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PHYSICO-CHEMICAL AND RADIOLOGICAL CHARACTERIZATION OF PHOSPHOGYPSUM FOR ITS VALORISATION IN CEMENT MORTAR

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INTRODUCTION

PHOSPHOGYPSUM STACK: OVER 100 Mt – 1000 ha.

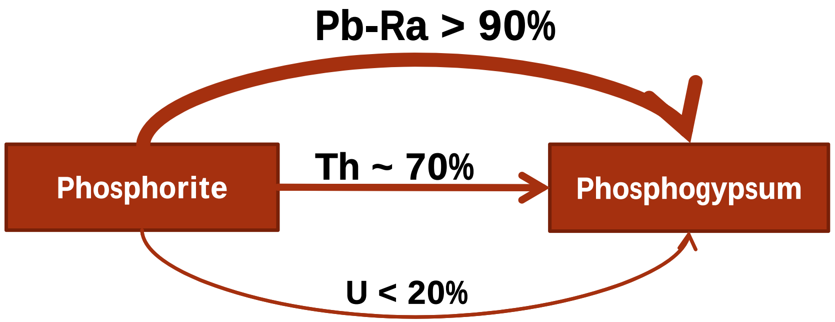
$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 \rightarrow 6\ H_3PO_4 + 10\ CaSO_4 \cdot 2H_2O + 2HF$

INTRODUCTION

NORM (NATURALLY OCCURRING RADIOACTIVE MATERIAL)

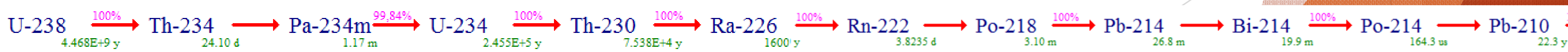
$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 \rightarrow 6\ H_3PO_4 + 10\ CaSO_4 \cdot 2H_2O + 2HF$ (1.66 kg of PG per kg of treated P)

Series	^{238}U	^{232}Th	^{40}K
Phosphorite (Bq Kg^{-1})	1500	<20	<30
Typical Soil (Bq Kg^{-1})	40	40	500



PG (Bq/kg)	
^{234}U	55 ± 20
^{230}Th	466 ± 51
^{226}Ra	693 ± 17
^{210}Pb	771 ± 29

Secular equilibrium in Phosphorite (same activity concentration for all radionuclides):



OBJECTIVES

- **APPLICATION OF PHOSPHOGYPSUM IN CIVIL ENGINEERING**

  - The main objective is to use the **Phosphogypsum as Setting Retarders** to replace the natural gypsum **in Cement Mortar**.

  - **Physico-chemical and Radiological Characterization of Mortars and their Raw Materials, and their Environmental Implications**

MATERIALS AND METHODS

RAW MATERIALS:

- **PHOSPHOGYPSUM** *(PG)*
- **NATURAL GYPSUM** *(NG)*
- **CLINKER** *(CK)*
- **NORMALIZED SAND** *(S)*

CEMENT MORTARS: **Curing conditions: 20 ºC,100% humidity**

	C-OPC-M	PG-M	NG/PG-M
CK (wt%)	21	21	21
S (wt%)	67	67	67
NG (wt%)	1.1	-	0.55
PG (wt%)	-	1.1	0.55
W (wt%)	11	11	11
ADITIVE (wt%)	-	0.20	0.20

MATERIALS AND METHODS

- **CHARACTERIZATION METHODS:**
  - **X RAY FLUORESCENCE (XRF)**
  - **X RAY DIFFRACTION (XRD)**
  - **ICP-MS/OES**
  - **GRANULOMETRY ANALISYS**
  - **ELECTRONIC MICROSCOPY (SEM-EDS)**
  - **GAMMA SPECTROMETRY ANALYSIS**
  - **LIXIVIATION TEST (UNE-EN 12457-4)**

RESULTS: XRF

RAW MATERIALS														
	Al (%)	**Ca (%)**	**Cu (%)**	**F (%)**	**Fe (%)**	**K (%)**	**Mg (%)**	**Mn (%)**	**Ni (%)**	**P (%)**	**Pb (%)**	**S (%)**	**Si (%)**	**P.C. (%)**
NG	1.43	15.7	ND	ND	1	0.9	2.2	0.03	ND	0.01	0.01	9.73	3.34	37.3
PG	0.08	22.5	ND	1.26	0.03	ND	ND	ND	ND	0.22	ND	16.7	0.40	23.7
CK	1.49	49.3	0.05	ND	3.8	0.26	0.37	0.03	0.01	0.07	0.04	0.79	8.40	1.00
S	2.06	0.08	0.02	ND	0.5	1.26	0.2	ND	ND	0.02	0.01	0.01	42.7	1.34

CEMENT MORTARS														
	Al (%)	Ca (%)	Cu (%)	F (%)	Fe (%)	K (%)	Mg (%)	Mn (%)	Ni (%)	P (%)	Pb (%)	S (%)	Si (%)	P.C. (%)
C-OPC	1.34	10.9	0.04	ND	1.60	0.56	0.24	0.02	0.02	0.06	0.02	0.81	30.3	6.37
NG-M	2.74	11.6	0.06	ND	2.41	1.22	0.37	0.03	ND	0.06	0.03	0.64	30.2	10.4
PG-M	1.23	10.7	0.03	ND	1.55	0.53	0.21	0.02	ND	0.06	0.02	1.04	29.9	6.69
NG/PG-M	2.62	11.3	0.03	ND	2.32	1.05	0.37	0.04	ND	0.06	0.04	0.96	30.2	11.9

RESULTS: XRD (RAW MATERIALS)

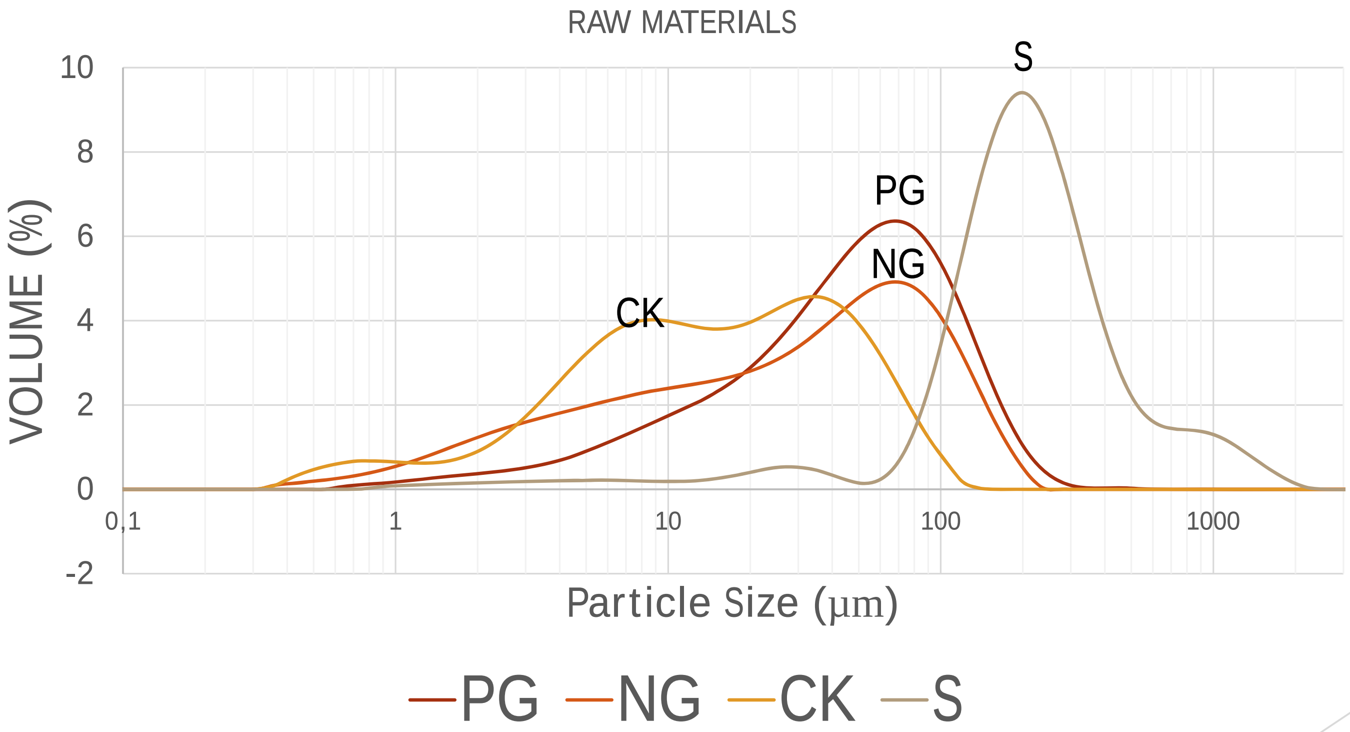
	PG (%)	NG (%)
Gypsum ($CaSO_4 \cdot 2H_2O$)	98	92
Bassanite ($CaSO_4 \cdot 1/2H_2O$)	n.d	1.5
Anhydrite ($CaSO_4$)	n.d	<1
Dolomite ($CaMg(CO_3)_2$	n.d	5.6
Magnetite (Fe_2O_3)	n.d	<1
Chukhrovite ($Ca_4AlSi(SO_4)F_{13} \cdot 12(H_2O)$)	<1	n.d
Quartz (SiO_2)	<1	<1

	CK (%)
Alite (Ca_3SiO_5) (C3S)	**66**
Larnite (Ca_3SiO_4) (C2S)	**9.3**
Brownmillerite ($AlCa_2FeO_5$) (C2AF)	**8.4**
$Al_2Ca_4Fe_2O_{10}$ (C4AF)	**6.1**
$Al_2Ca_3O_6$ (C3A)	**3.1**
Fayalite (Fe_2SiO_4)	2.3
Portlandite ($Ca(OH)_2$)	3.3
Lime (CaO)	1.7

	S (%)
Quartz (SiO_2)	100

RESULTS: GRANULOMETRY ANALYSIS

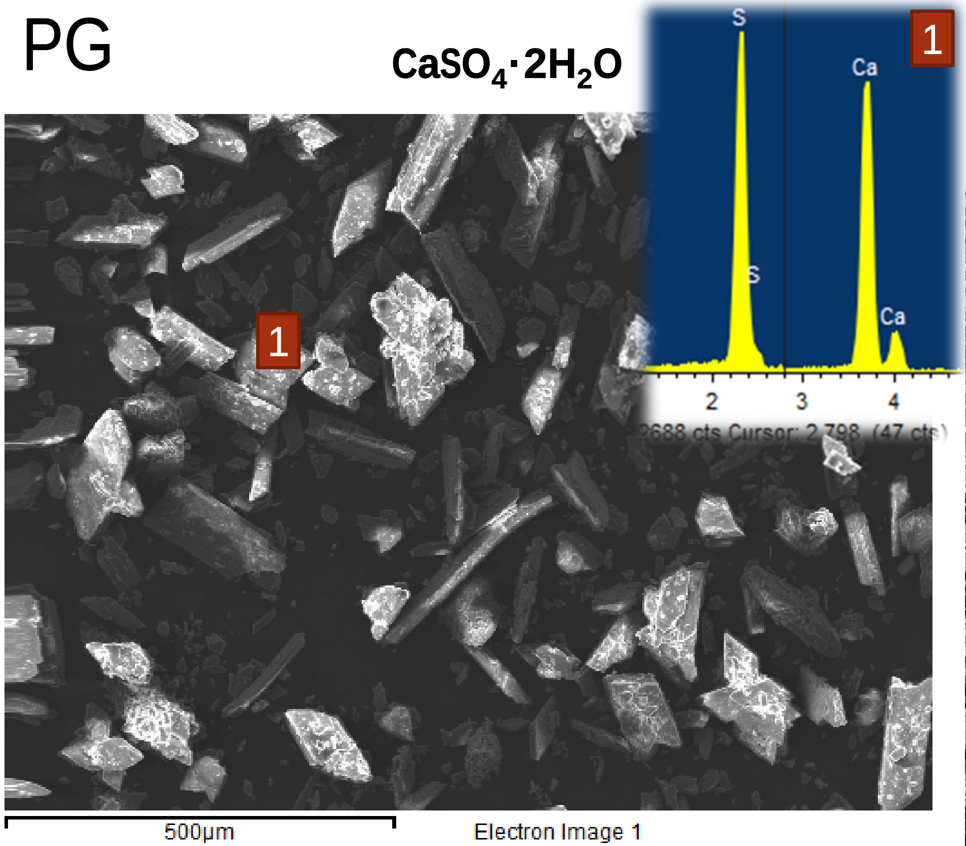
Clay: < 4 µm
Silt: 4 – 62 µm
Sand: 62 – 2000 µm
Gravel: > 2000 µm



RESULTS: SEM-EDS (RAW MATERIALS)

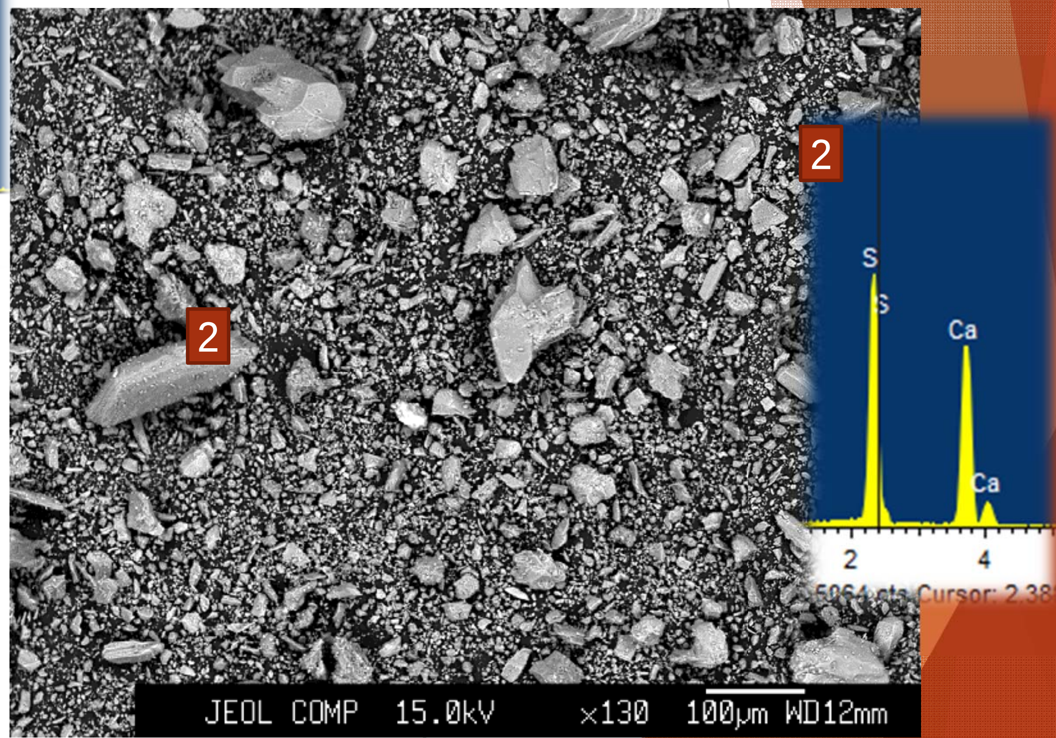
PG

$CaSO_4 \cdot 2H_2O$



$CaSO_4 \cdot 2H_2O$

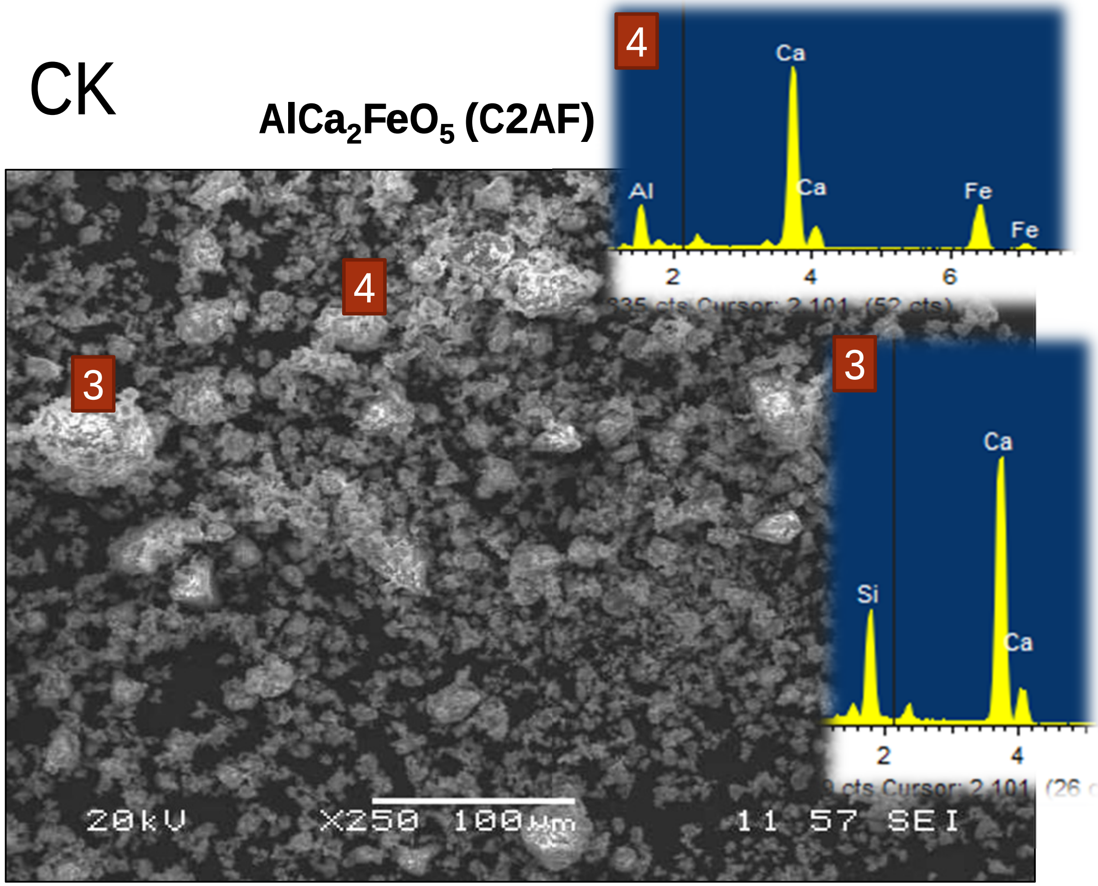
NG



RESULTS: SEM-EDS (RAW MATERIALS)

CK

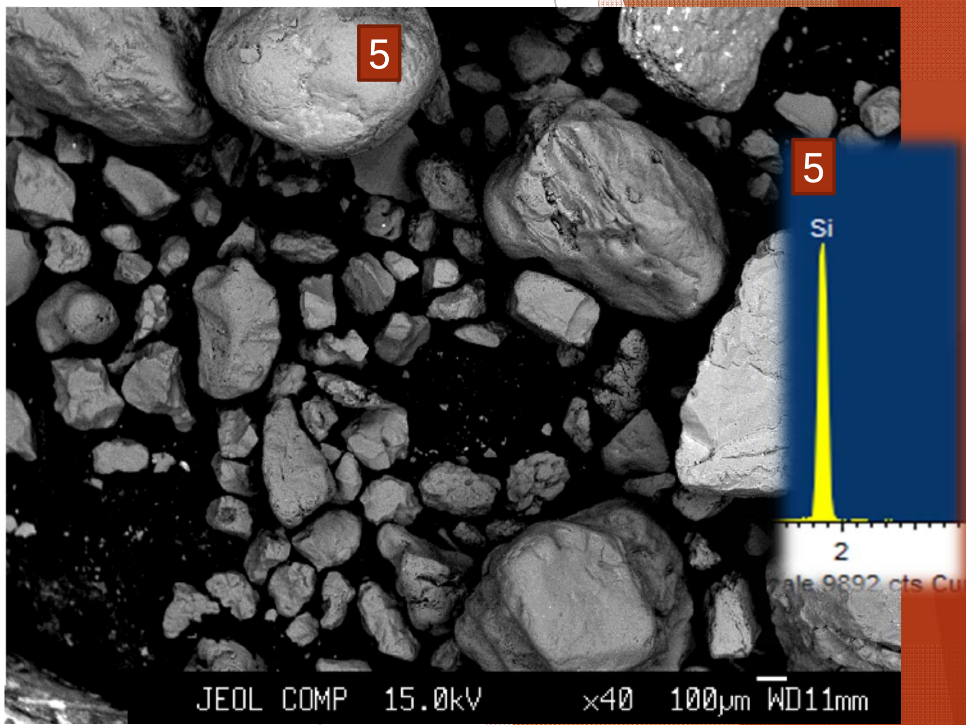
$AlCa_2FeO_5$ (C2AF)



Ca_3SiO_5 (C3S)

S

SiO_2



RESULTS: MORTARS

- **MAIN REACTIONS DURING CURING OF MORTARS:**

Tri- calcium silicates (C3S)

$2(CaO)_3(SiO_2) + 7H_2O \rightarrow \mathbf{(CaO)_3(SiO_2)\cdot 4(H_2O)} + \mathbf{3Ca(OH)_2}$

AMORFOUS (C-S-H) | PORTLANDITE

Di- calcium silicates (C2S)

$2(CaO)_2(SiO_2) + 5H_2O \rightarrow \mathbf{(CaO)_3(SiO_2)\cdot 4(H_2O)} + \mathbf{Ca(OH)_2}$

AMORFOUS (C-S-H) | PORTLANDITE

Calcium aluminate (C3A) in presence of gypsum

$(CaO)_3(Al_2O_3) + 3\ CaSO_4\cdot 2(H_2O) + 26\ H_2O \rightarrow \mathbf{(CaO)_3(Al_2O_3)(CaSO_4)_3\cdot 32(H_2O)}$

Ettringite

RESULTS: XRD MORTARS

	C-OPC-M (%)	PG-M (%)	NG/PG-M (%)
Quartz (SiO_2)	71.2	71.3	69.8
Portlandite ($Ca(OH)_2$)	9.3	12.2	10.4
Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26(H_2O)$)	6.8	8.3	8.3
Brownmillerite ($AlCa_2FeO_5$) (C2AF)	3.2	2.7	2.8
Alite (Ca_3SiO_5) (C3S)	3.7	2.7	2.4
Calcite ($CaCO_3$)	5.8	2.6	6.3

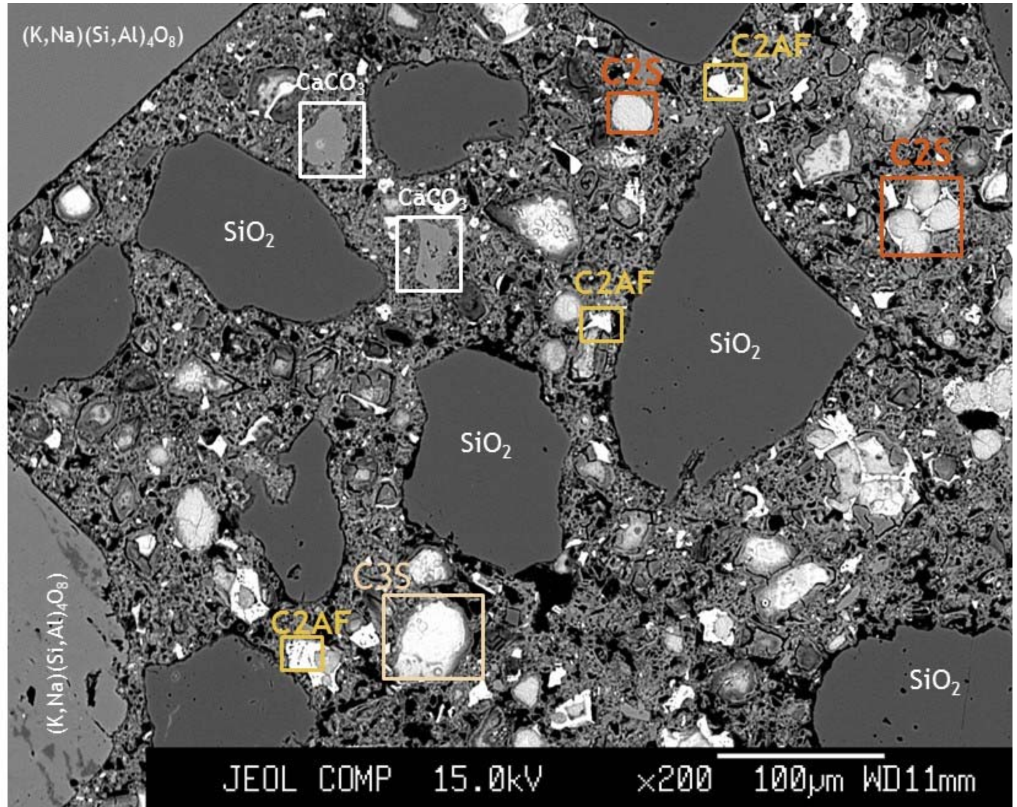
C3S: (CaO)$_3$(SiO$_2$)

C2S: (CaO)$_2$(SiO$_2$)

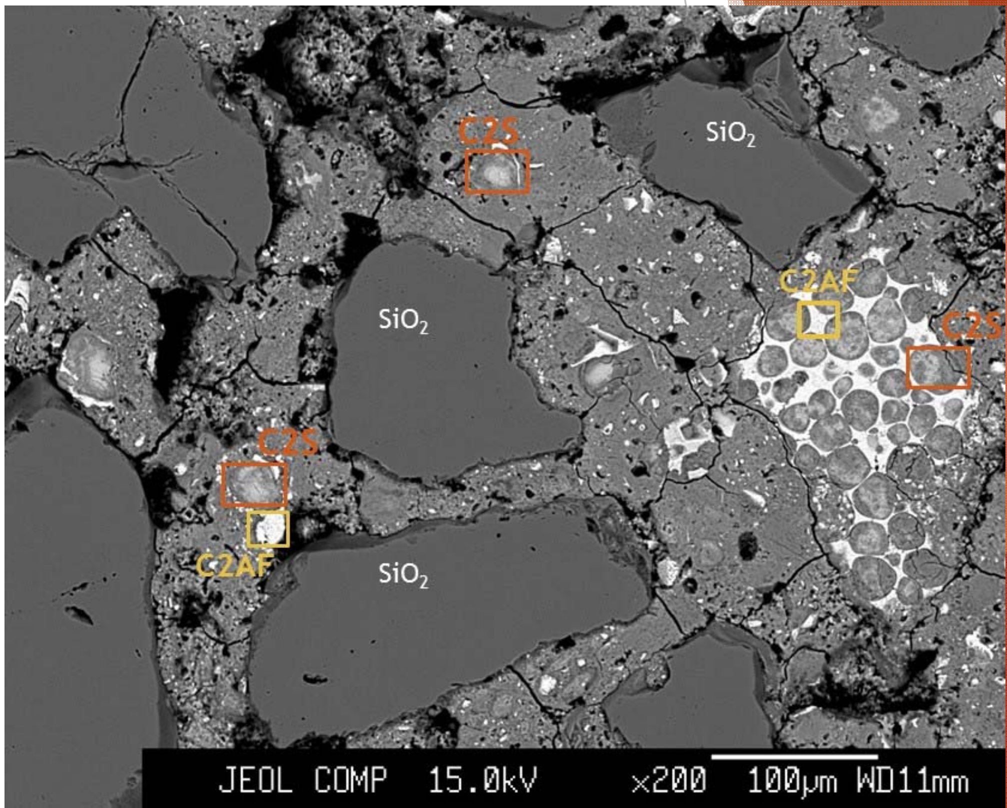
C2AF: (CaO)$_2$(Al$_2$O$_3$)(FeO)

RESULTS: SEM-EDS MORTARS

C-OPC-M



PG-M



RESULTS: LIXIVIATION TEST MORTARS

R.D. 1481/2001 which regulates the disposal of waste by landfill.

LIXIVIATION TEST ACCORDING TO UNE-EN 12457-4.

				NO HAZARDOUS	HAZARDOUS
	C-OPC (mg/kg)	PG-M (mg/kg)	NG/PG-M (mg/kg)	L/S = 10 (mg/kg)	L/S = 10 (mg/kg)
Cr	0.15	0.04	0.05	0,5 - 10	10 - 70
Ni	<LD	0.02	0.01	0,4 - 10	10 - 40
Cu	<LD	<LD	<LD	2 - 50	50 - 100
Zn	0.03	0.01	0.03	4 - 50	50 - 200
As	<LD	0.01	<LD	0,5 - 2	2 - 25
Se	<LD	<LD	<LD	0,1 - 0,5	0,5 - 7
Mo	0.07	0.15	0.10	0,5 - 10	10 - 30
Cd	<LD	0.01	<LD	0,04 - 1	1 - 5
Sb	0.0005	0.002	0.0005	0,06 - 0,7	0,7 - 5
Ba	6.4	0.63	0.38	20 - 100	100 - 300
Hg	<LD	<LD	<LD	0,01 - 0,2	0,2 - 2
Pb	0.12	<LD	0.06	0,5 - 10	50

RESULTS: MORTARS

European Union Regulation: Radiation protection 112

	C-OPC	PG-M	NG/PG-M
	Bq/kg	Bq/kg	Bq/kg
^{234}Th	7.9±4.1	10.0±4.4	10.7±4.4
^{226}Ra	7.2±0.8	13.3±0.8	14.3±1.0
^{210}Pb	12.2±3.9	29.7±4.6	13.3±5.0
^{228}Ra	6.6±1.4	8.8±1.3	17.3±1.9
^{228}Th	6.6±1.2	6.7±1.0	12.2±1.6
^{40}K	104±7	123±7	155±11
INDEX I	0.12	0.14	0.13

$I=(^{226}Ra/300)+(^{228}Ra/200)+(^{40}K/3000) < 1$ (materials used in bulk amounts, e.g. concrete)

FINALS REMARKS

- This study was carry out to use the **phosphogypsum as setting retarders** to replace the natural gypsum **in cement mortar.**
- **Physico-chemical and Radiological Characterization** of mortars and their raw materials have been performed.
- Several mortars have been manufactured by **according to regulations of building materials.**
- The **composition and mineral phases** of mortar cement manufactured of PG **are the expected and similar that were found in the control mortar.**
- **Lixiviation test and radiological risk index reveal that the mortars do not involve radiological either environmental risks.**

ACCORDING TO THE RESULTS THERE ARE NOT SIGNIFICANT DIFFERENCES BETWEEN MANUFACTURED MORTARS WITH NG AND PG

THANK YOU FOR YOUR ATTENTION

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