

EFFECT OF TEMPERATURE ON THE ALKALI ACTIVATION OF CONTINUOUS CASTING STAINLESS STEEL SLAG

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Summary

Continuous casting slag from stainless steel production containing non-hydraulic minerals was activated in alkaline solutions at elevated temperature by steam curing. A steam curing cycle of 24 hours including 16 hours of steam curing was used to provide the elevated temperatures of 60 °C, 70 °C, 80 °C, 90 °C, 100 °C and 110 °C. The compressive strength of the mortars prepared using the slag was found to increase steadily with the increase in the steam curing temperature. Na activators generated higher compressive strength than K activator though Na activated mortars showed higher porosity. Presence of CSH as reaction product was evident by thermal and FT-IR analysis.

Keywords: stainless steel slag, alkali-activation, steam-curing, TGA, porosity, SEM, FTIR

1 Introduction

Stainless steel production results in the generation of different kinds of slags at different stages of processing. At the final stage of processing in a continuous casting (CtCs) pot, CtCs slag is generated. This slag is distinct by its unique dusty appearance. Hence, unlike other stainless steel slags, it cannot be valorised as aggregates. The dusty appearance is related to the mineralogy of the slag. CtCs slag contains high amount of dicalcium silicate (C_2S) which goes through several polymorphic transformations during cooling; $\alpha C_2S \rightarrow \beta C_2S$ at 675 °C and $\beta C_2S \rightarrow \gamma C_2S$ at 490 °C. The $\beta \rightarrow \gamma$ transformation is accompanied by a volume increase of approximately 12%, which leads to high internal stresses in the

solid slag (β polymorph) and finally causes the slag to self-pulverise, leading to the final dusty appearance [1].

A high CaO content in the CtCs slag gives it a compositional resemblance to ordinary Portland cement, although in terms of mineral composition, most minerals present in the CtCs slag, unlike Portland cement, are non-hydraulic. In previous studies the authors found that CtCs slags exhibit certain binding capabilities under the influence of alkaline activators at elevated temperatures (steam curing) [2]. Most studies on alkali-activated systems are on amorphous materials and a detailed study on the effect of temperature on the hydration reaction in crystalline slags is scarce. In the current study different steam curing temperatures have been tried to stimulate binding reactions in CtCs slag to investigate the influence on the hydration reaction, compressive strength and microstructure of the resulting material.

2 Materials and methods

The CtCs slag was obtained from a stainless steel producing plant. For the current study, fractions finer than 80 μm (CtCs_80) were used. The characterisation of oxide content was carried out by X-ray fluorescence (XRF) analysis and the phase compositions were identified by quantitative X-ray diffraction (QXRD). 5 M Sodium hydroxide (NaOH) mixed along with sodium silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) and 5 M potassium hydroxide (KOH) mixed with potassium silicate, $\text{K}_2\text{O} \cdot \text{SiO}_2$ was used as alkaline activator. The hydroxide to silicate ratio was kept at 50:50.

The activator to slag ratio was kept at 0.7. A 24-hour steam curing cycle with 16 hours of steam curing time was followed to provide accelerated curing condition. Open porosity of the slag mortars was determined after 28 days of curing (EN 1936). The hydration reactions on the powdered vacuum dried slag pastes after 28 days of hydration were followed by thermogravimetric analysis (TGA), electron microscopy in secondary electron mode and Fourier transform infrared spectroscopy (FT-IR).

3 Results and discussion

The mineral quantities of CtCs_80 are shown in **Tab. 1**. It can be observed that, dicalcium silicate in the γ -form ($\gamma\text{-C}_2\text{S}$) is the most predominant mineral. It is present in two forms, γ -1 possibly has some substitutions and the normal form γ -2. The fluorine containing mineral cuspidine is also seen in the slag. This is due to the addition of CaF_2 in the continuous casting pot to lower the melting temperature of the slag. It can be noted that none of the minerals present in the slag are hydraulic and the slag is highly crystalline ($\approx 90\%$).

Tab. 1 Mineral composition of CtCs_80 by QXRD analysis

Minerals	C_2S γ -1	C_2S γ -2	Merwinite	Cuspidine	Periclase	Bredigite	Fluorite	Unknown/ amorphous
CtCs_80	14	35	4	16	10	9	3	9

It was found that at 28 days, the improvement in compressive strength at 110 $^\circ\text{C}$ was more than 5 times compared to that at 60 $^\circ\text{C}$. Also was interesting to note is that the strength of mortar samples with K activator approximately matched the strength of mortar samples

with Na activator at 10 °C lower curing temperatures. This indicates that Na activator is better at activating the binding reactions in the slag.

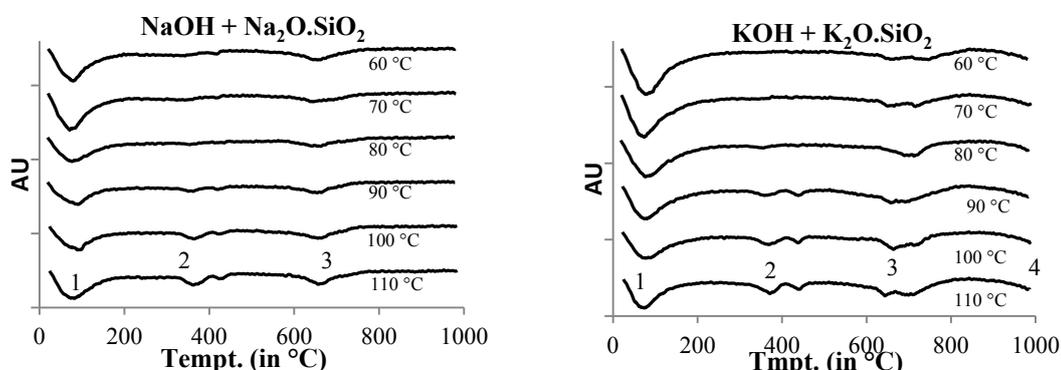


Fig. 1 DTG curve of CtCs_80 slag at different steam curing temperatures at 28 days

Nevertheless, the derivative of thermogravimetric analysis (DTG) on activated slag at 28 days (**Fig. 1**) shows that the main reaction products are similar. Peak 1 is in the dehydration range of C-S-H, which can form due to the hydration of crystalline calcium silicate phases. Peak 2, appears more dominantly at higher curing temperatures, corresponds to brucite which can form due to the hydration of periclase or magnesium containing silicate phases. Peak 3 represents calcium carbonate, formed due the carbonation of mineral phases. An additional peak (peak 4) that is observed to appear in the K activator at 1000 °C can be associated with K_2CO_3 .

Tab. 2 Open porosity of slag mortars at 28 days

Temperature/Porosity %	60 °C	70 °C	80 °C	90 °C	100 °C	110 °C
NaOH + $Na_2O.SiO_2$	24.22	24.39	24.58	24.49	24.3	23.04
KOH + $K_2O.SiO_2$	22.39	22.91	22.15	21.09	22.31	21.65

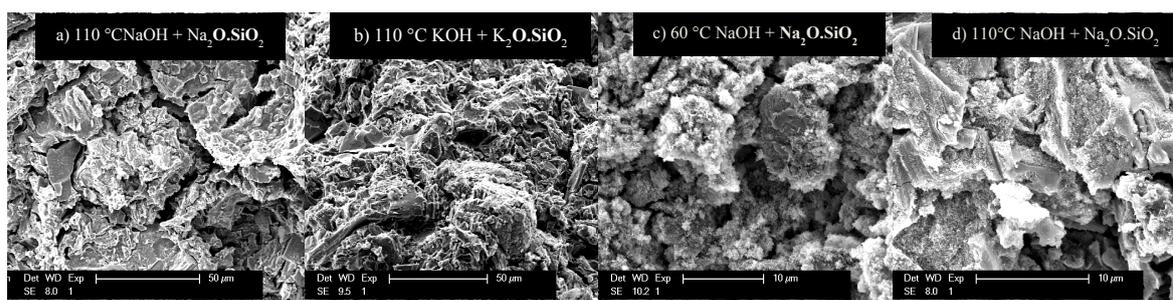


Fig. 2 SEM images of CtCs_80 slag paste at 28 days

Despite the striking difference in compressive strength of the mortars, there is no major difference in the open porosity of the slag mortars (**Tab. 2**) at different curing temperatures, although comparing the figures at 60 °C and 110 °C, a decrease can be observed. It can be observed that slag pastes activated with Na activator appear to be cracked and eroded whereas paste sample activated with K activator appears to be more homogenous. **Fig. 2 c, d** show the difference in microstructure of the reaction products at 60 °C and 110 °C with Na activator. At 60 °C the reaction products appear much smaller, needle like and dense. At

110 °C the matrix looks more consolidated and the reaction products are more dispersed. Also, higher quantities of reaction products were observed at 110 °C during the analysis.

Further insight in the reaction products can be observed by the FT-IR analysis in **Fig. 3**. It can be seen that different alkaline activator and different curing temperatures form similar reaction products. This is also seen in the DTG results. The peak at 860 cm⁻¹ (peak 1) in slag represents γ -C₂S. The peak at 970 cm⁻¹ (peak 2) can be assigned to Si–O stretching vibrations in C-S-H in the Q² tetrahedra. The band in the range 1400–1500 cm⁻¹ (peak 3) corresponds to the asymmetric stretching of CO₃²⁻.

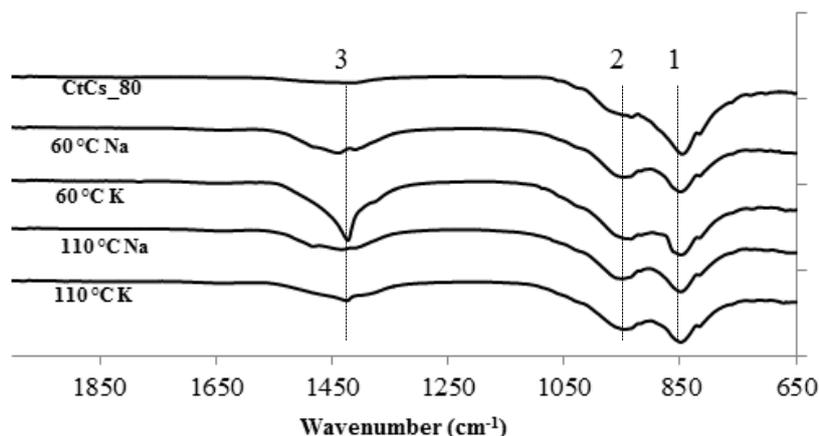


Fig. 3 FT-IR pattern of CtCs_80 slag at 28 days of hydration

4 Conclusions

CtCs slag containing a high amount of CaO and non-hydraulic minerals shows considerable hydration reaction capabilities at high temperatures under alkaline environment. Significant increase in the compressive strength of slag mortars is seen as the steam curing temperature is increased with the Na activator resulting in a higher strength. Formation of C-S-H in reaction product is confirmed in DTG and FT-IR studies. SEM and open porosity results show formation of a denser matrix with the K activator as compared to the Na activator.

References

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