Management and valorisation of wastes and co-products from the TiO_2 pigment industry

M. Contreras[1)*], M.J. Gázquez[1)], S.M. Pérez-Moreno[1)], M. Romero[2)], and J.P. Bolívar[1)]

1) Department of Applied Physics, University of Huelva, Campus de Excelencia Internacional del Mar (CEIMAR), 21071 Huelva, Spain.

2) Group of vitreous and ceramic materials, Department of construction materials, Institute of Building Sciences Eduardo Torroja IETcc-CSIC, Madrid 28033, Spain

(*) Corresponding author: Juan Pedro Bolívar, email: bolivar@uhu.es phones: +34959219793 - +34669754251

Abstract

This work analyses and evaluates potential applications for several inorganic wastes and intermediate materials, called co-products, generated in the TiO_2 pigment production industry through the sulphate method. For this purpose, a physical-chemical characterisation of the input materials (ilmenite and slag), wastes (sludge and red gypsum), and co-products (two ferrous sulphates, mono and hepta-hydrated) was carried out. In addition, because the TiO_2 pigment production activity is a NORM (Naturally Occurring Radioactive Material) industry, a radiological characterisation was also undertaken.

The main objective was to gain basic information for the application (actual or potential) of these co-products and wastes in fields such as agriculture, construction, and civil engineering. For each specific application of these wastes and co-products, additional studies were carried out to evaluate their appropriateness with respect to technical properties and their health and environmental impact. The results obtained in this work have revealed several lines of research with potential commercial applications.

Keywords: TiO_2 industry, NORM wastes, management, valorisation, civil engineering.

1. Introduction

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

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

Titanium dioxide (TiO_2) pigment is a white powder with high opacity and brilliant whiteness. These properties have made it a valuable pigment for many applications in paints, plastic goods, inks and paper, among others. There are two chemical methods for obtaining TiO_2, one using sulphate, and the other chloride. It is estimated that about 65 % of the world's production is derived from the chloride process, while 70 % of the European production takes the sulphate route.

One European centre of production is located in southwestern Spain, in the vicinity of Huelva. This factory uses the sulphate method for producing dioxide pigments. In addition to the main TiO_2 pigment production, four different co-products and wastes result from the process (Figure 1) [8,9].

The industrial process followed at the Huelva TiO_2 factory begins with the acid digestion of the feedstock [8,9]. A controlled blend of ilmenite (ILM) and slag (SLAG) (85 % ilmenite and 15 % slag) is mixed with highly concentrated sulphuric acid (H_2SO_4 98 %), and acid (H_2SO_4 80 %) recycled from the chemical process. The resulting liquor contains titanyl sulphate ($TiOSO_4$) in solution, which goes into a clarification tank where the un-dissolved solids (SLUDGE) are separated by flocculation (decantation) and posterior filtration. Then, the clarified liquor, in which the TiO_2 is dissolved as titanyl sulphate, is hydrolysed with steam in order to produce the precipitation of hydrated titanium. The TiO_2 pulp is then separated from the mother liquor (called “strong acid”) by vacuum filters. The TiO_2 cake is washed again with water, producing a liquor called “weak acid”, and then placed in in rotary kilns for the removal of its water content and some traces of sulphur. The resulting final solid is calcinated, milled, coated, washed, dried, and finely, micronized to be packed for commercial distribution.

Historically, the TiO_2 process has undergone significant development in relation to the treatment of the two waste products generated by the process (strong and weak acid). In the 1970s the factory was designed to discharge the strong acid into the deep sea in the Gulf of Cadiz at a point 40 miles from the coast, considered to pose minimal potential environmental impact. Curiously, this requirement was stricter than that imposed on other similar industries in Europe, where the strong acid was pumped into the sea only two kilometres from the coast.

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

This Directive:

- Prohibited the dumping of any solid waste, strong acid waste, treatment waste, weak acid waste, or neutralized waste, with effect from 15 June 1993.
- Specified a reduction in the discharge of SO_x arising from digestion and calcination steps in the manufacture of titanium dioxide, to a value of not more than 10 kg of SO_2 equivalent per ton of titanium dioxide produced with effect from 1 January 1995.
- Classified solid wastes taking into account the type of management, and attending to their nature.

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

Firstly, the strong acidfrom the TiO_2 precipitation and lixiviation stages is pumped to crystallisers and concentrated, precipitating the solid heptahydrated ferrous sulphate ($FeSO_4 \cdot 7H_2O$), commonly known as “copperas” (COP), which is extracted by centrifugation [8,9]. The remaining strong acid containing some additional amounts of Fe, is further concentrated by multi-stage evaporation until the precipitation of monohydrated ferrous sulphate ($FeSO_4 \cdot H_2O$), called “monohydrate” (MON), which is separated by filtration. The resulting strong sulphuric acid is concentrated again (H_2SO_4, 80 %), and is recycled into the process at the digestion stage of the raw material (see Figure 1).

The final weak acid stream is treated in a neutralization plant by adding calcium hydroxide and magnesium hydroxide, generating a waste called red gypsum(RG), formed mainly of artificial gypsum ($CaSO_4 \cdot 2H_2O$), and iron hydroxides, while the resulting clean stream is released into the estuary (Figure 1).

Around 142,000 metric tonnes of raw material (ILM) are processed annually in the Huelva factory, generating the following amounts of dry co-products and waste per kilogram of raw material: 0.10 kg of SLUDGE, 0.33 kg of RG, 0.64 kg of MON, 0.70 kg of COP, and 0.4 8kg of TiO_2pigment.

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

In view of the above, the main objective of this paper is to specify the physicochemical and radioactive characterization of the raw materials, co-products and waste from the TiO_2 pigment industry, and to apply this information in the valorisation of the waste in the production of new materials with commercial applications.

2. Materials and methods

2.1. Materials

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

2.2. Methods

2.2.1 Characterisation techniques

The identification of the mineral phases was performed by the XRD technique (X-ray diffraction) in a Bruker diffractometer (model D8 Advance), using Cu Kα radiation operating at a current of 30 mA, and a voltage of 40 kV. Data were recorded in the 5–70º 2Ɵ range (step size 0.019736º and 0.5 s duration for each step). For Rietveld quantitative phase analysis, finely powdered samples were mixed with 30 % high purity calcined α-Al_2O_3 as internal standard. The mixture was homogenized by hand milling for 5 minutes in an agate mortar with acetone. Powder diffraction patterns suitable for performing the Rietveld analysis were collected by step-scanning in the 10º-70º (2Ɵ) range, with steps of 0.03º and a duration of 8 s for each step.

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

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

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

Thermal behaviour was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (SETARAM model Labsys) on powdered samples (size particle = 80–100 µm). DSC/TGA scans were performed in platinum crucibles under a flow of air between 25 ºC and 1450ºC at 50 ºC min^{-1}, taking calcined Al_2O_3 as reference material. The DSC/TG curves were normalised with respect to the sample weight.

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

2.2.2. Technological characterisation

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

The sintering behaviour of ceramic was evaluated in terms of water absorption, apparent porosity and bulk density. The water absorption, E (wt. %), was measured according to EN ISO 10545-3 [15] for ten representative specimens. The apparent porosity and the bulk density were measured according to ASTMC373-88 [16], which involves drying the test specimens to constant mass. After impregnation, the mass of each specimen while suspended in water was determined along with their saturated mass. The apparent porosity, P (%), expresses the relationship of the volume of open pores with the exterior volume of the specimen. The bulk density, B (g cm^{-3}), of a specimen is the quotient of its dry mass divided by the exterior volume, including pores. In addition, the linear shrinkage, LS (%) and the bending strength, BS (MPa), was measured according to EN 843-1 [17].

2.2.3. Fire-resistance tests

Fire-resistance test standards are stipulated in the regulation UNE-EN 13501-1 [18]. This test requires that one of the sides of the plate be exposed to a standard temperature curve defined by the equation $T = 20 + 345 \log10 (8t + 1)$, where T is the oven temperature (ºC), and t is the time (min) from the beginning of the test. The temperature of the unexposed side is measured by means of three Pt-100 thermocouple probes. The test is concluded when the temperature of one of the thermocouples on the unexposed surface of the plate is either above 180 ºC, or the average temperature of all the thermocouples exceeds 140 ºC + $T_{Env.}$, where T_{Env}. is the ambient temperature when the product was tested at 23 ºC. In the event of the test material fracturing or losing structural stability, the trial is discontinued, a circumstance which did not occur in any of the tests performed.

3. Results and discussion

3.1. Characterization of raw materials, co-products and waste

3.1.1. Mineralogical characterization

Details of the mineralogical composition determined by XRD is given in Table 1.The ilmenite ore shows a non-uniform mineralogical composition with the following species: ilmenite ($FeTiO_3$) comprising 71 % of the total, compensated by the presence of rutile (TiO_2) and pseudo-rutile ($Fe^{3+}{}_2Ti_3O_9$), 7 % and 20 % respectively. Slag is a product resulting from the smelting of ilmenite, a process that upgrades the ilmenite concentrate, yielding a TiO_2-rich slag as a primary product and marketable iron metal as co-product [19,20]. The uniformity in the mineralogical composition of slag samples analysed is very high, identifying armalcolite ($(Mg,Fe^{2+})Ti_2O_5$), at 90 % as main mineral species.

The properties of waste and co-products are dependent upon the nature of the ilmenite ore used, the type of process employed and the plant operation efficiency. The mineralogical analysis of the SLUDGE shows ilmenite (22 %) and rutile (34 %), and additionally some previously undetected species in the raw material, such as Fe and Ti oxides ($Fe_3Ti_3O_{10}$), zircon ($ZrSiO_4$) and quartz (SiO_2): 18.2 %, 13 % and 12.1 %, respectively. The detection and quantification of these new mineralogical phases cannot be considered as surprising, since all these species are insoluble in sulphuric acid [8]. By contrast, the mineralogical composition of red gypsum is very homogeneous, with gypsum as the main mineral compound ($CaSO_4 \cdot 2H_2O$), consistent with the expected results. The only point of interest to add is that all the samples analysed have a small fraction (5 %) of titanium and iron oxides, as confirmed by the elemental analysis performed (see below) [9,21].

The co-products (copperas and monohydrate) show a high degree of instability. Although theoretically it could be expected that 100 % of the COP should be melanterite ($FeSO_4 \cdot 7H_2O$), a small amount of rozenite ($FeSO_4 \cdot 4H_2O$) was found (see Table 1). These results can be explained by the tendency of the heptahydrated ferrous sulphate to lose a fraction of its water content and to transform into a mineral form containing only four water molecules. With respect to MON, theoretically it would also be expected that 100 % should be szomolnokite ($FeSO_4 \cdot$H2O), but the presence of a significant proportion (22 %) of rozenite was also found (Table 1). In this case, the opposite tendency to that of copperas is observed, since the monohydrate ferrous sulphate tends to end up with a content of four water molecules, in order to form the most stable hydrated ferrous sulphate compound [22].

3.1.2. Elemental composition

The major elements in the ilmenite ore, expressed as oxides, are Fe_2O_3 and TiO_2, 44 % and 50 % respectively (Table 2). In addition, percentages of SiO_2, Al_2O_3 and MnO can be observed as major impurities associated with the pseudorutile [23]. The slag, in addition to Fe_2O_3 and TiO_2 (11 % and 75 %, respectively), also contains significant levels of several metals such as Si, Al and Mg oxides (2.5 %, 2.3 % and 5 %, respectively).

Sludge has TiO_2 as the main element (52 %), containing considerable amounts of Fe_2O_3 (14 %), SiO_2 (17 %), SO_3 (6.1 %) and ZrO_2 (2.3 %), being compatible with mineral phases obtained by XRD. The predominant compounds in red gypsum are CaO and SO_3 (33 % and 27 %, respectively), also showing a relatively high titanium and iron content (7.6 % TiO_2 and 14 % Fe_2O_3) (Table 2).

The co-products, copperas and monohydrate, contain mainly SO_3 (22 %- 25 %) and Fe_2O_3 (31 %- 39 %) respectively, as was expected, consistent with their mineralogical composition. MON (monohydrate) presents considerable levels of oxide impurities (Al, Mn or Ti), which can be accounted for by the fact that it is formed by the concentration of strong sulphuric acid and that consequently there is precipitation of the dissolved salts it contains. However, the COP (copperas), coming from the crystallization process, shows a high degree of purity (Table 2).

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

3.1.3. Radioactivity characterization

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

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

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

3.2. Applications

3.2.1 Co-products for agricultural use

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

3.2.2. Potential applications for waste

Sludge and red gypsum are currently disposed of in landfills. On this point, our research team has carried out several projects exploring the potential of these wastes in fields as diverse as civil engineering, building construction and CO_2 sequestration.

3.2.2.1. The use of sludge and red gypsum in commercial cement manufacture

The composition of natural gypsum, $CaSO_4.2H_2O$, makes it an ideal set retardant (in concentrations of between 3 and 5 %) in the manufacture of commercial Portland cement [30]. We therefore set out to examine the possibility of replacing natural gypsum with red gypsum in the manufacture of cements [31], and likewise, the potential of sludge as a direct additive to the cement [32].

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

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

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

3.2.2.2. Sludge as an additive in the manufacture of Sulphur Polymer Cements (SPCs)

In this section, we report on our investigation into the valorisation and stabilization of sludge as an additive in the manufacture of sulphur polymer cements (SPCs), and in particular, the mechanical properties and potential environmental impact [36]. For the study we used granular elemental sulphur (99.4 wt %, size < 60 mm, type Rubber Sul 10) (Repsol-YPF, Madrid, Spain), gravel (< 6.3 mm), and a siliceous sand (< 4 mm). A modified sulphur-containing polymer, STX (STARcrete™ Technologies Inc., Quebec, Canada), was used as a thermoplastic material. Three SPCs were manufactured with differing amounts of sludge (10, 20 and 30 % w/w: SPC17-10, SPC21-20 and SPC21-30, respectively), and their performance measured against a control, SPC (SPC21-0), with no sludge and a sample of Ordinary Portland Cement (OPC). To prepare the SPCs, the aggregates (gravel, sand and sludge) were first heated in an oven to 135-140 ºC for 4 h, and the sulphur was liquefied in a mixing bowl within the same temperature range for 10 min. Then, these materials were mixed into a homogeneous viscous paste and at this point, STX was added, stirring for 4-5 min at 140-145 ºC. Finally, the mix was placed in preheated (120 ºC) steel moulds (40x40x160 mm) over a vibration table set at 3000 rpm for 30 s to compact the cements before storing them at room temperature for 24 h. The hardened SPCs casts were then demoulded.

Figure 4 shows the flexural and compressive strength values and the mechanical behaviour of the cements. As can be seen, performance improves as the proportion of sludge increases, up to 20 %. However, the addition of more sulphur (i.e., in the SPC21-30 mixture) produced a thick layer of sulphur around the aggregates, increasing the brittleness of the final composite. SPC21-20 produces the highest values in terms of flexural and compressive strength, at 13 and 64 MPa, respectively. These values are similar to, or even better than, those obtained for OPC and other wastes used in SPC manufacture [37–39]. In addition, it is important to note that the mechanical behaviour of the SPC cements is optimum at 24 hours, whereas for OPC (ordinary Portland cement) the maximum strength is achieved at 28 days, at which point SPC21-20 returned a WAC value of 0.6 kg m^{-2}, slightly lower than the 0.9 kg m^{-2} of SPC21-0. However, both values are lower than those reported for Portland cements [40,41]. SPC21-20 would therefore appear to be a very impermeable SPC.

3.2.2.3. Sludge as an additive in the manufacture of ceramics

Sludge contains a high level of iron oxide ($Fe_2O_3 \approx 10$ %), like red stoneware, which is made from natural clays with a high iron oxide content ($Fe_2O_3 > 7$ %). This led us to consider its valorisation as an additive in ceramic tiles [42,43]. Mixtures of a commercial red stoneware (RSM) with different concentrations of sludge (3, 5, 7, 10, 30 and 50 %) were shaped by uniaxial pressing (Nannetti S hydraulic press) at 40 MPa in a steel die, in order to obtain tiles measuring 50x50x5 mm, which were fired in an electric furnace at 1150ºC following a fast-firing process for eight minutes. The results, shown in Figure 5, indicate that linear shrinkage increases with the concentration of sludge, with values <7 %. Lower values are advantageous because they reduce cracking and volume changes during firing. Also, apparent porosity generally increases with the concentration of sludge. This physical property is very important and is directly related to water absorption [44] and open porosity. Moreover, water absorption decreases with the addition of 3 % and 5 % of sludge (2.82 and 2.48 %, respectively), facilitating the subsequent sintering, drying stages, freeze–thaw cycles and stain resistance. The bulk density increases with the concentration of sludge up to 10 % due to the high density of sludge (3.7 g cm^{-3}). Bending strength increases with the addition of sludge up to 10 %, due to the beneficial effect of ilmenite on sintering during firing as denoted by the decrease in porosity (Figure 5). On the other hand, bending strength values in the 70/30 and 50/50 samples decreases due to the increase of interconnecting open pores. In any case, bending strength values for the 7/3 and 95/5 mixtures are above the minimum value of 30 MPa required by standard EN 14411 for tiles in the BIb group. Likewise, the corresponding values for the 100/0, 93/7 and 90/10 samples are greater than 22 MPa, the minimum value for tiles in the BIIa group, while the 70/30 and 50/50 samples produced values above the minimum value of 18 MPa required for tiles in the BIIb group [45].

3.2.2.4. Waste products as fire-resistant materials

The Thermal characteristics of red gypsum and sludge as additives were examined with a view to their potential as building materials for firewall insulation [21]. A low-cost manufacturing method was used to produce plates measuring 25x25cm, with thicknesses of 1.5 and 2.5cm, using different compositions (P1: 100 % red gypsum; P2: 75 % red gypsum and 25 % sludge; P3: 80 % red gypsum, 15 % sludge and 5 % vermiculite and P4: 100 % Pladur®),. The thermal insulation capacity of the resulting plates was evaluated in accordance with the EN-1363-1 standard.

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

3.2.2.5. Waste as a means of CO_2 sequestration

Finally, red gypsum was evaluated as a source of calcium for CO_2 sequestration by an indirect carbonation process [53]. The process can be conceptually divided into two steps: (a) red gypsum dissolution (eq. 1), and (b) subsequent carbon sequestration (eq. 2). In order to induce the carbonation process, the extraction of calcium from the sample was required beforehand. For this, two different extraction routes were applied (the NaOH andNH_4OH pathways). The entire experimental procedure is explained in equations 1 and 2; full details of the methodology can be found elsewhere [54].

$CaSO_42H_2O$ + [2NaOH or $2NH_4OH$] > $Ca(OH)_2$ + [Na_2SO_4 or $(NH_4)2SO_4$] + $2H_2O$ (1)

$Ca(OH)_2 + CO_2 > CaCO_3 + H_2O$ (2)

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

3.3 Environmental Implications

In summary, we have seen that TiO_2 industry generates two different co-products (copperas and monohydrate) and two residues (sludge and red gypsum). The environmental and occupational radiological impact of the by-products generated is quite limited (Figure 2). The negligible environmental impact of copperas and monohydrate holds not only from the radiological point of view. In relation to heavy metals and/or toxic elements (Table 3), the results for copperas indicate that this co-product is relatively free of trace elements, which is not surprising given its formation process (crystallisation). The concentrations of heavy metals found in the copperas are lower than those found in typical soils (see Table 3), with the exception of Zn and, especially, Cd. By contrast, monohydrate presents heavy metals in similar amounts to those found in phosphate fertilizers used worldwide without any environmental restrictions [2].

The management of sludge and red gypsum is one of the most serious problems currently faced by the TiO_2 pigment industry. Both are mixed in the plant and depleted in natural radionuclides, causing a dilution in the radioactivity associated with them.

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

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

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

This index should not exceed one ($I \leq 1$) for any material used in bulk quantities, e.g., cement, concrete, etc., and six ($I \leq 6$) for superficial materials, e.g. tiles, boards, and so on, to ensure that the external dosage to which occupants are exposed does not exceed the reference value of 1mSv $year^{-1}$ [57]. Figure 7 shows the different index, I, obtained for all the materials analysed. The index (I) for samples RGA, RGB, RGC and SA shows that the value is below one, and consequently, these samples can be used without restrictions. On the other hand, sample SB presents the index slightly above one, while SC has a value close to 2, which is unacceptable from a radiological point of view. Furthermore, the radiological index for all the SPC cements exceeded 1. Nevertheless, these cements could have other civil construction applications, e.g., in marine platforms or bridges, since their radiological impact on the environment can be considered negligible.

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

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

4. Conclusions

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

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

Sludge coming from the TiO_2 pigment production is a good additive (up to 10 %) in the manufacture of red stoneware ceramic bodies, having a beneficial effect to the sintering processes, improving the bending strength (up to 15 %) and reducing both apparent porosity and water absorption (up to 50 %). This waste can be also applied in the manufacturing of fire resistance plates.

Finally, red gypsum can be used as a source of calcium for CO_2 sequestration by an indirect carbonation, obtaining carbonation efficiencies of about 90 % and 65 % with

$NaOH$ and NH_4OH, respectively. In general, the levels of pollutants in the final calcite were comparable to the ones found for typical unperturbed soils.

Acknowledgements

This work has been partially supported by the Government of Andalusia through the project “Characterization and modelling of the phosphogypsum stacks from Huelva for their environmental management and control” (Ref.: P10-RNM-6300). PhD student M. Contreras would like to expresses his gratitude for the research contract granted him through The Fellowship Training Program of the University Teaching Staff; reference AP2010-2746, financed by the Spanish Ministry of Education, Culture and Sport (MECD). This is publication No. 119 from the CEIMAR Publication Series.

References

[1] Kacimi, L.; Simon-Masseron, A.; Ghomari, A.; Derriche, Z.: Reduction of linkerization temperature by using phosphogypsum, J. Hazard. MaterB137, 129–137 (2006).

[2] Kuryatnyk, T-; Angulski da Luz, C.; Ambroise, J.; Pera, J.: Valorization of phosphogypsum as hydraulic binder. J. Hazard. Mater. 160, 681–7 (2008).

[3] De Michelis, I.; Ferella, F.; Beolchini, F.; Olivieri, A.; Vegliό, F.: Characterisation and classification of solid wastes coming from reductive acid leaching of low grade manganiferous ore. J. Hazard. Mater. (2008) doi:10.1016/j.jhazmat.2008.06.024.

[4] Liu, T.; Lin, C.; Wu, Y.: Characterization of red mud derived of from a combined Bayer process and bauxite calcination method. J. Hazard. Mater.146, 255–261 (2007).

[5] Deydier, E.; Guilet, R.; Sarda, S.; Sharrock, P.: Physical and chemical characterization of crude meat and bone meal combustion residue: “waste or raw material?”, J. Hazard. Mater. B121, 141–148 (2005).

[6] Shen, W.; Zhou, M.; Ma, W.; Hu, J.; Cai, Z.: Investigation on the application of steel slag-fly ash-phosphogypsum solidified material as road base material. J. Hazard. Mater. (2007) doi:10.1016/j.jhazmat.2008.07.125.

[7] Potgieter, J.H.; Horne, K.A.; Potgieter, S.S.; Wirth, W.: An evaluation of the incorporation of a titanium dioxide producer’s waste material in Portland cement clinker, Materials Letters. 57, 157–163 (2002).

[8] McNulty, G.S.: Production of titanium dioxide. Plenary lecture. NORM V International Conference Sevilla Spain, 19-22 March 2007. ISBN 978-92-0-101508-2.

[9] Gázquez, M. J., Bolívar, J. P, Garcia-Tenorio, R.; Vaca, F.: Physicochemical characterization of raw materials and co-products from the titanium dioxide industry. J. Hazard. Mater.166, 2, (2009) 1429-1440 (2009).

[10] Lozano, R.L.; Bolívar, J.P.; San Miguel, E.G.; García-Tenorio, R.; Gázquez, M.J.: An accurate method to measure alpha-emitting natural radionuclides in atmospheric filters: application in two NORM industries. Nucl. Instrum. Methods. A.659, 557–68 (2011).

[11] Hurtado, S.; García-Tenorio, R.; García-León, M.: ^{210}Pb determination in lead shields for low-level gamma-spectrometry applying two independent radiometric techniques. Nucl. Instrum. Meth. Section A. 497, 381-388 (2003).

[12] AENOR (Asociación Española de Normalización y Certificación-Spanish Association for Standardisation and Certification). UNE-EN 196-1: Métodos de ensayo de cementos. Parte 1: Determinación de resistencias mecánicas (Methods of testing cement - Part 1: Determination of strength). 2005.

[13] AENOR (Asociación Española de Normalización y Certificación-Spanish Association for Standardisation and Certification). UNE-EN 480-5: Aditivos para hormigones, morteros y pastas. Métodos de ensayo. Parte 5: Determinación de la absorción capilar (Admixtures for Concrete, Mortar and Grout. Test Methods. Part 5: Determination of Capillary Absorption). 2006.

[14] AENOR (Asociación Española de Normalización y Certificación-Spanish Association for Standardisation and Certification). UNE-EN 196-3: Métodos de ensayo de cementos. Parte 3: Determinación del tiempo de fraguado y de la estabilidad de volumen (Methods of testing cement - Part 3: Determination of setting times and soundness). 2005.

[15] ISO (International Organization for Standardization). 10545-3: Ceramic tiles. Part 3: Determination of water absorption, apparent porosity, apparent relative density and bulk density. 1997.

[16] ASTM (American Society for Testing and Materials) C373-88. Standard test method for water adsorption, bulk density, apparent porosity and apparent specific gravity of fired white ware products. 1999.

[17] AENOR (Asociación Española de Normalización y Certificación-Spanish Association for Standardisation and Certification). EN 843-1: Cerámicas técnicas avanzadas. Cerámicas monolíticas. Propiedades mecánicas a temperatura ambiente. Parte 1: Determinación de la resistencia a la flexión (Ratificada por AENOR en enero de 2007.) (Advanced technical ceramics. Monolithic ceramics. Mechanical properties at room temperature. Part. I: Determination of flexural strength). 2006.

[18] AENOR (Asociación Española de Normalización y Certificación-Spanish Association for Standardisation and Certification). UNE-EN 13501-1: Clasificación en función del comportamiento frente al fuego de los productos de construcción y elementos para la edificación. Parte 1: Clasificación a partir de datos obtenidos en ensayos de reacción al fuego (Fire classification of construction products and building elements - Part 1: Classification using data from reaction to fire tests). 2010.

[19] Sahoo, P.K.; Galgali, R.K.; Singh, S.K.; Bhattacharyee, S.; Mishra, P.K; Mahanty, B.C.: Preparation of titania-rich slag by plasma smelting of ilmenite, Scandinavian. J. Metallurgy. 28, 6,243–248 (1999).

[20] Pourabdoli, M.; Raygan, S.; Abdizadeh, H.; Hanaei, K.: Production of high titania slag by electro-slag crucible melting (ECSM) process. Int. J. Miner. Process. 78, 3, 175–181 (2006).

[21] Pérez-Moreno, S.M.; Gázquez, M.J.; Barneto, A.G.; Bolívar, J.P.: Thermal characterization of new fire-insulating materials from industrial inorganicTiO_2 wastes. Thermochim. Acta. 552, 114–122 (2013).

[22] Wang, T.; Debelak, K.A.; Roth, J.A.: Dehydration of iron (II) sulphate heptahydrate. Thermochim. Acta. 462, 1, 89-93 (2007).

[23] Pownceby, I.M.; Sparrow, J.G.; Fisher-White, J.M.: Mineralogical characterization of eucla basin ilmenite concentrates—first results from a new global resource. Miner. Eng. 21, 587–597 (2008).

[24] Gao, R.: Composition of the Continental Crust, Treatise of Geochemistry.Elsevier.3, 1–64 (2003).

[25] United Nations Scientific Committee on the effects of Atomic Radiation (UNSCEAR). Report of the United Nations scientific committee on the effects of atomic radiation. New York: United Nations; 2000.

[26] Mabuchi, H.: On the volatility of some polonium compounds. J. Inorg. Nucl. Chem.25, 657–660 (1963).

[27] United Nations Scientific Committee on the effects of Atomic Radiation (UNSCEAR). Sources, effects and risks of ionizing radiation. Report to the General Assembly, with annexes. New York: United Nations; 1988.

[28] Gázquez, M.J.; Mantero, J.; Bolívar, J.P.: Physico-chemical and radioactive characterization of TiO_2 undissolved mud for its valorisation. J. Hazard. Mater.191, 269–276 (2011).

[29] Orihuela, D.L.; Marijuan, J.L.: Sulfatos de hierro: su uso agrícola. Ed. University of Huelva. (In Spanish), Huelva, Spain. (2003). ISBN: 9788495699749.

[30] Potgieter, J.H.; Potgieter, S.S.; McCrindle, R.I.: A comparison of the performance of various synthetic gypsums in plant trials during the manufacturing of OPC clinker. Cem. Concr. Res. 34, 2245–2250 (2004).

[31] Gázquez, M.J.; Bolívar, J.P.; Vaca, F.; Garcia-Tenorio, R.; Mena--Nieto, A.: Use of the “red gypsum” industrial waste as substitute of natural gypsum for commercial cements manufacturing. Mater. Construc, (2011). doi:10.3989/mc.2011.63910 ISSN: 0465-2746.

[32] Gázquez, M.J.: Characterization and recovery of waste generated in the industry for the production of titanium dioxide (Caracterización y valorización de residuos generados en la industria de producción de dióxido de titanio). University of Huelva; (2010).

[33] Chandara, C.; Azizi Mohd Azizl, K.; Arifin Ahmad, Z; Sakai, E.: Use of waste gypsum to replace natural gypsum as set retarders in Portland cement. Waste. Manage. 29, 1675–1679 (2009).

[34] Vangelatos, I.; Angelopoulos, G.N.; Boufournos, D.: Utilization of ferroalumina as raw material in the production of Ordinary Portland Cement. J. Hazard. Mater.168, 473–478 (2009).

[35] Özkul, M.H.: Utilisation of citro- and desul phogypsum as set retarders in Portland cement. Cem. Concr. Res.30, 1755–1758 (2000).

[36] M. Contreras, M.; Gázquez, M.J.; García-Díaz, I.-,Alguacil, F.J.; López, F.A.; Bolívar, J.P.: Valorization of ilmenite mud waste for the manufacturing of Sulfur polymer cements. J. Environ. Manage. 128, 625-630 (2013).

[37] López, F.A., Román, C.P., Padilla, I., López-Delgado, A., Alguacil, F.J.: The application of sulfur concrete to the stabilization of Hg-contaminated soil. Proceedings of the 1stSpanish National Conference on Advances in Materials Recycling and Eco-Energy (RECIMAT'09) Madrid, Spain, November 12-13. 38-41, 978-84-7292-3980-0 (2009),

[38] López, F.A., Gázquez, M.J., Alguacil, F.J., Bolivar, J.P., García-Díaz, I., López Coto, I.: Microencapsulation of phosphogypsum into a sulfur polymer matrix: physico chemical and radiological characterization. J. Hazard. Mater. 192, 234-245 (2011).

[39] Mohamed, O.A.M.; Gamal, M.: Sulfur based hazardous waste solidification. Environ. Geol. 53, 159-175 (2007).

[40] Khatib, J.M.; Roger, M.: Absorption characteristics of metakaolin concrete.Cem. Concr. Res. 34 (1), 19-29 (2004).

[41] Medeiros, M.H.F.: Helene, P.: Surface treatment of reinforced concrete inmarine environment: influence on chloride diffusion coefficient and capillarywater absorption. Constr. Build. Mater. 23 (3), 1476-1484 (2009).

[42] Contreras, M.; Martín, M.I.: Gázquez, M.J.; Romero, M.; Bolívar, J.P.: Valorisation of ilmenite mud waste in the manufacture of commercial ceramic. Constr. Build. Mater. 72, 31–40 (2014).

[43] Contreras, M.; Martín, M.I.; Gázquez, M.J.; Romero, M.; Bolívar, J.P.: Manufacture of ceramic bodies by using a mud waste from the TiO_2pigment industry. Key. Eng. Mater. 663, 75-85 (2016).

[44] Raigón-Pichardo, M.; García-Ramos, G.; Sánchez-Soto, P.J.: Characterization of a waste washing solid product of mining granitic tin-bearing sands and its application as ceramic raw material. Resour. Conserv. Recycl. 17(2), 109–24 (1996).

[45] AENOR (Asociación Española de Normalización y Certificación-Spanish Association for Standardisation and Certification). UNE-EN 14411: Baldosas cerámicas. Definiciones, clasificación, características, evaluación de la conformidad y marcado (Ceramic tiles. Definitions, clasifications, characteristics and marking). 2003

[46] Leiva, C.; Vilches, L.F.; Vale, J.; Fernández-Pereira, C.: Influence of type of ash on the fire resistance characteristics of ash-enriched mortars. Fuel. 84, 1433–1439 (2005).

[47] Leiva, C.; Vilches, L.F.; Vale, J.; Fernández-Pereira, C.: Fire resistance of biomass ash panels used for internal partitions in buildings. Fire Safety J. 44, 622–628 (2009).

[48] Leiva, C.; Vilches, L.F.; Vale, J.; Olivares, J.; Fernández-Pereira, C.: Effect of carbonaceous matter contents on the fire resistance and mechanical properties of coal fly ash enriched mortars. Fuel. 87, 2977–2982 (2008).

[49] Leiva, C.; Garcia Arenas, C.; Vilches, L.F.; Vale, J.; Giménez, A.; Ballesteros, J.C.; Fernandez-Pereira, C.: Use of FGD gypsum in fire resistant panels. Waste. Manage. 30, 1123–1129 (2010).

[50] Vilches, L.F.; Fernández-Pereira, C.; Olivares del Valle, J.; Vale, J.: Recycling potential of coal fly ash and titanium waste as new fireproof products, Chem. Eng. J. 95, 155–161 (2003).

[51] Vilches, L.F.; Leiva, C.; Vale, J.; Fernández-Pereira, C.: Insulating capacity of fly ash pastes used for passive protection against fire. Cement. Concrete. Compos. 27, 776–781 (2005).

[52] García Arenas, C.; Marrero, M.; Leiva, C.;Solís-Guzmán, J.; Vilches Arenas, L.F.: High fire resistances in blocks containing coal combustion fly ashes and bottom ash. Waste. Manage. 31, (2011) 1783–1789 (2011).

[53] Pérez-Moreno, S.M.; Gázquez, M.J.; Bolívar, J.P.: CO_2 sequestration by indirect carbonation of artificial gypsum generated in the manufacture of titanium dioxide pigments. Chem. Eng. J. 262, 737–746 (2015).

[54] Cárdenas-Escudero, C.; Morales-Flórez, V.; Pérez-López, R.; Santos, A.; Esquivas, L.: Procedure to use phosphogypsum industrial waste for mineral CO_2sequestration, J. Hazard. Mater. 196, 431–435 (2011).

[55] Contreras, M.; Pérez-López, R.; Gázquez, M.J.; Morales-Flórez, V.; Santos, A.; Esquivias, L.; Bolívar, J.P.: Fractionation and fluxes of metals and radionuclides during the recycling process of phosphogypsum wastes applied to mineral CO_2 sequestration. Waste. Manage. 45, (2015) 412–419 (2015).

[56] Directive 2013/59/EURATOM, of 5 December 2013. Laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation.

[57] Kovler, K.: Radiological constraints of using building materials and industrialby-products. Constr. Build. Mater. 23, 246–253 (2009).

[58] U.S. EPA, Test Methods for Evaluating Solid Waste - Physical Chemical Methods, SW-846, U.S. Environmental Protection Agency, Washington, DC, 1997.

[59] Hierro, A.; Martín, J.E.; Olías, M.; García, C.; Bolivar, J.P.: Uranium behaviour during a tidal cycle in an estuarine system affected by acid mine drainage. Chem. Geo. 342, 110-118 (2013).

FIGURE AND TABLE CAPTIONS

Figure 1. Detailed diagram of the TiO_2 extraction by sulphate way

Figure 2. Activity concentration in Bq kg^{-1} of each materials used in the Huelva TiO_2 industry.

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

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

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

Figure 6. Insulating capacity of the plates tested.

Figure 7. Index "I" obtained for all analysed materials in the different applications. The limit I value is indicated according bulk ($I \leq 1$) or superficial materials ($I \leq 6$) [57].

Table 1. Average (five samples) mineralogical composition (%) of raw materials, co-products and wastes in the Huelva TiO_2 industry.

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

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

Table 4. Setting times established following a normalized protocol (UNE-EN 196-3) for the various cements and for ordinary Portland cement (OPC) taken as reference. Optimum W/C ratios are also shown.

Table 5. The carbonation efficiency (CE) in different experiments.