Steelmaking Slags as Raw Material for Sulphoaluminate Belite Cement

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Licentiate Thesis

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Abstract

The present work was undertaken as part of the research in the Minerals and Metals Recycling research centre, MiMeR. The course of the thesis is attributed to metallurgical slags from the steelmaking industry and the possible use of such by-products as raw material for sulphoaluminate belite cement (SAB). Implementing steel slags into the production of cement could contribute to the steel industry's possibility of increasing the recirculation. In addition to the previous objective, the introduction of slag into the cement manufacturing can also facilitate the reduction of carbon dioxide emissions as well as lowering the overall energy consumption during the manufacturing. The reason for this is that the SAB system enables the reduction of the lime saturation factor (LSF) which in turn implies that less limestone is needed in the raw meal. Additionally, the firing temperature can be reduced by about 100-150 °C, since dicalcium silicate and sulphoaluminate are formed already at approximately 1200-1250 °C. In any event, one should remember that this is not intended to be a final solution for the recycling of slag, nor a replacement for already accepted cement materials. A number of applications currently exist where ordinary Portland cement (OPC) is used, but in cases where the OPC could be replaced with other type of cements, e.g. SAB cement, the possibility of using residues material in cement applications is increased. Considering the clinker covered within this work, possible applications are those where slow hydraulic properties are suitable.

The behaviour of high temperature reactions of tested mixtures was investigated using thermogravimetric analysis coupled with a quadrupole mass spectrometer. Mineralogical observations were carried out with x-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The results proved that steelmaking slags have the potential to work as raw material, since sulphoaluminate along with polymorphs of dicalcium silicate and ferrite phases were detected after firing at 1200 °C in an air atmosphere.

The hydraulic properties of the specimens were analysed through conduction calorimetry, XRD, differential scanning calorimetry (DSC) as was the mechanical strength of the specimens when hydrated for 2 and 28 days. The compressive strength was in accordance with that suggested in the literature for slow hardening SAB cement. Both mixtures tested behaved the same with regard to heat development as well as the amount of AFt formed during the first 24 hours of the hydration.

List of Papers

The Licentiate Thesis is a summary of the following two papers,

- I. Seelmaking Slags as Raw Material for Sulphoaluminate Belite Cement

ADOLFSSON D., MENAD N., VIGGH E., and BJÖRKMAN B.

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- II. Hydraulic Properties of Sulphoaluminate Belite Cement Based on Steelmaking slags

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D. Adolfsson’s contribution to the papers:

- Firing of briquettes as well as the sample preparation before and after these trials.
- Simultaneous thermal analyses (STA), XRD and SEM-analyses
- Report compilation and interpretation

Papers not appended in the thesis:

- Steelmaking Slags as Raw Material for Calcium Sulphoaluminate Belite Cement
ADOLFSSON D. and VIGGH E. O.

The paper was presented by D. Adolfsson at the conference Securing the Future, 2005, in Skellefteå.

- Treatments of AOD Slag to Enhance Recycling and Resource Conservation
YANG Q., ENGSTRÖM F., TOSSAVAINEN M., and
ADOLFSSON D.

The paper was presented by Q. Yang at the conference Securing the Future, 2005, in Skellefteå.

- Thermodynamic Considerations of the Crystallisation Behaviour of Steelmaking Slags
ENGSTRÖM F., ADOLFSSON D., YANG Q., SAMUELSSON C., and
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1. Introduction

1.1 Background

There are good reasons for trying to implement the use of metallurgical by-products in the manufacturing of cement or alternatively as filler in the cement/concrete. One good reason is the limitation of a significant amount of slag being dumped each year. Another reason is the potential for decreasing energy consumption as well as decreasing carbon dioxide emissions within the cement industry.

So far steel slag has not been used very extensively in cement production. Recently, according to figure 1, only 1 % of the European steel slag was used for cement production in the year 2004 ¹. This might be partly explained in terms of classification as to whether it is considered as a product or waste. From a practical point of view, it is important to avoid fluctuations in the composition. Although the presence of free lime could be an advantage, acting as an activator if blended with Portland cement, it might still cause trouble in terms of expansion. Apart from free lime (CaO), MgO might also be the cause of volumetric expansion as it also reacts with water to form magnesium hydroxide and thereby limits the practical use of a cement within civil engineering. The volumetric factor is at least one limitation to be mentioned in relation to construction. Fluctuations

though, can be compensated for if the material is blended with, for instance, ground granulated blast furnace slag, GGBS ².

Fig. 1. The use of steelmaking slags in Europe 2004 ¹.

Alternatives to ordinary Portland cement (OPC) of which the sulphoaluminate belite cement (SAB) is an important option, have been and are still under investigation. The advantage of producing SAB compared to OPC is the reduction of the lime saturation factor (LSF), which enables the reduction of CO₂ emissions ³, but also the firing temperature which can be lowered by about 100-150 °C ⁴. The latter is possible to accomplish since both sulphoaluminate and dicalcium silicate are formed at lower temperatures, at which tricalcium silicate is not formed. Furthermore, since large amounts of steelmaking slags cannot be introduced into ordinary cement production due to heavy metals and free MgO (which in the OPC is suggested to be lower than 5 %), it is reasonable to look for alternative

compositions which are accompanied by the possibility of saving energy as well as decreasing the release of carbon dioxide emissions.

A lot of research has been done in the field of SAB cement especially in the area of civil engineering. The use and development of sulpho- and ferroaluminate cements in China are, for instance, very well reviewed by Zhang et al.⁵. However, other investigations, where raw materials other than virgin materials are used, have been completed. Arjunan et al.⁶ obtained similar results as those obtained with OPC when using bag house dust, low-calcium fly ash (Class F fly ash) and scrubber sludge in different proportions. The aim was to produce environmentally friendly cement. Low-temperature phases were detected and the usefulness was, for instance, confirmed by the compressive strength. Another example comes from the properties of blended SAB cement as investigated by Zivica⁷. For the synthesis of SAB cement, a mixture of limestone, gypsum, fly ash and pyrite ash was used and heated at 1250 °C. The SAB cement was further mixed with 5, 15, and 30 % granulated BF slag, fly ash, and silica fume, respectively. It was partly concluded that SAB blends with additions of 5-15 % portions of pozzolana seemed to be optimal. Furthermore, the effect of blending was stated as being dependent on the activity of pozzolans and the properties of the SAB cement, in relation to the content of β -C₂S. A more theoretical work was performed by Majling et al.,⁸ where the objective was to forecast the mineralogical composition of SAB cement based on fly ash using modified Bouge computations. A relationship was established between the raw

material and the mineralogical composition of clinker material which was considered very useful in the further development of SAB cements based on fly ash. The present work is focused on the potential of steelmaking slag, when it is the major part of a raw material used for SAB cement. Four different mixtures were prepared from various proportions of common steelmaking slags, i.e. MixA, MixB, MixC and MixD. The high temperature reactions in tested mixtures were investigated using thermogravimetric analysis coupled with a quadrupole mass spectrometer. Mineralogical observations were carried out using x-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The hydraulic properties of the specimens were analysed through conduction calorimetry, XRD, differential scanning calorimetry (DSC) as well as testing of the mechanical strength of the specimens when hydrated for 2 and 28 days.

1.2 Ordinary Portland cement

OPC is well known and traditionally used within the field of civil engineering. Additionally, the raw materials are rather cheap. However, since the raw meal is based on limestone and clay, the manufacturing is accompanied by a significant amount of carbon dioxide and high energy demands during firing of the raw meal and grinding of the final clinker. OPC consists of four major crystalline phases, see table 1.

Table 1.
The main crystalline phases in OPC.

Compound	Oxide composition	Abbreviation
Tricalcium silicate	$3\text{CaO}\cdot\text{SiO}_2$	C_3S
Dicalcium silicate	$2\text{CaO}\cdot\text{SiO}_2$	C_2S
Tricalcium aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	C_3A
Tetracalcium aluminoferrite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	C_4AF

Normally, the content of C_3S is in the range of 50-65 %, C_2S 15-25 %, C_3A 8-14 % and C_4AF 8-12 % ⁹. Silicates provide strength to the cement as it reacts with water. The strength of the material early on is due to the C_3S , while C_2S is of more importance after 28 days.

1.3 Steelmaking slags

Slag from the steelmaking industry can be generated either from integrated steel plants or scrap based steel production. The different types of slag within the integrated plants are blast furnace (BF), basic oxygen furnace (BOF) and ladle slag. In scrap based production, the categorisation would entitle them: electric arc furnace (EAF), argon oxygen decarburisation (AOD), as well as ladle slag. There are a number of reasons for using slag in the steelmaking process. One purpose is to extract metal oxides and impurities from the metal bath into the slag. Additionally, it acts as a thermal insulator.

1.3.1 Generation of BF slag

There have been different ideas of how to use slags within the cement area. Most widely used is the BF slag, which can be used either as it is, if granulated, or blended with OPC, i.e. slag cement.

The BF process in Sweden is run with iron ore pellets, i.e. hematite, and it produces approximately 150 kg slag/t hot metal. Coke is used as a reduction agent as it produces CO (g) after reaction with oxygen. The overall reaction between CO (g) and iron oxide can be written as follows, $\text{Fe}_2\text{O}_3 + 3\text{CO(g)} \rightarrow 2\text{Fe} + 3\text{CO}_2\text{(g)}$ ¹⁰. The liquid slag (when used for cement) is usually granulated (quenched in water) since the granulation offers a very amorphous material (glassy phase) which is easy to grind, resulting in excellent hydraulic properties. Main minerals which usually occur in this by-product are melilite ($2\text{CaO} \cdot (\text{Al,Fe})(\text{Al,Si})\text{O}_3 \cdot \text{SiO}_2$), merwinite ($3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), and wollastonite ($(\text{Ca,Mg})\text{O} \cdot \text{SiO}_2$) ¹¹. It is, however, sometimes appropriate to further activate the slag by increasing the lime content and thereby the basicity or by other means. Generally, granulated BF slag is considered to have slow hardening hydraulic properties if compared to OPC. However, tests of highly aged slag have proven that it becomes at least as strong as OPC does after 28 days of hydration and thereafter, it continues to increase in strength and does not level off as the OPC does ¹².

1.3.2 Generation of BOF slag

In the BOF converter, the melted iron is mixed with steel scrap. Thereafter, oxygen with reasonably high pressure is blown towards the surface of the melt in order to reduce the carbon content. There are, however, techniques where oxygen can be injected from the bottom too. At this stage of the process, slag formers are added as well i.e. burned lime and/or dolomite lime. The most important reactions taking place are ¹³,

Other elements such as vanadium and phosphor are converted into oxides in the slag as well. In order to dissolve the lime more quickly it is possible to add CaF_2 . The latter enables the reduction of the melting point of the lime. As the lime dissolves into the slag, the viscosity will increase. Consequently, the fluidity of the slag starts to decrease compared to the properties of the individual constituents, mainly SiO_2 , MnO and FeO . At the time the steel is being tapped from the converter, some alloying elements are added. BOF slag is normally air cooled and consists basically of C_3S , C_2S , $(\text{Fe, Mg, Mn})\text{O}$, C_2F and free lime. Most of the iron occurs mainly as wuestite (FeO) but can

also be present as hematite ¹⁴. The BOF slag most often does not disintegrate, i.e. no phase transformation of $\beta\text{-C}_2\text{S} \rightarrow \gamma\text{-C}_2\text{S}$, since the phosphor has a stabilising effect on the $\beta\text{-C}_2\text{S}$ ¹⁴. In those cases where the slag consists of a high amount of C_3S , the tricalcium silicate usually decomposes to the non-hydraulic and disintegrating $\gamma\text{-C}_2\text{S}$ due to slow cooling conditions. However, free lime and periclase hydrate when in contact with water. As a result, the use and availability in the field of civil engineering is limited due to volumetric expansion. Possible variation in the composition is usually dependent on the raw materials used, as well as the practice in both process and slag handling. The typical level of BOF slag produced within a Swedish steel plant reaches about 100-120 kg per tonne of steel.

1.3.3 Generation of EAF slag

EAF slag originates from the electric arc furnace, which is a unit operation within the scrap based steelmaking production. The formation of slag is essentially based on additions of burned lime, dolomite and possibly also fluorspar and sand, ¹¹. In Sweden, the slag is produced in the ratio of approximately 90 kg per tonne of steel, on average. It is generally accepted that the hydraulic properties of these slags increase with higher basicity, i.e. higher content of CaO. If dolomite is used during the process, the presence of MgO will increase as well ¹⁵. The main difference between BOF slag and EAF slag is probably the presence of free lime which in EAF slags is of a lower magnitude. However, the amount of free MgO that remains in the slag gives problems with regard to volumetric expansion. Primary minerals to be found in the final slag are merwinite (C_3MS_2), $(Fe, Mg)_2SiO_4$, C_3S , C_2S , C_4AF , C_2F and solid solutions of $(Ca, Fe, Mn, Mg)O$ ¹⁶.

1.3.4 Generation of AOD slag

The principal difference between the AOD process of stainless steel production compared to the BOF at integrated steel plants is the use of Ar-gas in addition to oxygen. The reaction between an oxygen-argon mixture and the steel bath lowers the carbon content in the steel bath, while at the same time, the oxidation of chromium to the slag can be kept at a low level. In the beginning of the operation, silica and manganese originating from the scrap is oxidised. After the blowing operation, the slag will consist of these elements along with the addition of lime and usually also fluorspar, made during the process. The top-slag (after the decarburisation period) usually reaches a level of 70 kg per tonne of steel ¹⁷.

1.3.5 Generation of secondary metallurgical slags

There are different kinds of secondary metallurgical slags, i.e. slags from the refining of the steel in ladle metallurgy. The composition might vary somewhat depending on the steel grade, but the final mineralogical composition can be summarised as follows: dicalcium silicate, merwinite, calcium aluminates, as well as free lime and periclase.

1.4 Sulphoaluminate belite cement

SAB cement refers to the phase assemblage $C-S-A-\bar{S}$ ¹⁸, and the major phases present within the system are given in table 2. Since the belite phase (C_2S) itself does not bring any high early strength to the cement activation of the hydration mechanism is needed³. Basically, this is the role of sulphoaluminate ($C_4A_3\bar{S}$) as its properties substitute for those of tricalcium silicate in order to provide sufficient early strength. Depending on what properties are required for a specific application, the quantity of each phase present can be adjusted. High amounts of sulphoaluminate provide high early strength to the cement, but it also contributes to good corrosion resistance and controllable expansion⁵. Generally, raw materials used for this type of cement are limestone, bauxite and gypsum, which are calcined at 1300-1350 °C¹⁹. Another possible alumina source according to Glasser and Zhang¹⁹ could be red mud, a by-product from the Bayer process.

Table 2.
The main crystalline phases in the SAB system.

Compound	Oxide composition	Abbreviation
Yeeliminite	$4CaO \cdot 3Al_2O_3 \cdot SO_3$	$C_4A_3\bar{S}$
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S
Calcium sulphate	$CaO \cdot SO_3$	$C\bar{S}$
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF
Free lime	CaO	C

1.4.1 Hydration of dicalcium silicate

Dicalcium silicate contributes to the late strength of the cement, as in OPC. The hydration product produced is very similar to the calcium silicate hydrate gels (C-S-H) formed through tricalcium silicate ²⁰, according to the following overall reactions (5) and (6) ²¹,

analogous to,

Since calcium sulphate is present, the C-S-H might be slightly modified in terms of having some sulphate incorporated in the structure ²¹.

1.4.2 Hydration of sulphoaluminate

The function of sulphoaluminate is the same as for tricalcium silicate in Portland cement, but forms instead ettringite ($C_6A\bar{S}_3H_{32}$) also abbreviated AFt, after reaction with calcium sulphate and water. Both of the following reactions give the overall hydration mechanism for sulphoaluminate, however, the second one is considered in case of expansion ²².

1.4.3 Hydration of the ferrite phase

In OPC, tricalcium aluminate reacts very quickly with water and gypsum to form AFt. Further on, AFt continues to react with C_3A to form monosulphate (AFm). The ferrite phases follow the same sequence as tricalcium aluminate, but much more slowly, with respect to the formation of AFt. The overall reaction can be written according to reaction (9) (unbalanced),

Still, this is also a relatively rapid reaction and takes place at the very early stage of hydration. As in the case of C_3A , C_4AF forms AFt and contributes both to the early and late strength of the cement in the SAB system¹⁸. Since no tricalcium aluminate is present in the SAB system, there will be no competition between the two phases regarding the reactivity with calcium sulphate²⁰ and, thus, the ferrite phase will be considerably more reactive in the SAB cement in comparison to the OPC system. In addition, the absence of C_3A also prevents a reaction between the latter and ettringite to form monosulphate.

1.4.4 Hydration periods

Considering OPC, different periods are usually discussed in the following order: the initial period, the dormant period, the acceleration phase, the deceleration phase, and an ever-slowng reaction phase ²³. In the first period, hydrolysis and release of ions into the solution take place, and the reactions are characterised as very rapid and exothermic ²⁰. Within the first couple of minutes, the heat evolved is due to the hydration of sulphate, the formation of AFt, as well as the wetting ²⁴. Then, after the dormant period, which might last between 30 minutes and 2 hours, the next heat liberated is attributed to the hydration of C₃S, and after approximately 12-15 hours of hydration, AFt will react with aluminates to form “monosulphate” (AFm) ²⁴. An important difference between the OPC and the SAB system is the final products. The SAB paste generally is constituted by AFt, AFm, alumina, and ferrite gel ⁵. The AFt phase, however, is not a final product of the OPC paste. The hydration periods previously discussed are believed to be somewhat applicable to the SAB system as assumed in the further discussion.

2. Material and experimental procedure

2.1 Material

Steelmaking slags and additives were combined according to table 3, as predicted by using modified Bouge calculations. The calculation is based on a chemical analysis from which a mass balance can be performed. Since there are five initial phases to be considered, the mass balance contained five different linear equations according to the general matrix given below,

$$\mathbf{Ax}=\mathbf{b} \Leftrightarrow \begin{bmatrix} a_{11} & a_{12} & \cdots \\ a_{21} & a_{22} & \cdots \\ a_{31} & \vdots & \\ \vdots & & \end{bmatrix} \cdot \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \end{bmatrix}.$$

The variables in the matrix refer to the weight fraction of each oxide in question, in relation to the actual mineral it makes up. Thus, $a_{11}=(M_{\text{CaO}}/M_{\text{C}_2\text{S}})$ and b_1 = total fraction CaO, i.e. the amount given from chemical analyses, and, finally, the $x_1= \text{C}_2\text{S}$ phase can be calculated. The same method is applied to SiO_2 , Al_2O_3 , Fe_2O_3 and SO_3 . From this system of equations, the potential phase composition can be estimated by finding the inverse matrix, $\mathbf{A}^{-1}$, when $\det(\mathbf{A}) \neq 0$. Since this is only a mass balance, there are no thermodynamic or kinetic considerations within the calculations.

Four mixtures were prepared, i.e. MixA, MixB, MixC, and MixD (see table 3). The fractions of each slag given within each mixture exemplify possible combinations giving the desirable phase composition i.e. the fractions given are not a unique solution, and thus other combinations are possible as well. The aim of this work was to combine different slags in such a way that it could demonstrate the potential of all kinds of steelmaking slags. MixA contained 70 % slag, of which 55 % was AOD slag and 15 % ladle slag, along with limestone, gypsum and an alumina rich material, containing 10 % of each additive. MixB contained 64 % slag, of which only 14 % represents AOD slag in this mixture.

Table 3.
Mixtures prepared in wt-%.

Material	Mix A	Mix B	Mix C	Mix D
AOD slag	55	14	-	-
EAF	-	25	25	-
BOF	-	-	14	-
Ladle slag	15	25	25	100
Gypsum	10	5	5	-
Alumina*	10	6	6	-
Limestone	10	25	25	-
Total	100	100	100	100

* The alumina source consists approximately of 5 wt-% CaO, 74 wt-% Al₂O₃ and 21 % SiO₂

The rest of the slag content consisted of 25 % ladle slag and 25 % EAF slag, resulting in a higher total amount of additives, i.e. 25 % limestone, 6 % alumina and 5 % gypsum. MixC was more or less the same as MixB. The only difference was the substitution of 14 % AOD slag by BOF slag. Finally, MixD only consisted of ladle slag.

In table 4, the analysed chemical composition of each mixture is presented, along with the calculated potential phase composition. It is important to point out that, in the chemical analyses, iron is given as Fe_{tot} and sulphur as elemental, S^0 . However, in the mass balance discussed, these elements have been recalculated as Fe_2O_3 and SO_3 and, thus, all iron present is assumed to be Fe_2O_3 and sulphur, as SO_3 . In addition, since only five linear equations have been chosen, the total phase composition of the desired phase assemblage will not be 100 %.

Table 4.
Analysed chemical composition of each mixture in wt-%.

Mixture	CaO	SiO ₂	Al ₂ O ₃	Fe _{tot}	MgO	S _{Leco}	C _{Leco}
Mix A	46.5	20.2	15.5	2.7	4.3	2.0	1.4
Mix B	40.7	12.7	14.1	8.9	6.3	0.9	3.0
Mix C	39.2	9.7	13.6	11.0	7.4	0.9	2.9
Mix D	45.5	18.8	20.3	1.1	9.7	1.3	1.0

Calculated potential phase composition in wt-%							
Mixture	C_2S	$C_4A_3\bar{S}$	C_4AF	$C\bar{S}$	C	Total	LSF
Mix A	58	26	12	3	-	99	0.60
Mix B	36	12	39	1	-	88	0.67
Mix C	28	7	48	2	-	85	0.73
Mix D	54	38	5	-	-	97	0.58

The result of the mass balance indicates that, dicalcium silicate is expected to be one the dominating mineral in each mixture. The main difference is the amount of ferrites and sulphoaluminate. Both MixB and MixC give a considerably higher amount of ferrites, i.e. 39 wt-% and 48 wt-% respectively, while sulphoaluminate is estimated to be 26 wt-% in MixA and 38 wt-% in MixD.

2.1.1 Particle size distribution

The fineness of samples before and after firing was determined by a Malvern 2000, which is an optical sizing unit, and the measurement was performed by Cementa Research AB, Sweden. Figure 5a-d, in paper 1 show the particle size distribution before firing. These figures reveal that MixB gives a $d_{50} \approx 15 \mu\text{m}$ while other mixtures reach approximately $d_{50} \approx 20 \mu\text{m}$.

2.2 Experimental procedure

2.2.1 Thermal analysis

The measurements of the thermal analysis coupled with quadrupole mass spectrometer, QMG 420, were carried out simultaneously using the Netzsch STA 409 equipment shown in figure 2. 100-mg test materials were contained in an alumina crucible and subjected to a programmed heating of 10 K/min in an air atmosphere, in the temperature range of 25 to 1400 °C. A TG/DTA (thermogravimetric and differential thermal analyses) sample holder with an alumina crucible was positioned on a radiation shield in order to protect the balance. In order to correct for the Buynce effect, an empty crucible was run (correction data) before analysing the sample, i.e. the investigated samples were tested in the mode TG/DTA sample + correction. The gases formed during the reaction were identified using quadrupole mass spectrometer (QMS) measurements connected to the STA equipment. In a high-frequency, quadrupole electric field, it is possible to separate ions according to their mass/charge ratio.

Fig. 2. Schematic of Netzsch STA 409.

2.2.2 Sample preparation and firing of briquettes

Each slag was crushed, using a jaw crusher, and divided into representative samples using a rotary splitter and ground in a rod mill for approximately 25 minutes. The slags were further combined to produce the mixtures given in table 3. In order to get a good homogenisation and a fairly fine powder-like material, the mixtures were once again introduced to a rod mill and run for approximately 60 minutes. The ground mixtures were prepared as briquettes with the approximate dimension of $\varnothing \times H$, i.e. 2x4 cm before firing in order to get good contact between particles and then dried in an oven for 24 hours at 100 °C. The briquettes were fired in a furnace with an air atmosphere at 1200 °C for approximately 30 minutes followed by

water cooling. The cooled briquettes were dried in an oven for 24 hours at 100 °C and then examined by x-ray diffraction, XRD and scanning electron microscopy, SEM.

2.2.3 XRD and SEM analyses

A Siemens D5000 X-ray powder diffractometer with CuK α radiation at 40 kV and 40 mA was used in order to identify crystalline clinker phases before and after firing of briquettes. The analyses were run with step scan, i.e. 4 seconds per step in the $\sin 2\theta$ -range 10-90°.

Observations of sulphoaluminate and AFt in the investigated samples were performed with SEM using a Phillips XL 30 equipped with energy dispersive spectra, EDS in the 20 keV range. The material was first dispersed (10 - 20 mg) in a few millilitres of ethanol, and then, while sonicating, a sample of the pulp was taken out with a pipette. One drop was placed on a double sided carbon tape. Thereafter, the samples were sputter coated with gold.

2.2.4 Conduction calorimetry

Isothermal calorimetry was performed on a TAM air (Thermal Activity Monitor) instrument from Thermometric using glass ampoules. The instrument is an 8-channel heat flow calorimeter for heat flow measurements in the milliwatt range and the measurement was performed on mixtures and an ordinary Portland cement. Duplicate samples were performed using, 100 ml /sample with a w/c-ratio =0.5 for 24 hours at 20 °C. The tests were performed by Cementa Research AB, Sweden.

2.2.5 Preparation of mortars

The fired briquettes were ground with a rod mill for 25 minutes followed by a vibration mill for 25 minutes. Next, the material was run through a magnetic separation and then divided into three representative samples using a Jones riffle. In one of the dividers, 5 % gypsum was added, and in a second one, 10 % gypsum was added, while the third sample was left untreated with regard to the addition of gypsum. The three dividers were then once again ground separately with a vibration mill in order to get a close particle size distribution and good homogenisation of those to which additions of sulphate were made. Finally, material from all three of the samples was taken out using a Jones Riffle for further determination of the particle size distribution of each sample.

2.2.6 Compressive strength

Mortar prisms with the dimension of 25x25x285 mm were prepared and tested by Cementa Research AB, Sweden. The material was blended with sand and water in the ratio 3:1:0.5 and hydrated for 2 and 28 days. In the first 24 hours, the mortars cured in a moisture chamber with 95 % relative humidity at 20 °C. Thereafter, the moulds were cured in water at 20 °C until the mechanical strength was tested.

2.2.7 X-ray diffraction, XRD, - observation of AFt

Confirmation of AFt was carried out on a Phillips X'pert Pro diffractometer with CuK α radiation and an “X’celerator” detector. The scanning was made after 24 hours between 7-50° in the sin2 θ -range and performed by Cementa Research AB, Sweden.

2.2.8 Differential scanning calorimetry, DSC

The DSC experiment was run on a DSC 7 Perkins Elmer Differential Scanning Calorimeter to analyse the formation of AFt. This was performed by mixing a sample with water, but in order to stop the hydration, acetone was added. Thereafter, the sample was filtered and the moisture mass which was left was ground and heated with the DSC instrument (20 °C/min) as well as analyzed by XRD in order to confirm the presence of AFt. The tests were performed by Cementa Research AB, Sweden.

3. Results and Discussion

3.1 Simultaneous Thermal Analysis, STA

TG/DTA measurements in an air atmosphere were carried out for all mixtures, see table 5.

Table 5.

Weight loss in wt-% and gas release in ion current observed by TG/DTA/QMS-analyses at specific temperature ranges.

Mixture	Temperature range			Total weight loss
	100-150°C	700-800°C	1300-1400°C	
MixA	-3.56	-4.23	-3.61	-11.4
MixB	-1.35	-9.35	-2.15	-12.9
MixC	-1.57	-9.05	-1.80	-12.4
MixD	-1.02	-2.49	-0.05	-3.6
Gases in ion current $10 \cdot 10^{-10}/\text{A}$				
	H ₂ O	CO ₂	SO ₂	
MixA	3.5	2.8	0.4	
MixB	1.4	5.6	-	
MixC	1.5	5.6	0.2	
MixD	0.43	0.98	-	

The results show that the highest weight loss is obtained in the temperature range of 700-800 °C, see table 5. This weight loss is especially pronounced for MixB and MixC with about 9 wt-%, each. That implies a weight loss of approximately 7 and 5 wt-% more than was observed for MixA and MixD, where losses of only 4 and 2.5 wt-% were reached, respectively. In any event, since more calcite exists from the start in MixB and MixC, it should consequently result in a higher percentage of weight loss at the given temperature. It also implies that much less CO₂ is released compared to OPC, where the CO₂ emissions generally reach about 40 %. In general, the calcination starts at 700 °C, according to reaction (10), and the maximum is reached between 750-800 °C, independently of the composition of the mixture in question (table 5).

The Differential Thermogravimetry results, DTG (given in paper 1), show agreement with the corresponding gas emissions, i.e., the released moisture and carbon dioxide emissions, at the aforementioned temperatures. The last small effect at rather high temperature, i.e. 1300-1400 °C, is related to the evaporation of sulphur dioxide due to the decomposition of gypsum. The SO₂ emissions, however, were only registered in the case of MixA and MixC, which can also be seen from the results of the evaporated gases in table 5. Although MixB and MixC are very similar in composition and behave very much the same, no sulphur dioxide could be detected from MixB. The sulphur present is presumably consumed in the clinker formation.

The weight loss for MixD in this temperature range was 0.05 wt-%, which is neglectably low.

The various reactions taking place are partly related to the formation of sulphoaluminate. From a general point of view, the process, it starts at approximately 1000 °C, according to reaction (11), and depending on which mixture is being used. In the context of kinetics, the firing conditions strongly influence the completeness of formation, as well as the amount of mineralising elements.

In slags, where dicalcium silicate already is present, the polymorphic transformation of $\gamma \rightarrow \alpha'_L$ usually takes place at 900 °C and, furthermore, $\alpha'_L \rightarrow \alpha'_H$ at 1180 °C²⁵. These kinds of transition states also contribute to the observations made by DTA. Subsequently, different reactions take place simultaneously resulting in overlapping endothermic and exothermic sequences. As a result, each peak obtained cannot be easily designated to a specific reaction, e.g. whether it is a matter of phase transformation or mineralising reactions occurring. Complete data with figures of the TG/DTA/QMS results are found in paper 1.

3.2 Furnace trials

While all mixtures have white and grey nuances in colour before being fired, figure 3, the difference in composition becomes clear afterwards, indicating the formation of new phases in different proportions. While MixA and MixD are somewhat light brown and light green, it can be noticed that MixB and MixC are rather dark brown (figure 3). The brown colour is especially sharp in the case of MixC.

Fig. 3. Mixtures before and after firing, giving the differences in colour.

3.3 X-ray diffraction, XRD

XRD analyses were carried out in order to determine the clinker forming reactions that have occurred. The analyses of the investigated samples are summarized in table 6. In the raw material of MixA, XRD revealed the presence of calcite, merwinite, calcium silicate (non-hydraulic), and akermanite as major phases. After the mixture was fired, none of these phases appeared. Instead, sulphoaluminate, also referred as yeeliminite, was detected along with bredigite, which is an α' -structure of dicalcium silicate. Apparently, calcite reacted with alumina and sulphate to form the sulphoaluminate phase, as expected. It is not clear, though, to what extent the mayenite phase reacted with the calcium sulphate present, forming sulphoaluminate. In any event, since no mayenite or other alumina phase was detected afterwards with the exception of sulphoaluminate, its contribution to the formation of sulphoaluminate can be assumed. The latter is presumably applicable in the case of MixD, too. Without any additives at all, a single ladle slag fired at 1200 °C forms all the desired clinker minerals, along with some free periclase, already present from the start. Since no alumina and sulphate were added, it is reasonable to assume that mayenite, being one of the major minerals in this material, reacts with gypsum to form sulphoaluminate. However, it could also be that the mayenite partly contributes to the brownmillerite formation in this case. Furthermore, in the ladle slag, tricalcium aluminate was found which also could contribute to the

sulphoaluminate formation. Silicates present in MixA and MixD, such as akermanite and merwinite, are believed to be part of the formation of bredigite, and larnite, as would be expected. The raw meal of MixB and MixC contained the same minerals, but in different proportions. Apart from additives, the major phases detected were calcium silicate, mayenite, periclase and wuestite. Important differences were detected after firing. The clinker material of MixB agreed better with the estimated phase composition, according to the modified Bouge calculation, than MixC did. MixB gave higher intensities of sulphoaluminate and brownmillerite than MixC which instead contained a calcium magnesium alumina iron silicate structure. All together, substituting AOD slag by BOF slag clearly influences the final composition. The latter, detail, however, does not generally imply that AOD slag is preferable.

It is worthwhile to mention that the light green colour observed in figure 3 for MixA and MixD could be due to the non-hydraulic phase $2\text{C}_2\text{S}\cdot\text{CaSO}_4$, which is not unreasonable to assume at the temperature in question, as α' - C_2S reacts with CaSO_4 ²⁶. However, since this phase was not detected by XRD, the likely amount is approximately < 3 % otherwise it would have been detected.

Table 6.

The most abundant minerals detected by x-ray diffraction before and after firing. B=before firing and A= after firing.

Nr.	Mineral		Mix A		Mix B		Mix C		Mix D	
	Name	Chemical formula	B	A	B	A	B	A	B	A
1	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$								
2	Calcite	CaCO_3								
3	Corundum	Al_2O_3								
4	Periclase	MgO								
5	Calcium silicate	$\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$								
6	Mayenite	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$								
7	Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$								
8	Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$								
9	Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$								
10	Wuestite	FeO								
11	Yeeliminite	$4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$								
12	Bredigite	$\text{Ca}_{1.7}\text{Mg}_{0.3}\text{SiO}_4$								
13	Lamite	$\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$								
14	Brownmillerite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$								
15	(Ca,Mg, Al, Fe) silicate	$\text{Ca}_2\text{Mg}_{0.2}\text{AlFe}_{0.6}\text{Si}_{0.2}\text{O}_5$								
16	Calcium iron oxide	CaFeO_3								
17	iron	Fe								

3.4 Scanning electron microscopy, SEM, - observation of sulphoaluminate

SEM analyses were performed to actually view the presence of sulphoaluminate. Figure 4a-d, show the observations from the sulphoaluminate phase. Figure 4a represents what was found in MixA, i.e. a hexagonal tabular structure²⁶, and the composition of that structure is confirmed by the energy spectra, EDS. The same kind of structure can be seen in Mixes B-D, and is confirmed with EDS analyses (see figures 4b-d). The general impression of the samples was that a larger amount of sulphoaluminate was formed in MixA, in comparison to MixB, MixC, and MixD.

Fig. 4a. SEM/EDS of MixA.

Fig. 4b. SEM/EDS of MixB.

Fig. 4c. SEM/EDS of MixC.

Fig. 4d. SEM/EDS of MixD.

3.5 Particle size distribution of mortars

From figure 5, it can be seen that all samples of MixB are clearly finer and possess lesser variation among individuals of the same mixture compared to those of MixA. All MixB-samples have a $d_{80} \approx 50 \mu\text{m}$, while MixA 0% and MixA 10 %, approximately reach a $d_{80} \approx 80 \mu\text{m}$, and MixA 5% a $d_{80} \approx 70 \mu\text{m}$, i.e. somewhat finer. The difference is partly assumed to be due to the presence of a varying content of metal drops in MixA, but it could also be explained in terms of grindability. The magnetic separation of metal drops in the slag from production of ordinary steel is much easier than for those originating from the stainless steelmaking process. In MixA there is a substantial amount of AOD slag, i.e. 55 %. All MixB blends give an acceptable particle size distribution, and instead of differing among individual samples, the blends are very closely distributed. It is well known that the particle size is an extremely important parameter, since it has a considerable affect on the hydration mechanism and thereby the final strength of the cement/concrete.

Fig. 5. Particle size distribution of MixA and MixB with and without addition of gypsum.

3.6 Compressive strength

The results for the compressive strength are listed in table 7. The value given for each mixture represents the mean value of four tests and was measured after 2 and 28 days, according to standards.

Table 7.
Compressive strength developed for each mixture of MixA and MixB after 2 and 28 days of hydration.

Specimen	Compressive strength (MPa)	
	2 days	28 days
MixA 0% Gypsum	0	7.0
MixA 5% Gypsum	4.2	8.5
MixA 10% Gypsum	4.0	8.3
MixB 0% Gypsum	3.7	12.0
MixB 5% Gypsum	7.5	13.5
MixB 10% Gypsum	7.6	12.3

Apparently, all MixA samples possess hydraulic properties that are lower than those of MixB. The compressive strength of MixB is almost twice as high after two days of hydration. At the level of 28 days of hydration, MixA 5% increased by 4.3 MPa, yielding 8.5 MPa, which is significantly lower than MixB 5%, the strength of which was determined to be 13.5 MPa. If no addition of gypsum was added, the mortar of MixB 0% measured 3.7 MPa after 2 days, but that is markedly higher than MixA 0%, which did not provide any strength at

all. However, even when gypsum was added, it did not bring a result as satisfactory as that of MixB, independent of the amount of gypsum added. In MixB, the composition is estimated to have approximately 40 wt-% of calcium ferrite, but only about 10 wt-% is contained in MixA. The result of this is a remarkable difference in compressive strength. In this case, the ferrite phase provides both the early strength and the final strength of the SAB cement. It has been stated that calcium ferrite phases possess higher reactivity in SAB compositions compared to OPC¹⁸.

The results show that mortars of MixB measured strengths in accordance to that suggested in the literature for slow hardening cement based on the C-S-A-S system¹⁸. The results obtained also imply that there is a saturation point at about 5% with regard to the addition of gypsum. Going from 0% to 5%, there is a considerable increase in strength. If 10% of gypsum is added instead, the compressive strength remains almost the same as if 5% is added, regardless of mixture composition.

3.7 Conduction calorimetry

Conduction calorimetry was performed on MixA 5% and MixB 5%, chosen based on the compressive strength results and on a commercial OPC. The heat generated from these samples as function of time is shown in figure 6. MixA 5% and MixB 5% give roughly the same pattern, although MixA 5% seems to react slightly faster for the first seven hours but does not release as much heat as MixB 5%. Still, both mixtures reach their maximum within 10 hours, after which both of them also start to level off. The OPC sample reacts much more than MixA 5% and MixB 5% and reaches its maximum after approximately 10 hours until it levels off. However, the heat liberation for OPC does not level off as quickly as in MixA 5% and MixB 5%.

Fig. 6. Results of calorimetry of mixtures compared to an ordinary Portland cement, OPC.

The AFt is formed according to reactions (7), (8) and (9), i.e. water and calcium sulphate react with sulphoaluminate or ferrites instead of tricalcium aluminate. In this investigation, it is believed to be mainly reaction (7) that takes place in these mixtures in relation to the hydration of sulphoaluminate, since no calcium hydroxide is expected before mixing with water. However, polymorphs of C_2S will contribute to reaction (8) through Ca^{2+} ions as C_2S dissolves, hence, the Ca^{2+} ions react with OH^- ions to form $Ca(OH)_2$. Furthermore, there will be a contribution to AFt formation from the ferrite phases which follow the same sequence of reactions as the aluminates in OPC, though this reaction is reported to be much slower in rate. Considering the modified Bouge calculations, it can be assumed that the influence of heat developed due to hydration of ferrites is more pronounced in MixB than in MixA. As shown in figure 6, the first few minutes of heat liberation is the same for all samples. The initial period is characterised by wetting, producing very rapid exothermic reactions, as expected. The dormant period seems to last longer for MixB, but both MixA 5% and MixB 5% show a very strong and intense increase in reaction activity when the dormant period ends, while the acceleration period lasts at least 1.5 hours for both MixA and MixB. After approximately 10 hours, both MixA and MixB start to level off dramatically and the heat liberation becomes very weak further on. Significant heat which is evolved in the early hours is related to the formation of AFt, and it is well known that a substantial amount of sulphoaluminate present in any SAB composition is consumed in parallel to AFt formation, i.e. 60-70 % of the

sulphoaluminate is usually consumed within the first 24 hours¹⁸. The formation of AFt is not the only reaction which takes place, but it is surely the dominating reaction, as is supposed at early stages when SAB compositions hydrate.

3.8 Measurement of AFt

The formation of AFt was confirmed by the XRD patterns given in figure 7. MixA 5% and MixB 5% have a similar diffractogram and both give a much higher intensity of AFt than OPC. Furthermore, as expected, Ca(OH)_2 can be observed for OPC, indicating the silicates are being dissolved when mixed with water.

Fig. 7. X-ray diffraction patterns indicating formation of AFt after 24 hours of hydration.

The amount of AFt formation was analysed by differential scanning calorimetry (DSC). The first peak, in figure 8 of each sample, belongs to acetone, and the heat accompanied with the AFt present was distinguished and identified at approximately 150°C. Since the amount could not be quantified, it is only the relative amount between the mixtures that can be evaluated. From figure 8, it can be noted that the amount of AFt is rather equal for MixA 5% and MixB 5% during the first 24 hours.

Fig. 8. The relative amount of AFt formed in mixtures.

All together, it can be concluded that the formation of AFt after a few hours is more accelerated in MixA 5% and MixB 5% in comparison to the formation of AFt in OPC. The amount of tricalcium silicate in OPC tested is approximately 54 %, which is much more than the expected amount of sulphoaluminate in MixA and MixB. As a result,

the OPC obtained more lasting heat development, to which the ferrites and dicalcium silicate reactions also contribute.

3.9 Scanning electron microscopy, SEM, - observation of AFt

In both photos of MixA 5% as well as MixB 5% (figures 9a-b), needle-like crystals (AFt) can be observed in the matrix using SEM. The analyses are made after two days of hydration.

Fig. 9a. SEM/EDS MixA 5% 2 days hydration.

Fig. 9b. SEM/EDS MixB 5% 2 days hydration.

3.10 Concluding remarks MixA and MixB

The first part of the work considered four different mixtures based on steelmaking slag. The investigation of hydraulic properties, however, only concerned MixA and MixB with different additions of gypsum. The reason for not investigating MixC and MixD was basically a matter of time. MixD, which only consisted of a ladle slag was chosen based on its original composition, i.e. high content of alumina in comparison to other slags, which is a very favourable property in this case. It would, however, not be realistic to produce a commercial clinker based on only ladle slag, since there cannot be sufficient of volumes provided. MixC and MixB were very close in composition with regard to the raw meal, but the final composition was considered to be more promising for both MixA and MixB, since both of these compositions agreed better with those estimated through the modified Bouge equations. The latter, however, does not mean that MixC can be excluded based on the argument that it does not possess good hydraulic properties!

Regarding MixA and MixB, is it true that MixB would be preferable in comparison to MixA? From the compressive strength point of view it is true until 28 days of hydration. However, MixA consists mainly of dicalcium silicate and sulphoaluminate according to the XRD results, and it has already been stated that the properties of dicalcium silicate are of utmost importance for strength development after

28 days. The amount of dicalcium silicate in MixB is less, and therefore, it could be that the later strength development of MixB starts to level off earlier than MixA. As a result, it could be possible that MixA in the long term provides better strength than MixB, though that is something which needs to be investigated further. Finally, all mixtures tested are possible slag combinations, but at this stage of the investigation, the different mixtures are mainly aimed at highlighting the potential of slags as raw material, thus, optimisation is possible, depending on the requirements of any application that might be considered.

4. Conclusions

- Steelmaking slags have potential to work as raw material for sulphotoaluminate belite cement, (SAB cement).
- The results from XRD reveals formation of clinker phases such as sulphotoaluminate, $C_4A_3\bar{S}$, polymorphs of dicalcium silicate, i.e. α' - C_2S and β - C_2S , as well as ferrite phases. The formation of sulphotoaluminate was also confirmed through SEM-analyses.
- After 2 and 28 days, the strength of MixB agrees with that suggested in the literature for a slow hardening SAB composition. The reason for MixA being weaker until 28 days of hydration is believed to be a lack of ferrites in comparison to MixB.

5. Future work

The future work is suggested to be focused on high temperature reactions with regard to clinker formation. In parallel, it is also of interest to simulate the production of SAB clinker in a rotary kiln. In order to do so, thermodynamic data of sulphoaluminate, i.e. Gibbs free energy, must be determined or estimated through known estimation rules since it is not available in the literature. Furthermore, if the slags are going to be used as raw meal in a production line, it is important to be able to control the production in terms of getting an even final product/composition. Therefore, it will also be important to investigate the quantification of clinker phases. Finally, the leaching behaviour of the mixtures must be considered and analysed with respect to the content of heavy metals.

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**STEELMAKING SLAGS AS RAW MATERIAL FOR SULPHOALUMINATE
BELITE CEMENT**

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STEELMAKING SLAGS AS RAW MATERIAL FOR SULPHOALUMINATE BELITE CEMENT

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Abstract

In the present work, slags from the steelmaking industry are described and considered as potential raw material within the field of sulphotoaluminate belite cement (SAB). The objective is to investigate the possibility of using a substantial amount of steelmaking slags as raw meal in the manufacture of a sulphobelitic clinker. The aim is also to compare the influence of different slags in relation to the formation of sulphotoaluminate and other clinker phases needed. The behaviour of high temperature reactions was investigated by using thermogravimetric analysis coupled with a quadrupole mass spectrometer. Mineralogical observations were carried out through x-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Three different mixtures and a single ladle slag were prepared using modified Bouge calculations, which is characterised by the assessment of a potential phase composition in order to produce belite-rich cement activated with sulphotoaluminate. The results so far prove that steelmaking slags have the potential to work as raw material, since sulphotoaluminate along with polymorphs of dicalcium silicate and ferrite phases were detected after firing at 1200 °C in an air atmosphere.

Keywords: by-products, cement, sulphotoaluminate

1. Introduction

Ordinary Portland cement (OPC) is well known and traditionally used within civil engineering. Additionally, the raw material is rather cheap. However, since the raw meal is based on limestone and clay, the manufacturing will be accompanied by a significant amount of carbon dioxide and high energy demands during firing of the raw meal and grinding of the final clinker.

OPC consists of four major crystalline phases, i.e. tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF), (see figure 1). Normally, the content of C_3S is in the range of 50-65%, C_2S 15-25 %, C_3A 8-14 % and C_4AF 8-12 %¹. Silicates provide strength to the cement as it reacts with water. The strength of the material early on is due to the C_3S , while C_2S is more of importance after 28 days.

Fig. 1. Ternary phase diagram of the CaO - Al_2O_3 - SiO_2 assemblage.

Slag from steelmaking industry can be generated either from integrated steel plants or scrap based steel production. The different types of slag within the integrated plants are blast furnace (BF), basic oxygen furnace (BOF) and ladle slag. In scrap based production, the categorisation would entitle them: electric arc furnace (EAF), argon oxygen decarburisation (AOD) as well as ladle slag. Apart from the blast furnace process, the BOF and EAF slags are usually generated under oxidising conditions which contribute to the higher amount of iron content.

There have been different ideas of how to use slags within the cement area. Most widely used is the BF slag, which can be used either as it is or blended with OPC, i.e. slag cement. The slag is usually granulated since the granulation offers a very amorphous material which is easy to grind, resulting in excellent hydraulic properties. In any event, it is sometimes appropriate to further activate the slag by for instance increasing the lime content and thereby the basicity. The properties of BF slag regarding hydration and structure, are well described by Roy and Idorn, 1982 ².

Steel slag is distinguished from the BF slag with respect to the iron oxide content, but possible fluctuations in the composition along with excess of free lime is also something not totally unusual about this by-product ³. According to authors, there are basically two ways to proceed. One option is to use steel slag as raw material, fired with clay and limestone. A second possibility refers to a non-calcining process, where steel slag is blended with OPC or, alternatively, combined with BF slag and gypsum.

Generally, the chemical composition of steelmaking slags is very similar to that of OPC, i.e. all oxides present in OPC are also present in steel slags, ⁴. There are important differences, though, from a mineralogical point of view. In addition of being rich in wuestite, the amount of tricalcium silicate, which is considered to be the most important phase in OPC, is usually very low ⁵. Instead, the predominant phases are polymorphs of dicalcium silicate but, also, different calcium (alumina) ferrites, solid solutions of (Ca, Fe, Mn, Mg)O, as well as olivine and merwinite ⁶. The amount of MgO in these slags is very dependent on the flux, as to whether dolomite or lime is being used in the steelmaking process ⁷.

So far steel slag has not been used very extensively in cement production. Recently, according to figure 2, only 1 % of the European steel slag was used for cement production in the year 2004. Partly, this might be explained in terms of classification as to whether it is considered as a product or waste. From a practical point of view, it is important to avoid fluctuations in the composition. Although the presence of free lime could be an advantage, acting as an activator if blended with OPC, it might still cause trouble in terms of expansion. However, apart from free lime, MgO might be the cause of volumetric unsoundness as it also reacts with water to form magnesium hydroxide. The volumetric factor is at least one limitation to be mentioned in relation to construction. Fluctuations though, can be compensated for if the material is blended with, for instance, ground granulated blast furnace slag³.

Fig. 2. Use of steelmaking slags in Europe 2004⁸.

Alternatives to OPC, of which the sulphaaluminate belite cement, SAB, is an important option, have been and are still under investigation. SAB cement refers to the phase assemblage $C-S-A-\bar{S}$ ⁹, and the major phases present within the system are C_2S , $C_4A_3\bar{S}$, C_4AF , $C\bar{S}$ and C (see figure 3). Since the belite phase itself does not bring any high early strength to the cement, activation of the hydration mechanism is needed¹⁰. Basically, this is the role of sulphaaluminate, $C_4A_3\bar{S}$, as its properties substitute for those of tricalcium silicate in order to provide sufficient early strength.

Fig. 3. Ternary phase diagram showing the approximate composition of slow hardening SAB cements.

The advantage of producing SAB compared to OPC, is the reduction of the lime saturation factor (LSF) which enables the reduction of CO₂ emissions¹⁰, but also the firing temperature which can be lowered with about 100-150 °C¹¹. It is possible to accomplish the latter since both sulphoaluminate and dicalcium silicate are formed at lower temperatures at which the tricalcium silicate is not formed.

Depending on what properties are required for a specific application, the quantity of each phase present can be adjusted. High amounts of sulphoaluminate provide high early strength to the cement, but it also contributes to good corrosion resistance and controllable expansion¹². Generally, raw materials used for this type of cement are limestone, bauxite and gypsum, which are calcined at 1300-1350 °C¹³. Another possible alumina source according to Glasser and Zhang¹³ could be red mud, a by-product from the Bayer process.

A lot of research has been done in the field of SAB cement and, especially, in the area of civil engineering. The use and development of sulphy- and ferroaluminate cements in China are, for instance, very well reviewed by Zhang et al. ¹². However, other investigations, where raw materials other than virgin materials are used, have been completed. Arjunan et al. ¹⁴ got similar results as those gotten with OPC when using bag house dust, low-calcium fly ash (Class F fly ash) and scrubber sludge in different proportions. The aim was to produce environmentally friendly cement. Low-temperature phases were detected and the usefulness was, for instance, confirmed by the compressive strength. Another example comes from the properties of blended SAB cement as investigated by Zivica ¹⁵. For the synthesis of SAB cement, a mixture of limestone, gypsum, fly ash and pyrite ash was used and heated at 1250 °C. The SAB cement was further mixed with 5, 15, and 30 % granulated BF slag, fly ash, and silica fume, respectively. It was partly concluded that SAB blends with additions of 5-15% portions of pozzolana seemed to be optimal. Furthermore, the effect of blending was stated as being dependent on the activity of pozzolans and the properties of the SAB cement, in relation to the content of β -C₂S. A more theoretical work was performed by Majling et al. ¹⁶ where the objective was to forecast the mineralogical composition of SAB cement based on fly ash using modified Bouge computations. A relationship was established between raw material and the mineralogical composition of clinker material which is considered very useful in the further development of SAB cements based on fly ash. The present work, however, is focused on the potential of steelmaking slag, when it is the major part of raw material used for SAB cement. Since all of the different slags are believed to be able to meet the compositional requirements in relation to the content of dicalcium silicate, the materials are assumed to possess enough quality to work as a raw material for slow hardening SAB cement without any unreasonable amounts of additives in the raw meal. At the same time, by combining different steelmaking slags, possible fluctuations can be compensated for as well as having the ability of providing enough of slag volumes.

2. Material and experimental procedure

2.1 Material

Raw materials were combined according to table 1, as predicted by using modified Bouge calculations. The calculation is based on a chemical analysis from which a mass balance can be performed. Since there are five initial phases to be considered, the mass balance will contain five different linear equations according to the general matrix given below,

$$\mathbf{Ax}=\mathbf{b} \Leftrightarrow \begin{bmatrix} a_{11} & a_{12} & \cdots \\ a_{21} & a_{22} & \cdots \\ a_{31} & \vdots & \\ \vdots & & \end{bmatrix} \cdot \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \end{bmatrix}.$$

The variables in the matrix refer to the weight fraction of each oxide in question, in relation to the actual mineral it is being part of. Thus, $a_{11} = (M_{\text{CaO}}/M_{\text{C}_2\text{S}})$ and $b_1 =$ total fraction CaO, i.e. the amount given from chemical analyses, and, finally, the $x_1 = \text{C}_2\text{S}$ phase can be calculated. The same method is applied to SiO_2 , Al_2O_3 , Fe_2O_3 and SO_3 . From this system of equations, the potential phase composition can be estimated by finding the inverse matrix, $\mathbf{A}^{-1}$, when $\det(\mathbf{A}) \neq 0$. Since this is only a mass balance, there are no thermodynamic or kinetic considerations within the calculations.

Four mixtures were prepared, i.e. MixA, MixB, MixC, and MixD (see table 1). MixA contains 70 % slag, of which 55 % is AOD slag and 15 % ladle slag, along with limestone, gypsum and an alumina rich material, containing 10 % of each additive. MixB contains 64 % slag of which only 14 % represents AOD slag, in this mixture.

Table 1.
Mixtures prepared in wt-%.

Material	Mix A	Mix B	Mix C	Mix D
AOD slag	55	14	-	-
EAf	-	25	25	-
BOF	-	-	14	-
Ladle slag	15	25	25	100
Gypsum	10	5	5	-
Alumina*	10	6	6	-
Limestone	10	25	25	-
total	100	100	100	100

* The alumina source consists approximately of 5 wt-% CaO, 74 wt-% Al_2O_3 and 21 % SiO_2

The rest of the slag content consists of 25 % ladle slag and 25 % EAF slag, resulting in a higher total amount of additives, i.e. 25 % limestone, 6 % alumina and 5 % gypsum. MixC is more or less the same as MixB. The only difference is the substitution of 14 % AOD slag by BOF slag. Finally, we looked at MixD, which only consists of ladle slag.

In table 2, the analysed chemical composition of each mixture is presented, along with the calculated potential phase composition. Chemical analysis of each slag used is typical as those given by Tossavainen et al¹⁷, and Yang et al¹⁸. It is important to point out, that, in the chemical analyses (table 2), iron is given as Fe_{tot} and sulphur as elemental, S⁰. However, in the mass balance discussed, these elements have been recalculated as Fe₂O₃ and SO₃ and, thus, all iron present is assumed to be Fe₂O₃ and sulphur, as SO₃. In addition, since only five linear equations have been chosen, the total phase composition of the desired phase assemblage will not be 100 %. The other elements are either considered as individual minerals and/or elements which are incorporated in the structure of expected minerals such as dicalcium silicate. It is worthwhile to mention that minor percentages of MnO, P₂O₅, K₂O, V₂O₅, TiO₂ and Cr₂O₃ were detected too. The level of these oxides measured 2.5 wt-% in MixA (of which 1.5 wt-% is Cr₂O₃), 3.3 wt-% in MixB (of which 1 wt-% is Cr₂O₃ and 1.7 wt-% MnO), 4.3 wt-% in MixC (of which 0.7 wt-% is Cr₂O₃, 0.8 wt-% V₂O₅ and 2 wt-% MnO) and finally 1.8 wt-% in MixD (of which 1 wt-% is TiO₂). The rest of the excess in weight (not specified in table 2) refers to oxygen being part of the calcium carbonate structure as well as the gypsum and iron compound.

Table 2.

Analysed chemical composition of each mixture in wt-%.

Mixture	CaO	SiO ₂	Al ₂ O ₃	Fe _{tot}	MgO	S _{Leco}	C _{Leco}
Mix A	46.5	20.2	15.5	2.7	4.3	2.0	1.4
Mix B	40.7	12.7	14.1	8.9	6.3	0.9	3.0
Mix C	39.2	9.7	13.6	11.0	7.4	0.9	2.9
Mix D	45.5	18.8	20.3	1.1	9.7	1.3	1.0

Calculated potential phase composition in wt-%

Mixture	C ₂ S	C ₄ A ₃ S̄	C ₄ AF	C ₃ S̄	C	Total	LSF
Mix A	58	26	12	3	-	99	0.60
Mix B	36	12	39	1	-	88	0.67
Mix C	28	7	48	2	-	85	0.73
Mix D	54	38	5	-	-	97	0.58

The result of the mass balance indicates that dicalcium silicate is expected to be one of the dominating mineral in each mixture. The main difference is the amount of ferrites and sulphoaluminate. Sulphoaluminate was estimated to be 26 wt-% in MixA and 38 wt-% in MixD, while both MixB and MixC give a considerably higher amount of ferrites, i.e. 39 wt-% and 48 wt-% respectively. However, since AOD slag is replaced by BOF slag in MixC, the total iron content should increase, resulting in a higher amount of ferrite within the composition. A high amount of C₄AF is a good thing, since this compound contributes to both the early and late strength in the SAB system⁹.

2.2 Experimental procedure

2.2.1 Thermal analysis

The measurements of the thermal analysis coupled with quadrupole mass spectrometer, QMG 420, were carried out simultaneously using the Netzsch STA 409 equipment shown in figure 4. 100-mg test materials were contained in an alumina crucible and subjected to a programmed heating of 10 K/min in an air atmosphere, in the temperature range of 25 to 1400 °C. A TG/DTA (thermogravimetric and differential thermal analyses) sample holder with an alumina crucible is positioned on a radiation shield in order to protect the balance. The investigated samples can be tested in the mode TG/DTA sample + correction, i.e. in order to avoid problems with Buynce effect, an empty crucible is run (correction data) before analysing the sample. The gases formed during the reaction were identified using quadrupole mass spectrometer (QMS) measurements connected with STA equipment. In a high-frequency, quadrupole electric field, it is possible to separate ions according to their mass/charge ratio (m/e) (see figure 4).

Fig. 4. Schematic of Netzsch STA 409.

2.2.2 Sample preparation and firing of briquettes

Each slag was crushed, using a jaw crusher, and divided into representative samples using a rotary splitter and ground in a rod mill for approximately 25 minutes. The slags were further combined to produce the mixtures given in table 1. In order to get a good homogenisation and a fairly fine powder-like material, the mixtures were once again introduced to a rod mill and run for approximately 60 minutes. The ground mixtures were prepared as briquettes with the approximate dimension of $\phi \times H$, i.e. 2x4 cm before firing in order to get good contact between particles, and then dried in an oven for 24h at 100 °C. The briquettes were fired in a furnace with an air atmosphere at 1200 °C for approximately 30 minutes followed by water cooling. The cooled briquettes were dried in an oven for 24 h at 100 °C and then examined by XRD and SEM.

2.2.3 Particle size distribution

Before firing the mixtures, the particle size distribution was determined with a Malvern 2000, and the results are given in figure 5a-d. From those figures, it can be seen that all mixtures except MixB give a similar distribution. MixB gives a $d_{50} \approx 15 \mu\text{m}$ while other mixtures reach approximately $d_{50} \approx 20 \mu\text{m}$. It can therefore be stated that all the mixtures are powder-like materials and that there is nothing critical about MixB being finer than the others and vice verse, according to later results.

Fig. 5a. Particle size distribution of MixA.

Fig. 5b. Particle size distribution of MixB.

Fig. 5c. Particle size distribution of MixC.

Fig. 5d. Particle size distribution of MixD.

2.2.4 XRD and SEM analyses

A Siemens D5000 X-ray powder diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 40 mA was used. The analyses were run with step scan, i.e. 4 seconds per step in the 10-90 2-theta range.

Observations of sulphotoaluminate in the investigated samples were performed with SEM using a Phillips XL 30 equipped with energy dispersive spectra, EDS in the 20 keV range. The material was first dispersed (10 - 20 mg) in a few millilitres of ethanol, and then, while sonicating, a sample of the pulp was taken out with a pipette. One drop was placed on a double sided carbon tape. Thereafter, the samples were sputter coated with gold.

3. Results and Discussion

3.1 Results of Simultaneous Thermal Analysis, STA

Contemporary thermoanalytic equipment like the Netzsch STA 409, offer very useful measurements in order to analyse the behaviour of materials heated in controlled atmospheres. The results of the mixtures are compiled in figure 6a-d. The figures basically depict the behaviour of the different mixtures when heated until 1400 °C in an air atmosphere. In the approximate temperature range, 1100-1300 °C, clinker formation can be noted and the area is highlighted with a circle. However, from the marked areas, it is not by any means a trivial and straightforward task to exactly tell which reaction refers to which peak, since many reactions take place simultaneously, resulting in overlapping endothermic and exothermic sequences. The TG results provide the relative differences in weight loss between tested samples. It can be seen very clearly that the most significant weight loss is especially pronounced in MixB and MixC with about 9 wt-%, respectively. According to table 3, which summarises differences in weight loss, as well as detected gases of each mixture, the results indicate a weight loss of approximately 7 and 5 wt-% more than was observed for MixA and MixD, where a loss of only 4 and 2.5 wt-% were reached, respectively. In any event, since more calcite exists from the start in MixB and MixC, it should consequently result in a higher percentage of loss. It also implies that much less CO₂ is released as compared to OPC, where the CO₂ emissions generally reach about 40 %.

On closer examination of the TG/DTG, Differential Thermogravimetry, there are basically three distinct effects which can easily be distinguished in sample MixA, MixB, and MixC. The first effect at 100-150°C refers to physical water. The amount of water is practically the same, apart from MixA giving 3.6 loss in wt-% compared to the approximately 1.5 wt-% in the other mixtures. This peak is accompanied further on by an even broader and more pronounced peak, which is recognised as decomposition of calcium carbonate according to reaction (1). Depending on which mixture is being discussed, a maximum is reached at slightly different temperatures. However, in general, the calcination starts at 700 °C and the maximum is reached between 750-800 °C, independent of mixture in question (see table 3). The DTG results show agreement with the corresponding gas profiles, i.e. implying the released moisture and carbon dioxide emissions at the aforementioned temperatures. The last small effect at rather high temperature, i.e. 1300-1400 °C is related to the evaporation of sulphur dioxide due to the decomposition of gypsum. The SO₂ emissions, however, were only registered in the case of MixA and

MixC, and can also be viewed in the results of gases. Although MixB and MixC are very similar in composition and behave very much the same, no sulphur dioxide could be detected from MixB. As an explanation, the sulphate present is presumably consumed in relation to the clinker formation, i.e. no saturation of sulphate, which is also believed to be the case in MixC, keeping in mind that the level of sulphur dioxide observed in MixC only reaches 0.2 in ion current. Furthermore, a weight loss of 0.05 wt-% with regard to MixD is considered to be neglected and of no importance, since it is so considerably low.

After the broad endothermic peak already discussed, a small exothermic reaction was detected in relation to MixA and MixD. This peak was found at 1000 °C in MixD and at 1130 °C in MixA. Next, this reaction was followed by a distinct endothermic effect at 1150 °C in MixA. The corresponding reaction appears at 1180 °C in MixB, MixC, and MixD. Thereafter, in all the samples, this pattern repeats itself by having shifting effects due to small endothermic and exothermic reactions. A more pronounced reaction was recorded at 1300 °C in the case of MixC and MixD, and was not as sharp in the other discussed materials at the same temperature. The various reactions taking place is partly related to the formation of sulphoaluminate. From a general point of view, it starts at approximately 1000 °C, according to reaction (2), and depending on which mixture. In the context of kinetics, the firing conditions strongly influences the completeness of formation, as well as the amount of mineralising elements. In slags, where dicalcium silicate already is present, the polymorphic transformation of $\gamma \rightarrow \alpha'_L$ usually takes place at 900 °C and, furthermore, $\alpha'_L \rightarrow \alpha'_H$ at 1180 °C¹⁹. These kinds of transition states also contribute to the observations made by DTA.

Fig. 6a. TG/DTA/QMS results of MixA.

Fig. 6b. TG/DTA/QMS results of MixB.

Fig. 6c. TG/DTA/QMS results of MixC.

Fig. 6d. TG/DTA/QMS results of MixD.

Table 3.

Weight loss in wt-% and gas releases in ion current observed by TG/DTA/QMS-analyses at specific temperature ranges.

Mixture	Temperature range			Total weight loss
	100-150°C	700-800°C	1300-1400°C	
MixA	-3.56	-4.23	-3.61	-11.4
MixB	-1.35	-9.35	-2.15	-12.9
MixC	-1.57	-9.05	-1.80	-12.4
MixD	-1.02	-2.49	-0.05	-3.6

	Gases in ion current $10 \cdot 10^{-10}/A$		
	H ₂ O	CO ₂	SO ₂
MixA	3.5	2.8	0.4
MixB	1.4	5.6	-
MixC	1.5	5.6	0.2
MixD	0.43	0.98	-

3.2 Furnace trials

3.2.1 Physical data before and after firing

In addition to particle size distribution, some other physical data were analysed before and after firing of the briquettes. The density is of the same magnitude before and after firing. The same result can be applied to all other data measured and presented in table 4, i.e. porosity.

Table 4.

Physical constants of mixtures compared before and after firing.

Mixture	Before firing			After firing	
	Density (kg/m ³)	Blaine (m ² /kg)	Porosity	Density (kg/m ³)	Porosity
Mix A	2965	683	0.50	3097	0.45
Mix B	3139	609	0.53	3318	0.50
Mix C	3192	591	0.50	3348	0.50
Mix D	3047	501	0.50	3090	0.45

More interesting, though, is the change in colour seen in figure 7. While all mixtures have white and grey nuances in colour before being fired, the difference in composition becomes clear afterwards, thus indicating the formation of new phases and in different proportions. While MixA and MixD are somewhat light brown and light green, it can be easily noticed that MixB and MixC are rather dark brown. The brown colour is especially sharp in the case of MixC. It should be pointed out that the light green colour in MixA and MixD could be due to the non-hydraulic phase $2C_2S \cdot CaSO_4$, which is not unreasonable to achieve at the temperature in question, when α' - C_2S reacts with $CaSO_4$ ²⁰. However, as shall be seen, this phase was not detected by x-ray diffraction, and therefore, if present, the amount should be quite low, (approximately < 3 %), otherwise it would have been detected.

Fig. 7. Mixtures before and after firing, showing differences in colour.

3.3 X-ray diffraction, XRD

X-ray diffraction analyses of the samples are summarized in table 5, which gives a good overall picture of what has been formed, as well as that which has disappeared from the starting mixtures, while figure 8 provides the XRD pattern of MixA before and after firing as an example of all the patterns recorded. In the raw material of MixA, XRD revealed the presence of calcite, merwinite, calcium silicate (non-hydraulic), and akermanite as major phases. After the mixture was fired, none of these phases appeared. Instead, sulphoaluminate, also referred as yeeliminite, was detected along with bredigite, which is an α' -structure of dicalcium silicate. Apparently, calcite has reacted with alumina and sulphate to form the sulphoaluminate phase, as expected. It is not clear though, what the role of mayenite has been, regarding the formation of sulphoaluminate in other words, to what extent this phase reacted with the calcium sulphate present. In any event, since no mayenite or other alumina phase was detected afterwards except for sulphoaluminate, its contribution to the formation of sulphoaluminate can be assumed. The latter is presumably applicable in the case of MixD too. Without any additives at all, a single ladle slag fired at 1200 °C forms all the desired clinker minerals, along with some free periclase, already present from the start. Since no alumina and sulphate were added, it is reasonable that mayenite, being one of the major minerals in this material, reacts with gypsum to form sulphoaluminate. However, in the ladle slag tricalcium aluminate was found (as well in the beginning) and should therefore not be overlooked with regard to the sulphoaluminate formation. Silicates present in MixA and MixD, such as akermanite and merwinite, are believed to be part of the formation of bredigite, and calcium silicate in relation to the beta structure of dicalcium silicate, as the temperature in question provides the polymorphic transformation of this mineral.

The raw meal of MixB and MixC could be said to be constituted of the same minerals, but in different proportions. Apart from additives, the major phases detected were periclase, calcium silicate, mayenite, and wuestite. Still, important differences were detected after firing. The clinker material of MixB seemed more promising than MixC, in view of the better intensities of sulphoaluminate and formation of brownmillerite (instead of the calcium magnesium alumina iron silicate structure which was obtained in MixC). All together, substituting AOD slag by BOF slag clearly, in this case, influences the final composition. The latter, however, does not in general imply that AOD slag is preferable. What could be stated is that AOD slag might be more suitable in a starting mixture similar to that of MixB.

Fig. 8. X-ray diffraction pattern of MixA.

Table 5.

The most abundant minerals found with x-ray diffraction before and after firing. B=Before firing and A=After firing.

Nr.	Mineral		Mix A		Mix B		Mix C		Mix D	
	Name	Chemical formula	B	A	B	A	B	A	B	A
1	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$								
2	Calcite	CaCO_3								
3	Corundum	Al_2O_3								
4	Periclase	MgO								
5	Calcium silicate	$\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$								
6	Mayenite	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$								
7	Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$								
8	Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$								
9	Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$								
10	Wuestite	FeO								
11	Yeeliminite	$4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$								
12	Bredigite	$\text{Ca}_{1.7}\text{Mg}_{0.3}\text{SiO}_4$								
13	Larnite	$\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$								
14	Brownmillerite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$								
15	(Ca,Mg, Al,Fe) silicate	$\text{Ca}_2\text{Mg}_{0.2}\text{AlFe}_{0.6}\text{Si}_{0.2}\text{O}_5$								
16	Calcium iron oxide	CaFeO_3								
17	iron	Fe								

3.4 Scanning electron microscopy, SEM

SEM analyses were performed to actually view the presence of sulphoaluminate. Figure 9a-d, show the observations made of the sulphoaluminate phase. Figure 9a represents what was found in MixA, i.e. a hexagonal tabular structure²⁰, and the composition of that structure is confirmed by the energy spectra, EDS. The same kind of structure is viewed in MixB-D, and is confirmed with EDS as in MixA (see figure 9b-d). The general impression was that a larger amount of sulphoaluminate was formed in MixA, as compared to MixB, MixC, and MixD where it seemed to be less. However, quantification of clinker phases is beyond the scope of this work, but needs to be investigated in future work.

Fig. 9a. SEM/EDS of MixA.

Fig. 9b. SEM/EDS of MixB.

Fig. 9c. SEM/EDS of MixC.

Fig. 9d. SEM/EDS of MixD.

4. Conclusions

The work covers analyses of four different mixtures containing high amounts of steelmaking slag from the steelmaking industry in Sweden. The goal was to produce belite rich cement activated with sulphotoaluminate. Thermal analyses coupled with a mass spectrometer, XRD and SEM were used for the characterisation of the mixtures' behaviour. The results reveal formation of clinker phases such as sulphotoaluminate, $C_4A_3\bar{S}$, and polymorphs of dicalcium silicate, i.e. α' - C_2S and β - C_2S . The next step, however, is to investigate the hydraulic properties, and further on, it will also be necessary to try to quantify the clinker phases obtained.

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ON STEELMAKING SLAGS**

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HYDRAULIC PROPERTIES OF SULPHOALUMINATE BELITE CEMENT BASED ON STEELMAKING SLAGS

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Abstract

Steelmaking slags were combined based on modified Bouge calculations in order to produce a belite-rich clinker activated with sulphoaluminate. The experiments were conducted on two different mixtures based on steelmaking slags along with additives, i.e. MixA and MixB. The objective of the present work is to investigate the hydraulic properties of the specimens, using conduction calorimetry, XRD, and DSC as well as to measure the mechanical strength of the specimens when hydrated for 2 and 28 days. The compressive strength was in accordance with that suggested in the literature for slow hardening SAB cement. Both mixtures behaved the same with regard to heat development as well as the amount of AFt formed during the first 24 hours of the hydration.

Keywords: By-product, Hydration; Sulphoaluminate

1. Introduction

Each year, large amounts of slag are generated in the steelmaking industry. In parallel, it is important to find ways of reducing energy consumption and carbon dioxide emissions within the cement industry. Therefore, as investigated in part 1 of this work ¹, steelmaking slag was used as raw meal along with other additives for the formation of sulphoaluminate belite cement (SAB) which was fired at 1200°C in an air atmosphere. The results from that work proved that steelmaking slags have the potential to work as raw materials. This part, however, is focused on the hydraulic properties where two of those investigated mixtures, MixA and MixB with regard to the formation of SAB clinkers are further examined.

There are important differences in the hydration reactions between ordinary Portland cement (OPC) and SAB clinkers which need to be clarified. In both types formation of ettringite (AFt) will take place, but it is not formed by the same reactants. In relation to the OPC, different periods are usually discussed in the following order, the initial period, the dormant period, the acceleration phase, the deceleration phase, and an ever-slowng reaction phase ². In the first period, hydrolysis and release of ions into the solution take place, and the reaction is characterised as very rapid and exothermic ³. Within the first couple of minutes, the heat evolved is due to the hydration of sulphate, the formation of AFt according to chemical reaction (1), as well as the wetting ⁴. After the dormant period which might last between 30 minutes and 2 hours the next heat liberated is attributed to the hydration of tricalcium silicate (C₃S). After approximately 12-15 hours of hydration, AFt will react with tricalcium aluminate (C₃A) to form monosulphate ⁴ (AFm) according to chemical reaction (2). In the SAB system, however, the AFt is formed when sulphoaluminate as well as the ferrite phases (which follow the same sequence as C₃A) react with the present calcium sulphate and water. Reaction (3) ⁵ gives the overall hydration mechanism for sulphoaluminate, and in the case of expansion ettringite is produced according to reaction (4) ⁵. It can therefore be concluded that AFt is not a final product of the OPC system, while the SAB paste generally is constituted by AFt, AFm, alumina, and ferrite gel ⁶.

2. Material and experimental procedure

2.1. Material

Slags were combined according to table 1 (i.e. estimated by using modified Bouge calculations). In MixA there is mainly AOD (argon oxygen decarburization) slag (i.e. 55 wt-% but also 15 wt-% of ladle slag blended with gypsum, alumina, and calcium carbonate, 10 wt-% of each additive). In addition to AOD slag, which only made up 14 wt-% of MixB, and ladle slag, which made up 25 wt-%, MixB also contains 25 wt-% EAF (electric arc furnace) slag, along with 25 wt-% limestone and minor percentages of alumina and sulphate, (5 and 6 wt-% respectively). In table 2, the chemical composition is presented, as well as the potential phase composition. The phase composition is calculated based on the results presented in part 1 of this work ¹.

The ferrite phase is calculated to be 39 wt-% in MixB but only 12 wt-% in MixA which creates the greatest difference between the mixtures in view of the final composition. Dicalcium silicate is expected to be higher in MixA, with a value of 58 wt-% compared to 36 wt-% in MixB. The same kind of difference is seen for sulphoaluminate, i.e. 26 wt-% in MixA and 12 wt-% in MixB.

Table 1.
Mixtures prepared.

Mix A	wt-%	Mix B	wt-%
AOD slag	55	AOD slag	14
Ladle slag	15	EAF slag	25
Calcium sulphate	10	Ladle slag	25
Alumina*	10	Calcium sulphate	5
Limestone	10	Alumina*	6
		Limestone	25
Total	100	Total	100

* The same alumina source as used in part 1¹.

Table 2.
Calculated and analysed chemical composition of each mixture prepared and potential phase composition in wt-%.

Mixture	CaO	SiO ₂	Al ₂ O ₃	Fe _{tot}	MgO	S _{Leco}
Mix A	46.5	20.2	15.5	2.7	4.3	2.0
Mix B	40.7	12.7	14.1	8.9	6.3	0.9

Calculated Phase Composition in wt-%						
Mixture	C ₂ S	C ₄ A ₃ $\bar{S}$	C ₄ AF	C $\bar{S}$	C	Total
Mix A	58	26	12	3	-	99
Mix B	36	12	39	1	-	88

2.2. Experimental procedure

Each slag was crushed, using a jaw crusher, divided into representative samples using a rotary splitter and ground in a rod mill for approximately 25 minutes. The slags were further combined to produce MixA and MixB as given in table 1. In order to achieve good homogenisation and a fairly fine powder-like material, the mixtures were once again introduced to a rod mill and ground for approximately 60 minutes. The ground mixtures were prepared as briquettes with the approximate dimension of $\varnothing \times H$, i.e. 2x4 cm before firing in order to get good contact between particles and then dried in an oven for 24h at 100 °C. The briquettes were fired in a furnace in an air atmosphere at 1200 °C for approximately 30 minutes. This was followed by water cooling. The cooled briquettes were dried in an oven for 24 h at 100 °C. Thereafter, the briquettes were ground with a rod mill for 25 minutes followed by a vibration mill for 25 minutes. Next, the material was run through a magnetic separation and then divided into three representative samples using a Jones riffle. In one of the dividers, 5 % gypsum was added, and in a second one, 10 % gypsum was added, while the third sample was left untreated with regard to the addition of gypsum. The three dividers were then once again ground separately with a vibration mill in order to get a close particle size distribution and good homogenisation of those to which additions of gypsum were made. Finally, material from all three of the samples was taken out using a Jones Riffle for further determination of the particle size distribution of each sample.

2.2.1. Particle size distribution

The fineness of the samples prepared was determined by a Malvern 2000, which is an optical sizing unit, and the measurement was performed by Cementa Research AB, Sweden.

2.2.2. Compressive Strength

Mortar prisms with the dimension of 25x25x285 mm were prepared and tested by Cementa Research AB, Sweden. The material was blended with sand and water in the ratio 3:1:0.5 and hydrated for 2 and 28 days. In the first 24 hours, the mortars cured in a moisture chamber with 95 % relative humidity at 20 °C. Thereafter, the moulds were cured in water at 20 °C until the mechanical strength was tested.

2.2.3. Calorimetry

Isothermal calorimetry was performed on a TAM air (Thermal Activity Monitor) instrument from Thermometric using glass ampoules. The instrument is an 8-channel heat flow calorimeter for heat flow measurements in the milliwatt range and the measurement was performed on mixtures and an OPC. Duplicate samples were performed using, 100 ml/sample with a w/c-ratio =0.5 for 24 hours at 20 °C. The tests were performed by Cementa Research AB, Sweden.

2.2.4. X-ray diffraction, XRD

Confirmation of Aft was carried out on a Phillips X'pert Pro diffractometer with CuK α radiation and an "X'celerator" detector. The scanning was carried out after 24 hours between 7-50 degrees in the 2-theta range and performed by Cementa Research AB, Sweden.

2.2.5. Differential scanning calorimetry, DSC

The DSC experiment was run on a DSC 7 Perkins Elmer Differential Scanning Calorimeter to analyse the formation of AFt. This was performed by mixing a sample with water, but in order to stop the hydration, acetone was added. Thereafter, the sample was filtered and the moisture mass which was left was ground and heated with the DSC instrument (20°C/min) as well as analyzed by XRD in order to confirm the presence of AFt. The tests were performed by Cements Research AB, Sweden.

2.2.6. Scanning electron microscopy, SEM

The SEM analyses were performed in the 20 keV range with a Phillips XL 30 equipped with energy dispersive spectra (EDS) which enables chemical mapping. The material was first dispersed (10 - 20 mg) in a few millilitres of ethanol, and then, while sonicating, a sample of the pulp was taken out with a pipette. One drop was placed on a double sided carbon tape. Thereafter, the samples were sputter coated with gold.

3. Results and discussion

3.1. Particle size distribution

Fig. 1. Particle size distribution of MixA and MixB with and without addition of sulphate.

From figure 1, it can be seen that all samples of MixB are clearly finer and possess a much better consistency in among individuals of the same mixture compared to those of MixA. All MixB-samples have a $d_{80} \approx 50 \mu\text{m}$, while MixA 0% and MixA 10%, approximately reach a $d_{80} \approx 80 \mu\text{m}$, and MixA 5% a $d_{80} \approx 70 \mu\text{m}$, i.e. somewhat finer. The difference is partly assumed to be due to the presence of metal drops, but it could also be explained in terms of grindability. The magnetic separation of by-products belonging to a non-stainless process is much easier than that originating from the stainless steelmaking process. In MixA there is a substantial amount of AOD slag, i.e. 55 %. All MixB blends give an acceptable particle size distribution, and instead of differing among individual samples, the blends are closely distributed. It is well known that the particle size is an extremely important parameter since it has a considerable affect on the hydration mechanism and thereby the final strength of the cement/concrete.

3.2. Compressive strength

The results for the compressive strength are listed in table 3. The value given for each mixture represents the mean value of four tests.

Table 3.
Compressive strength developed for each mixture of MixA and MixB after 2 and 28 days of hydration.

Specimen	Compressive strength (MPa)	
	2 days	28 days
MixA 0% Gypsum	0	7.0
MixA 5% Gypsum	4.2	8.5
MixA 10% Gypsum	4.0	8.3
MixB 0% Gypsum	3.7	12.0
MixB 5% Gypsum	7.5	13.5
MixB 10% Gypsum	7.6	12.3

Apparently, all MixA samples possess hydraulic properties that are lower than those of MixB. The compressive strength of MixB is almost twice as high after two days of hydration. At the level of 28 days of hydration, MixA 5% increased by 4.3 MPa, yielding 8.5 MPa, which is significantly lower than MixB 5%, the strength of which was determined to be 13.5 MPa. If no addition of gypsum was added, the mortar of MixB 0% measured 3.7 MPa after 2 days, but that is markedly higher than MixA 0%, which did not provide any strength at all. However, even when gypsum was added, it did not bring a result as satisfactory as that of MixB, independent of the amount of gypsum added. In MixB, the composition is estimated to have approximately 40 wt-% of calcium ferrite, but only about 10 wt-% is contained in MixA. The result of this is a remarkable difference in compressive strength. In this case, the ferrite phase provides both the early strength and the final strength of the SAB cement. It has been stated that calcium ferrite phases possess higher reactivity in SAB compositions compared to OPC ⁷. The results show that mortars of MixB measured strengths in accordance with what is suggested in the literature for a slow hardening composition based on the C – S – A – S⁻ system ⁷. The results obtained also imply that there

is a saturation point at about 5 % with regard to the addition of gypsum. Going from 0 % to 5 %, there is a considerable increase in strength. If 10 % of gypsum is added instead, the compressive strength remains almost the same as if 5 % is added, regardless of the mixture composition.

3.3. Conduction calorimetry

The conduction calorimetry was performed on MixA 5% and MixB 5%, chosen based on the compressive strength results and on a commercial OPC. The heat generated from these samples as function of time is shown in figure 2. MixA 5% and MixB 5% give roughly the same pattern, although MixA 5% seems to react slightly faster for the first seven hours but does not release as much heat as MixB 5%. Still, both mixtures reach their maximum within 10 hours after which both of them also start to level off. The OPC sample reacts much more than MixA 5% and MixB 5% and reaches its maximum after approximately 10 hours until it levels off. However, the heat liberation for OPC does not level off as quickly as in MixA 5% and MixB 5%.

Fig. 2. Results of calorimetry of mixtures compared to an, OPC.

The Aft is formed according to reactions (3) and (4), i.e. water and calcium sulphate react with sulphoaluminate instead of tricalcium aluminate. In this investigation, it is believed to be mainly reaction (3) that takes place in these mixtures, since no calcium hydroxide is expected before mixing with water, but polymorphs of C_2S will

contribute to reaction (4) by Ca^{2+} ions when C_2S dissolves, and thus react with OH^- ions to form $\text{Ca}(\text{OH})_2$. Furthermore, there will also be a contribution to Aft formation from the ferrite phases which follow the aluminates in OPC, though this reaction is reported to be much slower in rate. Considering the modified Bouge calculations, it can be assumed that the influence of heat developed due to hydration of ferrites is more pronounced in MixB than in MixA. As shown in figure 2, the first few minutes of heat liberation is the same for all samples. The initial period is characterised by wetting, producing very rapid exothermic reactions, as expected. The dormant period seems to last longer for MixB, but both MixA 5% and MixB 5% show a very strong and intense increase in reaction activity when the dormant period ends while the acceleration period lasts at least 1.5 hours for both MixA and MixB. After approximately 10 hours, both MixA and MixB start to level off dramatically and the heat liberation becomes very weak further on. Significant heat which is evolved in early hours is related to the formation of Aft, and it is well known that a substantial amount of sulphoaluminate present in any SAB composition is consumed in parallel to the Aft formation i.e. 60-70 % of the sulphoaluminate is usually consumed within the first 24 hours ⁷. The formation of Aft is not the only reaction which takes place, but it is surely the dominating reaction, as is supposed at early stages when SAB compositions hydrate.

3.4. Measurement of AFt

The formation of AFt was confirmed by the x-ray patterns given in figure 3. MixA 5% and MixB 5% have a similar diffractogram and both give a much higher intensity of AFt than OPC. Furthermore, as expected, Ca(OH)_2 can be observed for OPC, indicating the silicates being dissolved when mixed with water.

Fig. 3. X-ray diffraction patterns indicating formation of AFt.

The amount of AFt formation was analysed by differential scanning calorimetry (DSC). The first peak, in figure 4 of each sample belongs to acetone, and the heat accompanied with the AFt present was distinguished at approximately 150 °C. Since the amount could not be quantified, it is only the relative amount between the mixtures that can be evaluated. From figure 4, it can be noted that the amount of AFt is rather equal for MixA 5% and MixB 5% during the first 24 hours.

Fig. 4. The relative amount of AFt formed in mixtures.

All together, it can be concluded that the formation of AFt after a few hours is more accelerated in MixA 5% and MixB 5% in comparison to the formation of AFt in OPC. The amount of tricalcium silicate in OPC tested is approximately 54 %, which is much more than the expected amount of sulphaaluminate in MixA and MixB. As a result, the OPC obtained the more lasting heat development, to which the ferrites and dicalcium silicate reactions also contribute.

3.5. Scanning electron microscopy (SEM)

In both photos (figures 5a-b), needle-like crystals (Aft) can be observed in the matrix using SEM. The analyses are made after 2 days of hydration.

Fig. 5a. SEM MixA 5% 2 days hydration.

Fig. 5b. SEM MixB 5% 2 days hydration.

4. Conclusions

The results of the hydraulic properties of two SAB clinkers based on a large amount of steelmaking slags are covered in the present work. The results revealed a better usefulness for MixB mortars with regard to the compressive strength until 28 days of the hydration. After 2 and 28 days, the strength agrees to that suggested in the literature for a slow hardening SAB composition. The reason why MixA measured lower values in strength is believed to be a lack of ferrites in comparison to MixB. Nonetheless, whether the strength of MixA mortars is low or high enough depends on what application it is considered for. In future work it will be important to investigate the leaching behaviour of the materials as well as the quantity of each clinker phase present. If the slags are going to be used as raw meal in a production line, it is important to be able to control the production in terms of getting an even final product/composition, but that is beyond the scope of this paper.

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