



# Cementitious binders from activated stainless steel refining slag and the effect of alkali solutions



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## HIGHLIGHTS

- Alkalis and steam curing transform a non-hydraulic slag into a cementitious binder.
- Silicates in the activation solution lead to higher compressive strength.
- Thermal and FT-IR analysis indicate presence of C–S–H and carbonated phases.
- QXRD analysis shows decrease in dicalcium silicates and bredigite with time.
- Batch leaching shows lower leaching for K activator compared to Na.

## ARTICLE INFO

### Article history:

Received 12 June 2014

Received in revised form

14 December 2014

Accepted 23 December 2014

Available online 30 December 2014

### Keywords:

Stainless steel slag

Alkali activated cement

Compressive strength

Phase analysis

Thermal analysis

Leaching

## ABSTRACT

With an aim of producing high value cementitious binder, stainless steel refining slag containing a high amount of CaO in  $\gamma$ -dicalcium silicate form was activated with NaOH and Na-silicate as well as KOH and K-silicate solutions, followed by steam curing at 80 °C. Higher levels of alkali-silicate in the activating solution resulted in higher cumulative heat suggesting accelerated reaction kinetics. With respect to compressive strength, higher levels of alkali silicate resulted in higher strength and the mortars with Na activator were found to have higher early strength than the ones with K activator. The long term strength was found to be similar, regardless of the alkali metal. Thermogravimetric, QXRD and FTIR analyses showed an increase in the amount of reaction products (C–S–H type) over time, further confirming the reactivity of the crystalline slag. Batch leaching results showed lower leaching of heavy metals and metalloids with K activator compared to the Na activator. These results demonstrate that the alkali type and the ratio of hydroxide to silicates have a significant impact on the hydration and mechanical strength development of the stainless steel slag. The above findings can aid in the recycling and valorization of these type of slags which otherwise end up landfilled.

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## 1. Introduction

Various slags are generated in the production of stainless steel from scrap metal during the different stages of metal processing. The final phase of the metallurgical operation is carried out in a continuous casting ladle where slag is used as a covering layer for the molten metal to prevent its oxidation and minimize heat losses among others. Stainless steel refining (SSR) slag is generated as residue during this process. In terms of chemistry, SSR slag is

rich in calcium oxide (CaO), a major part of which is present in the form of dicalcium silicate (C<sub>2</sub>S). C<sub>2</sub>S goes through several polymorphic transformations as the molten slag cools down; of particular interest is the  $\beta$ -C<sub>2</sub>S  $\rightarrow$   $\gamma$ -C<sub>2</sub>S 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 and finally causes the slag to self-pulverize [1,2], leading to its typical dusty appearance. Powdered slag is not only a liability in terms of processing and handling, requiring more space for storage, it also has little market value as compared to other stable stainless steel slags which are sold as aggregates for road construction [3]. A possible valorization application for this waste is yet to be found.

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Steel slag has been found to exhibit cementitious properties under the influence of chemical activators [4]. The susceptibility of the materials to activation and hydration depends on the phase composition and fineness of the slag and the type of activator used [5]. In the present case, the CaO content of the SSR slag suggests that it has potential for alkali activation. However, the materials generally studied for alkali activation, like GGBFS, fly ash and metakaolin, are vitreous/highly amorphous. This is already a challenge for the alkali activation of SSR slag considering the fact that it is highly crystalline, with phases such as  $\gamma$ -C<sub>2</sub>S, bredigite and merwinite, which are considered to be non-hydraulic. Indeed, it has been suggested that crystalline structures do not provide sufficient reactivity [6], although few works on similar crystalline slags have been reported. For example, Duda studied the reactivity and compressive strength potential of crystalline Linz–Donawitz (LD) slags by milling and blending them with blast furnace slag. The author used NaOH as activator and found that hydration reactions were initiated in the crystalline LD slag blends [7]. Zhang et al. [8] found that crystalline basic oxygen furnace steel slag used as 30–60% replacement in cement have strength properties similar to OPC. Setién et al. [9] studied the chemical, mineralogical and microstructural properties of crystalline ladle furnace slag and suggested that the slag has capabilities for potential application as construction material. Shi [10] in his works on crystalline ladle slag found that, when blended with blast furnace slag, they show significant cementitious properties in the presence of alkaline activator which improves with the increasing fineness of the material. In another work, Shi and Hu [11] showed that considerable compressive strengths can be achieved by mixing crystalline ladle slag with siliceous materials under autoclave curing at 175 °C for 4 h. Rodriguez et al. [12] showed that partial replacement of cement and sand by ladle slags results in improvements in the sustainability and economic savings in sand and cement. Kriskova et al. [13–15] have shown that the hydraulic behavior of crystalline slags or of particular phases relevant to metallurgical processing is greatly modified after mechanical and chemical activation.

Since the nature and composition of the residues vary from plant to plant and mineral additions may be limited by their local availability, in the current work the slag is used as the lone source of binder. Silicates of sodium and potassium were mixed with the respective hydroxides in different proportions to study the hydraulic properties with the aim to assess the potential valorization of SSR slag as a cementitious binder.

## 2. Materials and methods

The SSR slag was obtained from a stainless steel plant. The fraction of the slag finer than 45  $\mu$ m (SSR.45) was used for experiments. This fraction consisted of more than 50 wt% of the total slag. The chemical analysis of the slag was determined by wavelength dispersive X-ray fluorescence (XRF) spectrometry (Philips PW 2400), quantified using the Super Q software. The particle densities of the different fractions of the slag were determined by pycnometer analysis [16] and the specific surface area was determined by Blaine [17] and BET analysis [18]. The particle size distribution of the slag was determined by wet laser diffraction (Malvern Mastersizer). The microstructural investigation of the SSR.45 slag sample was done by scanning electron microscopy (SEM XL30, Philips) whereas EPMA was also employed for mapping (Jeol JXA-8530F EPMA).

Solutions of 5 M sodium hydroxide (NaOH) and potassium hydroxide (KOH) were prepared with distilled water. The alkaline solutions were mixed with commercial sodium silicate (ABCR GmbH & Co. KG, 39–40% silicates in water) and potassium silicate (R&D Lab. Ltd., weight ratio, silicate to K<sub>2</sub>O = 1.40:1–1.45:1, total alkali as K<sub>2</sub>O = 21.1–22.1%). 5 M NaOH solution was mixed with Na-

**Table 1**  
Oxide composition of SSR.45 slag by XRF analysis.

Compound	CaO*	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>
Wt %	58.37	30.31	7.41	1.31	1.09	0.44

\* Including the Ca in CaF<sub>2</sub>, which is not detectable by XRF.

silicate at mass ratios of 75:25 (Na:Si–75:25), 50:50 (Na:Si–50:50) and 25:75 (Na:Si–25:75) to give a resulting modulus (molar ratio of silicate to Na<sub>2</sub>O) of 0.7, 1.4 and 2.3, respectively. Similarly, 5 M KOH solution was combined with K-silicate at a mass ratio of 75:25 (K:Si–75:25), 50:50 (K:Si–50:50) and 25:75 (K:Si–25:75) to give a resulting modulus (molar ratio of silicate to K<sub>2</sub>O) of 0.7, 1.4 and 1.9 respectively.

In order to study the heat evolution during hydration of the alkali activated slags, isothermal conduction calorimetry was performed on slag pastes (slag + activator) using a TAM Air Calorimeter. The heat evolution was monitored at 80 °C.

Quantitative X-ray diffraction (QXRD) data were collected using a Philips Analytical PW 1710 diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) operating at 45 kV and 35 mA. The samples were scanned over a range of 10–70° 2 $\theta$ . The scans were measured in step scan mode at 2 s per 0.02° 2 $\theta$ . A 10 wt% ZnO internal standard was added to the samples to determine the amorphous phase content. Phase identification was carried out using the DiffracPlus EVA software. The Topas Academic v4.1 software was used for Rietveld quantitative phase analysis. The quantification results are referred to 100 g of unhydrated slag. Further description about the procedure and the CIF files for detected phases has been provided in the Supplementary documents (Table 1).

Thermogravimetric analysis (TGA) was carried out using Netzsch STA 409 PC DSC-TGA equipment, under N<sub>2</sub> flow atmosphere (60 ml/min) over a temperature range of 20–1000 °C at a controlled heating rate of 10 °C/min.

Fourier transform-infrared (FTIR) spectra were recorded on a PerkinElmer Frontier spectrometer running in attenuated total reflectance (ATR), in the region of 4000–650 cm<sup>-1</sup> at a resolution of 1 cm<sup>-1</sup>.

Mortar samples were prepared using SSR.45 slag, 0–5 mm sand (in a weight ratio of 1:3 slag to sand) and activator in the weight ratio of 0.7 to that of slag. The mixing and casting was performed in accordance with EN196-6 [17]. The three different combinations of hydroxide to silicate ratio identical to isothermal calorimetry were used for the preparation of the slag mortars. Elevated temperature curing was provided in a steam curing chamber. The steam curing cycle involved pre-steaming period of 24 h at standard laboratory conditions (20 °C, 60% RH), followed by curing in a steam curing chamber at 80 °C for 24 h and cooling for 24 h. After the three day steam curing cycle, the samples were cured in a moist room (20 °C, >90% RH). Mortar samples were taken at 3, 7, 28 and 90 days for the measurement of compressive strength.

The samples for TGA, XRD and FTIR were prepared with slag paste activated with Na:Si–50:50 and K:Si–50:50 activating solution following the curing conditions as in the preparation of the mortars. The activator to slag weight ratio was kept 0.7. Samples

**Table 2**  
Phase composition of SSR.45 slag by QXRD analysis.

Phase name	Wt%
Bredigite, Ca <sub>7</sub> Mg(SiO <sub>4</sub> ) <sub>4</sub>	10
$\gamma$ -C <sub>2</sub> S, Ca <sub>2</sub> SiO <sub>4</sub>	51
Cuspidine, CaSi <sub>2</sub> O <sub>7</sub> (F,OH) <sub>2</sub>	15
Fluorite, CaF <sub>2</sub>	3
Merwinite, Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>	3
Periclase, MgO	10
Unknown/amorphous	8

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