

DEVELOPMENT OF A LABORATORY METHOD FOR CHARACTERISATION OF MOULD POWDER MELTING RATE

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ABSTRACT

For high quality continuous casting of steel, it is necessary to fine-tune mould powder composition in order to optimize melting properties and generate a sufficiently deep layer of molten slag. Most steelmakers are casting a variety of steel grades, formats and casting speeds. Hence a number of different mould powders are required to achieve excellent casting conditions. Today work to optimize the melting rate of mould powders is mostly done by 'trial and error', which is a time consuming method and can also be very risky due to the danger of 'break outs'. For this reason a laboratory method for comparative testing has been developed at Swerea KIMAB which resembles the actual process, whereby a continuous melting of mould powder is achieved with a controlled temperature and slag thickness. With this method it is possible to measure and learn more about the melting properties of different mould powders and thereby reduce the number of process trials in the steel plants.

INTRODUCTION

A schematic drawing of the upper part of the mould for continuous casting is shown in Figure 1.

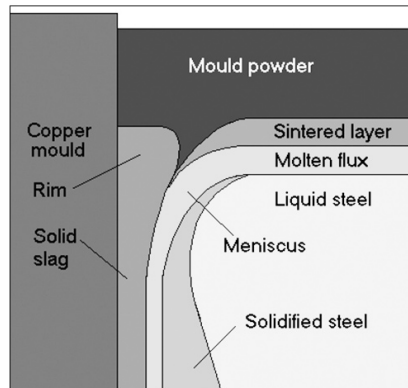


Figure 1: Schematic presentation of shell formation in mould

The mould powder has a number of functions to fulfill in the casting process, such as:

- Protect the steel meniscus from oxidation and thermally insulate the steel surface
- Lubricate the steel shell and reduce the friction between shell and mould
- Absorb inclusions floating up from the steel
- Provide an optimum level of horizontal heat transfer between the solidifying steel shell and the mould
- Chemically insulate the contact between the carbon rich mould powder and the steel.

Good powder performance requires a safe feeding of the mould slag around the whole periphery of the mould throughout the whole casting sequence. The depth of the molten slag pool is a balance between melting rate of the mould powder and the consumption of mould slag. It is also important that the whole bath is covered with a sufficient layer of molten slag of 10-15 mm in thickness. If some parts are not covered with slag the steel surface will go *dry* that means high friction and low cooling which will lead to an increased risk of break outs and surface defects.

The work to attain optimal mould slag thickness is mostly done by trial and error and there is a great need for a laboratory method where the melting rate can be tested in a more controlled and cheaper way than industrial plant trials.

THEORY OF MOULD POWDER MELTING

Mould powder in a liquid state consists of oxides, mainly silicon, alkali, alkaline-earth oxides and fluorides. The liquid slag has an ionic nature. The building block of most mould powders is the SiO_4^{4-} tetrahedron, which has the ability to create a three-dimensional network if the concentration is sufficiently high. The network will be broken down with the addition of cations, such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ and Li^+ . Fluorine decreases the binding force and consequently the viscosity of the slag system.

The desired properties of a mould powder can be achieved with several different combinations of chemical composition. Table 1 shows the ranges of different components that are commonly used in mould powders both for continuous and ingot casting.

Table 1: Typical chemical compositions of mould powders (wt-%)

Network (glass) formers	SiO ₂	17-56
	Al ₂ O ₃	0-13
	TiO ₂	0-5
Network breakers, basic oxides	CaO	22-45
	MgO	0-10
	BaO	0-10
Network breakers, alkali	Na ₂ O	0-20
	K ₂ O	0-5
	Li ₂ O	0-5
Network breakers, fluidizers	F	2-15
	MnO	0-5
	Fe ₂ O ₃	0-10
Melt speed control	C	2-20

The desired chemical composition can be obtained from a variety of raw material combinations. For the most part, cost and environmental concerns drive the raw material selection. With the exception of a few synthetic products such as cement and prefused materials, most raw materials are open-pit mined minerals and can have considerable variations in composition from batch to batch. For that reason, it is preferable that a mould powder be composed of a number of different raw materials. Some common raw material sources for mould powder production are listed in Table 2.

Table 2: Raw materials for mould powder production

SiO ₂	Feldspar, wollastonite, perlite, spodumine, cullet (crushed glass), fly-ash, quartz dust
CaO	Lime, limestone, wollastonite, cement, slags
Na ₂ O/K ₂ O	Sodium carbonate, potash, feldspar, sodium silicate, cullet (crushed glass)
F	Fluorspar, sodium fluoride, cryolite, hexafluorosilicate
Li ₂ O	Spodumine, lithium carbonate
C	Carbon black, coke dust, fine graphite, fly-ash

A large number of factors influence the melting rate of a mould powder and these are presented in diagrammatic form in Figure 2 [1].

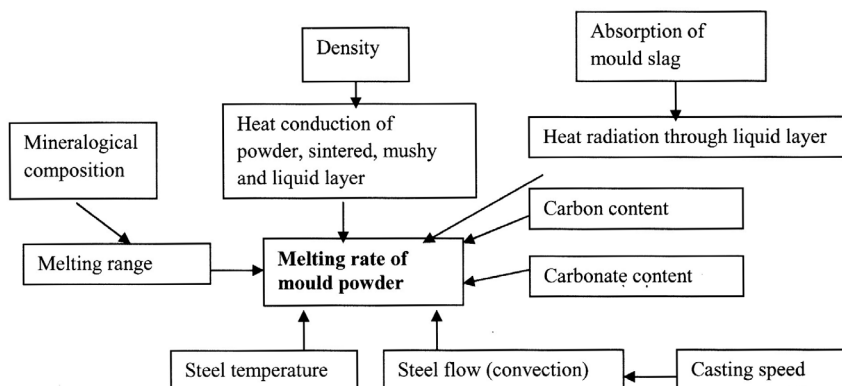


Figure 2: Schematic diagram showing the factors affecting the melting rate of mould powder

To construct a laboratory method to measure the melting rate of mould powders, the dominating factors which must be considered are:

- Heat flux through mould slag
- Content and type of free carbon in the mould powder
- Content of carbonates
- Oxidation and elimination of carbon.

Heat Flux Through Mould Slag

The total heat flux through the mould slag consists of three components:

- Heat flux by radiation
- Heat flux by conduction
- Heat flux by convection.

The heat flux by convection can be regarded as small because of a thin liquid slag layer. Also the conductive heat flux is low in mould slags according to [2].

The dominating factor regarding the heat flux is radiation. The radiative heat flux for a media between two infinite parallel plates with two different temperatures and emissivity's can, according to Deissler's equation, be written as:

$$q_{rad} = \beta(T_1^4 - T_2^4) \quad (1)$$

where:

$$\beta = \frac{n^2 \sigma}{\left(0.75\alpha d + \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1\right)} \quad (2)$$

The refractive index can be assumed to be 1.6 for all amorphous mould slags and with knowledge of its thickness, emission factors and temperature an approximate estimation with Deissler's equation regarding heat flux due to radiation can be done if the absorption index is known. The major part of heat flux by radiation through mould slags is within the infrared wave length of 0.7 – 3.0 μm and the absorption of slags must be determined in this region.

The elements that influence the absorption coefficient are mainly transition metal oxides, such as FeO, MnO, Cr_2O_3 and NiO. From investigation [3] a formula of the absorption at the wavelength of 2 μm was formulated as:

$$\alpha_{2\mu} = 30 + 910(\text{wt}\% \text{FeO}) + 5(\text{wt}\% \text{MnO}) + 390(\text{wt}\% \text{Cr}_2\text{O}_3) + 370(\text{wt}\% \text{Cr}_2\text{O}_3)^2 \quad (3)$$

An example of a calculation performed by Swerea KIMAB regarding the total heat flux for a commercial mould slag as a function of slag thickness according to Equation 1 is shown in Figure 3 for two steel temperatures, 1460 and 1520°C.

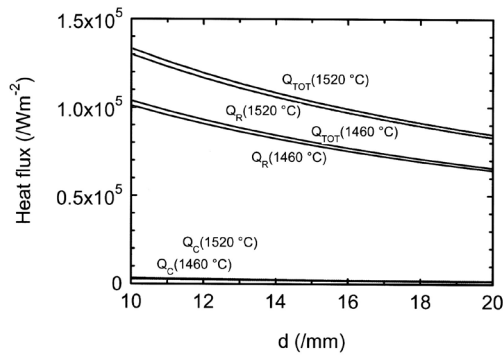


Figure 3: Heat flux through a mould powder slag. Q_c =Heat flux by conduction, Q_R =Heat flux by radiation, Q_{TOT} =Total heat flux

From Figure 3 the following conclusions can be drawn:

- Heat flux by convection is negligibly only 2-3% of total heat flux
- The heat flux is approx. 30% larger at a steel temperature of 1520°C (low carbon steel) compared to 1460°C (stainless steel)
- Increase of slag thickness will decrease the radiated heat flux due to higher absorption.

Influence of Carbon on Melting Properties of Mould Powder

Addition of free carbon to the mould powder is the most efficient way to control the melting speed. While mould powders are composed of a mixture of mineral components with a high melting point and fluxing agents, for example CaF_2 and Na_2O , the carbon particles delays the contact and sintering of the minerals. The carbon also delays the agglomeration of the slag droplets. The effect of carbon on melting speed is correlated to both the amount- and particle size of the carbon with finer carbon being much more effective in reducing melting speed. The particle size is dependent on the carbon source, which is illustrated in Table 3.

Table 3: Typical particle size and burn temperature for different carbon types [4]

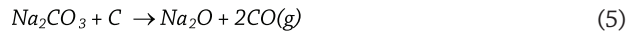
Type of carbon	Particle size, μm	Burn temperature, °C
Carbon black	0.028	386 - 522
Metallurgic coke	20	511 - 718
Graphite	74	613 - 897
Fine graphite	1.36	613 - 897

For melting of a mould powder to take place the carbon must be burnt either by oxidation from the air or by other oxidation agents as from the decarbonation of carbonates or to a minor extent from the reduction of iron oxide in the mould powder.

Influence of Carbonates on Melting Properties of Mould Powder

Temperature measurements from mould powder and mould slags collected during continuous casting is shown in Figure 4 [5]. It can be seen that the temperature increases quickly in the sintered layer around 750°C. This is because the carbonate, in this case 12.5 wt-% sodium carbonate, has gone through the majority of its energy demanding

thermal decomposition, which takes place between 550°C and 850°C. Decomposition of sodium carbonate (or other carbonates of other metals such as K and Li) can take place via two reactions:



Both reactions are endothermic. Up to around 700°C reaction (4) is expected to be dominant. Above that, reaction (5) will dominate

The effect of carbonates on the melting properties of mould powder is complex though, because it effects the melting in three ways, depending on amount of carbonates and free carbon:

- Decreased melting speed because of the cooling effect of the endothermic reactions (4) and (5)
- Increased melting speed because of reaction (4) and (5) which contributes to the elimination of carbon
- Increased melting speed because of convective gas heat transfer through the powder bed.

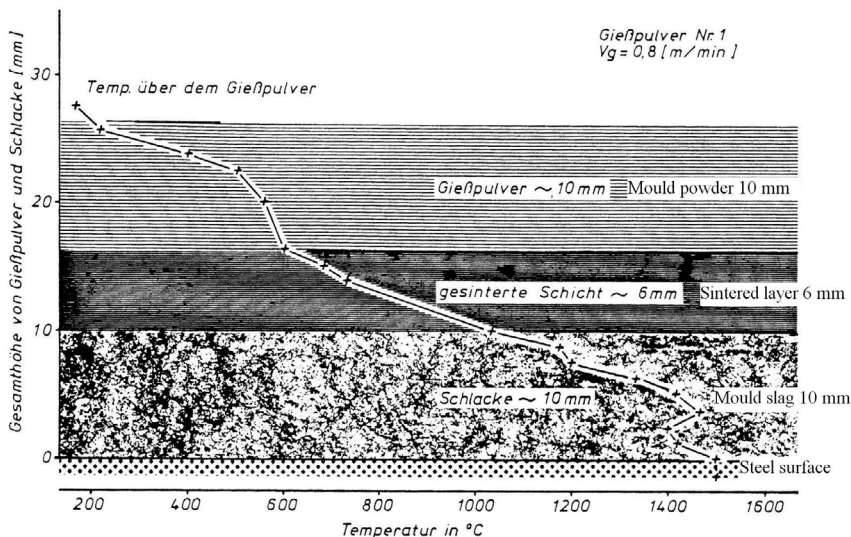


Figure 4: Temperature in mould powder and mould slag [5]

METHODOLOGY

From the theoretical survey regarding the main factors controlling the melting of mould powders the following demands can be put on a laboratory method for characterization of mould powder melting rate:

- The temperature of the bottom plate must be controlled at an aim temperature which resembles the steel temperature, e.g. 1500°C
- The slag thickness must be held at a controlled and stable thickness, e.g. 10 mm. This in turn demands a method with constant melting and flow of slag

- To control the burning of carbon, it must be possible to add air and force it on the powder layer in a controlled way (argon is forced through powder layer on most casters).

A number of laboratory methods have been developed during the years to measure the melting rate of mould powders subjected to unidirectional heat flow, simulating the casting conditions.

The methods can be divided into 3 groups:

- Crucible tests [6, 7]
- Molten slag drip test [8, 9]
- Mould powder on steel surface [10, 11].

All methods have disadvantages in one or another way. The methods in references 6, 7, 10 and 11 create an increasing slag layer and by that a growing absorption of radiation and as a consequence a decreasing powder melting rate and will not fully simulate the real process with a constant melting of mould powder and consumption of mould slag. The method described in references 8 and 9 does not have a constant slag thickness and also showed to be out of function for granulated mould powders because they fall out of the slag melting device due to their good fluidity. Of these reasons a new method for comparative testing was developed at Swerea KIMAB. This work was started as part of a Masters Thesis [12] which provides a basis for further development.

A schematic drawing of the equipment is shown in Figure 5b and the equipment during a trial at the laboratory at Swerea KIMAB is shown in Figure 5a. The mould powder is added via a water-cooled inlet cone into a graphite crucible, which is heated with an induction aggregate. The bottom temperature is computer-regulated at a temperature of 1500°C, with the aid of the signal from a thermocouple. The depth of the slag is kept at a defined value of 10 mm by a siphon construction of the cylinder walls which also prevents the granulated mould powder from flowing out of the crucible at start of the testing. During testing the mould powder is manually fed into the graphite crucible to a defined height and a defined flow of air is put upon the mould powder surface. The mould slag flows through the elongated openings in the crucible and the mould powder consumption is noted at certain intervals. The result from the testing is presented in the unit $\text{kg/m}^2 \cdot \text{s}$, that is, consumption as a unit of time in relation to the bottom area of the crucible.

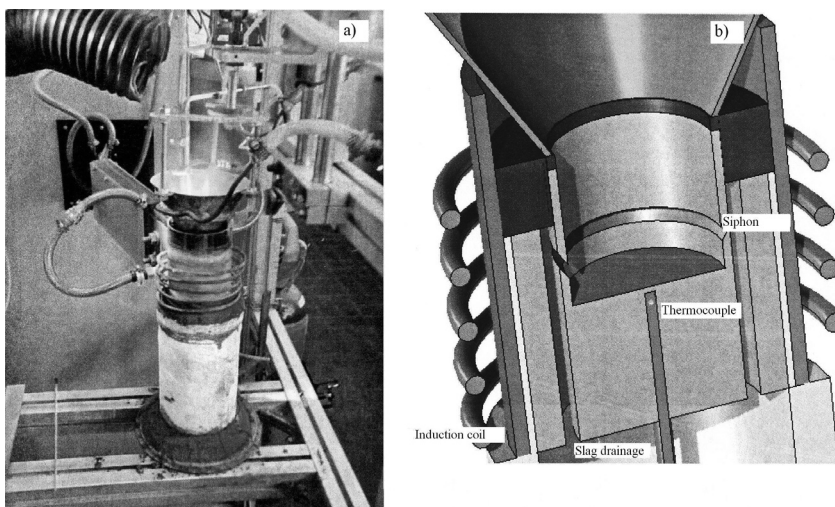


Figure 5: (a) Laboratory equipment during a trial, (b) schematic drawing of the test equipment

RESULTS AND DISCUSSION

To show the melting behavior of mould powders used for different casting process the test results of three mould powders is presented:

- A is used for continuous casting of stainless steels with $T_{liq} \sim 1460^{\circ}\text{C}$
- B is used for continuous casting of low carbon steels with $T_{liq} \sim 1510^{\circ}\text{C}$
- C is a fly ash based mould powder used for ingot casting of low carbon steels.

Table 4 shows the chemical composition for three tested mould powders.

Table 4: Chemical composition of tested mould powders

wt- %	Powder A	Powder B	Powder C
SiO ₂	29.0	30.7	38.0 – 48.0
CaO+MgO	34.3	38.0	2.0 – 8.0
Al ₂ O ₃	6.7	6.5	18.0 – 26.0
Fe ₂ O ₃	0.8	< 0.6	4.0 – 9.0
MnO	2.7	-	-
Na ₂ O*	8.0	8.4	9.0 – 11.0
F	7.9	9.1	-
Carbon free	1.13	3.6	3.0 – 4.0

* As carbonate

The result from the testing of the three powders is shown in Figure 6.

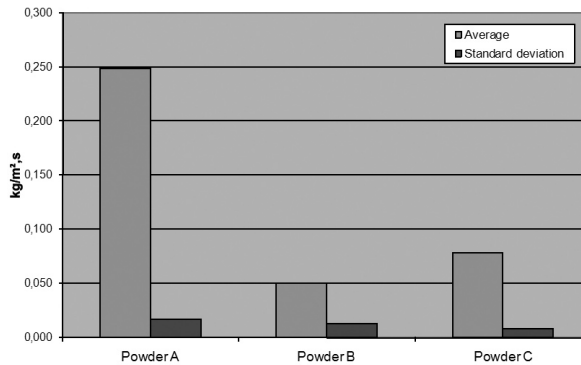


Figure 6: Results from testing of melting rate

To explain the results, the carbon consumption due to chemical reactions has been analyzed which is shown in Table 5 based on an amount of 100 grams of mould powder.

Table 5: Theoretical calculation of decarbonation, iron reduction and oxygen demand

	Powder A	Powder B	Powder C
Na ₂ CO ₃ (gram)	13.48	14.36	17.1
Carbon consumption for decarbonation (gram) Na ₂ CO ₃ +C → Na ₂ O+2CO(g)	1.55	1.63	1.94
Carbon consumption for reduction of iron oxide (gram) Fe ₂ O ₃ +C → 2FeO+CO(g)	0.06	0.03	0.49
Demand of extra oxygen for carbon burning (Ndm ³) 2C+O ₂ (g) → 2CO(g)	-	1.81	1.01
Air consumption for carbon burning (Ndm ³)	-	8.64	4.79

Comments:

- The low free carbon content of powder A explains its high melting rate. The CO₂ generated from the decarbonation is enough to burn off the carbon, no extra oxygen is needed which is a combination of a low content of free carbon and a rather high content of sodium carbonate.
- Powder B and C have about the same amount of free carbon but the melting rate of powder C is larger. The explanation is a higher amount of decarbonating components in powder C and also because it is based on fly ash its free carbon has of larger particle size (compared to mould powder B) which are less effective reducing the melting rate. The free carbon of mould powder B consists only of carbon black with very small particle size (see Table 3).

CONCLUSIONS

Based on the theory of the main factors which influence the melting rate of mould powders, a laboratory method for comparative testing has been constructed. The results from testing of a number of different commercial mould powders show a good resemblance to experience from trials at the steel plants. Especially wide format continuous casting of stainless steels has shown to be difficult to optimize regarding mould powder melting speed, due the low heat generated in the mould. The liquidus temperature as well as the fluid flow is low. Plant trials has shown that a reduction of the free carbon content from 3 to 1.2 wt-% results in an increase of mould slag depth from 4 to 10 mm.

NOMENCLATURE

α = Average absorption coefficient.

n = Refractive index.

ε_1 = Emissivity of plate 1 (steel surface).

ε_2 = Emissivity of plate 2 (sintered mould powder).

d = Thickness of media (slag thickness).

σ = Stefan Boltzmann's constant.

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