

# Steelmaking slags as raw material for calcium sulfoaluminate belite cement

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## Abstract

In the steelmaking industry there is a need for recycling of by-products and development of new products. At the same time it is important to find ways of reducing the energy consumption as well as carbon dioxide emissions during the manufacture of cement. One option available, as an alternative to ordinary Portland cement, is to produce a belite-rich cement activated with calcium sulfoaluminate,  $C_4A_3\bar{S}$ .

In this project which is undertaken as part of MiMeR, (Minerals and Metals Recycling Research centre), the last alternative is investigated by using metallurgical slags as the main component, but also additions of calcium carbonate, anhydrite and aluminium oxide. The results show similar behaviour of two different mixtures analysed with TG/DTA and X-ray powder diffraction at three different temperatures, 750°C, 1200°C and 1320°C. In both mixtures formation of  $C_4A_3\bar{S}$  was found along with other hydraulic minerals.

## Introduction

There are good reasons using industrial by-products as a raw material or as an admixture to cement and concrete. Considering the oxide composition of slags and fly ashes, it is reasonably sound using these materials, in the production of special cements, i.e. as an alternative to ordinary Portland cement. The advantage of producing such cement provides the possibility to decrease the burning temperature as well as less calcium carbonate needed in the raw mixture, i.e. the lime saturation factor might be held in the interval of 80-85 %, which enable the reduce of carbon dioxide emissions (Popescu et al., 2003; Sharp et al., 1999), and does not adversely effect the quality of the final clinker.

In the present work, two different raw mixtures were prepared by using modified Bouge computations (Majling et al., 1999) in order to estimate the amounts of each material needed. The mixtures consist mainly of slags but also additions of calcium carbonate, anhydrite and aluminium oxide. The objective is to illustrate the possibility of using by-products as a raw material in the manufacture of cement and to compare the influence of different amounts of different products.

## Experiment

Raw materials were combined according to table 1, i.e. estimated by using modified Bouge computations. In table 2 the chemical analysis are presented, both calculated and analysed.

**Table 1** *Mixtures prepared*

<b>SAB mix 1</b>		<b>SAB mix 3-LB</b>	
<b>components</b>	<b>wt-%</b>	<b>components</b>	<b>wt-%</b>
AOD slag	55	AOD slag	14
Ladle slag	15	EAF slag	25
Anhydrite	10	Ladle slag	25
Aluminium oxide	10	Anhydrite	5
Lime	10	Aluminium oxide	6
		Lime	25
	100		100

*AOD*= Argon Oxygen Decarburization, *EAF*= Electric Arc Furnace

**Table 2** *Calculated and analysed chemical composition for each mixture prepared*

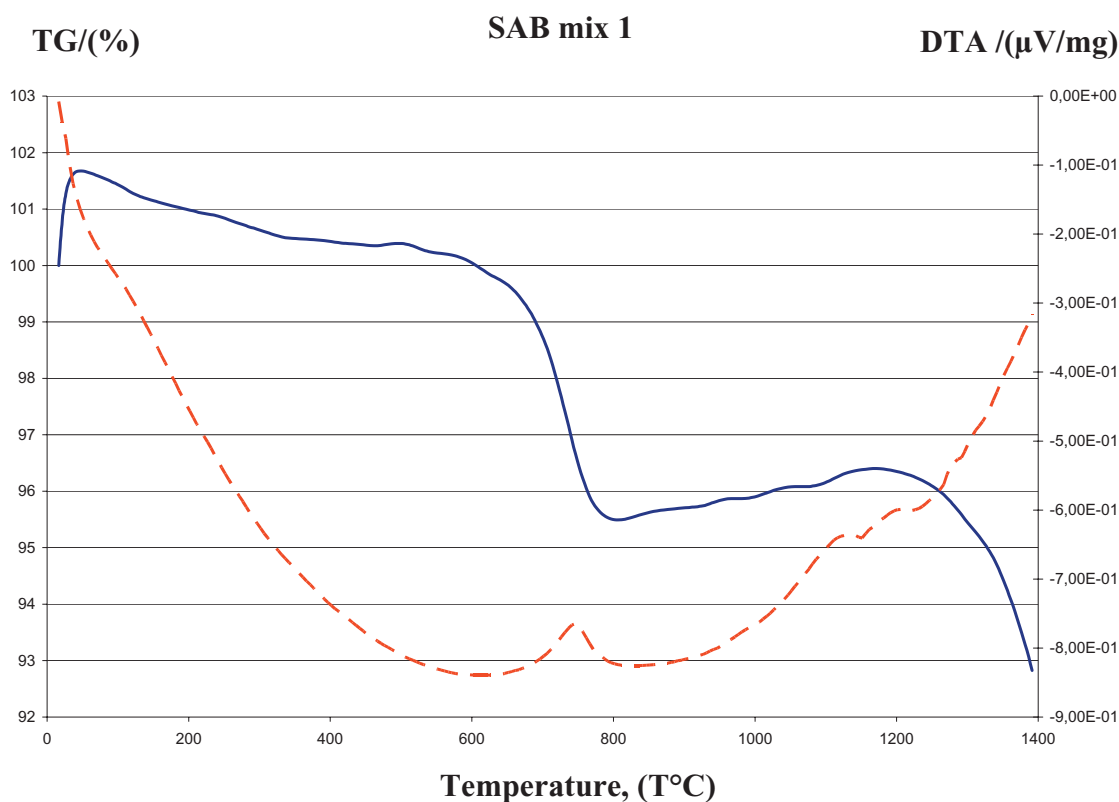
<b>Mixture</b>	<b>CaO</b>	<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fetot</b>	<b>MgO</b>	<b>S</b>	<b>others</b>	<b>total</b>
<b>SAB mix 1 calculated</b>	46.1	17.14	12.41	1.09	4.22	5.28	13.76	100
<b>SAB mix 1 analysed</b>	49.52	19.31	16.42	1.59	4.28	2.64	6.24	100
<b>SAB mix 3-LB calculated</b>	41.26	11.18	11.37	9.76	5.76	2.58	18.09	100
<b>SAB mix 3-LB analysed</b>	43.24	10.67	14.26	8.86	5.72	1.13	16.12	100

For Thermo-Gravimetric (TG) and Differential Thermal Analysis (DTA) a Netzsch STA 409 instrument was used. The samples were heated 10°C per minute in air until the temperature reached 1400°C. No correction was run.

Material used in the furnace trials, was prepared as pellets by mixing the material with water and then dried prior introduction to the furnace. Considered temperatures were chosen based on the TG/DTA results, i.e. 750°C, 1200°C and 1320°C. The pellets were burned for 15 minutes at 750°C, and 20 minutes at 1200°C and 1320°C, before rapidly cooled in water. After cooling the samples were dried and prepared for X-ray diffraction analysis. A Siemens D5000 X-ray powder diffractometer with CuK $\alpha$  radiation at 40 kV and 40 mA was used.

## Results and Discussion

The results of TG/DTA, SAB mix1 are presented in figure 1 and SAB mix3-LB in figure 2.



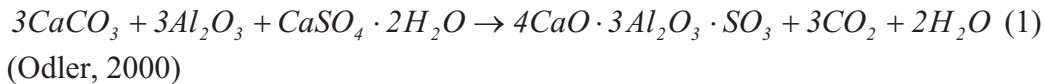
**Fig. 1** Results of TG/DTA, SAB mix1 Red line (---) = DTA, Blue line = TG

The TG results, in figure 1, indicate a decrease in mass at approximately 680°C, i.e. 4.67 % and which give rise to a pronounced endothermic peak according to the DTA curve, reaching a maximum at 749°C. The reaction occurring corresponds to CO<sub>2</sub> release,  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ , and was detected by mass spectrometer. It is reasonably sound to observe dissociation of calcium carbonate at these temperatures. Moreover, calculations imply that the detected CO<sub>2</sub> originates from the added 10 % of calcium carbonate.

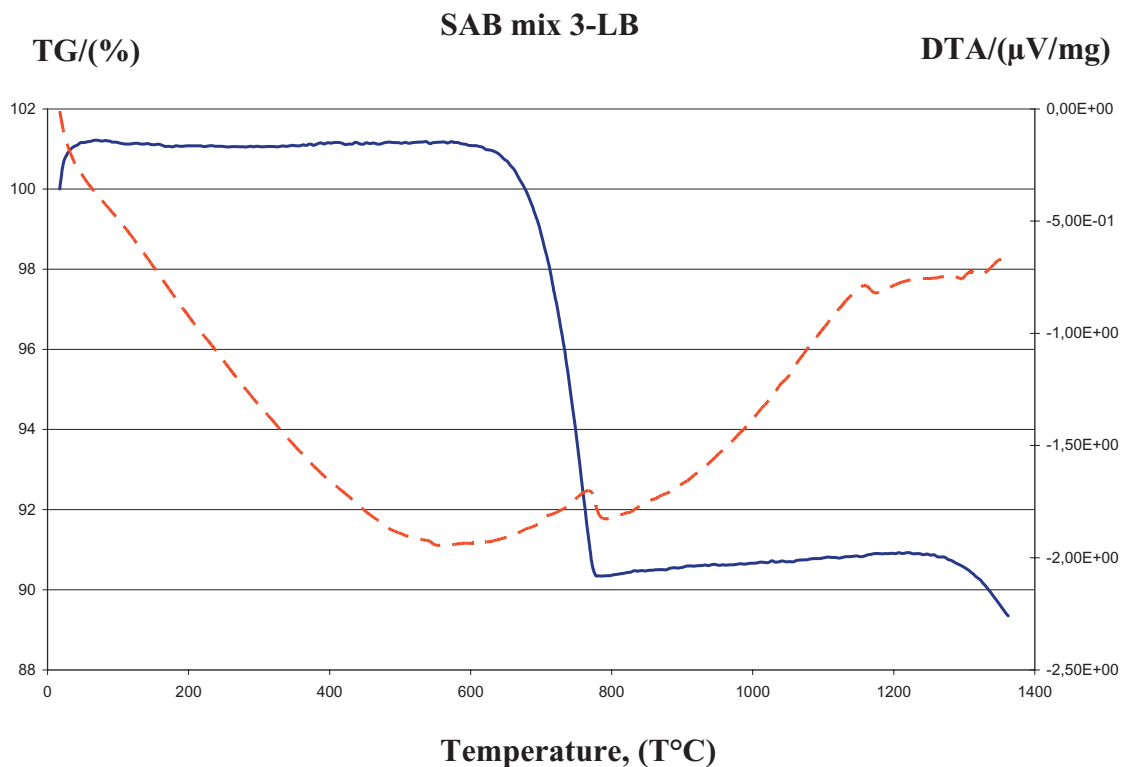
In the range of 800°C to 1200°C the sample tends to increase slightly in weight, probably due to an oxidation of the material. The second most important weight loss to be noticed starts at 1324°C. The mass change is related to SO<sub>2</sub> releases and was determined to 3.68 %.

Apparently, there are phase transitions in the composition between 1100°C and 1280°C. The transitions are confirmed by one exothermic peak at 1149°C and an endothermic peak at 1278°C, without any change in mass. In this particular temperature range, i.e.

1000-1250°C, the formation of calcium sulfoaluminate is suggested by literature (Odler, 2000). The overall reaction usually taking place can be written as:



It is, however, necessary to point out that anhydrite was used in the experiments and not gypsum as written in the chemical reaction. It is very important that aluminosulfate is formed during the burning otherwise the properties of the final clinker will fall, having in mind it is supposed to substitute tricalcium silicate found in ordinary Portland cement and thereby provide early strength to the cement until the hydration reaches approximately 28 days.



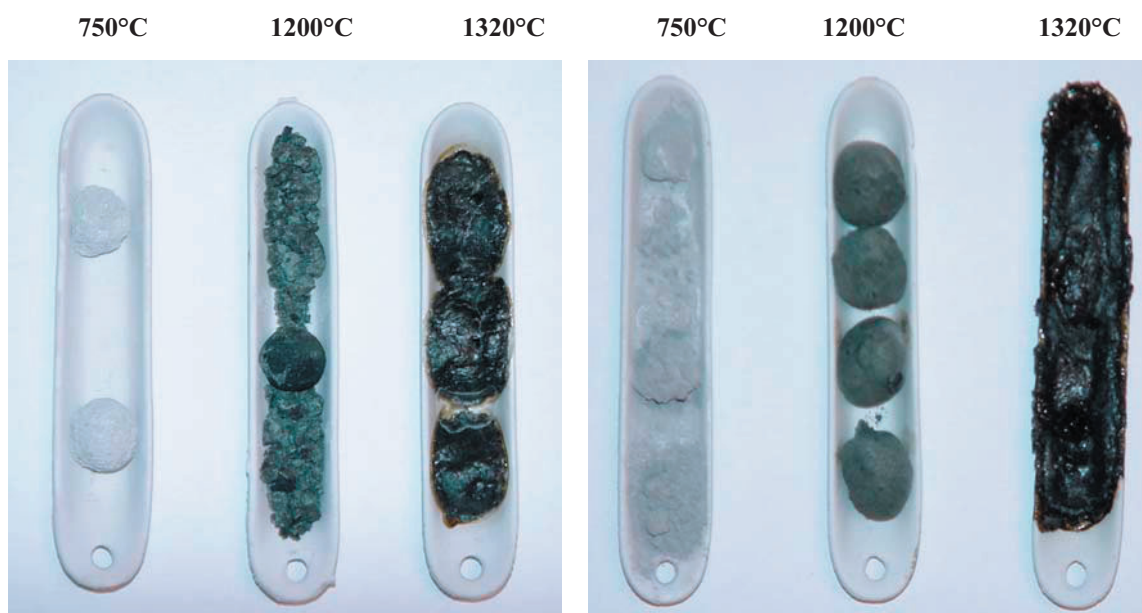
**Fig. 2** Results of TG/DTA, SAB mix3-LB Red line (---) = DTA, Blue line= TG

The results in figure 2 are very similar to those of SAB mix 1 already discussed in figure 1. The weight loss starting at 705°C corresponds to the releases of carbon dioxide and was determined to 10.77 % (which refers to added carbonates, 25%) and at the same time there is a distinct endothermic peak at the DTA-curve reaching a maximum at 768°C. The other weight loss, i.e. 1.62 % at 1300°C, relates to SO<sub>2</sub> emissions. No other possible gases which could have been found were detected, i.e. alkalis, chlorines and carbon monoxide. This result applies to both mixtures. The increase in mass at 800°C until approximately 1200°C is due to a small oxidation of the sample.

As in the first case, there is a phase transition taking place in between 1150°C until 1320°C, which represents a small endothermic peak at 1170°C and another two, but exothermic at 1296°C and 1320°C. One important transformation is of course the formation of aluminosulfate which shall be seen in the other results and another would be the formation of tricalcium aluminate, but this must be analysed further. It is, however, not likely to refer any of these peaks to the release of SO<sub>2</sub>.

### Furnace Trials

At 750°C the pellets exploded when cooled, independent of mixture, figure 3 and figure 4. As a result, only two pellets are left in the case of SAB mix 1, figure 3. The phase transition earlier discussed can also be seen in figure 3 and figure 4 for each mixture, i.e. both mixtures shift their colour from grey to green after rapidly cooled. In figure 3 it looks like the pellets have fallen apart at 1200°C, this is, however, not the case as these pellets remained intact even after cooling just like pellets of SAB mix3-LB at 1200°C in figure 4. At 1320°C both mixtures start to smelt especially when it comes to SAB mix3-LB. This is not a preferable result at all and it needs to be considered further.



**Fig. 3** SAB mix 1 after burning

**Fig. 4** SAB mix 3-LB after burning

### X-ray powder diffraction

The x-ray patterns shown in figure 5 and figure 6 confirm the transformations taking place at different stages in the burning process. The identified minerals are marked with numbers ranging from 1-9, figure 5 and 1-11 in figure 6. Peaks denoted 1 in figure 5 at 1200°C and 1320°C confirm the formation of aluminosulfate. Apparently, the intensity of these peaks is less at 1320°C. This result agrees with the literature, saying that aluminosulfate starts to decompose at temperatures above 1200°C and react with free lime to yield tricalcium aluminate, (Odler, 2000).

It is generally accepted that dicalcium silicate can exist in at least five different polymorphs and switch between these structures when heated or cooled, (Chan et al., 1992). Thereby,  $\gamma$ -2CaO·SiO<sub>2</sub>, found at 750°C, in figure 5 (and the least hydraulic polymorph), is probably a reason of finding  $\beta$ -2CaO·SiO<sub>2</sub> and  $\alpha$ -2CaO·SiO<sub>2</sub>, i.e. Larnite and Bredigite at high temperatures. Another possible source of finding Larnite and Bredigite is of course the calcium carbonate added to the raw mixture which also is consumed during the formation of aluminosulfate. At 750°C, the  $\gamma$ -2CaO·SiO<sub>2</sub> was not expected, i.e.  $\beta$ -2CaO·SiO<sub>2</sub> was supposed to be detected. However, these kinds of reactions are known to be very slow and as an explanation, the phenomenon of finding  $\gamma$ -2CaO·SiO<sub>2</sub> instead of  $\beta$ -2CaO·SiO<sub>2</sub> could be described in terms of kinetics.

Other minerals found at 750°C, i.e. CaSO<sub>4</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> are also believed to be consumed during phase transitions, which then would be the explanation to why these components not appear at higher temperatures. CaSO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> are already mentioned in relation to the TG/DTA results. MgO, on the other hand seems to contribute to the formation of Bredigite though it is likely that the manganese atoms, being part of the Bredigite structure most probably originally belongs to the MgO registered at 750°C, although this must be analysed further.

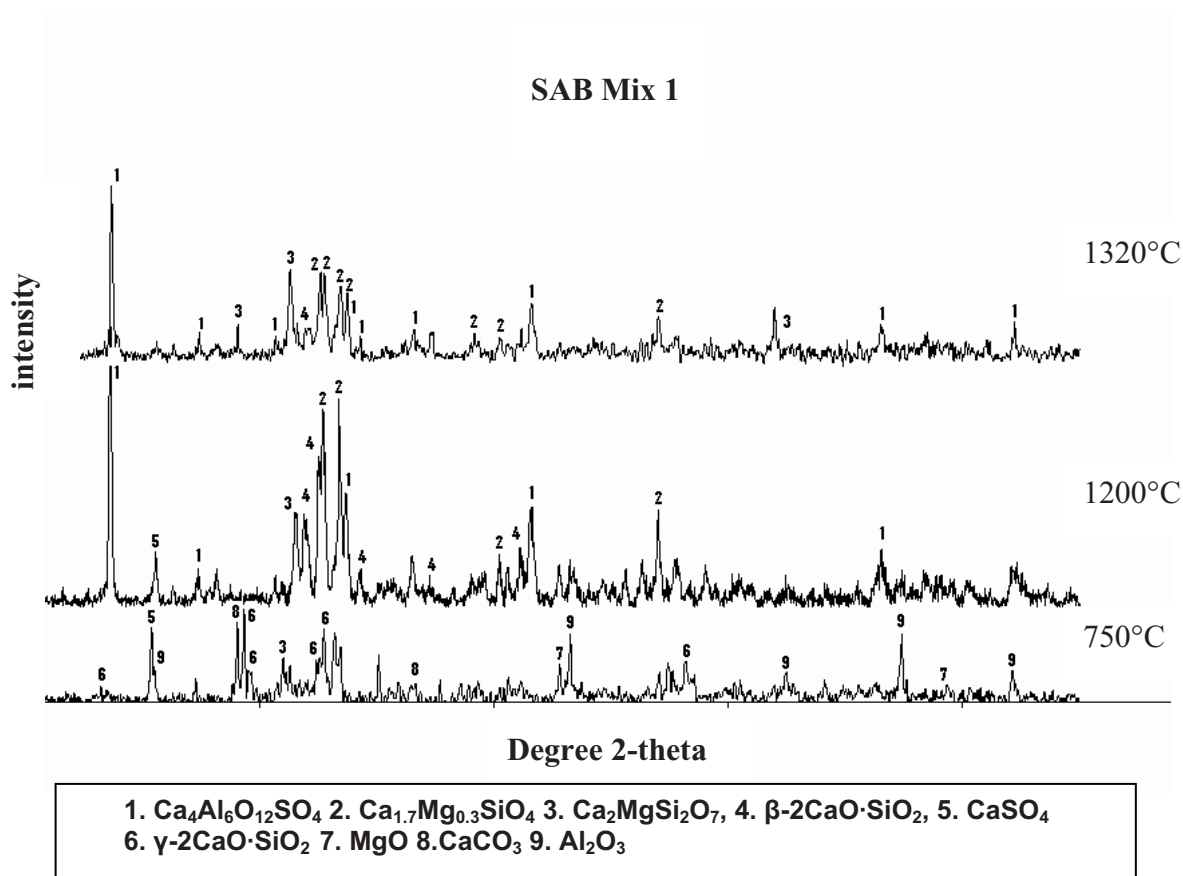
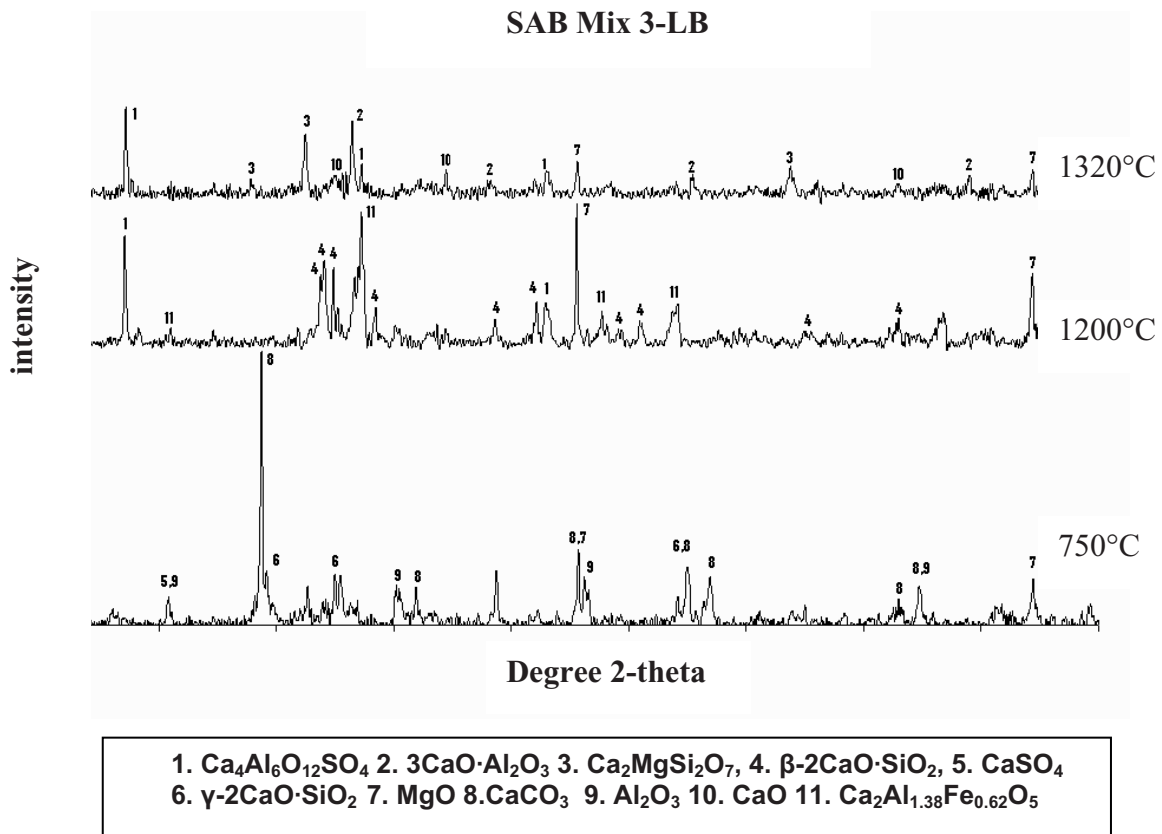


Fig. 5 X-ray diffractograms of SAB mix 1 at different temperatures

The results obtained for SAB mix3-LB is very similar to those discussed for SAB mix1 regarding phase transformation. In the pattern describing the phases at 1200°C aluminosulfate was detected along with a new phase,  $\text{Ca}_2\text{Al}_{1.38}\text{Fe}_{0.65}\text{O}_5$ , but also  $\beta\text{-2CaO}\cdot\text{SiO}_2$  and free Periclase, which did not appear at the corresponding temperature in mixture 1. Then, on the other hand, there was no Bredigite found which in contrast was observed in mixture 1. At 1320°C, tricalcium aluminate (third most important clinker mineral in ordinary Portland cement) appeared, as well as Akermanite, which was found at all stages in relation to mixture 1, with varied intensity. The reason of finding tricalcium aluminate is probably due to decomposition of calcium sulfoaluminate mentioned, followed by the reaction with free lime. In addition to that, small peaks belonging to free MgO were detected and also small amounts of free lime.



**Fig. 6** X-ray diffractograms of SAB mix3-LB at different temperatures

## Conclusions

In both mixtures, calcium sulfoaluminate,  $C_4A_3\bar{S}$ , was formed during the burning. This is a very important result since it is supposed to provide early strength by substituting tricalcium silicate found in ordinary Portland cement. It was determined that measured  $CO_2$  releases in fact originate from the added calcium carbonate which in turn is much less than that of raw mixtures based on limestone and clay, i.e. approximately 45 % compared to 4.7 % in SAB mix1 and 10.8 % in SAB mix3-LB.

Next important step in the evaluation of the materials is to prepare moulds and estimate the hydraulic properties. If the moulds provide reasonable strength, the lime saturation factor would not be of any particular concern. Moreover, since mainly slags are used it should be possible to keep the burning temperature at  $1200^\circ C$ , since the content of dicalcium silicate in slags is high, i.e. there is only a need of controlling the phase transformation of dicalcium silicate and the formation of aluminosulfate to gain a material possessing hydraulic behaviour. That requires of course that there is enough dicalcium silicate present in the raw mixture.

## References

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