Management and Valorisation of Wastes and Co-products from the TiO₂ Pigment Industry

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Abstract

This work analyses and evaluates potential applications for several inorganic wastes and intermediate materials, called co-products, generated in the TiO₂ pigment production industry through the sulphate method. For this purpose, a physical–chemical characterisation of the input materials (ilmenite and slag), wastes (sludge and red gypsum), and co-products (two ferrous sulphates, mono and hepta-hydrated) was carried out. In addition, because the TiO₂ pigment production activity is a Naturally Occurring Radioactive Material industry, a radiological characterisation was also undertaken. The main objective was to gain basic information for the application (actual or potential) of these co-products and wastes in fields such as agriculture, construction, and civil engineering. For each specific application of these wastes and co-products, additional studies were carried out to evaluate their appropriateness with respect to technical properties and their health and environmental impact. The results obtained in this work have revealed several lines of research with potential commercial applications.

Keywords

TiO₂ industry; NORM wastes; Management; Valorisation; Civil engineering

Introduction

There is currently growing interest in what is known as the circular economy. In a circular economy the utility of products is maximised on the one hand by extending their lifespan through in-built restorability (as opposed to inbuilt obsolescence), and on the other by enabling components and materials to be re-used in the production cycle, thus producing minimal wastage. It contrasts with a linear model, in which a ‘take, make, dispose’ approach requires large quantities of cheap, easily accessible materials and energy. The attraction of a circular economy is that it recognises the physical limits of resources and the importance of safeguarding the environment whilst providing a viable business alternative. An important area of the circular economy is the valorisation of the waste generated in the production and final consumption of the goods.

In this sense, it is important to note that industrial waste recycling is a growth area in the majority of industrial processes. The protection of health and the environment are of great importance; moreover, the economic benefits accruing from waste recycling must not be ignored [1–4]. The minimisation of waste disposal, avoiding its direct release into the environment, could lead to the production of co-products with economic value and broad applications [5–7]. In addition, the environmental and health impact of these co-products should comply with existing regulations at national and/or international level.

Titanium dioxide (TiO₂) pigment is a white powder with high opacity and brilliant whiteness. These properties have made it a valuable pigment for many applications in paints, plastic goods, inks and paper, among others. There are two chemical methods for obtaining TiO₂, one using sulphate, and the other chloride. It is estimated that about 65 % of the world’s production is derived from the chloride process, while 70 % of the European production takes the sulphate route.

One European centre of production is located in southwestern Spain, in the vicinity of Huelva. This factory uses the sulphate method for producing dioxide pigments. In addition to the main TiO₂ pigment production, four different co-products and wastes result from the process (Fig. 1) [8, 9].

The industrial process followed at the Huelva TiO₂ factory begins with the acid digestion of the feedstock [8, 9]. A controlled blend of ilmenite (ILM) and slag (SLAG) (85 % ilmenite and 15 % slag) is mixed with highly concentrated sulphuric acid (H₂SO₄, 98 %), and acid (H₂SO₄, 80 %) recycled from the chemical process. The resulting liquor contains titanyl sulphate (TiOSO₄)

in solution, which goes into a clarification tank where the un-dissolved solids (SLUDGE) are separated by flocculation (decantation) and posterior filtration. Then, the clarified liquor, in which the TiO₂ is dissolved as titanyl sulphate, is hydrolysed with steam in order to produce

Fig. 1 Detailed diagram of the TiO₂ extraction by sulphate way

the precipitation of hydrated titanium. The TiO₂ pulp is then separated from the mother liquor (called “strong acid”) by vacuum filters. The TiO₂ cake is washed again with water, producing a liquor called “weak acid”, and then placed in rotary kilns for the removal of its water content and some traces of sulphur. The resulting final solid is calcinated, milled, coated, washed, dried, and finely, micronized to be packed for commercial distribution.

Historically, the TiO₂ process has undergone significant development in relation to the treatment of the two waste products generated by the process (strong and weak acid). In the 1970s the factory was designed to discharge the strong acid into the deep sea in the Gulf of Cadiz at a point 40 miles from the coast, considered to pose minimal potential environmental impact. Curiously, this requirement was stricter than that imposed on other similar industries in Europe, where the strong acid was pumped into the sea only two kilometres from the coast.

Subsequently, in the early 1990s, the Council Directive 92/112/EEC of 15 December 1992, established procedures for harmonizing the programmes for the reduction and eventual elimination of pollution caused by waste from the titanium dioxide industry.

This Directive:

- Prohibited the dumping of any solid waste, strong acid waste, treatment waste, weak acid waste, or neutralized waste, with effect from 15 June 1993.
- Specified a reduction in the discharge of SO_x arising from digestion and calcination steps in the manufacture of titanium dioxide, to a value of not more than 10 kg of SO₂ equivalent per ton of titanium dioxide produced with effect from 1 January 1995.
- Classified solid wastes taking into account the type of management, and attending to their nature.

In response to the need to eliminate the discharge of effluents into the sea, huge technical and environmental modifications were carried out in the Huelva plant with significant success and the last dump was made on May 31, 1993. The new processes introduced in the factory in order to reduce the pollutant effluents released into the estuary of Huelva to a negligible concentration can be summarized as follows.

Firstly, the strong acid from the TiO₂ precipitation and lixiviation stages is pumped to crystallisers and concentrated, precipitating the solid heptahydrated ferrous sulphate (FeSO₄ · 7H₂O), commonly known as “copperas” (COP), which is extracted by centrifugation [8, 9]. The remaining strong acid containing some additional amounts of Fe, is further concentrated by multi-stage evaporation until the precipitation of monohydrated ferrous sulphate (FeSO₄ · H₂O), called “monohydrate” (MON), which is separated by filtration. The resulting strong sulphuric acid is concentrated again (H₂SO₄, 80 %), and is recycled into the process at the digestion stage of the raw material (see Fig. 1).

The final weak acid stream is treated in a neutralization plant by adding calcium hydroxide and magnesium hydroxide, generating a waste called red gypsum(RG), formed mainly of artificial gypsum (CaSO₄ · 2H₂O), and iron hydroxides, while the resulting clean stream is released into the estuary (Fig. 1).

Around 142,000 metric tonnes of raw material (ILM) are processed annually in the Huelva factory, generating the following amounts of dry co-products and waste per kilogram of raw material: 0.10 kg of SLUDGE, 0.33 kg of RG, 0.64 kg of MON, 0.70 kg of COP, and 0.48 kg of TiO₂ pigment.

Additionally, we must take into account that the production of titanium dioxide is a Naturally Occurring Radioactive Material (NORM) industrial process as ilmenite has enhanced levels of natural radionuclides from both the uranium and thorium series. The input of radionuclides occurs throughout the process among the different coproducts and waste generated.

In view of the above, the main objective of this paper is to specify the physicochemical and radioactive characterization of the raw materials, co-products and waste from the TiO₂ pigment industry, and to apply this information in the valorisation of the waste in the production of new materials with commercial applications.

Materials and Methods

Materials

The samples of raw materials (ilmenite and slag), wastes (red gypsum and sludge) and co-products (ferrous sulphates, hepta- and monohydrated) were provided for use in this study by the titanium dioxide production plant 12 km from the city of Huelva. Five sampling campaigns were organised during a period of 1 month, taking place every 6 days. The objective was to analyse the possible temporal variability in the characteristics of the materials, and to obtain representative samples to be used in the new manufactured materials. After collection, the raw materials were dried at 105 °C, while wastes and co-products were dried at 45 °C to prevent excessive dehydration.

Methods

Characterisation Techniques

The identification of the mineral phases was performed by the XRD technique (X-ray diffraction) in a Bruker diffractometer (model D8 Advance), using Cu K α radiation operating at a current of 30 mA, and a voltage of 40 kV. Data were recorded in the 5°–70° 2 θ range (step size 0.019736° and 0.5 s duration for each step). For Rietveld quantitative phase analysis, finely powdered samples were mixed with 30 % high purity calcined α -Al₂O₃ as internal standard. The mixture was homogenized by hand milling for 5 min in an agate mortar with acetone. Powder diffraction patterns suitable for performing the Rietveld analysis were collected by step-scanning in the 10°–70° (2 θ) range, with steps of 0.03° and a duration of 8 s for each step.

The microstructures of all applications were examined by field emission scanning electron microscopy (FESEM) (HITACHI model S-4800) operating at 20 kV. Granulometric analyses were performed using a Mastersize 2000 APA granulometer (Malvern Instruments Ltd.).

The major elements were measured for X-ray fluorescence (XRF) using a Bruker S4 Pioneer system with the following characteristics: 4 kW, front window and Rh anode; five analysing crystals—LIF200, Ge, PET, OVO55 and OVOC, and two X-ray detectors.

Trace elements analysis was performed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry), using an HP branded computer model HP4500® and by ICP-OES (Inductively Coupled Plasma Optical Emissions Spectrometer) using a Jobin–Yvon ULTIMA 2.

Thermal behaviour was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (SETARAM model Labsys) on powdered samples (size particle = 80–100 µm). DSC/TGA scans were performed in platinum crucibles under a flow of air between 25 and 1450 °C at 50 °C min⁻¹, taking calcined Al₂O₃ as reference material. The DSC/TG curves were normalised with respect to the sample weight.

The activity concentrations of radionuclides were measured by high-resolution low-background gamma spectrometry with high-purity germanium detectors (HPGe). In addition, the concentrations of Th-isotopes (²³²Th, ²³⁰Th), U-isotopes (²³⁴U, ²³⁸U) and ²¹⁰Po were determined by the alpha spectrometry technique with ion implanted Si detectors (PIPS detectors) [10, 11].

Technological Characterisation

The sintering behaviour of cements was evaluated in terms of compressive (Cs) and flexural (Fs) strength, and water absorption by capillarity (WAC). The compressive (Cs) and flexural (Fs) strengths were measured according to standard UNE 196-1:2005 [12], using an Autotest 200-10-W universal press (Ibertest). The coefficient of water absorption by capillarity was determined gravimetrically according to standard UNE-EN480-5:2006 [13]. The water/cement ratio (W/C) is one of the first parameters that must be calculated to ensure the optimal behaviour of the final cements and concretes. A normalized Vicat apparatus with a rod 50 mm in length and 10 mm in diameter was used. Another important property of commercial cement is its setting time. The protocol used to measure this records the depth of penetration of the needle in the mould at different positions [14].

The sintering behaviour of ceramic was evaluated in terms of water absorption, apparent porosity and bulk density. The water absorption, E (wt%), was measured according to EN ISO

10545-3 [15] for ten representative specimens. The apparent porosity and the bulk density were measured according to ASTM C373-88 [16], which involves drying the test specimens to constant mass. After impregnation, the mass of each specimen while suspended in water was determined along with their saturated mass. The apparent porosity, P (%), expresses the relationship of the volume of open pores with the exterior volume of the specimen. The bulk density, B (g cm⁻³), of a specimen is the quotient of its dry mass divided by the exterior volume, including pores. In addition, the linear shrinkage, LS (%) and the bending strength, BS (MPa), was measured according to EN 843-1 [17].

Fire-Resistance Tests

Fire-resistance test standards are stipulated in the regulation UNE-EN 13501-1 [18]. This test requires that one of the sides of the plate be exposed to a standard temperature curve defined by the equation $T = 20 + 345 \log_{10}(8t + 1)$, where T is the oven temperature (°C), and t is the time (min) from the beginning of the test. The temperature of the unexposed side is measured by means of three Pt-100 thermocouple probes. The test is concluded when the temperature of one of the thermocouples on the unexposed surface of the plate is either above 180 °C, or the average temperature of all the thermocouples exceeds $140\text{ °C} + T_{\text{Env.}}$, where $T_{\text{Env.}}$ is the ambient temperature when the product was tested at 23 °C. In the event of the test material fracturing or losing structural stability, the trial is discontinued, a circumstance which did not occur in any of the tests performed.

Results and Discussion

Characterization of Raw Materials, Co-products and Waste

Mineralogical Characterization

Details of the mineralogical composition determined by XRD is given in Table 1. The ilmenite ore shows a nonuniform mineralogical composition with the following species: ilmenite (FeTiO₃) comprising 71 % of the total, compensated by the presence of rutile (TiO₂) and pseudorutile (Fe₂³⁺Ti₃O₉), 7 and 20 % respectively. Slag is a product resulting from the smelting of ilmenite, a process that upgrades the ilmenite concentrate, yielding a TiO₂-rich slag as a primary product and marketable iron metal as coproduct [19, 20]. The uniformity in the mineralogical composition of slag samples analysed is very high, identifying armalcolite ((Mg,Fe²⁺)Ti₂O₅), at 90 % as main mineral species.

Table 1 Average (five samples) mineralogical composition (%) of raw materials, co-products and wastes in the Huelva TiO₂ industry

	Mineral phases
ILM	Ilmenite (71 ± 11 %); Pseudorutile (20 ± 7 %); Rutile (7.0 ± 2.4 %)
SLAG	Armstrongite (91 ± 3 %); Rutile (8.4 ± 2.4 %)
SLUDGE	Rutile (34 ± 4 %); Ilmenite (22 ± 3 %); Ti and Fe oxides ($\text{Fe}_3\text{Ti}_3\text{O}_{10}$) (18 ± 2 %); Quartz (13 ± 3 %); Zircon (12 ± 2 %)
RG	Gypsum (95 ± 1 %); Ti and Fe oxides (5 ± 1 %)
COP	Melanterite (66.6 ± 20.9 %); Rozenite (33.4 ± 17.8 %)
MON	Szomolnokite (77.6 ± 20.9 %); Rozenite (22.4 ± 4.0 %)

Mineral phases with lower concentration of 5 % are not detected

The properties of waste and co-products are dependent upon the nature of the ilmenite ore used, the type of process employed and the plant operation efficiency. The mineralogical analysis of the SLUDGE shows ilmenite (22 %) and rutile (34 %), and additionally some previously undetected species in the raw material, such as Fe and Ti oxides ($\text{Fe}_3\text{Ti}_3\text{O}_{10}$), zircon (ZrSiO_4) and quartz (SiO_2): 18.2, 13 and 12.1 %, respectively. The detection and quantification of these new mineralogical phases cannot be considered as surprising, since all these species are insoluble in sulphuric acid [8]. By contrast, the mineralogical composition of red gypsum is very homogeneous, with gypsum as the main mineral compound ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), consistent with the expected results. The only point of interest to add is that all the samples analysed have a small fraction (5 %) of titanium and iron oxides, as confirmed by the elemental analysis performed (see below) [9, 21].

The co-products (copperas and monohydrate) show a high degree of instability. Although theoretically it could be expected that 100 % of the COP should be melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), a small amount of rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) was found (see Table 1). These results can be explained by the tendency of the heptahydrated ferrous sulphate to lose a fraction of its water content and to transform into a mineral form containing only four water molecules. With respect to MON, theoretically it would also be expected that 100 % should be szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$), but the presence of a significant proportion (22 %) of rozenite was also found (Table 1). In this case, the opposite tendency to that of copperas is observed, since the monohydrate ferrous sulphate tends to end up with a content of four water molecules, in order to form the most stable hydrated ferrous sulphate compound [22].

Elemental Composition

The major elements in the ilmenite ore, expressed as oxides, are Fe₂O₃ and TiO₂, 44 and 50 % respectively (Table 2). In addition, percentages of SiO₂, Al₂O₃ and MnO can be observed as major impurities associated with the pseudorutile [23]. The slag, in addition to Fe₂O₃ and TiO₂ (11 and 75 %, respectively), also contains significant levels of several metals such as Si, Al and Mg oxides (2.5, 2.3 and 5 %, respectively).

Sludge has TiO₂ as the main element (52 %), containing considerable amounts of Fe₂O₃ (14 %), SiO₂ (17 %), SO₃ (6.1 %) and ZrO₂ (2.3 %), being compatible with mineral phases obtained by XRD. The predominant compounds in red gypsum are CaO and SO₃ (33 and 27 %, respectively), also showing a relatively high titanium and iron content (7.6 % TiO₂ and 14 % Fe₂O₃) (Table 2).

The co-products, copperas and monohydrate, contain mainly SO₃ (22–25 %) and Fe₂O₃ (31–39 %) respectively, as was expected, consistent with their mineralogical composition. MON (monohydrate) presents considerable levels of oxide impurities (Al, Mn or Ti), which can be accounted for by the fact that it is formed by the concentration of strong sulphuric acid and that consequently there is precipitation of the dissolved salts it contains. However, the COP (copperas), coming from the crystallization process, shows a high degree of purity (Table 2).

Table 2 Average concentrations (%) of major elements by XRF in the raw materials, co-products and wastes

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	TiO ₂	SO ₃	ZrO ₂
ILM	0.71 ± 0.09	0.71 ± 0.09	44 ± 1	1.30 ± 0.05	0.32 ± 0.07	0.05 ± 0.01	49.6 ± 0.3	<0.01	0.34 ± 0.01
SLAG	2.5 ± 0.04	2.34 ± 0.01	10.7 ± 0.2	0.26 ± 0.01	5.06 ± 0.03	0.56 ± 0.01	75.3 ± 0.2	0.17 ± 0.02	0.05 ± 0.01
SLUDGE	17 ± 1	3.6 ± 0.2	14.0 ± 0.4	0.45 ± 0.02	1.33 ± 0.02	0.71 ± 0.02	52 ± 1	6.1 ± 0.7	2.32 ± 0.19
RG	1.2 ± 0.2	1.4 ± 0.2	14 ± 2	0.35 ± 0.04	1.4 ± 0.2	33 ± 2	7.6 ± 1.2	27 ± 1	<0.01
COP	<0.01	0.06 ± 0.01	39 ± 3	0.35 ± 0.04	0.25 ± 0.03	<0.01	0.18 ± 0.02	22 ± 2	<0.01
MON	<0.01	1.1 ± 0.3	31 ± 2	1.4 ± 0.1	0.61 ± 0.12	0.09 ± 0.03	2.9 ± 0.3	25 ± 1	<0.01
SOIL ^a	66.6	15.4	5.04	0.1	2.48	3.59	0.64	<0.01	0.02

^a Continental crust composition [25]

The trace elements (Table 3) in most of the materials were at concentrations either higher than (Cr, Cd, Pb, Zn and especially V) or similar to (Ni and Cu) the continental crust composition [24]. Furthermore, most trace elements analysed in the sludge, such as V, Cr, Zn, As, Cd, and Pb, show high enrichment factors in comparison with a typical soil: 10, 6, 3, 12, 7 and 16, respectively [24]. On the other hand, copperas allows us to conclude that this co-product is quite free from trace elements, which is not surprising given its formation by crystallisation.

Table 3 Average composition of trace elements (mg kg⁻¹) by ICP-OES in the materials analysed

	V	Cr	Ni	Cu	Zn	As	Cd	Pb
ILM	940 ± 45	344 ± 60	15 ± 2	41 ± 6	296 ± 28	22 ± 2	2.7 ± 0.3	135 ± 10
SLAG	3131 ± 28	1126 ± 102	6.6 ± 0.7	32 ± 3	35 ± 7	0.41 ± 0.12	2.3 ± 0.2	36 ± 7
SLUDGE	940 ± 12	518 ± 26	13 ± 1	278 ± 10	193 ± 11	57 ± 4	0.60 ± 0.06	278 ± 7
RG	277 ± 10	133 ± 4	31 ± 4	12 ± 1	225 ± 12	12 ± 1	1.04 ± 0.10	35 ± 2
COP	25 ± 3	10 ± 1	11 ± 1	<0.01	299 ± 34	0.25 ± 0.03	3.3 ± 0.4	46 ± 6
MON	1105 ± 86	467 ± 27	28 ± 1	<0.01	749 ± 55	1.32 ± 0.09	0.87 ± 0.04	45 ± 3
SOIL	97	92	47	28	67	4.8	0.09	17

^a Continental crust composition [25]

Radioactivity Characterization

It was noted in the introduction that ilmenite ore is a NORM material since it is enriched in natural radionuclides from both the Th- and U-series (in secular equilibrium), with a mean concentration of about 100 and 400 Bq kg⁻¹ for ²³⁸U and ²³²Th radionuclides, respectively (Fig. 2). On the other hand, it can be observed that the radionuclide levels for slag are very much lower than those found in typical undisturbed soils (25 Bq kg⁻¹ of ²³⁸U and ²³²Th in secular equilibrium with their daughters) [25, 26]. Therefore, the use of this material in the production process will have a very positive radiological effect.

Fig. 2 Activity concentration in Bq kg⁻¹ of each materials used in the Huelva TiO₂ industry

By contrast, sludge contains radionuclide concentrations higher than 1 Bq g⁻¹, which is the EU threshold for defining Naturally Occurring Radioactive Material (NORM) waste [27]. The ²²⁶Ra and ²²⁸Ra radionuclides contain the highest activity concentrations, around 800 and 2500 Bq kg⁻¹, respectively, which is around eight times the levels originally present in the raw material (ilmenite). Bearing in mind that 1 g of ilmenite produces 0.10 g of dry sludge, it is possible to deduce that practically 100 % of the radium present in the raw material remains bound to the sludge. This can be accounted for by the fact that radium sulphate is insoluble in a sulphuric medium [28]. Furthermore, red gypsum is slowly enriched in ²³²Th, ²²⁸Th and ²²⁸Ra, in comparison with an unperturbed soil, presenting activity concentrations of 127, 124 and 91 Bq kg⁻¹, respectively (Fig. 2).

The co-product COPPERAS is practically free of radioactivity and below the levels typical of undisturbed soils (20–40 Bq kg⁻¹) [25]. By contrast, monohydrate presents particularly active concentration of uranium and thorium isotopes of the same order as ilmenite (around 300 and 100 Bq kg⁻¹ for the Th and U-series).

Applications

Co-products for Agricultural Use

COP (ferrous sulphate heptahydrated) and MON (commercially known as Sulfafer) are well known compounds with uses in various fields. The classic market has been agriculture. The iron contained in COP is in a ferrous state, and is therefore readily assimilated by plants. As a result, it is used to supply iron to prevent chlorosis in plants, especially citrus trees. The presence of iron promotes the formation of chlorophyll, making for better plant growth. Moreover, COP contains sulphuric acid, which enables the solubilisation of other cations such as magnesium and phosphorus, as well as other metals such as zinc, copper, and manganese, which are essential trace elements in plant development. In addition, it is also used as an agent to fight plagues of snails, which damage the plantations, especially in the early stages of growth [29]. In alkaline soils, MON can be used directly, in appropriate doses, to acidify the soil, and mixed with manure produces compost more quickly, because the presence of free acid accelerates the decomposition of organic matter. At the same time, it has good agronomic properties due to its significant iron content that can be easily assimilated by plants.

Potential Applications for Waste

Sludge and red gypsum are currently disposed of in landfills. On this point, our research team has carried out several projects exploring the potential of these wastes in fields as diverse as civil engineering, building construction and CO₂ sequestration.

Use of Sludge and Red Gypsum in Commercial Cement Manufacture. The composition of natural gypsum, CaSO₄·2H₂O, makes it an ideal set retardant (in concentrations of between 3 and 5 %) in the manufacture of commercial Portland cement [30]. We therefore set out to examine the possibility of replacing natural gypsum with red gypsum in the manufacture of cements [31], and likewise, the potential of sludge as a direct additive to the cement [32].

The following mixtures were tested: RGA (97.5 % linker to 2.5 % red gypsum), RGB (95 % clinker to 5 % red gypsum), RGC (90 % clinker to 10 % red gypsum), SA (97.5 % cement to 2.5 % sludge), SB (95 % cement to 5 % sludge) and SC (90 % cement to 10 % sludge). These tests analysed and evaluated the main mechanical, elastic and thermodynamic properties of cements manufactured according to the different proportions of red gypsum and sludge listed above. The properties of these new cements were compared with those of ordinary Portland cement Type I (97 % clinker and 3 % natural gypsum, with a compressive strength category of 52.5 N mm⁻²). The first stage was to determine the appropriate water/cement (W/C) ratio by weight in order to obtain a “normal” consistency in the paste formed [12].

Figure 3 presents the results for compressive and flexural strength. The results show that the mechanical behaviour of the cements improves with the proportion of red gypsum in clinker, the resistance values obtained being very close to those of commercial cement (52.5 MPa). The best values in flexural and compressive strength were in RGC (10 % RG). Our results also indicate that the behaviour of these mortars is similar to, or even better than, those obtained for the other wastes high in gypsum content currently used in cement manufacturing [10, 33, 34]. On the other hand, the addition of a little sludge to the cement (2.5 and 5 %) improves the values of mechanical strength. In particular, after 2 days the addition of 2.5 % sludge did not affect the bending strength but the compressive strength increased by approximately 10 %. After 28 days, these values decreased slightly, although the resistance category of 52.5 was not affected [10].

Fig. 3 Compressive and flexural strength behaviour of cement produced and Ordinary Portland Cement (OPC)

The W/C ratios are all quite similar (Table 4), with no significant differences between the test cements and ordinary Portland cement (OPC). Indeed, the performance results are comparable to those observed in other cements formed with gypsum-enriched waste [33]. Table 4 shows how the incorporation of red gypsum and sludge produces setting times that fall within those required by legislation. For the RGC cement (10 % RG), there is an increase in comparison with commercial cement of 55.4 % (from 139 to 216 min) and 56.7 % (from 224 to 351 min) in the initial and final setting times respectively, similar to the results obtained for other wastes with high gypsum content [30, 34, 35]. By contrast, the hardening times for samples SA (2.5 % sludge) and SB (5 % sludge) are 43 and 35 min respectively, a reduction of 50 and 59 % on the times of the commercial cement taken as reference. Both sets of results fall within the values established in the standard UNE-EN 196-3 [12].

Table 4 Setting times established following a normalized protocol (UNE-EN 196-3) for the various cements and for ordinary Portland cement (OPC) taken as reference

	Optimum W/C	Initial setting time (min)	Final setting time (min)	Δt (min)
RGA	0.286	82	129	47
RGB	0.272	108	298	190
RGC	0.294	216	351	135
SA	0.268	158	201	43
SB	0.274	171	206	35
SC	0.281	203	263	60
OPC	0.266	139	224	85

Optimum W/C ratios are also shown

Sludge as an Additive in the Manufacture of Sulphur Polymer Cements (SPCs). In this section, we report on our investigation into the valorisation and stabilization of sludge as an additive in the manufacture of sulphur polymer cements (SPCs), and in particular, the mechanical properties and potential environmental impact [36]. For the study we used granular elemental sulphur (99.4 wt%, size <60 mm, type Rubber Sul 10) (Repsol-YPF, Madrid, Spain), gravel (<6.3 mm), and a siliceous sand (<4 mm). A modified sulphur-containing polymer, STX (STARcrete™ Technologies Inc., Quebec, Canada), was used as a thermoplastic material. Three SPCs were manufactured with differing amounts of sludge (10, 20 and 30 %w/w: SPC17-10, SPC21-20 and SPC21-30, respectively), and their performance measured against a control, SPC (SPC21-0), with no sludge and a sample of Ordinary Portland Cement (OPC). To prepare the SPCs, the aggregates (gravel, sand and sludge) were first heated in an oven to 135–140 °C for 4 h, and the sulphur was liquefied in a mixing bowl within the same temperatura range for 10 min. Then, these materials were mixed into a homogeneous viscous paste and at this point, STX was added, stirring for 4–5 min at 140–145 °C. Finally, the mix was placed in preheated (120 °C) steel moulds (40 x 40 x 160 mm) over a vibration table set at 3000 rpm for 30 s to compact the cements before storing them at room temperature for 24 h. The hardened SPCs casts were then demoulded.

Figure 4 shows the flexural and compressive strength values and the mechanical behaviour of the cements. As can be seen, performance improves as the proportion of sludge increases, up to 20 %. However, the addition of more sulphur (i.e., in the SPC21-30 mixture) produced a thick layer of sulphur around the aggregates, increasing the brittleness of the final composite. SPC21-20 produces the highest values in terms of flexural and compressive strength, at 13 and 64 MPa,

respectively. These values are similar to, or even better than, those obtained for OPC and other wastes used in SPC manufacture [37–39]. In addition, it is important to note that the mechanical behaviour of the SPC cements is optimum at 24 h, whereas for OPC (ordinary Portland cement) the maximum strength is achieved at 28 days, at which point SPC21-20 returned a WAC value of 0.6 kg m⁻², slightly lower than the 0.9 kg m⁻² of SPC21-0. However, both values are lower than those reported for Portland cements [40, 41]. SPC21-20 would therefore appear to be a very impermeable SPC.

Fig. 4 Flexural and compressive strengths (MPa) and water absorption (kg m⁻²) of the SPCs and Ordinary Portland Cement (OPC)

Sludge as an Additive in the Manufacture of Ceramic. Sludge contains a high level of iron oxide (Fe₂O₃ ≈ 10 %), like red stoneware, which is made from natural clays with a high iron oxide content (Fe₂O₃ > 7 %). This led us to consider its valorisation as an additive in ceramic tiles [42, 43]. Mixtures of a commercial red stoneware (RSM) with different concentrations of sludge (3, 5, 7, 10, 30 and 50 %) were shaped by uniaxial pressing (Nannetti S hydraulic press) at 40 MPa in a steel die, in order to obtain tiles measuring 50 x 50 x 5 mm, which were fired in an electric furnace at 1150 °C following a fast-firing process for eight minutes. The results, shown in Fig. 5, indicate that linear shrinkage increases with the concentration of sludge, with

values < 7 %. Lower values are advantageous because they reduce cracking and volume changes during firing. Also, apparent porosity generally increases with the concentration of sludge. This physical property is very important and is directly related to water absorption [44] and open porosity. Moreover, water absorption decreases with the addition of 3 and 5 % of sludge (2.82 and 2.48 %, respectively), facilitating the subsequent sintering, drying stages, freeze–thaw cycles and stain resistance. The bulk density increases with the concentration of sludge up to 10 % due to the high density of sludge (3.7 g cm⁻³). Bending strength increases with the addition of sludge up to 10 %, due to the beneficial effect of ilmenite on sintering during firing as denoted by the decrease in porosity (Fig. 5). On the other hand, bending strength values in the 70/30 and 50/50 samples decreases due to the increase of interconnecting open pores. In any case, bending strength values for the 7/3 and 95/5 mixtures are above the minimum value of 30 MPa required by standard EN 14411 for tiles in the BIb group. Likewise, the corresponding values for the 100/0, 93/7 and 90/10 samples are greater than 22 MPa, the minimum value for tiles in the BIIa group, while the 70/30 and 50/50 samples produced values above the minimum value of 18 MPa required for tiles in the BIIb group [45].

Waste Products as Fire-Resistant Materials. The characteristics of red gypsum and sludge as additives were examined with a view to their potential as building materials for firewall insulation [21]. A low-cost manufacturing method was used to produce plates measuring 25 x 25 cm, with thicknesses of 1.5 and 2.5 cm, using different compositions (P1: 100 % red gypsum; P2: 75 % red gypsum and 25 % sludge; P3: 80 % red gypsum, 15 % sludge and 5 % vermiculite and P4: 100 % Pladur®). The thermal insulation capacity of the resulting plates was evaluated in accordance with the EN-1363-1 standard.

Figure 6 indicates that plates 1–3 have similar insulating properties, much better and more varied than Pladur, the temperature of which increased rapidly, indicating its very low thermal insulation properties. These results are consistent with other authors [46–52]. The tests demonstrate that plates 2 and 3 have the best capacity for fire resistance within most thermal ranges. Moreover, the addition of sludge significantly improves thermal insulation, mainly due to its highly refractory mineral phases. One final point is that no smoke or odours from the plates were emitted at any time during the test.

Fig. 5 Linear shrinkage and technological properties of fired tiles. Results show average values of 10 measurements

Waste as a Means of CO₂ Sequestration. Finally, red gypsum was evaluated as a source of calcium for CO₂ sequestration by an indirect carbonation process [53]. The process can be conceptually divided into two steps: (a) red gypsum dissolution (Eq. 1), and (b) subsequent carbon sequestration (Eq. 2). In order to induce the carbonation process, the extraction of calcium from the sample was required beforehand. For this, two different extraction routes were applied (the NaOH and NH₄OH pathways). The entire experimental procedure is explained in Eqs. (1) and (2); full details of the methodology can be found elsewhere [54].

Fig. 6 Insulating capacity of the plates tested

Carbonation efficiency was evaluated (Table 5), with the highest values being obtained for NaOH, at approximately 92 %, consistent with other studies [55]. Ammonium hydroxide showed lower efficiencies (64 %), most likely because it is a weak alkali and does not completely dissociate the calcium from the gypsum, thus producing an insufficient concentration of hydroxyl ions to react with the whole sample, and as consequence causing a decrease in the carbonation efficiency.

Table 5 The carbonation efficiency (CE) in different experiments

	CaO (%) ^a	CO ₂ (%) ^b	CaCO ₃ (%) ^c	Experimental mass ^d	CaCO ₃ (%) ^e	CE (%)
RG	28 ± 2		50 ± 4 ^f	50 ± 2	25 ± 2 ^f	
NaOH		31 ± 2	71 ± 4	32 ± 1	23 ± 1	92 ± 6
NH ₄ OH		20 ± 1	46 ± 2	35 ± 1	16 ± 1	64 ± 5

^a Percent of CaO in red gypsum from XRF results

^b Percent of CO₂ in C1 and C2 (product of carbonation process) from TGA results

^c Percent of CaCO₃ calculated from CaO(%) or CO₂(%) data

^d Mass (g) of samples in the experiment

^e Mass (g) of CaCO₃ calculated in the samples from experimental data

^f Data of theoretical CaCO₃ formed from red gypsum

Environmental Implications

In summary, we have seen that TiO₂ industry generates two different co-products (copperas and monohydrate) and two residues (sludge and red gypsum). The environmental and occupational radiological impact of the by-products generated is quite limited (Fig. 2). The negligible environmental impact of copperas and monohydrate holds not only from the radiological point of view. In relation to heavy metals and/or toxic elements (Table 3), the results for copperas indicate that this co-product is relatively free of trace elements, which is not surprising given its formation process (crystallisation). The concentrations of heavy metals found in the copperas are lower than those found in typical soils (see Table 3), with the exception of Zn and, especially, Cd. By contrast, monohydrate presents heavy metals in similar amounts to those found in phosphate fertilizers used worldwide without any environmental restrictions [2].

The management of sludge and red gypsum is one of the most serious problems currently faced by the TiO₂ pigment industry. Both are mixed in the plant and depleted in natural radionuclides, causing a dilution in the radioactivity associated with them.

So as to evaluate the radiological suitability of these wastes for the construction industry, we checked them against the EU reference values for natural radionuclide concentrations in building materials [56]. These values constitute an external risk index (I), also called activity concentration index, and are calculated by the following Eq. (3):

$$I = \frac{C_{^{226}\text{Ra}}}{300 \text{ Bq/kg}} + \frac{C_{^{232}\text{Th}}}{200 \text{ Bq/kg}} + \frac{C_{^{40}\text{K}}}{3000 \text{ Bq/kg}}, \quad (3)$$

where $C_{^{226}\text{Ra}}$, $C_{^{232}\text{Th}}$, and $C_{^{40}\text{K}}$ are the activity concentrations for ^{226}Ra , ^{232}Th and ^{40}K , respectively, expressed in Bq kg⁻¹.

This index should not exceed one ($I \leq 1$) for any material used in bulk quantities, e.g., cement, concrete, etc., and six ($I \leq 6$) for superficial materials, e.g. tiles, boards, and so on, to ensure that the external dosage to which occupants are exposed does not exceed the reference value of 1 mSv year⁻¹ [57]. Figure 7 shows the different index, I, obtained for all the materials analysed. The index (I) for samples RGA, RGB, RGC and SA shows that the value is below one, and consequently, these samples can be used without restrictions. On the other hand, sample SB presents the index slightly above one, while SC has a value close to 2, which is unacceptable

from a radiological point of view. Furthermore, the radiological index for all the SPC cements exceeded 1. Nevertheless, these cements could have other civil construction applications, e.g., in marine platforms or bridges, since their radiological impact on the environment can be considered negligible.

With regard to ceramic and fire-insulating materials (Fig. 7), the index “I” is lower than six for all analysed materials. This renders sludge a suitable material for use in the ceramic industry in comparison with other additives [57].

Fig. 7 Index “I” obtained for all analysed materials in the different applications. The limit I value is indicated according bulk (I B 1) or superficial materials (I B 6) [57]

Finally, to assess the environmental risks associated with the use of waste in the different applications, the TCLP leaching test (Toxicity Characteristic Leaching Procedure, US EPA) was carried out [58] to measure the pollutant (metals and radionuclides) concentrations in the leaching dissolutions. The results of this test were very low and well within the ecotoxicity limits set by the US EPA [58], with concentrations of radioisotopes in the SPC cements of the same order of magnitude as typical continental waters, indicating that their potential radiological impact is negligible [59].

Conclusions

This paper reviews the various waste valorisations developed in recent years by the Radiation and Environmental Research Group (FRYMA). From the results of this work, we can conclude that the research into construction and building materials has demonstrated the viability of the use of waste materials in practical applications.

Red gypsum can be used as a safe substitute for natural gypsum, and the addition of up to 5 % sludge as an additive in the manufacturing of Portland cement did not produce a reduction in the technical properties. Furthermore, the addition of sludge (up to 20 %) in SPC cements improved the mechanical properties used in the construction of non-residential buildings, according the activity concentration index. In addition, the mobility of the original pollutants in red gypsum and sludge are similar to those measured in standard reference cements formed with natural gypsum.

Sludge coming from the TiO₂ pigment production is a good additive (up to 10 %) in the manufacture of red stoneware ceramic bodies, having a beneficial effect to the sintering processes, improving the bending strength (up to 15 %) and reducing both apparent porosity and water absorption (up to 50 %). This waste can be also applied in the manufacturing of fire resistance plates.

Finally, red gypsum can be used as a source of calcium for CO₂ sequestration by an indirect carbonation, obtaining carbonation efficiencies of about 90 and 65 % with NaOH and NH₄OH, respectively. In general, the levels of pollutants in the final calcite were comparable to the ones found for typical unperturbed soils.

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