UTILIZATION OF SODIUM-RICH LEAD-ACID BATTERY SLAG AS ALKALINE ACTIVATOR FOR BLAST FURNACE SLAG

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Introduction

Slags from the recycling of lead-acid batteries cannot be easily valorised. Apart from their heavy metal content exceeding environmental legislation limits, the high sodium content (20-28 wt% Na_2O) provides the slag with unwanted reactivity when used as aggregate, making the resultant concrete vulnerable to alkali-silica reaction. An alternative valorisation route that exploits the high sodium content is the production of alkali-activated materials (AAM).

The use of non-ferrous metallurgical slags as silicate source for alkali-activated materials has become quite common in literature. Several publications show a satisfactory technical performance in terms of compressive strength evolution when the mixture is optimized.[1,2,3] The leaching behavior is being studied as well[4] and depends mainly on the cleanliness of the slag itself.[5] The non-ferrous slag has never been used as activator, although some secondary non-ferrous metal production slags contain significant quantities of Na.[5] The composition of these slags therefore comes closer to that of soda-lime silica glass, the waste of which has been used as source to produce alternative activators.[6,7] The reactivity of this glass is limited, requiring still high concentrations of NaOH to be able to exploit its silicon and sodium content. As a by-product of lead-acid battery recycling, the non-ferrous slags are present in liquid state, which allows chemical modification through addition of fluxes. Thus, before cooling, a chemical composition can be adjusted which is advantageous for the use of the slag as an alkaline activator.

Materials and methods

Slags from two non-ferrous metal producers are investigated as activators. Both slags were treated at high temperature and quenched in water before milling them to a powder. One slag was chemically modified using the additives in Table 1 at high temperature in an electric arc furnace. More information on the high temperature process can be found in the proceeding by Maier et al., the chemical composition from X-ray fluorescence (XRF) is shown for the main elements in Table 1.

Table 3: Chemical composition of the modified slags determined by XRF.

Additive	Addition (wt%)	SiO_2 (wt%)	Na_2O (wt%)	Fe_2O_3 (wt%)	Al_2O_3 (wt%)	CaO (wt%)
/	/	49.9	22.2	15.5	4.4	2.3
Al_2O_3	11	43.5	19.2	15.6	14.4	2.0
Al_2O_3	15	40.9	18.6	14.9	16.7	1.8
Al_2O_3	17	41.2	18.3	13.4	18.7	1.9
Al_2O_3 + C	15 + 1	42.6	18.9	11.9	17.4	2.1
Al_2O_3 + C	15 + 1.3	42.6	18.8	12.1	17.3	2.1
C	1.5	48.1	20.9	15.9	4.3	2.4
CaO	6	45.3	19.3	15.3	4.0	8.0
CaO + C	6 + 1.5	47.8	20.5	11.2	4.2	8.3
Al_2O_3 + CaO + C	15 + 6 + 1.5	43.4	16.8	7.8	17.1	8.0
Na_2O + C	8 + 1.5	49.4	25.2	9.5	4.3	2.4

To assess the reactivity of the slags, isothermal calorimetry was done. The heat release was monitored after mixing the slags with ground granulated blast furnace slag in a 1:1 mass ratio and water with a water/powder mass ratio of 0.4.

Compressive strength measurements were performed on mortar bars of 4 cm x 4 cm x 16 cm. Mortars were mixed in a Hobart mixer according to the procedure described in EN 196-1 with various ratios of blast furnace slag vs. Na-rich slag and the addition of water or NaOH solution. 1350 g of standard EN 196-1 sand was used for 450 g of powder. The tested mortars from 28 days strength tests were used for a batch leaching test. The crushed sample was immersed in water (water/solid mass ratio = 10) and shaken for 24 hours. The composition of the liquid was analyzed with a Varian Vista MPX inductively coupled plasma optical emission spectrometer.

Results and discussion

The first non-ferrous metal slag was used in an initial study to screen the mix-design. The binder was composed of the non-ferrous slag and blast furnace slag and reported using the wt% of non-ferrous metal slag in the binder. As liquid, water or 0.5 M NaOH was used. The compressive strength evolution of selected samples is presented in Figure 1. The late strength clearly benefits from higher wt% of non-ferrous slag in the binder, while to gain early strength it seems necessary to use NaOH in combination with a sufficient amount of non-ferrous slag. Comparing to the strength evolution of Portland cement, e.g. CEM I 52.5 N, there is a need for > 25 wt% of activator slag in the binder and NaOH solution. Observing the limited early strength, the concentration of the NaOH solution might need to be higher than 0.5 M.

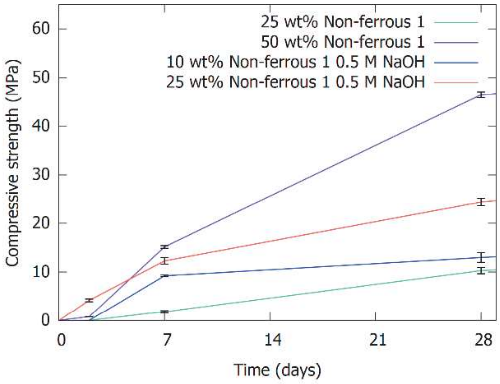

Figure 3: Compressive strength evolution of the mortars made with a binder composed of blast furnace slag and non-ferrous slag.

The chemical composition of the second non-ferrous slag was modified to optimize its reactivity. Only the addition of Na_2O significantly enhances the reactivity, while the addition of Al_2O_3 is detrimental for this goal.

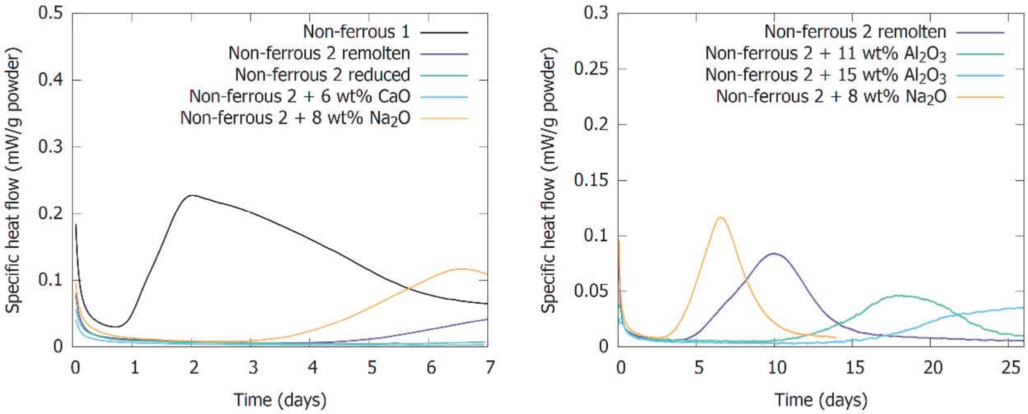

Figure 4: Heat flow obtained from isothermal calorimetry on mixtures with 50 wt% blast furnace slag and 50 wt% of non-ferrous slag.

Despite the increased reactivity seen in Figure 2, the compressive strength evolution was not significantly impacted by the addition of Na_2O, nor by addition of CaO (Figure 3). At this stage the strength is suitable for monolithic products such as façade bricks. The leaching behavior of all samples passed the Flemish legislation for use in construction materials. Table 2 shows example values for the sample with 40 wt% of non-ferrous slag with 8 wt% of Na_2O added.

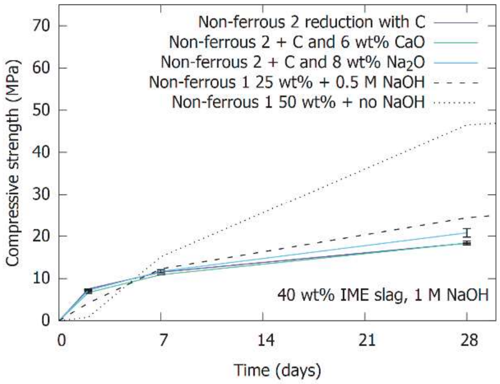

Figure 5: Compressive strength evolution of the mortars made with a binder composed of blast furnace slag and non-ferrous slag.

Table 2: Example batch leaching result for non-ferrous slag activated mortar compared to the Flemish VLAREMA limits for the leaching of heavy metals (B2.3.2). Between brackets are proposed limits for an upcoming update of the VLAREMA.

Element (mg/kg dm)	Pb	Cu	Ni	Zn	Ba	Mo	V
Sample	0.58	< 0.05	< 0.05	0.37	0.93	< 0.1	0.60
VLAREMA	1.3	0.5	0.75	2.8	(20)	(55)	(2.5)

Acknowledgements

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