

Article

A Review of the Commercial Uses of Sulphate Minerals from the Titanium Dioxide Pigment Industry: The Case of Huelva (Spain)

Manuel Jesús Gázquez ^{1,*}, Manuel Contreras ², Silvia María Pérez-Moreno ², Jose Luis Guerrero ², Melquiades Casas-Ruiz ¹ and Juan Pedro Bolívar ²

¹ Department of Applied Physics, Marine Research Institute (INMAR), University of Cadiz, 11510 Cádiz, Spain; melquiades.casas@uca.es

² Department of Integrated Sciences, Faculty of Experimental Sciences, University of Huelva, 21007 Huelva, Spain; manuel.contreras@dfa.uhu.es (M.C.); silvia.perez@dcu.uhu.es (S.M.P.-M.); joseluis.guerrero@dfa.uhu.es (J.L.G.); bolivar@uhu.es (J.P.B.)

* Correspondence: manueljesus.gazquez@uca.es



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Abstract: This study was focused on the historical evolution of the waste management policy carried out by the Spanish industry devoted to titanium dioxide pigments manufacturing for minimising its environmental impact. This challenge was achieved by modifying the original chemical process and converting the originally dissolved sulphate and sulphuric acid present in the final streams of the factory into sulphate minerals (melanterite $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, szomolnokite $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). These by-products were physicochemically, mineralogically and radiologically characterised in order to gain basic information for its subsequent commercial use. Some of the uses summarised in this study for both ferrous sulphates are as a supplier of iron to prevent chlorosis, animal food, manufacture of cement (to reduce Cr VI), primary flocculants for ferrous sulphates, magnetite nanoparticle and nano- Fe_2O_3 formation, production of magnetite concentrate, remediation of polluted soils with metals, and treatment of wastewaters. Red gypsum was analysed as a substitute for natural gypsum in the manufacture of cement, construction materials, inhibitor in soil erosion, and the immobilisation of heavy metals in agricultural soils and carbonation processes.

Keywords: TiO_2 industry; ferrous sulphate heptahydrate; ferrous sulphate monohydrate; red gypsum; uses of sulphate minerals; NORM industries

1. Introduction

In any industrial process, the generation of wastes that could cause a potential environmental impact is almost unavoidable. In this sense, we should think it possible to develop industrial processes that are sustainable and compatible with the conservation of the environment by using the waste generated in these processes as raw materials (by-products) for new commercial products [1,2]. This is the basic principle for “Industrial Ecology”, where the valorisation of industrial waste is a steadily rising research field [3,4].

Globally, in order to achieve sustainable development, awareness about resource scarcity and environmental pollution is increasing. In this sense, legislative progress plays an increasingly important role. In particular, one of the strategic lines of EU policies aims to ensure the implementation and development of “Industrial Ecology” carrying out efficient use of raw materials, thus minimising the generation of wastes (Directive 2008 [5]). For some years, European and national policies on waste management have favoured the re-use and valorisation of waste in preference to just disposal. Thus, Directive 2008 [5] showed high novelty in the context of end-of-waste (EOW) conditions. Thus, several wastes can lose their waste status when they have undergone a recovery operation (including recycling), complying with the following conditions:

- (1) The substance or object is commonly used for specific purposes;
- (2) A market or demand exists for such a substance or object;
- (3) The substance or object fulfils the technical requirements for specific purposes and meets the existing legislation and standards applicable to products;
- (4) The use of the substance or object will not lead to overall adverse environmental or human health impacts.

The implementation of this polity will contribute significantly to solve two main problems, the final disposal of the waste in the landfill and, on the other hand, raw material savings in some commercial materials by using the obtained by-products in several industrial processes, so increasing the competitiveness of these companies [6–8].

It is therefore essential that the industries become aware of the aspects raised as minimisation and waste treatment, achieving a significant cost reduction. European and national policies on waste management have for some years favoured the re-use and valorisation of waste in preference to just disposal. In addition, environmental benefits providing a proper waste recovery represents, in certain industrial sectors, an excellent alternative to the management of them [9,10].

In this work, we analysed the historical evolution of the chemical process of one industry devoted to titanium dioxide pigment manufacturing and the reduction of the environmental issues generated with the implementation of the improvements in the waste treatment. Three sulphate minerals were generated in the factory used as a case study as new co-products with many commercial applications (ferrous sulphate heptahydrate, ferrous sulphate monohydrate, and red gypsum), which were thoroughly characterised. Finally, the commonest commercial uses of these by-products were analysed.

2. TiO₂ Industrial Process

2.1. Historical Evolution of the Industrial Process

Titanium dioxide is a white, solid, and inorganic compound usually used as pigment due to its light scattering power, showing a very high refractive index of 2.70 in comparison with values of 2.02 and 1.57 for zinc oxide and china clay materials, respectively, which are used as white pigments.

Currently, about 93–95% of the titanium ore extracted in the world is treated to generate titanium dioxide pigments [11]. There are two industrial processes to obtain TiO₂ pigments, chloride (~60% of the world production) and sulphate (~40% of the total) routes [12,13]. In this case, the most interesting process is the sulphate route because some sulphates minerals are generated as by-products. In this work, an industry devoted to the titanium dioxide pigments manufacture (sulphate route) located 10 km from the city of Huelva, Spain, was studied (Tioxide Europe S.L.). In addition, we analysed the evolution over time, and the adaptation to the legislative changes carried out in order to minimise the environmental impact of the industrial process by implementing a wide recycling strategy.

Historically, the raw material used by the sulphate route has been ilmenite (FeTiO₃) from Australia, a mineral composed of approximately 50% of titanium dioxide and 50% iron oxides. Initially, in the early 1970s when the industry began its production, the industrial process consisted of three main steps:

- (1) Acid attack in the digestion step: This step began with the mixture of sulphuric acid and raw material (ilmenite);
- (2) The resulting mixture was sent to a decantation zone, where mud was separated and transferred to a boat and sent offshore (more than 40 miles into the Gulf of Cadiz) in a zone of minimal environmental impact. This mud was mainly composed of all un-attacked minerals from the raw materials;
- (3) The sample containing titanium and iron in solution was treated, precipitating the titanium contents in the liquid fraction and the resulting liquor (20–25% H₂SO₄, usually named strong acid) containing sulphuric acid and iron salts, which was mixed with the previously obtained mud and sent offshore.

Later, changes in environmental directives led to the implementation of important changes in the above mentioned industrial process. Thus, the Council Directive of 20 February 1978 on waste from the titanium dioxide industry [14] gave guidelines in relation to the prevention and progressive reduction of pollution caused by waste from the titanium dioxide industry. The aim of this directive was to ensure that waste was disposed of without endangering human health and without harming the environment, encouraging recycling and the prevention and processing of waste. Thus, in the mid-1980s, changes in the manufacturing process of TiO_2 were carried out. From then on, the strong acid from the filtration step was pumped into crystallisers where iron sulphate was removed as ferrous sulphate heptahydrate (solid material usually called copperas). Additionally, the liquor obtained, formed by recycled acid, was sent to the digestion steps, and used again in the process.

However, it was in the mid-1990s, when the new regulations took effect, that radical changes in the industrial process were carried out. Thus, Directive 92/112/EEC was applied to solid waste, strong acid waste, weak acid waste, neutralised waste, treatment waste and dust [15]. The dumping of any waste from ships or aircraft was prohibited as of 15 June 1993. In addition, discharges into territorial waters and the high sea of solid waste and strong acid waste from existing industrial establishments using either process or of treatment waste from existing industrial establishments using the sulphate process were prohibited from that date. In this sense, solids wastes should be classified, taking into account the type of management, attending to their nature.

Taking into account the limitations given by the previously cited Directive in relation to the elimination of the discharges of effluents to the sea, deep technical achievements were carried out in Huelva's titanium dioxide pigment industry in order to ensure compliance with the regulations and ensure environmental protection. The last dumping was made on 31 May 1993.

Thus, the industrial process is schematised in Figure 1. The process begins with the acid attack with sulphuric acid (H_2SO_4 98% (~160,000 t), recycled H_2SO_4 80% (~70,000 t) and recycled H_2SO_4 65% (~30,000 t) of the raw material (ilmenite FeTiO_3 , ~142,000 t per year), previously dried and milled under 60 microns in the digestion step (~200 °C) [12]. The recycled acid is needed in order to reach the optimum ratio mass sulphuric acid/mass of TiO_2 of 1.85. The reaction is produced in a discontinuous (~20–21 t in each charge) process over 8 h following Equation (1):

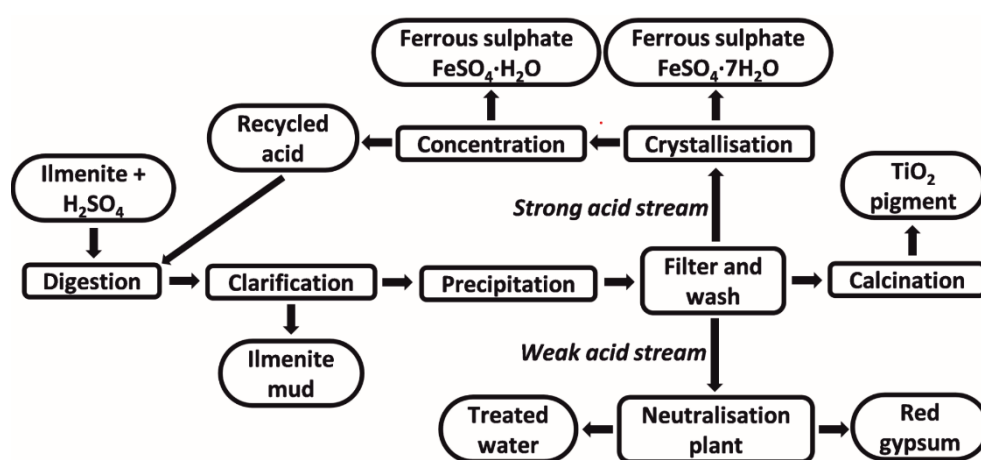
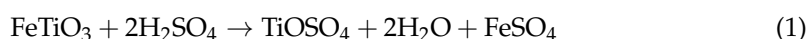
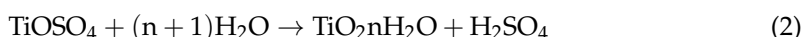


Figure 1. Schematic process of titanium dioxide pigment production by the sulphate route.

At this point, and with the aim to ensure that all the iron is reduced and therefore remains in solution, the resulting liquor from the digestion step is passed by scrap (Fe^{3+} to

Fe^{2+}). The resulting liquor is stored in a clarification tank, where the undissolved solids (usually called ilmenite mud or unattached) are separated from the solution by flocculation, decantation, and subsequent filtration. This mud (~30,000 t per year) is the first solid waste obtained and is formed by refractory elements which have not been attacked by sulphuric acid. Currently, this mud is neutralised and disposed of in landfills.

Then, the clarified liquor is hydrolysed with the aim to produce the precipitation of hydrated titanium, see Equation (2). Then, the TiO_2 is separated by vacuum filters (called “Moore filters”) from the mother liquor (usually named “strong” acid, 20–25% H_2SO_4). The treatment of this mother liquor will be detailed later.



After separation, the filtered TiO_2 is washed with water with the aim to remove the remaining impurities, which can diminish the quality of the final product. The water collected in this final wash, usually called weak acid stream (Figure 1), is sent to the neutralisation plant where calcium hydroxide is added, generating the third by-product, named red gypsum, and water which can be discharged to the environment.

Once the TiO_2 has been obtained, the sample is sent to rotary kilns in order to remove the water remnant and some traces of sulphur. The resulting solid is cooled and finely ground (“micronised”) before being packed for commercial distribution.

The production of titanium dioxide is classed as a NORM industry (Naturally Occurring Radioactive Material) due to ilmenite containing high levels of natural radionuclides from both uranium and thorium series (~100 and 400 Bq/kg, respectively) [15,16]. The content of these radionuclides is finally distributed in the by-products and waste generated since the TiO_2 pigment is practically pure and free of traces of metals and radionuclides. For that reason, an exhaustive radiological study was carried out in the Huelva’s factory, being published by the Nuclear Security Council (CSN) in their technical reports series in 2010 [17]. In this study, it was demonstrated that the annual effective doses received by the personnel performing their working activities in these plants were clearly below 1 mSv/y.

2.2. Treatment of Acid Streams

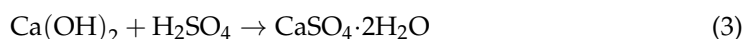
As mentioned above, since there was no treatment of acid currents, the effluent was discharged directly into the sea at the beginning of the industrial activity. Due to the growing environmental awareness of society, the factory located in Huelva made enormous technical and environmental improvements with significant success. Therefore, a thorough study of the operating parameters of the TiO_2 pigment plant and acid effluent concentration plant was carried out over five years. In addition, the most acceptable materials were established for use in the strong effluent concentration stage related to the corrosivity of concentrated sulphuric acid at elevated temperature. The most common materials in the factory are Teflon, several alloys, and graphite, although the latter is being replaced by a more resistant material such as tantalum. Subsequently, an industrial-scale plant was built, managing to recycle all the strong effluent generated.

To remove most of the sulphate in the form of solid ferrous sulphate heptahydrate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, it is necessary to pump the strong acid obtained after the TiO_2 separation step to crystallisers (Figure 1). This is thus known as copperas (COP), normally thickened and extracted by centrifugation. This primary crystallised by-product of the titanium dioxide production process can be washed with water in order to achieve appropriate levels of quality and purity.

Later, a multi-stage process of evaporation to re-concentrate the remaining strong acid to be re-used in the first digestion step is used. This process leaves the remaining ferrous sulphate present at high temperature in a monohydrated form instead of the heptahydrated form. Ferrous sulphate monohydrate, or $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (MON), is a solid material formed in the re-concentration phase, separated through filtration (Figure 1). The production of both copperas and monohydrate has a benign environmental impact. It actually enables the use

of high iron concentrated ilmenite as the production of COP and MON reduces the need for treatment of the main TiO_2 plant effluent.

In the last stages of the TiO_2 washings, a third and final by-product is formed. The liquid stream is sent to the neutralisation plant, Figure 1, where lime is added, creating a new by-product usually called red gypsum (RG) mainly composed of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and iron hydroxides with a significant percentage of particles (90%) < 63 μm in size [12], according to the reactions:



After separating the red gypsum through filtration, part of the water is recycled, with another part released into the river. The level of pollution of this water is considerably lower than the limits imposed by the Spanish Government.

The generated by-products at the Huelva factory are as follows: 142,000 metric tonnes of raw material are annually processed (ilmenite) with 160,000 metric tonnes of sulphuric acid concentrated (98% *w/w*) and 100,000 metric tonnes of recycled sulphuric acid, generating 70,000 metric tonnes of red gypsum (40% of humidity), 140,000 metric tonnes of copperas (35% of humidity), and 125,000 metric tonnes of monohydrate (9% of humidity) [12].

To summarise, the titanium dioxide industrial process generates three sulphate minerals as by-products. Thus, ferrous sulphates, both hepta- and monohydrated, are generated during the treatment of the mother liquor. Then, by washing the TiO_2 pulp, the resulting weak acid leads to the generation of a third by-product, calcium sulphate dihydrate (red gypsum) and cleaner water [12,13].

3. Characterisation of the Samples

As a previous step of the valorisation process is required for the by-products, it is important to know the physico-chemical and radiological composition of samples. The most important results consulted in the bibliography are shown in this section.

3.1. Mineralogical Composition

The ilmenite was mainly composed of 75% of ilmenite (FeTiO_3), 7% of rutile (TiO_2), and 18% of pseudo-rutile ($\text{Fe}^{3+}_2\text{Ti}_3\text{O}_9$) [18,19]. In relation to the obtained ferrous sulphate during the process, copperas is mainly formed by melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and ferrous sulphate monohydrate composed of the szomolnokite mineral form ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$). In both samples, a non-negligible fraction of rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) was identified [13]. These results can be explained in relation to the stability of the mineral phases due to rozenite being the most stable form, according to a previous study [20]. Thus, heptahydrated ferrous sulphate tends to lose a fraction of the hydration water and on the contrary monohydrated ferrous sulphate tends to gain structural water, passing to a mineral form with four water molecules.

Finally, taking into account the information gained by XRD analysis, we show that the mineralogical form of the red gypsum samples was gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), their mineralogical composition being homogeneous and in agreement with the expected results [12,21].

3.2. Major Elements

The major elements in the raw material (ilmenite) were iron and titanium, with average concentrations around 45% and 50%, respectively [12,18], with the rest of the measured metals being lower than 1.5% (Table 1). Additionally, high uniformity found between the five analysed samples was noted.

Table 1. Average concentration (%) of major elements in raw material (ilmenite), and sulphate minerals (copperas, monohydrate, and red gypsum) uncertainties are given as 1σ (standard deviation) [12].

	Ilmenite	Copperas	Monohydrate	Red Gypsum
SiO ₂	1.13 ± 0.25	<0.01	<0.01	1.2 ± 0.2
Al ₂ O ₃	1.10 ± 0.21	0.06 ± 0.01	1.1 ± 0.3	1.4 ± 0.2
FeO _T	44 ± 1	39 ± 3	31 ± 2	14 ± 2
MnO	1.30 ± 0.05	0.35 ± 0.04	1.4 ± 0.1	0.35 ± 0.04
MgO	0.32 ± 0.07	0.25 ± 0.03	0.61 ± 0.12	1.4 ± 0.2
CaO	0.05 ± 0.01	<0.01	0.09 ± 0.03	33 ± 2
TiO ₂	49.6 ± 0.3	0.18 ± 0.02	2.9 ± 0.3	7.6 ± 1.2
SO ₃	<0.01	22 ± 2	25 ± 1	27 ± 1
L.O.I.	<0.01	39 ± 2	41 ± 3	21 ± 2

L.O.I.: Loss on Ignition.

In Table 1, we observed that both the ferrous sulphates were mainly composed of SO₃ (22% for copperas and 28% for monohydrate) and FeO_T (39% and 32% for copperas and monohydrate, respectively), as expected with regards to the previous results obtained by XRD. On the other hand, monohydrate samples contained significant concentrations of metals such as Al, Mn, Mg or Ti, around one order of magnitude higher than the copperas.

This fact is a consequence of the formation process of both iron salts, copperas coming from the crystallisation process and monohydrate obtained after the concentration and co-precipitation processes, so remaining more enriched of metals in relation to copperas. As can be seen, the total sum of the major elements for red gypsum, copperas and monohydrate were lower than 100%, and this fact was due to the L.O.I value, around 40% for both ferrous sulphates and 21% for red gypsum.

The third by-product, or waste depending on the country where the factory is located, the red gypsum, was mainly composed of SO₃ and CaO with concentrations of 27% and 33%, respectively. These concentrations are in agreement with the mineralogical results obtained by X-ray diffraction, and the content of calcium is similar to that obtained for natural gypsum [21,22]. Finally, and taking into account that red gypsum is generated in the neutralisation plant (see Figure 1), mixing the weak acid with lime, it is possible to explain the titanium dioxide content near to 8%, also showing a high concentration of iron oxide (14%), being the element that gives the characteristic red colour to this sample. Additionally, red gypsum also contains non-negligible concentrations of Al₂O₃ (0.69%), SiO₂ (0.17%), and MgO (0.38%).

3.3. Trace Elements

In Table 2, the main toxic trace elements for ilmenite, copperas, monohydrate, and red gypsum are detailed. Ilmenite showed, in all cases, higher concentrations of trace elements than the continental crust composition. In relation to both the ferrous sulphates, it can be seen that monohydrate was more enriched in trace elements than copperas mainly due to their formation processes, copperas by crystallisation and monohydrate by concentration and subsequent precipitation. Copperas showed lower concentrations of the trace elements analysed, excluding Pb, and with Cd being 30 times higher in comparison to the typical soils (Table 2). On the contrary, ferrous sulphate monohydrate had, in general, a higher concentration of trace metals such as Cr, Zn, Cd, Pb, U, and Th, than typical soils, especially Cr and Zn. Finally, red gypsum showed moderate concentrations of the trace elements analysed, particularly Zn and Cd.

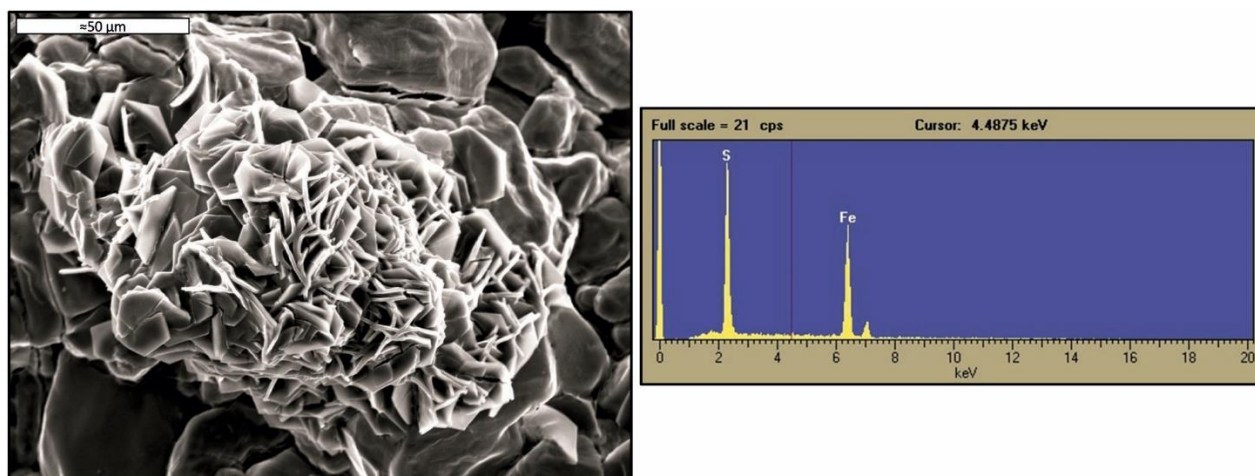
Table 2. Average composition of trace elements ($\pm$ standard deviation, mg/kg), in the raw materials and by-products generated in the titanium dioxide plant [12,13]. (*) Continental crust composition [23].

	Ilmenite	Copperas	Monohydrate	Red Gypsum	(*)
Cr	344 $\pm$ 60	10 $\pm$ 1	467 $\pm$ 27	133 $\pm$ 4	92
Cu	41 $\pm$ 6	<0.01	<0.01	12 $\pm$ 1	28
Zn	296 $\pm$ 28	299 $\pm$ 34	749 $\pm$ 55	225 $\pm$ 12	67
As	22 $\pm$ 2	0.25 $\pm$ 0.03	1.32 $\pm$ 0.09	12 $\pm$ 1	4.8
Cd	2.7 $\pm$ 0.3	3.3 $\pm$ 0.4	0.87 $\pm$ 0.04	1.0 $\pm$ 0.1	0.09
Pb	135 $\pm$ 10	46 $\pm$ 6	45 $\pm$ 3	35 $\pm$ 2	17
Th	97 $\pm$ 9	3.1 $\pm$ 0.5	92 $\pm$ 5	30 $\pm$ 1	11
U	6.5 $\pm$ 0.7	0.11 $\pm$ 0.01	5.0 $\pm$ 0.2	1.7 $\pm$ 0.2	2.7

3.4. Scanning Electron Microscopy

All these waste and co-products have been analysed in many papers, and similar results were obtained here [21,22,24–28], so we will summarise the results obtained in the case of the Huelva industry.

The SEM-EDX analyses of copperas produced at Huelva are shown in Figure 2. In the SEM images, a granular habit and size greater than 500 μ m can be observed (left image). Furthermore, pseudohexagonal iron sulphate crystal aggregates with the “rosette” texture were identified (right image). Moreover, the elemental analysis of the surface was also obtained using Energy Dispersive X-ray spectroscopy (EDX). The study revealed the presence of Fe and S, as was expected from the previous XRF results.

**Figure 2.** SEM-EDX analysis of copperas [12].

According to the SEM-EDX analysis of the monohydrated ferrous sulphate (Figure 3), granular aggregates and interconnected tabular crystals with a size greater than 50 μ m were clearly observed, which is a characteristic of szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$). Additionally, some metals such as aluminium, titanium and manganese were also observed, in contrast with the copperas samples, where the EDX spectrum was free of metals, so corroborating previous analyses made by XRF for both ferrous sulphates, Figure 2.

Finally, we could observe that red gypsum was composed of prismatic crystals, mainly formed by Ca and S (point 1 of Figure 4), similar to natural gypsum [22] but showing additionally significant amounts of iron [29]. In addition, small particles containing high concentrations of Fe, Ti, Al, Si, and Mg were also observed together with red gypsum in the neutralisation process (see point 2 of Figure 4). As can be seen in the EDX spectrum, the iron content was not negligible, corroborating the previous results obtained by XRF and XRD (>10% of Fe).

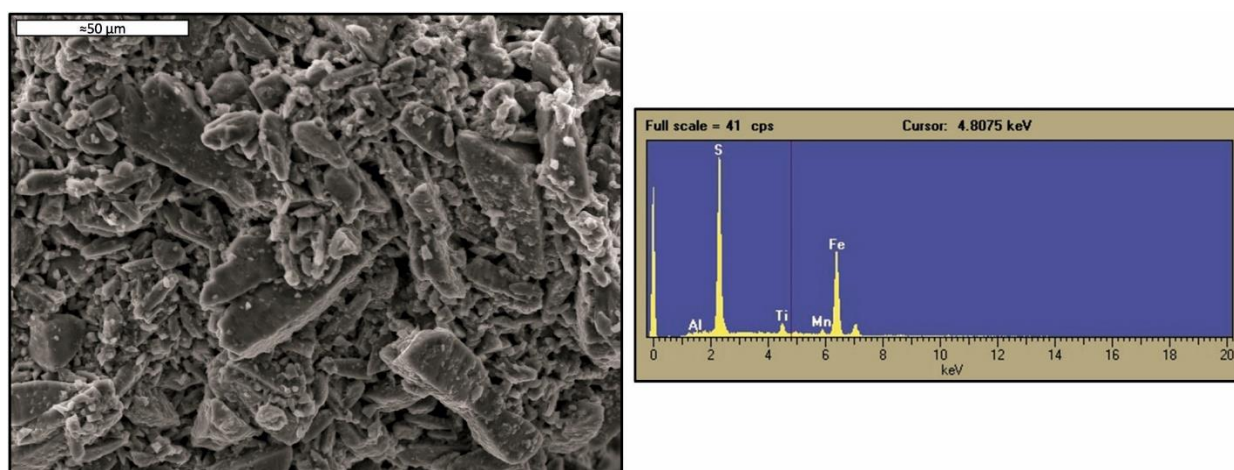


Figure 3. SEM-EDX analysis of a monohydrate sample [12].

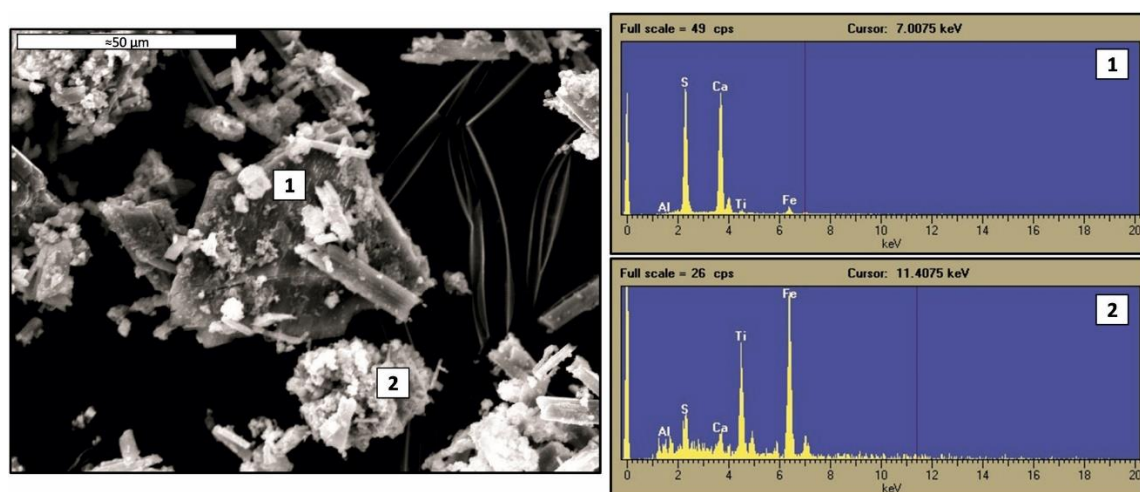


Figure 4. SEM-EDX specific analysis of gypsum particle [12].

3.5. Radioactive Characterisation

Table 3 shows the activity concentration of several radionuclides from both the uranium and thorium series. Ilmenite was enriched in natural radionuclides from both the Th and U series (in secular equilibrium), containing ~ 400 Bq/kg for ^{238}U and ^{232}Th radionuclides (Table 3), around ten times the equivalent of radium and higher than those found in typical unperturbed soil (35 Bq/kg for ^{238}U and ^{232}Th in secular equilibrium with their daughters) [30,31]. It is important to note that ilmenite only contains 20 Bq/kg of ^{40}K , an activity concentration much lower than unperturbed soil (500 Bq/kg) [30].

Table 3. Activity concentration (Bq/kg) of raw material (ilmenite) and by-products. (red gypsum, cooperas and monohydrate) by alpha and gamma spectrometry [12].

	Code	Ilmenite	Red Gypsum	Cooperas	Monohydrate
Alpha Spectrometry	^{210}Po	96 ± 9	14.0 ± 2.0	5.7 ± 0.7	22 ± 3
	^{238}U	116 ± 10	19.0 ± 1.0	0.90 ± 0.10	53 ± 4
	^{232}Th	315 ± 20	127 ± 8	8.0 ± 0.9	365 ± 18
	^{230}Th	95 ± 5	43 ± 3	3.5 ± 1.2	114 ± 6
Gamma Spectrometry	^{226}Ra	86 ± 5	14.0 ± 1.0	4.5 ± 1.0	9.2 ± 1.0
	^{228}Ra	300 ± 20	91 ± 4	6.3 ± 1.3	43 ± 3
	^{40}K	30 ± 5	<18	<14	<14

In relation to by-products, Table 3 shows that copperas was practically radioactive free, the activity concentration of all radionuclides being lower than a typical soil. On the contrary, monohydrated presented similar values of ^{232}Th and ^{230}Th as ilmenite, 365 and 114 Bq/kg, respectively, a fact which must be considered in future commercial applications. The different radiological content is due to the different ferrous sulphate's formation processes, copperas by crystallisation and monohydrate by concentration, causing the precipitation of metals and radionuclides. Finally, red gypsum was only enriched in ^{232}Th , and ^{228}Ra , in relation to unperturbed soil, 127 and 91 Bq/kg, respectively. On the other hand, the uranium series were similar to typical undisturbed soils (35 Bq/kg) [30].

4. Commercial Applications of Sulphates from the Titanium Dioxide Industry

The correct valorisation process comes with unique advantages and challenges for the factory:

- Development of new lines of Research and Development (R&D), with the aim to introduce changes in the production processes that entail improvements in order to achieve the minimisation of the produced waste;
- Improvement of the public image of the industry thanks to the valorisation process of the waste, minimising the environmental pollution;
- Improvement in competitiveness, increasing sales and market share and reducing costs related to the management of waste.

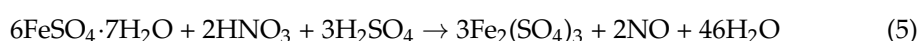
Ferrous sulphate heptahydrate is a material that has been widely used for a long period of time. It is also known as copperas, green vitriol, or melanterite. In recent times new advanced applications have been developed to allow the discovery of markets for the total production of this iron compound.

Traditionally, copperas has been widely used as a supplier of soluble iron in the field of agriculture, with the aim of preventing chlorosis in flora, mainly in citrus [32]. Thus, iron promotes the growth and development of plants, increasing chlorophyll formation and making photosynthetic action more effective. Additionally, ferrous sulphate is also used to prevent the plagues of snails that harm plants, especially in the early stages of growth [32].

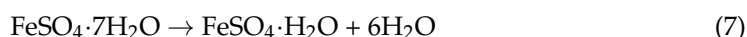
Directive 2003/53/EC of the European Parliament and the Council of 18 June 2003, relating to restriction on the marketing and use of certain dangerous substances and preparations for cement, cautions the use of Cr (VI) [33]. Cement must not be used if it contains, when hydrated, more than 0.0002% soluble chromium VI of the total dry weight of the cement. The purpose of this legislation is to minimise the possibility of an allergic reaction known as dermatitis, which can be caused by water-soluble chromium VI. Thus, it is important to note that ferrous sulphate is also used in the manufacture of cement as a reducing agent for chromium VI [12,34].

Additionally, it is well known that iron, in ferrous form, is an essential element for animal nutrition because it is in a suitable form to produce haemoglobin in the early stages of animal development. Ferrous sulphate monohydrate is the best for this due to it being a dry product with high iron content, although the heptahydrated form can be used [35,36]. Some studies have been carried out in order to demonstrate the utility of iron in the diet of chickens, being directly responsible for the formation of haemoglobin [37,38].

On the other hand, it is possible to produce ferric sulphate in order to remove the colloidal substances [34]. This ferric sulphate is obtained from ferrous sulphate by two different routes: one of them by direct oxidation of ferrous sulphate by using high temperature ($T \geq 150\text{ }^{\circ}\text{C}$) and pressure ($P \approx 15\text{ atm}$) with sulphuric acid and oxygen, and the second one from mixing the ferrous sulphate with nitric and sulphuric acids, according to the following chemical reactions:



Copperas is also used as a flocculant in the cleaning of wastewater, removing the contained phosphates with the aim to avoid the eutrophication of water bodies [28]. Ren et al. [24] used pyrite as a reducing agent under nitrogen protection to break down ferrous sulphate waste, obtaining porous magnetite nanoparticles (FeFe_2O_4) generally used as a water purifying agent. This nanometer magnetite was also sinterised by a microwave-assisted reduction method, which is a promising prospect for applications in water-based pigments [25]. Ferrous sulphates, heptahydrate and monohydrate, can be used in the manufacture of iron pigments for ink [26], being transformed into oxide by roasting, according to the chemical reactions:



It can also be used to produce nano- Fe_2O_3 ($\alpha\text{-Fe}_2\text{O}_3$), a typical nanomaterial with a small size, which is widely used in the pigment field, by a novel process of the reduction of ferrous sulphate with coke [27]. In addition, it can be used to prepare spinel-structured magnesium ferrite (n-type semiconducting material) particles with a micrometre size (usually used in catalysis, adsorption, sensors, and magnetic technologies), through the solid-phase reaction between ferrous sulphate, magnesium sulphate, and pyrite under a reducing atmosphere, with the following reaction:



The above takes full advantage of sulphur and iron resources contained in the by-products [39].

Ferrous sulphate from the titanium dioxide industry is also used to obtain concentrate magnetite (Fe_3O_4) by co-precipitation with calcium hydroxide as the precipitator. Fe^{2+} ions were precipitated as $\text{Fe}(\text{OH})_2$ and subsequently converted into Fe_3O_4 by air oxidation and heating, remaining blended with gypsum. Two options to separate the concentrated magnetite were tested, firstly by magnetic separation [40] and secondly by using polyethylene glycol (PEG) as a dispersant [41]. Additionally, the ferrous sulphate was studied as the main component to synthesise cubic inverse spinel copper magnesium ferrite nanoparticles (CMFNPs), one of the most important magnetic n-type semiconducting materials, by using the solid-phase reduction method [42].

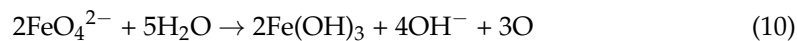
In the field of agriculture, the most important applications have been researched, taking into account the following:

- Fe^{2+} iron can be directly assimilated by plants;
- The solubilisation of several cations (magnesium or phosphorus) is carried out by using sulphuric acid;
- Other elements such as zinc, copper, and manganese are important trace elements in plant growth.

In this sense, and due to the widespread use in agriculture, this has allowed the commercialisation of different granulated co-products by the Huelva factory where the ferrous sulphate was mixed with magnesium sulphate (commercial name fillmag), magnesium sulphate (commercial name tiomag), assailable phosphorous (commercial name fosfermag) and assailable phosphorus and potassium (commercial name PKMag) with high value in the agricultural field. Therefore, at appropriate doses, the ferrous sulphate monohydrated is used directly in alkaline soil, generating the acidification of the soil to be mixed with manure products and/or compost. Additionally, the presence of free acid accelerates the decomposition of organic matter, giving good agronomic properties due to the addition of a significant amount of iron which can be assimilated by plants.

Other applications of ferrous sulphate are its use as a source of iron in the production of alkali ferrates, mainly sodium ferrate, using gas–solid reactions [43]. The term “ferrate” is used to name compounds containing iron in an oxidation state higher than $\text{Fe}(\text{III})$. These

compounds are mainly used for water treatment due to their powerful oxidising capacity (oxidation of organic materials, biocide agent), and additionally by using the flocculating property of the generated ferric hydroxide, according to the reaction [44]:



This reaction generates a basic media that produces the co-precipitation of heavy metals onto hydroxides [44]. Additionally, ferrates have a significant role in environmental engineering since they are used in many applications such as sludge treatment, treatment of emerging organic pollutants, and water disinfection, among others [45].

Ferrous sulphate is also usually used in the remediation of polluted soils with heavy metals such as arsenic and vanadium, amongst others, and in the treatment of wastewater with inorganic components. Thus, the realgar tailings (where the main components are As, Si, Ca, and S) abandoned in mining areas are Fe-deficient. For that reason, ferrous sulphate was used in order to enhance the transformation of Ca–As and S–As species to more stable Fe–As species, reducing the As leaching concentration [46]. Additionally, microwave irradiation was studied in order to enhance the long term stability of arsenic (As) in FeSO_4 -treated realgar tailings. The obtained results showed that the efficiency of As stabilisation was increased up to values near to 99.5%, 1.35 fold of that the treatment without the application of microwaves [47]. Similarly, the soil contaminated with vanadium can have a potential health risk to humans, animals, and plants in a direct way or through the food chain. The stabilisation treatment, converting pollutant metals into less soluble and mobile forms, plays an important role. The use of ferrous sulphate allows the stabilisation of V onto ferrihydrite [48].

Nitroaromatic compounds (nitrobenzene and nitrophenols, 4-Nitro-phenol (4-NP) and 2,4-dinitro-phenol (2,4-DNP)) from the production and use of dyes, pesticides, and pharmaceuticals, are considered environmental pollutants. They are usually found in wastewater, and their detoxification is very difficult due to their resistance to oxidation. In this sense, a Fenton oxidation treatment by using ferrous sulphate as a source of iron catalyst was analysed, and it was concluded that it could be utilised effectively [49].

The consulted literature for red gypsum or titanium gypsum shows that studies about its potential valorisation are growing in importance. For example, the red gypsum can be used for cement production as a binder [50], green concrete [51], calcium sulpho-aluminate cement [52], foamed concrete [53], cementitious materials [54], and the production of anhydrite [55] and eco-friendly road base materials [56]. Taking into account the composition of this co-product (mainly composed by gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and knowing that the natural gypsum must be added in a range between 3% and 5% to clinker as a set retardant for the manufacture of commercial cement, the replacement of natural gypsum by red gypsum has been carried out with promising results [29].

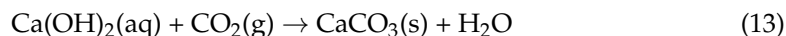
Additionally, red gypsum has been analysed as an inhibitor of soil erosion (reducing runoffs and total soil loss), soil degradation, a heavy metals fixer in polluted soils [21], and for covering trenches or filling of abandoned mines [57]. Thus, for example, it can reduce the Cd, As and Pb absorption and bioavailability in rice grown in polluted paddy soils with heavy metals, resulting in a decrease of pH and dissolved organic carbon (DOC), thereby improving the rice plants growth. Additionally, the relative abundance of sulphate-reducing bacteria increased with the use of red gypsum [58]. On the other hand, mixtures of red gypsum with sewage sludge have been analysed as an alternative for landfill cover, showing that hydraulic conductivity was not affected and the risk of cracking was minimised when the content of gypsum was high enough [59]. In addition, taking into account the composition of red gypsum (Fe, Ca, Al, Mg, Mn, S, and other elements), a flora inventory in a red gypsum-formed landfill located at the Ochsenfeld site in eastern France was analysed in order to establish the main chemical drivers of the native spontaneous vegetation that occurred after 10 years of inactivity [60].

Other research has been conducted to valorise red gypsum in the carbonatation process through CO_2 sequestration. Direct and indirect processes have been studied by several

authors. The indirect process requires the previous extraction of calcium from the sample. For this, several extraction agents have been used, for example, Na(OH) and NH₄(OH) pathways [61,62], obtaining CaCO₃ and NaSO₄ or (NH₄)SO₄ respectively, as final products following the reactions:



Subsequently, the solid Ca(OH)₂ formed was dissolved in water with a flow of CO₂, with the reaction:



On the other hand, the accelerated mineral carbonation process was analysed by using sulphuric acid as an extractant agent of calcium ions. Then, the carbonation process was carried out with an aqueous solution containing red gypsum, CO₂, and mono-ethanolamine (MEA) in order to absorb the highest quantity of CO₂ possible so as to maximise the precipitation of calcite [63]. Additionally, direct aqueous mineral carbonation of red gypsum has been investigated, obtaining CaCO₃ and FeCO₃ as the final products [64]. This method should be developed because the obtained carbonates purity and carbonation efficiency are still very low. In the case of red gypsum showing a higher content of iron (red gypsum coming from Malaysia), it is possible to obtain iron carbonate (FeCO₃) through the carbonation process [65] with high purity and carbonation efficiency.

5. Summary

This paper provides a compilation of the commercial uses of sulphate minerals obtained as co-products in the titanium dioxide pigment industry. It has also been demonstrated that this industry is a NORM activity because it uses as a raw material an ore called ilmenite that contains levels of natural radionuclides about 10–15 times higher than those measured in unperturbed soils.

This work has also shown how a chemical industry that was very pollutant at the beginning of the 1970s has been changing production processes, little by little over the last decades, to achieve a practically zero-waste production, as the new working philosophy allows them to produce new materials (co-products) with high commercial value.

Some of the uses summarised in this study for ferrous sulphates are as a supplier of iron to prevent chlorosis, animal food, manufacture of cement, primary flocculants, magnetite nanoparticle and nano-Fe₂O₃ formation, production of magnetite concentrate, remediation of polluted soils, and the treatment of wastewater. Red gypsum was analysed as a substitute for natural gypsum in the manufacture of cement, construction materials, immobilisation of heavy metals in agricultural soils, and carbonation processes.

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