

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Characterization and Valorization of Norm Wastes for Construction Materials

Irene García-Díaz, Manuel Jesus Gázquez,
Juan Pedro Bolivar and Felix Antonio López

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/63196>

Abstract

The recycling of waste generated by industrial production processes is a topic of considerable environmental and economic interest. The minimization of waste disposal, avoiding its direct release into the environment, generates environmental benefits for industries in addition to the manufacture of the main product. Some of these wastes, measured by their radioactive element content, may be considered as naturally occurring radioactive material (NORM). Two of these NORMs are phosphogypsum (PG) and ilmenite mud (IM) come from the fertilizer industry and TiO₂ pigment industry, respectively. This chapter discusses the viability of valorization and/or recycling of PG and IM in the manufacture of sulfur polymer cement/concrete, Portland cement, and ceramic materials.

Keywords: Phosphogypsum, Ilmenite mud, sulfur polymer concrete/cement, portland cement, ceramic

1. Introduction

Some minerals or raw materials used in industrial process can contain radionuclides at concentrations which cannot be disregarded. The main natural radionuclides derive from the ²³⁸U and ²³²Th decay series. In some cases, industrial processing can lead to further enhancement of the concentrations in the product, by-product or in the waste materials.

These materials are known as naturally occurring radioactive material (NORM) used to describe materials that contain radioactive elements, radionuclides, found in the natural

environment. Long-lived radioactive elements of interest include uranium, thorium, and potassium, and any of their radioactive decay products such as radium and radon. However, the term is used more specifically for all naturally occurring radioactive materials where human activities have increased the potential for exposure compared with the unaltered situation. Sometimes artificially concentrated NORM is called technologically enhanced naturally occurring radioactive material (TENORM).

Environmental management of NORMs has taken on a new urgency in the last few decades. Increasingly, the governments are adopting more stringent regulations on radiation and environmental protection in general. Nowadays, the recycling and/or valorization of wastes generated by different industries are increasing exponentially [1–6]. Reduction in the disposal of these wastes has environmental and economic benefits for the industries and for the population.

This chapter is focused mainly in the valorization for construction materials of two NORMs coming from the fertilizer industry – phosphogypsum (PG) and the TiO_2 pigment industry – ilmenite mud (IM).

1.1. Fertilizer industry: phosphogypsum

The continuous rise in world population increases the demand for food production which involves a constant increase in the use of phosphate fertilizer [7] and the development of chemical industries related to their production. Phosphate rocks are used for manufacturing phosphoric acid and chemical fertilizers. These are mainly composed of carbonate fluorapatite ($\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6\text{CaCO}_3$), quartz, goethite; minor mounts of Al-phosphates, anatase, monazite,

Country	^{238}U	^{232}Th	^{226}Ra	^{228}Ra
USA	259–3700	3.7–22	1540	–
USA:Florida	1500–1900	16–59	1800	–
Brazil	114–880	204–753	330–700	350–1550
Chile	40	30	40	–
Algeria	1295	56	1150	–
Morocco	1500–1700	10–200	1500–1700	–
Senegal	1332	67	1370	–
Tunisia	590	92	520	–
Egypt	1520	26	1370	–
Jordan	1300–1850	–	–	–
Australia	15–90	5–47	28–90	–

Source: IAEA Tech Report 419, p. 90.

Table 1. Activity concentration (Bq/kg) of radionuclides present in different phosphate rock samples.

barite, magnetite; and heavy metals and trace elements (Cd, Ni, As, and Sr) [8, 9]. The phosphate rock also contains certain levels of natural radioactivity being a major NORM due to its uranium (^{238}U) and thorium (^{232}Th) content [10], **Table 1**. So the fertilizer industry has an impact in conventional and radioactive environmental contamination [11, 12].

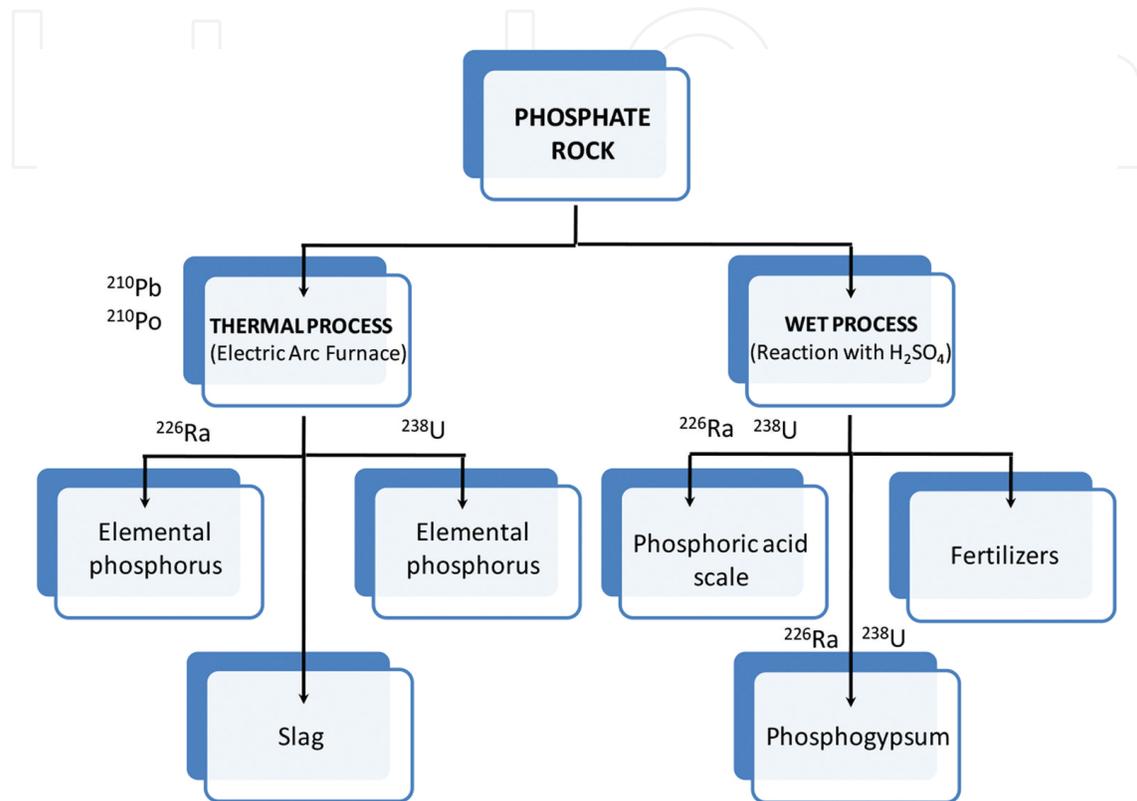
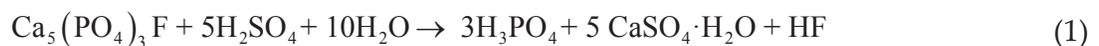


Figure 1. Schematic of phosphate processing [13].

Phosphate ore is processed to obtain phosphoric acid by the dry thermal or the wet acid methods, **Figure 1** [13].

Currently, over 90% of phosphoric acid production is by the wet acid method, involving the chemical attack of phosphate rock ore with sulfuric acid, generating a waste called phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Eq. (1). This process is economic, however, large amounts of PG are generated—around 5 tons per ton of phosphate rock.



$\text{CaSO}_4 \cdot \text{H}_2\text{O}$ is the main component of phosphogypsum, making up over 90% of it. Other impurities such as residual acids, fluorides (NaF , Na_3AlF_6 , Na_3FeF_6 , Na_2SiF_6 , CaF_2), fluoride sulfate ions, H_3PO_4 , $\text{Ca}_3(\text{PO}_4)_2$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{H}_2\text{PO}_4)2\text{H}_2\text{O}$, residual acids, some trace metals (e.g., Cr, Cu, Zn and Cd), and organic matter can be attached to the surface of the

gypsum crystals [13–16]. Due to the residual acid compounds, PG has a pH 3 and is thus classed as an acidic by-product.

The wet process causes the selective separation and concentration of naturally occurring radionuclides present in phosphate rock. Depending on the source rock, PG can contain as much as 60 times the level of radionuclides normally found prior to processing, with around 80% of ^{226}Ra , 86% of U, and 70% of Th ending up in the phosphoric acid, **Table 2** [13]. In particular, a great variation of ^{226}Ra activity is observed depending on the nature of the phosphate rock. For example, this ranges between 15 Bq/kg in Sweden and 114 Bq/kg in Florida. It is important to be aware of this radionuclide content due to the fact that ^{226}Ra produces radon gas (^{222}Rn) which has a short half-life of 3.8 days and is therefore highly active, that is, has a high radiation output and can cause significant damage to internal organs. High levels of ^{238}U and ^{210}Po activity have also been reported by various authors.

Country	Refs.	PG rock origin	^{238}U	^{236}Ra	^{210}Pb	^{210}Po	^{230}Th
Indonesia	[17]	Pt PetrokimiaGresik	43	473	480	450	–
China	[17]	Keiyan	15	85	82	82	
India	[17]	Vadorado	60	510	490	420	
Egypt	[17]	Nile Valley Rock	–	100	–	445	–
Florida	[14]	Central Florida	130	1140	1370	1030	113
Australia	[14]	Numerous	10	500	–	–	–
Sweden	[14]	Kola (USSR)	390	15	–	–	–
Spain	[18]	Morocco	140	620	–	82	280

Table 2. Radiochemical analyses of different PG types (Bq/kg) [13].

PG is stored without any prior treatment, requires a large land area, and can cause serious environmental contamination of soils, water, and the atmosphere. So PG management is one of the most serious problems currently faced by the phosphate industry.

1.2. TiO_2 industry: ilmenite mud

The titanium product most widely used is not in the form of titanium metal or alloy. It is a white powder—titanium dioxide (TiO_2) pigment. Because it provides whiteness and opacity, this is widely used in a huge range of products and industries from coatings and plastics, printing inks, as flux in glass manufacture, filler material for paper industries and rubber. It is also an important substance, although not used in such high volumes, in important sectors such as pharmaceuticals, foodstuffs, and cosmetics [19, 20]. The annual TiO_2 worldwide production is around 4.5 million t [21].

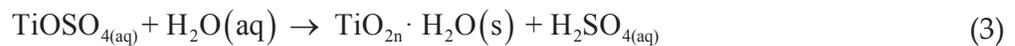
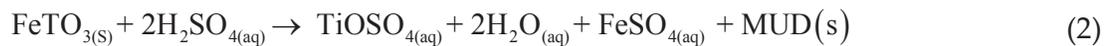
Two different commercial processes are used in TiO_2 pigment production—the chloride process using chloride gas and the sulfate process using concentrated sulfuric acid. Around

60% of total TiO₂ production is by the chloride process and 40% by the sulfate process [20–22].

The main feedstocks for the TiO₂ industry are rutile, synthetic rutile, and chloride slag, all used in the chloride route, and ilmenite and sulfate slag, used for the sulfate process. These ores can contain levels of naturally occurring radioactive material so this is a NORM industry, **Table 3**.

In the sulfate route, the main raw material used to produce TiO₂ is ilmenite ore (FeTiO₃). This contains approximately 43–65% TiO₂. A titanium slag (a co-product of the ilmenite ore coming from smelting process) which contains 70–80% titanium dioxide [23–25] is also used. The ilmenite contains around 300 Bq/kg of the radionuclides from the thorium series and around 100 Bq/kg for the radionuclides of the uranium series. This requires it to be classed as a NORM industry [26].

TiO₂ production begins with a highly exothermic reaction involving the digestion of a mix of ilmenite and titanium slag by highly concentrated (98%) sulfuric acid and water. The general steps for the digestion reaction are dissolution of the raw material, given in Eq. (2), followed by TiO₂ precipitation, Eq. (3).



Raw materials	TiO ₂ (%)	²³⁸ U	²³² Th (Bq/g)
Rutile	93–96	100–740	80–360
Synthetic Rutile	88–95	40–80	140–1900
Chloride slag	85–86	2–80	1–120
Sulfate slag	79–86	2–80	10–120
Ilmenite	45–65	100–10,000	80–200

Table 3. Radionuclide activity of raw materials used in TiO₂ production (Bq/kg) [21].

After the sulfuric acid dissolution, the liquid contains titanylsulfate (TiOSO₄) and iron sulfate (FeSO₄). The liquor is then passed to a clarification tank, where the un-dissolved ore (solid ilmenite mud) is separated by flocculation and filtration. It is then neutralized and stored in a safe area (**Figure 2**).

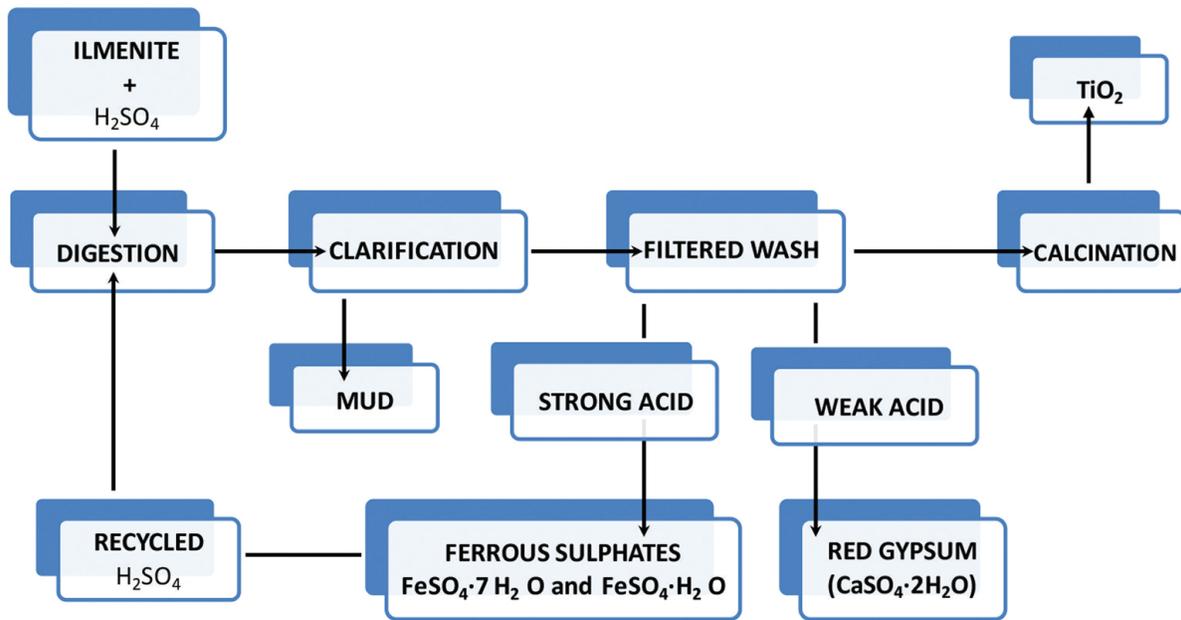


Figure 2. Sulfate route to TiO_2 production.

After ilmenite mud separation, the TiO_2 is precipitated from the clarified liquor by boiling it for several hours followed by cooling. Then, the $\text{TiO}_{2(s)}$ is separated by vacuum filters from the liquor, which is a “strong” acid, with a content 20–25% H_2SO_4 . After filtration, the hydrated titanium dioxide slurry is placed in rotatory kilns where the TiO_2 crystals grow to their final size and the water and sulfur traces are removed [25]. The production of half a ton of TiO_2 pigment requires one ton of raw materials.

During the feedstock digestion with sulfuric acid, the radionuclides are distributed; U and Th believe will pass forward in liquor; Ra has low solubility and suggests 75–95% is not digested; and Pb has low solubility and expects majority to remain in the solid phase. Considering that after the digestion, the solid volume is reduced by a factor of 5–6 and the overall impact of the radionuclides activity in the residue, ilmenite mud, is increased. The activity concentration for the ilmenite mud is typically given as, ^{238}U series = 600–1000 Bq/kg (in a feedstock 100–200 Bq/kg) and ^{232}Th series = 1200–2500 Bq/kg (in a feedstock 400–500 Bq/kg) [24, 26].

The ilmenite mud remaining at the end is enriched in radium isotopes, ^{226}Ra (860 Bq/kg) and ^{228}Ra (2590 Bq/kg) as well as ^{40}K (280 Bq/kg). The increased radium concentration is due to the insolubility of radium as a sulfate [21]. The relatively high concentration of ^{40}K in ilmenite mud is because the main form of ^{40}K (the raw material had 18 Bq/kg) in the feedstock, and this remains unaltered by the process [24].

So the ilmenite mud is a highly acid waste that contains a large amount of natural radionuclides and also certain metals. All of these can adversely affect the environment and must be managed adequately.

2. Norm wastes application for construction materials

2.1. Physico-chemical and radiological characterization of raw material

Table 4 shows the chemical composition for the major elements in PG and IM and in the raw materials [gravel, sand, red stoneware (RSM), and clinker] used in the various valorization processes. The PG and IM were collected from a PG piles and TiO₂ factory located at the Southwest Spain in the city of Huelva, respectively.

	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	TiO ₂	SO ₃	P ₂ O ₅	K ₂ O	Na ₂ O
PG	2.43	0.40	40.3	0.23	0.04	0.04	52.4	0.95	0.03	0.13
IM	11.9	1.44	0.73	12.5	0.94	52.9	7.79	0.02	0.16	0.16
Gravel	29.1	1.27	57.8	0.8	0.63	0.13	0.27	–	0.25	–
Sand	79.9	10.8	0.42	0.74	0.26	0.11	–	–	5.3	1.78
RSM	62.0	19.9	2.10	7.39	1.73	1.67	0.06	–	4.20	0.58
Clinker	22.0	5.3	66	2.8	1.4	–	0.53	–	1.0	0.04

Table 4. Concentration (%) of major elements.

PG is composed of 40% CaO and 54% SO₃. The main mineralogical phases by X-ray diffraction (XRD) are gypsum (CaSO₄·2H₂O) and basanite (CaSO₄·1/2H₂O). Also, a 0.95% of P₂O₅ is founded in PG sample, which remains later the washing in the industrial process [27].

The IM sample had a high concentration of titanium oxides (53%) and appreciable amounts of iron and silicon oxides (12.5 and 11.9%, respectively). Similar compositions have been observed elsewhere [24]. In the ilmenite mud, ilmenite (22%) and rutile (34%) were the main mineral phases observed by XRD. Other species such as Fe and Ti oxides (Fe₃Ti₃O₁₀), zircon (ZrSiO₄), and quartz (SiO₂) at 18.2, 13, and 12.1%, respectively, were also present.

In relation to the valorization studies for these industrial wastes, it is important take into account the particle sizes. The d (0.5) value of the particles of phosphogypsum and mud measured was ≤53 and 30 μm, respectively.

To evaluate the potential radiological impacts of these wastes when used in the production of building materials, the EU has proposed reference values for the natural radionuclide concentrations [28], defining an external risk index (I), also called the activity concentration index, according to the following equation:

$$I = \frac{C_{226\text{Ra}}}{300} + \frac{C_{332\text{Th}}}{200} + \frac{C_{40\text{K}}}{300} \quad (4)$$

where C_{226Ra}, C_{232Th}, and C_{40K} are the activity concentrations for ²²⁶Ra, ²³²Th, and ⁴⁰K, respectively, expressed in Bq/kg.

This index should not exceed one ($I \leq 1$) for any material used in bulk quantities, for example, cement or concrete. It should not exceed six ($I \leq 6$) for superficial materials, for example, tiles or boards. This is to ensure that the external dose received by occupants does not exceed the reference value of 1 mSv/year [28–29]. Other countries use the equivalent radium concentration parameter, $Ra(eq)$, given in Eq. (5):

$$Ra(eq) = C(^{226}\text{Ra}) + 1.43C(^{228}\text{Ra}) + 0.077C(^{40}\text{K}), \quad (5)$$

where $C(^{226}\text{Ra})$, $C(^{228}\text{Ra})$, and $C(^{40}\text{K})$ are the activity concentrations for ^{226}Ra , ^{228}Ra , and ^{40}K in Bq/kg, respectively. Three hundred and seventy Bq/kg is taken as the reference.

The concentration of natural radionuclides from the ^{238}U decay series in phosphate rock (PR) used in Huelva was around 1650 Bq/kg (Table 5). This is over 50 times higher than the concentrations in unperturbed soils which are around 25 Bq/kg of ^{238}U and ^{232}Th [30]. Ilmenite ore (ILM) is also a NORM mineral since it is high in natural radionuclides from both the Th and U series with a total concentration of over 400 Bq/kg for ^{238}U and ^{232}Th nuclides [24].

Code	^{210}Pb	^{238}U	^{232}Th	^{226}Ra	^{228}Ra	^{40}K	I	Ra(eq)
PR	1600 ± 90	1650 ± 70	25 ± 2	1580 ± 80	22 ± 2	<18	5.4	1612
PG	624 ± 37	97 ± 6	8.2 ± 1.0	589 ± 34	8 ± 1	<18	3.9	621
ILM	82 ± 4	105 ± 10	315 ± 20	110 ± 10	300 ± 20	30 ± 5	1.9	541
IM	247 ± 11	184 ± 12	250 ± 15	521 ± 30	1919 ± 112	334 ± 21	11.4	3291

Table 5. Natural radionuclide concentrations (Bq/kg) and radium equivalent (Bq/kg) and external risk index (I) calculated in raw materials and NORM wastes.

The activity concentration of ^{238}U and ^{226}Ra in the pure PG used in this work is around 100 and 600 Bq/kg, respectively, which are significantly higher than the average world-wide values from unperturbed soils. The ilmenite mud (IM) also has a total radionuclide concentration higher than 1000 Bq/kg. ^{226}Ra and ^{228}Ra are the radionuclides with the highest activity concentrations in IM at around 500 and 2000 Bq/kg, respectively. This is a considerable fraction of the radioactivity content originally present in the raw material.

2.2. Use of phosphogypsum and ilmenite mud in sulfur polymer cement/concrete manufacturing

The manufacture of Portland cement is associated with a high energy consumption (850 kcal/kg of clinker) due to the high temperature required to produce Portland cement clinker (around 4500°C). This has negative environmental effects as around 850 kg of CO_2 is emitted into the atmosphere per ton of clinker produced, as well as other greenhouse gases and NO_x and SO_x . It also involves massive quarrying for raw materials (1.7 ton to produce 1 ton of clinker) [3, 4].

In contrast, the manufacture of traditional binders such as sulfur polymer concretes (SPCs) does not require a heavy energy input. SPCs are based basically in the sulfur properties. To manufacture, a thermoplastic material is melted and mixed with an aggregate after which the mixture poured, molded and allowed to harden. These materials have been studied extensively over the past few decades.

Various trials have been carried out in which sulfur was used as the basis of construction materials [31–34]. In these studies, SPCs were prepared by heating of a mix of elemental sulfur (un-modified sulfur) and mineral aggregates. However, the SPCs manufactured using elemental sulfur exhibited durability problems. They failed under repetitive cycles of freezing and thawing, humid conditions, or immersion in water [31, 35].

Extensive research has established the reason for the failure of these SPCs and determined ways of preventing it. When the hot mixture of elemental sulfur and aggregate is cooled to cast SPCs the liquid sulfur binder crystallizes at 114°C as monoclinic sulfur ($S\beta$) with a decrease in volume of around a 7%. When the temperature goes below 96°C, the $S\beta$ begins to transform to orthorhombic sulfur $S\alpha$ which is the stable form of sulfur at ambient temperature [35]. This transformation is rapid (<24 hours) and causes the material failure. The $S\alpha$ form is denser than $S\beta$. In the material, high strength is induced by the change in the material. Thus, the sulfur binder can become highly stressed and cause durability problems, mainly when it is exposed to water conditions.

It is necessary modify the sulfur-based concrete to reduce the expansion and contraction during thermal cycling and achieved a product with good durability. Several chemical substances to inhibit the transformation of monoclinic to orthorhombic sulfur and to improve SPC products have been studied. Such modifiers are now available. Among the modifiers, commonly used are dicyclopentadiene (DCPD) or a combination of dicyclopentadiene, cyclopentadiene, and dipentene [31–36].

Sulfur concrete has properties, which for certain applications are superior to Portland cement concrete (PCC). Compared to traditional PCC, the main advantage of sulfur concrete is its high durability. SPC is also resistant to aggressive chemical environments and has good mechanical properties, high frost resistance, low absorbability, antiseptic qualities, water resistance, and good thermal insulating and dielectric properties [37]. SPCs have a fast setting time reaching nearly full mechanical strength in <24 hours. These features make SPCs an ideal material for a wide range of applications in different fields, such as in road and railway infrastructure, hydrotechnical constructions, waste water treatment plants, and landfills [37]. Due to their generally good properties and higher adhesive strength, SPCs are can also be used for stabilization/solidification in aggregate recycling and radioactive waste storage [35, 38–40].

Valorization of PG and IM by incorporating them into sulfur polymer concretes was studied by the authors of this chapter.

Different mixtures were prepared with percentages of PG and IM between 10 and 30 wt%. Each sample was denominated as SPC-XPG-Y and SPC-XIM-Y, where “X” is the percentage wt% of elemental sulfur and “Y” is the percentage wt% of phosphogypsum or ilmenite mud of the mixture. The reference sample was SPC.

The SPCs were prepared by first heating the aggregates (gravel/sand and NORM waste) at 130–135°C for 4 h. Then, the sulfur, gravel, sand, and NORM waste are heated together in a preheated mixing bowl, where the temperature is controlled at 135–140°C for 10 minutes. After this time, the modified sulfur STX™ is added with continuous mixing. Finally, the mixture is stirred at 140–145°C for 4–5 minutes. The molds (4 × 40 × 160 mm) are preheated to approximately 120°C before adding the sulfur polymer concrete. The material is compacted using a vibration table at 3000 rpm for 30 seconds. The storage of the moulds is done at a room temperature. The specimens are de-molded 24 hours after placement in the steel moulds.

The compressive Cs and flexural strength Fs in SPC cements are shown in **Table 6**. The compressive strength of the SPCs has values between 55–62 MPa for PG and 58–64 MPa for IM. These values are in line with those reported by other authors. For example, López et al. [38] present values of 54 and 58 MPa for metacinnabar SPC with sulfur/HgS ratios of 0.4 and 2.6, respectively. Abdel-Mohsen et al. [31] obtained a compressive strength of 54 MPa for SPC with fly ash, where the sulfur/fly ash proportion was 0.9. SPCs with lead wastes, have been studied by Lin et al. [39], and the final compressive strength of the SPC was 48.5 MPa. Between 65 and 73 MPa was the SPC strength obtained using a recycled aggregate coming from the ceramic industry [40].

	Fs (Mpa)	Cs (Mpa)	Ratios sulfur/waste
SPC-21	7.07 ± 0.66	57.70 ± 1.98	–
SPC-17PG-10	9.36 ± 0.24	55.41 ± 1.37	1.70
SPC-19PG20	11.20 ± 0.14	62.11 ± 0.86	0.95
SPC-21PG30	10.72 ± 0.60	56.76 ± 5.20	0.70
SPC-17IM10	9.83 ± 1.82	58.45 ± 1.62	1.70
SPC-21IM20	13.25 ± 0.77	64.38 ± 1.62	1.05
SPC-21IM30	9.40 ± 0.52	36.77 ± 2.58	0.70

Table 6. Values of compressive strength (Cs) and flexural strength (Fs) in the SPCs at 1 day old the ratios of sulfur to waste.

These results can be compared with Portland cement, which has a Cs > 52.5 MPa. At 28 days of curing Portland cement has a flexural strength of 10.1 ± 1.2 MPa and compressive strength of 61.3 ± 1.0 MPa [41]. These values of strength are similar or slightly lower than the values obtained for the SPC with a percentage of between 20 and 30% of PG or between 10 and 20% of IM at 1 day old.

The strength obtained tends to increase as the sulfur/waste ratio increases up to between 0.95 and 1.05 (**Table 6**). A thin layer of sulfur-coated PG particles is a good binder for aggregates increasing the mechanical strength. However, a decrease in the compressive strength is observed with a larger proportions of sulfur. This is due to the fact that this level of sulfur increases the thickness of the sulfur layer around the particles and leads to brittleness.

Table 7 shows the water activity coefficient (WAC) results recorded for SPC-21PG-30 and SPC-21IM-20. Water absorption by capillarity was studied gravimetrically in prismatic concrete specimens (50 × 29 × 9 mm) in water at room temperature. The water level was sufficient to wet only the lower surface of the test specimens. After 28 days, the WAC coefficient values of the samples are very low and certainly less than that of the SPC. However, all WAC values for SPC-PG and SPC-IM samples are smaller than those for concrete made from Portland cement as reported by several authors [42, 43]. WAC coefficients of 5.0 and 6.2 kg/m² after 28 days of immersion in water are measured for an ordinary Portland cement and for a concrete made of Brazilian Portland cement (CPII E-02) (slag-modified Portland cement), respectively. The use of a sulfur/modified sulfur mix reduces the WAC coefficient producing a very impermeable concrete.

Mixture	Water absorption (g cm ⁻²)			
	3 hours	72 hours	7 days	28 days
SPC 21	0.07	0.20	0.30	0.90
SPC-21PG-30	0.10	0.16	0.20	1.20
SPC-21IM-20	0.01	0.04	0.05	0.06

Table 7. Water absorption by capillarity as a function of time for cement with and without mud.

	SPC-17PG-10	SPC-19PG-20	SPC-21PG-30	SPC17-IM-10	SPC21-IM-20	SPC21-IM-30
%Waste	10	20	30	10	20	30
²¹⁰ Pb	70 ± 5.0	143 ± 9.0	219 ± 13.0	28 ± 4	40 ± 4	76 ± 7
²³⁸ U(²³⁴ Th)	21 ± 2.0	12 ± 2.0	38 ± 3.0	25 ± 4	61 ± 5	84 ± 7
²³² Th(²¹² Pb)	9.4 ± 0.7	8.6 ± 0.6	8.1 ± 0.5	54 ± 3	115 ± 7	182 ± 11
²²⁶ Ra	63 ± 4.0	115 ± 7.0	179 ± 11.0	51 ± 3	123 ± 7	194 ± 11
²²⁸ Th	8.7 ± 0.7	<6	6.8 ± 0.7	50 ± 2	100 ± 6	168 ± 11
²²⁸ Ra(²²⁸ Ac)	8.6 ± 0.8	8.8 ± 0.8	6.9 ± 0.7	212 ± 13	426 ± 26	674 ± 39
⁴⁰ K	528 ± 32.0	394 ± 24.0	347 ± 21	512 ± 31	493 ± 32	413 ± 24
INDEX "I"	0.43	0.56	0.75	1.40	2.70	4.20
Ra(eq) (Bq/kg)	117	253	158	394	770	1189

The radium equivalent activity and the activity concentration index "I" are also given.

Table 8. Natural radionuclide concentration (Bq/kg) in SPC samples.

Taking into account that the wastes come from a NORM industry, it is necessary to carry out a radioactivity characterization of the SPCs obtained (**Table 8**). The radionuclides with the highest activity concentration in the PG-SPCs are ²²⁶Ra (and its daughters of short half life) and ⁴⁰K. As expected, the activity concentration of ²²⁶Ra shows a linear dependence ($y = 5.49x + 8.95$;

$R^2 = 0.9988$) on the percentage (x) of PG added. However, ^{40}K concentration decreases linearly ($y = -5.82x + 529$; $R^2 = 0.9041$). This is due to the fact that the potassium content in PG is practically negligible (<18 Bq/kg for ^{40}K , or $<0.06\%$ in natural potassium).

In SPC-IM samples, the radionuclide with the highest activity concentration is ^{228}Ra . The activity concentration of ^{228}Ra also shows a linear dependence ($y = 18.7x + 59.6$; $R^2 = 0.9976$) on the percentage (x) of IM added to the SPC-IM samples. A similar behavior was showed for ^{210}Pb , ^{234}Th , and ^{232}Th . In relation to the ^{40}K , the activity concentration decreases when we increase the IM content in the sample.

The activity concentration index (I) in the SPC-PG samples is below the EU reference values for bulk building materials (Table 8). The Ra(eq) is also below the threshold of 370 Bq/kg considered in USA and some other countries. However, in the SPC-IM samples, the index I is higher than the EU reference values for materials used in bulk amounts. Nevertheless, these could have other civil construction applications, for example, in marine platforms or bridges. The values of Ra(eq) are also higher than the reference level of 370 Bq/kg.

Due to the high radionuclide content to assess the risk of the use is important study the environmental mobility of these. In relation to the toxicity characteristic leaching procedure leaching test (TCLP, USEPA) [44], it can be confirmed that none of the radionuclides ^{234}Th , ^{226}Ra , ^{228}Ra , ^{40}K , and ^{210}Pb were detected in the leachates as their concentrations were below 1 Bq/L (leaching coefficients $\text{LC} < 0.1\%$).

Sample	pH	Ac (wt%)	^{238}U (Bq/L)	^{210}Pb (Bq/L)	^{210}Pb Lc (%)	^{238}U Lc (%)
SPC-21	2	1.63	0.078 ± 0.003	<0.01	<0.01	0.27
	4	1.01	0.143 ± 0.012	0.039 ± 0.019	0.19	0.48
	6	1.25	0.078 ± 0.005	0.017 ± 0.011	0.09	0.26
	8	0.95	0.0106 ± 0.0003	<0.01	<0.01	0.03
	10	0.75	<0.01	<0.01	<0.01	<0.01
SPC-21PG-30	2	1.50	1.09 ± 0.05	0.97 ± 0.07	1.17	0.18
	4	1.89	0.73 ± 0.05	0.15 ± 0.03	0.78	0.03
	6	1.99	1.14 ± 0.04	0.067 ± 0.017	1.22	0.01
	8	1.46	0.09 ± 0.03	<0.01	0.09	<0.01
	10	0.87	0.05 ± 0.01	<0.01	0.05	<0.01
SPC-21IM-20	2	0.37	0.463 ± 0.025	0.871 ± 0.020	0.86	0.26
	4	0.36	0.363 ± 0.078	0.891 ± 0.027	0.88	0.30
	6	0.34	0.340 ± 0.020	0.862 ± 0.020	0.84	0.20
	8	0.38	0.111 ± 0.008	0.906 ± 0.023	0.90	0.18
	10	0.46	0.009 ± 0.004	0.807 ± 0.026	0.77	0.05

Table 9. ^{238}U and ^{210}Po concentration and leaching coefficients with respect to pH.

In acidic media, pH 2 and 4, the concentration of ^{238}U in SPC-21 was between 0.078 and 0.143 Bq/L and for pH 8 0.011 Bq/L. These values are in agreement with those recorded for inland

water bodies which are between 0.005 and 0.5 Bq/L [45]. The SPC-21PG-30 leachate has a mean ^{238}U concentration of around 1 Bq/L in acidic media higher than SPC-21, falling to 0.07 Bq/L for basic media (close to the upper limits allowed for groundwater affected by mining residues [1 Bq/L]) [46]. This, plus the results outlined in **Table 9**, shows that the contamination of water by uranium isotopes by SPCs containing 30% waste would be negligible.

The activity concentration of ^{210}Po in SPC-21 is between 0.039 and 0.017 Bq/L for acid media, below the mean 0.01 Bq/L recorded for basic media. In acid media, the ^{210}Po concentration is higher in SPC-21PG-30 with values around the levels for inland water bodies but lower at pH of 8 and 10, that is, 0.01 Bq/L. The ^{238}U concentration is around twice that of ^{210}Po in the leaching so Po tends to be more strongly fixed to a particular material than U.

The activity concentration of ^{238}U in the acidic media in SPC-21IM-30 is around 0.38 Bq/L, this value falling between 0.1 and 0.009 Bq/L for pH = 8 and 10, respectively. The contamination of water by uranium isotopes due to the SPC-IM would be negligible. At all pH values, the ^{210}Po concentration is very similar, around 0.8 Bq/L, with the leaching coefficient for ^{210}Po being in general higher than for ^{238}U by a factor of 3. For pH = 10, it can be higher by a factor of 15.

This result confirms that phosphogypsum and ilmenite mud can be successfully immobilized and valorized in the manufacture of SPC construction materials, which also allow for the safe disposal of waste sulfur.

2.3. Use of ilmenite mud in commercial cement manufacturing

Industrial wastes are widely used within the cement industry [3, 4, 47–49] either as partial or total substitution of raw material in clinker production or as an addition to clinker for cement production. In addition, it is important to note that the use in cement production of waste generated in several industrial activities should be undertaken with caution. Certain requirements should be met: (a) the physical and chemical properties of the cement generated should be at least comparable to the physical and chemical properties of the “normal” cement; and (b) the “new” cement should not cause any additional environmental problems (in other words, one environmental problem should not be replaced by another).

It is known that the moderate addition (5% or less) of pure TiO_2 in the manufacture of Portland clinker increases the hydraulic activity (the capacity to react with water in order to gain high resistance) of the cement, acts as a mineralizer, reduces the porosity and increases the resistance [50, 51].

Taking into account that IM contains around 50% TiO_2 , we decided to explore the effects of adding the ilmenite mud (IM) directly to cement. The mixtures were IMA (97.5% Cem–2.5% IM), IMB (95% Cem–5% IM) and IMC (90% Cem–10% IM). Below we analyze and evaluate the main mechanical, elastic and thermodynamic properties of these cements. Their properties were compared with those of ordinary Portland cement (OPC)—Type I (clinker 97% and natural gypsum 3%) with compressive strength around 52.5 N/mm².

The first step after the formation of the three dried mixtures of clinker with ilmenite mud was to determine the appropriate water/cement (W/C) relation in weight terms for obtaining a

“normal” consistency of the paste formed [52]. The results of experimentation show that the optimum water–cement ratio for each of the samples was 0.27 for OPC, IMA, and IMB and 0.28 for IMC. The setting times of the three cements formed using different proportions of IM as an additive were obtained with a Vicat apparatus [52]. The setting time for OPC is 139 min. This time is extended to 158, 171, and 203 min for IMA, IMB, and IMC, respectively. On the other hand, the final setting time was 224 for OPC, and 201, 206, and 263 min for IMA, IMB, and IMC. The setting times for the three IM cements are comparable to those obtained for commercial cement and fulfill the requirements of national legislation. Note that the initial and final setting times are prolonged by increasing the proportion of IM used.

Mechanical resistance tests (compressive and flexural strength) were carried out for the new cements with ilmenite mud added and for the commercial cement (CEM). The results obtained are given in **Table 10**

Sample	Flexural strength		Compressive strength	
	2 days	28 days	2 days	28 days
Commercial cement (CEM)	6.8±0.3	10.1±1.2	34.4±0.4	61.3±1.1
IMA (2.5% IM)	6.8±0.1	9.8±0.6	38.1±1.4	55.3±1.9
IMB (5% IM)	6.7±0.3	9.0±0.3	34.8±0.9	55.9±1.3
IMC (10% IM)	4.8±0.3	8.0±0.2	24.2±0.8	45.5±1.0

Table 10. Compressive and flexural strength values (MPa) of new cement produced by adding IM to OPC (ordinary Portland cement).

These results show that the addition of a little ilmenite mud to the cement (2.5 and 5%) improves the mechanical strength. In particular, after to 2 days, the bending strength of the new cement that had 2.5% IM added is not affected but its compressive strength increased by approximately a 10%. After 28 days, the values decrease slightly, but is still within acceptable limits (>52.5 MPa) [42].

In order to analyze the possible risks of short-time expansion, which can affect the ilmenite mud cements formed, the Le Chatelier test was performed [52]. The results obtained for the new cements show that the presence of IM in the cements formed does not cause any significant modification in their expansion behavior in comparison with the commercial cement. This applies irrespective of the proportion of IM used as an additive, within the range tested.

Calorimetric analyses of the three IM cements were performed (**Table 11**) in order to determine the total heat liberated in their hydration process. These values clearly indicate that the addition of IM diminishes the rate of heat release in the acceleration–deceleration peak, down to 12.4 kJ/kg h in the IMC sample. This is 28% lower than that obtained for the commercial cement. The addition of IM also retards the appearance of this peak until 7.23 h in the IMB sample or 8.61 h in the IMC sample. The total heat liberated in the cements formed with IM is slightly lower in all the samples, at around 245 kJ/kg.

Sample	Acceleration–deceleration peak			Total heat after 60 hours (kJ/kg)
	V(kJ/kg h)	t _v (h)	Q _v (kJ/kg)	
Cement	17.60	6.40	86.4	254.3
Clinker	12.50	7.20	71.4	258.3
IMA	16.06	6.85	73.0	240.0
IMB	14.90	7.23	71.8	247.0
IMC	12.40	8.61	67.5	245.0

Table 11. Calorimetric analysis of the new cement obtained with IM, clinker and cement taken as reference.

Finally, a thorough analysis from the environmental point of view was carried out. The external risk index (I) of samples was measured. For IMA, the value is 0.68, that is, below unity. Therefore, this sample can be used without restrictions. However, sample IMB presents an index slightly above unity at 1.09. IMC has a value close to 2 which is a problem from a radiological point of view. In relation with radium-equivalent Ra(eq), the values obtained for IMA, IMB, and IMC were 190, 308, and 544 Bq/kg, respectively, showing that IMA and IMB are below the 370 Bq/kg level, but IMC is above it.

To assess the risk of the use of IM to the environment, a TCLP leaching test was carried out [29]. The pollutant concentrations (metals and radionuclides) in the leaching solutions obtained from the mobility tests were measured. The leaching test shows that the concentrations of radioisotopes are of the same order of magnitude as typical ones in continental waters [53], and it can be ensured that their potential radiological impact is negligible.

	IMC	CEM	US EPA
Cr	70	89	5000
As	2.7	1.1	5000
Se	22	16	1000
Cd	<1	<1	1000
Ba	330	317	100,000
Pb	8.8	8.8	5000
Ti	2.7	<1	–
Fe	<1	<1	–

Limit values given in the US EPA standard.

Table 12. Leachability concentrations of metals (µg/L) obtained by TCLP test from the CEM and IMC samples.

The content of Cr(VI) in the samples must also be analyzed, because European directive [54] prohibits the marketing and use of cement which, when hydrated, contains more than 2 mg/kg of water-soluble hexavalent chromium, determined as percentage by mass of dry

cement. In **Table 12**, we can see that the concentration of Cr (total) in the IMC sample is $70 \mu\text{g/L}$ and taking into account that the dilution factor used was 20, the final concentration of Cr by mass of dry cement is 1.4 mg/kg , lower than 2 mg/kg . Also, values for other heavy metals are similar or even lesser than the cement taken as reference.

In order to gain a better understanding of how the ilmenite mud impurities are incorporated in the final cement product, a detailed study by SEM was made of the IMC cement sample. This sample is the one that contains the biggest proportion of ilmenite mud (10%). In **Figure 3**, one can see a main dark matrix (point 1) corresponding to the cement formed, with a composition typical of a calcium silicate hydrate (C–S–H) gel and a Ca–Si ratio = 2.2 ± 0.1 . The bright particles embedded in the matrix are formed by iron plus titanium (point 2). This can be deduced from the corresponding X-ray spectra obtained by XRMA at these points, which are also shown in **Figure 3**.

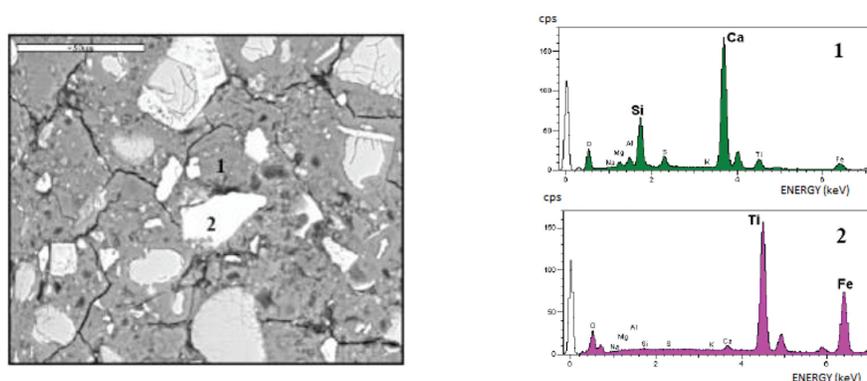


Figure 3. SEM image obtained in the BSE mode of the cement formed by mixing conventional clinker with 10% IM (IMC sample). The X-ray spectra corresponding to the numbered points in the image are also shown.

All the SEM-XRMA results indicate that the particles trapped in the matrix are high in iron and titanium. This is important because it reduces the potential leaching of the iron and titanium contaminants in the cement formed and, consequently, limits their potential harm to the environment.

2.4. Ilmenite mud as additive in the manufacture of ceramic

In line with the research to date, and noting the composition of the IM [24], another possible valorization method for IM is its use in the production of ceramic tiles. Three fundamental factors need to be borne in mind when considering the possibility of using ceramic tiles for the recycling of IM. Firstly, it is essential to study whether the presence of this residue modifies the mechanical properties of the tile compared with commercial tile. Secondly, these studies require prior physico-chemical analysis (elemental, mineralogical, and morphology) of the waste and the components used in the generation of tile tested. Finally, it is essential to check its environmental impact mainly associated to the potential problem of leaching of metals and radionuclides included in the tile matrix [55–58].

Ilmenite mud exhibits a high content of iron oxide ($\text{Fe}_2\text{O}_3 \approx 10\%$). This is a similar value to that of red stoneware (RSM) which is made from natural clays with high iron oxide content ($\text{Fe}_2\text{O}_3 > 7\%$), (Table 4). For this reason, its valorization in ceramic tiles has been trialed [59]. Mixtures of a commercial red stoneware (RSM) with different concentrations of ilmenite mud (3, 5, 7, 10, 30, and 50%) were shaped by uniaxial pressing (Nannetti S hydraulic press) at 40 MPa in a steel die to produce tiles measuring $50 \times 50 \times 5$ mm, which were fired in an electric furnace at 1150°C following a fast-firing process for 8 minutes.

The sintering behavior of the ceramic was evaluated on the basis of water absorption, apparent porosity, and bulk density. The water absorption E (wt%), was measured according to EN ISO 10545-3 [60] for ten representative specimens. The apparent porosity and the bulk density were measured according to ASTM C373-88 [61]. Also, the linear shrinkage, LS (%), and the bending strength, BS (MPa), were measured according to EN 843-1 [62].

The results shown in Table 13 indicate that the linear shrinkage increases with the concentration of ilmenite mud showing values up to 7%. Lower values are advantageous because they reduce cracking and volume changes during firing. Also, apparent porosity generally increases with the concentration of ilmenite mud. This physical property is very important, and it is directly related with the water absorption and open porosity [63]. Moreover, the water absorption decreases with the addition of 3 and 5% of sludge (2.82 and 2.48%, respectively). In accordance with the European Standard EN 14411 [64], tiles are categorized according to the water absorption coefficient (E). So tiles with low water absorption belong to group I, which in turn, is divided in two sub-groups (a) $E \leq 0.5\%$ (called BIa group) and (b) $0.5\% < E \leq 3\%$ (called BIb group). Tiles with $3\% < E \leq 6\%$ and $6\% < E \leq 10\%$ belong to the BIIa and BIIb groups, respectively. This fact is important because of low values of both E and P provides a high resistance to freeze-thaw cycles, requiring less drying time.

RSM/IM (%)	Linear shrinkage LS (%)	Apparent porosity P (%)	Water absorption E (wt%)	Bulk density B ($\text{g}\cdot\text{cm}^{-3}$)	Bending strength BS (MPa)
100/0	3.8 ± 0.1	12.5 ± 0.7	5.30 ± 0.06	2.36 ± 0.02	35.1 ± 0.9
97/3	5.6 ± 0.1	6.71 ± 0.3	2.82 ± 0.05	2.38 ± 0.04	41.1 ± 0.8
95/5	6.0 ± 0.1	5.98 ± 0.2	2.48 ± 0.03	2.42 ± 0.05	40.2 ± 0.8
93/7	6.0 ± 0.1	10.0 ± 0.5	4.18 ± 0.04	2.40 ± 0.03	37.5 ± 0.7
90/10	6.4 ± 0.2	12.0 ± 0.7	4.72 ± 0.06	2.55 ± 0.03	36.5 ± 0.7
70/30	6.3 ± 0.1	19.8 ± 0.8	9.02 ± 0.10	2.22 ± 0.02	33.2 ± 0.8
50/50	6.6 ± 0.1	20.9 ± 0.9	9.18 ± 0.12	2.27 ± 0.05	30.8 ± 0.9

Table 13. Linear shrinkage and technological properties of fired tiles (results show the average values of 10 measurements).

The bulk density increases with the concentration of sludge up to 10% due to the high density of sludge (3.7 g cm^{-3}). The bending strength increases with the addition of IM up to 10% due

to the beneficial effect of ilmenite on sintering during firing as denoted by the decrease in porosity (**Table 13**).

The 97/3 and 95/5 samples show the highest values of bending strength, that is, 41 and 40 MPa, respectively. These are above 30 MPa, the minimum value required for group BIb [64]. On the other hand, values corresponding to 100/0, 93/7, and 90/10 samples are greater than for the BIIa group (22 MPa). Finally, in the 70/30 and 50/50 samples, bending strength decreases due to the increase of interconnecting open pores.

In order to analyze how the ilmenite mud is incorporated to the final product, a detailed study by FESEM was made. The images (**Figure 4**) show good sintering and a homogeneous microstructure free of internal defects such as cracks.

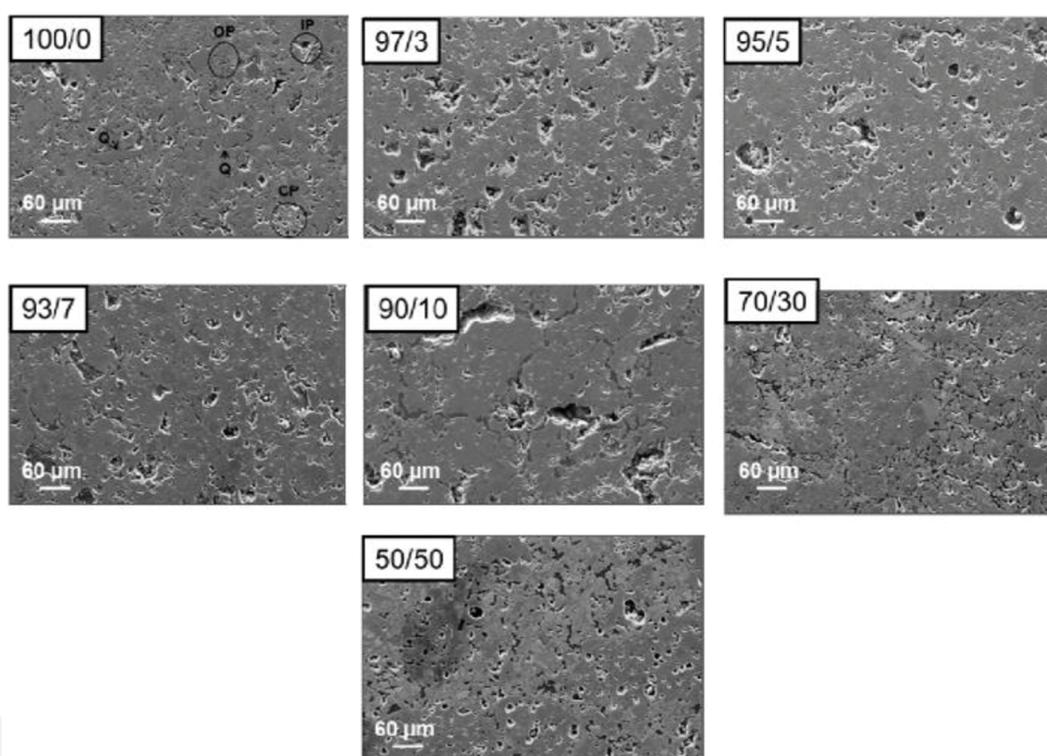


Figure 4. Secondary electron images (low magnification) on polished surfaces of fired tiles. Q: quartz; OP: open porosity; CP: closed porosity; and IP: interparticle porosity.

It is important to note the existence of both open (<math><5\ \mu\text{m}</math>) and closed (<math><10\ \mu\text{m}</math>) pores in the samples. Once the allotropic transformation is carried out at

Recall that the original mud had a total radionuclide concentration of 2000–3000 Bq/kg, with the highest activity concentrations for ^{226}Ra and ^{228}Ra being around 500 and 2000 Bq/kg, respectively, (**Table 5**). In the tiles, the activity concentration of these radionuclides increased with increasing ilmenite mud content, as did those of ^{228}Ra , ^{228}Th , and ^{238}U . The activity

concentration of ^{40}K was constant in all samples. The index (I) for ceramic samples is lower than six for all of the analyzed materials. This means that ilmenite mud suitable material for use in the ceramic industry in comparison with other additives [66].

A TCLP leaching test was also applied to evaluate the potential environmental impacts generated by hazardous metals and radionuclides contained in tiles. The results indicate that increasing the proportion of ilmenite mud in mixture decreases the leached metals. Obviously, the firing process makes metal less leachable. These values are lower than the limits imposed by the US EPA and will not have a significant impact when this material is released into the environment. The only exception is ^{210}Po (Table 14).

	^{238}U	TF	^{234}U	TF	^{232}Th	TF	^{230}Th	TF	^{210}Po	TF
RSM	29±3	1.5	36±4	1.8	50±17	1.7	129±28	7.6	7.3±1.9	0.4
97/3	10.1±2.1	0.6	10.1±2.1	0.5	18±6	0.6	54±10	2.5	12±2	0.7
95/5	4.8±1.4	0.2	6.3±1.7	0.3	33±11	1.0	75±17	3.0	9.6±1.9	0.6
93/7	6.3±1.4	0.3	5.1±1.2	0.3	10.5±3.6	0.4	24±5	1.3	10.8±2.9	0.3
90/10	6.4±1.4	0.4	6.4±1.4	0.4	5.1±1.6	0.2	8.0±2.0	0.4	5.5±0.8	0.3
IM	2.1±0.7	0.1	5.3±1.2	0.3	37±9	1.0	99±18	4.3	9.7±2.8	0.1

Transfer factor (%) in TCLP.

Table 14. Average concentration (mBq/L) of each sample analyzed by alpha spectrometry.

The motilities of U- and Th-isotopes are of the same order of magnitude for the various samples studied, that is, 10–100 mBq/L, apart from Po which is one order of magnitude lower (<10 mBq/L). This fact is explained by the tendency of Po to bind onto the particulate material [15].

Therefore, that the impact of the use of ilmenite mud as an additive in ceramics is negligible from the environmental point of view.

Author details

Irene García-Díaz¹, Manuel Jesus Gázquez², Juan Pedro Bolivar³ and Felix Antonio López^{1*}

*Address all correspondence to: flopez@cenim.csic.es

¹ National Center for Metallurgical Research (CENIM), CSIC, Madrid, Spain

² Department of Applied Physics, Cádiz University, Cádiz, Spain

³ Department of Applied Physics, Huelva University, Huelva, Spain

References

- [1] Kuryatnyk T, Angulski da Luz C, Ambroise J, Pera J. Valorization of phosphogypsum as hydraulic binders. *Journal of Hazardous Materials* 2008;160:681–687. doi:10.1016/j.jhazmat.2008.03.014
- [2] Samara M, Lafhai Z, Chapiseau C. Valorization of stabilized river sediments in fired clay bricks: factory scale experiment. *Journal of Hazardous Materials* 2009;163:701–710. doi:10.1016/j.jhazmat.2008.07.13
- [3] Puertas F, García-Díaz I, Palacios M, Gazulla MF, Gómez MP, Orduña M. Clinkers and cements obtained from raw mix containing ceramic wastes as raw materials: characterization hydration and leaching studies. *Cement and Concrete Composites* 2010;32:175–186. doi:10.1016/j.cemconcomp.2009.11.011
- [4] García-Díaz I, Palomo JG, Puertas F. Belite cements obtained from ceramic wastes and the mineral pair $\text{CaF}_2/\text{CaSO}_4$. *Cement and Concrete Composites* 2011;33:1063–1070. doi:10.1016/j.cemconcomp.2011.06.003
- [5] Pérez-Moreno SM, Gázquez MJ, Bolívar JP. CO_2 sequestration by indirect carbonation of artificial gypsum generated in the manufacture of titanium dioxide pigments. *Chemical Engineering Journal* 2015;262:737–746. doi:10.1016/j.cej.2014.10.023
- [6] Ribeiro MCS, Meira-Castro AC, Silva FG, Santos J, Meixedo JP, Fúza A, Dinis ML, Alfim MR. Re-use assessment of thermoset composite wastes as aggregate and filler replacement for concrete–polymer composite materials: a case study regarding GFRP pultrusion wastes. *Resources, Conservation and Recycling* 2015;104:417–426. doi:10.1016/j.resconrec.2013.10.001
- [7] Ajmal PY, Bhangare RC, Tiwari M, Sahu SK, Pandit GG. External gamma radiation levels and natural radioactivity in soil around a phosphate fertilizer plant at Mumbai. *Journal of Radioanalytical and Nuclear Chemistry* 2014;300:23–27. doi:10.1007/s10967-014-2941-4
- [8] Carbonell-Barrachina A, DeLaune RD, Jugsujinda A. Phosphogypsum chemistry under highly anoxic conditions. *Waste Management* 2002;22:657–665. doi:10.1016/S0956-053X(01)00052-6
- [9] Oliveira SMB, Imbernon RA. Weathering alteration and related REE concentration in the Catalão I carbonatite complex, Central Brazil. *Journal of South American Earth Sciences* 1998;11:379–388.
- [10] Olszewski G, Borylo A, Skwarzec B. Uranium (^{234}U , ^{235}U and ^{238}U) contamination of the environment surrounding phosphogypsum waste heap in Wiślinka (Northern Poland). *Journal of Environmental Radioactivity* 2015;146:56–66. doi:10.1016/j.jenvrad.2015.04.001

- [11] NafehKassir L, Lartiges B, Ouaini N. Effects of fertilizer industry emissions on local soil contamination: a case study of a phosphate plant on the east Mediterranean coast. *Environmental Technology* 2012;33:873–885. doi:10.1080/09593330.2011.601765
- [12] Ayadi A, Chorriba A, Fourati A, Gargouri-Bouزيد R. Investigation of the effect of phosphogypsum amendment on two *Arabidopsis thaliana* ecotype growth and development. *Environmental Technology* 2015;36:1547–1555. doi:10.1080/09593330.2014.997296
- [13] Tayibi H, Choura M, López FA, Alguar FJ, López-Delgado A. Environmental impact and management of phosphogypsum. *Journal of Environmental Management* 2009;90:2377–2386. doi:0.1016/j.jenvman.2009.03.007
- [14] Rutherford PM, Dudas MJ, Arocena JM. Heterogeneous distribution of radionuclides barium and strontium in phosphogypsum by-product. *Science of the Total Environment* 1996;180:201–209.
- [15] Berish CW. Potential environmental hazards of phosphogypsum storage in Central Florida. Proceedings of the third international symposium on phosphogypsum, Orlando, FL, FIPR Pub. No. 01060083; 1990;2:1–29.
- [16] Kacimi L, Simon-Masseron A, Ghomari A, Derriche Z. Reduction of clinkerization temperature by using phosphogypsum. *Journal of Hazardous Materials* 2006;137:129–137. doi:10.1016/j.jhazmat.2005.12.053
- [17] Burnett WC, Schultz MK, Carter DH. Radionuclide flow during the conversion of phosphogypsum to ammonium sulfate. *Journal of Environmental Radioactivity* 1996;32:33–51. doi:10.1016/0265-931X(95)00078-O
- [18] Borrego E, Mas JL, Martín JE, Bolívar JP, Vaca F, Aguado JL. Radioactivity levels in aerosol particles surrounding a large TENORM waste repository after application of preliminary restoration work. *Science of the Total Environment* 2007;377:27–35. doi:10.1016/j.scitotenv.2007.01.098
- [19] Zhang W, Zhu Z, Cheng CY. A literature review of titanium metallurgical processes. *Hydrometallurgy* 2011;108:177–188. doi:10.1016/j.hydromet.2011.04.005
- [20] Gázquez MJ, Bolivar JP, García-Tenorio R, Vaca F. A review of the production cycle of titanium dioxide pigment. *Materials Sciences and Applications* 2014;5:441–458. doi:10.4236/msa.2014.57048
- [21] McNulty GS. Production of titanium dioxide. PlenayLecture. NORM V International Conference, Sevilla, 19–22 March 2007, pp. 169–188
- [22] Shon HY, Zhou L. The chlorination kinetics of beneficiated ilmenite particles by Co + Cl₂ mixtures. *Chemical Engineering Journal* 1999;72:37–42. doi:10.1016/S1385-8947(98)00139-9

- [23] Chernet T. Applied mineralogical studies on Australian sand ilmenite concentrate with special reference to its behavior in the sulphate process. *Minerals Engineering* 1999;12:485–49. doi:10.1016/S0892-6875(99)00035-7
- [24] Gázquez MJ, Mantero J, Bolívar JP, García-Tenorio R, Vaca F, Lozano RL. Physicochemical and radioactive characterization of TiO₂ undissolved mud for its valorization. *Journal of Hazardous Materials* 2011;191:269–276. doi:10.1016/j.jhazmat.2011.04.075
- [25] Gázquez MJ, Bolívar JP, García-Tenorio R, Vaca F. Physicochemical characterization of raw materials and co-products from the titanium dioxide industry. *Journal of Hazardous Materials* 2009;166:1429–1440. doi:10.1016/j.jhazmat.2008.12.067
- [26] Mantero J, Gázquez MJ, Bolívar JP, García-Tenorio R, Vaca F. Radioactive characterization of the main materials involved in the titanium dioxide production process and their environmental radiological impact. *Journal of Environmental Radioactivity* 2013;120:26–32. doi:10.1016/j.jenvrad.2013.01.002
- [27] Kovler, K. Radiological constraints of using building materials and industrial by-products. *Construction and Building Materials* 2009;23:246–253. doi:10.1016/j.conbuildmat.2007.12.010
- [28] Rentería-Villalobos M, Vioque I, Mantero J, Manjón G. Radiological, chemical and morphological characterizations of phosphate rock and phosphogypsum from phosphoric acid factories in SW Spain. *Journal of Hazardous Materials* 2010;182:193–203. doi:10.1016/j.jhazmat.2010.04.116
- [29] Directive 2013/59/EURATOM, of 5 December 2013. Laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation.
- [30] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Sources, effects and risks of ionizing radiation. Report to the General Assembly, with annexes. New York: United Nations; 1988.
- [31] Abdel-Mohsen O, El Gamal MM. Sulfur based hazardous waste solidification. *Environmental Geology* 2007;53:159–175. doi:10.1007/s00254-006-061-4
- [32] Bacon RF, Davis HS. Recent advances in the American sulfur industry. *Chemical Metallurgical Engineering* 1921;24:65–72.
- [33] Duecker WW. Admixtures improve properties of sulfur cements. *Chemical Metallurgical Engineering* 1934;41:583–586.
- [34] Kobbe WH. New uses for sulfur in industry. *Industrial and Engineering Chemistry* 1994;16:1026–1028.
- [35] Moon J, Kal PD, Milina L, Norhtrup PA. Characterization of sustainable sulfur polymer concrete using activated filler. *Cement and Concrete Composites* 2016;67:20–29. doi:10.1016/j.cem.concomp.2015.12.002
- [36] Seunggun Y, Hyuk K, Hyuk RN, Bo-In P, No Kyung P, Heon-Jin C, Sung-Churl C, Goo DK. Preparation and characterization of a new cement based composite with sulfur

- polymer. *Royal Society of Chemistry Advances* 2015;5:36030–36035. doi:10.1039/c5ra02281a
- [37] Książek M. The influence of penetrating special polymer sulfur binder-polymerized sulfur applied as the industrial waste material concrete. *Composites: Part B* 2014;62:137–142. doi:10.1016/j.compositesb.2014.02.027
- [38] López F.A., Gázquez M., Alguacil F.J., Bolivar J.P., García-Díaz I., López-Coto I., Microencapsulation of phosphogypsum into a sulfur polymer matrix: Physico-chemical and radiological characterization, *Journal of Hazardous Materials* 2011;192:234–245. doi:10.1016/j.jhazmat.2011.05.010
- [39] Lin SL, Lai JS, Chian ESK. Modification of sulfur polymer cement (SPC) stabilization and solidification (S/S) process. *Waste Management* 1995;15: 441–7. doi:10.1016/0956-053X(95)00049-6
- [40] Sandrolini F, Manzi S, Andrucci A. Sulfur–polymer matrix composites from particulate wastes: a sustainable route to advanced materials. *Composites Part A: Applied Science and Manufacturing* 2006;37:695–702. doi:10.1016/J.compositesa.2005.07.004
- [41] UNE-EN 196-1. Método de ensayo de cementos. Parte 1: Determinación de resistencias mecánicas
- [42] Medeiros MHF, Helene P. Surface treatment of reinforced concrete in marine environment: influence on chloride diffusion coefficient and capillary water absorption. *Construction and Building Materials* 2009;23:1476–1484. doi:10.1016/j.conbuildmat.2008.06.013
- [43] Khatib JM, Clay RM. Absorption characteristics of metakaolin concrete. *Cement and Concrete Research* 2004;34:19–29. doi:10.1016/S0008-8846(03)00188-1
- [44] US EPA. Test Methods for Evaluating Solid Waste Physical Chemical Methods, SW-846, US Environmental Protection Agency, Washington, DC, (1997). <http://www.epa.gov/SW-846/main.htm>
- [45] Mas JL, García-León M, García-Tenorio R, Bolívar JP. Radionuclide concentrations in water. In: *Radionuclide Concentrations in Food and the Environment*, (2006), Ed. E. Nollet, M. Pöschl, pp. 59–113 Taylor & Francis Group. Boca Raton London New York.
- [46] Bolivar JP, Martín JE, García-Tenorio R, Pérez-Moreno JP, Mas JL. Behaviour and fluxes of natural radionuclides in the production process of a phosphoric acid plant. *Applied Radiation and Isotopes* 2009;67:345–356. doi:10.1016/j.apradiso.2008.10.012
- [47] Chen G, Lee H, Young KL, Yue PL, Wong A, Tao T, Choi KK. Glass recycling in cement production: an innovative approach. *Waste Management* 2002;22:747–53. doi:10.1016/S0956-053X(02)00047-8

- [48] Shia C, Meyer C, Behnood A. Utilization of copper slag in cement and concrete. *Resource Conservation and Recycling* 2008;52:1115–20. doi:10.1016/j.resconrec.2008.06.008
- [49] Shih P-H, Chang J-E, Lu H-C, Chiang L-C. Reuse of heavy metal-containing sludges in cement production. *Cement and Concrete Research* 2005;35:2110–5. doi:10.1016/j.cemconres.2005.08.006
- [50] Potgieter JH, Horne KA, Potgieter SS, Wirth W. An evaluation of the incorporation of a titanium dioxide producer's waste material in Portland cement clinker. *Materials Letters* 2002;57:157–163. doi:10.1016/S0167-577X(02)00723-1
- [51] Katyal NK, Alhuwalia SC, Parkash R. Influence of TiO₂ on the hydration of tricalcium silicate. *Cement and Concrete Research* 1999;29:1851–1855. doi:10.1016/S0008-8846(99)00171-4
- [52] UNE-EN 196-3, 2005. Methods of testing cement – Part 3: determination of setting times and soundness.
- [53] Hierro A, Martín JE, Olías M, García C, Bolivar JP. Uranium behaviour during a tidal cycle in an estuarine system affected by acid mine drainage (AMD). *Chemical Geology* 2013;342:110–118. doi:10.1016/j.chemgeo.2013.01.021
- [54] Directive 2003/53/EC The 26th amendment of the Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement).
- [55] Andres A, Fernandez-Gómez N, Rivero-Gutierrez S, Viguri JR. 2005. Reusing of waste materials in ceramic: analysis of scientific-technical information. *Proceedings of the 10th Mediterranean Congress on Chemical Engineering*.
- [56] Romero M, Andrés A, Alonso R, Viguri J, Rincón JM. Sintering behaviour of ceramic bodies from contaminated marine sediments. *Ceramics International* 2008;34:1917–1924. doi:10.1016/j.ceramint.2007.07.002
- [57] Tay J-H, Show K-Y. 1999. Constructive sludge disposal option converting sludge into innovative civil engineering materials. *Proceedings of the 7th IAWQ Asia-Pacific Regional Conference, Taipei, Taiwan*. pp. 1023–1028.
- [58] Weng C-H, Lin D-F, Chiang P-C. Utilization of sludge as brick materials. *Duecker, Advances in Environmental Research* 2003;7:679–685. doi:10.1016/S1093-019(02)00037-0 2003.
- [59] Contreras M, Martín MI, Gázquez MJ, Romero M, Bolívar JP. Valorisation of ilmenite mud waste in the manufacture of commercial ceramics. *Construction and Building Materials* 2014;72:31–40. doi:10.1016/j.conbuildmat.2014.08.091
- [60] ISO 10545-3:1997. Ceramic tiles. Part 3: determination of water absorption, apparent porosity, apparent relative density and bulk density.

- [61] ASTM C373-88:1999. Standard test method for water adsorption, bulk density, apparent porosity and apparent specific gravity of fired white ware products.
- [62] EN 843-1:2006. Advanced technical ceramics. Monolithic ceramics. Mechanical properties at room temperature. Part. I: Determination of flexural strength.
- [63] Raigón-Pichardo M, García-Ramos G, Sánchez-Soto PJ. Characterization of a waste washing solid product of mining granitic tin-bearing sands and its application as ceramic raw material. *Resource Conservation and Recycling* 1996;17:109–24. doi:10.1016/0921-3449(96)01108-1
- [64] EN 14411:2003. Ceramic tiles. Definitions, classifications, characteristics and marking.
- [65] De Noni A, Hotza D, Cantavella V, Sanchez E. Effect of quartz particle size on the mechanical behaviour of porcelain tile subjected to different cooling rates. *Journal of the European Ceramic Society* 2009;29:1039–1046. doi:10.1016/j.jeurceramsoc.2008.07.052
- [66] Kovler K. Radiological constraints of using building materials and industrial by-products. *Construction and Building Materials* 2009;23: 246–253. doi:10.1016/j.conbuildmat.2007.12.010

