Recycling wastes coming from the pigment TiO_2 industry

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Abstract

A big factory devoted to the pigment TiO_2 production is located at Huelva city (South-West Spain), which generates big amounts of two wastes. The first one is called “red gypsum” (RG), which is mainly formed by calcium-ferrous sulphates, while the second waste is named “ilmenite mud”,comingfrom the digestion step of the raw material (ilmenite), and for that this contains a high proportion of refractory minerals (zircon, rutile, etc.).

In order to have a deep knowledge of the wastes to be used in their future applications microscopic studies were performed by applying scanning electron microscopy with X-ray microanalysis (SEM–XRMA), while the mineralogical compositions were carried out by means of the X-ray diffraction (XRD) technique. The concentrations of its major elements were determined by X-ray fluorescence (XRF), while heavy metals and other trace elements were ascertained through Inductively Coupled Plasma Mass Spectrometry (ICP- MS).

The results obtained in this work have revealed several lines of research with potential applications. The refractory properties of mineral phases observed in the mud from un-dissolved ilmeniteleading to a possible use in the ceramic industry, oras additive in the manufacture of cement. In addition, the environmental impacts (heavy metals leached and radionuclides content) are practically negligible.

1. Introduction

In the last decades, the recycling of waste material generated in the industrial production processes is being the subject of a deeply research. The protection of health and the environment are of great importance, although the economic benefits accruing from waste recycling cannot be neglected either [1-4]. The minimisation of waste disposal, or of its direct release into the environment, generates not only health and environmental benefits but also could lead to the production of co-products with economic value and broad applications, performing the appropriate treatment in the waste generated.

In this context the recovery of wastes currently generated in most industrial processes is the subject of a thorough investigation [5-7]. One well-known potential use of some industrial wastes is through their incorporation as secondary raw materials in the manufacture of construction materials, as for example in ceramic and cement production [8-12].

Pigment TiO_2 production begins with the mixing of ilmenite (Fe_2TiO_3) with highly concentrated sulphuric acid (80-95%) [13]. The liquor generated goes to a clarification tank where the un-attacked solid –called “ilmenite mud” (MUD) - is allowed to settle. Then this mud is separated from the liquor by a process of decantation and filtration, and finally stored in a safety area. Mud contains enhanced concentration of heavy metals and refractory mineral.

The red gypsum (RG), emerges in the final stage of the industrial process of titanium dioxide manufacturing, where a low acidic liquid stream composed primarily of sulfuric acid (H_2SO_4) and iron sulfates ($FeSO_4$, $Fe_2(SO_4)_3$) is treated in a neutralization plant. In this plant, calcium hydroxide and magnesite are added to the weak acid stream in order to precipitate the dissolved materials in the stream, and the red gypsum is finally obtained by filtration [13]. RG is mainly formed by CaSO4 2H2O as crystalline phase and iron oxides as a amorphous phase.

The magnitude of this generated waste is around 30,000 and 70,000 tons per year of mud and RG, respectively. Currently these wastes have no commercial value and are disposed of in an authorized and controlled repository area.

In addition to note that the feedstock used in the process (ilmenite) presents enhanced levels of radionuclides from the natural uranium and thorium series (about ten times more radioactive than a typical soil), implying this fact that TiO_2 production industry be considered as NORM industry (Naturally Occurring Radiactive Material) [15]. For that, in previous studies [14] it has been obtained that the mud contains a total concentration of radionuclides of about 3000 Bq kg^{-1} in equivalent radium, which is greater than 1 Bqg^{-1}, the reference level to be considered a material as NORM waste by the IAEA [15]. This aspect has to be taken into account in the study of environmental implication when the valorisation is carried out

The main objective of this work is to evaluate the alternative uses of red gypsum and mud in the manufacture of commercial cement and ceramics, trying to cover in each application two objectives. Firstly, to verify that the final products manufactured verify the required technological properties, and secondly to demonstrate that theirenvironmental implications is negligible.

2. Materials and Methods

2.1 Materials

The waste (mud andred gypsum) used in thisstudy werecollected from a titanium dioxide production plant located 12kmfrom the city ofHuelva (southwestSpain). Fivesampling campaignswere organized for a period ofone month, with asampling taking place every six days, to evaluate thepossible temporal variabilityof the characteristicsof these wastes.After collection, all sampleswere dried at60 °C (at this low temperature red gypsum does not lose its hydration), until reachingconstant weightbefore analysis.

The first objective of our work was to check the possibility of substituting natural gypsum for RG as a set retardant in the manufacture of cement, mixtures of varying percentages of RG were added to conventional clinker (YA 97.5% (see Table 1). The properties of these mixtures were compared to those of commercial cement (CEM), which has the following characteristics: its compressive strength category is 52.5 N/mm^2, and is composed of a mixture of clinker (97%) and natural gypsum (3%). The clinker used for the three mixtures with RG is a standard clinker Portland.

Table 1.Proportions of clinker and red gypsum used in the three cements formed for this study. The characteristics of the commercial cement taken as reference are also given.

Name	CEM I, 52.5 N/SR	Clinker	Red Gypsum
CEM	100	-	-
YA	-	97.5	2.5
YB	-	95	5
YC	-	90	10

Once the different raw materials were characterized, we analyzed various mixtures of clinker-RG in order to measure their viability as commercial cements. This evaluation was performed following the test quality protocols established in Spanish legislation.

On the other hand, in the case of mud, several mixtures with commercial red stoneware (RSM [code sample 100/0]) and different concentrations of ilmenite mud (3, 5, 7, 10, 30 and 50%, code samples 97/3, 95/5, 93/7, 90/10, 70/30 and 50/50 respectively) were prepared and studied their main technical properties. This new mixtures were compared with a ceramic commercial, called red stoneware (RSM).

2.2. Methods used for physicochemicaland radioactive characterization

2.2.1. Mineralogy

The mineralogical study was performed by applying the X-ray diffraction technique, and in particular, the disoriented dust method with a Bruker D8 Advance system. For these analyses, we used the k$_{\square}$radiation of Cu, excited by 50 mA of intensity and 40 kV of voltage.The mineralogical quantification of all the analyzed samples was performed using Bruker EVA software with internal standards, noting that this technique is only valid for analyzing crystalline compounds.

2.2.2. Chemical Analysis

The major elements were determined by applying the X-ray fluorescence (XRF) technique with a Philips PW-1004 X-ray system equipped with a tube of Sc-Mo and five different analyzer crystals. The spectra obtained were analyzed using super-Q manager software.

As this technique requires a maximum homogenization of the sample to be analyzed, the procedure was as follows: one gram of each dry sample and 10 grams of lithium tetraborate (material used for melting) were mixed with five drops of lithium iodide at 20%. Each mixture was then placed in a crucible of Pt-Au, and set in a special furnace to fuse the sample. The final result was homogeneous glass samples ready for measurement. DNC-1 Standard has been used, and the different between the certificated and determinate values is less than 4.8%.

The inductively coupled plasma mass spectrometry (ICP-MS) technique was used to determine the trace elements. The determinations were achieved following the total dissolution by microwave acid digestion (hydrochloric, hydrofluoric, nitric and percloric acids) of the samples, and their later dilution for placement in the ICP-MS system as 2% nitric acid solutions. SRM 1643-e standard has been used and the different between the certificated and determinate values is around 2-10%.

2.2.3. Laser granulometry

The grain sizeanalysis have been performed by using a Sympatecdiffractometer that operates in a range between 0.90 and 175 µm. This technique is based on the incidence of a monochromatic laser beam through a non-reactive liquid carrying the sample to be analyzed. To provoke the total dispersion of the samples in the non-reactive liquid, isopropylic alcohol was used to remove the electronic and Van der Waals forces between the particles.

2.2.4. Radiometric measurements

Gamma measurements were carried out using an XtRa coaxial Ge detector (Canberra), with 38% relative efficiency and FWHM of 0.95 keV at the 122 keV line of ^{57}Co and 1.9 keV at the 1333 keV line of ^{60}Co. The detector was coupled to a conventional electronic chain, including a multichannel analyser and was shielded with Fe 15 cm thick.

Th and U isotopes activity concentrations were determined in the samples by alpha-particle spectrometry. For the determination of these isotopes by alpha-particle spectrometry in the samples, a sequential well-established radiochemical method to the samples was applied [16]. In this method, the isotopes are electrodeposited onto stainless steel planchets after its isolation from the bulk matrixes. The planchets were measured using an EG&G Ortec alpha spectrometry system with ion-implanted silicon detectors. Counting times ranged from 2 days to 4 days, depending on the activity concentrations and the recovery obtained in the chemical separation.

2.2.5. Pollutant mobility tests

To assess the risks of the use of twowastes, from an environmental perspective, the TCLP leaching test (Toxicity Characteristic Leaching Procedure, USEPA) was carried out [17]. The pollutant concentrations in the leaching dissolutions obtained from the mobility tests were analyzed by ICP-MS. In addition, the concentrations of different radionuclides contained in the leaching dissolutions were analyzed by both alpha and gamma spectrometry techniques.

2.3. Methods to evaluate the generated new cements

In order to measure the setting times and water cement ratio, a normalized Vicat apparatus with a rod 50 mm in length and 10 mm in diameter was used for this purpose, and various moulds of the three mixtures were fabricated with different W/C proportions. All the moulds were 40 mm in height, and in the shape of a truncated cone with lower and upper diameters of 70 and 80 mm, respectively. For each mixture, the optimum W/C ratio corresponded to the penetration of the rod in the mould to a depth of 34 mm.

The setting times of the three cements formed by using different proportions of red gypsum as an additive were also obtained with a Vicat apparatus, equipped in this instance with a normalized noodle with a 1.13 mm diameter. All the cements were analyzed as pastes formed with the previously determined optimum W/C ratios. The national protocol for achieving setting times is UNE-EN 196-3 [18], which is based on the study of the depth of penetration of the noodle in the mould at different positions.

For the mechanical resistant test, mortars (sand and cement mixed in a proportion of 3:1) were used to conduct tests to evaluate the compressive and flexural strength of the cements formed with RG. These mortars were made from sand with a SiO_2 content of about 99% in mass.

Once the different mortars were formed, their binding and compressive resistances were measured in prismatic test samples (40 x 40 x 160 mm) 2 and 28 days after their formation, EN 196-1 [19]. Flexural resistance was determined by applying the method of centered and concentrated loads to the prismatic samples, while the compressive tests were performed using the broken prismatic samples in the flexural tests, over surfaces of 40 x 40 mm.

Mortar samples (under the same conditions and sand/cement proportions as for the mechanical tests) were also made to determine the linear retraction in the RG cements that occurs due to their progressive dryness. The mortars were tested in accordance with regulation ASTM C 596-89 [20]. Special moulds were filled with the mortar samples for this purpose, as described in this protocol.

2.4.Technological characterization of new obtained ceramics

In relation with the use of mud in ceramics, different properties of the material was measured and compared with a commercial ceramic material. The sintering behaviour of tiles was evaluated on the basis of water absorption, apparent porosity and bulk density. The water absorption was measured according to EN ISO 10545-3 [19] for ten representative specimens. The water absorption coefficient, E (dry wt.%), was calculated by the equation:

$$E = [(m_2 - m_1)/m_1] \times 100 \qquad [1]$$

where m_2 (g) is the mass of wet specimen and m_1 (g)is the mass of dry specimen.

In addition, the apparent porosity and the bulk density were measured according to ASTM C373-88 [20], which involves drying the test specimens to constant mass (D). The test was carried out on ten representative specimens. After impregnation, the mass (S) of each specimen while suspended in water and their saturated mass (M) was determined. The apparent porosity, P (%), expresses the relationship of the volume of open pores with the exterior volume of the specimen and is calculated as follows:

$$P = [(M - D)/(\rho \cdot V)] \times 100 \qquad [2]$$

where V (cm^3) is the exterior volume (V = M - S) and ρ is the density of the water 1 g cm^{-3}.

The bulk density, B (g cm^{-3}), of a specimen is the quotient of its dry mass divided by the exterior volume, including pores:

$$B = D/V \qquad [3]$$

Linear shrinkage, LS (%), was calculated by the equation:

$$LS = (L_i - L_f) \times 100/L_i \qquad [4]$$

where L_i (mm) is the specimen lengthwithout firing and L_f (mm) is the specimen lengthafter firing.

On the other hand, bending strength, BS (MPa), was measured according to EN 843-1 [21] in an electronic universal tester (Servosis model ME-402/01) on ten test specimens for each sintered temperature by a three-point loading test with a span of 32 mm and a crosshead speed of 1 mm/min.

3. Results and discussion

3.1. Characterization of wastes

In the ilmenite (raw material)analysed samples, the following species remain dominant: ilmenite ($FeTiO_3$), rutile (TiO_2) and pseudo-rutile ($Fe^{3+}_2Ti_3O_9$), while in the mud sample several crystalline phases are observed asilmenite ($FeTiO_3$) and rutile (TiO_2) as main components, which are minerals remaining from the used raw material. Additionally otherphases are detected such as zircon ($ZrSiO_4$), quartz (SiO_2), and Fe and Ti oxides ($Fe_3Ti_3O_{10}$). The presence of rutile and the detection in the mud of the aforementioned mineral phases (zircon and quartz) cannot be considered as surprising, since all of these speciespresent in the raw material,are insoluble in sulphuric acid[21]. Finally, we have to highlight an important feature of this waste; all mineral phases are highly refractory. This condition reveals interesting perspectives for the analysis of their possible use in ceramic.

In the red gypsum sample, the crystalline phases observed are mainly gypsum or calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) and iron and titanium oxides. We must consider that this type of analysis the amorphous sample is not detectable. It can be shown, based on the composition of the major elements and their stoichiometry, the sample of red gypsum is made approximately 76% of $CaSO_4{\cdot}2H_2O$, indicating that comprises approximately 24% of amorphous phase [13].

Table 2 shows the concentrations of major elements (%) of the studied samples. In relation to the majority metals, ilmenite has the following composition: Fe_2O_3 (44 %) and TiO_2 (~50 %), with low percentages of SiO_2 (0.7 %), MnO (1.3 %) and MgO (0.33 %), [22]. In addition, ilmenite mud is mainly composed of TiO_2 (53 %), which corresponds to approximately with the 5 % of total input of titanium contained in the ilmenite (raw material). Moreover, contains a high percentage of SiO_2 (18 %), coming from the quartz phaseand ZrO_2 (2.1 %) associated with the zircon phase. The high content of Fe_2O_3 (11 %) comes from the iron and titanium oxides ($Fe_3Ti_3O_{10}$) and ilmenite ($FeTiO_3$), previously identified as crystalline phases in XRD analysis.

Table 2. Concentration (%) of major elements in the materials under study. The total iron content is given as Fe2O3. (*) Continental crust composition[23].The uncertainty is given by the standard deviation of the mean.

	Ilmenite	Mud	Red gypsum	(*)
SiO_2	0.85 ± 0.09	18 ± 1	1.2 ± 0.2	67
Al_2O_3	0.71 ± 0.09	2.5 ± 0.2	1.4 ± 0.2	15
Fe_2O_3	44 ± 1	11 ± 1	14 ± 2	5.0
MnO	1.3 ± 0.1	0.36 ± 0.01	0.35 ± 0.04	0.10
MgO	0.32 ± 0.07	0.38 ± 0.02	1.4 ± 0.2	2.5
CaO	0.05 ± 0.01	0.75 ± 0.01	33 ± 2	3.6
TiO_2	49.6 ± 0.3	53 ± 1	7.6 ± 1.2	0.64
SO_3	<0.01	6.1 ± 0.7	27 ± 1	-
ZrO_2	0.15±0.03	2.1 ± 0.4	< 0.01	0.02
LOI	<0.01	< 0.01	13 ± 1	-

On the other hand, the composition of red gypsum is expected according to the bibliography [13] and consistent with their mineralogy, having as major components SO_3 and CaO, with 27 and 33% respectively, quite similar to natural gypsum [24]. Moreover, we must remember that this waste is generated by neutralization of the weak acid effluent obtained in the latter stages of washing and leaching of TiO_2 pulp with calcium hydroxide and magnesite ($MgCO_3$). This explains the appearance of a high content of titanium in this waste, 7.6% TiO_2. This weak acid is also composed of sulfuric acid (H_2SO_4) and trace amounts of iron sulphate.

Trace element concentrations for each waste sample, together with the average concentrations found for the same elements in the raw material, are compiled in Table 3.For comparison purposes, the same table also shows the average concentrations of the same elements which can be associated to a typical soil (continental crust composition) since the wastes (mud and RG) under analysis can reach through their potential applications the environment, and the levels of metals and other compounds form the samples should not greatly exceed those found in uncontaminated soils in order to assure minimal environmental impact.

Table 3. Average compositions of trace elements (ppm). (*) Continental crust composition. [23]. The uncertainty is given by the standard deviation of the mean

Elements	**ILMENITE**	**MUD**	**RG**	**Soil***
Cr	344 ± 134	518 ± 51	133 ± 8	92
Co	59 ± 14	16 ± 3	12 ± 1	17.3
Ni	15 ± 5	13 ± 1	31 ± 8	47
Cu	41 ± 13	278 ± 18	12 ± 1	28
Zn	296 ± 63	193 ±21	225 ±3 0	67
As	22 ± 5	57 ± 11	12 ± 1	4.8
Cd	2.7 ± 0.7	0.60 ± 0.11	1.04 ± 0.09	0.09
Pb	135 ± 23	278 ± 16	35 ± 5	17
Th	97 ± 19	70 ± 8	30 ± 2	10.5
U	6.5 ± 1.5	7.9 ± 0.9	1.70 ± 0.29	2.7

In the aforementioned Table it is observed that trace element concentrations for the raw material samples are relatively uniform, and only average values are presented. The Co and Cd concentrations are a factor of approximately 3-4 times higher in the raw material than in mud, while other elements, such as Cr, Cu, As, Pb, and U, present clearly lower concentrations in the raw material. On the other hand, most trace elements analysed in the mud samples, such as Cr, Zn, As, Cd, and Pb, show high enrichment factors: 6, 3, 12, 7 and 16 respectively, in relation to a typical soil,Table 3. It is also interesting to point out that the concentration of Th in the mud samples is high, with values of 70 mg/kg, 6-7 times higher than a typical soil, but lower than the concentration found for the raw material. At the same time, the concentration of U in mud is relatively high, 7 times higher than in undisturbed soils, and higher, by a factor of 2-3, than in the raw material.

In relation with RG,comparing the results in Table 3, we observe that the majority of heavy metal concentrations in the RG are similar or slightly upper than in the reference soils, with the exception of Co and Ni, and are similar to data in the literature [13,25]. Also of interest arethe relatively high levels of thorium found in the RG, which is not surprising given that the raw material used in the titanium dioxide pigment industry (ilmenite) is practically a NORM material (mineral enriched in natural radionuclides).

In addition, one very important aspect to take into account in cement and ceramics industries is the grain size of the materials used. The data obtained shows that RG has a maximum granulometric distribution of around 40 µm, while in the mud sample the 89 % of the particles are below of 60 µm. These results clearly indicate that both studied wastes can be used in the selected applications.

Finally, and taking into account that the titanium dioxide pigment is a NORM industry, it is necessary a radiological characterization of the wastes.In Table 4, we can see that ilmenite is a NORM mineral due to its enrichment in natural radionuclides from the Th and U series, with a total concentration of some 500 Bq kg^{-1} for ^{238}U and ^{232}Th, around 20 times upper than a typical undisturbed soil (20-30 Bq kg^{-1}) [26].

Table 4. Average concentrations of dry Bq kg^{-1} activity of natural radionuclides in the ILM, MUD and RG samples.

	^{238}U	**^{226}Ra**	**^{232}Th**	**^{228}Ra**	**^{40}K**
ILM	95 ± 10	86 ± 5	315 ± 20	301 ± 20	30 ± 5
MUD	91 ± 5	457 ± 19	78 ± 3	1158 ± 48	477 ± 30
RG	20 ± 1	14 ± 1	127 ± 3	91 ± 3	12 ± 2

The radioactive content for RG is moderate, indicating that a minority fraction of the content in the treated raw material is accumulated in this co-product, for example 127 Bq kg^{-1232}Th and 91 Bq kg^{-1} for ^{228}Ra. No radiological concern then appears associated to the potential use of RG in cement.However, the activity concentrations in the mud samples are far from negligible, which implies that this waste should also be considered and treated as a NORM. The mud contains a total concentration of radionuclides greater than 1 Bq/g [15], which is a considerable fraction of the radioactivity content originally present in the raw materials. In fact, it is possible to deduce that practically all the radium present in the raw material is associated to the mud sample. This fact can be explained by taking into account the insolubility of radium as sulphate [21], which is the existing medium in the digestion step (concentrated sulphuric acid).

3.2. Application of red gypsum in cement manufacture

The first step after the formation of the three dried mixtures of clinker with red gypsum (see Table 1) was to determine the appropriate water/cement (W/C) relation in weight terms for obtaining a “normal” consistency of the paste formed, as defined in the UNE-EN 196-3 regulation in the Spanish law. A normalized Vicat apparatus was used for this purpose, and various moulds of the three mixtures were fabricated with different W/C proportions. All the moulds were 40 mm in height, with a shape of a truncated cone with lower and upper diameters of 70 and 80 mm, respectively. For each mixture, the optimum W/C ratio corresponded to the penetration of the rod in the mould to a depth of 34 mm.

The optimum W/C ratios for the three different cements formed with red gypsum are shown in table 5. This table also presents the optimum W/C ratio obtained for the commercial cement used as reference. All the W/C ratios are quite similar, with no significant differences found between the commercial and red gypsum cements.

Table 5. Setting times determined following a normalized protocol for the various cements formed by using different proportions of red gypsum. For comparison, the setting times determined for the commercial cement taken as reference in this work are shown.

Sample	Optimum W/C	Initial setting time (min)	Final setting time (min)
(CEM) Commercial cement	0.27	139	224
YA (2.5% RG)	0.29	82	129
YB (5% RG)	0.27	108	298
YC (10% RG)	0.29	216	351

The data show that the addition of red gypsum in the proportions used in this work leads to setting times that are within those required by national legislation (initial setting time > 45min and final setting time <720 min), and it is noteworthy that the initial and final setting times are prolonged by increasing the proportion of red gypsum used as an additive in cement fabrication, further underlining the role of red gypsum as a retardant in the hardening of cement. Adding higher percentages of red gypsum extends the initial and final setting times. For the YC cement (10% red gypsum) these increases are of 55.4% (from 139 to 216 min) and 56.7% (from 224 to 351 min) in the initial and final setting times, respectively, in relation to the commercial cement.

In relation with mechanical resistance tests, mortars (sand and cement mixed in a proportion of 3:1) were used to conduct tests to evaluate the compressive and flexural strength of the cements formed with red gypsum. These mortars were made from sand with a SiO_2 content of about 99% in mass. The binding and compressive resistances of the mortars were measured in prismatic test samples (40 x 40 x 160 mm) 2 and 28 days after their formation. Flexural resistance was determined by applying the method of centered and concentrated loads to the prismatic samples, while the compressive tests were performed using the broken prismatic samples in the flexural tests, over surfaces of 40 x 40 mm.

The resistances to flexion and compression determined through these tests for the three red gypsum cements analyzed in this work are given in Table 6. Each result in this table is the average of three tests performed on three different samples formed from the same paste. The same table also shows the comparative results for the commercial cement (CEM).

Table 6. Values of flexural and compressive resistances (MPa) determined in the three types of red gypsum cements analyzed in this work. For comparison, the results obtained with the same tests for the commercial cement (CEM) taken as reference are also shown.

Sample	W/C	Flexural strength		Compressive strength	
		2 days	28 days	2 days	28 days
Comercial cement (CEM)	0.40	6.8±0.33	10.1 ± 1.2	34.4 ± 0.4	61.3 ± 1.0
YA (2.5% red gypsrum)	0.54	4.2±0.15	9.8 ± 0.6	17.8 ± 0.3	51.7 ± 0.6
YB (5% red gypsum)	0.52	5.4±0.25	8.2 ± 2.7	23.1 ± 0.3	57.9 ± 1.0
YC (10% red gypsum)	0.52	7.6±0.80	10.8 ± 0.8	31.5 ± 0.8	59.6 ± 1.5

The critical evaluation of the results in Table 6 leads to the following conclusion: it seems that the mechanical behaviour of the cements formed improves when more red gypsum is added to the cements, thereby approaching the resistance values of the commercial cement. In fact, in the YC sample (10% red gypsum) the mechanical resistance values are similar to those for the commercial cement. This is important, as it supports the use of red gypsum as an additive in the formation of cements and because it is possible to reduce the amount of clinker used, with all the economic benefits that this entails (cost savings). In this sense, it is necessary to remember that the commercial cement taken as reference in our study is approximately 97% clinker and 3% natural gypsum.

In addition, mortar samples (under the same conditions and sand/cement proportions as for the mechanical tests) were made to determine the linear retraction in the red gypsum cements that occurs due to their progressive dryness. The mortars were tested in accordance with regulation ASTM C 596-89: “Standard Test Method for Drying Shrinkage of Mortar Containing Portland Cement”. The linear retraction values were determined in prismatic test samples (25.4 x 25.4 x 287 mm), and the results from the three red gypsum cements and the commercial cement are shown in Figure 1.

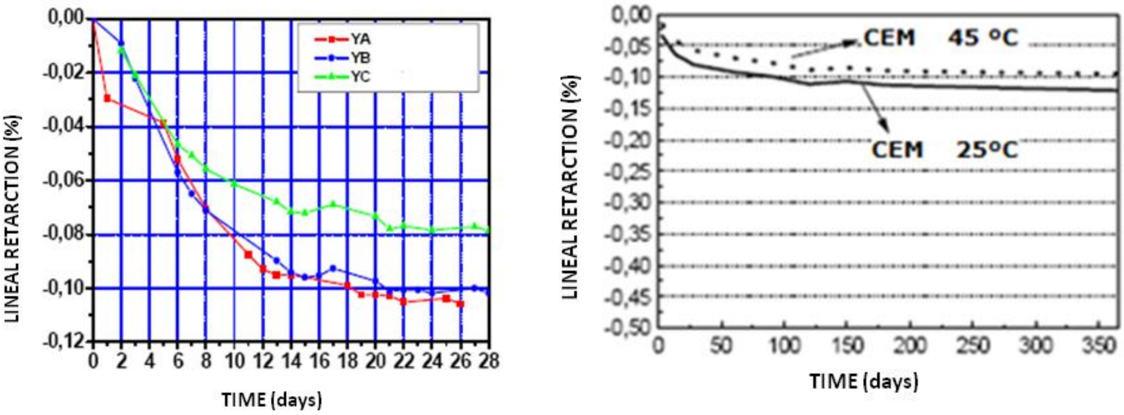

Figure 1. Linear retraction curves obtained for the three cements formed with red gypsum (left). For comparison, the linear retraction curves for the commercial cement at 25 °C y 45 °C are also shown (right).

Here we observe how the major retractions occur during the first days of reaction. Then as the cement hydratationtimes progress, the linear retractions diminish until to be practically constant in the final days.The results also show that the addition of red gypsum to the clinker improves the linear retraction of the cements formed in comparison to the commercial cement. As higher percentages of red gypsum are added to the cement, lower retractions are produced.

Finally, we have assessed the environmental impact of the use of red gypsum in cement manufacturing. Table 7 shows the critical concentration values and leachability test results from the RG cements, YC and CEM samples.

Table 7. Critical concentration values [27] and leachability of metals from the RG cements YC, RG sample and reference cement (CEM).

Concentration in solid samples (mgkg^{-1})			**Leaching TCLP test (μg L^{-1})**		
Element	Critical concentration	RG	RG	YC	CEM
As	20-50	10	1.8	1.9	1.1
Cd	3-8	1	<0.1	<0.1	<0.1
Co	25-50	16	65	<0.1	<0.1
Cr	75-100	109	103	82	89
Ni	100	30	176	4.1	3.3
Pb	100-400	19	8.0	8.3	2.9
Zn	70-400	212	-	-	-

As observed in this table, RG metal concentrations are lower than the ecotoxicity limits. Only Cr concentration is slightly higher than this threshold. On the other hand, the chemical mobility (i.e. leachability) of the trace elements from the cement is also important for the evaluation of the potential environmental impact. TCLP test is extensively used to characterize hazardous potential of wastes. In this regard, some metals such as Cr(VI) can be readily released from the cement phase into the mixing water while the weathering of the hardened cement paste under the influence of rain water, ground water or other factors such as biological activity which leads to the mobility of metals from the cement. Due to the high toxicity of hexavalent Cr, a European directive [28] has been issued limiting the content of water-soluble Cr (VI) in cement to a maximal concentration of 2 mgkg^{-1}.

In Table 7 are shown the lixiviation results carried out to the sample YC (10% RG), to the reference cement CEM and to the RG sample. It is possible to observe that in any test, i.e for any analyzed sample, the Cr concentration in the leachate is not higher that the limit value of 2 mg kg^{-1} established in the regulation [28].

3.3 Application of ilmenite mud in the manufacture of ceramic as additive

In order to carry out the evaluation of the ilmenite mud in ceramic, several mixtures with red stoneware (RSM) were prepared, as we mentioned in material section. The mixtures moistened by spraying with distilled water (6 wt %) and then shaped by uniaxial pressing (Nannetti S hydraulic press) at 40 MPa in a steel die, to obtain tiles measuring 50 x 50 x 5 mm. These tiles werefired in an electric furnace at 1150 ºC for eight minutes following the fast-firing process recommended by the red stoneware supplier.

The RSM analysis reported mainly SiO_2 (62 wt.%), Al_2O_3 (20 wt.%), Fe_2O_3 (7.4 wt.%), K_2O (4.2 wt.%) and CaO (2.1 wt.%), and trace elements (As, Cr, Cu, Pb, Cd and Zn) containing concentrations below 0.1% .

In relation with technological properties, Table 8indicate that the linear shrinkage increases due to the concentration of ilmenite mud also increasing. Lower values are advantageous for traditional ceramics manufacturing because it reduces cracking and volume changes during firing. The linear shrinkage of samples fired at 1150 °C showed values < 7%.

Table 8. Linear shrinkage and technological properties of fired tiles.The averagesand standard uncertainties were calculated by using 10 measurements.

RSM/MUD	Linear shrinkage LS (%)	Apparent porosity P (%)	Water absorption E (wt.%)	Bulk density B (g·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

The apparent porosity generally increases with the concentration of ilmenite mud; therefore the water absorption also follows this trend as both properties are directly related. Moreover the water absorption decreases by adding 3 and 5% of ilmenite mud (2.82 and 2.48 wt.% respectively), facilitating the sintering. In accordance to the European Standard EN 14411 [29] the products with water absorption coefficient (E) $0.5\% < E \leq 3\%$ belongs to the BI_b group and the materials with $3\% < E \leq 6\%$ belongs to the BII_a group.

The bulk density increases with the concentration of ilmenite mud until 10%. It is due to the density of un-dissolved mud is 3.7 $g \cdot cm^{-3}$.When it is higher than 30% of mud it decreases radically, due to the increase in the porosity.The bending strength increased with the sintering due to the decreasing of porosity. The addition of mud up to 5%, table 8, lowers the rupture tension due to the increasing in porosity. These results are upper 30 MPa, minimum value required in standard EN 14411.

The study of environmental implications is necessary, because as we saw previously, ilmentemud had a total radionuclide concentration (2.0–3.0 Bq g^{-1}) that surpassed the 1 Bq g^{-1} EU safety thresholds for naturally occurring radioactive material (NORM) wastes (IAEA). The radionuclides with the highest activity concentrations were ^{226}Ra and ^{228}Ra at around 800 and 2500Bq kg^{-1} respectively, table 4. In the mixtures, the activity concentration of these radionuclides increased with increasing mud content, as did those of ^{228}Ra, ^{228}Th, and ^{238}U, while the activity concentration of ^{40}K is practically constant, table 9.

Table 9. Concentration in $Bqkg^{-1}$ of each simple analyzed by alpha and gamma spectrometry. External risk rate "I" in samples and raw material

	^{238}U	**^{226}Ra**	**^{232}Th**	**^{228}Ra**	**^{40}K**	**"I"**
100/0	35 ± 2	50 ± 1	60 ± 2	61 ± 2	1104 ± 16	0.84
97-3	37 ± 2	55 ± 1	62 ± 2	97 ± 3	1154 ± 15	1.05
95-5	44 ± 2	72 ± 2	59 ± 2	127 ± 4	1182 ± 18	1.27
93-7	40 ± 2	79 ± 2	59 ± 4	141 ± 5	1158 ± 23	1.35
90-10	37 ± 2	75 ± 2	63 ± 5	139 ± 5	1124 ± 24	1.32
MUD	91 ± 6	457 ± 19	78 ± 3	1158 ± 48	477 ± 30	7.47

The radioactive content of the mud samples introduces the question of whether this waste can be valorised as building material. To this end, European Union proposes reference values for the natural radionuclide concentrations in building materials [30], defining an external risk index (*I*), also called activity concentration index, Equation (5).

$$I = C(^{226}Ra)/300 + C(^{228}Ra)/200 + C(^{40}K)/3000 \qquad [5]$$

where $C^{226}Ra$, $C^{228}Ra$, $C^{40}K$ are the concentrations of the activities of ^{226}Ra, ^{228}Ra and ^{40}K respectively, expressed in $Bqkg^{-1}$.

This index should not exceed the value $I \leq 1$ for materials used in bulk amounts, e.g. concrete, or $I \leq 6$ for superficial materials and those with restricted use, e.g. tiles, boards, etc., to ensure that the additional external dose received by occupants living in buildings constructed with these materials do not exceed the reference value of 1 mSv $year^{-1}$.Table 9 shows that in the sample tiles, index I is significantly lower than the reference value of 6. This fact makes the un-dissolved mud a material to be used in the ceramic industry in comparison to other additives [31-32].

Finally, the TCLP test was carried out to evaluate the potential environmental impact generated by hazardous metals contained in the ceramics tiles. Table 10 shows that the amount of leached metalsincreases with the proportion of mud. Attending to these data is concluded that the firing process makes metal less leachable. The leached metals values are clearly lower than the limits imposed by US EPA [17]; these data indicate that the metal concentrations are below the limits, and will not have a significant impact when this material is released into the environment.

Table 10. Leachability concentrations of metals (μgL^{-1}) obtained by TCLP test from the raw materials and tile. Transfer factor (%) into liquid phase of TCLP. Limit values given in the U.S. EPA standard.

	RSM		**97/3**	**95/5**	**93/7**	**90/10**		**MUD**		**U.S.EPA**
	$\mu g \cdot L^{-1}$	*%*	$\mu g \cdot L^{-1}$	$\mu g \cdot L^{-1}$	$\mu g \cdot L^{-1}$	$\mu g \cdot L^{-1}$	*%*	$\mu g \cdot L^{-1}$	*%*	$\mu g \cdot L^{-1}$
As	110	2.0	40	40	60	60	4.0	< 30	0.46	5000
Cd	22	*N.M.*	24	24	23	23	*N.M.*	< 2	*N.M.*	1000
Cr	200	0.58	200	200	240	220	3.41	< 20	0.04	5000
Fe	2100	0.01	3220	3200	3040	3000	10.93	40	0.01	**-**
Pb	100	0.51	300	20	150	110	3.24	< 10	0.07	5000
Sr	60	1.11	60	50	40	40	0.71	< 10	0.15	**-**
Ti	< 10	0.01	< 10	20	< 10	< 10	0.02	10	0.09	**-**
Zn	41	0.31	138	103	122	101	0.75	6	0.77	25000

4. Conclusions

The present study was focused on the characterization of two waste (red gypsum and mud) generated in the industry of titanium dioxide pigments, pretending to study their behaviour and environmental implications in the manufacture of commercial cement and ceramics.

After a detailed physicochemical characterization of the raw materials and cements usedin the manufacturing of the cements and ceramics of this work, and the performance of an ample set of physico-mechanical and chemical tests, it has been demonstrated thatRG can be safely applied as a substitute for natural gypsum in the fabrication of commercial cements without decreasing the quality of the cements generated, and without causing any environmental impact. A proportion of RG as high as 10% could be used forthe manufacture of cements complying with all the quality requirements of theSpanish legislation. In addition, the availability and low cost of RG make it attractive as raw material for the production of cement with further benefits including the mitigation of the waste management problems associated with their disposal and pollution control, and the likely reduction in operating costs i.e. mining and raw material processing costs.

In the use of mud in ceramics, the technological properties are compatible or even better than the commercial sample taken as reference. We have demonstrated that he addition of ilmenite mud as additive (3-7%) has a beneficial role as agent in sintering, decreasing both the apparent porosity and water absorption. These facts facilitate the drying stage through the decrease in the water absorption. The BI_a group is formed by the addition of 3-5% of un-dissolved mud, with a water absorption of $0.5\% < E \leq 3\%$and required a minimum bending strength of 22MPa (tiles obtained exceed this value). The other group (BII_b), is formed by the tiles 93/7 and 90/10, with a water absorption of $3\% < E \leq 6\%$ and a minimum bending strength of 18MPa, tiles that exceed clearly this minimum value.

Finally, in both applications, the environmental implication (heavy metals leached and radionuclides content), are practically negligible.

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