NOVEL INORGANIC PRODUCTS BASED ON INDUSTRIAL WASTES

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Motivation

Search for environmental-friendly solutions involving materials recycling:

- Preservation of primary (non-renewable) resources

- Wastes looked as secondary raw materials:

  (i) Why the use of ceramic products as recycling ?

  (ii) What products ? Traditional ceramics/cement and minor incorporation ?

  (iii) Waste-based formulations ? Value-added products ? Why ***inorganic pigments*** *?*

which wastes ?

- Metal-rich sludges (e.g. Al-anodising and surface coating industrial processes – Ni/cr plating);

- Inorganic non-metallic wastes:
    - sludge generated in potable water filtration/cleaning operations;
    - sludge and fines from cutting/sawing of natural stones;
    - foundry sand;
    - red mud;
    - ash, etc …

These materials are often classed as non-hazardous but are produced in high daily amounts, which means high transportation costs for disposal.

Introduction

?

Waste → ***Raw Material***

Separation / Mixture → Homogeneity

Milling ? Washing ? Drying ? Calcination ?

Raw Material "Re-design"

Incorporation in a ceramic/cement matrix

Novel Product

How ?

Wastes characterization

(a) Chemical and mineralogical/phases (XRF/XRD);
(b) Thermal behavior (DTA/TG/DSC);
(c) Grain size distribution;
(d) Toxicity (leaching tests): **DIN 38414-S4**

Wastes pre-treatment/adaptation ?

(a) Collection of representative samples;
(b) Mixing and homogenization;
(c) Milling ? Drying ?
(d) …

Why belite-based clinker ?

- Belite and sulfobelite cements might reduce the impact on the environment and global warming, caused by the production of Ordinary Portland Cement (OPC).

- The lower required amount of carbonates and the concomitant reduction of CO_2 emissions, resulting from the lower firing temperature when compared to OPC clinker, are important advantages of those alternative formulations.

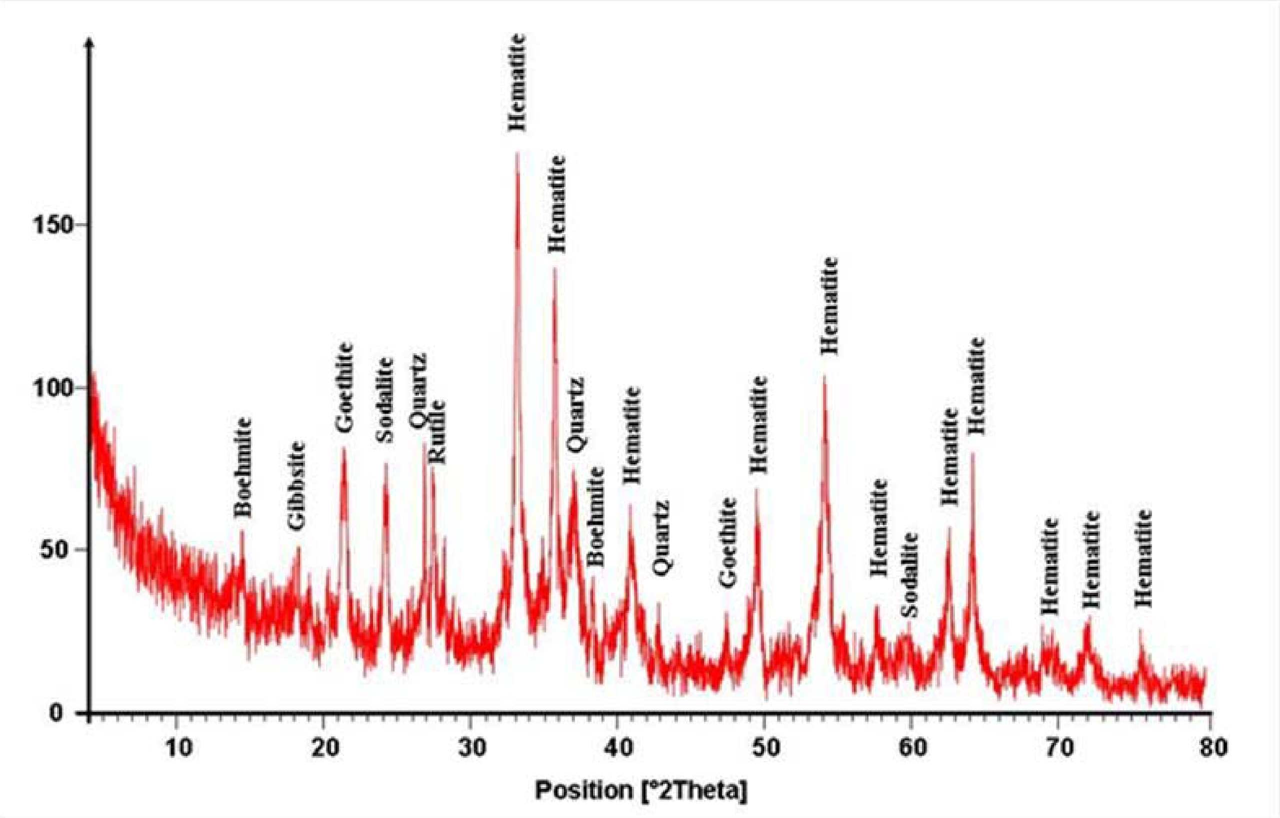
- Major drawback is the slower hardening rate, which might be partially solved by forming tetracalcium trialuminate sulfate ($C_4A_3\check{S}$).

- Production/consuming amounts are high, as with common cements, so it is adaptable for wastes generated in huge quantities, as the red mud. This waste might be a useful source of alumina and iron oxide !

- Several other wastes might be used: Al-anodising sludge; marble sawing dust/sludge; foundry sand.

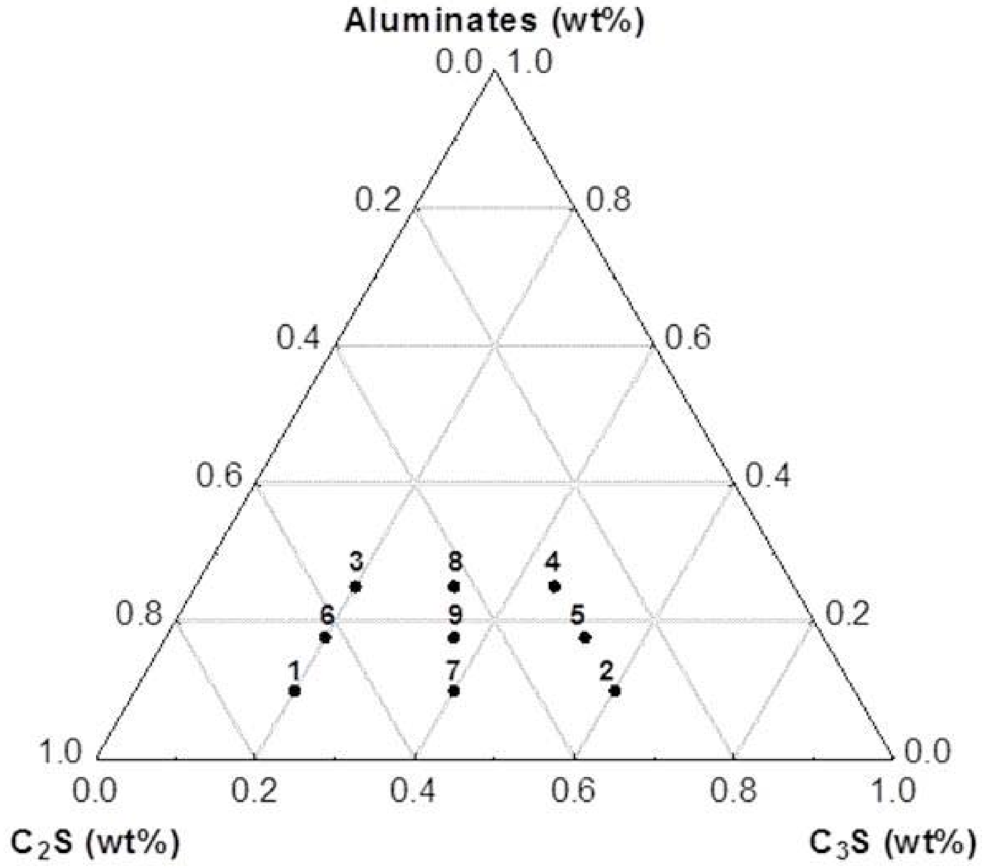
Red mud characterisation

Component	RM (wt.%)
CaO	3.27
SiO_2	5.54
Al_2O_3	18.8
Fe_2O_3	51.8
SO_3	0.23
TiO_2	11.2
Na_2O	6.84
K_2O	0.08
MnO	0.04



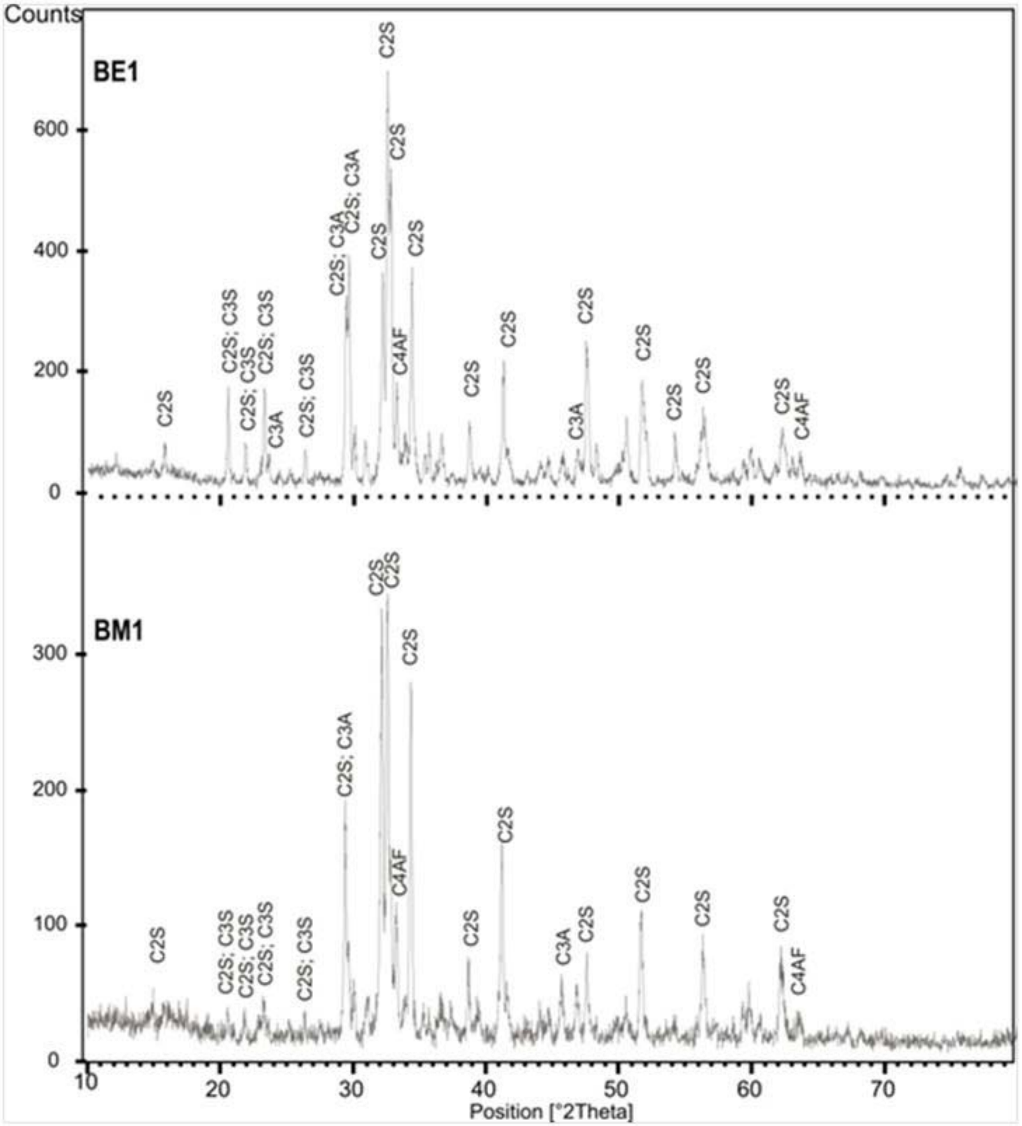
Clinker formulations

Formulations	BE1	BE2	BE3	BE4	RM1	RM2	RM3	RM4
Fe_2O_3	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
RM	-	-	-	-	2.83	2.77	4.92	7.09



Clinker formation and characterisation

- The firing cycle was the following: 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 hours, (e) fast cooling in air.



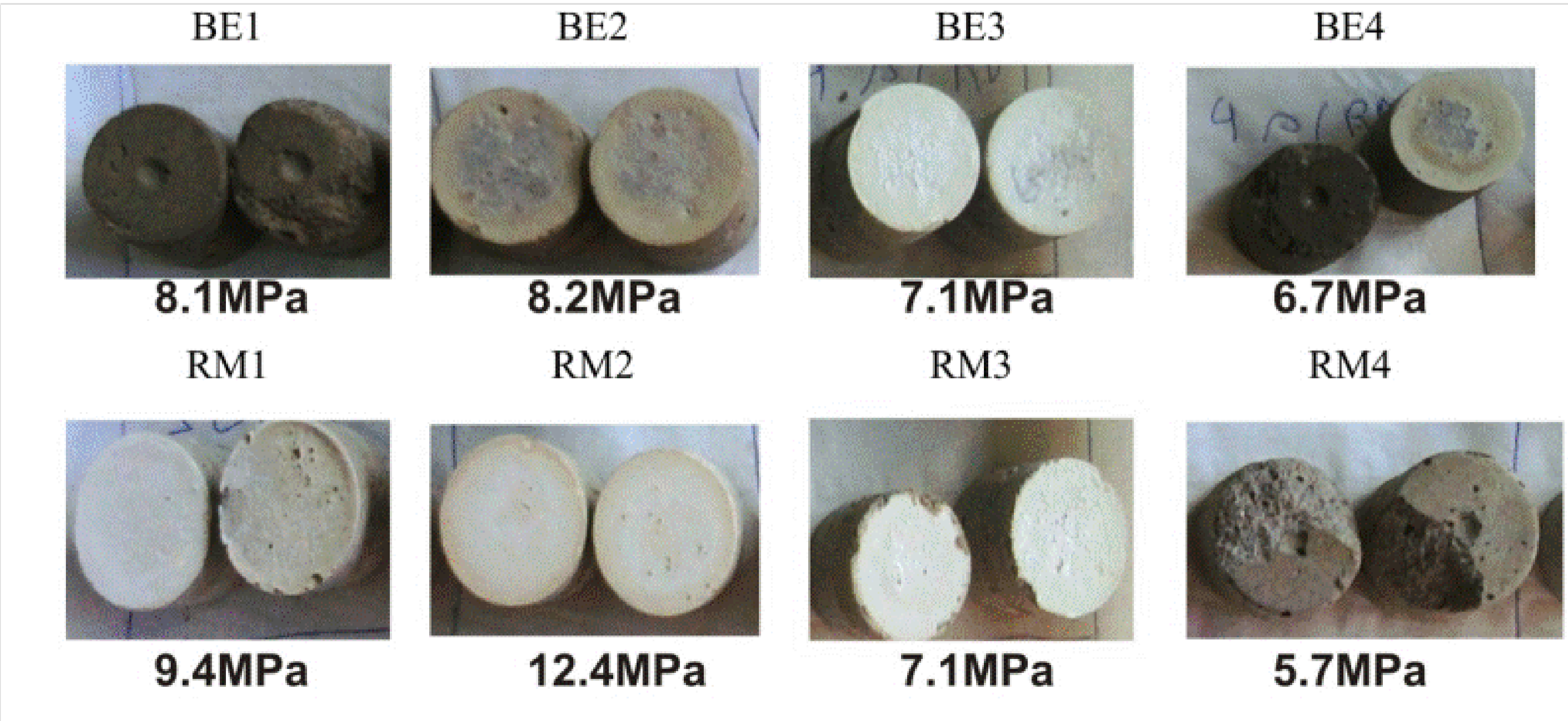
Clinker characterisation

- The quantitative phase analysis was performed using TOPAS 4.2 - BRUKER software following RIR (Reference Intensity Ratio) and Rietveld refinement techniques

Formulations	BE1	BE2	BE3	BE4	RM1	RM2	RM3	RM4
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

Mortars characterisation

- 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). The binder/aggregate and water/binder ratio in weight used were 1:1 and 0.7, respectively.
- Mortars were cured with 66% relative humidity and 22ºC up to 7 days.



L. Senff, A. Castela, W. Hajjaji, D. Hotza, J.A. Labrincha, Construction and Building Materials, 25[8], 3410-3416 (2011)

Why geopolymers ?

- Binders with lower impact on the environment and global warming, and demanding lower production energy.

- Metakaolin or fly ash might be activated (amorphous aluminosilicates). Also adaptable for highly alkaline waste streams (red mud ?).

- Good chemical resistance in acidic media; better fire resistance than OPC concrete.

- The need of an alkaline activator (soda, water glass) instead water to initiate the binding process, is one relevant drawback (liquid alkaline waste stream?).

- Tendency for efflorescences formation and hardening too fast !

Geopolymers

- Geopolymers were produced by using metakaolin 1200S (MK) (AGS Mineraux, France), alone and mixed with red mud.

- 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 to dissolve the solid compounds and combine all sodium ions.

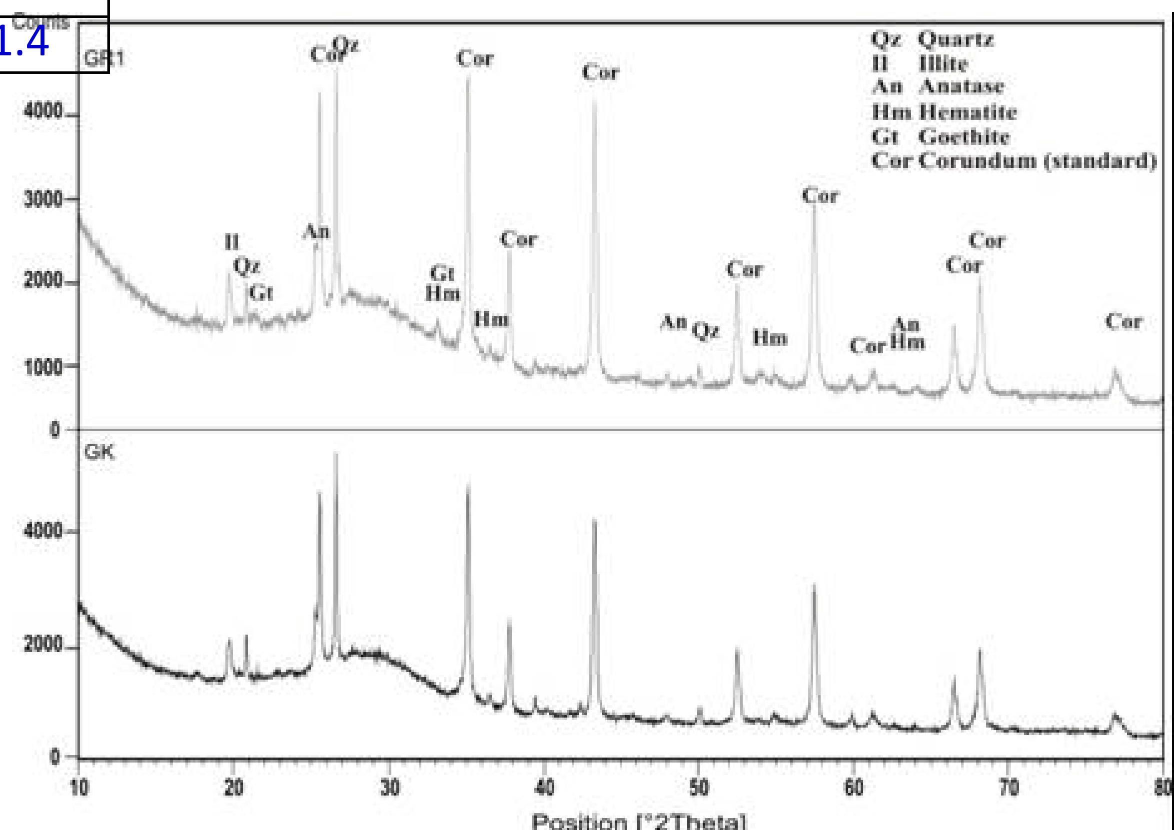
- In terms of molar ratios the target was: $SiO_2/Al_2O_3 = 1$, $Na_2O/Al_2O_3 = 1.11$.

- When used, as substitute of metakaolin in the proportions (wt%) of 1/4 (G1) and 1/10 (G2), the red mud was previously ball-milled for 30 min.

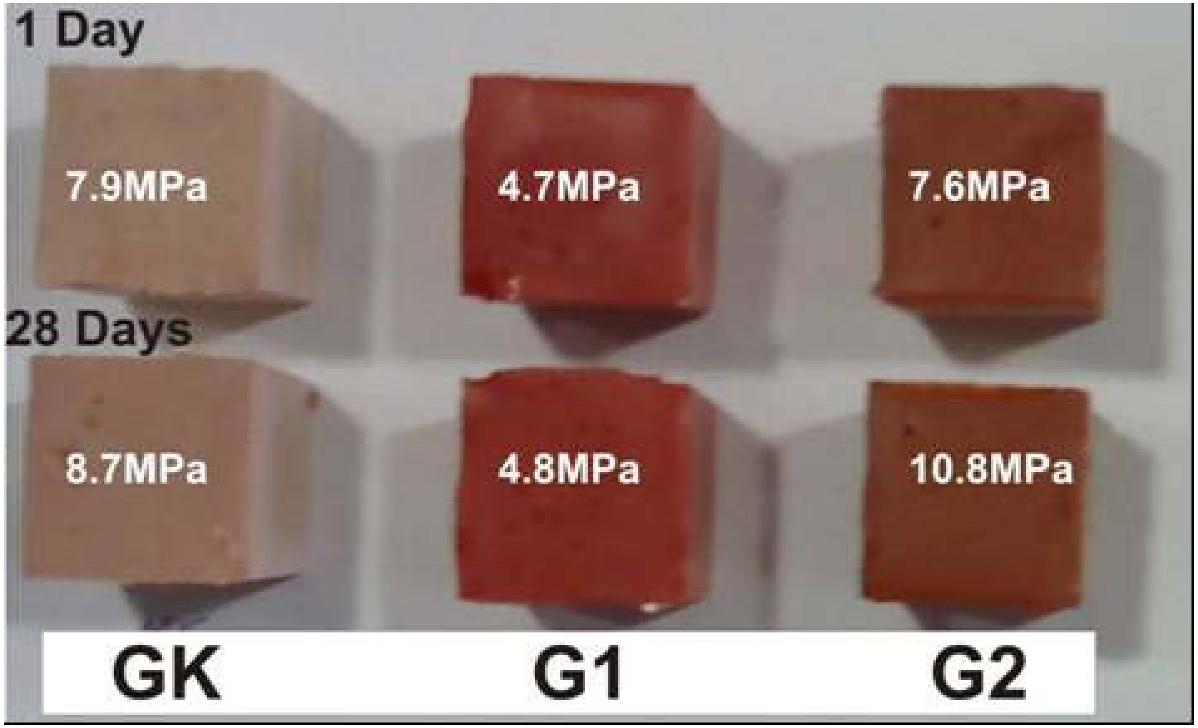
- The pastes were immediately poured into 20x20x20 mm cubic moulds and placed in the oven at 50°C for 24 h and after they were left at room temperature for one day.

Geopolymers

Formulations	GK	GR1	GR2
Na_2SiO_3	41.0	41.0	41.0
NaOH	11.1	11.1	11.1
MK	48.0	36.0	43.2
RM	-	12.0	4.80
Hematite	-	0.70	1.50
Spinel	-	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



Geopolymers



- The use of red mud to obtain geopolymers is feasible, since samples cured for 28 days showed interesting compressive resistance.

- However, further studies are required to optimize the correct proportion 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.

- Distinct wastes might added to be activated (e.g. biomass fly ash).

Why ceramic pigments ?

- The hazardous classification of certain wastes is due to their relatively high concentration of metallic species (transition/heavy) that are, at the same time, currently used as chromophores.

- The sintering of pigments at high temperature (> 1000°C) might promote the combination of hazardous/chromophore species with the matrix components, so assuring efficient inertization. Then the pigment is used/added (in minor amounts) to colouring another product (e.g. glaze).

- However, chemical and granulometric characteristics should be strictly controlled in order to get stable/reproducible colors (suitable for wastes insertion ?).

- Production/consuming amounts are relatively small, so adaptable for hazardous wastes generated in modest quantities (high cost for land filling).

Ceramic pigments

• There has been a great interest in the dyes industry for developing high stable pigments that show intense tonalities and comply with technological and environmental demands:

- use of alternative and less expensive raw materials.

• ***Are some selected wastes good candidates ?***

Ceramic pigments

A suitable ceramic pigment might fulfill the following requirements:

High coloring power – minimum amount to reach intense hue.

Thermal stability – the basic crystalline structure should be stable at high (preparation and use) temperatures.

Insolubility in (glassy) matrixes – the pigment should remain chemically independent of the matrix where it was added, to get stable and homogeneous coloration.

No changes of matrix properties – physical and chemical characteristics of the matrix should remain unchanged by adding the pigment (e.g., mechanical strength, hardness, thermal expansion coefficient, etc).

Are some selected wastes good candidates ?

Which wastes ?

- Several industrial wastes have been investigated for this purpose, in particular metal-rich sludges:

  - Al-rich sludge generated in the wastewater treatment unit of anodizing or surface coating industrial processes (AS)

  - galvanizing sludge from the Cr/Ni plating (GS),

  - iron-rich sludge generated in the steel wiredrawing (IS)

  Other:

  - foundry sand (FS)

  - marble sawing sludge (MS)

  - etc …

How ?

XRF of wastes after drying at 110ºC (LOI at 1000°C)

	AS	MS	FS	GS	IS
Al_2O_3	**35.3**	0.14	0.20	4.73	0.14
SiO_2	1.19	0.64	**97.7**	0.17	0.41
Fe_2O_3	1.41	0.24	1.12	1.57	**62.1**
CaO	2.99	**55.5**	0.20	19.5	5.31
Na_2O	0.35	-	-	3.42	2.61
K_2O	0.07	0.11	0.26	0.19	-
MgO	0.34	0.31	-	1.02	0.21
TiO_2	-	0.02	0.20	-	-
Cr_2O_3	-	-	0.20	**12.8**	0.09
NiO	-	-	-	**17.4**	0.01
SO_3	16.7	-	-	10.6	0.11
P_2O_5	-	-	-	8.75	3.09
LOI	40.0	43.0	0.20	20.7	25.2

AS

GS

IS

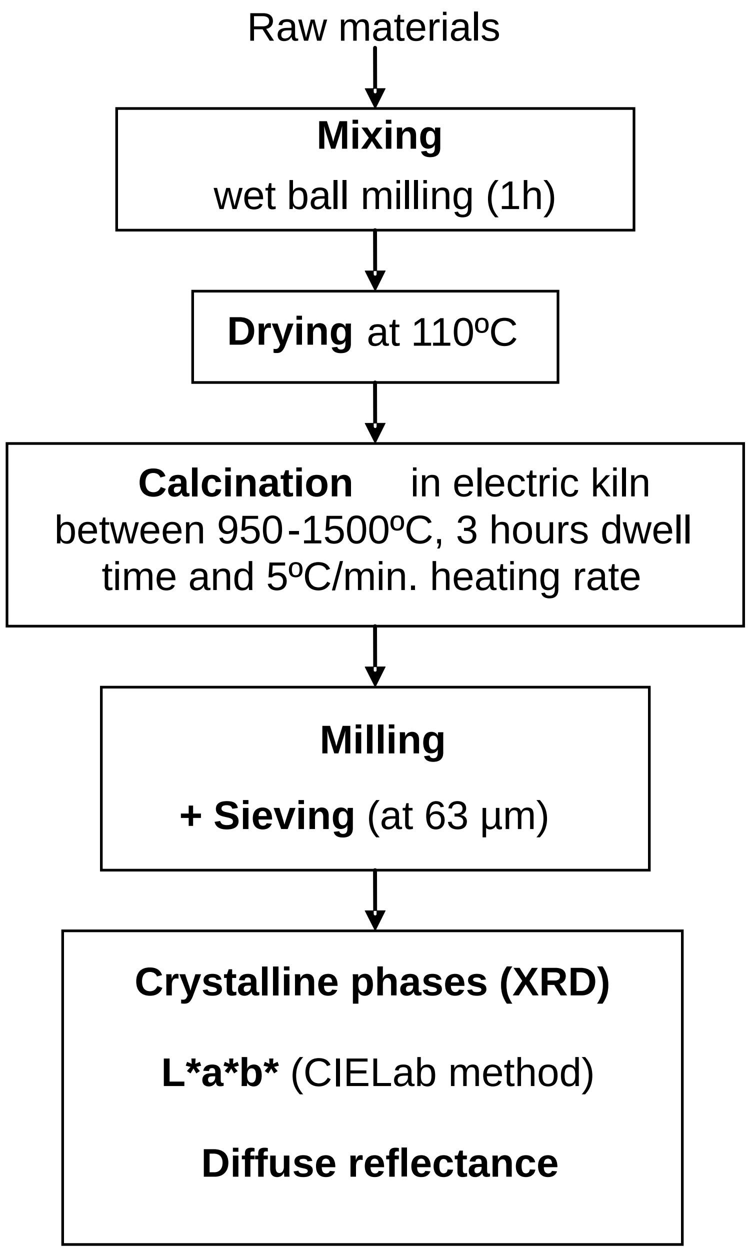
How ?

Chemical composition (wt.%) of commercial reagents (LOI at 1000°C), used to compose the replicas

	Alumina (Alcoa CT 3000)	Calcite (Calcitec M1)	Silica (Sibelco P5000)	Cobalt II Oxide (Panreac)	Cassiterite (CCT MP 889)	Titania (Kronos)	Ni(II) acetate (Riedel)	Cr(III) nitrate (Fluka)	Fe(III) Oxide (Riedel)
Al_2O_3	98.7	0.10	0.10	-	-	-	-	-	-
SiO_2	0.20	0.10	99.0	-	-	-	-	-	-
Fe_2O_3	0.37	0.07	0.06	-	-	0.03	-	-	99.0
CaO	0.10	55.6	0.10	-	-	-	-	-	-
MgO	0.01	0.22	0.07	-	-	-	-	-	-
TiO_2	0.06	0.01	0.01	-	-	99.3	-	-	-
SnO_2	-	-	-	-	99.9	-	-	-	-
Co_3O_4	-	-	-	99.9	-	-	-	-	-
Cr_2O_3	-	-	-	-	-	-	-	37.50	-
NiO	-	-	-	-	-	-	30.0	-	-
LOI	0.50	43.9	0.50	-	-	0.10	-	-	-

How ?

- pigments were prepared by the solid state reaction method:



Pigments applications

Pigments

↓

Adding to commercial glazes/ceramic bodies
(4-10 wt%)

↓

Mixing

↓

Application

↓

Firing
(also in industrial furnaces)

↓

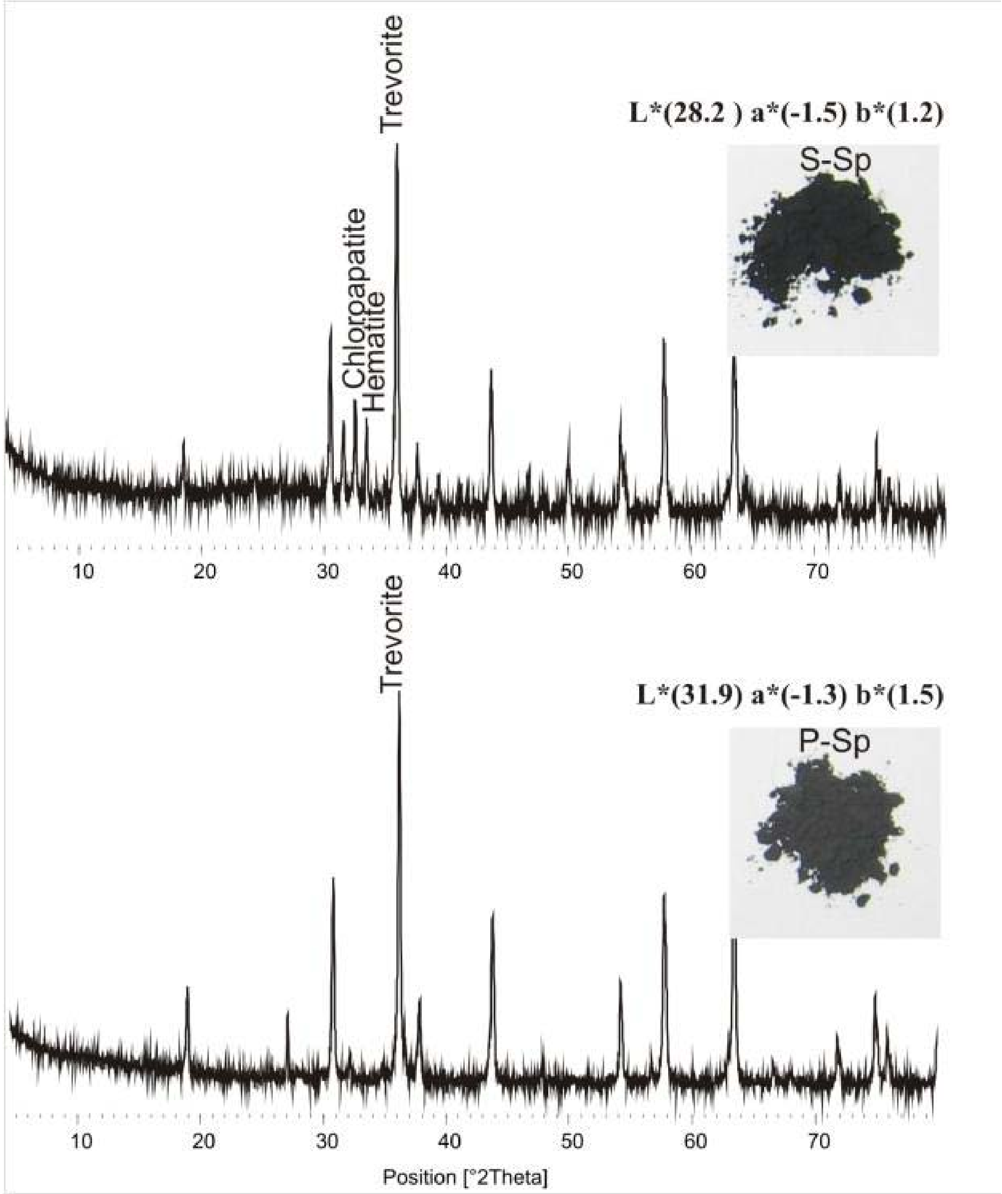
Characterization
(CIEL*a*b*, gloss, defects)

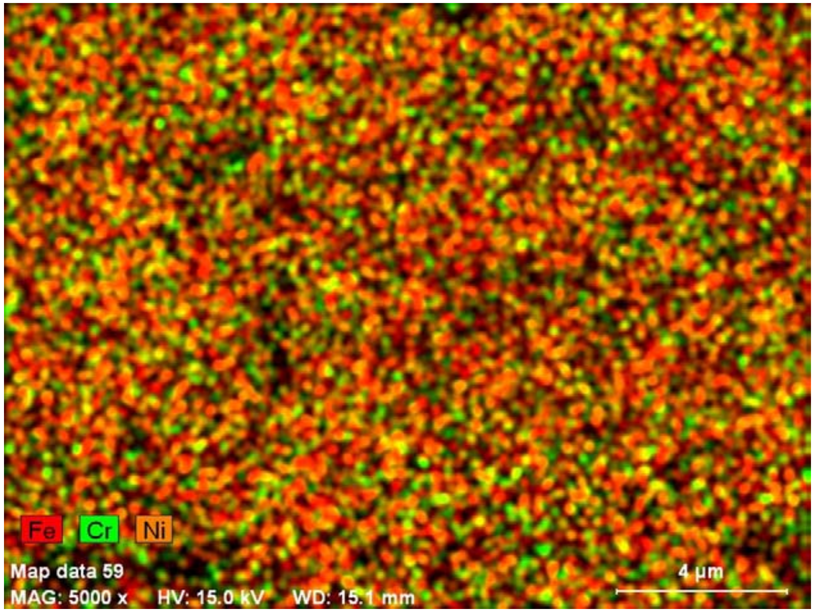
Black spinel

Components, sample reference and calcination temperature of the black spinel pigments $(Fe,Ni)(Fe,Cr)_2O_4$.
P = pure/commercial reagents; S = wastes based formulations.

	T (°C)	Ni(II) acetate	Cr(III) acetate	GS	Fe(III) oxide	IS
P-Sp	1200	29.05	39.97	-	7.98	-
S-Sp	1000	-	-	60	-	40

Black spinel



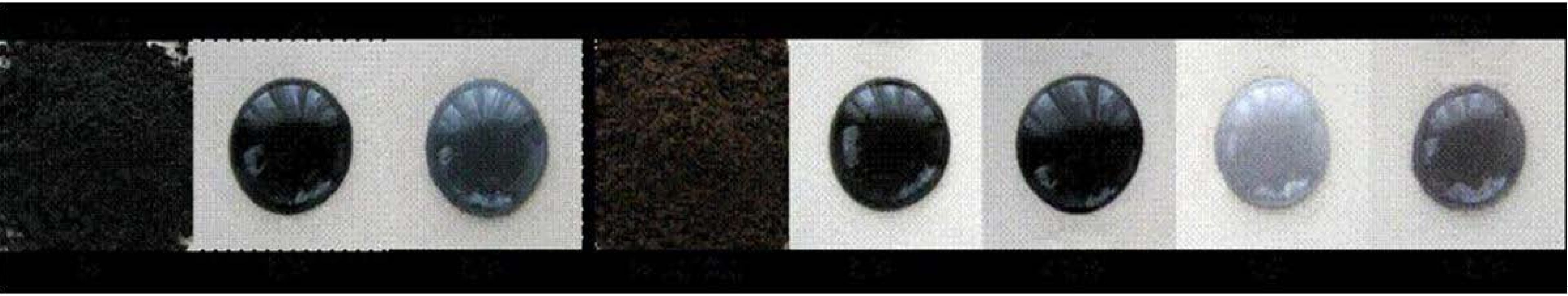


EDX mapping of spinel grains: (Fe+Cr):(Ni+Zn+Cu) ratio ~ 2

X-ray diffraction data, L*a*b* colorimetric values and aspect of black pigments. Trevorite = $Fe(Ni,Fe)O_4$

Black spinel

- Pigment based on chrome-iron-nickel spinel $(Fe,Ni)(Fe,Cr)_2O_4$ exclusively formulated with industrial wastes was successfully prepared.
- Wastes-based formulations can be sintered at lower temperatures than the commercial one (1000°C vs. 1200°C), due to the presence of fluxing/mineralizing agents in the complex sludges.
- Major drawback is the requirement of relatively higher additions in order to equalize the brightness in opaque glazes reached by the commercial pigment.
- Also tendency to get brownish hues.



W. Hajjaji, M.P. Seabra, J.A. Labrincha, Journal of Hazardous Materials, 185[2-3] 619-625 (2011)

Hibonite blue

- Calcium hexaluminate ($CaAl_{12}O_{19}$ or $CaO.6Al_2O_3$) occurs in nature as the mineral hibonite and presents the magnetoplumbite-type structure (space group P63/mmc, Z=2) whose general crystallochemical formula is $A^{[12]}\ M1^{[6]}\ M2_2^{[5]}\ M3_2^{[4]}\ M4_2^{[6]}\ M5_6^{[6]}\ O_{19}$.
- Calcium occurs in 12-fold coordination (site A), whereas Al^{3+} ions are distributed over five different coordination sites, including three distinct octahedral (M1, M4 and M5), one tetrahedral (M3) and an unusual trigonal bipyramidal (M2) providing a five-fold coordination by oxygen ions.
- Of great importance is the tendency of M^{2+} ions to be hosted at the M3 site, while M^{4+} and M^{5+} ions are preferentially accommodated at the M4 site.

- **Sintering temperature > 1500ºC.**

Never tested as pigment structure ?

Formulation change to co-generate hibonite + anorthite/gehlenite:

T ≤ 1400ºC

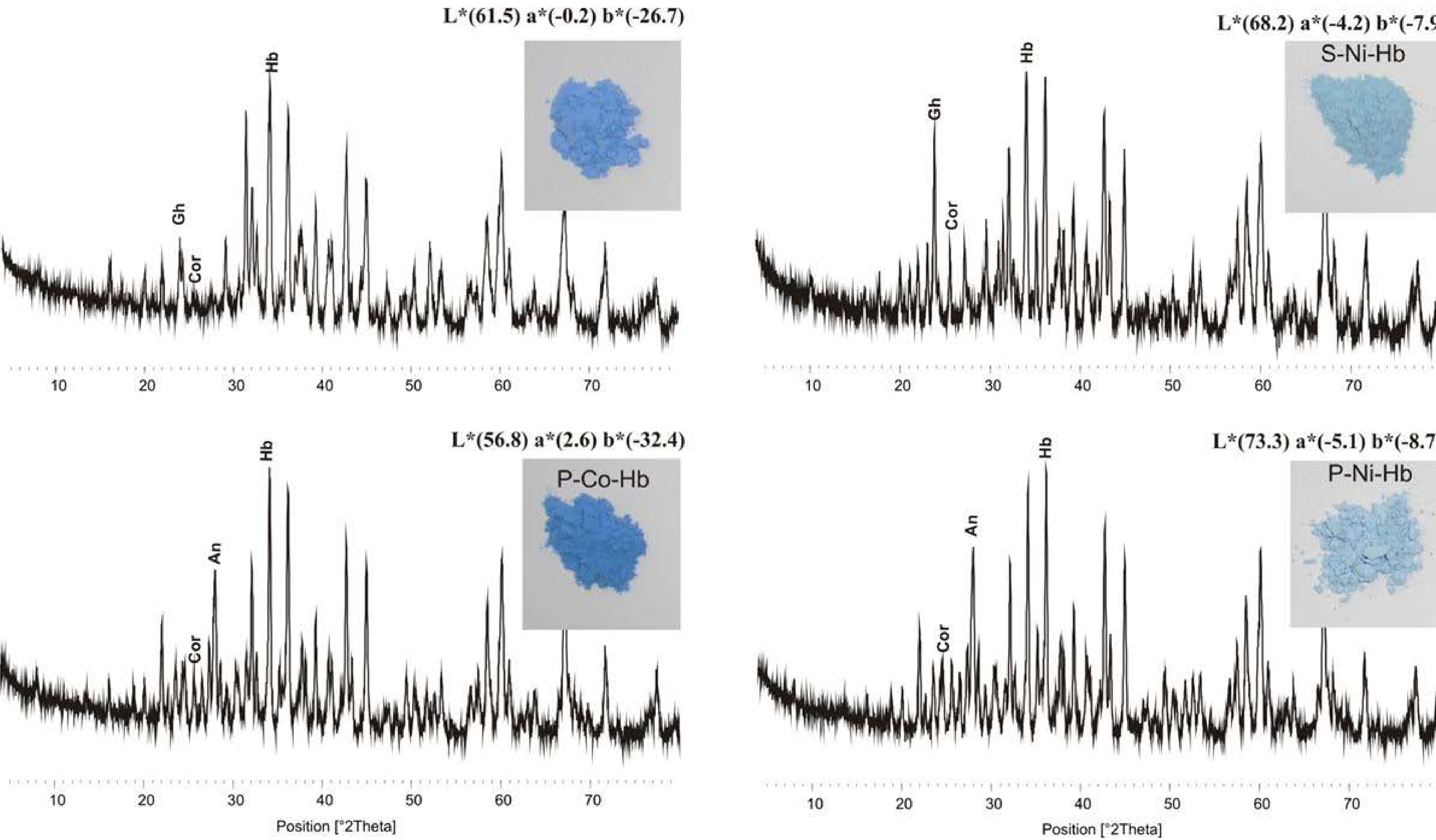
Hibonite blue

Components, sample reference and calcination temperature of the pigments.
P = pure/commercial reagents; S = wastes containing formulations.

	T (ºC)	Alumina (Alcoa CT 3000)	AS	Calcite (Calcitec M1)	MS	Silica (Sibelco P 5000)	FS	Cobalt II Oxide (Panreac)	Titania (Kronos)	Ni(II) acetate (Riedel)
P-Co-Hb	1350	65.0	-	19.0	-	11.4	-	2.3	2.3	-
S-Co-Hb	1350	-	80.8	-	13.0	-	4.2	1.0	1.0	-
P-Ni-Hb	1400	61.8	-	17.7	-	10.6	-	-	2.1	7.7
S-Ni-Hb	1400	-	76.3	-	12.0	-	3.9	-	0.9	6.9

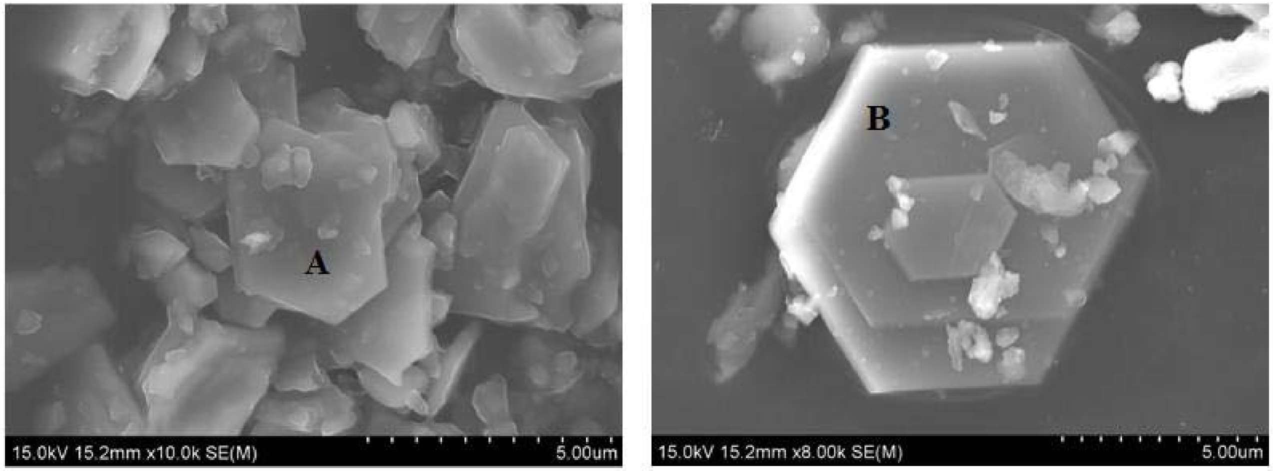
- Ti is used for charge compensation of Co_{Al} substitution.
- Another set of tests were conducted with GS as source of Ni

Hibonite blue



X-ray diffraction data, L*a*b* colorimetric values and aspect of hibonite based pigments

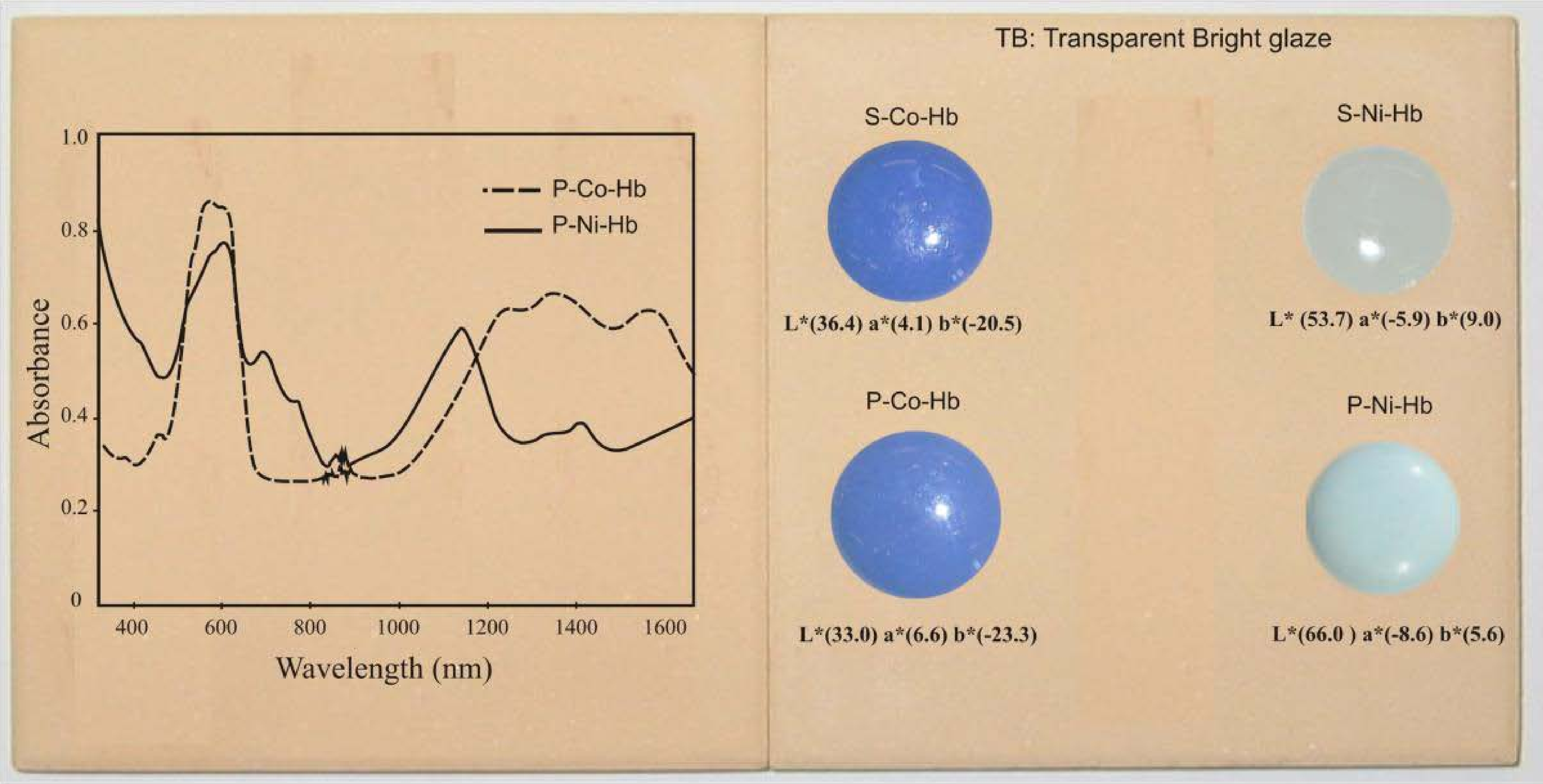
Hibonite blue



Elements (at.%)	Particle A	Particle B
Calcium	3.49	3.48
Aluminium	35.39	36.35
Titanium	1.28	0.81
Cobalt	1.21	0.75
Silicon	0.29	0.35
Oxygen	58.35	58.25

A. Leite, G. Costa, W. Hajjaji, M.J. Ribeiro, P. Seabra, J.A. Labrincha, Dyes and Pigments, 81, 211-217 (2009).

Hibonite blue pigments



The colour is due to the incorporation of cobalt/nickel in tetrahedral positions, as confirmed by the UV-Vis-NIR absorption spectra by transitions from $^4A_2(F)$ to the excited $^4T_1(F)$ and $^4T_1(P)$ states.

W. Hajjaji, P. Seabra, J.A. Labrincha, Dyes and Pigments, 83, 385-390 (2009).

Hibonite blue

- Ni (turquoise hue) or Co might be used as coloring elements: the chromatic mechanism is due to incorporation of Ni^{2+} or Co^{2+} in tetrahedral coordination, likely occurring at the site M3 of the hibonite lattice, where it partially substitutes the Al^{3+} ion.

- Relative amount of Co is much lower than in commercial pigments (more than 20x) and sintering temperature is acceptable (1300-1500°C).

- But coloring power is also lower.

G. Costa, M.J. Ribeiro, W. Hajjaji, M.P. Seabra, J.A. Labrincha, M. Dondi, G. Cruciani, J. Europ. Ceram. Soc., 29, 2671-2678 (2009).

More colours

- Brown Corundum, $(Fe,Al)_2O_3$
- Green Corundum, $(Cr,Al)_2O_3$
- Victoria green, $Ca_3Cr_2Si_3O_{12}$
- Violet cassiterite, $(Sn,Cr)O_2$
- Brown spinel, $(Zn,Fe)(Fe,Cr)_2O_4$
- Pink malayaite sphene, $Ca(Sn,Cr)SiO_5$
- Etc ...

W. Hajjaji, M.P. Seabra, G. Costa, M.J. Ribeiro, C. Zanelli, M. Dondi, J.A. Labrincha, J. Europ. Ceram. Soc., 32[4] 753-764 (2012)