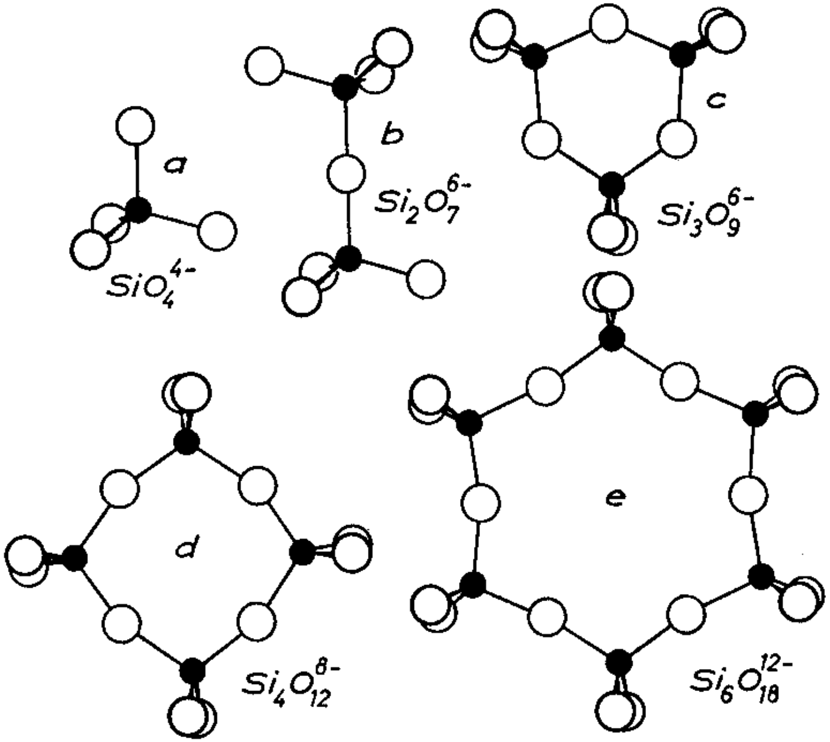
Atomic arrangement in vitreous silica



Schematic drawing of a two-dimensional structureof a soda-lime-silicate glass

Viscosity

Typical structure elements in mould slags



Discrete silicate anions. Filled circles = Si, unfilled = O

Viscosity

Effect of Alumina

Alumina is an amphoter oxide but in mould slags with a large amount of both alkali and alkaline earth oxides it will become a network builder.

$Al_2O_3 + Na_2O \text{ --> } 2(NaAlO_2)$

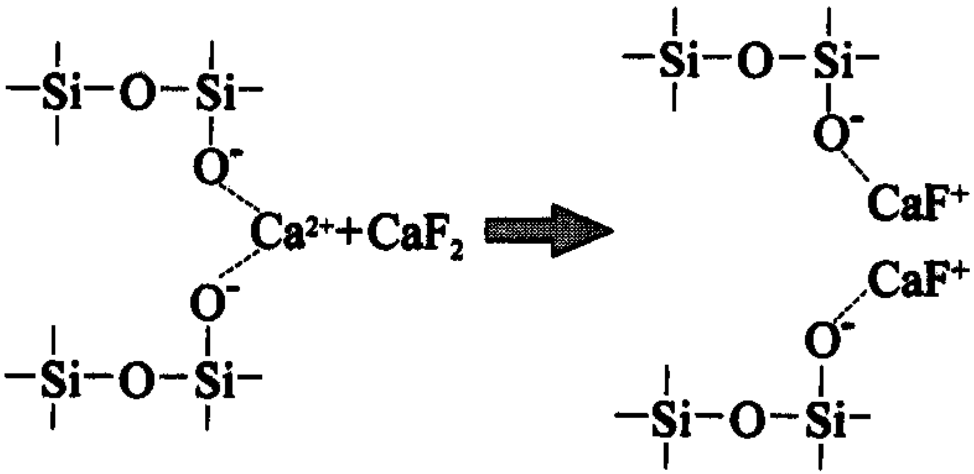
Since the oxygen supplied by Na_2O are consumed in the formation of the aluminium-oxygen tetrahedra, they are not available for the formation of NBO.

K.C. Mills, *The structure of silicate melts*, National Physical Laboratory, 1991

Viscosity

Effect of fluorine

CaF_2 addition breaks the electrostatic bindings between the silicate anions and the divalent calcium ions because CaF^+ ion pairs are added to the silicate anions. Since this reduces the resistance of flow, the viscosity is lowered.



M.Hayashi et al, *Effect of Fluorine on Silicate Network for CaO-CaF_2-SiO_2-FeO_x Glasses*, ISIJ International, Vol. 42, 2002, No. 4.

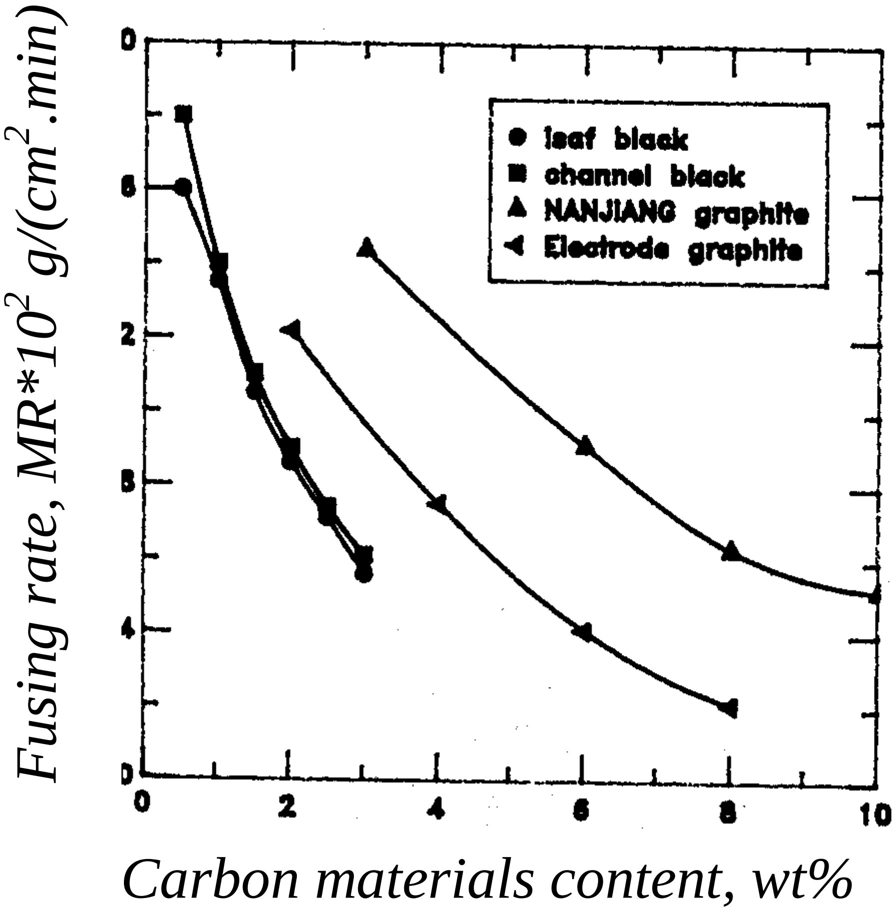
Melting rate

The melting rate controls to a large extent the thickness of the melted slag layer and is an important factor for opimisation of the process.

- Optimal slagg layer thickness is 10-15 mm.
- If the slag layer is too thin the steel will become carburized, unmelt slag patches will occur as surface defects and worse of all the result can be a breakout because of too high friction between steel shell and mould.
- If the slag layer is too thick at thick crystallised rim will emerge at the meniscus which will disturb the solidification process and cause surface defects on the steel.

Melting rate

Content and grain size of free carbon is the major controlling component in mould powders.



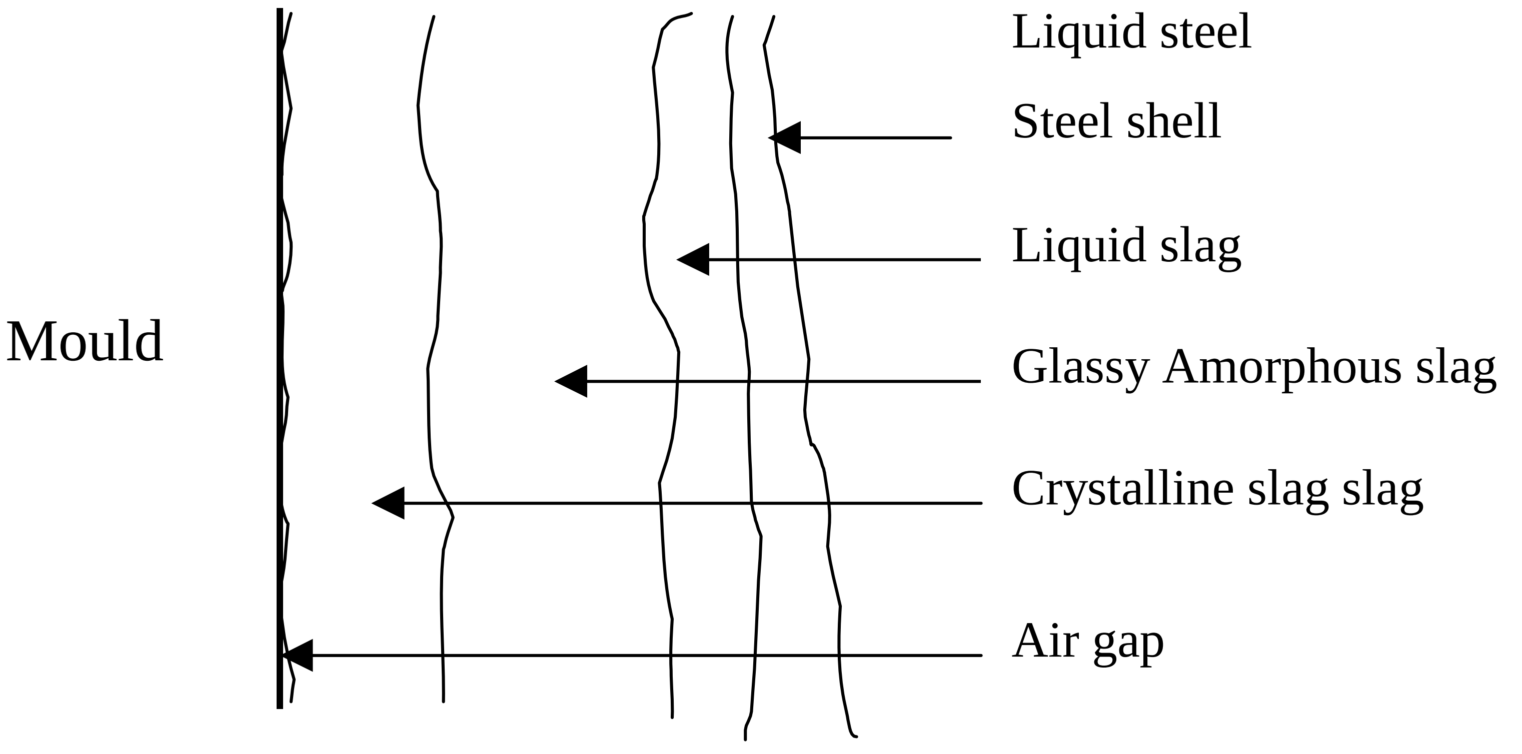
Heat flux

The heat flux through the slag layer controls the solidification rate of the steel. For some steels this must be high and others especially crack-sensitive grades the solidification speed ought to be low. This can be controlled with choice of mould slag composition. The heat flux consists of the following components:

- Thermal conductivity of slag melt, amorphous and crystalline layer.
- Thermal resistance in gap between mould and slag controlled by surface roughness.
- Thermal radiation.
- Thickness of the different layers.

Heat flux

Heat flux from liquid steel to the water cooled cupper mould



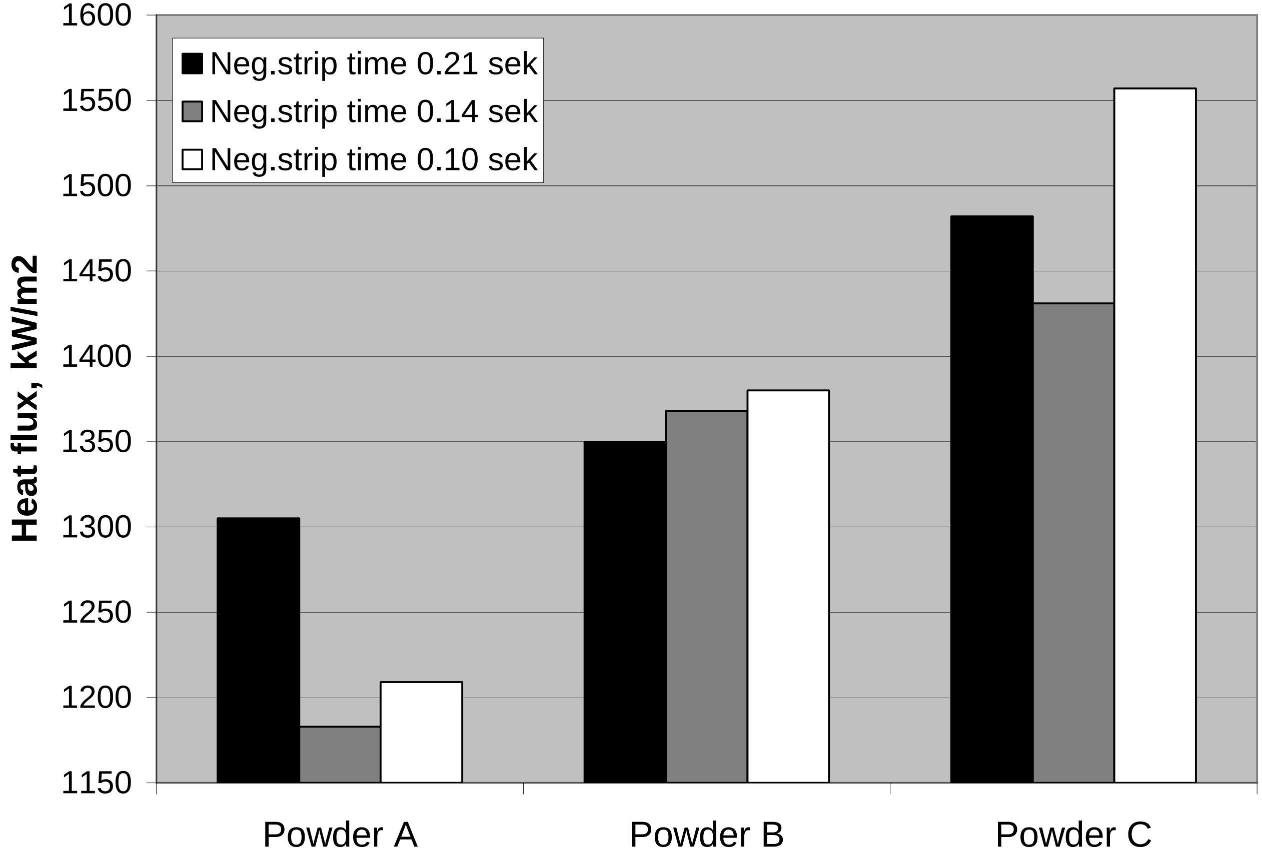
Heat flux

	Soft cooling slag	**Hard cooling slag**
Crystallinity	High	Low
Basicicty	High	Low
Heat flux by radiation	Very low	High
Absorption coefficient, α	High	Low
Air gap width (contact resistance)	High	Low

α (at 2 μm) ~ 30 + 5(%MnO) + 910*(%FeO) + 390(Cr_2O_3) + 370(Cr_2O_3)

Heat flux

Heat flux in mould for three mould slags with different basicity



Bas = 1.19 Bas = 1.06 Bas = 0.88

C-Å. Däcker, T.Sohlgren, *Influence of Mould- Powder, Geometry and Oscillation on Heat transfer and Slab Quality for a Micro-Alloyed Peritectic Steel*, 5th European Continuous Casting Conference, 2005

Composition design

	Impact on Viscosity
Basicity CaO/SiO_2	Decrease
Al_2O_3	Increase
Na_2O, K_2O	Decrease
CaO, MgO	Decrease
CaF_2	Decrease

	Impact on Heat flux
Basicity CaO/SiO_2	Decrease
Viscosity	Decrease
Absorption, FeO, Cr_2O_3	Decrease

	Impact on melting rate
Content of free carbon	Decrease
Carbonates	Increase
Absorption, FeO, Cr_2O_3	Decrease
Steel temperature	Increase
Argon purging in mould	Increase

Composition design – example for carbon steels

Rough classification for slab casting at medium casting speeds

Steel type	Class A	Class B	Class C
Carbon steels, C_P (wt-%)	0,09-0,14	<0,09, 0,14-0.5	> 0.5
Melting point	High	Middle	Low
Meniscus shell strength	High	Low	Low
Meniscus shell behaviour	Depression	Sticking	Sticking
Shell surface appearance	Rough	Smooth	Smooth
Mould heat flux control	Soft cooling	Hard cooling	Hard cooling
Basicity of mould slag	High	Low	Low
Melting rate of mould powder	Low	Middle	High
Content of free carbon	High	High	Medium

Characterisation of properties

Property	Method	Standard
Melting characteristics	Melt behaviour of briquette	DIN 51730
Melting rate	No available method at the moment	-
Viscosity	Rotating cylinder method	ASTM C1276-94, not in use in Europe
Heat flux	Laser Flash - method	-
Thermal conductivity	Hot-wire method	-
Absorption coefficient	FTIR - spectroscopy	-
Crystallisation temperature	DTA, Break temperature by viscosity	-
Rate of crystallinity	No available method at the moment	-

Characterisation of properties

Result from measurement of thermal conductivity of a mould slag made at KIMAB with the Hot wire method