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CHARACTERIZATION AND VALORISATION OF NORM WASTES; APPLICATION TO THE TiO_2 PRODUCTION INDUSTRY

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Abstract

The present study was focused to characterize the raw materials, wastes and several co-products from titanium dioxide industry, in particular their elemental composition (major, minor and trace elements), mineralogy, and radioactive contents, with the objective to apply this knowledge to valorize these materials in fields such as construction, civil engineering, fertilizers manufacturing, etc.

Keywords: Ilmenite, red gypsum, waste, valorisation, titanium dioxide.

INTRODUCTION

The recycling of waste material generated in the majority of industrial production processes is the subject nowadays of more and more research for several reasons. The protection of health and the environment are of great importance, although the economic benefits accruing from waste recycling cannot be neglected either [1–2]. The minimization of waste disposal, avoiding its direct release into the environment, generates not only health and environmental benefits in several industrial processes, in addition to the generation of the main product; the appropriate treatment of a fraction of the waste generated could lead to the production of co-products with economic value and broad applications [3].

There is a paradigmatic NORM industry (NORM = Naturally Occurring Radioactive Material) hat applies widely the recycling strategy. It is located in the province of Huelva and produces titanium dioxide pigments, and two different co-products obtained as a consequence of the treatment of waste generated throughout the process.

Two raw materials are used as feedstock in titanium dioxide production at the Huelva factory: ilmenite ($FeTiO_3$) and slag. Ilmenite is a heavy mineral containing approximately 43–65 % titanium dioxide [4], and can be considered as a NORM material because generally contains enhanced amounts of uranium and thorium depending deeply from this geological origin. The titaniferous slag, which contains 70–80 % in titanium dioxide, is a co-product resulting of the smelting of ilmenite [5]. The oldest and most common process for titanium dioxide production is the sulphate process (see Fig 1), being its main steps the followings:

1. Digestion of the ore (*batch operation*): A carefully controlled blend of illmenite and slag is mixed with highly concentrated sulphuric acid (80–95 %) to digest the TiO_2 containing feedstock.
The resulting liquor contains titanyl sulphate ($TiOSO_4$) and iron sulphate ($FeSO_4$) dissolved in sulphuric acid. To ensure that all the Fe is in dissolution, the liquor is passed through a bath of scrap metal (Fe reduction step).

2. Clarification of the resulting liquor: The reduced liquor flows into a clarification tank where the un-dissolved solids (mud) are separated from the solution by flocculation and filtration.

3. Titanium dioxide precipitation: The clarified liquor is then hydrolyzed in order

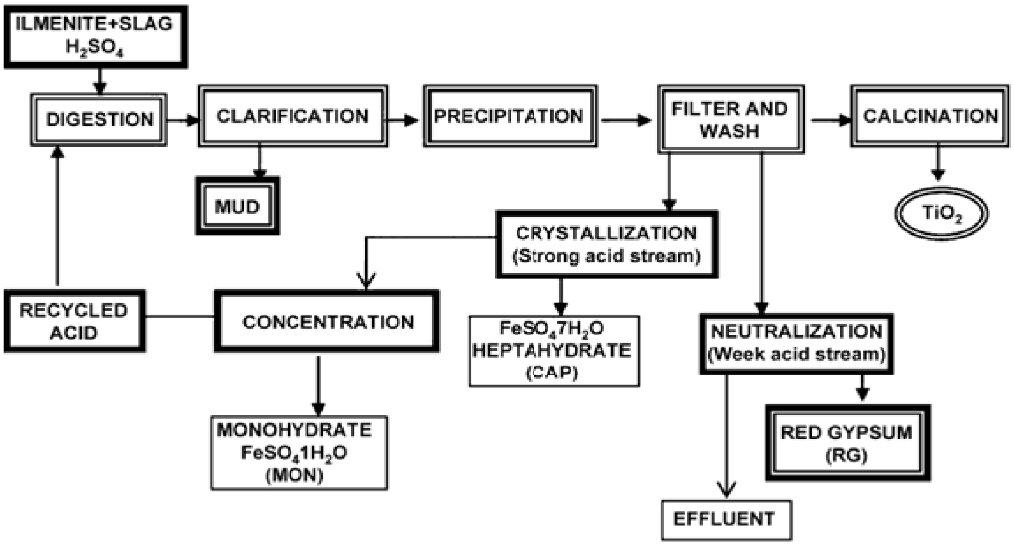

Figure 1. Diagram of the sulphate process used in the Huelva factory for TiO_2 production.

to produce the precipitation of hydrated titanium.

4. Hydrated TiO_2 separation: The hydrated TiO_2 after its precipitation is separated from the mother liquor by vacuum filters (called “Moore filters”).This liquor can be considered one by-product, and it is treated for the generation of two co-products, as will be detailed later.

5. TiO_2 washing: After the separation of the mother liquor, the filtered TiO_2 cake is washed with water in order to remove the remaining impurities. The generated weak acid solution used in this final wash can be considered, in principle, a waste of the process.

6. The TiO_2 pulp is then placed in rotary kilns for the removal its water content and some traces of sulphur. The resulting solid is cooled, milled, coated, washed, dried and finely ground (“micronized”), before be it packed for commercial distribution.

Initially, the first by-product, i.e. the mother liquor (“strong” acid, 20–25 % H_2SO_4) is pumped into a batch cooler crystallizers, where the iron is removed as solid ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$). This constitutes the first co-product of the TiO_2 process, commonly known as cooperas (CAP). The remaining strong acid is then re-concentrated for its reuse in the initial digestion step, being precipitated in this process ferrous sulphate monohydrate (MON), forming a second co-product that is separated by filtration. Then, the resulting clean sulphuric acid can be recycled and be introduced in the illmenite digestion step.

On the other hand, the weak sulphuric acid coming from the washing of the TiO_2 pulp, it is also processed by sending it into a neutralization plant, where by the addition of lime, or limestone, to the weak acid stream, it is generated a solid waste called red gypsum (RG), which is formed mainly of di-hydrated calcium sulphate ($CaSO_4{\cdot}2H_2O$) and iron hydroxides, which give it a red color, according to the following reactions:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4{\cdot}2H_2O$$

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$$

The magnitude of the co-products generated at the Huelva factory is reflected clearly in the following figures: annually, around 142,000 t of raw material are processed (85 % illmenite and 15 % slag), with the generation of 70,000 t of RG, 140,000 t of CAP and 125,000 t of MON.

EXPERIMENTAL

The samples of raw materials (illmenite and slag), co-products (CAP and MON) and the waste (RG) used in this study have been collected from a titanium dioxide production plant 12 km from the city of Huelva, in south-western Spain. Five sampling campaigns were organized during a period of 1 month, taking theses mentioned samples every 6 days in order to analyze the possible temporal variability in the industrial process. After collection, the raw materials were dried at 105 °C until reaching a constant weight, while the co-products and RG were dried at 45 °C to avoid the loss of their hydration water.

The mineralogical compositions were analyzed by means of the X-ray diffraction (XRD) technique. The concentrations of major elements, heavy metals, and other trace elements were determined by X-ray fluorescence (XRF) and ICP-MS, respectively. Additionally, the activity concentrations of natural radionuclides in these materials were determined by both alpha-particle and gamma spectrometry with semiconductor detectors.

RESULTS AND DISCUSSION

In Table 1, we can see that ilmenite is a NORM mineral due to its enrichment by natural radionuclides from the Th and U series, with a total concentration of some 500 Bq/kg for ^{238}U and ^{232}Th. The figures for slag are lower than those found in typical undisturbed soil (20-30 Bq/kg) [7].

Table 1. Average concentrations of dry Bq/kg activity of natural radionuclides in the raw material, co-products and RG. Relative Humidity R.H (%). N.D. Under Detection.

	HR	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{40}K
ILM	4	95± 10	110±10	420±15	440±30	30±5
SLAG	3	5.9±0.6	6.1±0.6	14 ± 1	9.0±0.4	N.D
CAP	40.3	1.5±0.2	N.D.	13 ± 2	4 ± 1	N.D.
MON	4.2	53 ± 2	9.1± 0.4	365±13	43±2	N.D.
RG	46.3	20 ± 1	14 ± 1	127 ± 3	91± 3	12±2

The CAP activity concentrations are less than 10 Bq/kg, so its use in any application is not restricted by its radioactive properties. By contrast, MON has high levels of Th isotopes, particularly ^{232}Th and ^{228}Th, as well as an appreciable fraction of the initial U that enters the process with the ilmenite.

The radioactive content for RG) is moderate, indicating that a minority fraction of the initial content (for the Th and U isotopes) in the treated raw material accumulates in this co-product.

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 %), [4]. By contrast, the slag is much richer in titanium than the ilmenite (75 % TiO_2), as expected, but poorer in iron (11 % F_2O_3) [6]. On the other hand, CAP ($FeSO_4 \cdot 7H_2O$) and MON ($FeSO_4 \cdot 1H_2O$) yield high percentages of iron (~ 30 %) and sulphur (~ 25 %), as expected, which corroborates what XRD obtained. Due to its formation process, the CAP (achieved by crystallization) contains a lower proportion of metals than the MON (by precipitation).

The levels of radionuclides and heavy metals in CAP and MON are not a problem in present commercial applications. Copperas is currently being used as a basic soil amendment, animal feed and a primary flocculant in the production of liquid and solid ferrous sulphate for waste water treatments. As for the monohydrate, it is valued as a fertilizer for soils that are poor in iron, and as an additive in the cement industry for the reduction of Cr (VI). Lastly, the majority composition of RG is: 27 % SO_3 and 33 % of CaO, with $CaSO_4 \cdot 2H_2O$ being the dominant crystalline phase, but with a significant iron hydroxide content (12 %) which gives it its characteristic dark red colour [8]. Also surprising is this co-product's high titanium content (~7 % TiO_2), which has led the industry to seriously investigate ways of recovering it.

Research is currently focused on replacing natural gypsum in cement with red gypsum (clinker + natural gypsum) as a setting retardant. The first trials have begun, with the mixing of 10 % RG with 90 % clinker (RG1) and comparing the result with Type I (95 % clinker) 52.5 N/SR commercial cement (CEM). Table 2 shows the preliminary results of tests for resistance and setting time. The behaviour of the RG sample studied is similar to that of commercial cement, and the figures fall within the RC-08 Spanish Regulations.

Tabla 2. Figures relating to bending and compression (MPa). Initial setting time T_i, final Setting timeT_f (min).

	Bending		Compression		Setting	
	2days	28days	2 days	28days	T_i	T_f
CEM	6.8±0.3	10.1±1.2	34.4±0.4	61.3±1.0	139	224
RG1	7.6±0.8	10.8±0.8	31.5±0.8	59.6±1.5	216	351

In order to carry out the radiological evaluation and to check what kind of material can be used in construction, the EU has established criteria in its "Radiation Protection 112" document [9] that defines the rate of external risk (I) as:

$$I = \frac{C_{226_{Ra}}}{300\ Bqkg^{-1}} + \frac{C_{228_{Ra}}}{200\ Bqkg^{-1}} + \frac{C_{40_{k}}}{3000\ Bqkg^{-1}}$$

where C_{226Ra}, C_{228Ra}, C_{40K} are the concentrations of the activities of ^{226}Ra, ^{228}Ra and ^{40}K, respectively, in the construction material on trial. When applying this radiological criterion, we find that red gypsum can be used as a component of construction materials in any proportion with no radiological consequences.

CONCLUSIONS

The present study has been made to acquire detailed information on the composition of raw materials, co-products and waste from the process to obtain TiO2.

Once these three have been typified from the physical, chemical and radiological viewpoint, we have confirmed that the concentrations of metals and radionuclides in the CAP and MON co-products are within the European regulations pertaining to applications. RG, is now being used as a substitute for natural gypsum in cement production. The preliminary results indicate that it can be used without the cement losing any of its mechanical properties.

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