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POTENTIAL VALORIZATIONS OF ARTIFICIAL GYPSUM GENERATED IN THE MANUFACTURE OF TITANIUM DIOXIDE PIGMENTS

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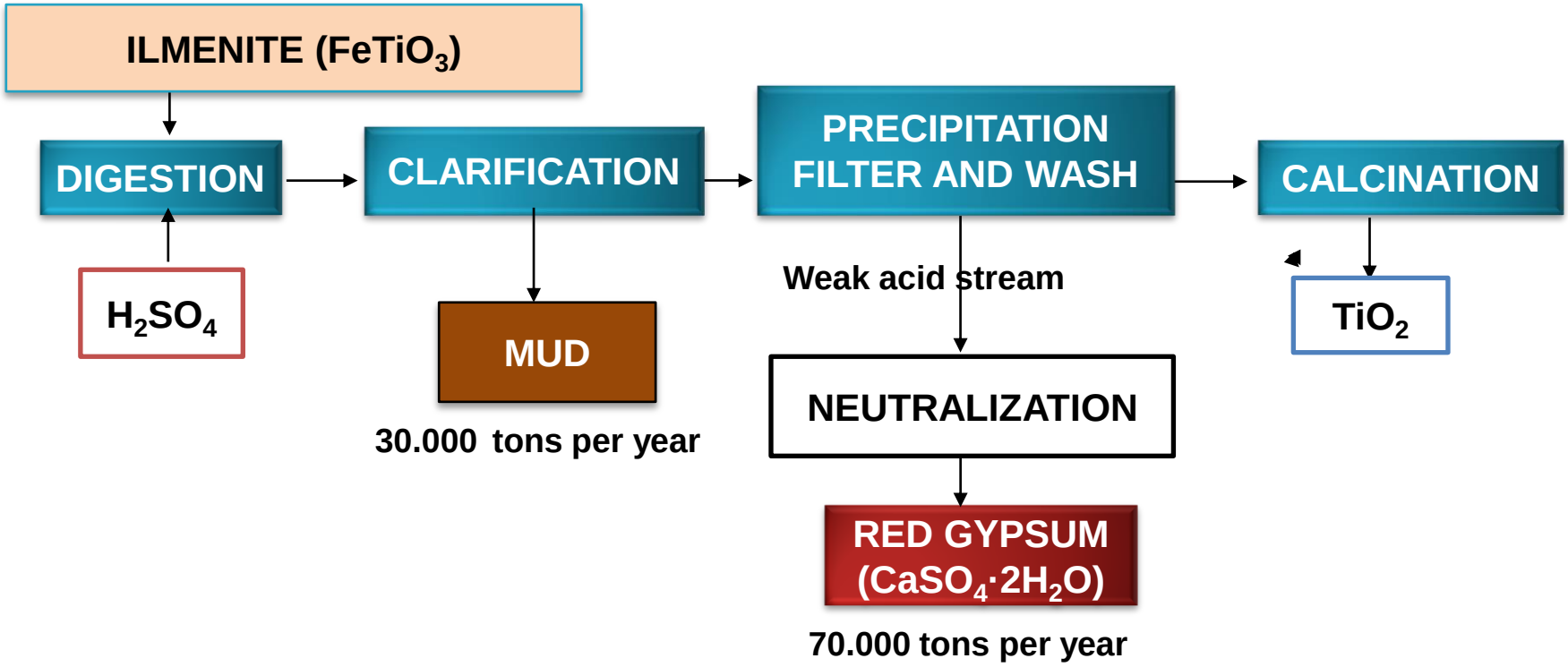
INTRODUCTION

- Globally **huge amounts of inorganic industrial wastes** are generated and their management **represents a high cost and an environmental problem.**
- **The development of technologies and new applications** to valorize these wastes is **of increasing importance.**
- The factory of **Tioxide-Huelva** is the only one in Spain devoted to the **TiO_2 production**.
- Two **residues, red gypsum (RG) and un-attacked ilmenite mud (MUD)** have been studied.

INDUSTRIAL PROCESS



Currently these wastes **have no commercial value** and **are disposed of in an authorized and controlled repository area**

OBJECTIVES

1. Use of RG and MUD as building materials **for fire-resistant panels.**

2. Use of RG as a calcium source for **carbon dioxide sequestration.**

CHARACTERIZATION METHODS

- X-Ray fluorescence (XRF)
- X-Ray difraction (XRD)
- Inductively coupled plasma-mass spectrometry (ICP-MS)
- Granulometry analysis
- Thermogravimetric analysis (TGA)
- Scanning electron microscopy (SEM-EDS)

MATERIALS

- MUD and RG samples were collected every 5 days for 1 month, in order to evaluate the possible temporal variability of the characteristics of these material
- In order to carry out the applications studied in this work, several materials as Pladur, vermiculite and NaOH were used.

RESULTS AND DISCUSSION

- **WASTE CHARACTERIZATION**
- **APPLICATIONS 1**
- **APPLICATIONS 2**

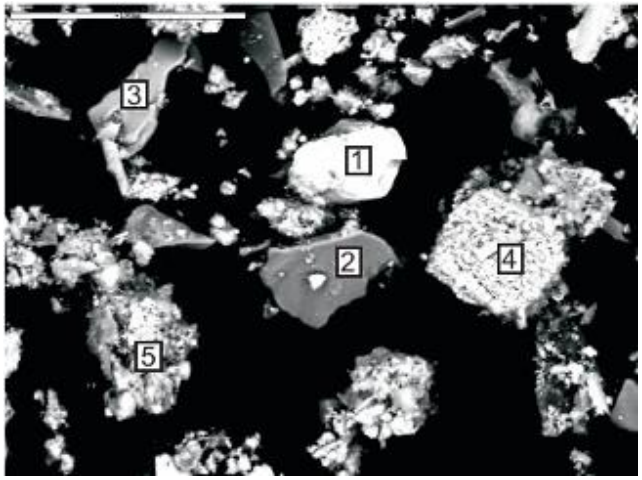
WASTE CHARACTERIZATION

MUD AND RED GYPSUM

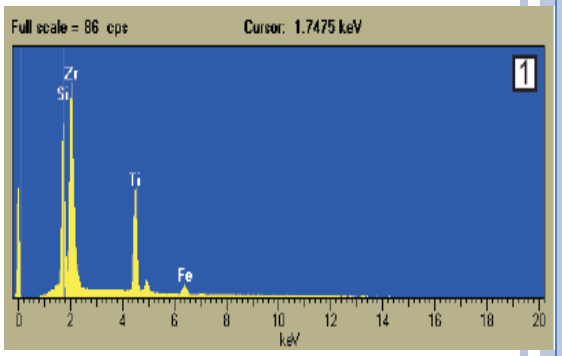
MUD

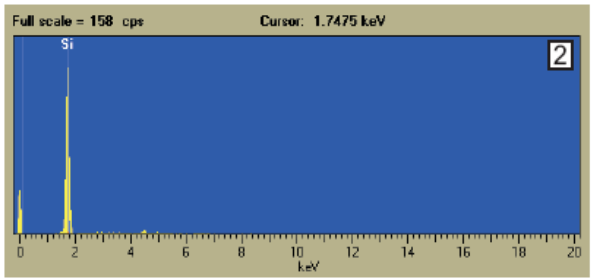
SiO_2	**18±1**
Al_2O_3	2.5±0.2
$FeO_{(T)}$	**11±1**
MnO	0.36±0.01
MgO	0.38±0.02
CaO	0.75±0.01
SO_3	**6.1±0.7**
TiO_2	**53±1**
ZrO_2	4.2±0.1

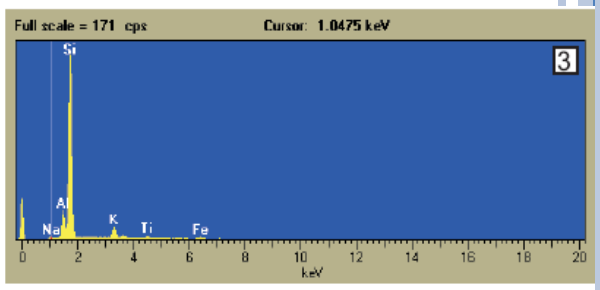
Concentration (%) of major elements by XRF

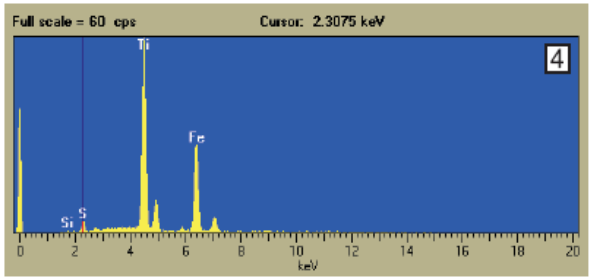


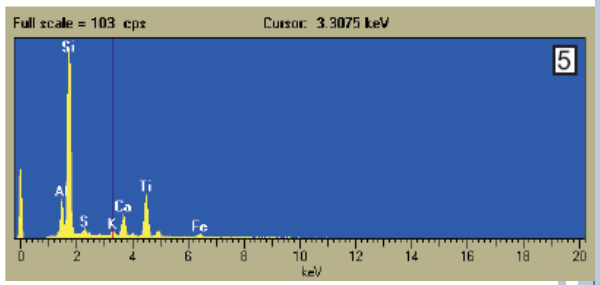
Granulometry ~ 40 µm











SEM analysis of MUD and their X-ray spectra

Mineralogical composition by XRD: **ilmenite ($FeTiO_3$), rutile (TiO_2), Zircon ($ZrSiO_4$), Quartz (SiO_2)**

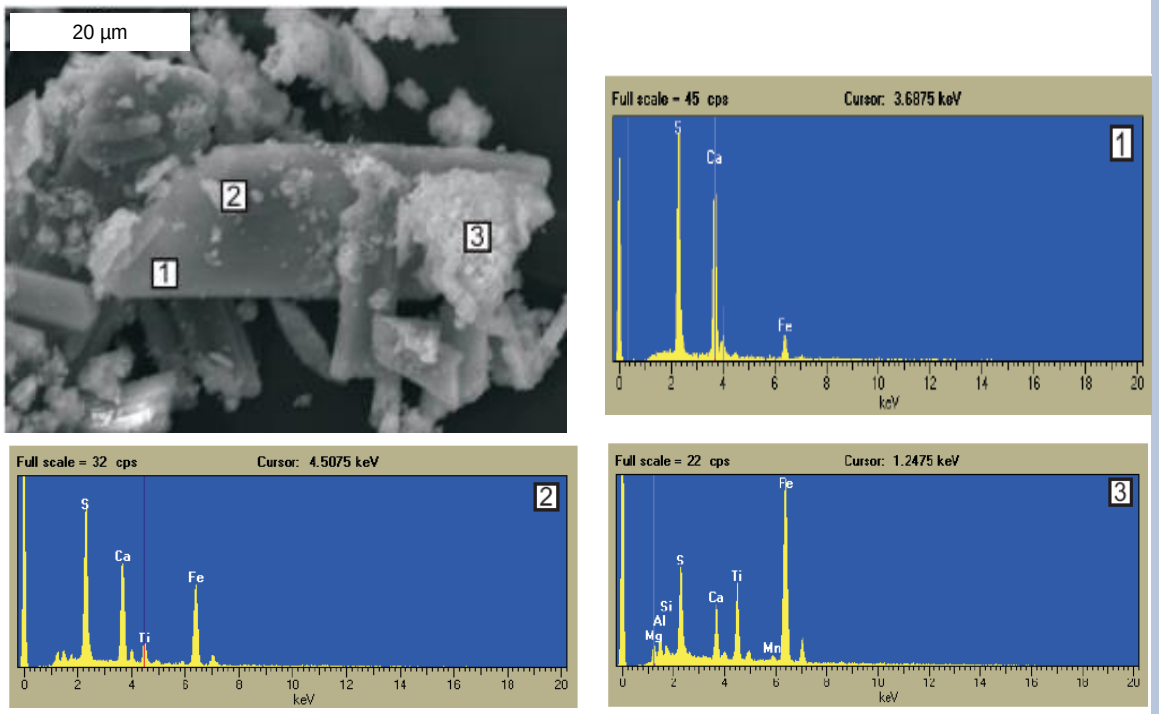
Mineral phases are highly refractory

RED GYPSUM

Granulometry ~ 60 µm

SiO_2	1.2±0.2
Al_2O_3	1.4±0.2
$FeO_{(T)}$	**14±2**
MnO	0.35±0.04
MgO	1.4±0.2
CaO	**33±2**
SO_3	**27±1**
TiO_2	7.6±1.2

Concentration (%) of major elements by XRF



SEM analysis of RG and their X-ray spectra

Mineralogical composition by DRX: **Gypsum ($CaSO_4 \cdot 2H_2O$) and iron and titanium oxides**

APPLICATION 1

RG and MUD as building materials for fire-resistant panels

Code	RG	MUD	Vermiculite
Plate 1	100 %	-	-
Plate 2	75 %	25%	-
Plate 3	80%	15%	5%

Vermiculite was used to increase the insulating capacity of plates.

Pladur (R) was used as typical building material.

Plates were made using a low cost **manufacturing method**:

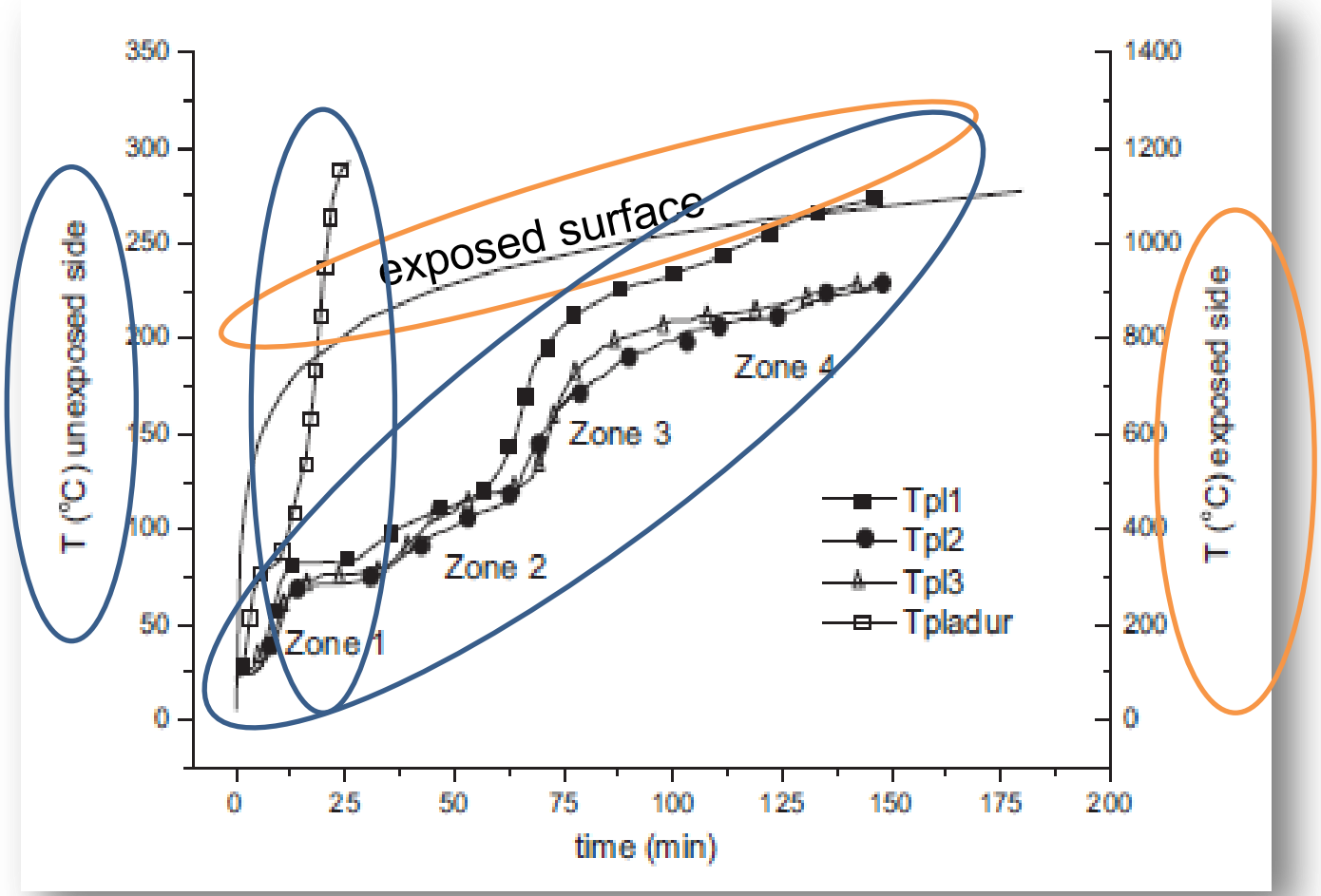
- The components were mixed with water, in different percentages.
- The pastes obtained were poured into a 25 x 25 cm by 2.8 cm thick molds and were dried for 25 days at ambient temperature.

FIRE-RESISTANCE TESTS

The fire-resistance capacity was evaluated in agreement to EN-1363-1 standard, which established a temperature (T) versus the time (t) inside an oven by the equation: **$T = 20+345 \cdot \log10(8t+1)$**, where T is the internal temperature (°C), and t is the time (minutes) from the beginning of the test.

The experiment is finished when:

- The temperature of one of the thermocouples on the non-exposed surface of the material is above 180 ºC.
- The average temperature of all the thermocouples on the non-exposed surface is above 140 ºC + Tenv (environmental temperature).



Plates 1–3: similar insulating behavior, much better than Pladur®.

The addition of mud improves thermal insulation significantly, mainly due to its highly refractory mineral phases. (Plate 2 and 3 better than 1)

The **influence of vermiculite** on the material **is negligible.**

Concentration values (µg/L) of leachability of trace elements from the plates and limits values of TCLP test .

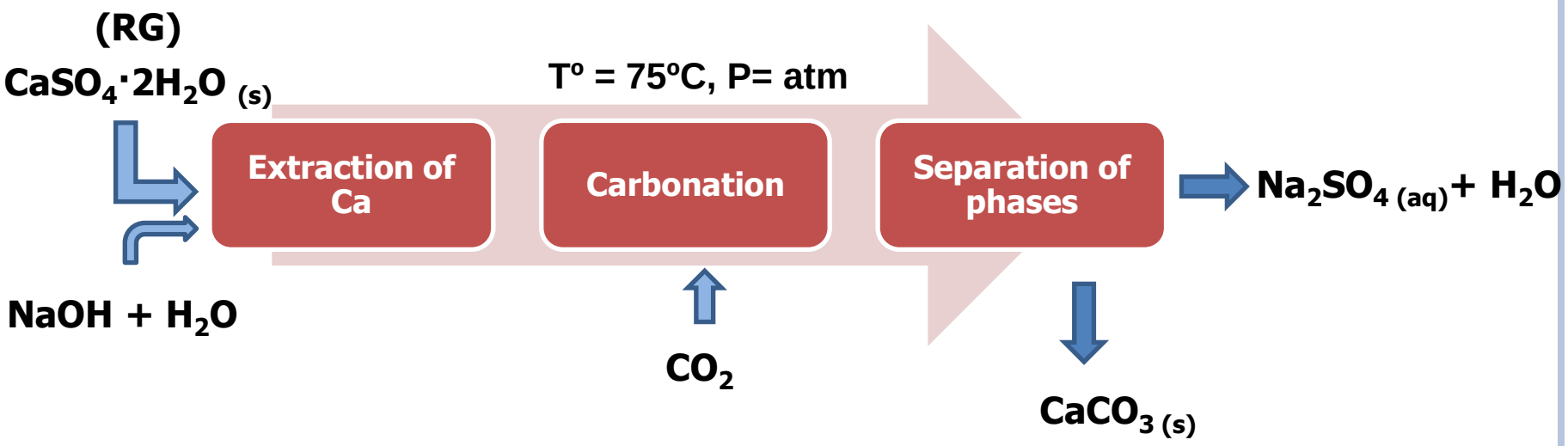
	As	Cd	Co	Se	Cr	Cu	Ni	Pb	Sr	V	Zn
Plate 2	<1	<1	5.2±0.4	<1	1.7±0.2	25.7±1.8	42±5	<1	336±11	<1	39±3
Plate 3	<1	1.9±0.1	8.5±0.5	<1	2.1±0.2	47.2±2.2	68±3	<1	330±10	<1	71±4
U.S. EPA	5000	1000	-	1000	5000	-	-	5000	-	-	-

The **leaching test** shows a **metals concentration lower than regulatory limits by EPA** for TCLP test.

APPLICATION 2

RG as a calcium source for carbon dioxide sequestration.

CARBONATION PROCESS



Theoretical Global Reaction:

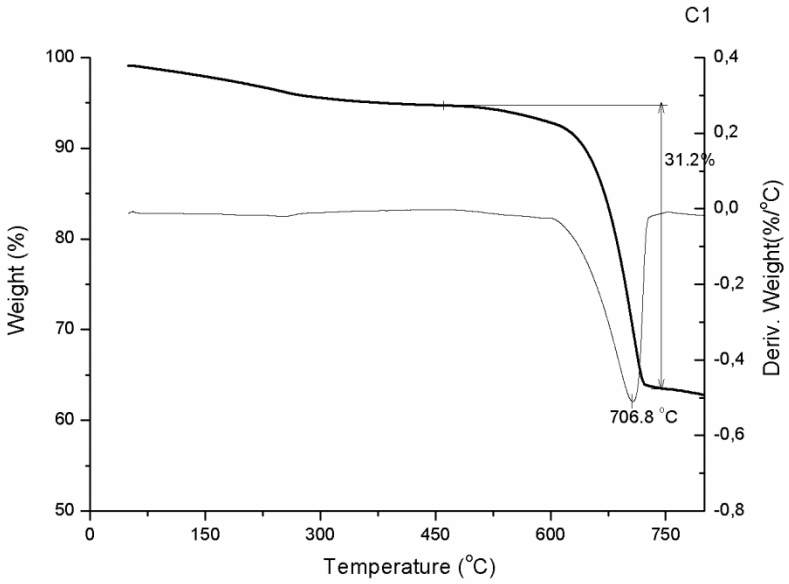
$$CaSO_4 \cdot 2H_2O_{(s)} + 2\,NaOH_{(aq)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)} + Na_2SO_{4\,(aq)} + H_2O$$

Concentration (%) of major elements and the transfer factor (%) in the brackets

	RG	Carbonated fraction	Sulphate fraction
SiO_2	0.74±0.05	1.2±0.1 (103±11)	0.35±0.03 (38±4)
Al_2O_3	0.75±0.02	1.0±0.1 (84±8)	0.04±0.01 (4.4±1.1)
Fe_2O_3	7.3±2.0	9.0±2.5 (79±30)	0.03±0.01 (0.34±0.15)
MnO	0.25±0.07	0.30±0.08 (76±29)	0.01±0.01 (3.3±3.4)
MgO	0.77±0.05	0.30±0.02 (25±2)	0.95±0. 06 (101±9)
CaO	28±2	47±3 (106±10)	1.8±0.1 (5.3±0.5)
Na_2O	0.18±0.01	0.50±0.03 (0.84±0.07)	37±3 (80±8)
K_2O	0.03±0.01	0.04±0.01 (84±35)	0.01±0.0 1 (27±20)
TiO_2	3.8±0.1	4.7±0.1 (79±3)	0.02±0.010 (0.43±0.21)
P_2O_5	0.05±0.01	0.05±0.01 (64±18)	0.01±0.01 (17±17)
SO_3	34±1	2.1±0.1 (4.0±1.0)	35±1 (85±4)

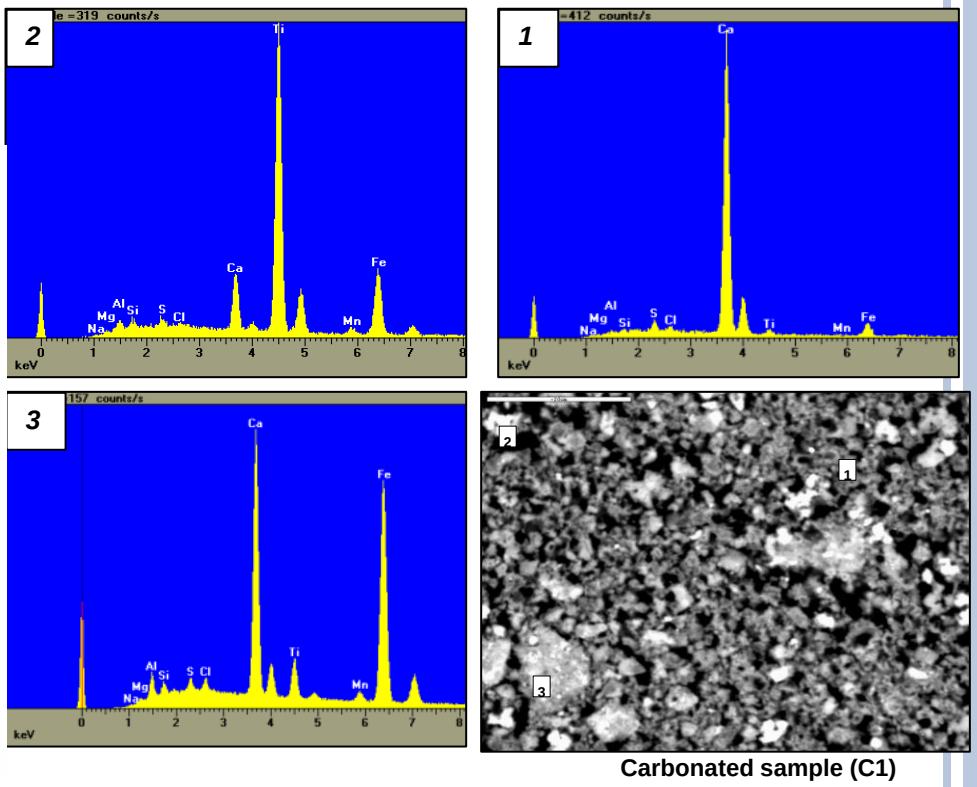
Mineralogical composition by XRD: Calcite ($CaCO_3$) and rutile (TiO_2).

Thermogravimetric analysis results



$$CaCO_3 \rightarrow CaO + CO_2$$

SEM analysis and their corresponding X-ray spectra



Carbonated sample (C1)

Particles present a poorly developed rectangular shape which is characteristic of calcite ($CaCO_3$)

Co_2 SEQUESTRATION EFFICIENCY (C_E)

$$C_E(\%) = \left(\frac{X_{exp}}{X_{theo}}\right) x\ 100$$

Where:

X exp ~ calcium in form of carbonate generated in the process

X theo ~ total calcium in the red gypsum

$$C_E = 92 \pm 6\ \%$$

CONCLUSIONS

APPLICATION 1: USE OF RG AS BUILDING MATERIALS FOR FIRE-RESISTANT PANELS

- Fire-resistance Test demonstrate that the **plates perform better than some materials used in construction such as Pladur®.** The tested material also **possesses acceptable mechanical properties** that showed **no noticeable distortion or breakage** during the test. Although, the mechanical properties of plates must be study.

- Also, it was conducted **leaching tests** using the **TCLP procedure** and **results** showed **a negligible environmental impact.**

APPLICATION 2: USE OF RG A CALCIUM SOURCE FOR CARBON DIOXIDE SEQUESTRATION

- The **products** of RG carbonation, using NaOH as extracting agents, are: **$CaCO_3$** and **Na_2SO_4.**

- The **pollutants remain almost completely into the carbonation fraction**, whereas the sulphate fraction is very clean. The **environmental implications** of both of them are **negligible for future applications.**

- The **carbonation efficiency** obtained is **very high under experimental conditions.**

Final remarks

- This study was carried out to evaluate the use of RG as building materials for fire-resistant panels and a calcium source for carbon dioxide sequestration, owing to its high content of Ca.
- Previously, it was necessary an exhaustive characterization of raw materials and later, a study of new materials obtained or products was made.
- Preliminary results show that these residues are viable in the studied applications.
- And the environmental implications are considered as negligible.

THANK YOU FOR YOUR ATTENTION

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