

# ALKALI ACTIVATION OF SYNTHETIC GAMMA DI-CALCIUM SILICATE WITH PURE CALCINED NATURAL CLAYS

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## Introduction

Stainless steel slag such as Argon Oxygen Decarburisation (AOD) and continuous casting (CC) slag are crystalline in nature and primarily rich in gamma di-calcium silicate ( $\text{Y-C}_2\text{S}$ ), which has poor hydraulic properties. Therefore, the use of these slags as a hydraulic binder is unfavourable in building materials. Recent study<sup>1</sup> has examined the effectiveness of mechanical and chemical activation of  $\text{Y-C}_2\text{S}$ ; these activations increased the hydraulic reactivity of  $\text{Y-C}_2\text{S}$  and transformed it into a reactive hydraulic component. The aim of this investigation is to transform the synthetic  $\text{Y-C}_2\text{S}$  into a single reactive binder system by mixing it with pure calcined natural clays such as kaolinite, Na- and Ca- montmorillonite and to study the effect of using clays on the hydraulic properties. Using pure calcined natural clays as a source of aluminosilicate promotes the formation of three-dimensional aluminosilicate network of zeolite, which gives the binding property to the binder.

## Materials and Methods

Three pure and calcined clays were used in this study, one kaolinite and two montmorillonites. Kaolinite (KGa-1b), Na-montmorillonite (SWy-3), and Ca-montmorillonite (STx-1b) were obtained from the Clay Minerals Society repository. The two-montmorillonite clays undergo a purification process using Jackson-treatment method<sup>2</sup> in order to remove the residual impurities of titanium dioxides, carbonates, quartz, and organic materials, which may influence the activity of the clays. The fraction less than  $2\text{ }\mu\text{m}$  was separated by centrifugation to obtain smectite, which contains less than 2% impurities. Thereafter, Kaolinite and montmorillonite were calcined in a laboratory programmable fixed-bed furnace at  $700^\circ\text{C}$  and  $800^\circ\text{C}$  respectively. Gamma di-calcium silicate was produced using chemical grade silicon dioxide and carbonates which were mixed for 24 hours in an ethanol suspension using 10 mm zirconia milling balls, and sintered at  $1450^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$  for 20 h. Subsequently, the sintered materials were cooled down to room temperature at a rate of  $1^\circ\text{C}/\text{min}$  and milled using high energy bead mill (Dispermat SL-12-C1, VMA), 100 g of synthetic  $\text{Y-C}_2\text{S}$  powder were milled in 500 ml of ethanol at 5000 rpm for 6 h using

1 mm ZrO<sub>2</sub> milling balls. The hydration reactivity has been studied by preparing calcined pure clay- Y-C<sub>2</sub>S mixtures. The mixtures of calcined pure clay and synthetic Y-C<sub>2</sub>S were dry mixed in a 1:1 weight ratio using tubular mixer for 2 h, 10M NaOH was added to the dry mix in a binder/ solution ratio of 1. The mixtures were stored in sealed containers. After 28 days, the pastes were freeze dried at 0.03 mbar and temperature of -62°C for 2 h to stop the hydration reactions<sup>3</sup>. The Freeze-drying is carried out using an Alpha 1-2 LD Martin Christ type freeze-dryer without pre-freezing the samples. The bulk chemical analysis of the pure calcined clays was measured by Varian 720Es ICP-OES. A lithium metaborate fusion was used as dissolution method. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. The samples were pre-treated by heating to 400°C for 12 h in a continuous N<sub>2</sub> gas flow. The measurement was performed on a Micrometrics Tristar 3000 using N<sub>2</sub> as an adsorbate. In order to monitor the hydraulic reactions of the new hydration products, isothermal conduction calorimetry (TAM Air Device, TA instruments) was used at a temperature of 20°C, with Clay to Y-C<sub>2</sub>S ratio equal to 1 and binder to liquid ratio of 1. In addition to a quantitative X-ray powder diffraction, the samples were mixed with 10% ZnO as internal standard. The XRD diffractions were recorded on a Philips PW 1830 diffractometer; samples were scanned over a range of 5 to 65° 2θ with step size of 0.02° 2θ and step time of 2 seconds.

## Results and Discussion

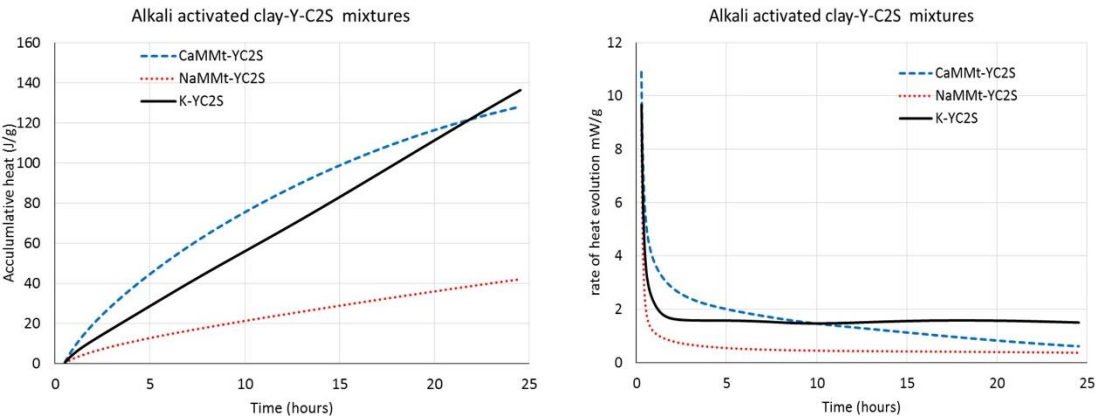
The chemical composition and the specific surface area of the unfired clays and synthetic Y-C<sub>2</sub>S are shown in Table 1. Si/Al ratio of kaolinite-1 was lower than the other clays due to the higher alumina content in kaolinite.

Figure 1 Shows that the rate of heat evolution of the Ca-MMt/YC<sub>2</sub>S mixture is slightly higher than K/YC<sub>2</sub>S and Na-MMt/YC<sub>2</sub>S mixtures, this is probably due to the high Si/Al ratio which enhance the dissolution reaction of the aluminosilicate oxides in addition to the high specific surface area which increase the reactivity of the materials, yet, the rate of the hydration reaction is slow for the three mixtures. The pattern doesn't show any early hydration peaks, one possible explanation for the prohibition of the reaction is that the system was under high alkalinity conditions, which hindered the formation of the reaction products by slowing solubility of Ca<sup>+2</sup> ions. The pattern of the accumulative heat of hydration shows that the total heat release with the Ca-MMt/YC<sub>2</sub>S is higher than K/YC<sub>2</sub>S and Na-MMt/YC<sub>2</sub>S. The same approach can be easily noted in Figure 2, where the XRD pattern of the raw materials and the alkali activated mixtures after 28 days of reaction. It's difficult to identify the reaction products from XRD; the amorphous nature of the hydration products might be the main reason in addition to the low amount of these products.

**Table 1:** Chemical composition, specific surface area and Si/Al ratio (calculated based on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of the unfired clay) of the raw materials

wt%	Kaolinite	Ca-MMT	Na-MMT	Y-C <sub>2</sub> S
Al <sub>2</sub> O <sub>3</sub> %	41.24	14.23	20.36	0.23
CaO %	0.04	2.33	0.14	64.30
FeO %	0.22	0.85	3.62	0.06
K <sub>2</sub> O %	0.00	0.07	0.11	0.00
MgO %	0.06	2.68	2.17	0.49
MnO %	0.00	0.01	0.00	0.03
Na <sub>2</sub> O %	0.08	0.15	2.91	0.08
SiO <sub>2</sub> %	47.65	63.03	61.60	34.73
TiO <sub>2</sub> %	1.78	0.22	0.14	0.03
LOI	8.70	15.5	8.8	
SSA (m <sup>2</sup> /g) unfired	11.01	75.30	30.83	8.84
Si/Al	1.0	3.8	2.6	

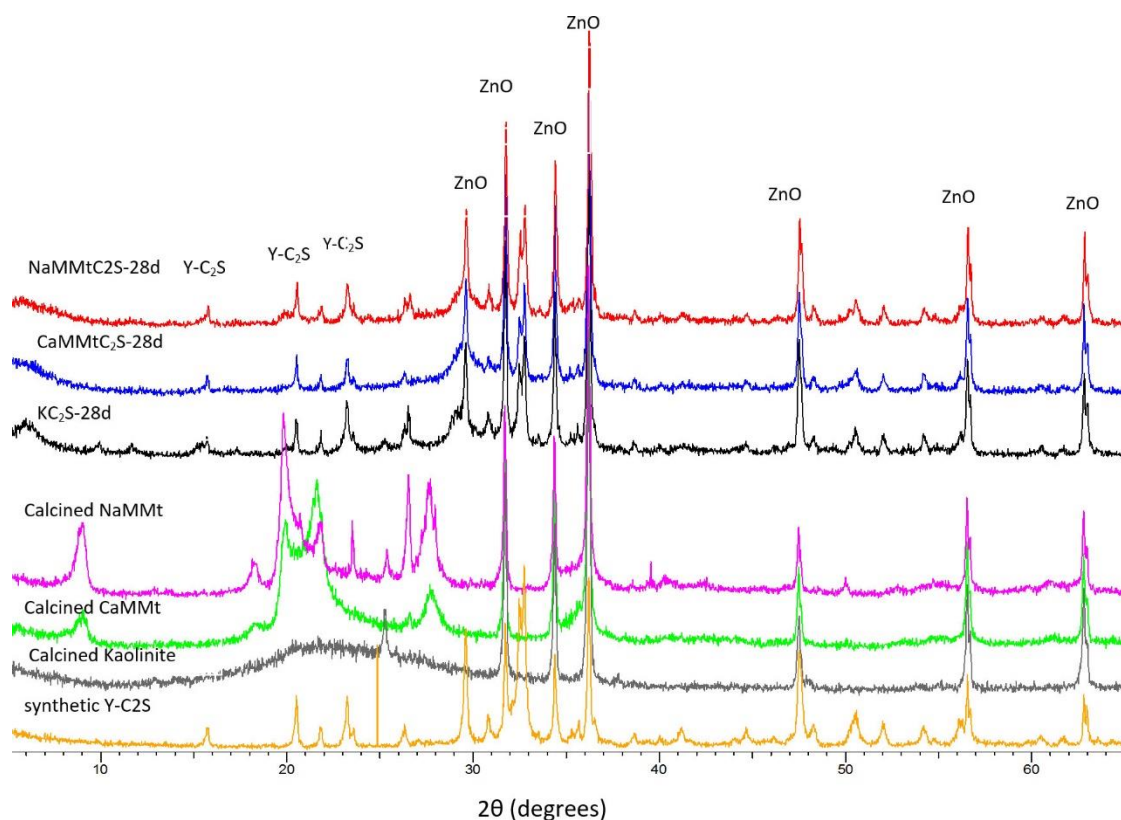
\*Ca-MMt is calcium montmorillonite, Na-MMt is sodium montmorillonite and K is Kaolinite



**Figure 1:** Isothermal conduction calorimetric of alkali activated clay- Y-C<sub>2</sub>S mixtures at 20°C

## Conclusions

There are no new crystalline peaks proving the presence of any reaction products resulting from the alkali activation of these clays with the synthetic YC<sub>2</sub>S, one might argue that crystalline C-S-H is not a product formed as a result of the alkaline activation of these mixtures under the conditions and parameters used in this investigation.



**Figure 2:** XQRD pattern of alkali activated clay/Y-C<sub>2</sub>S mixtures at 28d and the raw materials

## References

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