REACTIVITY OF NON-FERROUS METALLURGICAL SLAGS AND SLUDGES MEASURED BY THE RILEM R3 TEST

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Introduction

Non-ferrous metallurgy residues are challenging materials to recycle. First, their environmental quality is often problematic, and second, their technical properties barely meet, if at all, the requirements of low value construction applications.[1,2] The H2020 METGROW+ project aims to reach near zero-waste solutions for low grade residues by 1) recovering more valuable metals, while at the same time 2) removing harmful substances, and 3) upgrading the technical quality of the cleaned mineral residue in added value construction materials such as cement or binder components.

While test methods are in place to screen the environmental quality of a final residue, current standard reactivity testing methods for cement constituents such as supplementary cementitious materials (SCMs) are felt to fall short on many levels. Therefore, a rapid, robust and reliable (R3) reactivity test method was developed.[3,4] The test established a relationship between strength development and heat flow or bound water of model pastes of the SCM with slaked lime and additional alkalis for a range of conventional SCMs such as coal combustion fly ashes, natural pozzolans and iron blast furnace slags.[5] In a next step a wider range of materials are tested that are currently not used as SCM. This contribution shows the results of the SCM reactivity tests on residues from non-ferrous metallurgy slags and sludges.

Materials

A range of Zn and Ni production residues were selected for SCM reactivity testing. Table 1 provides a summary of the material designation, the mineralogical make-up, and the production process. The materials optionally underwent further metallurgical processing for additional metal recovery. In the plasma-pyro treatments the residues are remolten under reducing conditions at 1200 or 1600°C, and metals are recovered from the resulting metal fumes and bullion. The purified vitrified slag is evaluated for use as SCM. In the bioleaching treatments the residues are leached using (organic) acids produced by *in-situ* or ex situ bacteria. In acid leaching the residue was leached using a $NaHSO_4$ solution. Metals are extracted from the leaching solution; the solid residue was used for SCM reactivity testing.

All final, cleaned residues were dried and milled using a RETSCH 400 Planetary Ball mill to the typical fineness of cement constituents. A median volumetric mean particle size (d_{50}) of less than 25 µm was targeted.

Table 1: Summary of material properties, origin and treatments

Material	Abbrev.	Mineralogy	Process	Additional treatments
Goethite filter cake	GFC	Goethite, gypsum, franklinite, jarosite	Zn production	Plasma-pyro (T)
Jarosite filter cake	JFC	Jarosite, sulphur, gypsum, sphalerite	Zn production	Plasma-pyro (T), acid leaching (L)
Fayalite slag	FS	Fayalite, magnetite, amorphous	Ni production	Plasma-pyro (T), bioleaching (B)
Fe-Ni slag	FNS	Fayalite, diopside, amorphous phase	Historic Ni production	-

Methods

The R3 reactivity test was used to assess the reactivity of the treated residues in a lime-alkali sulphate system,[3-5] further experimental details and correlations between calorimetry test results, bound water contents and compressive strength data can be found in Li *et al.*[5]. The isothermal calorimetry data are complemented with XRD data to establish the reaction kinetics and mechanisms. Hydration stopped model pastes were measured.[6] Phase identification was carried out using HighScore Plus v4.8.

Results

The R3 reactivity test cumulative heat measurements are plotted in Figure 1. Three classes of heat release are distinguished: low, medium and high. Low heat release means little chemical reactivity of the treated residue, “medium” corresponds to the heat release of typical siliceous coal combustion fly ashes, “high” heat release is indicative of clear chemical reactivity of the residue with Portland cement. The classification of the residues is summarised in Table 2. Plasma-pyro treated goethite filter cake and in particular Fe-Ni slag show high chemical reactivity and thus show promise to be used as supplementary cementitious material. The 1600°C plasma-pyro treated residues invariably show higher heat release than the residues treated at 1200°C. The 1600°C plasma-pyro treatments invariably lead to an improvement of the reactivity of the residues. The effect of (bio)leaching treatments on SCM reactivity is disparate.

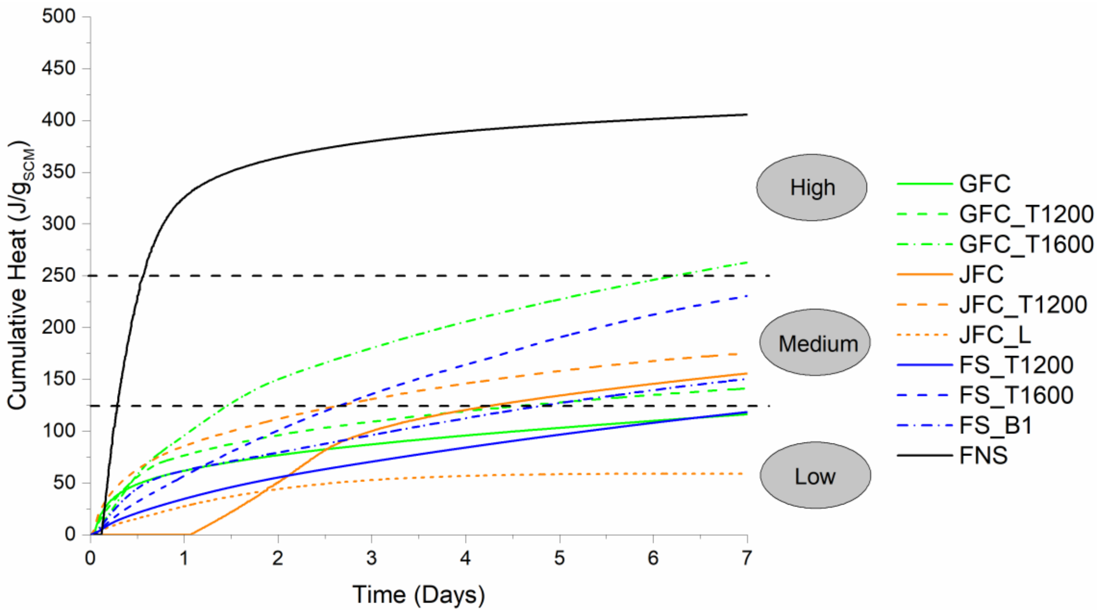

Figure 1: R3 calorimetry cumulative heat curves up to 7 days of reaction at 40°C

Table 2: Classification of residues as a function of cumulative heat released in the R3 test at 7 days of reaction

Material	High heat (> 250 J/g)	Medium heat (125-250 J/g)	Low heat (< 125 J/g)
Goethite filter cake	GFC_T1600	GFC_T1200	GFC
Jarosite filter cake		JFC_T1200 JFC	JFC_L
Fayalite slag		FS_T1600 FS_B1	FS_T1200
Fe-Ni slag	FNS		

The XRD analysis results are summarised in Table 3 and show that ettringite and AFm phases, mostly monosulphate, are the main crystalline hydration products. Such hydration products can be considered as beneficial and can contribute to strength development in Portland cement based concrete. It should be noted that C-S-H reaction products are difficult to identify by XRD. $Ca(OH)_2$ consumption is not always in line with the calorimetry results, this indicates different reaction mechanisms for the residues. High heat flow combined with little $Ca(OH)_2$ indicates latent hydraulic reactivity of the FNS sample. Alternatively, reaction of sulphur and $Ca(OH)_2$ leads to formation of gypsum in JFC. The screening test result interpretation can be confounded by the occurrence of additional reactions not leading to the formation of typical cement hydrates. In addition, formation of gypsum by reaction with $Ca(OH)_2$ is clearly undesirable as this may lead to internal sulfate attack, expansion and degradation of Portland cement based concretes.

Table 3: Crystalline reaction products identified and $Ca(OH)_2$ consumed in the hardened R3 model mixes grouped material

Material	Ettringite	AFm phases	Gypsum	$Ca(OH)_2$ consumed
Goethite filter cake				
GFC	++	+		+
GFC_T1200	+			-
GFC_T1600	+		+	++
Jarosite filter cake				
JFC	++		++	+
JFC_T1200			+	+
JFC_L	+	+	+	+
Fayalite slag				
FS_T1200			+	+
FS_T1600			+	++
FS_B	+	+		-
Fe-Ni slag				
FNS	++			-

Conclusion

A new test for material screening for use as SCM was applied to a selection of non-ferrous metallurgy residues. The effect of metal extraction treatments was evaluated. Fe-Ni slag and plasma-pyro treated goethite filter cake showed promising reactivity according to the R3 test. The presence of sulphur leading to gypsum formation in the jarosite filter cake residues may interfere with the interpretation of the test result for these residues.

Acknowledgement

The METGROW+ project has received funding from the European Union's Horizon 2020 programme under grant agreement Ni 690088.

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