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NOVEL INORGANIC PRODUCTS BASED ON INDUSTRIAL WASTES

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Abstract

This contribution reports the use of industrial slugdes obtained upon processing metallic materials: i) steel wiredrawing (F) ii) red mud (R) from alumina production from bauxite. Three distinct valorisation ways were explored, namely production of black ceramic pigments, belitic clinker, and geopolymers. The colourimetric behaviour of strontium hexaferrite pigments based on steel wiredrawing sludge is slightly poor than the one of formulations prepared from pure reagents. Particularly, L and b* coordinates are higher in the first case, meaning higher interference of green (-a*) and yellow (b*) undesirable hues. Belitic clinkers were produced by using red mud. Corresponding cements were then used to formulate mortars and their compressive strength was found similar to or better than the one of corresponding mortars prepared by using cement produced from pure chemicals. At the same time the relative amounts of C_3A and C_4AF diminished in the first case. Finally, the technological properties of geopolymers were affected by the addition of red mud. However, in small proportions the mechanical strength was improved at 28 days curing, certainly due to the high alkaline nature of this sludge.*

Introduction

Due to technological, commercial and environmental concerns there has been a great interest in evolving metal bearing by-materials in new applications. An innovative suggestion to decrease the price and, at the same time, to try to preserve natural resources was achieved by substituting wastes for pure reagents. This paper describes the use of industrial sludges generated upon processing metallic materials: i) steel wiredrawing (F); ii) red mud (R). These wastes might impose serious environmental problems due to the risks of contamination of surface and underground water resources, since they contain metallic oxide-bearing impurities.

In the past, the steel wiredrawing residue (F) was used for formulating spinel-based black ceramic pigments. This approach was successfully conducted after proper treatment and suitable combination with other industrial wastes. The obtained pigments showed interesting colouring power, and their stability also assured the desirable inertisation of hazardous species.[1]

The red mud (R) is generated in the Bayer process, commonly used to produce alumina from bauxite ore. This residue is highly alkaline (pH=10) and is produced in huge amounts, evacuated and confined in huge landfills.[2,3] Many recent studies and semi-industrial trials were directed to the incorporation of the red mud in construction materials;[4] traditional ceramics,[5] mortar and concrete,[6] cements,[7] lightweight aggregates[8] *etc*. The actual contribution describes its use as raw material in belitic clinkers and in the production of geopolymers that could be used for construction or restoration purposes.[9]

Materials and methods

In order to obtain fine and homogeneous slurries, all mixtures were wet ball-milled in water for 1 hour, and then dried at 110°C.

The formulations of pigments were prepared from pure reagents and from industrial wastes (steel wiredraw F; Table 1). The firing cycle was fixed as: heating rate = 5°C/min; 3 h dwell time at maximum temperature of 1050°C. Phase identification was carried out using X-ray diffraction (XRD, Rigaku Geigerflex D/max – Series). The L*a*b* colour measurements were obtained on a Konica Minolta Chroma Meter CR-400, using D65 illuminant and 10° standard observer (Y: 94.0, x: 0.3156, y: 0.3319) according to the CIE (Commission Internationale de l'Eclairage).[10]

To formulate belitic clinkers/cements we defined the required proportions of the main expected phases (C_2S, C_3S, C_4AF and C_3A), according to "design of experiments (DOE)" methodology[4] (see Table 2). Commercial silica (Sibelco P500), calcite (Calcite M1), alumina (Alcoa CT3000) and iron oxide (Sigma Aldrich) were used to produce four blank counterparts, while red mud (R) was used as a substitute of iron oxide in the other four set of samples. The calcination cycle was as follows: heating up to 1000°C at a rate = 15°C/min, (b) dwell-time 45 min (c) heating at 5°C/min up to 1350°C, (d) dwell-time of 5 h, (e) fast cooling in open air conditions. Finally, cements were obtained by adding 5 wt% gypsum to the milled clinker (particles < 63 μm). The mortars were produced by combining the obtained cements with commercial sand (average particle of 0.6 mm). Mortars were prepared through dry mixing of raw materials in a bag for 1 min, followed by mixing with water during 1 min and confectioned in cylindrical moulds (30x30 mm). The binder/aggregate and water/binder ratio in weight used were 1:1 and 0.7, respectively. After remolding, mortars were cured at 66% relative humidity and at 22°C up to 7 days.

Geopolymers were produced by using metakaolin 1200S (MK) (AGS Mineraux, France), alone and mixed with red mud. Their chemical composition is given in Table 1. In water medium, alkaline activators NaOH (ACS AR Analytical Reagent Grade Pellets) and hydrated sodium silicate (Merck, Germany, wt%; 8.5 Na_2O, 28.5 SiO_2, 63 H_2O) were used for dissolving the solid compounds and for combining all sodium ions. In terms of molar ratios the target was: SiO_2/Al_2O_3 = 1, Na_2O/Al_2O_3 = 1.[11] When used, as substitute of metakaolin in the proportions (wt%) of 1/4 (G1) and 1/10 (G2), red mud was previously ball-milled for 30 min. The pastes were immediately poured into 20x20x20 mm cubic moulds and placed in the oven at 50°C for 24 h and after they were left at room temperature for one day.

The phase compositions of clinkers and geopolymers were assessed with XRD, on a D8 ADVANCE, LynkEye detector-Bruker AXS diffractometer (Germany) that uses CuKa radiation in the 10-80° 2θ range, scan rate of 0.02° (2θ), and 185 s equivalents per step. The quantitative phase analysis was performed using TOPAS 4.2 - BRUKER software following RIR (Reference Intensity Ratio) and Rietveld refinement techniques. The experimental error is within 1%. The compressive strength was measured on a Shimazdu apparatus (Model: AG-X/R Refresh) and an average value was obtained by testing four specimens from the same sample.

Table 1: Average of XRF chemical compositions of the selected sludges

Oxides (wt%)	F	R
SiO_2	0.41	5.54
TiO_2	-	0.23
Al_2O_3	0.14	18.8
Fe_2O_3	62.1	51.8
CaO	5.31	3.27
Na_2O	2.61	6.84
MnO	0.37	0.04
ZnO	2.96	-
P_2O_5	3.09	-
SO_3	0.11	11.2
Others	0.32	0.08
LOI (at 1000°C)	21.2	1.90

(-) not detected, Others: MgO, NiO, Cr_2O_3, CuO, K_2O

Table 2: Formulations (wt%) and phase compositions (wt%) of tested products

	Pigments			Belitic clinkers								Geopolymers		
Formulations	SF1000°C	SF1050°C	SSF1050°C	BE1	BE2	BE3	BE4	RM1	RM2	RM3	RM4	GK	GR1	GR2
$SrCO_3$	9.45		6.09	-	-	-	-	-	-	-	-	-	-	-
Fe_2O_3	90.6		-	1.47	1.44	2.55	3.67	-	-	-	-	-	-	-
$CaCO_3$	-	-	-	79.2	82.3	79.3	78.9	79.0	82.1	79.0	78.4	-	-	-
SiO_2	-	-	-	17.4	14.4	14.8	12.6	17.2	14.2	14.5	12.2	-	-	-
Al_2O_3	-	-	-	1.95	1.91	3.40	4.90	1.42	1.39	2.47	3.56	-	-	-
Na_2SiO_3	-	-	-	-	-	-	-	-	-	-	-	41.0	41.0	41.0
NaOH	-	-	-	-	-	-	-	-	-	-	-	11.1	11.1	11.1
MK	-	-	-	-	-	-	-	-	-	-	-	48.0	36.0	43.2
F (sludge)	-	-	93.9	-	-	-	-	-	-	-	-	-	-	-
R	-	-	-	-	-	-	-	2.83	2.77	4.92	7.09	-	12.0	4.80
Compositions														
$SrFe_{12}O_{19}$	74.0	85.0	43.0	-	-	-	-	-	-	-	-	-	-	-
Hematite	26.0	15.0	32.0	-	-	-	-	-	-	-	-	-	0.70	1.50
Spinel	-	-	25.0	-	-	-	-	-	-	-	-	-	1.00	1.80
Quartz	-	-	-	-	-	-	-	-	-	-	-	2.30	2.60	2.40
Illite	-	-	-	-	-	-	-	-	-	-	-	5.60	3.70	2.50
Amorphous	-	-	-	-	-	-	-	-	-	-	-	91.5	91.7	91.4
C_2S	-	-	-	74.8	35.3	48.4	29.0	69.8	33.3	48.0	28.5	-	-	-
C_3S	-	-	-	15.6	53.5	30.7	45.5	19.8	54.7	29.2	50.5	-	-	-
C_4AF+ C_3A	-	-	-	9.6	11.2	20.9	25.5	10.4	12.0	22.8	21.0	-	-	-

Results

Ceramic Pigments

The XRD patterns of the fired powders are reported in Figure 1. They reveal the presence of three main phases; namely hexaferrite ($SrFe_{12}O_{19}$), hematite (Fe_2O_3) and spinel. Since Sr^{2+} cations are lager than Fe^{3+}, processing at higher temperatures is required for single-phase formation.[12]

The increase in the sintering temperature from 1000 to 1050°C enhances the amount of hexaferrite to 85% (Table 2). In waste based powders, the relative amount of SrM decreased, while the content of hematite and that of a newly formed iron spinel increased due to the presence of contaminants.

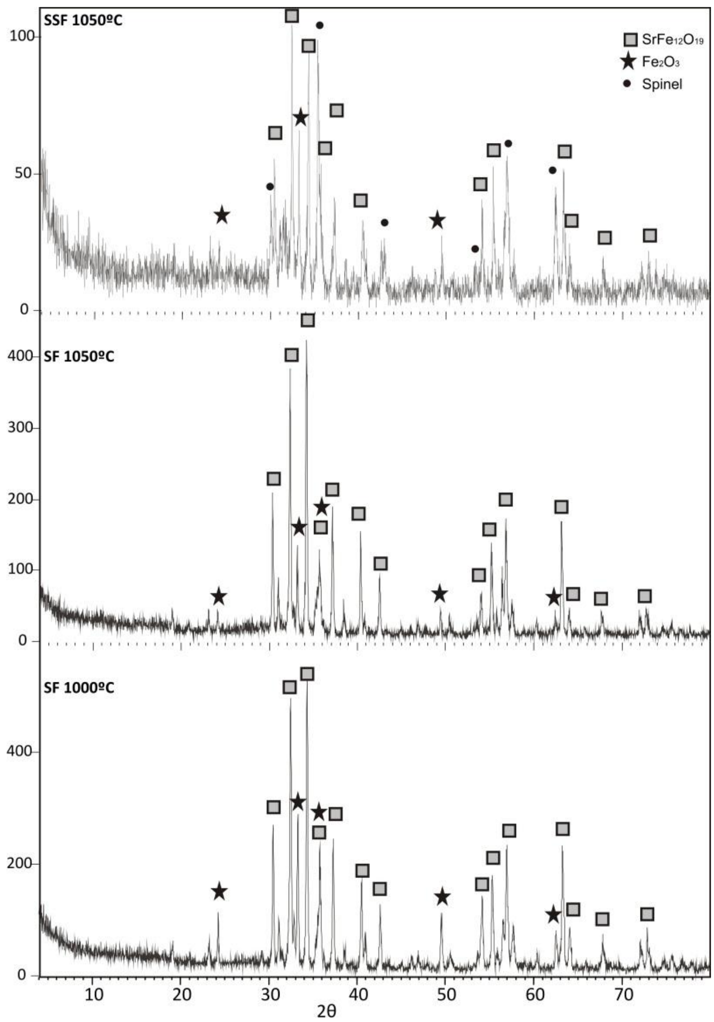

Figure 1: XRD patterns of the synthesised pigments

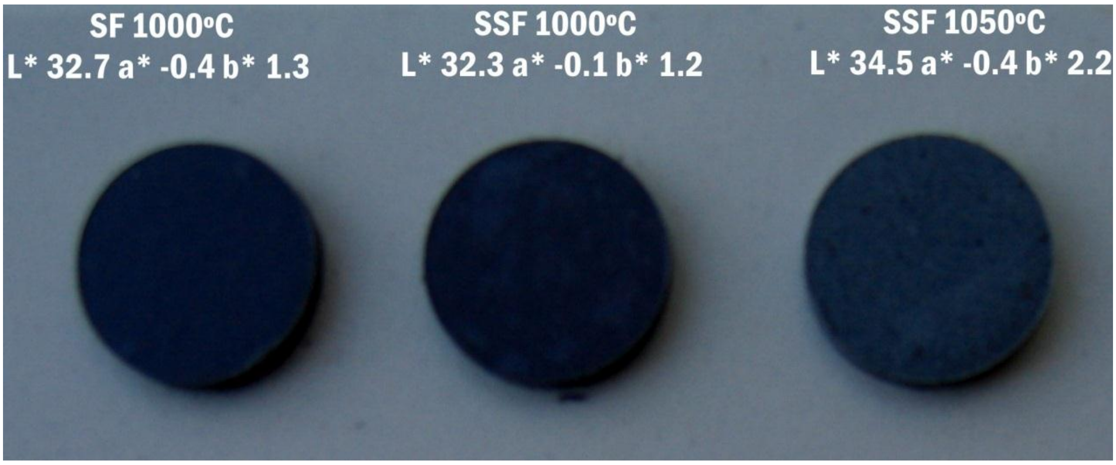

Figure 2: Black pigments and L*a*b* coordinates

The black pigments and their colourimetric parameters are presented in Figure 2. The brightness in pure based powders (SF) is close to 32 and is considered slightly inferior to that displayed by a commercial pigment (DCMA 13-50-9: L*a*b*=33.0/1.0/0.0).[13] At the same time, the current pigments exhibited stronger green (-a*) and yellow (b*) hues.

For the waste based product SSF, the L* and b* increased due to interference of contaminants and formation of multiple phases. However, the colour variance is minor and hard to detect by naked eye, and might also be easily corrected when the material is applied to colouring different products (ceramics and glazes).

Belitic clinker

Figure 3 shows the XRD patterns of clinkers based on pure reagents (BE1) and formulated with red mud (RM1). The quantification of the main phases C2S, C2S, C3A and C4AF is reported in Table 2. In general, changes in composition are easily recognised by compositional differences between BE and RM, but they are lower than 5%. Therefore, no significant changes are expected on the technical properties of the belitic clinkers.

Figure 4 shows images of mortars prepared by using the obtained clinkers, together with values of compressive strength of samples cured for 7 days. The mechanical strength is higher in products with lower amounts of aluminates (C_3A and C_4AF). Moreover, the addition of red mud increased the mechanical resistance of these materials. A contradictory behaviour is shown by BE4 and RM4 mortars, mostly related to the low C_2S content.

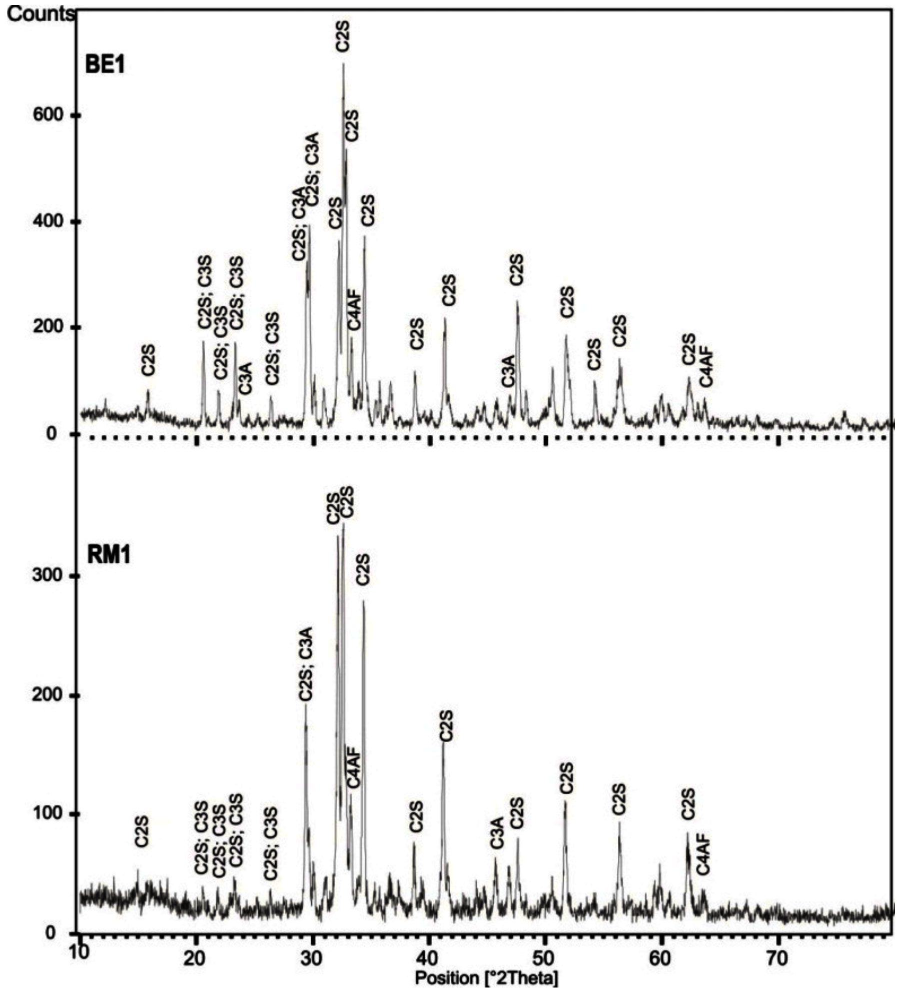

Figure 3: XRD patterns of clinkers based on pure reagents (BE1) and with addition of red mud (RM1)

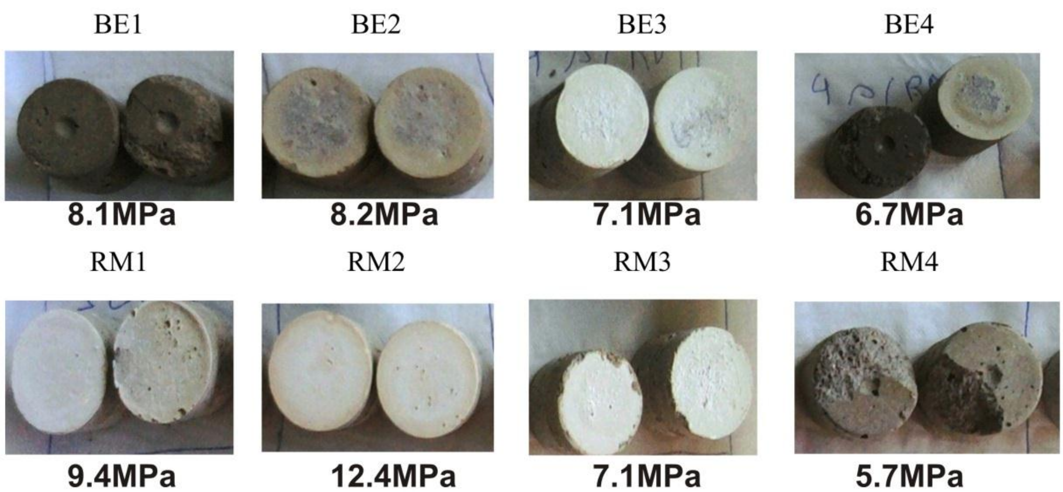

Figure 4: Mortars and respective compressive strength values at 7 days

Geopolymers

The fitted XRD patterns of GK, G1 and GR2 geopolymers and results of phase quantification are reported in Figure 5 and Table 2, respectively. The patterns show a broad reflection related to the amorphous content, like the one observed for metakaolin.[14] Nevertheless, the centre of this reflection is shifted to 2θ=29° due to changes on composition and structure when metakaolin is activated by NaOH and Na_2SiO_3 solution. This alkaline aluminosilicate is the dominant product corresponding to 90 wt% in all samples (Table 2). This suggests that a similar degree of geopolymerisation occurred even if the broad hump is slightly more pronounced in the MK geopolymer.

After 1 day curing, samples show maximum compressive strength of about 8 MPa (Figure 6). High content of R (G1) had an impact on the mechanical resistance, which tends to decrease to minimum values under 4.7 MPa. Geopolymers having lower SiO_2/Al_2O_3 molar ratios (G1 formulation corresponds to the lowest value) tend to be mechanically weaker than the other two. In the equivalent formulation prepared with red mud (sample G2; MK/red mud ratio = 1/10), the occurrence of iron seems to be compensated by the highly alkaline nature of the sludge and then the mechanical strength is comparable with GK.

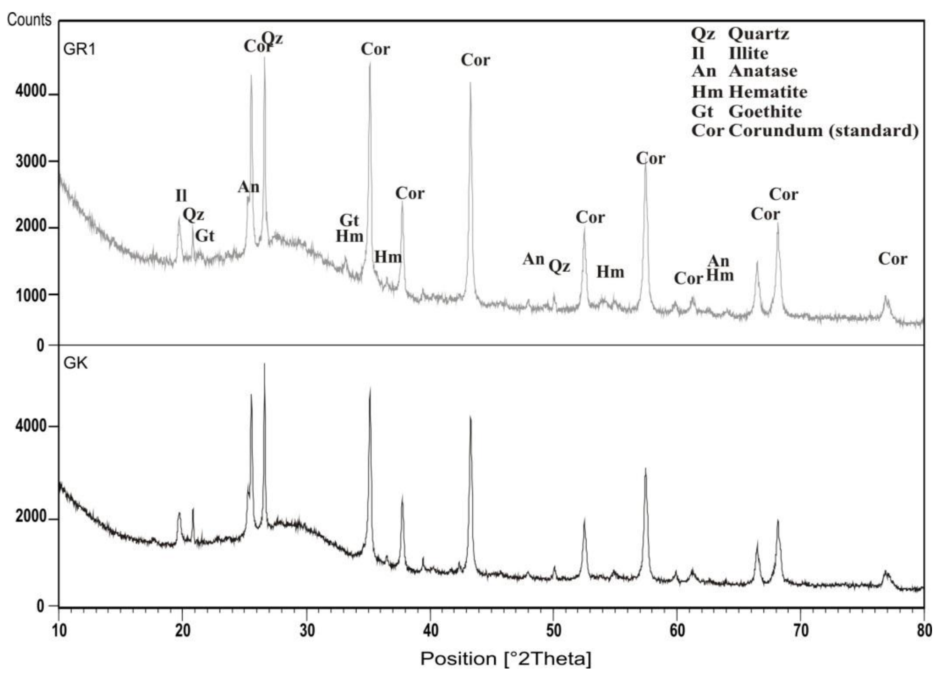

Figure 5: XRD patterns of the geopolymers (20 wt% corundum was added as standard)

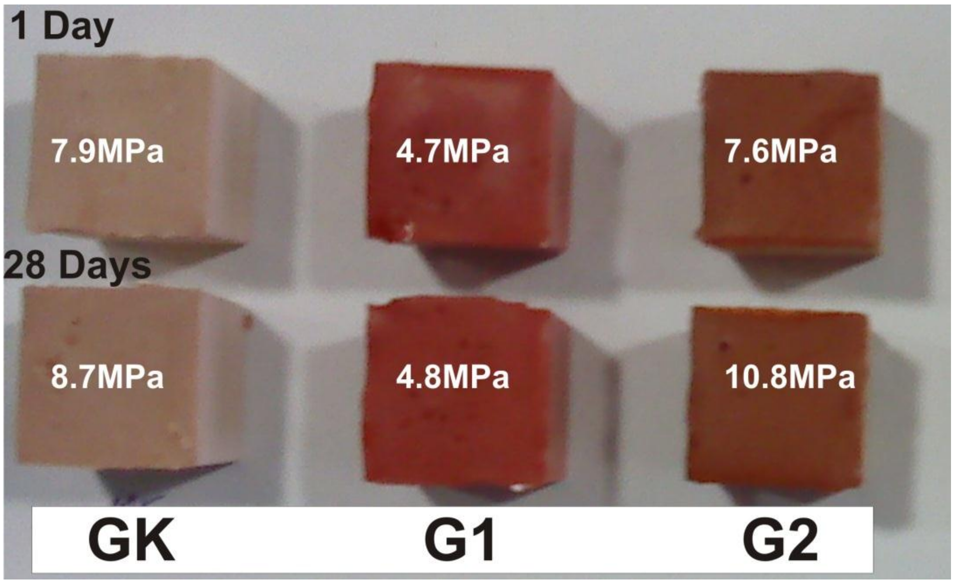

Figure 6: mechanical strength of GK, G1 and G2 geopolymers after curing during 1 and 28 days

Upon curing for 28 days, GK sample showed slight increase in the mechanical behaviour (Figure 6), related to the structural changes and degree of polymerisation. The progress in the mechanical strength of the sample G2, from 1 to 28 days, is rather evident.

Conclusions

In this work we achieved the following results:

- As expected from the initial formulations, the strontium hexaferrite is the major phase formed in the calcined powders. The pigments obtained from pure reagents exhibited a good black colour competing with commercial formulations, even if the b* (yellow) component is slightly higher. This parameter increased (2.2) along with the brightness (34.5) when the Fe-rich sludge was used to replace the commercial and pure source of iron in the mixture, leading to a barely-perceptible minor brown shadow.

- Belitic clinkers with balanced amounts of cementitious phases were produced at 1350°C. Mortars cured for 7 days produced from those clinkers/cements show mechanical strength that tends to increase when less amounts of aluminates (C_3A and C_4AF) are formed. Moreover, the addition of red mud increased the resistance of these materials.

- The use of red mud to obtain geopolymers is feasible since samples cured for 28 days showed good compressive resistance. However, further studies are required to optimise the correct proportioning of waste and metakaolin, as well as to adjust the processing conditions (*e.g.* curing). An increase in the mechanical strength of geopolymers is noticed with lower addition of red mud; G2 ratio 1/10.

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