VALORIZATION OF NORM WASTE FROM TITANIUM DIOXIDE INDUSTRY THROUGH COMMERCIAL PRODUCTS

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INTRODUCTION

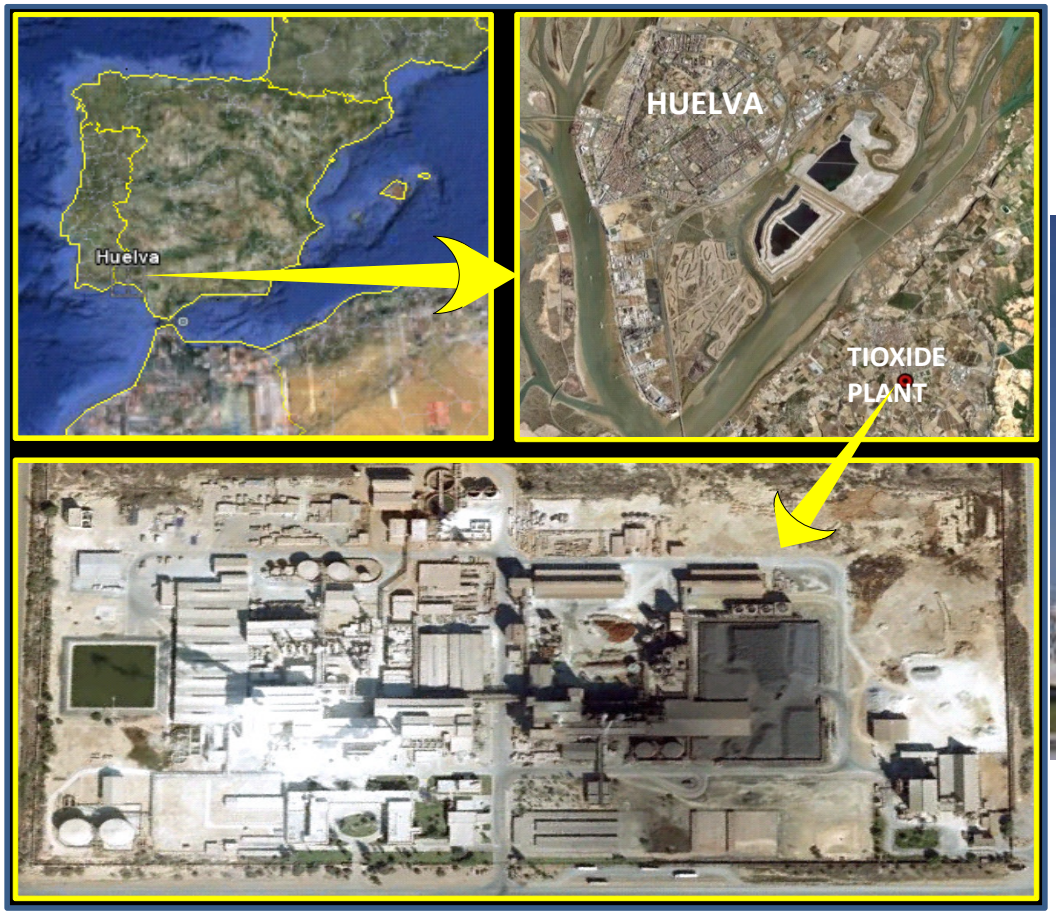
✓ **To valorize NORM waste adds to consider a new aspect: the radiological problem**

✓ **The present study has been carried out with the aim of evaluating the radiological problem related to the valorization of wastes and co-products from the TiO_2 NORM industry.**

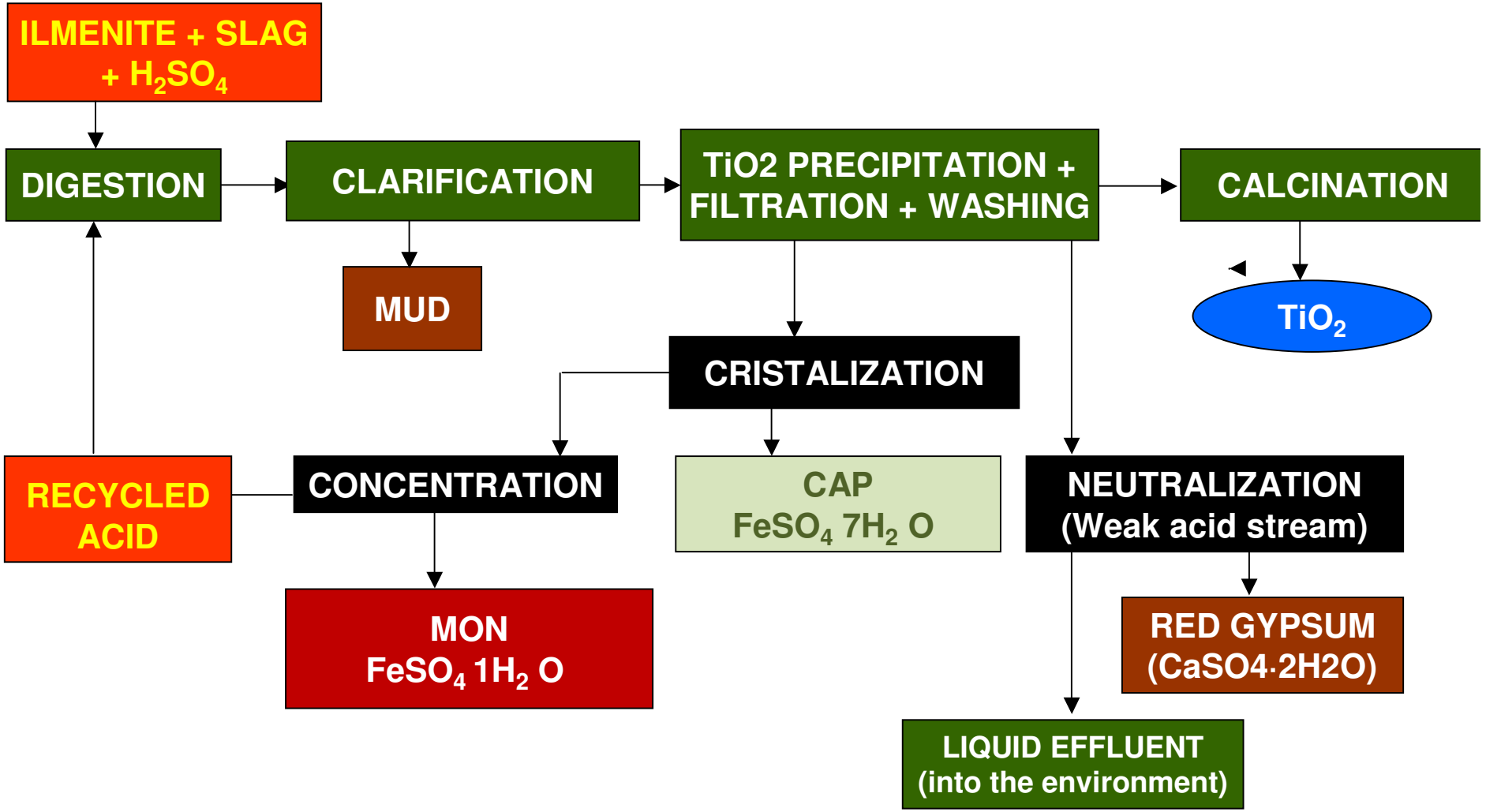
✓ **The factory of Tioxide-Huelva is the only one in Spain devoted to the titanium dioxide production.**

✓ **Two main residues generated in the TiO2 industry from Spain are: 1) Red Gypsum (RG), and 2) Un-attacked muds of ilmenite (MUD) from the mineral digestion.**

LOCATION



INDUSTRIAL PROCESS



OBJETIVES

✓ To characterize the raw materials (Ilmenite and SLAG), co-products (COP and MON) and waste (RG and MUD), elemental composition, trace elements, mineralogy, granulometry and radioactive contents were analyzed.

✓ To check the possibility of substituting natural gypsum (NG) for red gypsum (RG) in cement manufacturing.

✓ To evaluate the use of these wastes in the manufacture of several fire resistant materials for construction systems.

MATERIALS AND METHODS

✓ **5 samplings were done: ILM, SLAG, CAP, MON, MUD and RG samples were done (1 sampling every 5 days for 1 month), in order to evaluate the possible temporal variability in the properties of these materials.**

✓ **OPC (Ordinary Portland Cement: 52.5 MPa, 97 % Clinker + 3 % NG), clinker Portland and Vermiculite samples were also collected.**

✓ **Different measuring techniques were applied for materials characterization: alpha and gamma spectrometry, ICP-OES/MS, XRF, SEM, etc.**

ACTIVITY CONCENTRATIONS

Table 1. Activity concentration (Bq/kg) in different samples

	R.H.	^{238}U	^{230}Th	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{40}K
ILM	5.2	**95 ± 3**	85 ± 5	86 ± 5	84 ± 4	**335 ± 20**	301 ± 20	30 ± 2
SLAG	4.7	5.9 ± 0.7	19 ± 4	6.5 ± 0.7	<3	14 ± 3	9.0 ± 1.2	8 ± 1
COP	40	0.90 ± 0.10	4.5 ± 0.3	<4	11 ± 2	8.0 ± 0.9	<4	<4
MON	4.2	72 ± 2	114 ± 6	9.2 ± 0.6	18 ± 2	365 ± 18	43 ± 3	11 ± 2
RG	**46**	**19 ± 1**	**43 ± 3**	**14 ± 2**	**28 ± 4**	**152 ± 9**	**91 ± 4**	**12 ± 3**
MUD	**41**	**212 ± 25**	**45 ± 3**	**815 ± 30**	**277±17**	**353 ± 30**	**2580 ± 60**	**284 ± 10**
TiO_2	27	0.8 ± 0.2	-	5 ± 1	-	2.5 ± 0.1	15 ± 2	<4

143 000 t of ILMENITE+ 21 000 t SLAG

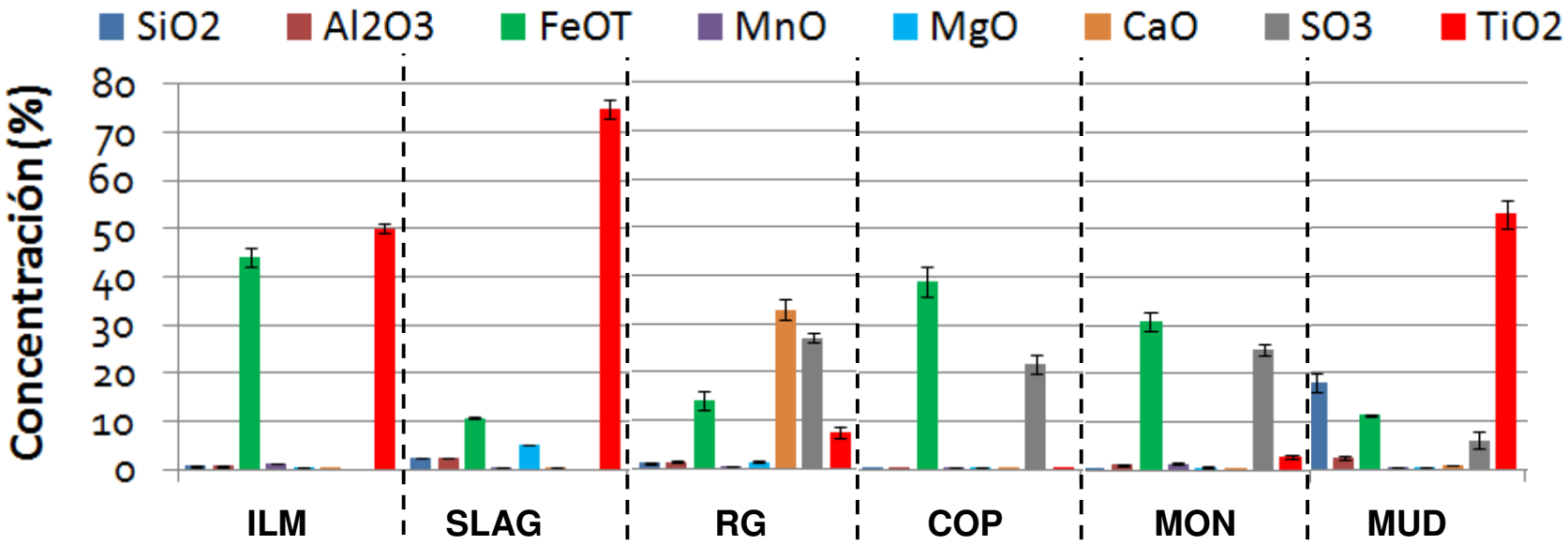
58 000 t of WET RED GYPSUM (RG)

185 000 t of COPPERAS (COP)

123 000 t of MONOHIDRATE (MON)

28 000 t of WET MUD (MUD)

MAJOR ELEMENTS



- **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.
- **COP** and **MON** have high percentages of Fe and S.
- **MUD** contains mainly TiO_2 (**≈ 5% of total TiO2**) and SiO_2.
- **Trace elements** have been also determined.

VALORIZATION OF COPPERAS AND MONOHYDRATE

COPPERAS

- **Copperas**, ferrous sulphate heptahydrated, has been used in the field of **agriculture**, as supplier of iron to prevent chlorosis in plants, especially in citrus, allowing a better plant growth.
- So is used as agent to **fight the plagues of snails** which damage the plantations, especially in the early stages of growth.
- It is also used in the **manufacture of cement** as **reducing agent of Cr (VI)**, attending to the EU Directive 2003/53/EC.
- Copperas has been also applied for the **purification of water** as flocculating and for **phosphate removal** in municipal and industrial sewage treatment plants to prevent eutrophication and to remove mainly the colloidal substances.
- Nowadays, all the produced Copperas is marketed.

MONOHYDRATE

- **Monohydrate Ferrous Sulphate** (MON) is used in the field of **feedstuffs** because is adequate to produce haemoglobin in the animal, especially in the early stages of their lives.
- In the **agricultural** field is used due to:

  1. The **iron in ferrous** state is directly assimilated by plants.
  2. The **sulfuric acid** allows the solubilization of other cations such as magnesium or phosphorus.
  3. **Metals** such as zinc, copper, and manganese are essential trace elements in plant development.

- In **alkaline soils**, can be used mixed in different composts since the presence of free acid accelerates the decomposition of the organic matter contained in the soil.

VALORISATION OF RED GYPSUM IN THE MANUFACTURING OF CEMENTS

- Currently RG is disposed of in authorized repository.

- We have analyzed to **substitute the NG (a setting retardant) for RG**.

- The mixtures (cements) manufactured were:

RG1 (90% CLINKER-10% RG), RG2 (95% CLINKER-5% RG) and RG3 (97.5% CLINKER-2.5 %RG).

- The properties of these cements were compared with a commercial cement CEM (type I 52.5 N/SR).

TEST

- Granulometry and XRD.
- Determination of water/cement ratio and soundness in paste by the Vicat method according to the EN 196-3.
- Determination of the 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.
- Final mortars were studied by SEM to analyze their micro-morphology.

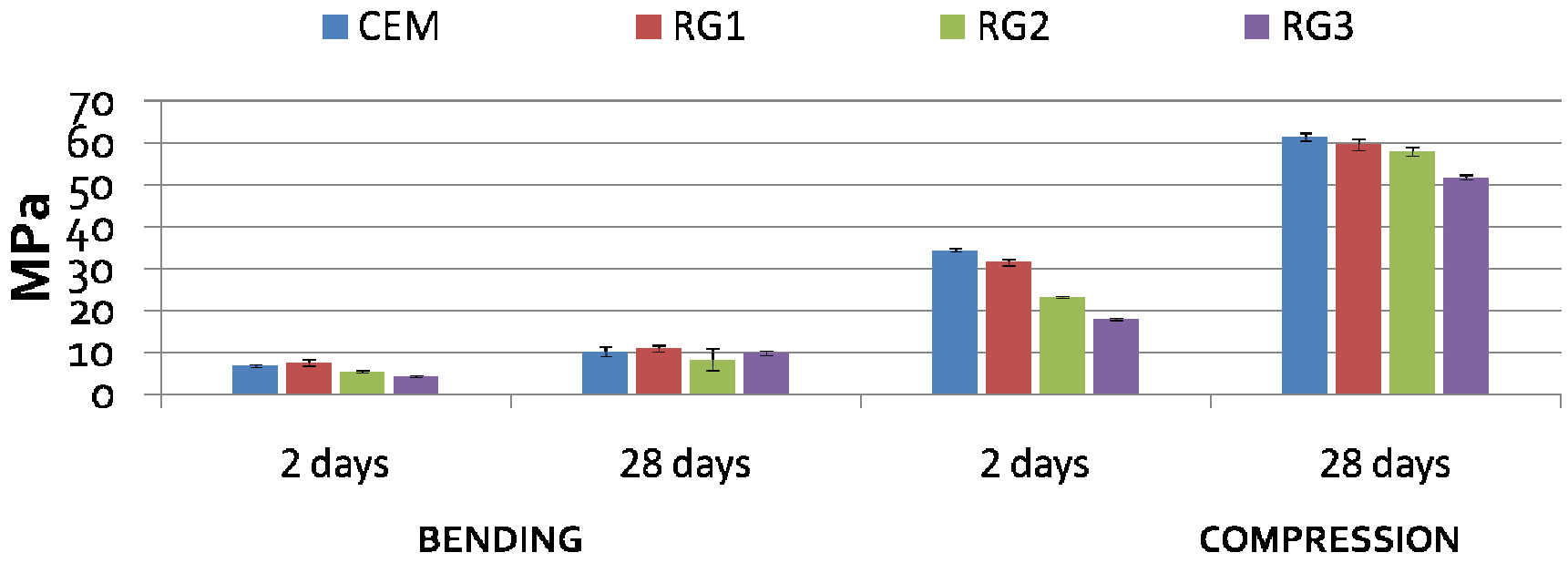
W/C RATIO, EXPANSION and SETTING TIMES

Table 3. 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	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

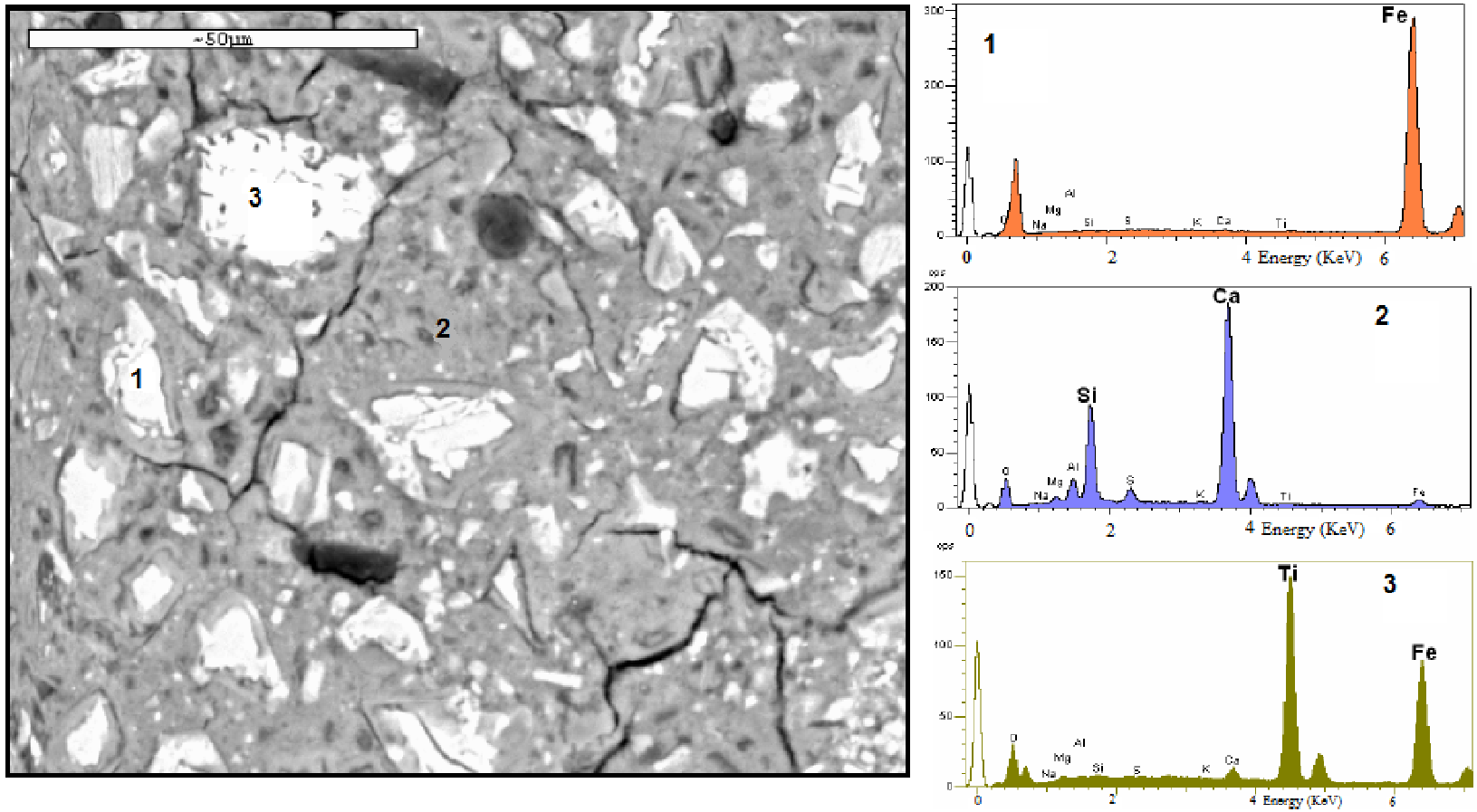
- All W/C ratios are similar to CEM.
- The values of expansion are less than 1 mm.
- Adding higher percentages of RG extends the initial and final setting times but always complying with Spanish law.

MECHANICAL STRENGTH TESTS



- The mechanical strength for breaking improves according to more RG is added.
- In the RG1 (10% of RG) cement the mechanical resistance is similar to the standard cement (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

- The EU has established criteria for buildings materials the Activity Concentration Index ("I").

- By applying this radiological index, we have found that RG can be used in any proportion with no radiological consequences.

VALORISATION OF RED GYPSUM + MUD

(Fire-resistant materials)

✓ Currently, the RG and MUD generated is disposed of in an authorized landfill.

✓ We have analyzed the possibilities for their use in the production of **fire resistant material** in buildings.

✓ **Vermiculite** (natural material) was added in order to reduce the density of the obtained plates.

Table 4. Proportions of MUD, RG and VER used in the different plates made.

Name	VER (%)	MUD (%)	RG (%)
Plate 1	Reference material (gypsum plaster)		
Plate 2	5	15	80
Plate 3	-	25	75
Plate 4	15	20	65
Plate 5	-	-	100

Plates were made by using a low cost manufacturing method:

✓The components were mixed with water, in different percentages, see table 4.

✓The obtained plates were introduced into molds 25 x 25 cm and 1.8 or 2.8 cm thickness, and were dried to their setting during 25 days at environmental temperature.

INSULATING TEST

The exposed side is subjected to the standard fire resistance curve:

$$T = 20 + 345 \cdot \log_{10}(8t+1)$$

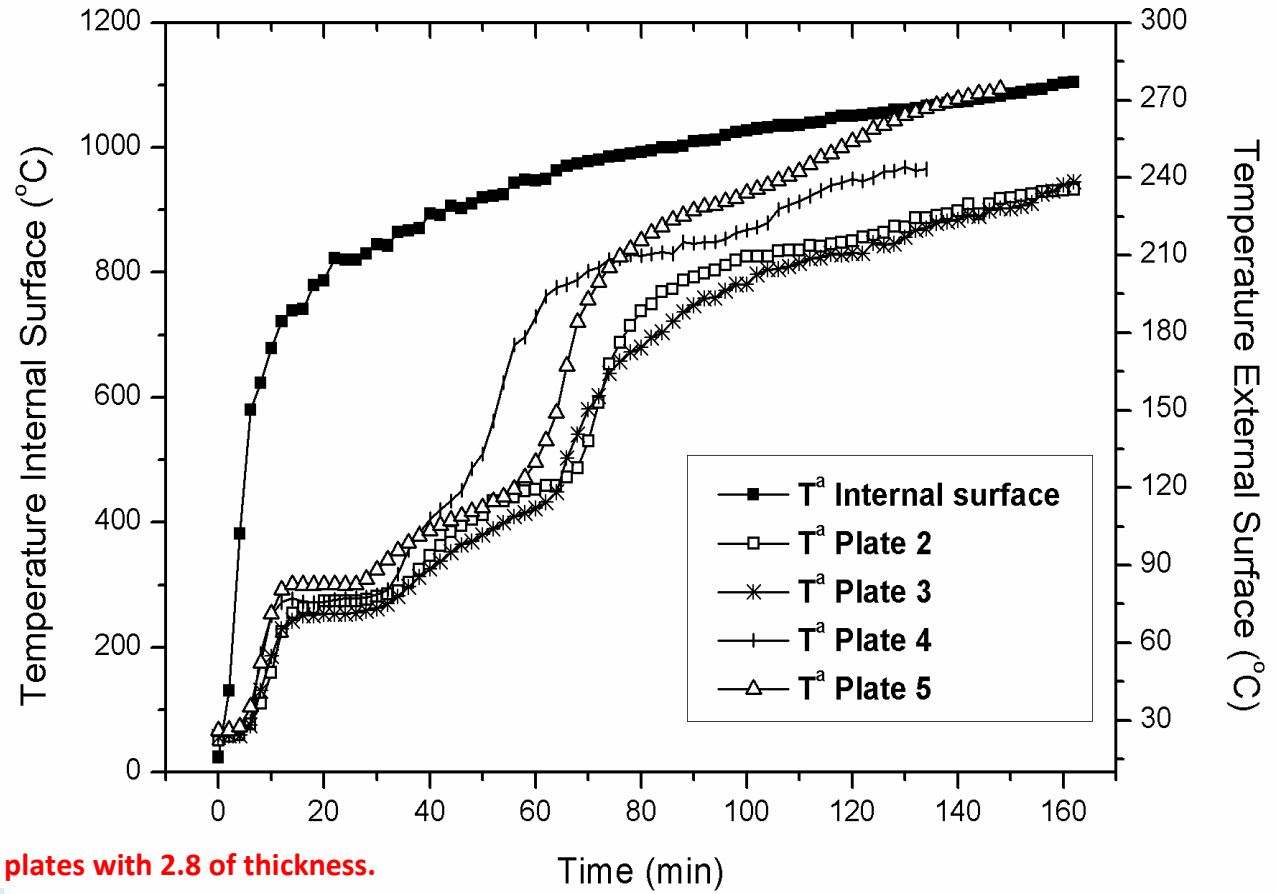
where T is the internal temperature (℃) of the oven, and t is the time (minutes) from the beginning of the test.

The plates are classified according to standard insulating tests (EN-1363-1) by measuring the time for that:

✓Temperature non-exposed surface is > 180 □C, or

✓Temperature non-exposed surface is > 140 □ C + T_{env}.

RESULTS OF INSULATING TESTS



plates with 2.8 of thickness.

- Plateau of loss of two molecules of water in CaSO4·2H2O
- Temp. non-exposed side has several regions with different behavior (slopes). Plates 2 and 3 give the best results (~ **20% MUD +80% RG**).
- The fire resistance is highly thickness dependant

RADIOLOGICAL EVALUATION

- Remembering that mud contains a concentration of **radium equivalent of about 4.5 Bq/g**.

- The radioactive content for red gypsum is moderate.

- Vermiculite present a high concentration of ^{40}K, around 1800 Bq/kg.

- Attending to the composition of plates index:

I = 0.74- 4.7 < 6 (EU recommendation for thin building systems, few cm thickness)

Table 5. *Concentration values* ***(µg/L****) of trace elements in solutions from the plate 2, plate 3 and limits values for the Toxicity Characteristic Leaching Procedure (****TCLP)*** *test.*

	As	Cd	Co	Se	Cr	Cu	Ni	Pb	Sr	V	Zn
Plate 3	**<1**	**1.9±0.1**	**8.5±0.5**	**<1**	**2.1±0.2**	**47.2±2.2**	**68±3**	**<1**	**330±10**	**<1**	**71±4**
Plate 2	**<1**	**<1**	**5.2±0.4**	**<1**	**1.7±0.2**	**25.7±1.8**	**42±5**	**<1**	**336±11**	**<1**	**39±3**

- TCLP tests were developed by US-EPA in the 80's to analyze the metals mobility in wastes.

- The leaching test shows metal concentrations in the leachates of plate 2 and 3 lower than regulatory limits for TCLP test.

CONCLUSIONS

- **Detailed information on the composition of raw materials, co-products and waste from the titanium dioxide pigment industry has been obtained and analyzed.**

- **It has been demonstrated that RG can be used for manufacturing of cements for substituting the NG**

- **This study has shown that plates manufactured with these wastes (RG + MUD) can be used for the construction of thermal insulator building walls.**

- **The results obtained for the Activity Concentration Index (I) and in the application of the Toxicity Characteristic Leaching Procedure (TCLP) tests to the manufactured products are between the limits established in Spain.**

Thank you for your attention

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MINIMIZATION AND ELIMINATION OF NORM WASTE FROM TITANIUM DIOXIDE INDUSTRY THROUGH THEIR VALORIZATION IN FINAL COMMERCIAL PRODUCTS

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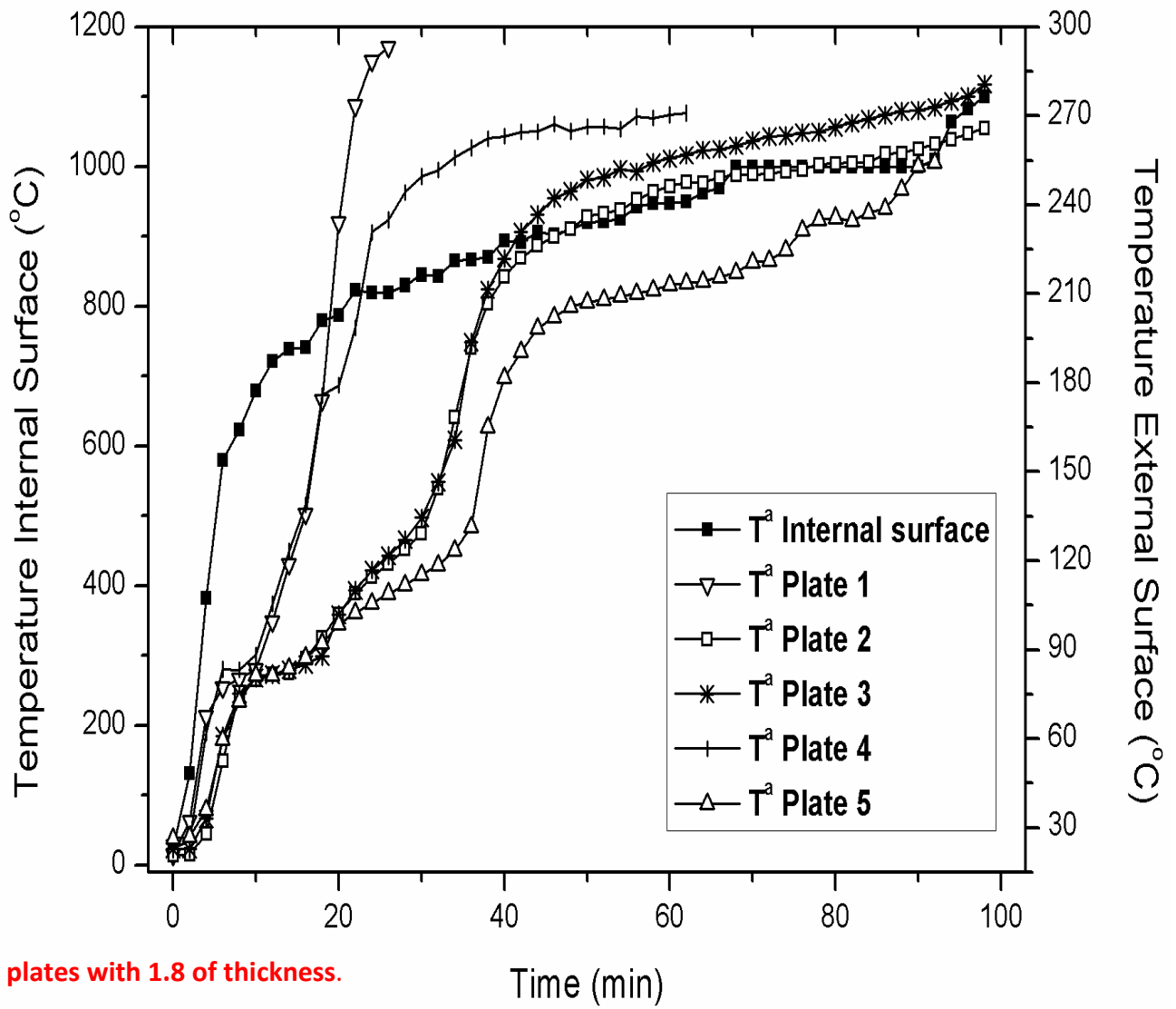
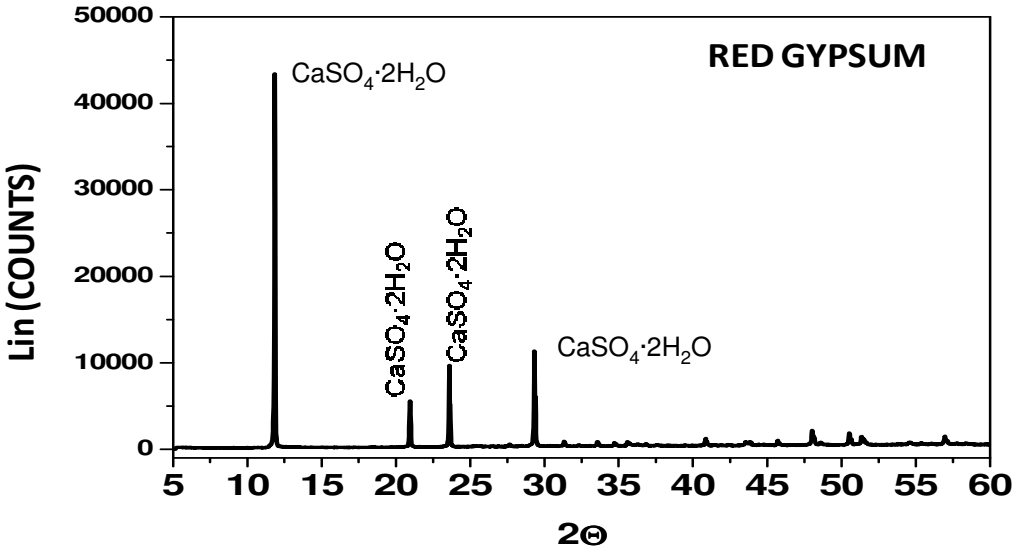
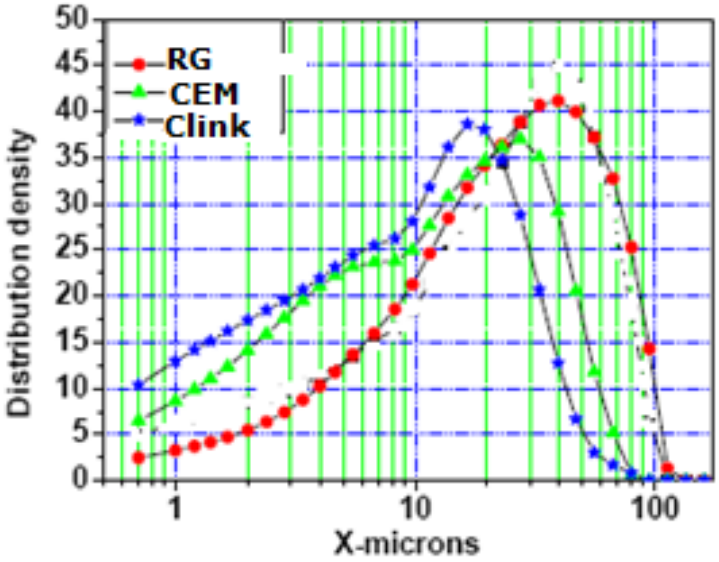


plates with 1.8 of thickness.

XRD and GRANULOMETRY





- The diffractogram obtained for RG is similar to NG.
- RG: its grain size distribution has a maximum around 40 μm, very similar to the standard cement (CEM)

TRACE ELEMENTS

Table 2. *Concentration (mg/kg) of trace elements.*

	ILM	SLAG	RG	COP	MON	MUD	SOIL
V	940 ± 100	3130 ± 60	277 ± 20	25 ± 7	**1100 ± 170**	**840 ± 90**	**97**
Cr	344 ± 134	1126 ± 212	133 ± 8	10 ± 3	**470 ± 60**	**518 ± 50**	**92**
Zn	300 ± 60	35 ± 12	230 ± 30	300 ± 70	**750 ± 110**	193 ± 11	**193**
As	22 ± 5	0.41 ± 0.23	12 ± 1	0.25 ± 0.06	1.3 ± 0.2	**57 ± 4**	**5**
Cd	2.7 ± 0.7	2.3 ± 0.5	1.04 ± 0.09	3.3 ± 0.7	**0.87 ± 0.09**	0.60 ± 0.06	**0.10**
Pb	135 ± 23	36 ± 13	35 ± 5	46 ± 14	45 ± 5	**278 ± 7**	**17**
Zr	1470 ± 290	324 ± 32	33 ± 2	1.8 ± 0.4	62 ± 3	**17200 ± 600**	**193**
Th	97 ± 19	4.2 ± 1.2	30 ± 2	3.1 ± 1.1	**92 ± 11**	**70 ± 4**	**10**
U	6.5 ± 1.5	0.77 ± 0.21	1.7 ± 0.3	0.11 ± 0.03	5.0 ± 0.4	**18 ± 1**	**3**

- 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.
- MUD contain a higher proportion of trace elements.