



	<b>Experiment title:</b> <b>Influence of Minor Elements, in particular SO<sub>3</sub>, on the Clinkerisation Process</b>	<b>Experiment number:</b> CH-1724
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## Report:

In commercial clinker all four major clinker phases ( $2\text{CaO}:\text{SiO}_2$  (C2S),  $3\text{CaO}:\text{SiO}_2$  (C3S),  $3\text{CaO}:\text{Al}_2\text{O}_3$  (C3A) and  $4\text{CaO}:\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$  (C4AF)) are present as solid solutions rather than as stoichiometric end-members because of the presence in the raw materials or in the fuels of minor constituents such as MgO,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  or  $\text{SO}_3$ . The addition of such minor components to the four major components influence the clinkerisation process, especially the phase relationships in the quaternary system  $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ , the basic system in the formation process of cement-clinker phases [1].

The purpose of these in-situ experiments is to better understand the details of the formation of the high temperature phases from the melt with appropriate composition.

Two basic samples with different composition as major oxide and two samples for each of them with different  $\text{SO}_3$  additions (0.75% and 1.5% respectively) were prepared.

The samples were previously pre-calcined and charged in platinum capillaries with an inner diameter of 0.52 mm and a wall thickness of 0.04 mm. Samples containing  $\text{SO}_3$  were sealed to avoid sulfate evaporation.

The heating system used was the optical furnace with halogen lamps [2] to heat the samples up to 1500 °C, then the samples were cooled down to 1200 °C with temperature steps of 25 or 50 °C.

The temperature in the furnace was estimated by using the platinum capillary as internal standard having known thermal expansion coefficient. The platinum (0 0 2) peak was used for calibration.

Fig. 1 shows some XRD pattern collected for one of the samples during heating from 700 °C to 1500 °C. Silicate phases formation and C2S polymorph transition are detectable.

The XRD powder patterns were analysed by Rietveld method, using the TOPAS software (vers. 2.1) [3].

Fig. 2 shows a plot of the calculated weight fractions for the phases for one sample during the heating up to maximum temperature (1500°C) and during the cooling up to temperatures below the eutectic point (1338 °C). CaO and Quartz react to form  $\alpha'$ -C2S. At ca. 1300 °C the C2S polymorph transition from  $\alpha'$  to  $\alpha$  is completed and C3S appears, reaching its maximum content just before the eutectic temperature. In the temperature range from 1332 to 1274 °C the aluminate phases (C3A and C4AF) appear, a great decrease in C3S content and the C2S polymorph transition from  $\alpha$  to  $\alpha'$  are observed.

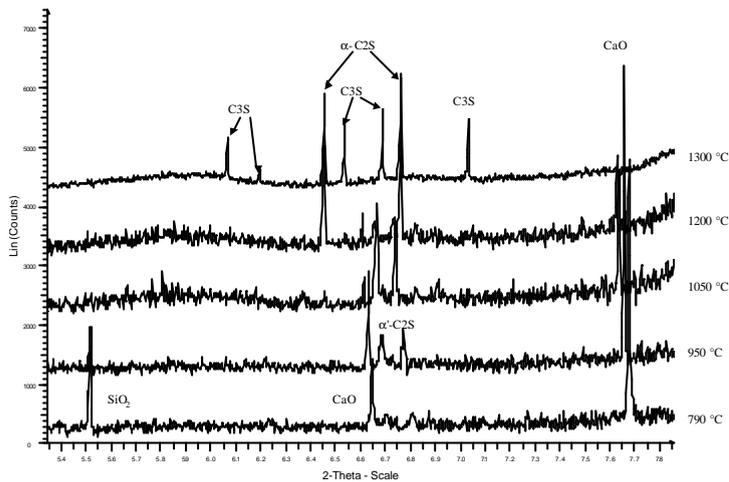


Fig. 1 – Some XRD patterns collected at different temperatures

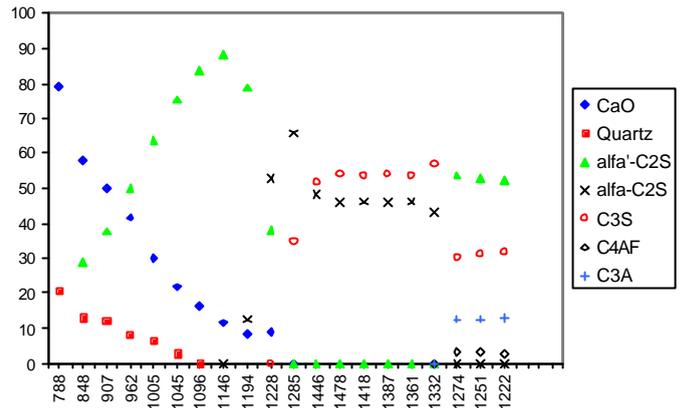


Fig. 2 – Plot of the calculated weight fraction of clinker phases during the heating and then the cooling of one sample

Fig. 3 show the plot of the C3S/C2S ratio obtained by Rietveld refinement for three different samples, with the same composition as main oxide but with different SO<sub>3</sub> contents during the cooling from the maximum temperature to a temperature below the eutectic point. Increasing the SO<sub>3</sub> in the sample causes a decreasing in the C3S/C2S ratio in the clinker, from 2.5 for the sample without SO<sub>3</sub> to less than 1 for the sample with 1.5% of SO<sub>3</sub> in agreement with data obtained by ex-situ experiments [4]. For samples with 0 and 0.75% of SO<sub>3</sub> the C3S/C2S ratio increase up to the eutectic point and in correspondence of the appearance of the aluminates phases a great decrease is observed. In the sample with 1.5% of SO<sub>3</sub> the C3S/C2S ratio decreases during the cooling. The presence of SO<sub>3</sub> seems to influence considerably the C3S/C2S ratio, and produces negligible variation in the transition temperatures.

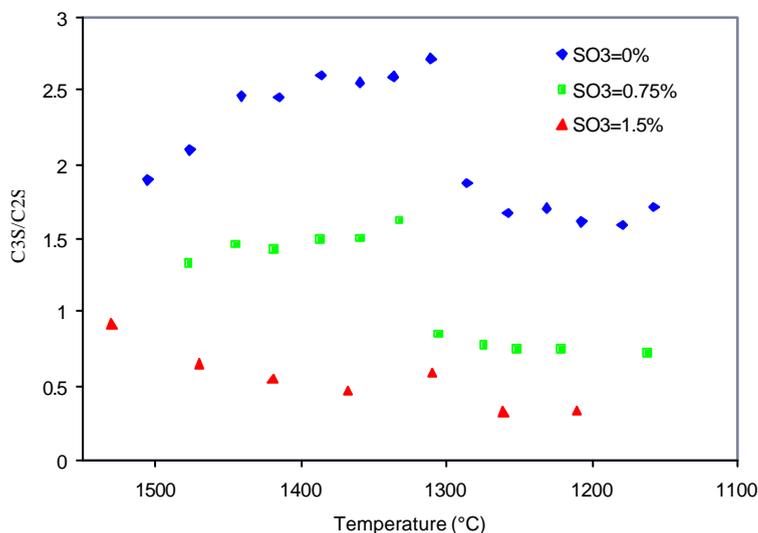


Fig. 3 – Plot of the C3S/C2S ratio during the cooling for three samples with different amount of SO<sub>3</sub>

## REFERENCES

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