PHYSICOCHEMICAL AND RADIOACTIVE CHARACTERIZATION OF CO-PRODUCTS FROM THE TITANIUM DIOXIDE NORM INDUSTRY FOR THEIR VALORISATION IN CEMENT MANUFACTURING.

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NORM VI

INTRODUCTION

- The present study has been carried out with the aim of tackling the problem of radiology in the waste and co-products of the NORM industry.

- The titanium dioxide NORM industry is the only one in Spain (Huntsman-Tioxide S.L.).

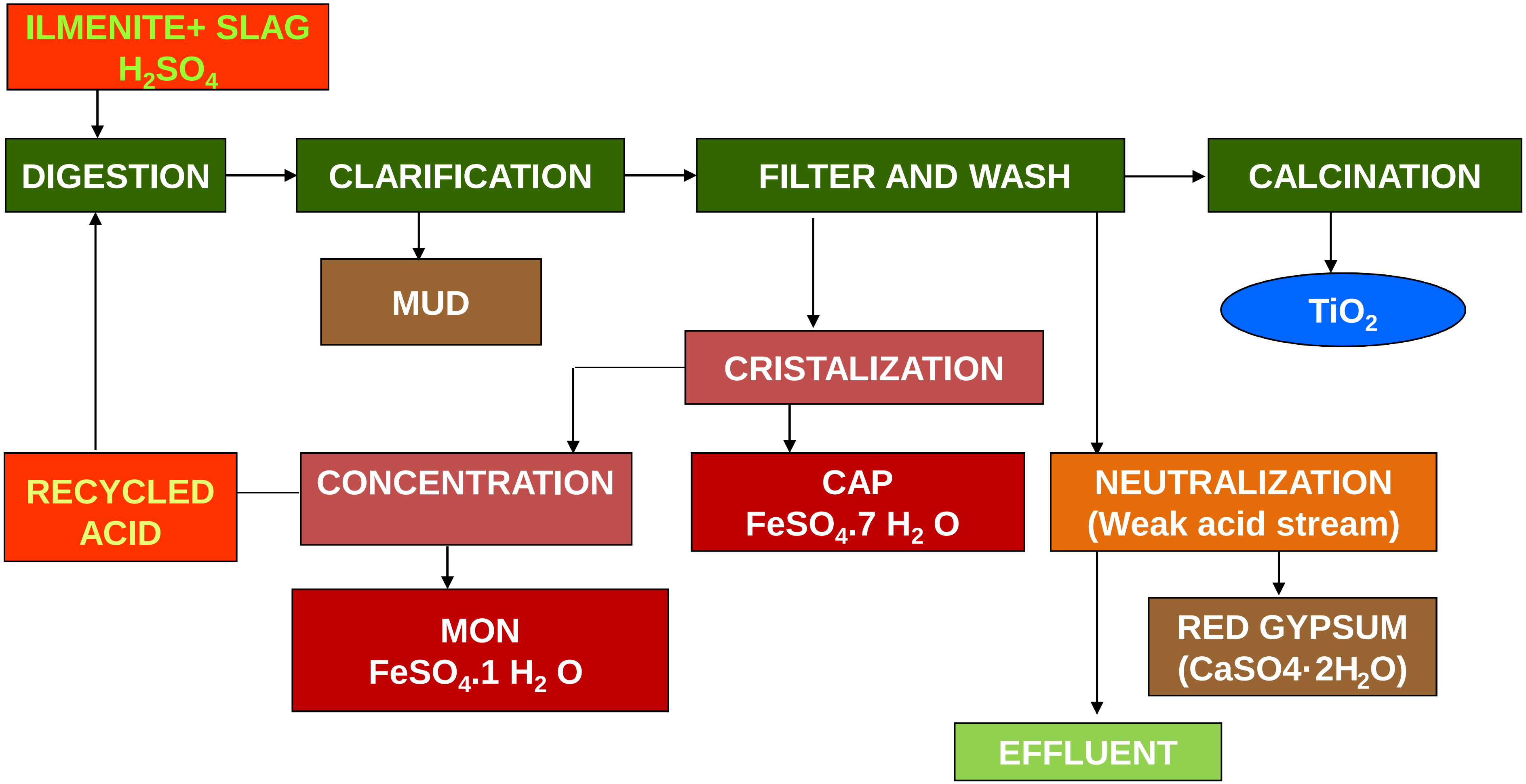
OBJECTIVES

- Firstly, to characterize the raw material, co-products and waste (elemental composition, mineralogy, granulometry and radioactive contents).

- Secondly, to check the possibility of substituting natural gypsum (NG) for red gypsum (RG) in cement manufacturing.

MATERIALS AND METHODS

MAIN STEPS OF PROCESS



MATERIALS

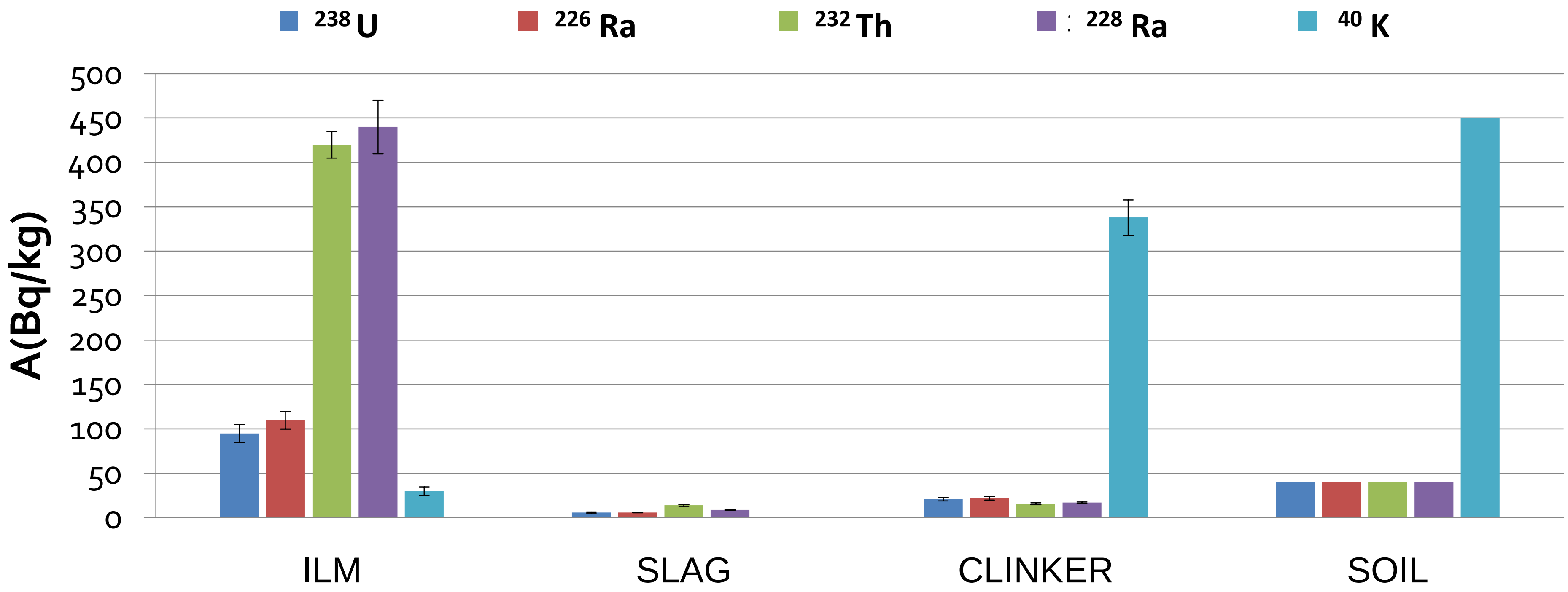
- ILM, SLAG, CAP, MON and RG samples were collected every 5 days for 1 month.
- OPC (Ordinary Portland Cement, 52.5 N/mm^2, 97 % Clinker + 3 % NG) and clinker Portland samples were also collected.

MEASUREMENT METHODS

- Alfa and gamma Spectrometry with semiconductor detectors (activity concentrations).
- XRD, X-Ray Diffraction (Mineralogical composition).
- SEM, Scanning Electron Microscopy
- XRF, X-Ray Fluorescence (major elements).
- ICP-MS, Inductively Coupled Plasma Mass Spectroscopy (trace elements).

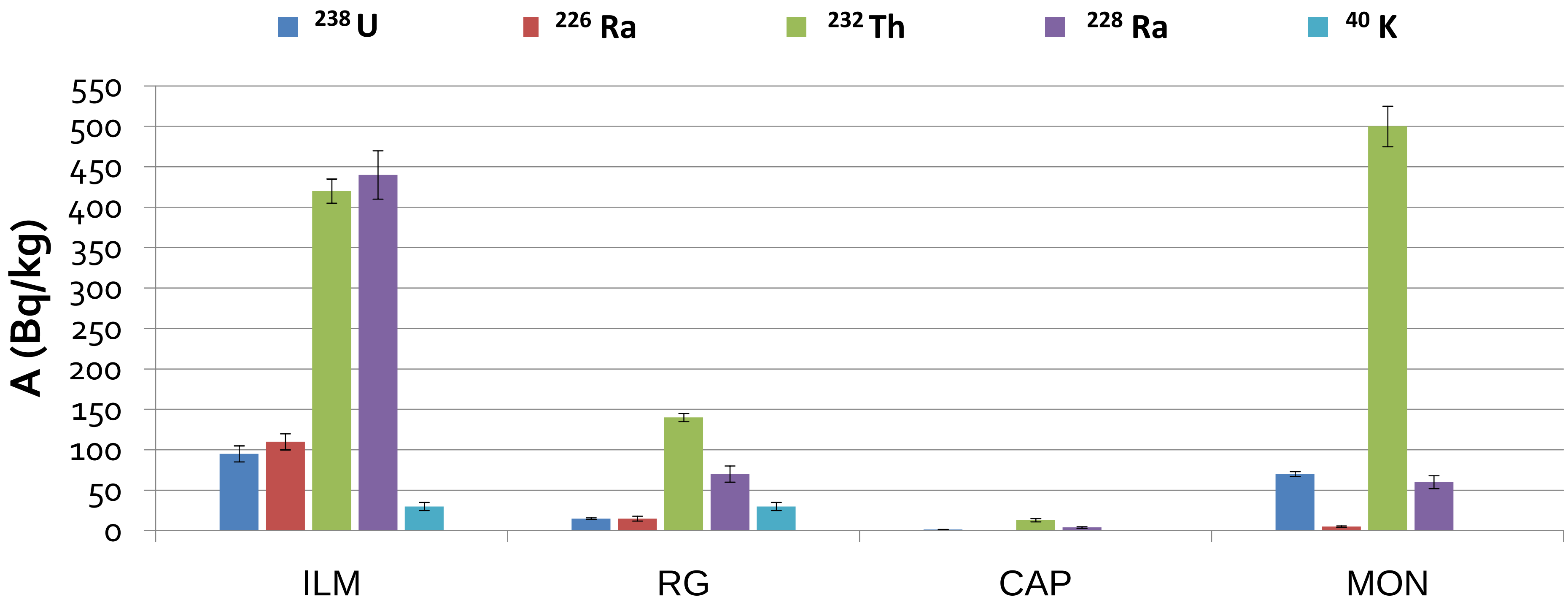
RESULTS

ACTIVITY CONCENTRATIONS (RAW MATERIALS)



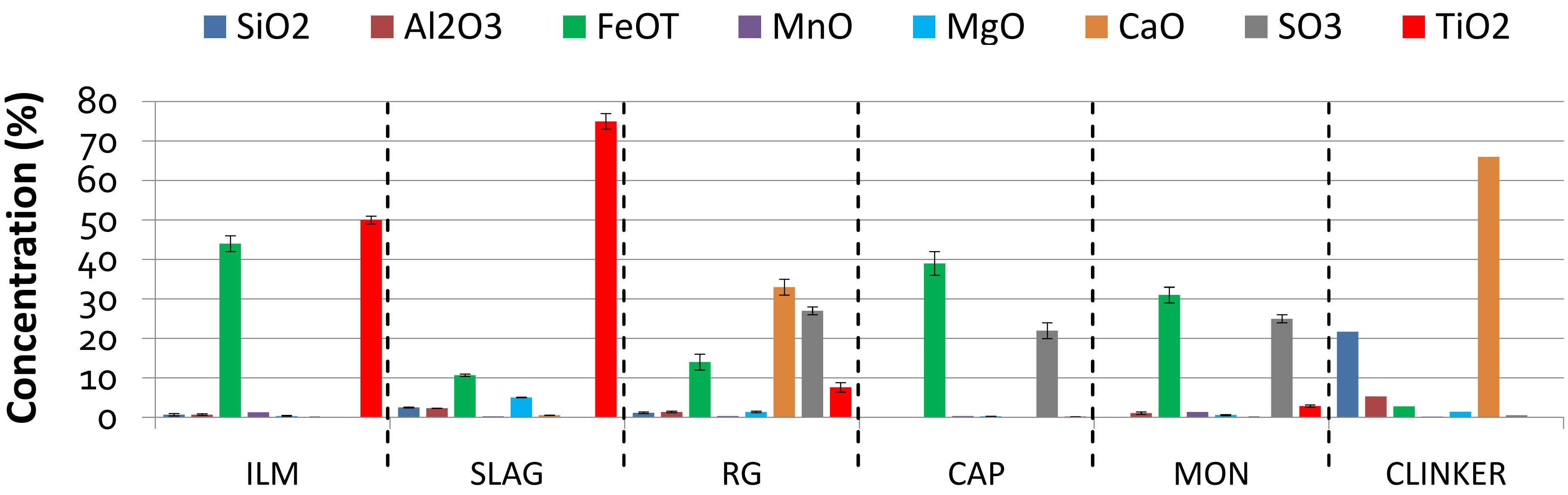
- ILM is a NORM mineral enriched by the natural radionuclides from the Th and U series.
- Radionuclide concentrations in SLAG are lower than soil, but these concentrations in clinker are similar to soil.

ACTIVITY CONCENTRATIONS
(CO-PRODUCTS and WASTE)



- The radioactivity content for RG is moderate.
- The CAP activity concentrations are less than 10 Bq/kg.
- MON has high levels of ^{232}Th and ^{238}U.

XRF



- ILM contains Fe and Ti. Slag has the highest concentration of Ti and low concentrations of Fe and Mg.
- RG contains mostly Ca and S, and traces of Fe and Ti.
- CAP and MON have high percentages of Fe and S.
- The concentrations of elements in clinker are standard.

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ICP/MS

Table 1. Concentration (mg/kg) of trace elements.

	ILM	SLAG	RG	CAP	MON	SOIL
V	940 ± 100	3130 ± 60	277 ± 20	25 ± 7	1100 ± 170	97
Cr	344 ± 134	1126 ± 212	133 ± 8	10 ± 3	470 ± 60	92
Zn	300 ± 60	35 ± 12	230 ± 30	300 ± 70	750 ± 110	193
As	22 ± 5	0.41 ± 0.23	12 ± 1	0.25 ± 0.06	1.3 ± 0.2	4.8
Cd	2.7 ± 0.7	2.3 ± 0.5	1.04 ± 0.09	3.3 ± 0.7	0.87 ± 0.09	0.09
Pb	135 ± 23	36 ± 13	35 ± 5	46 ± 14	45 ± 5	17
Th	97 ± 19	4.2 ± 1.2	30 ± 2	3.1 ± 1.1	92 ± 11	3.1
U	6.5 ± 1.5	0.77 ± 0.21	1.7 ± 0.3	0.11 ± 0.03	5.0 ± 0.4	2.7

- V and Cr concentrations are higher in slag than in ILM.
- RG contains a moderate concentration of trace elements.
- CAP is fairly free of trace elements. MON is enriched in trace elements.

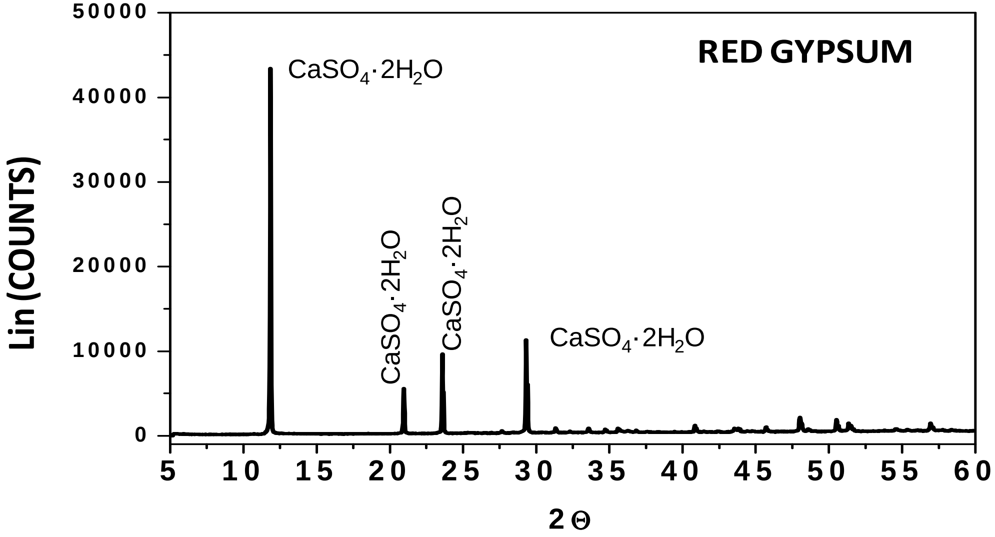
VALORISATION OF RED GYPSUM.

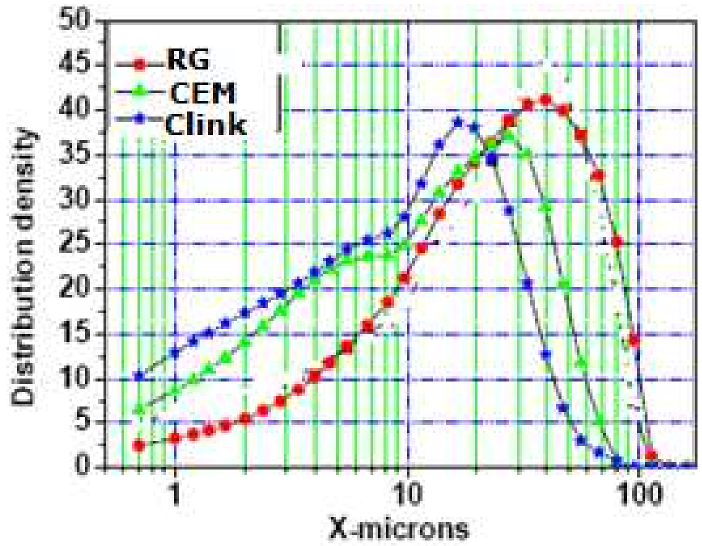
- Currently, the RG generated is disposed of in authorized area.
- We have analyzed the possibility of substituting NG for RG, as a setting retardant.
- The mixtures studied were: RG1 (90% CLINKER-10% RG), RG2 (95% CLINKER-5% RG) and RG3 (97.5% CLINKER-2.5 %RG).
- The properties of these mixtures were compared with a commercial cement CEM (type I 52.5 N/SR).

TESTS

- Granulometry and XRD.
- Determination of water/cement ratio in paste (Vicat) EN 196-3.
- Determination of expansion (Le-Chatelier),EN 196-3.
- The setting times in mortars (mixture of sand and cement, 3:1) for the three RG cements (Vicat), EN 196-3.
- Mechanical test in mortars, EN 196-1.
- Study by SEM.

XRD and GRANULOMETRY





- The difractogram obtained for RG is similar to NG.
- RG has a maximum granulometric distribution of around 40 µm

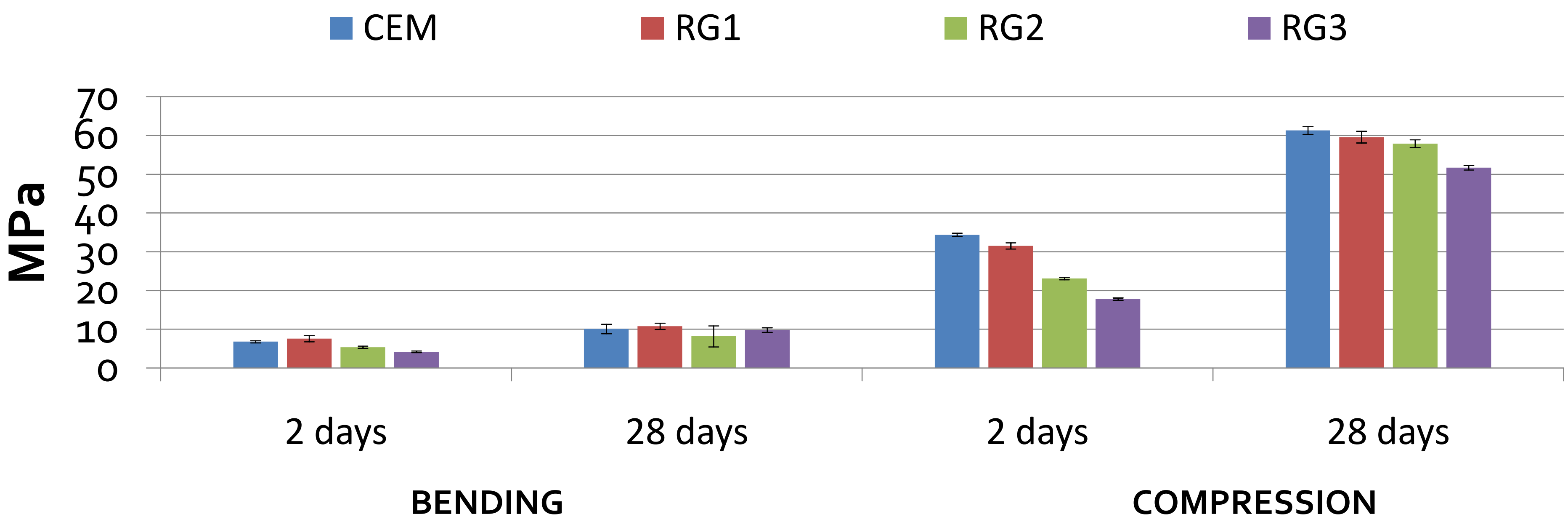
W/C, EXPANSION and SETTING TIMES

Table 2.- W/C ratios, setting times and expansion were determined following a normalized protocol using different proportions of red gypsum. For comparison, the commercial cements(CEM) taken as reference in this work are shown.

Sample	Optimum W/C	Initial setting times (min)	Final setting times (min)	Δt (min)	Expansion (mm)
CEM	0.27	139	224	85	2
RG1 (10% RG)	0.29	216	351	135	1
RG2 (5% RG)	0.27	108	298	190	1
RG3(2.5% RG)	0.29	82	129	47	1

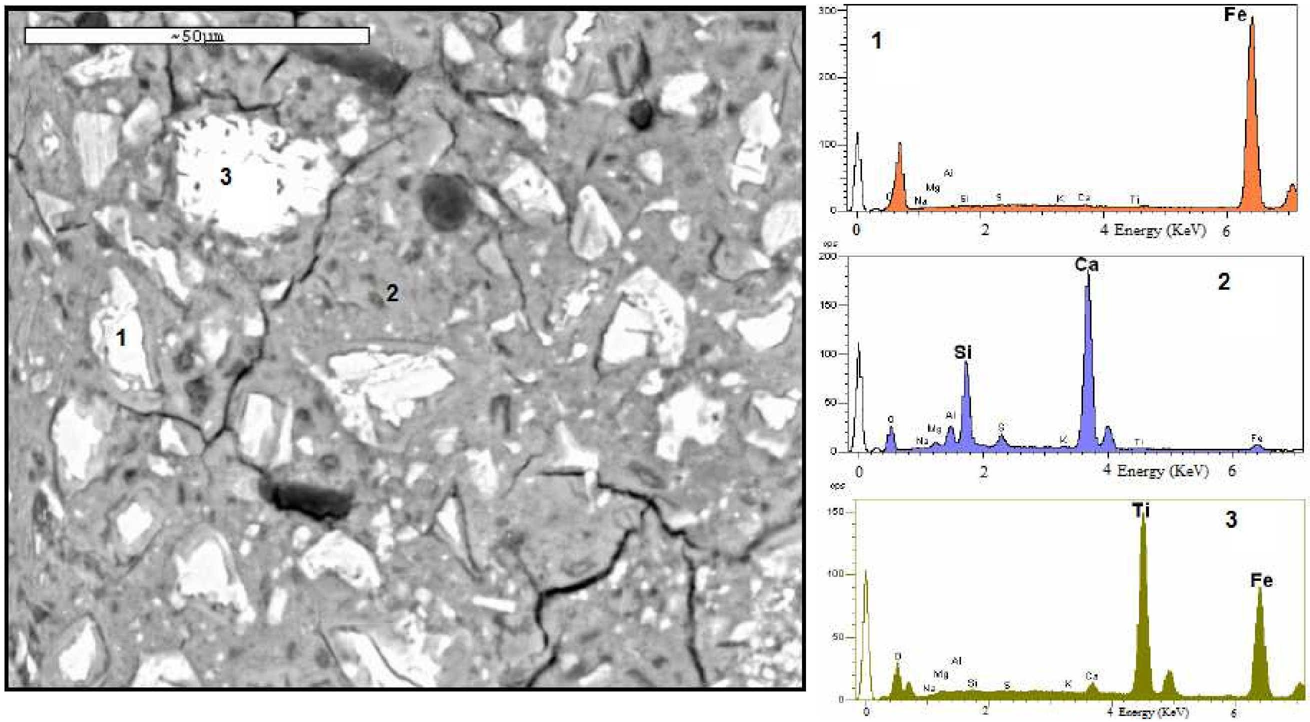
- All W/C ratios are similar to CEM.
- The values of expansion are less than 10 mm.
- Adding higher percentages of RG extends the initial and final setting times but always complying with Spanish law.

MECHANICAL TEST



- The mechanical behaviour of the cements formed improves when more RG is added.
- In the RG1 sample the mechanical resistance is similar to CEM.

SEM



- The SEM image enables us to confirm that RG has reacted completely with the mineral phases of the clinker.
- The major impurities, Fe and Ti, are trapped in the cement matrix.

RADIOLOGICAL EVALUATION

$$I = \frac{C_{^{226}Ra}}{300 \ Bqkg^{-1}} + \frac{C_{^{228}Ra}}{200 \ Bqkg^{-1}} + \frac{C_{^{40}k}}{3000 \ Bqkg^{-1}}$$

- The EU has established criteria that define the external risk rate "I" in building material.
- Applying these radiological criteria, we have found that RG can be used in any proportion with no radiological consequences.

CONCLUSIONS

- Detailed information on the composition of raw materials, co-products and waste used/generated in a titanium dioxide pigment industry has been obtained.
- From the radiological point of view we have confirmed that ilmenite is a NORM material and that the co-products, CAP and MON (with a well defined marked) fulfill the regulations.
- The research performed to analyses the possible use of RG in the productions of cement and mortars has allowed to concluded that this waste of the TiO2 industry can be used safely as a substitute on NG without decreasing the quality of the generated cements and without causing any detectable environmental impacts.

Thank you for your attention