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Valorisation of inorganic waste for obtaining construction materials

Memoria para optar al grado de doctor
presentada por:

Manuel Contreras Llanes

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Bajo la dirección de los doctores:

Juan Pedro Bolívar Raya

Manuel Jesús Gázquez González

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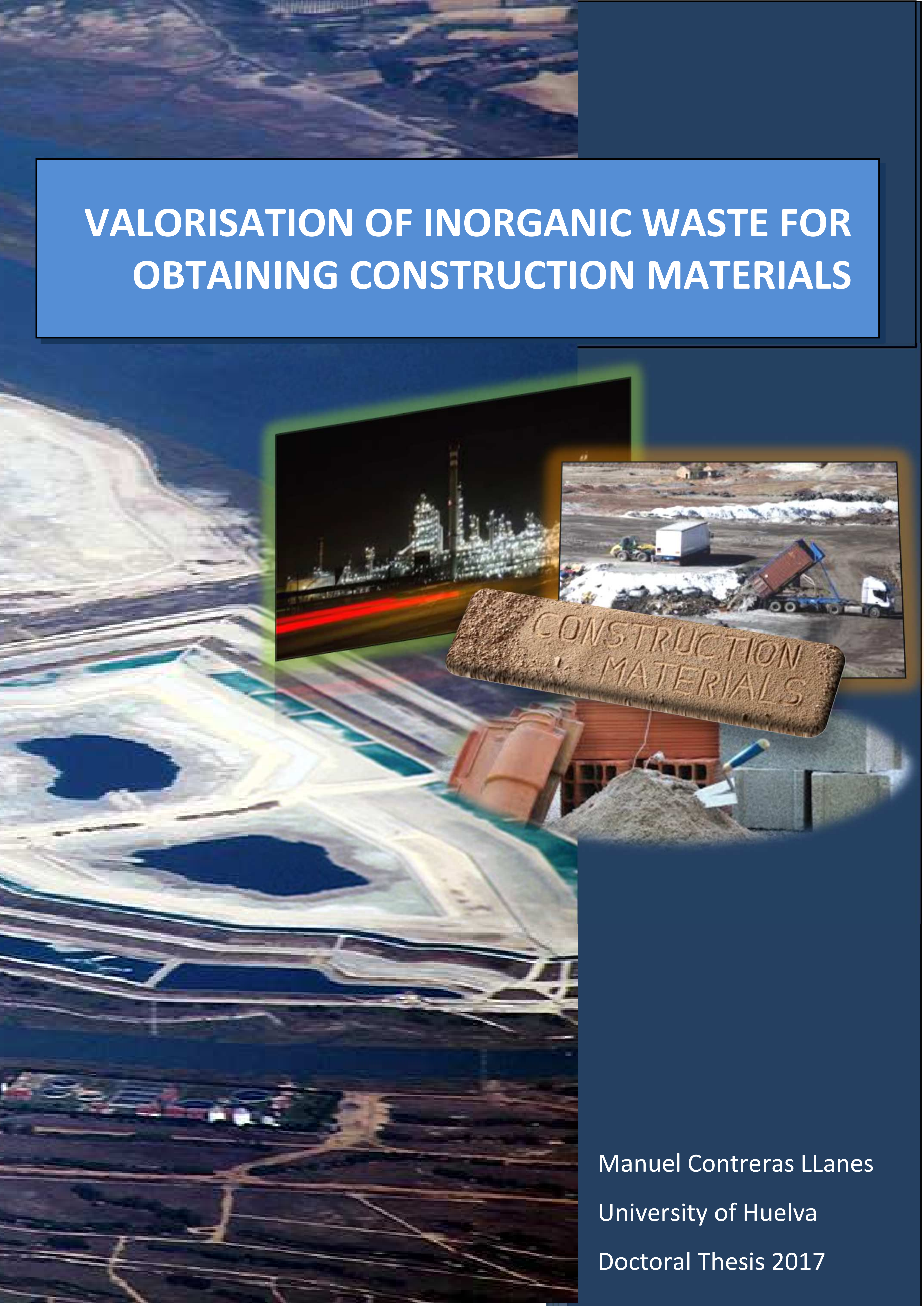
VALORISATION OF INORGANIC WASTE FOR OBTAINING CONSTRUCTION MATERIALS



Manuel Contreras LLanes

University of Huelva

Doctoral Thesis 2017

VALORISATION OF INORGANIC WASTE FOR OBTAINING CONSTRUCTION MATERIALS

Memoria presentada por:

MANUEL CONTRERAS LLANES

para optar al título de DOCTOR

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Tesis supervisada por:

Dr. Juan Pedro
Bolívar Raya

Dr. Manuel Jesús
Gázquez González

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RESUMEN

La generación de residuos, en general, aumenta según incrementa el grado de desarrollo tecnológico de una sociedad, por lo que el interés por la protección del medio ambiente y los riesgos para la salud han florecido en los últimos años. Por tanto, desarrollar estrategias que mejoren la gestión de los residuos tratando de alcanzar un desarrollo sostenible en el que se minimicen los recursos utilizados y los residuos generados es muy necesario, así como tratar de alcanzar una economía circular, incorporando los residuos y co-productos a nuevos materiales. Este enfoque ya ha sido incluido en las estrategias de la Unión Europea en materia de residuos, priorizando la prevención en la generación de residuos, así como el reciclaje y la valorización de estos como alternativa a su depósito en vertedero.

El objetivo principal de la presente Tesis Doctoral nace de la necesidad de desarrollar nuevas aplicaciones eficientes y de interés comercial en materiales de construcción (cerámicas, cementos y ladrillos), en base a diferentes porcentajes de tres tipos de residuos inorgánicos: (1) lodo de ilmenita generado en la producción de pigmento de TiO_2, (2) fosfoyeso procedente de la industria del H_3PO_4, y (3) residuos de construcción y demolición (RCD).

Para el estudio, tanto de la caracterización de los residuos como de los nuevos materiales diseñados, se han empleado diferentes técnicas instrumentales; entre otras, la difracción y la fluorescencia de rayos X (DRX/FRX), espectrometrías de masas o de emisión óptica con fuente de emisión por plasma de acoplamiento inductivo (ICP-MS/OES), análisis termo-gravimétrico y calorimétrico de barrido diferencial (TGA/DSC), y la microscopía electrónica de barrido (MEB). Las propiedades tecnológicas, como la resistencia, la absorción de agua, etc., han sido comparadas en relación a materiales comerciales tradicionales y evaluadas de acuerdo a los estándares técnicos establecidos. Como algunos de los residuos son considerados NORM (Naturally Occurring Radioactive Material = materiales radioactivos de origen natural), los materiales obtenidos fueron evaluados mediante espectrometría alfa y gamma, y

también se evaluaron las implicaciones ambientales de su utilización (estudios de lixiviación y radiológicos).

Los resultados más relevantes obtenidos de la presente Tesis Doctoral se pueden dividir en tres bloques:

Lodo de ilmenita

Una vez conocidas las propiedades físicas, químicas, granulométricas, micro-estructurales y radiológicas de este residuo se llevó a cabo el diseño de nuevos cementos poliméricos sulfurosos y cuerpos cerámicos, incorporando diferentes porcentajes. Los datos obtenidos demostraron que el lodo de ilmenita puede inmovilizarse y valorizarse con éxito al incluirlo como aditivo. Sus propiedades tecnológicas cumplieron sobradamente con los requisitos marcados en las diferentes regulaciones y, en algunos casos, fueron incluso mejores a las de los materiales de referencia. Finalmente, indicar que ambos materiales pueden ser usados sin generar problemas ambientales o de salud para las personas.

Fosfoyeso

Este residuo ha sido incluido como aditivo en cerámicas, las cuales has cumplido con las normativas internacionales vigentes en relación a las propiedades tecnológicas y con los requisitos ambientales establecidos. Incluso la adición de hasta 5 % de fosfoyeso mejora las propiedades tecnológicas en comparación al material de referencia.

Este residuo también ha sido estudiado como fuente de calcio para el secuestro mineral del CO_2 y obtención de calcita, obteniéndose altas eficiencias (96 %). El estudio de los flujos de metales y radionucleidos demostraron que la mayor parte de los contaminantes del fosfoyeso se transfieren a la calcita (> 95 %).

RCD

Este residuo ha sido reciclado como sustituto del agregado natural para la producción ladrillos. Los resultados muestran que pueden obtenerse ladrillos de bajo costo con excelentes propiedades físicas usando RCD como agregado, y cal o cemento como aglutinantes.

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ABSTRACT

Waste generation, in general, increases with technological development, consequently the interest in environmental protection and health risks have grown in recent years. Therefore, it is necessary to develop strategies that has a beneficial impact on waste reuse and management trying to achieve sustainable development in which the resources used and the waste generated are minimised, as well as trying to achieve a circular economy, incorporating waste and co-products to new materials. This approach has already been included in the European Union waste strategies, prioritizing the prevention in waste generation, as well as the recycling and valorisation of wastes as alternative to their landfilling disposal.

The main objective of this Doctoral Thesis was born out of the need to develop new efficient applications with commercial interest as construction materials (ceramics, cement and bricks), depending on the percentage of three types of inorganic residues: (1) Ilmenite mud generated in the production of TiO_2 pigment, (2) phosphogypsum from the H_3PO_4 industry, and (3) construction and demolition waste (CDW).

A number of instrumental techniques were deployed to characterise both the wastes used and the new materials designed, such as, X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), thermo-gravimetric analysis and differential scanning calorimetry (TGA/DSC) and scanning electron microscopy (SEM). In addition, the technological properties, such as resistance, water absorption, etc., have been compared in relation to traditional commercial materials and evaluated according to the established technical standards. Since, some of the wastes are considered NORM (Naturally Occurring Radioactive Material), the materials obtained were evaluated by alpha and gamma spectrometry, and the environmental implications (leaching and radiological studies) were evaluated.

The most prominent findings of the present research can be divided under three main headings:

Ilmenite mud

Once the physical, chemical, granulometric, micro-structural and radiological properties of this waste were known, the design of new sulphur polymer cements and ceramic bodies adding different percentages were carried out. The results shown that ilmenite mud could be successfully immobilised and valorised as an additive. Theirs technological properties are in agreement with the requirements established in each regulations and, in some cases, the results were even better than those obtained by the reference materials. Finally, it can be concluded that that both materials can be used with negligible environmental impact or health risk.

Phosphogypsum

This waste has been valorised as an additive in ceramic manufacturing, complying with the international regulations for both technological properties and environmental requirements. Moreover, the addition up to 5 wt.% of phosphogypsum improves the technological properties in relation to the reference material.

In addition, this waste has been studied as a calcium source for CO_2 mineral sequestration and calcite production with high efficiencies (96 %). The study of the fluxes of metals and radionuclides showed that most of the phosphogypsum pollutants are transferred to calcite (> 95%).

Construction and demolition waste (CDW)

This waste has been recycled as substitute of natural aggregates to produce bricks. The results shown that low cost bricks with excellent technological properties can be obtained using CDW as an aggregate and lime or cement, as binders.

CONTENTS

Chapter 1

Introduction

1.1 BACKGROUND

1.1.1 State of the Art

Nowadays, the environmental problems related to the production and elimination of the wastes have revealed as a great challenge. Waste generation tends to increase with population and economical growth, which could produce significant hazardous risks on the environment and the public health. For this reason, the minimisation, treatment, and valorisation of the waste is essential. This has led to an environmental awareness, trying to achieve sustainable development through its three main pillars: economic development, social development and environmental protection.

The idea of 'sustainable development' into the European waste policy has been incorporated. These policies should focus to reduce the amount of waste generated, pollutants at source, select the most appropriate treatments, promote recycling and, prioritising the valorisation before its disposal. Sustainable waste management requires considering the environmental impacts and health risk of waste disposal, and therefore the valorisation of waste constitute an excellent alternative to its storing in controlled landfills. This fact would involve both a saving of materials and avoiding the final disposal in landfills, with the consequent reduction of the future environmental impact and costs associated.

On the other hand, the circular economy recognises the physical limits of resources and the importance of safeguarding the environment whilst providing a viable business alternative. Thus, an important area in the circular economy is the valorisation of the waste generated. The valorisation of waste could generate co-products with potential economic value, especially, when the co-product obtained can successfully compete with the properties of traditional raw materials or are new materials developed for specific applications. Obviously, these co-products should comply with national and/or international policies ensuring a negligible environmental impact and health risks.

It is necessary to try a change about the negative vision associated with the word “waste, changing it into a positive vision. A waste should be seen as a new resource or raw material with possibility of being recycled in the manufacturing of new consumer products.

The current European Waste Strategy describes the policies concerning the recovery and disposal of waste. In this sense, the EU Directive 2008/98/EC sets the basic concepts and definitions related to waste managament, repealing certain previous Directives by incorporating all them into the Waste Framework Directive. This Directive lays down measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use.

For that reasons, it is important to note that this Directive incorporates a high novelty introducing the new concept on the “end-of-waste” status. Thus, several wastes can loss the waste status when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance 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 the 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.

These criteria should be established for specific materials by using the procedure described in Article 39 (2) of the Waste Framework Directive (2008/98/EC) (so called "comitology"). A mandate to set end-of-waste criteria was introduced to provide a high level of environmental protection and an environmental and economic benefit. They aim to further encourage recycling in the EU by creating legal certainty and a level playing field as well as removing unnecessary administrative burden. The criteria shall include limit values for pollutants where necessary and shall take into account any possible adverse environmental effects of the substance or object.

Consequently, developing technologies and new applications trying to find new applications to the generated wastes in order to reduce management costs and environmental pollution implication are required (Roy et al., 1992; Andres et al., 2005; Caligaris et al., 2000).

In our case, the valorisation of inorganic industrial waste as building materials avoid direct release into the environment of big amount of residual materials, reducing disposal costs and generating health and environmental benefits (Puertas et al., 2008; Quijornaa et al., 2008). It is expected that by 2020 new building structures will include at least 5 % of recycled materials (Freedonia, 2012).

Although valorisation is the best way to manage inorganic waste, there are still several obstacles to using these wastes in construction materials:

- Lack of confidence of clients and contractors.
- Uncertainty on its environmental benefits.
- Possible potential health hazards arising from the use of these materials.
- Lack of standards and specifications that producers can take into account.
- Low quality of the final product, owing to lack of knowledge of waste.
- Distance among disposal sites or waste generating activities and valorisation factories.

- Lack of a consistent supply of good quality valorised material that can satisfy existing demand.
- In the specific case of NORM[1] waste, which has a significant increase in natural occurring radioactivity, an assessment of the radiological risks of the application, as building materials are required.

In this sense, all aspects above mentioned must be taking into account in order to carry out a correct valorisation process.

In addition, reducing CO_2 emissions is an important task today. The targets established in the Kyoto Protocol cover the reduction of emissions in the six main greenhouse gases, as carbon dioxide, to achieve stabilisation in greenhouse gases concentration levels between 450 and 650 ppm CO_2-eq. Carbon dioxide equivalency is a quantity used to compare the emissions from various greenhouse gases, which describes the amount of CO_2 equivalent based upon their global warming potential.

A potential way to reduce CO_2 emissions, and hence, mitigate global warming, includes carbon sequestration technologies that are being widely studied worldwide. Nowadays, three possibilities for CO_2 sequestration are being applied: 1) aqueous carbon sequestration, 2) geological carbon sequestration, and 3) mineralogical carbon sequestration, which is the technique studied in the present thesis (Kirchofer et al., 2013).

Mineral carbonation has been proposed as one of the main methods for CO_2 sequestration, and is a promising approach to capture carbon dioxide into innocuous, stable and environmental benign carbonate mineral, fixing the carbon dioxide definitively. This technique involves a naturally occurring reaction in geological formations where aqueous ions

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[1] NORM (Naturally Occurring Radioactive Material): or radioactive materials, which occur naturally and where human activities can increase the exposure of people to ionizing radiation.

(mainly Ca^{2+} and Mg^{2+} resulting from silicates or oxides) react with CO_2 to form thermodynamically stable carbonate minerals, such as calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$).

This thesis is framed within the general objective on the possibility of recovery in the public and private sectors the inorganic waste streams, developing effective applications. In our case, we try to valorise in the building materials three different inorganic wastes (phosphogypsum, ilmenite mud, and construction and demolition waste), currently destined for landfill and without any commercial use. In addition, phosphogypsum was evaluated as a Ca source for CO_2 mineral sequestration studying the environmental implications concerning to the fractionation and fluxes of trace metals and radionuclides produced through the carbonation process.

Ilmenite mud and phosphogypsum are generated in two industrial processes, the titanium dioxide pigment production and the phosphoric acid manufacture, respectively, both placed in the industrial area of Huelva (Spain). In addition, both activities are NORM (Naturally Occurring Radioactive Material) industries, where the co-products and waste produced in the industrial process can be enhanced in natural radionuclides (IAEA, 2004).

The third waste is produced during the building operations, called construction and demolition waste (CDW), being the building materials account for about half of all materials used, and one half of the solid waste generated worldwide.

1.1.2 Waste generation

1.1.2.1 The TiO_2 pigment generation process

Contrary to popular belief titanium dioxide pigment production is the major consumer (approx. 96 %) of titanium minerals. The 4 % remaining is consumed by titanium metal and alloys manufacture. The annual worldwide production of titanium dioxide pigment is estimated over 5.6 million tonnes (3.7 proceeds via chloride and 1.9 by sulphate route) (USGS 2011). The main producer is China, annually 1.7 million tonnes, followed by Europe and North America, both with 1.4 million tonnes per year, approximately.

Titanium dioxide is the most commonly used white pigment due its brightness, whiteness, opacity, chemically resistant and non-toxic. The major market of titanium pigment is paint (57 %), followed by plastics and paper, with 24 % and 12 % respectively (Fig. 1.1). Furthermore, it is used in high-tech applications such as solar cells, glass manufacture, biomedical devices and air/water purification, cosmetics and food.

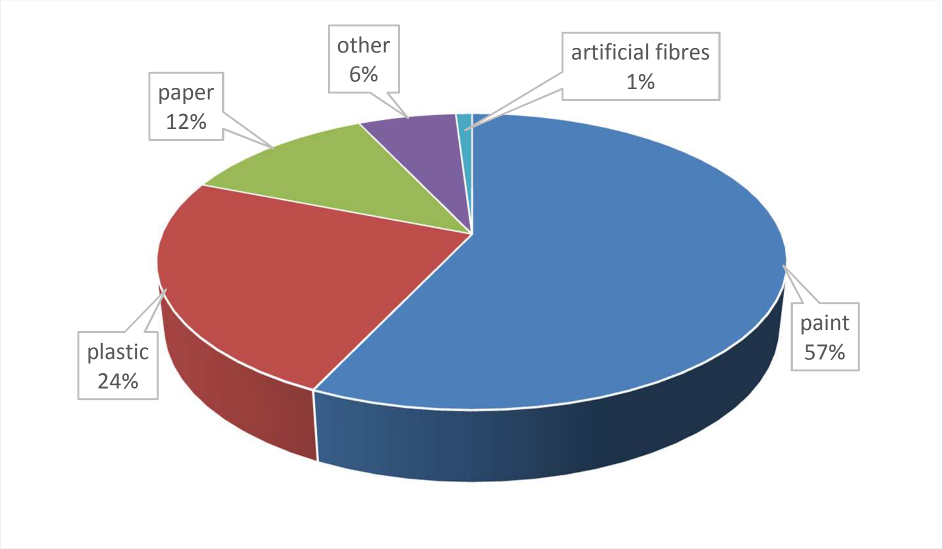

Figure 1.1. Uses of titanium dioxide pigment (https://goo.gl/bUqQeP)

The main processes for TiO_2 pigment manufacture are two, sulphate and chloride process, which use two principal ores, ilmenite (45-60 % of TiO_2) and rutile (up to 99 % TiO_2), respectively. Both processes differ in their chemistry and raw material requirements.

- The chloride method is the most common, 65 % of the world's titanium dioxide pigment production because produces a purer product and environmental friendly alternative. This method run as a continuous process, needs a high-grade ore, as rutile, which is mixed with coke (reducing agent) and gaseous chlorine at 900-

1000 ºC (McNulty, 2007). Then, the resulting gas stream containing titanium tetrachloride ($TiCl_4$) and impurities (McNulty, 2007; Braun et al., 1992) is purified and condensed. Finally, this liquid is oxided to form TiO_2 and release the chlorine is recycled back.

- The sulphate route employs a simple technology, run as a batch and uses lower grade ores (cheaper ore). However, this process generates large amounts of waste materials and acid, which is quite expensive the treatment.

The sulphate route is used in the 70 % of the European production (Gázquez et al., 2014). This method generates a large amount of by-products and waste, as ilmenite mud, object of study in this thesis. This waste is generated during the digestion of the feedstock (ilmenite ore) with highly concentrated sulphuric acid (80–95 %).

This chemical process involves four main stages (Fig. 1.2). The reaction begins with the digestion of the ore (Eq. 1.1):

$$FeTiO_3\ (s) + 2H_2SO_4\ (aq) \rightarrow FeSO_4\ (aq) + TiOSO_4\ (aq) + 2H_2O \qquad [Eq.\ 1.1]$$

Then, the process continues with the precipitation of the titanile sulphate ($TiOSO_4$), step called “clarification”, precipitating a hydrated TiO_2, which is subsequently separated by vacuum filters and later washed according Eq. 1.2:

$$TiOSO_4\ (aq) + (n+1)H_2O \rightarrow TiO_2 \cdot nH_2O\ (s) + H_2SO_4\ (aq) \qquad [Eq.\ 1.2]$$

Finally, the TiO_2 pulp is calcined for the removal of its water content and some traces of sulphur, metals, etc. (Eq. 1.3).

$$TiO_2 \cdot nH_2O\ (s) \rightarrow TiO_2\ (s) + nH_2O \qquad [Eq.\ 1.3]$$

The total reaction demands large quantities of sulphuric acid and produces copious amounts of acidic waste (concentrated and weak acid stream). This acidic waste could cause significant damage to the environment. Moreover, during the digestion stage is generated the ilmenite mud waste (undissolved ilmenite), which is passed to a clarification tank where is allowed to settle. This mud is finally separated from the liquor by decantation and filtration (Gázquez et al., 2011).

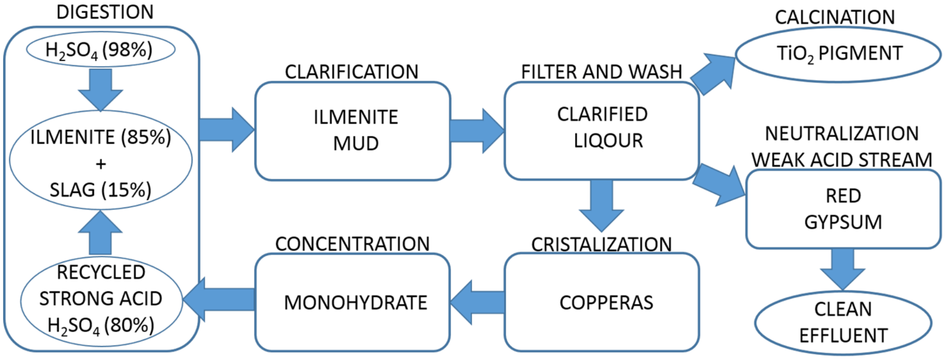

Figure 1.2. Diagram of the sulphate process used in the Huelva factory

About one tonne of raw material (ilmenite or ilmenite + slag[2]) is required to produce 0.5 tonnes of titanium dioxide pigment, which genarates 0.2 tonnes of ilmenite mud waste with no commercial application (Gázquez et al. 2011). The only titanium dioxide pigment production factory in Spain is placed in the city of Huelva (Fig. 1.3).

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[2] Titaniferous slag, containing 70–80 % titanium dioxide, is a co-product resulting of the smelting of ilmenite in order to decrease the reagent consumption and waste material accumulation in the subsequent pigment-making process, because the iron input in the titanium dioxide chemical process is reduced (Pistorius and Coetzee, 2003).

Figure 1.3. Location map of phosphoric acid plant

Dondi et al. (2010) have investigated the application in clay bricks manufacture but no further applications are documented in the literature. The main environmental implication associated to this waste is the presence of hazardous substances that could potentially damage the environment and health if not adequately managed (Gázquez et al., 2009). The ilmenite mud contains significant concentrations of heavy metals, radionuclides and residual sulphur, implying a highly acidic pH. Moreover, the ilmenite mud must to be stored in a controlled landfill repository because of has been classified as ‘‘hazardous waste’’ according the European legislation (Commission Decision 2000/532/EC as amended three times by the Commission Decisions 2001/118/EC, 2001/119/EC and 2001/573/EC). Therefore, the controlled disposal area must have adequate leachate collection, etc., to prevent the escape of potentially toxic elements. In addition, the ilmenite ore used in the TiO_2 pigment industrial process is classified as NORM due to the high activity concentration of natural radionuclides from both ^{238}U and ^{232}Th series (IAEA, 2004). Some of these radionuclides can be found enhanced in the ilmenite mud waste generated.

The treatment of the strong acid effluent generates two co-products, cooperas (140,000 tonnes) and monohydrate (125,000 tonnes), which are currently used commercially. On the other hand, the treatment of the weak acid stream produces red gypsum waste (70,000 tonnes) and clean water

(Fig. 1.2) (McNulty, 2007; Mantero et al., 2013; Gázquez et al., 2011) . The red gypsum and the ilmenite mud generated throughout the process are disposed of in a controlled industrial waste repository about 70 km from the factory.

1.1.2.2 Manufacturing process of phosphoric acid

Phosphoric acid (H_3PO_4) is demanded in many markets such as, chemical industry, fertilisers manufacture, food industry, metallurgy, etc. The worldwide production of phosphoric acid is estimated over 43 million tonnes P_2O_5 each year (FAO, 2015). The main producer is Asia, with an estimated production of 14 million tonnes per year. While, both North America and Europe produce annually 10 and 4 million tonnes, respectively.

Nowadays, the main worldwide use of phosphoric acid is the manufacture of phosphates fertilisers (80 %), but this proportion varies country by country (Fig. 1.4). The manufacture of fertilisers from phosphoric acid is used to rectify phosphorus deficiencies in soils. Furthermore, phosphoric acid is used in detergents as builder (12 %), in animal feeds manufacturing as additive (4 %), as food and drink additives and in some treatment process (4 %).

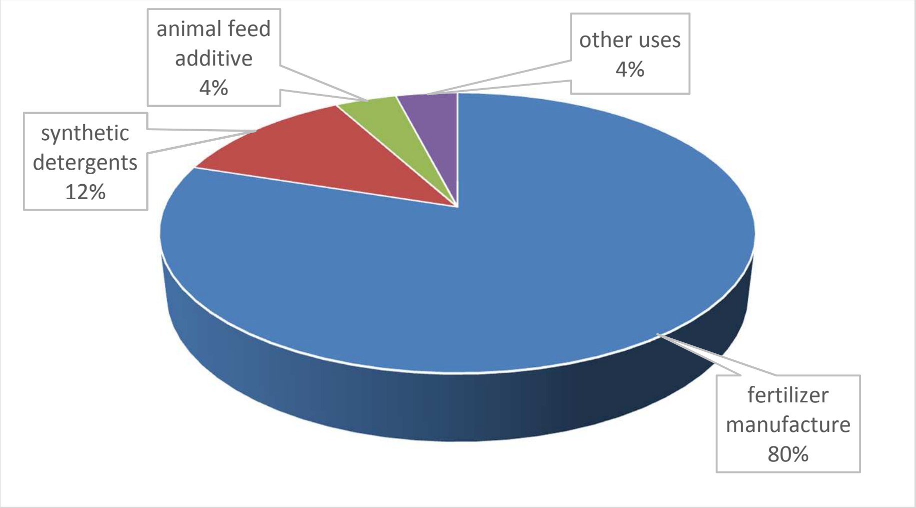

Figure 1.4. Uses of phosphoric acid (https://goo.gl/6ke1RG).

Manufacturing process for phosphoric acid present two main routes: 'wet' process and thermal process (Fig. 1.5).

- The 'wet' method is the most common, 90 % of phosphoric acid production (Becker, 1989), because it is the economic alternative. This method produces a low pure acid phosphoric but it is enough to be used in phosphate fertiliser's production, without further purification.

- The thermal route normally produces a high pure phosphoric acid highly concentrated. This method is hardly used because of the amount of energy that is needed. It is used in the manufacture of detergents, high-grade chemicals, food products and pharmaceuticals.

The 'wet' process is economic but generates a large amount of a gypsum-rich waste called phosphogypsum ($CaSO_4 \cdot 2H_2O$), studied in this thesis. It is generated during the acid attack with concentrated (93 %) sulphuric acid (H_2SO_4) of the fluorapatite ($Ca_5(PO_4)3F$), known as phosphate rock (Rutherford et al., 1994). The process comprises four stages: grinding, reaction, filtration and concentration and these are represented in Fig. 1.5. The chemical reaction of the industrial process can be summarised as shown in Eq. 1.4:

$$Ca_5(PO_4)_3F\ (s) + 5H_2SO_4\ (aq) + 10H_2O \rightarrow$$
$$3H_3PO_4\ (aq) + 5CaSO_4 \cdot 2H_2O\ (s) + HF\ (g) \qquad \text{[Eq. 1.4]}$$

This chemical reaction results in phosphoric acid, hydrofluoric acid[3] and calcium sulphate (gypsum), which is removed as phosphogypsum plus other insoluble impurities. The acids, H_3PO_4 and HF produced are cleaned, condensed and purified. On the other hand, once crystallised, the

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[3] Hydrogen fluoride is very soluble in water and this fact is used to control the gas level in the process. Hydrogen fluoride is collected and sent into a scrubber where is diluted in water producing a hydrofluoric acid weak effluent which is mixed with phosphogypsum waste and deposited in the stockpiles precipitating as hexafluorosilicic acid (H_2SiF_6).

phosphogypsum is separated from the liquid phase by filtration, mixed with water and stored in large stockpiles in areas close to fertiliser plants. The phosphogypsum waste of Huelva is generated as dehydrate ($CaSO_4 \cdot 2H_2O$).

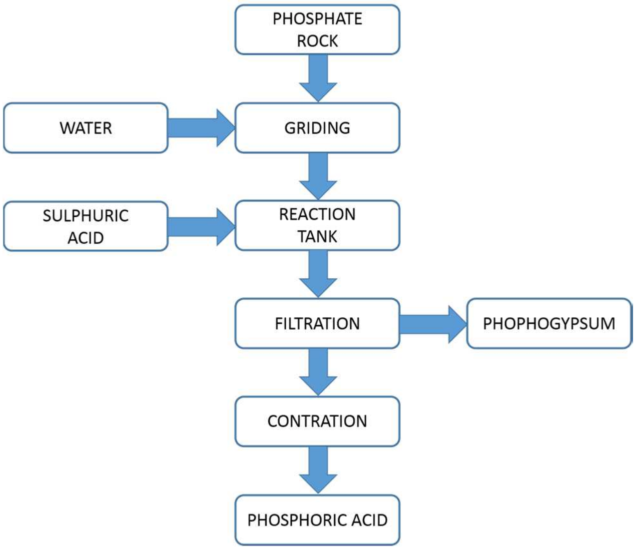

Figure 1.5. Scheme of the phosphate processes (USEPA, 1993).

Approximately, 5 tonnes of phosphogypsum are generated for producting every tonne of P_2O_5 manufactured. Worldwide phosphogypsum production is estimated to be around 280 Mt per year and only 15 % is recycled in agriculture (Yang et al., 2009; Parreira et al., 2003), amendment and reclamation of saline soils (Jacomino et al., 2009; Papastefanou et al., 2006), backfill for road construction (Al-Oudat et al., 1998a; Al-Oudat et al., 1998b), manufacture of Portland cement (Kim, 2010), Sulphur polymer cement (García-Díaz et al., 3013; López et al., 2011) and asphaltic bitumen (Cuadri et al., 2014).

The main restriction associated with the recycling of phosphogypsum is the presence of impurities, such as metals, potentially toxic elements and natural radionuclides from the ^{238}U decay series (Mas et al., 2006; Pérez-López et al., 2007). Previous research works (Bolivar et al. 2000) demonstrated that during the chemical attack of the phosphate rock, the impurities are partitioned according to their respective elementary chemical behaviour. Hazard trace elements such as, Sr, Cd and Y, and radionuclides. About 80 % of the ^{226}Ra, 90 % of the ^{210}Po and 20 % of the ^{238}U and ^{234}U originally in the phosphate rock goes into the phosphogypsum (Bolívar et al., 2009; Jacomino et al., 2009). Thus, phosphogypsum has been classified as Naturally Occurring Radioactive Material (NORM) (IAEA, 2004).

In Spain, the phosphoric acid production by via sulphate began in 1968 in the city of Huelva (SW Iberian Peninsula), and ended on the 31st December of 2010. The plants annually processed about 2 million tonnes of phosphate rock, generating 2.5 million tonnes of PG. Until 1998, approximately 80 % of the phosphogypsum generated wasn slurried with recycled water, pumped out of the fertiliser plant by a pipe system and then dumped to designed areas where the phosphogypsum eventually dries in stacks in the salt-marshes of the Tinto River. The remaining 20 % was released directly into the Tinto River. The area occupied by PG piles is over 1000 ha containing about 100 Mt without any commercial application. In Figure 1.6 the fertilisers complex, and the different zones occupied by the PG stacks are shown.

Figure 1.6. Location map of industrial complex and the phosphogypsum.

In 1992, the zone closed to the fertiliser complex of about 400 ha was restored by covering with a soil layer of 30 cm (restored zone #1), and also was restored the farthest area (around 170 ha) by using construction waste and soils (restored zone #2), which was finished around 2000 (Fig. 1.6). To develop economically viable and1.6).

Finally, to point out developing environmentally friendly applications using PG would mean seeing phosphogypsum stock-piles as a source of artificial gypsum resources, permitting future restoration of the zone, while economic development of the area is generated.

1.1.2.3 Construction and Demolition Waste (CDW)

Construction sector generates a vast amount of construction and demolition waste (CDW) every year, becoming a worldwide problem. This waste is produced mainly during building rehabilitation and demolition works. The European Union generates around 900 million tonnes per year of CDW, what represents 30 % of all wastes produced (Eurostat, 2010). In addition, the Construction & Demolition Recycling Association (CDRA) estimated that the generation of CDW in the United States is close to 400 million tonnes, which is estimated to represent 13–80 % of the entire mass of municipal solid wastes, depending of the developing degree of each country (Angulo, 2000).

Major components of CDW are very variable, including bricks, concrete, plaster, ceramics, glass, wood, asphalt, metal, soil, rock, etc. While most part of CDW is inert, it may contain some materials with potential impact on the human health and the environment (US EPA, 1998). Many researchers have shown that some CDW can contain elevated leachable heavy metal concentrations, particularly arsenic and lead (Tolaymat et al. 2004).

Since most countries have no specific processing plan for CDW, they are sent to landfill disposal, even more, in most the undeveloped countries are illegally dumped in urban areas, roads and unprepared places, polluting the environment, not only mechanically but also chemically. In the last years, governments have established a regulatory framework approved new recycling policies. As a result, the situation in the major cities is changing with the implantation of recycling plants. Although some separation of CDW components may occur at the construction or demolition site, most is recycled, separated and recovered at recycling plants (Townsend, 1998).

The average recycling CDW rate in Europe is 50 %, but this recycling rate in Spain is only the 15 % of the total production (Villoria et al., 2011) far away of the objective established by the Integrated Waste Management Plan (Directive 2008/98/EC). The global market for CDW is expected to increase 5.2 % this year, and again next year, up to 48.3 billion tonnes (Freedonia, 2012).

Several factors dictate the success of CDW recycling; it includes environmental and economic advantages, landfill fees reduction, minimisation of the environmental impact occurring in a disposal area, economic benefit in the reuse markets of recovered components and decrease the consumption and demand of natural resources.

CDW materials have been successfully recycled as base and sub-base of road construction (Bennert et al., 2000), paving projects (Arulrajah et al., 2014; Taha et al., 2002), footpaths (Arulrajah et al., 2013) and pipe-bedding (Rahman et al., 2014). Moreover, some researchers have developed new applications as building material, i.e. concrete brick and block (Neves-Monteiro & Fontes-Vieira, 2014; Poon et al., 2002), red ceramic (Acchar et al. 2009) and for concrete production (Martín-Morales et al. 2011; silva et al., 2014). Nowadays, it is necessary to develop new applications, manufacture new products, perform processes and find markets, to absorb and reduce the vast volume of CDW worldwide production. In light of the above, this thesis is aimed at appraising the recycling of CDW as new construction material.

1.2 OBJETIVES

The main objective of this thesis has been to find commercial applications to three different inorganic wastes. Two of them are inorganic industrial waste coming from Huelva, ilmenite mud waste generated by the TiO_2 pigment industry and phosphogypsum waste by the acid phosphoric process. At last, a third inorganic waste generated in the construction and demolition activities.

To achieve the main objective, the following specific objectives are established:

1. To develop an adequate protocol of action with the objective of carrying out a correct characterisation and subsequent valorisation of the wastes in study.
2. To characterise physically, chemically and mineralogically the waste to be evaluated, in order to know in depth their properties and their potential toxicity, paying special attention to the possible variation of these properties due to the change of raw materials.

3. To develop a radiological characterisation was carried out in order to guarantee the negligible environmental impact, since the industrial waste come from NORM industries.

4. To study the process of manufacture and formulation of the materials, depending on the properties to be achieved by the final product (ceramics, cement and brick), adjusting its formulation to the current regulations.

5. To measure the technological properties for each new material in the field of construction and civil engineering through the performance of specific tests (water absorption, breaking resistance, porosity, etc.).

6. To assess the environmental impact of the new materials tested by carrying out leaching tests and the relevant radiological measurements, taking into account the regulations in force for each of the future applications.

7. To evaluate the use of phosphogypsum for obtaining calcite from the CO_2 mineral sequestration process, and to assess the environmental impact of the co-products generated throughout the process.

8. To obtain the results and conclusions by analysing the obtained data, taking into account both the physical, chemical and radioactive characterisation, as well as the technological properties of the materials in question, as well as their environmental implications.

9. To write the papers related to objective of the thesis, and the final report summarising the methodology, results and conclusions of the thesis.

1.3 STRUCTURE OF THE THESIS

This work is structured in 4 chapters. In the chapter 1, called “Introduction”, the background of the problem, with a deeply detailed study of the processes describing the different production steps where the inorganic wastes studied are generated, objectives and structure of the thesis are presented.

In the following chapter 2 the materials and methods are shown. Firstly, sampling materials and sample pre-traetment are described. Then, the measuring techniques used for the characterisation of the wastes and materials have been summarised. Finally, the techniques used to evaluate the technological properties and the potential environmental risks are shown.

Chapter 3 is the core of this thesis where the results are presented, and it is divided in five sections. The first one (section 3.1) reports the possibility of manufacture sulphur polymer cements (SPCs) incorporating ilmenite mud waste, for use in concrete construction works and evaluate their mechanical properties and potential environmental impact. This work has been published in Journal of Environmental Management (Contreras et al., 2013).

Section 3.2 shows a study about the option of producing ceramic tiles by using ilmenite mud waste and comparing it with commercial ceramics, studying its technological properties and the environmental implications. This study has been published in Construction and Building Materials (Contreras et al., 2014).

Section 3.3 is concerned to study the use of phosphogypsum as additive in ceramic manufacturing. The ceramic bodies were produced at different fired temperature and phosphogypsum percentage. The technological properties results were compared with a standard red ceramic and the environmental impact evaluated. This work has been submitted for publication in Construction and Building Materials.

The section 3.4 is focused on the possibility of producing bricks, using waste lime or cement as binders, with construction and demolition waste (CDW) using the fraction below 4.8 mm, with no currently application, as substitute of natural aggregates. The technological properties were determined and compared with Brazilian, European and American standards, looking for commercial applications for this waste. This part has been published in Construction and Building Materials (Contreras et al., 2016).

Last section 3.5, evaluate the use of phosphogypsum wastes as a Ca source for producing calcite ($CaCO_3$) by reacting the PG with carbon dioxide, generating the consequence of mineral sequestration of CO_2. In this work has been also studied the fractionation and fluxes of heavy metals and radionuclides throughout the complete carbonation process. The results of this work were published in Waste Management (Contreras et al., 2015).

Finally, in the chapter 4 the main conclusions of this thesis are described, as well as new research lines for the future.

Chapter 2

Materials and Methods

This chapter aims to show the sampling and pre-treatment, materials, methods and equipment used in all the studies carried out in this doctoral thesis. Different characterisation techniques were used in this work: laser diffraction spectroscopy for grain size, X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC/TGA), alpha-particle spectrometry with PIPS detectors, gamma spectrometry with Ge detectors, radon exhalation rate by accumulation.

In addition, several technological properties were evaluated in order to check the behavior of new obtained materials. These properties were: water absorption by capillarity, water absorption, bulk density, apparent porosity, linear shrinkage, bending strength, compressive strength, flexural strength, TCLP leaching test, accelerated leach test, radiological implications (Index I) and data treatment. In the next section, the quality control applied will be described.

2.1 SAMPLINGS AND PRE-TREATMENTS

In this section a description of the sampling and pretreatments of the sample will be performed.

2.1.1 Samplings waste

The samplings were carried out in a different way:

(1) Ilmenite mud was supplied by TiO_2 pigment industry from the manufacture process. The sampling process was taking one sample every 5 days along one month to ensure the homogeneity of the waste produced (6 samples).

(2) Phosphogypsum was directly collected from the pile number 2, where a representative sampling of the area were developing by taking 10 samples at 50 cm in depth trying to avoid the superficial weathering

produced by the rain. Finally, the samples were mixed, dried and homogenized.

(3) Construction and demolition waste were obtained from two different cities from the São Paulo State (Brazil), in order to compare the heterogeneity between them. Firstly, five representative samples were collected from the transporting containers disposed at five work sites of construction and demolition in the city of Presidente Prudente, and secondly new samples from two different containers in a Construction and Demolition Waste (CDW) Recycling Plant in the city of São José do Rio Preto were taken.

2.1.2 Sample pre-treatment

After collection, the waste samples were preserved in plastic bags, and then, in the laboratory, they were dried at 60 ºC until constant weight. This temperature was selected to avoid structural water losses. Finally, the samples were grounded, sieved (< 65 μm), and homogenised.

The treatment to which the samples have been submitted to carry out the different measuring technique is exposed in the following section.

2.2 MEASURING TECHNIQUES

This second section we will outline the measurements techniques and equipment used in the physico-chemical and radiological characterisation of the collected samples and final materials.

2.2.1 Granulometry

Laser diffraction spectroscopy measures particle size distributions by determining the angular variation in intensity of light scattered when a laser beam passes through the suspended sample in water or another liquid where the sample is not soluble. The ISO 13320 (“Particle size analysis - Laser Diffraction methods - Part 1: General principles”) establishes Mie theory as the best option to determine the volume distribution of the particle size present in a granulated material.

Laser diffraction analysis, also known as laser diffraction spectroscopy, is a technology that utilises diffraction patterns of a laser beam passed through any object ranging from nanometers to millimeters in size to quickly measure geometrical dimensions of a particle. This process does not depend on volumetric flow rate, the amount of particles that passes through a surface over time. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analysed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter.

There are three main steps in the measurement process:

1. The sample must be prepared and dispersed to the correct concentration and then delivered to the optical bench. This is the purpose of the sample dispersion units.

2. The capturing of the scattering pattern from the prepared sample - known as "measurement". Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The detector array within the optical bench is made up of many individual detectors. Each detector collects the light scattering from a particular range of angles. A typical light scattering pattern is shown below (Fig. 2.1).

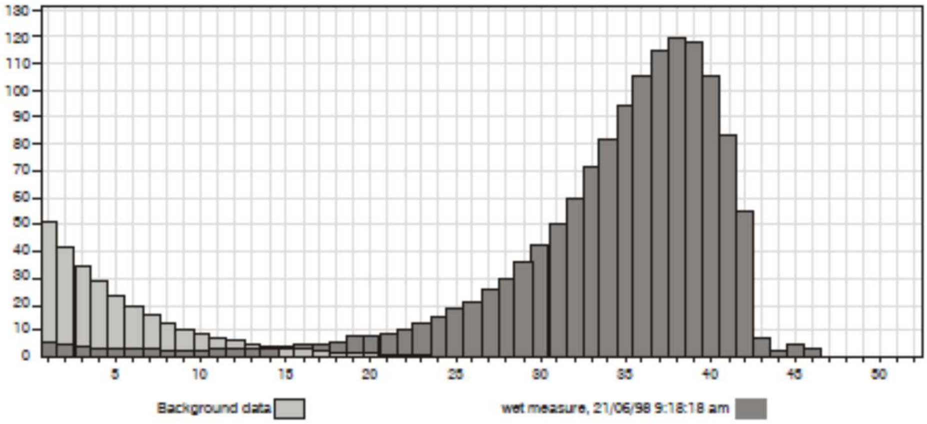

Figure 2.1. Typical light scattering patterns

Each bar in the histogram represents the light scattering from one of the detector elements (known as channel). The detector array takes many snapshots of the scattering pattern and averages the result to give a representative measurement.

3. Once the measurement is complete, the raw data from it is analysed by the software using the Mie theory. The resulting particle diameter is the geometric mean of the extreme values from each particular range.

The particle size analysis was performed by laser granulometry in wet suspensions with water as dispersant, using a Malvern Mastersizer 2000 particle sizer with 52 detectors and Hydro 2000M accessory, installed in the Central Research Services at the University of Huelva (Spain). The laser analyser provides the primary size information for particles in the 0.02 to 2000 μm range. For this, weight ranges from 20-30 g of each of sample were placed in beakers with 50 cm^3 of deionised water for 4 h. Subsequently, in order to facilitate the dispersion of the sample, all the beakers were subjected, for 10 minutes, to an ultrasonic bath at a constant temperature of 35 °C. They were then placed in a flask and mixed using a magnetic stirrer at a constant speed (700 rpm) to ensure the homogeneous distribution of the particles. Aliquots were then collected for granulometric analysis. The calibration method was performed with different certified reference materials: LTX3300C Nanosphere Size Standard; 2009A and 2009B Duke Polymer Microspheres Uniform Standards; 4009, 4009A and 4009B Duke Standards Microsphere Size Standards. Before each run, it is verified that the device parameters are in the range of measurement.

The program runs 10 countings on each aliquot (15 s measuring interval each) with 5 seconds delay between measurements. This assures, that if the sample is not dispersed completely and a change in the distribution curve occurred, then the analysis is re-run. In addition, three aliquots are measured and the results and standard deviation given. The accuracy of this method is ± 1 % on the Malvern and the instrument-to-instrument reproducibility is better than 1 % RSD.

2.2.2 XRD

X-ray diffraction (XRD) is a rapid analytical technique primarily used to study the internal structure of solids, in order to identify the crystalline phases present in a powdered sample. This procedure is based on the fact that each crystalline phase has its own characteristic diffractogram.

XRD analysis is based on constructive interference between a monochromatic X-rays beam and a crystalline sample. The interaction of the incident rays with the sample produces a diffracted ray, being the maximum of interference given by the Bragg's Law (Eq. 2.1):

$$n\lambda = 2\mathrm{d}\sin\theta \qquad \text{[Eq. 2.1]}$$

, where λ is the wavelength of the rays, θ is the angle between the incident rays and the surface of the crystal, d is the spacing between layers of atoms and n is the order of diffraction integer (integer number). The key component of all diffraction is the angle between the incident and diffracted rays.

X-ray diffractometers consist in an X-ray tube where electrons are produced and accelerated onto the target (Fig. 2.2). When electrons have sufficient energy to dislodge electrons of the target material, characteristic X-ray spectra are produced. The specific wavelengths are filtered by a crystal monochrometer to produce monochromatic X-rays. These X-rays are collimated and directed onto the sample, placed in a sample holder. The reffracted X-rays are detected by the counter. In addition, the X-ray tube and X- ray detector are installed in a rotation system around the sample holder.

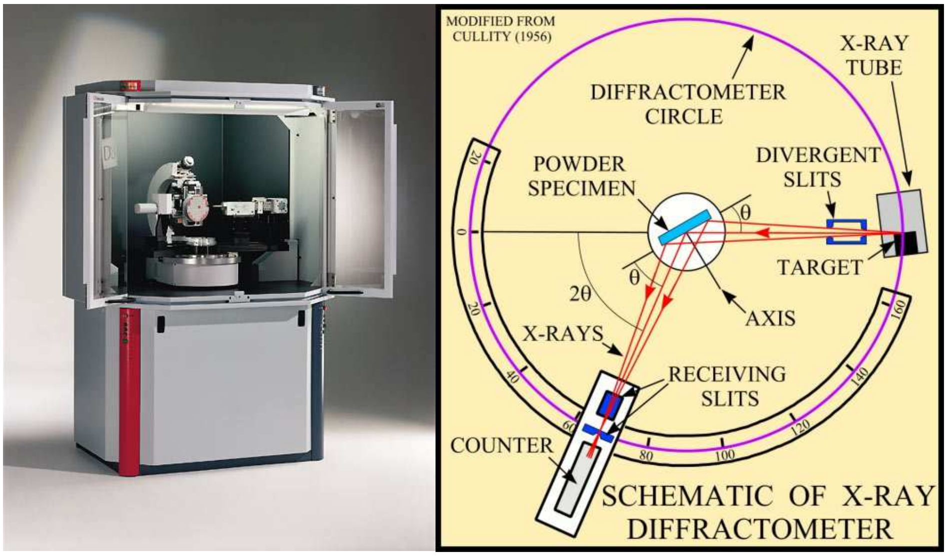

Figure 2.2. Bruker's X-ray Diffraction D8-Discover instrument and schematic of X-ray Diffractometer.

The characteristic x-ray diffraction pattern generated in a typical XRD analysis provides a unique "fingerprint" of the crystals present in the sample. When properly interpreted, by comparison with standard reference patterns and measurements, this fingerprint allows identification of the crystalline form.

The mineral characterisation of the powder samples was performed in the Central Research Services of the University of Huelva (Spain) by using a Bruker diffractometer (D8-Advance with $Cu_{K\alpha}$ radiation). Diffractometer settings were 40 kV, 30 mA, a scan range of 3-65° (2θ) with a step size of 0.02° and a counting time of 0.6 s per step. Under these measurement conditions, the detection limit was around 5 %. Similarly, at the University State of Sao Paulo (Brazil) in the laboratory of ceramic materials a Shimadzu diffractometer model XRD 6000, using $Cu_{K\alpha}$ radiation working at 1.2 kW (40 kV, 30 mA) was used. Data were recorded in the 5–60° (2θ) range (step size equal to 1° min^{-1}), obtaining under these set up a detection limit of about 3 %. The analyses were performed in triplicate to ensure reproducibility of the results.

The X-ray diffraction analysis has been performed according to the disoriented powder method. Random mounts are preferred when identification of phases in a specimen is required. In this type of mount, a few tenths of a gram (or more) of the material, as pure as possible are needed. The sample was grinded to a fine powder, typically less than 10 μm in size is preferred. Then, the sample was placed into a sample holder, smeared uniformly onto a glass slide, assuring a flat upper surface, packed into a sample container and sprinkled on double sticky tape. Care must be taken to create a flat upper surface and to achieve a random distribution of lattice orientations unless creating an oriented smear.

Analysis of diffraction patterns was performed with the software DIFFRAC-plus provided by Bruker, Search Match provider by Shimadzu, PDF Search (Powder Diffraction File) and X-Powder (Martín-Ramos, 2004). With this technique only crystalline phases with a percentage greater than 5 % are detected.

External standard and internal standard calibrations were preceded for achieving high accuracy in X-ray powder diffraction studies. As example, were used a single crystal Si specimen calibration standard for high-resolution XRD and alumina powder for quantitative analysis. The selected Standard Reference Materials (SRMs) were provided by the National Bureau of Standards (NBS). The statistical error of ± 5 % for major phases in an intensity-related quantitative analysis should be considered reasonable.

2.2.3 XRF

X-ray fluorescence (XRF) is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of characteristic energies. Theoretically this characteristic radiation permits to identify and quantify each element in the sample.

A XRF spectrometers consist of an X-ray tube that produces an intense X-ray beam onto the sample. The excited sample emits X-rays along a spectrum of wavelengths/energy characteristic of the types of atoms present in the sample. The atoms in the sample absorb X-ray energy by ionising, ejecting electrons from the lower (usually K and L) energy levels (Fig. 2.3). Electrons from outer levels replace the ejected electrons, and then energy is released in the form of emission of characteristic X-rays indicating the type of atom present.

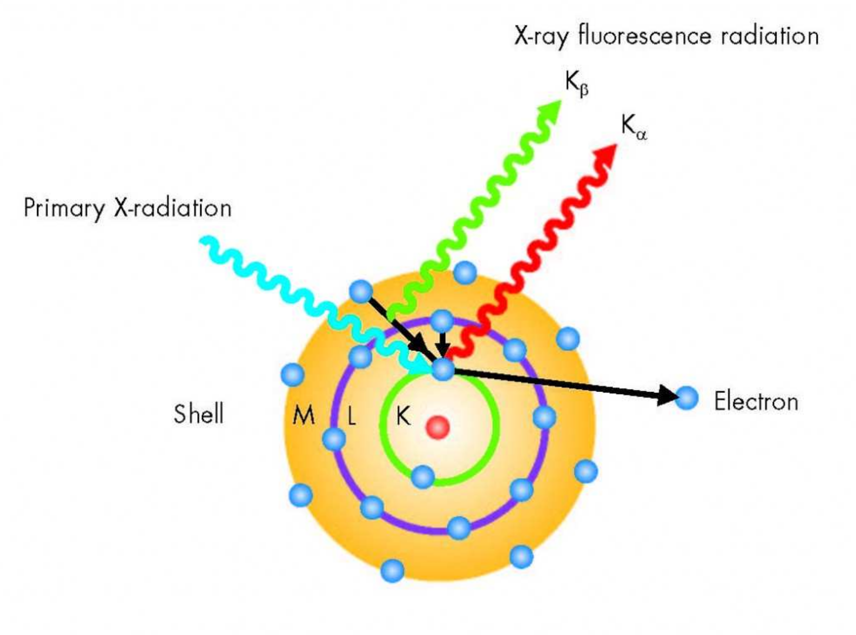

Figure 2.3. General scheme of X-ray fluorescence analysis.

The detectors are used to measure the intensity of the emitted beam. X-rays from the sample and a multichannel analyser assigns each detector pulse an energy value thus producing a spectrum. The intensity of the energy measured by these detectors is proportional to the abundance of the element in the sample. The exact value of this proportionality for each element is derived by comparison to mineral or rock standards whose composition is known from prior analyses by other techniques.

Two different XRF were used in the study:

- The wavelength dispersive X-ray fluorescence (WDXRF) analyser uses X-rays source emitting in all directions. A diffracting crystal is placed in the way of the emitted X-rays coming off the sample. An X-ray detector is position where it can detector the X-rays that are diffracted and scattered off the crystal. Depending on the spacing between the atoms of the crystal lattice (diffractive device) and its angle in relation to the sample and detector, specific wavelengths directed at the detector can be controlled. The angle can be changed in order to measure elements sequentially, or multiple crystals and detectors may be arrayed around a sample for simultaneous analysis.

- The energy dispersive X-ray fluorescence (EDXRF) analyser may be configured in two ways. The first way is direct excitation where the X-ray beam is pointed directly at the sample. A filter made may be placed between the source and sample to increase the excitation of the element of interest or reduce the background in the region of interest. The second way uses a secondary target, which is excited and fluoresces, used to excite the sample. A detector is positioned to measure the fluorescent and scattered

Major elements were determined by WDXRF technique in the Institute of Construction Sciences “Eduardo Torroja” (Madrid, Spain) using a Bruker S4 Pioneer system equipped with a X-ray tube of 4 kW, Rh front window and anode, five analysing crystals (LIF200, Ge, PET, OVO55 and OVOC) and two X-ray detectors, flow and scintillation. Flow detectors measure elements from C to Cu and scintillators from Cu to U. In addition, EDXRF technique was used at the University State of Sao Paulo (Brazil) in the laboratory of ceramic materials by a Bruker spectrometer S2 Ranger LE equipped with an X-ray tube of 50W (50 kV, 2 mA), anode of Pd, XFlash Silicon Drift Detector with resolution < 135 eV for $\mathrm{Mn}_{\mathrm{Ka}}$ and 100,000 cps.

These techniques require the samples under analysis to be as homogeneous as possible. Thus, 1 g of dry grounded sample was mixed with 10 g of lithium tetraborate and 5 drops of 20 % lithium iodide to form a homogenous glass ready for examination.

In general, elements with a concentration below 50 mg kg^{-1} (50 ppm) are difficult to detect. To decrease the air absorption of the elements with atomic number less than 21 (Sc), the operating pressure must be 0.1 torr.

The calibration method was performed with a standard containing an adequate number of elements to provide sufficient peaks for calibration. These peaks should be separated from other peaks by at least 3 to 4 keV to avoid confusion in assigning peaks to their corresponding elements. The calibration standards used are M.A.C.® 80090-20 X-Ray Fluorescence Universal Set 20 elements (Na, Mg, Al, Si, P, S, Cl, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Nb, Sn, Ba, W, Pb). In general, the detection limits according to the average and standard deviations from 6 blanks ranged from 1 to 100 ppm depending on each particular element. The analysis was performed in duplicate with differences below 5 % between them. The analytical accuracy was checked by the analysis of certified reference materials GBW 07238 (NCS DC 70006), SX18-04 and BIR-1a. The average accuracy of the measurements was < 5 %.

2.2.4 ICP-OES

The Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a trace-level elemental analysis technique that uses the emission spectra of a sample to identify, and quantify the elements through the measurement of the intensity of radiation emitted for element-specific.

Sample introduced into the ICP as liquid form is the most common technique for sample introduction, while the solid sample is converted into liquid by dissolving it into proper solvent. Liquid sample goes through different steps when injected to the ICP (Fig. 2.4).

The first process is called nebulisation, and it occurs when the sample is converted to an aerosol, a mist of finely divided droplet. The most commonly nebuliser is a concentric tube, where the sample is sucked into capillary tube by a high-pressure stream of Argon gas flowing around the tip of the tube. This pressure breaks the liquid into fine droplets in various sizes in the spray chamber.

In the spray chamber the large droplets go to drain the fine droplet carried to the torch. More than 99 % of the injected sample goes to drain and less than 1 % carried out to the torch.

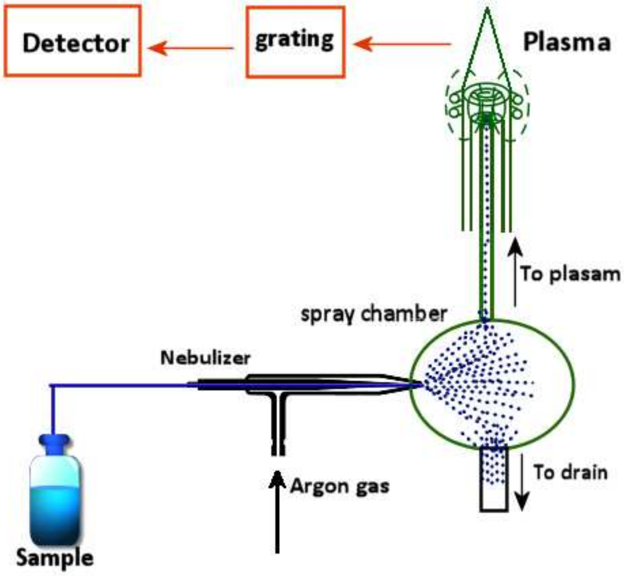

Figure 2.4. Diagram of Sample introduction to ICP-OES

The torch is consists of three concentric quartz tubes through which streams of argon gas flow. A spark from a Tesla coil initiates ionisation resulting ions and their associated electrons interact with the fluctuating magnetic field produced by the induction coil. Adding mechanical energy to the electrons/ions by the use of the induced field within the heart of the plasma in this manner is called “Inductively Coupling”.

A stable high temperature plasma of about 7000 K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles. The sample immediately collides with the electrons, charged ions in the plasma and is itself broken down into charged ions. The molecules break up into their respective atoms, which then lose electrons and recombine repeatedly in the plasma, giving off radiation at the characteristic wavelengths of the elements involved.

Transfer lenses are then used to focus the emitted light on a diffraction grating where it is separated into its component wavelengths in the optical emission spectrometer.

Within the optical chamber, after the light is separated into its different wavelengths, the light intensity is measured with a photomultiplier tube or tubes physically positioned to “view” the specific wavelength for each element line involved.

The intensity of each line is then compared to previously measured intensities of known concentrations of the elements, and their concentrations are then computed by interpolation along the calibration lines.

ICP-OES is suitable for the trace elements analysis present at high concentrations (100 ppb-1000 ppm), and is used for much type of matrices of environmental samples especially for high effect-matrix samples. Therefore, this technique is more robust than ICP-MS for analyzing samples as ground water, wastewater, soil, and solid waste. The element concentrations were carried out at the Activation Laboratories Ltd (ACTLABS, Ontario, Canada) using an ICP-OES Jobin Yvon JY ULTIMA 2 spectrometer.

Solid samples were digested following the four-acid method requiring HCl, $HClO_4$, HNO_3 and HF. Prior to digestion the samples were grounded to a powder. Samples are then dried at 80 ºC, and 0.5-0.2 g of sample is weighed into a Teflon vessel. The initial reagent mixture is 8 mL HCl, 7 mL HNO_3, 7 ml $HClO_4$, and 8 ml HF. The sample mixtures are evaporated completely. Another milliliter of $HClO_4$ and 2 mL of deionised water are added to each sample, and the solution is evaporated to dryness. Then 1 mL of aqua regia (3 parts HCl to 1 part HNO_3) is added to each sample and allowed to react for 15 minutes and finally evaporated. A solution of 9 mL 2 % HNO_3 is added to each sample and the vessel is heated until no evidence of remaining solids. Digested samples are then diluted at least 1:100 for analysis. Subsequent dilutions may be required if analyte concentrations are above the instrument’s linear range. Moreover, appropriate blank solutions are also necessary.

Multielement standard solutions were prepared from single certified standards supplied by SCP SCIENCE and prepared in a matrix of Milli-Q ultrapure water and nitric acid suprapur 2 % (v/v). The concentration of elements in the prepared standard were 0 (blank), 0.05, 0.5, 1, 5, 10, 25 and 50 ppm for all elements except Al and Fe. In these cases, 100 and 150 ppm respectively of each element were added to the previous concentrations. Detection limits were calculated by average and standard deviations from 10 blanks. Detection limits were below 0.1 mg L^{-1} for these elements. A triplicate analysis was performed in order to evaluate the analytical precision, showing differences below 5 % in all case. The analytical accuracy was checked by the analysis of certified reference material NIST-1640 (fresh-water-type).

2.2.5 ICP-MS

An ICP-MS technique has a multi-element character and a high sample throughput. While ICP-OES technique measures the radiation emitted by the different atoms through an optical detector, the ICP-MS detects the ions by using the mass spectrometer based on the mass-to-charge ratio (m/z).

The sample solution is introduced into the device by means of a peristaltic pump, then it becomes nebulised in a spray chamber, and finaly the aerosol is injected into an argon-plasma with a temperature of 6000-8000 K.

Then, the ions from the ICP source are collimated and focused into the entrance aperture of the mass spectrometer by the electrostatic lenses. Only a small amount part of the ions produced in the plasma further penetrate to the mass-spectrometer part.

The quadrupole mass spectrometer is the most common type of mass spectrometer used in atomic mass spectroscopy, which is a mass filter only allows ions having a limited range of m/z values reach the transducer. Ions that are not of the correct m/z collide with the rods or exit the path between the rods and are pumped out of the system. Quadrupole instruments easily resolve ions that differ in mass by one unit.

Each ion that exits from the mass spectrometer system hits the detector producing an electrical amplified signal proportional to its m/z ratio, producing finally a mass spectrum with peaks corresponding to the different mass/z ratios. The quantification is achieved by comparing the measured counts in an unknown sample with a standard containing a known amount concentration of the problem element.

ICP-MS is particularly suitable for isotope ratio studies and ultra-trace analysis of elements being the instrumental detection limits (IDL) in the range from 1 ppt to 10 ppb, depending of each particular element. In addition, this technique shows a wide dynamic range. On the contrary, this technique is not able to measure some non-metallic elements (e.g. S, P, Ti, Sc), which can be determine by ICP-OES.

ICP-MS is particularly suitable for isotope ratio studies and ultra trace analysis of elements being the instrumental detection limits (IDL) in the range from 1 ppt to 100 ppb, depending of each particular element. In addition, this technique shows a wide dynamic range. On the contrary, this technique is not able to measure some non-metallic elements (e.g. S, P, Ti, Sc), which can be determine by ICP-OES.

Trace elements were determined by ICP-MS (inductively coupled plasma mass spectrometry) after four-acid digestion at the Activation Laboratories Ltd (ACTLABS, Ontario, Canada) using an HP branded computer model HP4500, which meet the ISO/IEC 17025 Quality System standard. The quality control method included the use of a reagent blank, standard reference materials and replicates. The accuracy of the analytical data ranges from ± 5-10 %.

For analysis by ICP-MS, 0.2 g of sample was treated with hydrofluoric, hydrochloric, nitric and perchloric acids. Hydrofluoric acid was used to remove silica and release the chemical elements as ions. The nitric acid is an oxidant that was applied to prevent the volatilisation of certain elements and the perchloric acid and hydrochloric were used to eliminate the hydrofluoric acid residues, since this precipitates like fluoride. The amounts of nitric acid used were 7 mL, 8 mL of hydrofluoric acid, 8 mL of hydrochloric and 7 mL of perchloric acid. All samples were evaporated on a heating plate until dryness. After digestion, the final aliquot is adjusted to a 2 % solution in nitric acid with deonised water. Finally, the digested samples were dilutied 1:100 in order that the concentrations falls within the calibration range.

The calibration method was performed with a solution consisting of 10 ppb of ^{7}Li, ^{89}Y and ^{205}Tl. An external calibration was used, using a blank, and a multi-elemental certified standard solution of 1 ppb, 10 ppb, 50 ppb and 100 ppb. The sequence of analysis consisted of blank, st 1ppb, st 10ppb, st 50 ppb, st 100 ppb, then a series of 5 samples, monitor solution 10 ppb, again another 5 samples and monitor solution, etc. The monitor solution was used in the analysis sequence in order to control the drift of the equipment during the same.

The quality control of the measurements was done using certified reference materials (AGV-2, BCR-2, BHVO-1, SoNE-1), one duplicate at least every 15 samples, and procedure blanks. The instrument is recalibrated every 80 samples.

2.2.6 SEM

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 µm in width can be imaged in a scanning mode using conventional SEM techniques The SEM is also capable of performing analyses of selected point locations on the sample;

this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions by using Energy-Dispersive X-Ray Spectroscopy (EDS).

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathode luminescence–CL), and heat.

Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). Secondary electrons are emitted from the surface with a certain velocity that is determined by the levels and angles at the surface of the sample. The secondary electrons, strike the scintillator (fluorescing mirror) that produces photons. The location and intensity of illumination of the mirror vary depending on the properties of the secondary electrons. The signal produced is amplified and transduced to a video signal with the “topography” of the sample.

Moreover, there is a probability that some of the incident electrons will suffer a large deviation from the incident direction and be “reflected” backwards. These electrons are called “backscattered” electrons (BSE) and provide compositional information, since the BSE signal intensity of a material is proportional to its average atomic number. This implies that parts of a sample having different composition generate different intensity of backscattered electrons, although there is no difference of topography between them.

If an X-ray detector is incorporated, the characteristics X-rays generated by the electron beam are detected and analysed with an energy dispersive X-ray spectrometer (EDS). The EDS spectra can be used to obtain a qualitative and/or semi-quantitative elemental analysis at micrometer spatial resolution.

There are two main classes SEM techniques according to emission source: Scanning Electron Microscope (SEM) uses thermionic emitter and the Field Emission Scanning Electron Microscope (FESEM) uses a field emitter. Moreover, field emission Gun producing a cleaner image, less electrostatic distortions and spatial resolution < 2nm (that means 3 or 6 times better than SEM).

The microstructure was examined by field emission scanning electron microscopy (FE-SEM) in the Institute of Construction Sciences “Eduardo Torroja” (Madrid, Spain) using a HITACHI (model S-4800) microscope and JEOL (model JSM-5410) in the University of Huelva (Spain), both equipped with an Energy Dispersive Spectrometer (EDS) and a Back Scattered Electron (BSE) operating at 20 kV.

SEM specimens were embedded in epoxy resin (Araldite®), grinded with silicon carbide paper (SiC paper) and polished with 6, 3 and 1 µm diamond pastes after. The samples were washed with deisonised water and attacked with 5 % HF for 10 seconds, to highlight the developed phases. Chemically fixed material were ultrasonically washed with distilled water and ethyl alcohol and dried below the critical point to avoid damage of the fine structures due to surface tension. To facilitate their observation under the microscope, the samples are made conductive for current, so, the specimens were coated with a thin layer of Au-Pd in a Balzers SCD 050 sputter.

2.2.7 DSC/TG

Thermal analysis studies how the properties of materials change with temperature. This analysis typically measures heat flow, weight loss, or mechanical properties as a function of temperature. Several methods are commonly used, which are distinguished from one another by the measured property.

In this thesis were used two of these methods, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

- TGA is a method that measures the mass loss or gain due to decomposition, oxidation, or dehydration, as a function of temperature (thermal spectra) or isothermally as a function of time (with constant temperature and/or constant mass loss). The first derivative of the TG curve (DTG) is very useful, because it makes the noticing small features/boulders on the curve much easier (Fig 2.5).

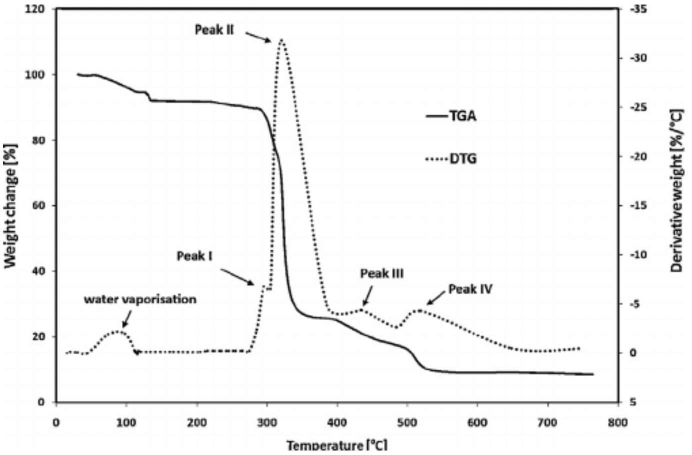

Figure 2.5. Example of TG/DTG curves

- DSC measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes (Fig. 2.6). DSC curve can provide information about physical phenomena, such as second-order phase transitions, including vaporisation, sublimation, absorption and desorption.

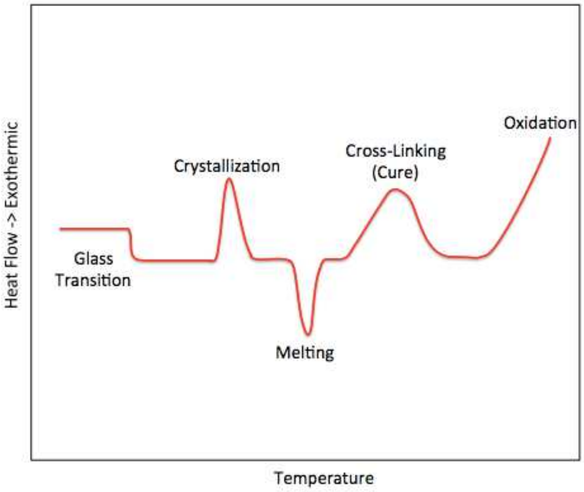

Figure 2.6. Typical DSC curve

A TGA analyser consists of a sample pan that is supported by a precision balance (± 0.0001 mg) (Fig. 2.7). The pan resides in a furnace and is heated or cooled during the experiment. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time. The atmosphere in the sample chamber may be purged with an inert gas to prevent oxidation or other undesired reactions. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. In addition, a cooling device is installed to help cool the sample.

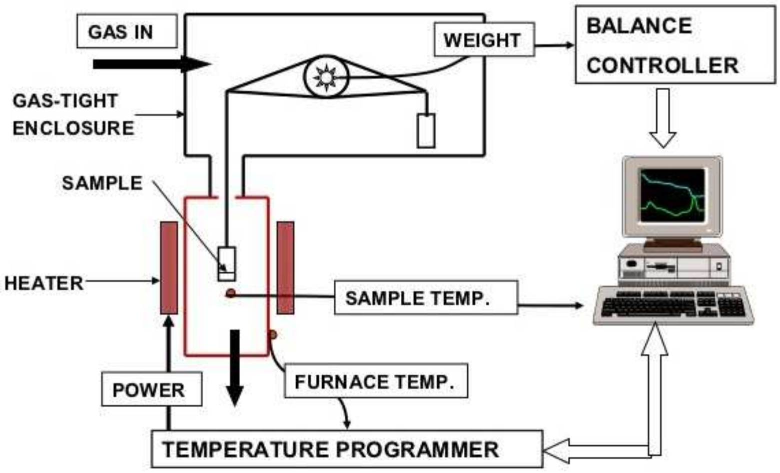

Figure 2.7. Chart diagram of the TG

On the other hand, in a DSC analyser (Fig. 2.8), the sample is placed in a suitable pan and sits upon a constantan disc on a platform in the DSC cell with chromel wafer and a chromel-alumel thermocouple under the constantan disc that measures the sample temperature. An empty reference pan sits on a symmetric platform in the furnace. This technique uses a reference material with a well-defined heat capacity over the range of temperatures. Generally, the temperature program for a DSC analysis is designed such that the sample and reference pan temperature increases linearly as a function of time and is maintained at nearly the same temperature throughout the experiment. However, owing to the heat capacity of the sample, there would be a temperature difference between the sample and reference pans, which is measured by area thermocouples, and the consequent heat flow is determined by the thermal equivalent of Ohm's law (Eq. 2.2):

$$q = \Delta T / R \qquad \text{[Eq. 2.2]}$$

, where q is "sample heat flow", ΔT is "temperature difference between sample and reference", and R is "resistance of thermoelectric disk".

The difference in the input energy required to match the temperature of the sample to that of the reference would be the amount of excess heat absorbed or released by the molecule in the sample (during an endothermic or exothermic process, respectively).

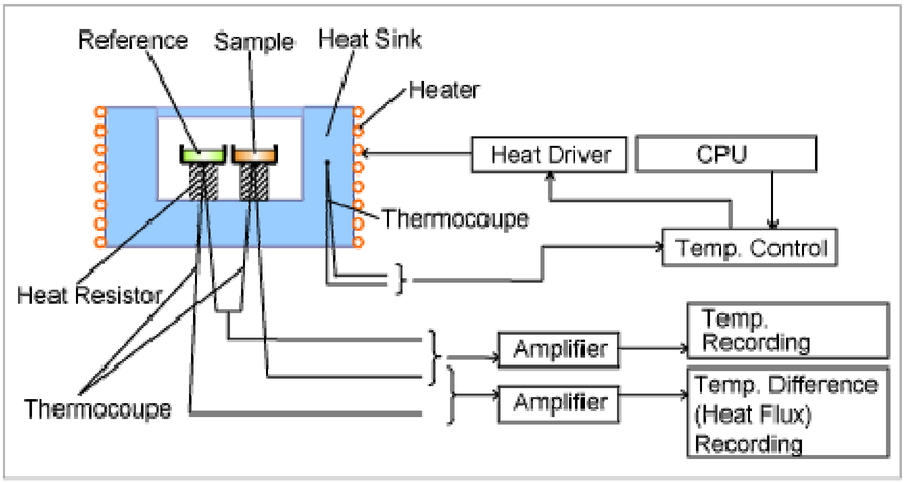

Figure 2.8. Chart diagram of DSC

The thermal behaviour on powder samples (size particle = 80-100 μm) was performed in the Institute of Construction Sciences "Eduardo Torroja" (Madrid, Spain) using DSC/TGA SETARAM, model Labsys, and at the University State of Sao Paulo (Brazil) in the laboratory of ceramic materials using a TA Instruments, model SDT Q600. DSC/TGA scans were performed between 25 ºC and 1450 ºC at 50 ºC min^{-1} in flowing air, platinum pan and calcined Al_2O_3 as reference material. The DSC/TG curves were normalised regarding the sample weight. The analysed material is finely ground and homogenised.

Samples can be analysed in the form of powder or small pieces with a sample size between 2 and 50 mg. It is better to have a large surface area exposed to the sample purge. Many small pieces of sample are better than one large chunk. At least, a minimum amount of 1 mg of sample is needed to run. If possible, the bottom of the pan with the sample material has to be covered. For best results, approximately the same sample weight during each experiment was used to ensure reproducibility.

To obtain accurate experimental results the thermal analyser was calibrated when running experiments and periodically thereafter. As a minimum, it was recalibrated anytime the beam set, experimental heating rate, or purge gas is changed. In addition, a blank test was performed.

The heat flow measurements and the temperature calibration were carried out using high purity standards (In, Sn, Bi, Pb and Au) with well-defined heat capacities.

DSC/TGA standard calibration includes the following procedures:

- TGA Weight Calibration: Calibration of the TGA weight signal.
- TA Baseline Calibration: Calibration of the Delta T signal. Baseline correction for a given scan rate (1 – 40 ºC min^{-1}).
- Temperature Calibration: Calibration of the temperature, heat of reaction, heat capacity scale.
- DSC Heat Flow Calibration: Calibration of the heat flow signal.

2.2.8 Alpha spectrometry

Alpha spectrometry is a technique based on the interaction of α-particles with matter, in order to detect and count them for analytical purpose, i.e., its aim is to determine the activity concentration of a specific radionuclide in a sample (Bq kg^{-1} or Bq m^{-3}). It is a powerful analytical method, extremely sensitive and specific for a large number of natural radionuclides (^{210}Po, U-isotopes, Th-isotopes, etc.) and anthropogenic (Pu-isotopes, Am-isotopes, etc.) alpha emitters in much type of samples. The application of this method requires minimisation of the alpha particle self-absorption effects at the source, since the alpha particles are absorbed in several micron of solid material.

The radioelements are firstly isolated and purified chemically before being either electroplated or auto-deposited on a thin layer of the sample uniformly and quantitatively onto an acceptable backing material in order to detect the emitted alpha particles.

2.2.8.1 Radiochemical method

A general radiochemical method to apply alpha-particle spectrometry with PIPS (Passivated Implanted Planar Silicon) detectors in Fig. 2.9 is shown. After the sample pretreatment (homogeneisation, calcination, co-precipitation, etc.), the tracers are added, and then the sample is dissolved with inorganic acid or by fusion. The next step will be to isolate the different radioelements of interest (in our case, U-isotopes, Th-isotopes and ^{210}Po). The radiochemical process ends with the manufacturing of the very thin radioactive source, usually by electrodeposition or microprecipitation.

The last step of the radiometric technique will be to take the alpha spectrum (counting), and posterior calculation of the activity concentration of each radionuclide of interest, and its uncertainty.

In our case, the method begins with the dissolution of the sample by using four strong acids (HCl, HNO_3, HF and $HClO_3$). And then actinides are isolated by using tributilphosphate (TBP), and purified with exchange resins. Then, the U- and Th-isotopes are electrodeposited onto stainless steel discs and, Po is self-deposited onto silver discs. Finally, the obtained discs are counted in an alpha spectrometer and the activity concentration calculated.

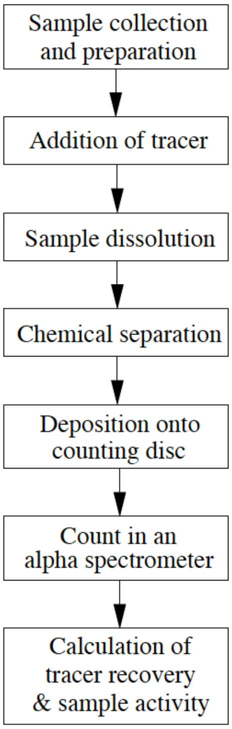

Figure 2.9. Blocks diagram of a generic radiometric method to measure radionuclides by alpha-particle spectrometry with PIPS detectors.

Step 1. Selection of the tracers

Due to the losses of radionuclides during the analytical separation processes, a known activity of an artificial radioactive isotope (same chemical behavior to the radionuclide of interest) was added in order to evaluate the recovery of the radiochemical process. The tracers used in this method (^{209}Po, ^{232}U and ^{229}Th), are shown in the Table 2.1. In addition, three conditions must be fulfilled in the selection of the tracers. Firstly, the emission energy must be different between the radionuclide (subject of study) and its tracer. Secondly, the tracer will be an isotope of the selected radionuclide (the same chemical behaviour) and finally the tracer must be artificial radionuclide, in order to ensure that the sample does not contain it.

Table 2.1

Information about the isotopes used as tracers in alpha spectrometry. With ± S is indicated the combined standard uncertainty of the Certified Reference Material (CRM).

Radionuclide	a (Bq L^{-1}) and Reference Date	$T_{1/2}$ (years)	Energy (MeV) and emission probability (%)
^{209}Po	105.6 ± 0.1 (15/03/1994)	102	4.88 (99 %)
^{229}Th	177.6 ± 1.1 (31/12/2007)	7340	4.797 (1.2 %), 4.814 (9.30 %); 4.837 (4.8 %); 4.845 (56.2 %); 4.901 (10.20 %); 4.967 (5.97 %); 4.978 (3.17 %); 5.050 (5.2 %); 5.052 (1.6 %)
^{232}U	72.5 ± 0.3 (25/03/2003)	69.8	5.32 (68 %) 5.27 (32 %)

Step 2. Digestion of the samples

The samples were subjected to a hard acid digestion in closed vessel (EPA 3050B) until near total dissolution. It is taken 0.2-0.5 g of sample and transferred to a Savillex with the tracers (^{209}Po, ^{229}Th and ^{232}U), in amounts according to the expected activity concentrations of the samples. After the addition of 9 mL HNO_3, 3 mL HF, and 2 mL H_2O_2, the Savillex is closed and put into the oven at 100 ºC for 24 h.

After this, it is taken from the oven, cooled, opened, and allowed to dry at environmental temperature and the sample is transferred to a Teflon vessel. The Savillex was washed with 5 mL of HCl and added to the Teflon vessel. Then, the sample is evaporated to dryness (maximum 80 °C) and 6 mL of $HClO_4$ is added and evaporated again to dryness, with the aim to remove the silicates (SiO_2).

Finally, it added 10 mL of HNO_3, and transferred the sample to a beaker, where it is evaporated to dryness and then to dissolve the sample residue in 10 mL of HNO_3.

Step 3. Radioelements sequential isolation based on TBP and Ion-exchange resins

This radiochemical method has been performed by our research group (Bolívar et al., 1995a) (Fig. 2.10), and is based on the property of TBP (tributyl phosphate, $C_{12}H_{27}PO_4$) to absorb the actinides.

The previous digested sample was added into a funnel with 5 mL of 8 M HNO_3 used to clean again the beaker. Five millilitre of TBP was added in the funnel and shaken for about 10 min, and settled for another 10 min without cover until the complete separation of phases. The previous two steps were repeated adding 10 mL of 8 M HNO_3 to the funnels to ensure complete separation. The aqueous phase (8 M HNO_3) contains ^{210}Po was collected in clean beakers and pass to the auto-deposition stage.

On the other hand, the organic phase that remains into the funnel contain the actinides (U and Th). The back-extraction of Th was conducted by adding 20 mL of xylene ($C_6H_8O_6$) and 15 mL of 1.5 M HCl to the organic phase in the separatory funnel, and shaken and settled for 10 min, each. The aqueous phase was separated (Th fraction) and this was repeated twice, using 15 mL of 1.5 M HCl. The beakers with aqueous solution pass to the thorium purification and separation by anion exchange resin.

To purify the Th fraction, which contains trace of U, a chromatography column is used. Previously, the sample is evaporated to dryness and the residue is dissolved with 5 mL of HNO_3 (65 %) and is again evaporated to dryness. Then, the column (height 4 cm and internal diameter 0.7 mm) is prepared with the addition of 3 g of AG1X8 Resin (100-200 mesh) and washed with 20 mL of 8 M HNO_3 with a flow of 0.8-1.0 mL min^{-1}. Then, the Th fraction is passed through the column to elute U and other interfering ions, and this solution was discarded. The thorium is extracted from the column with 40 mL of 9 M HCl. Finally, aqueous solution containing Th was saved until the electro-deposition stage.

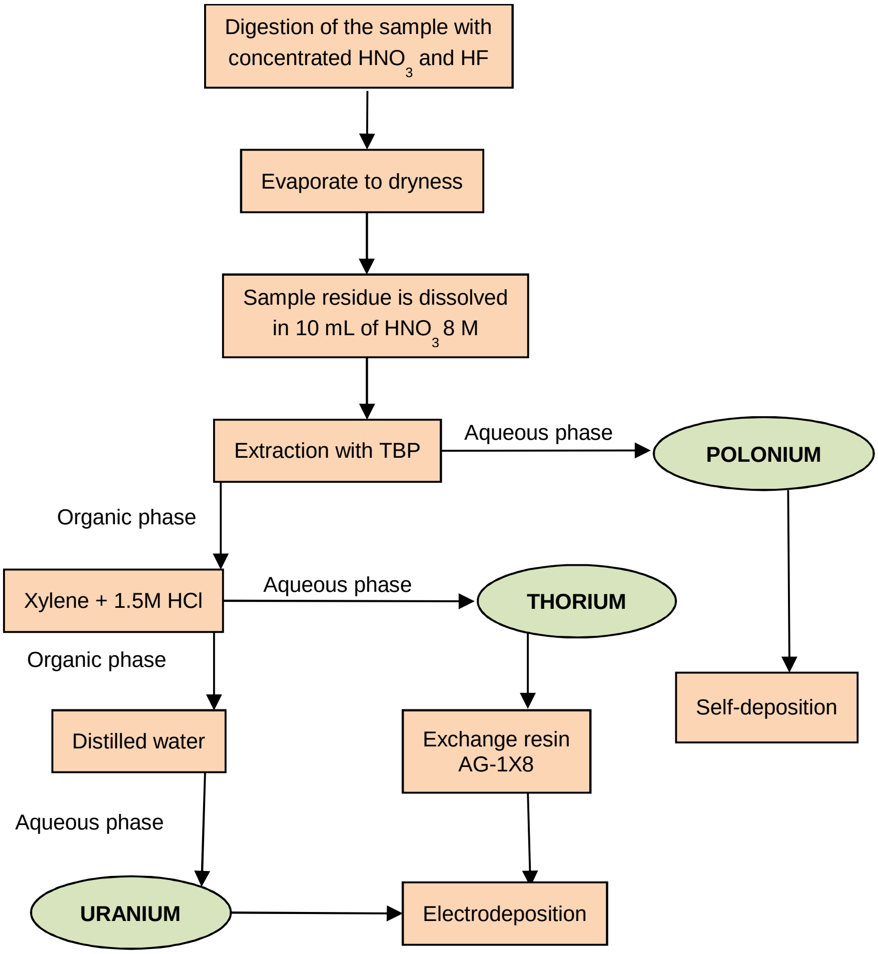

Figure 2.10. Diagram of TBP radiochemistry method.

At last, to extract and isolate the uranium from organic phase, 15 mL of distilled water was added to phase that remains into the funnel. Then, the funnels are agitated for 10 min and are settled for another 10 min. The uranium is back-extracted with water. The agitation steps are repeated with the previous addition of 15 mL of distilled water. To finish, the beakers with the aqueous solution containing U pass to the electro-deposition stage.

Step 4. Thin source preparation by self-deposition and electro-deposition

The isolation of ^{210}Po by self-deposition begins evaporating the sample to dryness. The temperature must be approximately 70-80 °C in order to avoid losses of polonium. The residue is dissolved with 5 mL of HCl, and then evaporated to dryness (this step is repeated twice). Then, the previous residue is dissolved with 10 mL of 2 M HCl, and about 50 mg of ascorbic acid for reduce Fe^{3+} to Fe^{2+}. Finally, the sample is filtered and transferred to self-deposition bottle. The bottles are placed in the mechanical agitator for at least 5 hours to ensure the Po isotopes are self-deposited onto silver discs.

For obtaining the thorium and uranium thin sources the electrodeposition technique is used. The sample was evaporated until 1 or 2 mL remained, and 1mL of 0.3 M Na_2SO_4 was added. Then, the sample was evaporated to dryness and the residue was dissolved with 0.3 mL of H_2SO_4, 4 mL of distilled water and 2 drops of Thymol blue (indicator). Previously, the electrodeposition cells were prepared and the sample was transferred into it, washing the beaker with approximately 5 mL of 1 % H_2SO_4. Drops of NH_3 (5 %) were added until pH 2.1-2.4 is reached (orange colour). At that moment, the electrodeposition is performed during 2 hours with 1.2 A electric current for Th. The electrodeposition times can be reduced for U (conditions: 1 hour with 1.2 A electric current). After the electrodeposition, the stainless steel disc is washed with distillated water, followed by iso-propanol, and dry at room temperature. Finally, the disc was saved into a little bag with the sample code until was analysed in an alpha spectrometric system with passivated implanted planar silicon (PIPS) detectors.

2.2.8.2 Alpha spectrometric system with passivated implanted planar silicon (PIPS) detectors

Silicon is mainly used semiconductor materials, for charged particle detectors. The silicon charged particle detector is a wafer of silicon having surface contacts forming a p-n junction. On the surface of the Si semiconductor, thin metal layers (gold and aluminium) are evaporated as doping impurities after chemical etching, as in the modern high-performance Passivated Implanted Planar Silicon (PIPS) detector.

In the detection process when an alpha particle enters the detector, it loses a small amount of energy in the thin entrance window. The vast majority of its energy is deposited in the depleted region of the detector diode (p-n junctions) by causing ionisation of the silicon atoms and free electron hole pairs (charge carriers). The energy necessary to form a single electron-hole is directly proportional to the energy of the stopped particle. The electric field in this region sweeps the electrons to one terminal and the holes to the other. This charge pulse is integrated in a charge sensitive preamplifier to yield the observed voltage pulse and perform the alpha spectrum.

The alfa spectrometry was performed using an EG&G Ortec system with an integrated Octete PC PLUS with eight chambers. Each chamber consists of 450 mm^2 ion-implanted silicon PIPS detector, each one housed inside a vacuum chamber. In addition, each alpha spectrometer chamber includes a vacuum gauge, variable detector bias supply, a preamplifier, a shaping amplifier with adjustable gain, pulse stretcher and bias amplifier, a test pulser generator with variable amplitude, and leakage current monitor. The detectors have a maximum FWHM (Full Width Half Maximum) of 20 keV by using a mono-energetic emission of ^{241}Am, with detection efficiency close to 25 % for distances less than 10 mm. A background counting rate less than 30 counts per day is expected in the energy range from 3-8 MeV, about $(1\text{-}2)\cdot 10^{-5}$ cps under a typical alpha peak, energy interval for the most interest natural alpha particle emitters. The detectors operate at a polarisation voltage of 50 V. The program used to control individually the spectrometer and for spectrum analysis and data evaluation was Maestro.

In order to quantify the activity concentrations of the different alpha particle emitters, it is necessary to identify them in the spectrum and to carry out an energy-channel calibration in the energy range 3-8 MeV. The detector response (channel) is directly proportional to the energy of the incident particle, and to find this relation consist the calibration channel-energy.

2.2.8.3 Counting efficiency

Several factors affect the absolute counting efficiency, as the detector size, the source-detector solid angle, and the intrinsic detention efficiency are the main factors. It is well know that for PIPS detectors the intrinsic detention efficiency is the unit (Vioque et al., 2002).

The absolute counting efficiency (ε) is defined as the number of detections without background (counts, N) in relation to the number of emissions of the radioactive source (N_0):

$$\varepsilon = \frac{N}{N_0} \qquad \text{[Eq. 2.3]}$$

Therefore, to determine experimentally the counting efficiency, a certified standard source with known activity (A_S) in the same geometry that sample is used, being the counting efficiency by the formula:

$$\varepsilon = \frac{(G - B)}{A_s \cdot P_S \cdot t} \qquad \text{[Eq. 2.4]}$$

, where G is the gross count of the peak, B the background, P_s is the emission probability of the standard source, and t the counting time.

2.2.8.4 Activity concentration calculation

The activity concentration (a) at the moment of the isolation (date, F_0) for a given alpha-emitter radionuclide can be calculated by applying the equation:

$$a = \frac{(G - B) \cdot P_0 \cdot m_0 \cdot a_0}{(G_0 - B_0) \cdot P \cdot m} \cdot e^{-\lambda_0 (F_0 - F_r)} \cdot e^{\lambda (F_1 - F_0)} \qquad \text{[Eq. 2.5]}$$

, where G is the total alpha counts in the peak of the radionuclide of interest, determined in the alpha spectrum obtained with a counting time t, G_0 is the net counts at the peak of tracer, P is the probability of the alpha emission in the peak of interest, P_0 probability of the alpha emission in the peak of interest for tracer (often is 1), m is the mass (or volume) of the sample, m_0 is the mass (or volume) taken from the certified standard tracer solution, a_0 tracer activity concentration at the reference date of the certificate, F_0 is the isolation date, F_1 is the counting date, F_r is the reference date for tracer activity concentration of the certificate (a_0).

The previous equation is valid if the contribution of the blank sample is negligible (blank activity = A_b), but in general this one has to be considered. Therefore, the real activity concentration of the sample (a_s) will be calculated trough the next expression:

$$a_s = a - A_b/m \qquad \text{[Eq. 2.6]}$$

The Yield (Y) of the radiochemical procedure is calculated as:

$$Y = \frac{G_0 - B_0}{\varepsilon P_0 m_0 a_0 t} \qquad \text{[Eq. 2.7]}$$

The average chemical yields obtained to ^{210}Po, Th and U radionuclides were 90, 60 and 80 %, respectively.

2.2.8.5 Lower limit of detection (LLD) and Minimum Detectable Activity (MDA)

The lower limit of detection (LLD) for any radionuclide is critically dependent on the detector background (B, counts), and procedure blank count rates. However, an attempt has been made to give typical limits for low background detectors, which is called the Instrumental LLD (ILLD) (Currie, 1968).

The ILLD (in counts) can be calculated by using the next formula derived by Lochamy (1981).

$$ILLD = k^2 + 2.8 \cdot k\sqrt{B} \qquad \text{[Eq. 2.8]}$$

, where k is the one-sided confidence factor, being k = 1.65 if a 95 % of confidence level is taken.

If the activity of the blank is negligible, the Minimum Detectable Activity (MDA) is given by:

$$MDA = \frac{ILLD\ (counts)}{\varepsilon \cdot Y \cdot t} = \frac{k^2 + 2.8 \cdot k\sqrt{B}}{\varepsilon \cdot Y \cdot t} = \frac{2.7 + 4.6\sqrt{B}}{\varepsilon \cdot Y \cdot t} \quad \text{[Eq. 2.9]}$$

But it is very common to find that the sample blank contains significantly activity above the background, and for these cases the valid alternative to assess the LLD is to use n replicate measurements of the sample blank by using an equation similar to the previous one (MARLAP, 2004):

$$LLD = k\sqrt{1 + \frac{1}{n}}\sigma_b \quad \text{[Eq. 2.10]}$$

, where σ_b denotes the standard deviation of the sample blank activity, n is the number of replicate blank measurements, and k is the quantile t-Student according to the number of freedom degrees (f = n-1). For example, for n = 10 blank samples, f = n-1 = 9, and k = 1.83 if a significant level α = 0.05 is taken, or k = 2.82 for α = 0.01. Therefore, a detection decision is made for a real sample by comparing the measured net activity to the critical net activity. This approach should work best if all samples and blanks are analysed under similar conditions, using instruments with similar counting efficiencies and background levels. It is important to point out that all samples and blanks must be corrected for instrument background (MARLAP, 2004).

The MDA is calculated by applying previous equation 2.9. In our laboratory the background counts is determined every month, and the blank average activity was calculated for five blanks: n = 4, f = 3, α = 0.05 → k = 2.3. Considering an average for yield of 80 %, the typical counting times of two days ($1.7 \cdot 10^5$ s), and a counting efficiency of 25 %, the MDA obtained for the radionuclides considered in this work ranged from 0.5 to 2.2 mBq.

2.2.8.6 Quality Control (QC)

The radiochemical method implemented at our laboratory is validated under a quality control system (QC) conformed by replicates, blanks, certified standard materials, and by participating in international and national intercomparison excercices.

The reference materials H1 (^{238}U), C1 (^{232}Th), and IAEA-327 have been used. Tables 2.2 shows that results obtained through TBP method were in agreement with the certified values IAEA-327 a soil from Moscow containing certified activity concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th at 95 % of confidence. Furthermore, the statistical parameter Z_{Score} was calculated as follow:

$$Z_{Score} = \frac{x_{meas} - \mu_{ref}}{\sqrt{\sigma_{meas}^2 + \sigma_{ref}^2}} \qquad \text{[Eq. 2.11]}$$

, where x_{meas} is the measured value, μ_{ref} is the reference value, σ_{meas} is the standard deviation of the measured value and σ_{ref} is the reference standard deviation.

Table. 2.2

Average activity concentrations (Bq kg^{-1}) of reference material IAEA-327 obtained through TBP radiochemical method and analysed by alpha spectrometry. Uncertainties are indicated as Standard Combined Uncertainty.

Radionuclide	Reference*	TBP	$\lvert Z_{Score}\rvert$**
^{238}U	32.8 ± 1.4	30 ± 3	0.76
^{234}U	32.4 ± 1.0	30 ± 2	1.11
^{232}Th	38.7± 1.5	38.5 ± 1.5	0.10
^{230}Th	34.1 ± 1.7	35.5 ± 1.4	0.63

[*] Certified activity concentration of the reference material IAEA-327

** $\lvert Z_{Score}\rvert \leq 2$ (no significant differences with a confidence level of 95 %)

All the results obtained shown $|Z_{Score}| \leq 2$ thus no significant differences between the reference material and the values measured with a confidence level of 95 %.

Tables 2.3 shows the activity concentrations obtained through TBP method compared to C1 and H1 reference materials. Both reference materials are solutions with known activity concentrations of ^{238}U (H1), and ^{232}Th (C1). The results were in agreement with the certified values.

Table. 2.3

Activity concentrations (Bq kg^{-1}) of reference materials C1 and H1. Uncertainties are indicated as Standard Combined Uncertainty.

Radionuclide	Reference*	TBP	$\|Z_{Score}\|$**
^{238}U	153.88 ± 1.05	157 ± 3	0.98
^{232}Th	97.09 ± 0.72	95.75 ± 1.64	0.42

* Certified activity concentration of the reference materials C1 and H1

** $|Z_{Score}| \leq 2$ (no significant differences with a confidence level of 95 %)

The Nuclear Safety Council (CSN) organises every year an intercomparison exercise with different type of samples (sediment, soil, filters, water, etc.). The results obtained in our laboratory and the reference values for a food ash are reported in Table 2.4, which are in accordance within 1σ of their nominal values.

Table. 2.4

Average activity concentrations (Bq kg^{-1}) of the food ash in the CSN-2010 inter-comparison exercise.

Radionuclide	Reference*	TBP	Z_{Score}**
^{238}U	27.3 ± 4.9	27.9 ± 1.0	0.13
^{234}U	28.5 ± 5.1	28.8 ± 1.0	0.07
^{230}Th	3.65 ± 0.66	4.30 ± 0.80	0.99

* Certified activity concentration of the reference material supplied by CSN

** $|Z_{Score}| \leq 2$ (no significant differences with a confidence level of 95 %)

2.2.9 Gamma spectrometry

Gamma ray spectrometry is an analytical non-destructive method that allows the identification and quantification of γ-emitting particles in a high variety of matrices. In one single measurement and with little physical sample preparation (efficiency is only dependent on physical parameters), gamma ray spectrometry detects several gamma-emitting radionuclides in the sample (multi-elemental). The measurement gives a spectrum of lines, being the amplitude of which is proportional to the activity of the radionuclide and its position on the horizontal axis gives its energy. Opposite the alpha-particle spectrometry, this method requires large sample masses, background gamma spectrum is higher and more complicated, detection efficiency varies with gamma energy, self-absorption of gamma radiation in the sample must be considered, and generally it is less sensitive than radiochemistry and.

The gamma spectrometry system used contains an Extended Range coaxial Ge Camberra detector (XtRa), model GX3519. The detector has a unique carbon composite thin-window (0.5 mm thick), 153 cm^3 active volume and 4 mm length from the detector to the carbon window, which extends the useful energy range down to 3 keV. Its relative efficiency in relation to a 3 x 3“ NaI(Tl) detector is 38 % and have FWHMs (Full Width Half Maximun) of 0.95 keV at 122 keV and 1.9 keV at 1330 keV. The detector is cooled to liquid nitrogen temperatures and coupled to a conventional electronic chain, including a PC-based 8K multichannel analyser and an ADC with Genie 2000 for data acquisition and analysis.

A reduction in the background was achieved by applying a shield constituted by an outer cylindrical lead layer of 10 cm thick to reduce the background radiation originating from building materials and cosmic rays surroundings. The lead shield is covered internally by a thin copper layer of 2 mm, whose mission is the attenuation of X-rays generated as consequence of the interaction between the outer radiation and the lead layer.

As the gamma spectrometry technique is a multi-element and non-destructive technique, the sample preparation was reduced to two main steps. The sample was dried to constant weight and grinded to homogenise the particle size. A representative aliquot between 50-100 g is placed in a cylindrical polyethylene container calibrated (see next section). The gamma spectrometric measurements were carried out during around 48 h.

2.2.9.1 Detector system calibration

The detector calibration has been performed, both energy and efficiency, in our research group (Bolivar et al., 1995a; Bolivar et al., 1996a; Pérez-Moreno et al, 2002). The cylindrical geometry was used according to polyethylene containers with 6.50 cm diameter and a variable sample height, between 0 and 5.0 cm. Furthermore, the self-absorption effect depends on the sample density and chemical composition, and, once the counting geometry is established, on the sample height.

The efficiency in the real sample (ε_S) is calculated multiplying the efficiency in the calibrating sample (ε_C) by the correction factor (*f*), which takes into account the self-absorption differences between both samples, so:

$$\varepsilon_S = f \cdot \varepsilon_c \qquad \text{[Eq. 2.12]}$$

The efficiency calibration method was performed using a standard mixed radionuclide source (IAEA-RGU-1, IAEA-RGTh-1, IAEA-RGK-1) of a known radionuclide concentration in ^{238}U and daughters, ^{232}Th and daughters, and ^{40}K. The full energy peak efficiency (*fεpε)* for the calibration sample (ε_C) was determined measuring the reference materials at different energies and heights (from 0 to 5 cm with intervals of 0.5 cm). The full energy peak efficiency was obtained according the following equation:

$$\varepsilon_C = \frac{N}{amP_\gamma t} = \varepsilon_C\left(E_\gamma, h\right) = \varepsilon_C(E_\gamma, m_C) \qquad \text{[Eq. 2.13]}$$

, where ε_C is the full energy peak efficiency for the calibration sample, *N* is the net area under the photo peak of interest, a (Bq kg^{-1}) is the ^{226}Ra activity concentration in reference sample, m (kg) the sample mass corresponding to a height h, P_γ is the probability of emission for the considered energy (E_γ) taken from tabulated data (Kocher, 1981), t the counting time, m_c (g) is the mass of calibration sample ($m_c = \pi r^2 \delta_c h = kh$), δ_c (g cm^{-3}) its apparent density and r (cm) the radius of cylindrical container.

The procedure of the calibration is explained with detail in Pérez-Moreno et al. (2002), being given the *fερε* for the calibrating sample by the equation:

$$\varepsilon_C = 14.52(E_\gamma)^{-0.95} \cdot e^{\left(-0.424(E_\gamma)^{-0.138} h\right)} \qquad \text{[Eq. 2.14]}$$

To point out that calibration sample has an apparent density of 1.60 g cm^{-3}, the radius of the cylindrical container is 3.25 cm, and h is the height (h) of sample in cm, and E_γ, in keV, is the energy of the considered gamma emission.

The correction factor (f) due to the different self-sorption between both the problem and the calibration samples was demonstrated in this paper that it is given by:

$$f = \frac{N_1}{N_2} = \frac{1 - e^{\mu \rho h}}{\mu \rho} \cdot \frac{\mu_c \rho_c}{1 - e^{-\mu_c \rho_c h}} \qquad \text{[Eq. 2.15]}$$

, where μ (cm^{-1}) is the self-attenuation coefficient, and ρ ins the apparent density of the sample. Therefore, in order to calculate the μ, it is convenient to know the composition of both sample and calibration matrix.

Finally, to point out that high energy (E_γ > 150 keV) samples containing elements with Z < 26 (Fe), it is possible to approximate the self-attenuation coefficient to the expression:

$$\begin{aligned} \eta(E_\gamma) = (0.556 \pm 0.013) - (0.113 \pm 0.004) Ln(E_\gamma) \\ + (0.0059 \pm 0.0003)[Ln(E_\gamma)]^2 \end{aligned} \qquad \text{[Eq. 2.16]}$$

By using these expressions, it is possible to calculate the *fερε* for any energy and sample type.

2.2.9.2 Activity concentration calculations

Once the detector has been calibrated, the samples under study were measured and the respective gamma-spectrum acquired. The activity concentration, a, for a given gamma-emitter radionuclide at the moment of the counting can be calculated by applying the equation:

$$a = \frac{G - F - B}{mtP_{\gamma}\varepsilon} \qquad \text{[Eq. 2.17]}$$

, where G is the total counts in the photopeak of the radionuclide of interest, determined in the sample with a counting time t; F is the number of counts in the photopeak of the radionuclide of interest, observed without any sample for the counting time t; B is the background due to the Compton component, m is the mass of the sample, P_{γ} is the intensity of the gamma emission, ε is the counting efficiency.

The standard uncertainty of the activity concentration (σ_a), and only considering the counting errors, is given by the next equation:

$$\sigma_a = a\frac{\sqrt{G - F - B}}{G + F + B} \qquad \text{[Eq. 2.18]}$$

2.2.9.3 Lower limit of detection (LLD) and Minimum Detectable Activity (MDA)

The background should be measured using a sample similar to measuring sample, but without any measurable amount of the radionuclide of interest. The second consideration is that the background counts are determined by taking a few channels on each side of the photopeak region of interest and fitting the points to form a continuous curve under the photopeak. The points on either side are used in this way to estimate the background that will be subtracted in the photopeak region.

The Lower Limit of Detection (LLD) it is calculated according to Currie (1968), and the equation at the 95 % confidence level is:

$$LLD = 2.72 + 3.30\sqrt{F + \sigma_F^2 + B + \sigma_B^2} \qquad \text{[Eq. 2.19]}$$

, where F is the background from ambient gamma radiation but may also be affected by the presence of radionuclides other than the one of interest in the sample, σ_F is the standard deviation of F, B is the continuous background, which is mainly due to the Compton component, and σ_B is the standard deviation of B.

The continuous background (B) due to the Compton component are given as follow:

$$B = \frac{N}{2n}(B_d + B_i) \qquad \text{[Eq. 2.20]}$$

, where N is the number of photons coming out from the real sample at the detector, B_d is the number of counts accumulated in the n channels before the interest peak region and B_i is the total counts in the n channels after of the interest peak region.

Equation 2.21 shows the formula to calculate the standard deviation of B:

$$\sigma_B^2 = \left(\frac{N}{2n}\right)^2 (B_d + B_i) \qquad \text{[Eq. 2.21]}$$

, where N is the number of photons coming out from the real sample at the detector, B_d is the number of counts accumulated in the n channels before the interest peak region and B_i is the total counts in the n channels after of the interest peak region.

The Minimum Detectable Activity (MDA) for a specific radionuclide, at 95 % of confidence level and at the moment of the counting, is given by:

$$MDA = \frac{LLD}{tP_\gamma \varepsilon} \qquad \text{[Eq. 2.22]}$$

, where LLD is the lower limit detection, *t* is the counting time, P_γ is the intensity of the gamma emission and ε is the counting efficiency.

Furthermore, the minimum detected activity concentration (Bq kg^{-1}, MDAC), was obtained as follow:

$$MDAC = \frac{MDA}{m} \quad \text{[Eq. 2.23]}$$

, where *MDA* (Bq kg^{-1}) is the minimum detectable activity and *m* (kg) is the mass of the sample.

2.2.9.4 Quality Control (QC)

The gamma spectrometry quality control has been performed by taken periodic blanks, certified reference materials (i.e., IAEA-327), replicates, and participating in national and international intercomparison exercises. Table 2.5 shows that results obtained were in agreement with the certified values within the confidence intervals (95 %).

Table. 2.5
Activity concentrations (Bq kg^{-1}) certified and measured in reference material IAEA-327 analysed by alpha spectrometry. Uncertainties as standard combined uncertainty

Radionuclide	Reference*	Measured	Z_{Score}**
^{228}Th	38.2 ± 1.0	33.5 ± 2.0	1.21
^{226}Ra	34.1 ± 1.4	30.3 ± 1.8	1.36
^{228}Ra	38.7 ± 1.4	33.5 ± 2.0	1,82
^{210}Pb	58.8 ± 4.9	65.2 ± 4.0	1.04
^{137}Cs	24.9 ± 0.6	23.5 ± 1.4	0.92
^{40}K	621 ± 9	710 ± 42	1.89

* Certified activity concentration of the reference material IAEA-327 at 95% of confidence level (k = 2).

** $|ZScore| \leq 2$ (no significant differences with a confidence level of 95 %)

The IAEA-CU-2008-03 organised a worldwide open proficiency exercise, which ^{226}Ra and ^{210}Pb were measured, in both spiked water and phosphogypsum (Table 2.6). The results are in accordance with the certified values, within 1σ of their nominal values. Z_{score} is calculated according equation 2.11.

Table. 2.6

Activity concentrations (Bq kg^{-1}) of the IAEA-CU inter-comparison exercise. Uncertainties as standard combined uncertainty

Radionuclide	Sample	Reference*	Measured	Z_{Score}**
^{226}Ra	W[1]	1.93 ± 0.09	2.02 ± 0.03	0.95
	P[2]	780 ± 31	862 ± 41	1.60
^{210}Pb	P[2]	680 ± 29	633 ± 39	0.97

* Certified activity concentration of the reference material supplied by IAEA-CU

** $|Z_{Score}| \leq 2$ (no significant differences with a confidence level of 95 %)

[1] spiked water

[2] phosphogypsum

Moreover, in the interlaboratory comparison organised by the Nuclear Safety Council (CSN) using food ash the measuring in our laboratory are in good agreement within the certified values (Table 2.7).

Table. 2.7

Activity concentrations (Bq kg^{-1}) certified and measured of the food ash in the CSN inter-comparison exercise.

Radionuclide	Reference*	Measured	Z_{Score}
234Th	23.9 ± 4.3	27.1 ± 4.4	0.52
^{228}Ra	5.25 ± 0.95	5.30 ± 1.00	0.04
^{228}Ac	5.26 ± 0.95	5.30 ± 0.90	0.03
^{228}Tl	1.77 ± 0.32	1.50 ± 0.26	-0.65
^{226}Ra	15.2 ± 2.7	15.3 ± 1.8	0.03
^{214}Pb	14.8 ± 2.7	15.3 ± 1.8	0.15
^{210}Pb	48.0 ± 8.6	50.9 ± 6.4	0.27
^{40}K	4593 ± 827	4700 ± 600	-0.10

* Certified activity concentration of the reference material supplied by CSN

** $|Z_{Score}| \leq 2$ (no significant differences with a confidence level of 95 %)

2.3 TECHNOLOGICAL PROPERTIES

The following section shows the protocols established and equipment used to evaluate the technological properties of the applications performed.

2.3.1 Water Absorption by Capillarity (WAC)

The European standard EN 480-5;2005 describes the determination of the water capillary absorption coefficient of concrete, mortars and grouts. It standard has been prepared by Technical Committee CEN/TC 104 “Concrete and related products” (2006).

Capillary water absorption coefficient is one of the most important features of a building material because it governs the liquid moisture movement into it and expresses the rate of absorption of water due to capillary forces for building materials. Thus, it must be taken into consideration when determining the hydrometric properties of the material.

Step 1. Preparation of test specimens

Mixing of the mortar was as described in EN 480-1:2014. Mortar specimens (40 x 40 x 160) mm^3 were prepared as described in EN 196-1: 2016, except that the moulds shall not be oiled.

When testing at equal w/c ratio, the water content of the admixture shall be taken into account when calculating the required water content of the mortar. Test mix has the same consistence as the control mix this is measured by using the workability meter in accordance with EN 413-2:2016.

Step 2. Curing of specimens

On both the control mix and the test mix, two series of measurements of capillary absorption, were carried out. The first series was performed on three specimens of test mix and three specimens of control mix after 7 days curing. The second series was carried out on the other specimens after 90 days curing. The specimens were demoulded after 24 h and further cured in the enclosure until 7 days and 90 days old respectively.

Step 3. Procedure

Materials for the control mix and test mix, and moulds were conditioned for at least 24 h before use. After drying, each sample at 50 °C in an oven until a constant mass was reached. The samples were conditioned by placing in an enclosure maintained at (20 ± 2) °C and (65 ± 5) % relative humidity.

The specimens were weighed (M_0) in the enclosure when 7 days or 90 days old as appropriate and placed vertically in a receptacle containing water at a constant level.

The samples rest on rods to allow free access of water to the base. The water level was maintained at (3 ± 1 mm) above the base of the specimen. Immediately after placing the specimens in position avoiding contact between them, the cover was placed on the receptacle.

At the beginning, the liquid being to moisten only the lower surfaces. The lower parts of the sides adjoining the inflow face were sealed with a polyethylene sheet to prevent any water being absorbed into their surface pores. Progressively, the position of the waterfront is gradually approaching the opposite side of the sample and capillary and viscous forces govern the water intake.

Finally, the quantity of the absorbed water was measured at standard time intervals by weighing the specimen. Each specimen was removed from the receptacle, wiped lightly with dry paper or cloth in order to remove any surplus water, and weighed (M_J). Each weighing should be completed as quickly as possible (typically within 30 s).

The WAC (g cm^{-2}) values were then determined using Eq. 2.24:

$$WAC = \frac{\Delta M}{A} = \frac{M_J - M_0}{16} \qquad \text{[Eq. 2.24]}$$

, where M_J (g) is the sample mass after 28 days, M_0 (g) is the initial mass, and ‘16’ the wetted surface area of the sample (4 x 4 cm^2).

All experiments were performed in triplicate and reference specimens were used. The reference mortar was as specified in EN 480-1. The test mix had the same consistence as the control mix as described in EN 480-1 or the test mix had the same water/cement ratio as the control mix. The water content of the admixture was taken into account when calculating the required water content of the test mix.

2.3.2 Water Absorption (WA or E), Bulk Density (BD) and Apparent Porosity (AP)

Water absorption is an essential parameter, not just for identifying the type of tile (product groups in standard EN 14411:2016, but also for advancing certain fundamental characteristics:

- Greater or lesser stain resistance in unglased tiles (UGL)
- Larger or smaller coefficient of moisture expansion based on greater or lesser porosity, related in turn to delayed crazing and the tile installation mode
- Resistance to frost/thaw cycles, this only being assured in tiles with $E \leq 0.5$ %
- Mechanical strength, this being greater in tiles with low absorption, at the same thickness
- The possibility of efflorescences appearing in UGL tiles of group III if the fixing background is not waterproofed

Water absorption capacity identifies the nature of the ceramic body in regard to internal structure, which is directly related to mechanical strength (measured by modulus of rupture and breaking strength) and to other characteristics that affect ceramic tile durability (particularly in unglased tiles), such as resistance to deep abrasion, stain resistance, and resistance to frost/thaw cycles, as well as to dimensional quality.

Water absorption, bulk density and apparent porosity were measured according to ISO 10545-3:1997 (Part 3 Determination of water absorption, apparent porosity, apparent relative density and bulk density) and ASTM C373-14:2014 (Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products, Ceramic Tiles, and Glass Tiles).

Step 1. Test sample preparation

This method is applicable to all ceramic tiles. The test was performed on 10 whole tiles in cases where the surface of each tile is less than 0.04 m^2; if greater than 0.04 m^2, 5 tiles will suffice. Every test sample weighed a minimum of 50 g.

Step 2. Test procedure

The specimens were dried in the oven at 110 ± 50 ºC, until it attains constant mass, and saved in the desiccators over silica gel, until cooled to room temperature. The specimens were weighed and placed vertically, with no contact between them, in deionised water. Maintain the water level 50 mm above the tiles throughout the test. Container should be kept at boiling point for two hours and allow the tiles to cool, still completely immersed in this water, overnight. Once the tiles have been removed from the container, excess water is removed with a chamois leather and tiles are then weighed, again as precisely as for dry weight. Finally, place the specimens in the wire basket that is immersed in water and determine the weight of each specimen to the nearest 0.01 g.

Step 3. Calculation

The absorption of water coefficient, E (dry wt.%), expressed as a percentage of the weight of the dry material, and was calculated by the equation:

$$E = \frac{m_w - m_d}{m_d} x\ 100 \qquad \text{[Eq. 2.25]}$$

, where m_w (g) is the mass of wet specimen and m_d (g) is the mass of dry specimen.

The apparent porosity, P (%), expresses the relationship of the volume of open pores with the exterior volume of the specimen and is calculated as follows:

$$P = \frac{m_w - m_d}{m_w - m_i} x\ 100 \qquad \text{[Eq. 2.26]}$$

, where m_i is the mass immersed in water.

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

$$BD = \frac{m_d}{m_w - m_i} x\ 100 \qquad \text{[Eq. 2.27]}$$

The water absorption was measured for ten or five representative specimens. The average absorption of water of the sample is determined by the arithmetic average of the individual results, and results must be rounded off to a single decimal place.

2.3.3 Linear Shrinkage (LS)

Linear firing shrinkage is a comparative indicator of the degree of vitrification. During the firing process, as a clay is fired higher it shrinks more and more and particles continue to pack together to a point of maximum shrinkage (after which swelling occurs as a precursor to melting). At this point, they begin to break down and react with each other, fluxes begin to melt and flow, and mineral grains seed the development of more stable forms.

This indicator was calculated according to the standard ASTM C-326-9:2009 (Standard Test Method for Drying and Firing Shrinkages of Ceramic Whiteware Clays).

The purpose of this test was to obtain values of shrinkage after firing process, under various processing conditions to enable designers to determine the proper size of fired specimens.

Linear shrinkage, *LS* (%), is the percent change in length or width of a test sample from dry to fired and was calculated by the equation:

$$LS = \frac{L_i - L_f}{L_i} x\ 100 \qquad \text{[Eq. 2.28]}$$

, where L_i (mm) is the specimen length without firing and L_f (mm) is the specimen length after firing.

The specimens were measured after and before firing on more than one dimension using a paquimeter Mitutoyo (precision of ± 0.01mm). Bending Strength (BS)

2.3.4 Bending Strength (BS)

Bending strength, also known as modulus of rupture, defined as the stress in a material just before it yields in a flexure test. The bending strength is an essential parameter, not just for identifying the type of tile (standard EN 14411), represents the highest stress experienced within the material.

This property was measured according to ISO 10545-4:2014 (Ceramic tiles - Part 4: Determination of modulus of rupture and breaking strength) and ASTM C674–13:2008 (Standard Test Methods for Flexural Properties of Ceramic Whiteware Materials). These methods must be applicable to all ceramic tiles.

Step 1. Test procedure

The sample piece is placed centrally across the two lower adjustable tension rods set a known distance apart (Fig.2.11). The load is applied evenly at a constant rate of increase of stress (1 N mm^{-2} s) by means of a third rod in contact with the proper surface, equidistant between the supporting rods. The test piece is subject to a three-point strain. At the optimum point, the test piece snapped, and the maximum finger on the dial gauge remain at the maximum point.

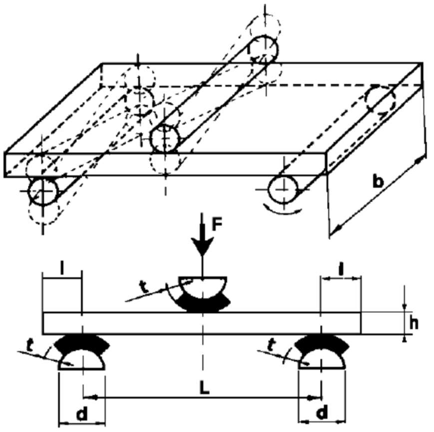

Figure 2.11. Loading system in the measurement of bending strength.

Step 2. Calculation

The resistance to bending (*BS*), expressed as N mm^{-2} or MPa is given by the following formula:

$$BS = \frac{3FL}{2bh} \qquad \text{[Eq. 2.29]}$$

, where *F* (N) is the breaking load, *L* (mm) is the span between the supporting rods, *b* (mm) is the width of the tile at the broken edge and *h* (mm) is the minimum thickness of the tile measured along the broken edge.

The resistance to bending was determined in an electronic universal tester (Servosis model ME-402/01) and in an Contenco (Model UMC-20T) testing machine on ten test specimens by a three-point loading test with a span of 32 mm and a crosshead speed of 1 mm min^{-1}.

The test was performed on whole tiles with a least ten tile for each test. The average resistance to bending of the sample is the arithmetic average of the individual results.

2.3.5 Compressive Strength (Cs) and Flexural Strength (Fs)

The compressive and flexural strengths of the cements and brick were measured according to standard EN 196-1:2005, Methods of testing cement. Part 1: Determination of strength.

This European norm described the method for the determination of the compressive and the flexural strength of cement mortar. The method applies to common cements and to other cements and materials, the standards for which call up this method. It may not apply to other cement types that have, for example, a very short initial setting time.

The method comprises the determination of the compressive and the flexural strength of prismatic test specimens 40 x 40 x 160 mm^3 in size according the norm.

The flexural strength (Fs) was calculated using the three-point loading method. The prisms were placed in the apparatus with one side face on the supporting rollers and with its longitudinal axis normal to the supports. The load was applied vertically by means of the loading roller to the opposite side face of the prism and increasing it smoothly at the rate of 50 ± 10 N s^{-1} until fracture. The prism halves were keep until tested in compression.

The flexural strength, Fs (MPa) is calculated as follows:

$$Fs = \frac{3F_f L}{b^3} \qquad \text{[Eq. 2.30]}$$

, where b (mm) is the side of the square section of the prism, F_f (N) is the load applied to the middle of the prism at fracture and L (mm) is the distance between the supports.

The procedure was developed using an Autotest 200-10-W universal press (Ibertest). All tests were performed in sextuplicate

The compressive strength was carried out by loading its side faces using the appropriate equipment. The prism halves were centered to the platens of the machine within ± 0.5 mm, and longitudinally. The load increased smoothly at the rate of 2400 ± 200 N s^{-1} over the entire load application until fracture.

The compressive strength, Cs (MPa) was calculated according eq. 2.29:

$$Cs = \frac{Fc}{S} \quad \text{[Eq. 2.31]}$$

, where Fc (N) is the maximum load at fracture and S (mm^2) is the cross section area (40 x 40 mm^2).

Compressive strength was measured using an EMIC apparatus, model DL-2000. Test result was defined as the arithmetic mean of the ten compressive strength determinations made on a set of three prisms. If one result within the ten determinations varied by more than ± 10 % from the mean, the set was discarded. The results shall comply with the requirements of standard EN 197-1:2011.

2.4 TECHNIQUES FOR ENVIRONMENTAL RISK EVALUATION

Finally, since these wastes are NORM (Naturally Occurring Radioactive Material) and even classified as hazardous, environmental implications and potential human risk of use the new materials have been evaluated according to the following methods:

2.4.1 TCLP leaching test

The potential environmental impact was evaluated according the method US EPA SW846-1311:1997 TCLP tests (Toxicity Characteristic Leaching Procedure) established by the Environmental Protection Agency (EPA). TCLP is designed to determine the mobility of both organic and inorganic pollutants present in solid and multi-phase wastes.

This method classifies waste as hazardous or non-hazardous based on its potential toxicity. If the extract from a representative sample contains any of the contaminants listed in U.S. EPA 40 CFR 261.24:2011 at the concentration equal to or greater than the respective value given is classified as hazardous.

Step 1. Preliminary Evaluations

Preliminary evaluation is performed on 100 g aliquot of waste. This aliquot may not actually undergo extraction. These preliminary evaluations included.

Calculation of the percent solids according the following equation:

$$Percent\ solids = \frac{Weight\ of\ Solid^{4}}{Total\ Weight\ of\ Waste}\ x100 \qquad \text{[Eq. 2.32]}$$

Any material that did not pass through a 9.5 mm (0.375 inch) standard sieve required size reduction.

Step 2. Selection of the Extraction Fluid

Determination of which of the two extraction fluids are to be used for the TCLP extraction of the waste. Extraction fluid is prepared in batches by the total number of extractions required.

Firstly, 5 g of the waste are transferred into a 500 mL Erlenmeyer flask with 96.5 mL of reagent water. It is covered with a watch glass, and stirred vigorously for 5 minutes using a magnetic stirrer. The pH is measured and recorded. If the pH < 5.0, then the extraction fluid #1 is used. If the pH > 5.0, then 3.5 mL 1N HCl is added, slurred briefly, covered with a watch glass and heated to 50 ºC for 10 minutes. The solution is cooled to room temperature and the pH measured. If the pH < 5.0, then the extraction fluid #1 is used. Oppositely, if the pH > 5.0, extraction fluid #2 has to be used.

Step 3. Preparation of the Extraction Fluids

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[4] The wastes used in this thesis are 100 % solids.

- Extraction Fluid #1 is prepared with the addition of 5.7 mL of glacial CH_3CH_2OOH and 64.3 ml of 1N NaOH diluted to a volume of 1L. When correctly prepared, the pH of this fluid is 4.93 ± 0.05.
- Extraction Fluid #2 is formulated diluting 5.7 mL of glacial CH_3CH_2OOH with reagent water to a volume of 1 L. When correctly prepared, the pH of this fluid is 2.88 ± 0.05.

Step 4. Extraction procedure

The amount of extraction fluid to add to the extractor vessel was determined as follows:

$$Weight\ of\ Extraction\ Fluid = \frac{20\ x\ \%\ Solids^{5}\ x\ Weight\ of\ Waste\ Filtered}{100} \quad [Eq.\ 2.33]$$

Slowly this amount of appropriate extraction fluid was added to the extractor vessel with the waste. A Teflon tape to the threads of the bottle was used and the vessels secured in the rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Then, the material in the extractor vessel was separated into its component liquid and solid phases by filtering through a new glass fiber filter. For final filtration of the TCLP extract, the glass fiber filter was changed, if necessary, to facilitate filtration.

Finally, the pH of the extract was recorded. Immediately aliquoted and preserved the extract for farther analysis. Metals aliquots were acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses was acidified and the extract analysed as

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[5] All the wastes used in this doctoral thesis are 100 % solids.

soon as possible. All aliquots were stored under refrigeration (4 ºC) until analysis.

The concentrations of metals and radionuclides in the leachates were determined by inductively coupled plasma optical emission spectrometry using a Jobin Yvon ULTIMA 2 apparatus and by alfa spectrometry, respectively.

The following general quality assurance procedures are applied during this procedure:

- All data was documented on TCLP Extraction Log/TCLP Extraction Fluid Preparation Log data sheets.
- The instrumentation was operated in accordance with the manufacturer's instructions. Equipment was checked-out procedures and calibration activities prior to commencing this procedure.
- A minimum of one blank (using the same extraction fluid as used for the samples) was analysed for every extractions series.
- Duplicate samples were processed for each samples. Duplicate samples were used to determine precision.

2.4.2 Accelerated leaching test for cements mortars

The mobility of radionuclides and metals in the manufactured cement were determined by leaching tests performed at different pH (López et al., 2011).

The test sample dimensions were 40 × 40 × 160 mm^3. All samples were submerged in demineralised water for 24 h. They were then dried, weighed, and then again submerged for 21 days in 250 ml of buffer solutions at different pH (2, 4, 6 , 8 and 10) (Panreac). After this time, the samples were air dried and weighed to make sure their weight had not changed by more than ± 2 g compared to their starting weights. The samples were then again submerged in their respective buffers for another 21 days. At the end of this period, they were again weighed and dried.

The coefficient of absorption, A_C (%), with respect to the pH was determined as follows:

$$A_c = \frac{P_{3i} - P_{1i}}{P_{1i}} \qquad \text{[Eq. 2.34]}$$

, where P_{3i} is the weight after 42 days of immersion, and P_{1i} the initial weight of each sample after immersion in water for 24 h.

Furthermore, after 42 days of experimental period, the solutions were filtered and their radionuclide and metals concentrations determined.

Moreover, leaching coefficient, Lc (%), for the radionuclides ^{238}U and ^{210}Po at the different pHs was calculated according to Eq. 2.35:

$$L_c = \frac{A_L\, V}{A_s\, P_{1i}} 100 \qquad \text{[Eq. 2.35]}$$

, where A_L (Bq L^{-1}) is the concentration of the corresponding radionuclide in the leachate, V (L) is the total volume of the solution after 42 days (0.250 L in all cases), A_S (Bq L^{-1}) is the concentration of the corresponding radionuclide in the concrete and P_{1i} (g) the weight of the concrete sample after 42 days of immersion in the corresponding buffer.

The concentrations of a number of metals in the leachates were determined by inductively coupled plasma optical emission spectrometry using a Jobin Yvon ULTIMA 2 apparatus. The system was calibrated using appropriate standards. Leachate samples were diluted to 2 % in a nitric acid solution for farther analyses. Moreover, ^{210}Po and ^{238}U was determined by alpha spectrometry.

2.4.3 Radiological implications in building materials

It is needed to evaluate the environmental impact when NORM (Naturally occurring radioactive materials) wastes are incorporated in building materials. In this sense, it is important to remember that both wastes studied in this thesis, phosphogypsum and ilmenite mud, are considered as NORM. Moreover, the activity concentrations of the nuclides in the final product should be measured in order to ensure the negligible environmental impact.

In order to evaluate this problem, Publication No. 112, from the monographic collection “Radiation Protection” issued by the European Union (Radiation Protection, 1999), defines an external risk index (I), also called an activity concentration index, Eq. (2.36), to ensure that external gamma dose rates inside a room from building materials does not exceed 1 mSv per year.

$$I = \frac{C_{226_{Ra}}}{300\,{}^{Bq}/_{kg}} + \frac{C_{232_{Th}}}{200\,{}^{Bq}/_{kg}} + \frac{C_{40_{K}}}{3000\,{}^{Bq}/_{kg}} \qquad \text{[Eq. 2.36]}$$

, where C(^{226}Ra), C(^{232}Th) and C(^{40}K) are the respective activity concentrations for ^{226}Ra, ^{232}Th and ^{40}K in the building material considered (expressed in Bq kg^{-1}).

The activity concentration index shall not exceed the following values depending on the dose criterion and the way and the amount the material is used in a building (Table 2.8). It is therefore recommended that controls should be based on a dose in the range 0.3-1 mSv a^{-1} (Kovler et al., 2009).

Table. 2.8

External risk (I) depending on the dose criterion and the way and the amount the material is used in a building.

Dose criterion	0.3 mSv a^{-1}	1 mSv a^{-1}
Materials used in bulk amounts, e.g. concrete	$I \leq 0.5$	$I \leq 1$
Superficial and other materials with restricted use: tiles, boards, etc.	$I \leq 2$	$I \leq 6$

2.4.4 Radon potential and exhalation rate

The fraction of the radon produced by the ^{226}Ra decay contained in the solid grains that reaches the air pores of the material is called emanation coefficient (ε), and then this radon can be transported through the pores into the surface of the solid material producing an exhalation rate (E, in Bq m^{-2} s^{-1}), or radon flux. In addition, the radon potential (Ω) is defined according to López-Coto et al. 2007:

$$\Omega = \varepsilon\, C_{Ra} \qquad \text{[Eq. 2.37]}$$

, where C_{Ra} (Bq kg^{-1}) in the activity concentration of ^{226}Ra in the material.

The radon emanation coefficient of samples was calculated based on López-Coto et al. method. A first measurement is carried out from the radon growth curve for each specimen in the accumulation chamber, and the exhalation rate is obtained. Secondly, a second measurement in the chamber by using a crushed portion of the specimen (about one third) is done, and then the emanation factor of the material is obtained.

The saturation radon concentration (C_{Rn}^{sat}) in the final steady-state (Bq m^{-3}), and the effective decay constant λ_{eff} are obtained fitting by the squared minimum method the following equation (s^{-1}):

$$C_{Rn}^{a}(t) = C_{Rn}^{sat} + C_{Rn}^{0} - C_{Rn}^{sat})e^{-\lambda_{eff}t} \qquad \text{[Eq. 2.38]}$$

, where C_{Rn}^{a} (Bq m^{-3}) is the radon concentration in the air of the chamber and C_{Rn}^{0} the initial background concentration (Bq m^{-3}).

In addition, the radon exhalation rate is obtained from the equation:

$$C_{Rn}^{sat} = \frac{E_0\, S}{\lambda_{eff}\, V_c} \qquad \text{[Eq. 2.39]}$$

, where E_0 is the sample exhalation rate (Bq m^{-2} s^{-1}), S is the exhalation surface (m^2) and V_c is the effective chamber volume available for accumulating radon (m^3).

On the another hand, by measuring the ^{226}Ra concentration in the material with a mass m, the radon potential and the emanation coefficients are calculated from the equation 2.37 and the following one:

$$\Omega = \frac{\lambda_{eff} V_c \, C_{Rn}^{sat}}{\lambda_{Rn} \, m} \qquad \text{[Eq. 2.40]}$$

, where λ_{Rn} is the radon decay constant (s^{-1}).

The radon measurements were done using two different radon detectors. The first one was an Alpha GUARD model PQ2000 PRO from Genitron Instruments (AG) with an ionisation chamber working in a range from 2 – 2 10^6 Bq m^{-3}, and a temporal resolution of 10 min. This detector was factory-calibrated and is traceable to PTB and NIST.

The second one detector is the Model 1027 from Sun Nuclear Corporation (SNC). This detector is based on the radon progeny electrodeposition, working in a range of 4 – 4 10^3 Bq m^{-3}, and typical temporal resolution of 1 h. This detector was calibrated at the Huelva University Radon Chamber, being the reference detector the NIST-traceable AG, and obtaining a calibration factor very close to the initial value obtained by the manufacturer (López-Coto et al., 2007). To study the worth conditions, samples were grounded, sieved and homogenised prior to place at least 10 g of powder sample in the detector containers. The analysis were performed in triplicate obtaining differences < 5% among the measurements.

Chapter 3

Results and Discussions

Chapter 3. Results and discussion

Los artículos que forman parte del apartado “Chapter 3”, han sido retirados de la tesis debido a restricciones relativas a derechos de autor. En sustitución de los artículos ofrecemos la siguiente información: referencia bibliográfica, enlace a la revista, y resumen.

- Contreras Llanes, M., Gázquez González, M.J., García Díaz, I., Alguacil, F.J., López, F.A., Bolivar Raya, J.P. (2013). “Valorisation of waste ilmenite mud in the manufacture of sulphur polymer cement”. Journal of Environmental Management, vol. 128, págs. 625-630. https://doi.org/10.1016/j.jenvman.2013.06.015

Enlace al texto completo del artículo (solo para miembros de la UHU):
https://doi.org/10.1016/j.jenvman.2013.06.015

RESUMEN:

This paper reports the preparation of sulphur polymer cements (SPCs) incorporating waste ilmenite mud for use in concrete construction works. The ilmenite mud raw material and the mud-containing SPCs (IMC-SPCs) were characterised physico-chemically and radiologically. The optimal IMC-SPC mixture had a sulphur/mud ratio (w/w) of 1.05 (mud dose 20 wt%); this cement showed the greatest compressive strength (64 MPa) and the lowest water absorption coefficient (0.4 g cm−2 at 28 days). Since ilmenite mud is enriched in natural radionuclides, such as radium isotopes (2.0·103 Bq kg−1228Ra and 5.0·102 Bq kg−1226Ra), the IMC-SPCs were subjected to leaching experiments, which showed their environmental impact to be negligible. The activity concentration indices for the different radionuclides in the IMC-SPCs containing 10% and 20% ilmenite mud met the demands of international standards for materials used in the construction of non-residential buildings.

- Contreras Llanes, M., Martín, M. I., Gázquez González, M. J., Romero, M., & Bolívar Raya, J. P. (2014). “Valorisation of ilmenite mud waste in the manufacture of commercial ceramic”. Construction and Building Materials, vol. 72, págs. 31-40. https://doi.org/10.1016/j.conbuildmat.2014.08.091

Enlace al texto completo del artículo (solo para miembros de la UHU):
https://doi.org/10.1016/j.conbuildmat.2014.08.091

RESUMEN:

This paper reports the results of a study focused on the production of ceramic tiles from ilmenite mud (MUD), a waste generated by the industry devoted to the TiO_2 pigment production. Ceramic tiles were produced from mixtures of a commercial red stoneware mixture (RSM) with different concentrations of mud (3, 5, 7, 10, 30 and 50 wt.%). The samples were sintered to simulate a fast-firing process. The sintering behaviour of the fired samples was evaluated according to ISO methodologies by linear shrinkage, water absorption and porosity measurements. Both green powder and fired samples were characterised by means of X-ray diffraction (XRD), differential scanning calorimetry (DSC/TG), field emission scanning electron microscopy (FESEM) and bending strength measurements. Moreover, since this activity is a NORM (Naturally Occurring Radioactive Material) industry, the radionuclides activity concentrations were measured by both gamma and alpha spectrometry techniques. Finally, the TCLP leaching test (Toxicity Characteristic Leaching Procedure, USEPA) was performed to assess the risks of the use of undissolved mud tiles from an environmental perspective. The results obtained demonstrated that ilmenite mud can be successfully valorisated in the manufacture of red stoneware ceramic bodies, with even better technological properties than commercial ones. The addition of mud as additive (from 3% to 10%) had 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%).

- Contreras Llanes, M., Teixeira, S.R., Santos, G.T.A., Gázquez González, M.J., Romero, M., Bolívar Raya, J.P. (2018). "Influence of the addition of phosphogypsum on some properties of ceramic tiles". Construction and Building Materials, vol. 175, págs. 588-600. https://doi.org/10.1016/j.conbuildmat.2018.04.131

Este artículo aparece en la tesis con el título: Manufacturing of red ceramic by using phosphogypsum waste (Under Review)

Enlace al texto completo del artículo (solo para miembros de la UHU):
https://doi.org/10.1016/j.conbuildmat.2018.04.131

RESUMEN:

Phosphogypsum (PG) is a waste from phosphoric acid production, and this work evaluates the use of PG as an additive in ceramic manufacturing. Ceramic samples were produced by adding different concentrations of PG (5, 7.5, and 10 wt%) to natural clay, and sintering at 950, 1050, and 1150 °C. Technological and mechanical properties of the obtained ceramics were evaluated. Moreover, the U.S. EPA's toxicity characteristic leaching procedure, Index "I", and the effective radium activity were calculated to evaluate the environmental risks. The use of PG improves the sintering behaviour and the bending strength, while also the environmental impact is negligible.

- Contreras, M., Teixeira, S.R., Lucas, M.C., Lima, L.C.N., Cardoso, D.S.L., da Silva, G.A.C., Gregorio, G.C., Souza, A.E. de, Santos, A. dos (2016). “Recycling of construction and demolition waste for producing new construction material (Brazil case-study)”. Construction and Building Materials, vol. 123, págs. 594-600. https://doi.org/10.1016/j.conbuildmat.2016.07.044

Enlace al texto completo del artículo (solo para miembros de la UHU):
https://doi.org/10.1016/j.conbuildmat.2016.07.044

RESUMEN:
Construction and demolition waste corresponds to 50% of all urban solid waste, usually it is dumped in improper places. This work reuses this waste as substitute of natural aggregate to produce bricks. Lime and cement were used as binding agents and were pressed using a uniaxial hydraulic press. After 21 days curing were submitted to compression tests, the probes presented an average resistance greater than 4 MPa, which is higher than standards. Water absorption, apparent porosity and density were also determined. The results show that it is possible to produce low-cost bricks with excellent physical properties using CDW as aggregate and lime or cement as additive.

- Contreras Llanes, M., Pérez López, R., Gázquez González, M.J., Morales Flórez, V., Santos, A., Esquivias, L., Bolívar Raya, J.P.: "Fractionation and fluxes of metals and radionuclides during the recycling process of phosphogypsum wastes applied to mineral CO2 sequestration". Waste Management. Vol. 45, págs. 412–419, (2015). DOI: 10.1016/j.wasman.2015.06.046

Enlace al texto completo del artículo (solo para miembros de la UHU):
https://doi.org/10.1016/j.conbuildmat.2016.07.044

RESUMEN:
The industry of phosphoric acid produces a calcium-rich by-product known as phosphogypsum, which is usually stored in large stacks of millions of tons. Up to now, no commercial application has been widely implemented for its reuse because of the significant presence of potentially toxic contaminants. This work confirmed that up to 96% of the calcium of phosphogypsum could be recycled for CO_2 mineral sequestration by a simple two-step process: alkaline dissolution and aqueous carbonation, under ambient pressure and temperature. This CO_2 sequestration process based on recycling phosphogypsum wastes would help to mitigate greenhouse gasses emissions. Yet this work goes beyond the validation of the sequestration procedure; it tracks the contaminants, such as trace metals or radionuclides, during the recycling process in the phosphogypsum. Thus, most of the contaminants were transferred from raw phosphogypsum to portlandite, obtained by dissolution of the phosphogypsum in soda, and from portlandite to calcite during aqueous carbonation. These findings provide

valuable information for managing phosphogypsum wastes and designing potential technological applications of the by-products of this environmentally–friendly proposal.

Chapter 4

General Conclusions

In this chapter, the general conclusions obtained in this doctoral thesis work are summarised, being the main objective the valorisation of three inorganic wastes (ilmenite mud, phosphogypsum and construction and demolition materials). This valorisation was carried out as additive in construction materials manufacturing and, on the other hand, a study on the fluxes of metals and radionuclides during the CO_2 sequestration process using phosphogypsum as source of Ca was developed.

Firstly, considering that ilmenite mud and phosphogypsum are materials generated in NORM industries, the implementation of an action protocol was necessary, in order to achieve a suitable valorisation of these hazardous wastes. In addition, an intensive bibliographic research has been done.

A deep characterisation was completed by analysing several physical and chemical properties, mineral phases by XRD, particle size distribution, major metals measured by FRX, trace elements measured by ICP-MS/OES, and the radiological properties.

The results obtained in this work has allowed us to draw the following main conclusions:

Ilmenite Mud Waste (IM)

1. It has been demonstrated that ilmenite mud can be successfully used in the manufacture of sulphur polymer cements (SPCs), and red stoneware ceramic bodies with similar or even better technological properties than standard commercial materials.
2. Ilmenite mud added up to 5 wt.% in red ceramic had a beneficial role as agent for the sintering processes, improving the bending strength (up to 15 %) respect to the reference commercial one, and reducing both apparent porosity and water absorption (up to 50 %).
3. The ceramic tiles containing ilmenite mud clearly exceed bending strength values required in the standard.

4. The addition up to 20 wt.% of ilmenite mud in SPCs (SPC21-20) improved the mechanical properties in relation to the reference material. In addition, water absorption by capillarity in SPCs containing ilmenite mud were slightly lower than SPC reference, and much lower than the normal values reported for Portland cements.

5. The leaching tests showed that the mobility of metals and radionuclides in the SPCs and red ceramic bodies was very low, and similar to the references materials. This fact showed that the metals and radionuclides are immobilised in the ceramic and cementation matrix avoiding their future release into the environment.

6. The radon levels and external dose received by occupants in buildings constructed with these ceramic bodies not exceed the limit established by the European Union. On the other hand, although not suitable for the construction of occupied buildings, SPC containing ilmenite mud could be safely used in concrete for construction in civil engineering.

Phosphogypsum Waste (PG)

1. The present study has proved that the manufacturing of ceramic tiles by using natural clays and PG as additive is suitable.

2. The addition of phosphosgypsum improves the sintering of the tile, reduces both the water absorption and apparent porosity, and, as consequence, a higher mechanical resistance compared to the reference samples is obtained. The improvement of the technological properties is associated to the formation of mullite above 950 °C, which produces a better sinterisation of the bulk material.

3. Linear shrinkage increases with temperature and decreases with the phosphogypsum percentage, reducing the deformation of the material during the firing process.

4. The metals and radionuclides are immobilised in the ceramic matrix avoiding the biodisponibility in the leachates, showing this fact that the potential environmental impact in future is negligible. The radiological index and the radon levels are in agreement with the EU regulations.

5. It has been demonstrated that PG can be used as source of calcium for the CO_2 sequestration as calcite, where up to 96 % of the calcium contained in the phosphogypsum could be recycled under ambient pressure and temperature.

6. Most of the trace metals and radionuclides (up to 97 %) in the carbonation process are transferred from phosphogypsum into the calcite, while the liquid phase of the carbonation process is free contaminants, and therefore the final solid sodium sulphate obtained.

7. Finally, to point out that calcite obtained by the CO_2 sequestration process is a NORM material according to Spanish regulation.

Construction and Demolition Waste (CDW)

1. It is possible to produce low-cost bricks for masonry walls using construction and demolition waste (CDW) as substitute of natural aggregate, showing similar or even better technical properties that commercial bricks. The binders used were recycled lime or cement.

2. The average CDW composition 50 % ceramic, 20 % concrete and 30 % mortar is a nice proportion to produce bricks.

3. Bricks containing up to 30 wt.% of CDW and cement as binder present the best technological properties. Furthermore, all the specimens studied present technological properties in agreements with the Brazilian, European and American regulations.

4. This improving in the mechanical resistance is due to the formation of new minerals phases during the hydration process. As example, the formation of portlandite and calcite as consequence of the

reaction between the hydrated lime together with some hydrated silicates.

Chapter 5

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Annex I

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Valorisation of waste ilmenite mud in the manufacture of sulphur polymer cement

Manuel Contreras [a], Manuel Jesús Gázquez [a,*], Irene García-Díaz [b], Francisco. J. Alguacil [b], Félix. A. López [b], Juan Pedro Bolívar [a]

[a] Departamento de Física Aplicada, Universidad de Huelva, Campus del Carmen, 21071 Huelva, Spain
[b] Centro Nacional de Investigaciones Metalúrgicas (CENIM), CSIC, Avda. Gregorio del Amo 8, 28040 Madrid, Spain

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ABSTRACT

This paper reports the preparation of sulphur polymer cements (SPCs) incorporating waste ilmenite mud for use in concrete construction works. The ilmenite mud raw material and the mud-containing SPCs (IMC-SPCs) were characterised physico-chemically and radiologically. The optimal IMC-SPC mixture had a sulphur/mud ratio (w/w) of 1.05 (mud dose 20 wt%); this cement showed the greatest compressive strength (64 MPa) and the lowest water absorption coefficient (0.4 g cm^{-2} at 28 days). Since ilmenite mud is enriched in natural radionuclides, such as radium isotopes ($2.0\cdot10^3$ Bq kg^{-1} ^{228}Ra and $5.0\cdot10^2$ Bq kg^{-1} ^{226}Ra), the IMC-SPCs were subjected to leaching experiments, which showed their environmental impact to be negligible. The activity concentration indices for the different radionuclides in the IMC-SPCs containing 10% and 20% ilmenite mud met the demands of international standards for materials used in the construction of non-residential buildings.

1. Introduction

The immobilisation/stabilisation of pollutants and the valorisation of hazardous industrial wastes is an area of great environmental and economic interest (Chen et al., 2010; Cruz-Yusta et al., 2011; Puertas et al., 2008; Yan et al., 2011). This paper describes the stabilisation and valorisation of waste ilmenite mud, generated in the titanium dioxide industry, as a component of sulphur polymer cement (SPC) that could be used in concrete construction works.

TiO_2 production begins with the mixing of ilmenite and highly concentrated sulphuric acid (80–95%). The liquor generated is passed to a clarification tank where the un-attacked solid – ilmenite mud – is allowed to settle. This mud is finally separated from the liquor by decantation and filtration (Gázquez et al., 2011). It is then neutralised and usually stored in a safe area.

Sulphur polymer cements have advantages over regular Portland cement in that they harden in under 24 h, are of high compressive strength, show resistance to fatigue, are little permeable to water, show exceptional resistance to acid and salt (allowing their use in aggressive environments such as sea water, and under all weather conditions), and are recyclable (ACI Committee 548, 1993; Amo and Gamal, 2009). In addition, SPC manufacture could make use of large amounts of sulphur waste, e.g., from oil refineries and the metallurgical industry. SPCs can also be used as stabilising agents for other kinds of waste (López et al., 2009, 2011; Mohamed and Gamal, 2007; Sandrolini et al., 2006a, b), including – potentially – ilmenite mud. Unfortunately, this type of mud contains relatively large amounts of natural radionuclides (Gázquez et al., 2011); its immobilisation in SPCs used in the construction of occupied buildings might therefore put people at risk. International recommendations exist (Radiation Protection 112, 1999) that propose reference values for natural radionuclide concentrations in building materials; Eq. (1) shows how the exposure risk index (I) is calculated:

$$I = \frac{C_{226_{Ra}}}{300\text{Bq/kg}} + \frac{C_{232_{Th}}}{300\text{Bq/kg}} + \frac{C_{40_{k}}}{3000\text{Bq/kg}} \quad (1)$$

where C(^{226}Ra), C(^{232}Th) and C(^{40}K) are the respective activity concentrations for ^{226}Ra, ^{232}Th and ^{40}K in the building material considered (expressed in Bq kg^{-1}). It is recommended that building material-induced indoor gamma doses do not exceed 1 mSv per year.

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* Corresponding author. Tel.: +34 959 21 97 98; fax: +34 959 21 97 77.
E-mail address: manuel.gazquez@dfa.uhu.es (M.J. Gázquez).

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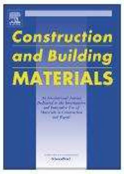

Valorisation of ilmenite mud waste in the manufacture of commercial ceramic

M. Contreras[a], M.I. Martín[b,1], M.J. Gázquez[a,*], M. Romero[b], J.P. Bolívar[a]

[a] Departamento de Fisica Aplicada, Universidad de Huelva, Campus de Excelencia Internacional del Mar (CEIMAR), 21071 Huelva, Spain
[b] Grupo de Materiales Vítreos y Cerámicos, Departamento de Construcción, Instituto de Ciencias de la Construcción Eduardo Torroja IETcc-CSIC, 28033 Madrid, Spain

HIGHLIGHTS

- Environmentally friendly ceramics were manufactured using waste ilmenite mud.
- First time that ceramics are manufactured by using mud from ilmenite.
- The new ceramics present better technological properties than commercial ceramics.
- The use of this waste produces negligible environmental impacts.

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ABSTRACT

This paper reports the results of a study focused on the production of ceramic tiles from ilmenite mud (MUD), a waste generated by the industry devoted to the TiO_2 pigment production. Ceramic tiles were produced from mixtures of a commercial red stoneware mixture (RSM) with different concentrations of mud (3, 5, 7, 10, 30 and 50 wt.%). The samples were sintered to simulate a fast-firing process. The sintering behaviour of the fired samples was evaluated according to ISO methodologies by linear shrinkage, water absorption and porosity measurements. Both green powder and fired samples were characterised by means of X-ray diffraction (XRD), differential scanning calorimetry (DSC/TG), field emission scanning electron microscopy (FESEM) and bending strength measurements. Moreover, since this activity is a NORM (Naturally Occurring Radioactive Material) industry, the radionuclides activity concentrations were measured by both gamma and alpha spectrometry techniques. Finally, the TCLP leaching test (Toxicity Characteristic Leaching Procedure, USEPA) was performed to assess the risks of the use of undissolved mud tiles from an environmental perspective. The results obtained demonstrated that ilmenite mud can be successfully valorisated in the manufacture of red stoneware ceramic bodies, with even better technological properties than commercial ones. The addition of mud as additive (from 3% to 10%) had 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%).

1. Introduction

Because of the depletion of natural resources, increasing greenhouse emissions and awareness of the need for sustainable development in terms of safe reuse of wastes, the transformation of these wastes into valuable materials (i.e. valorisation) is emerging as a strong trend. In this context and taking into account the growing awareness of the need for protection of health and environment, the recovery of wastes currently generated in most industrial processes is the subject of a thorough investigation [1–3]. The valorisation of wastes as secondary raw materials in the manufacture of construction materials could allay the problems associated with both the depletion of natural resources and the disposal of industrial wastes [4–7]. In this context the protection of health and environment is of great importance, although the economic benefits accruing from waste recycling must not be ignored [8,9].

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[*] Corresponding author at: Departamento Química, Universidad Técnica Particular de Loja, Loja, Ecuador.

E-mail address: manuel.gazquez@dfa.uhu.es (M.J. Gázquez).

[1] Present address: Departamento de Metalurgia Primaria y Reciclado de Materiales, Centro Nacional de Investigaciones Metalúrgicas, CENIM-CSIC, Grupo de Tecnologías Ecoinnovadoras aplicadas a Procesos Medioambientales, Reciclado de Materiales y Aprovechamiento Energético (TecnoEco).

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Recycling of construction and demolition waste for producing new construction material (Brazil case-study)

M. Contreras [a,*], S.R. Teixeira [b], M.C. Lucas [b], L.C.N. Lima [b], D.S.L. Cardoso [b], G.A.C. da Silva [b], G.C. Gregório [b], A.E. de Souza [b], A. dos Santos [c]

[a] *Department of Applied Physics, University of Huelva, Campus de Excelencia Internacional del Mar (CEIMAR), 21071 Huelva, Spain*
[b] *Universidade Estadual Paulista – UNESP, FCT/DFQB, Presidente Prudente – SP, Brazil*
[c] *Universidade do Oeste Paulista – UNOESTE, LABCIVIL, Presidente Prudente – SP, Brazil*

HIGHLIGHTS

- Low-cost bricks were manufactured using construction and demolition waste (CDW).
- Lime and cement used as binding agents mixed with CDW and water.
- The bricks present better technological properties than standards.
- The use of this waste reduce the raw materials demands and environmental impacts.

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ABSTRACT

Construction and demolition waste corresponds to 50% of all urban solid waste, usually it is dumped in improper places. This work reuses this waste as substitute of natural aggregate to produce bricks. Lime and cement were used as binding agents and were pressed using a uniaxial hydraulic press. After 21 days curing were submitted to compression tests, the probes presented an average resistance greater than 4 MPa, which is higher than standards. Water absorption, apparent porosity and density were also determined. The results show that it is possible to produce low-cost bricks with excellent physical properties using CDW as aggregate and lime or cement as additive.

1. Introduction

Construction demolition waste (CDW) is a worldwide problem. The estimated CDW production in Brazil is higher than 70 Mt/year (around 500 kg/year per capita), but this amount is variable and has correlation with the human development index (HDI). CDW represents the largest amount of municipal solid waste (in mass). The illegally dumped waste in urban areas, nearby creeks, roads and other unprepared places has substantial environmental and economical impacts resulting in financial problems for the community and public administration. In the last years, governments have approved new policies about responsibilities, dumping and recycling of waste in general. As a result, the situation in the major cities is changing with the implantation of recycling plants, but nowadays only a small part of the CDW is recovered.

On the other hand, recycling has another environmental and economic advantages, since it reduces the consumption of natural resources. So, there is a comprehensive array of research on the social and financial cost, production, characterization and recycling of this waste [1–4]. CDW recycling plants have been proved to be economically viable [5,6] as well as having a positive environmental impact [7,8].

However, it is essential to absorb the output from these plants by the market. In other words, there is a strong need to diversify the industrial applications of this waste. CDW materials have been evaluated and successfully implemented in recent years in several countries [9,10], and generally, it is used as raw mineral materials in paving projects [11–14], footpaths [15] and pipe-bedding [16]. Some author have focused in recycling CDW for concrete production

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[*] Corresponding author.
E-mail address: manuel.contreras@dfa.uhu.es (M. Contreras).

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Fractionation and fluxes of metals and radionuclides during the recycling process of phosphogypsum wastes applied to mineral CO_2 sequestration

M. Contreras [a], R. Pérez-López [b], M.J. Gázquez [a], V. Morales-Flórez [c,d], A. Santos [e], L. Esquivias [c,d], J.P. Bolívar [a,*]

[a] Department of Applied Physics, University of Huelva, Campus 'El Carmen', 21071 Huelva, Spain
[b] Department of Geology, University of Huelva, Campus 'El Carmen', 21071 Huelva, Spain
[c] Institute of Materials Science of Seville (CSIC-US), Av. Américo Vespucio, 49, 41092 Seville, Spain
[d] Department of Condensed Matter Physics, University of Seville, Av. Reina Mercedes, 41012 Seville, Spain
[e] Department Earth Sciences, University of Cádiz, Campus del Río San Pedro, Av. República Saharaui, 11510 Puerto Real, Spain

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ABSTRACT

The industry of phosphoric acid produces a calcium-rich by-product known as phosphogypsum, which is usually stored in large stacks of millions of tons. Up to now, no commercial application has been widely implemented for its reuse because of the significant presence of potentially toxic contaminants. This work confirmed that up to 96% of the calcium of phosphogypsum could be recycled for CO_2 mineral sequestration by a simple two-step process: alkaline dissolution and aqueous carbonation, under ambient pressure and temperature. This CO_2 sequestration process based on recycling phosphogypsum wastes would help to mitigate greenhouse gasses emissions. Yet this work goes beyond the validation of the sequestration procedure; it tracks the contaminants, such as trace metals or radionuclides, during the recycling process in the phosphogypsum. Thus, most of the contaminants were transferred from raw phosphogypsum to portlandite, obtained by dissolution of the phosphogypsum in soda, and from portlandite to calcite during aqueous carbonation. These findings provide valuable information for managing phosphogypsum wastes and designing potential technological applications of the by-products of this environmentally–friendly proposal.

1. Introduction

Industrial production of fertilisers from phosphate rock ore by the wet process produces a gypsum-rich by-product called phosphogypsum (*PG*, $CaSO_4 \cdot 2H_2O$). It is generated in the production of phosphoric acid (H_3PO_4) during the acid attack of apatite (mainly fluorapatite, $Ca_5(PO_4)_3F$) with sulphuric acid (H_2SO_4) (Rutherford et al., 1994). The chemical reaction of the industrial process can be written as follows:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \leftrightarrow 3H_3PO_4 + 5(CaSO_4 \cdot 2H_2O) + HF \quad (1)$$

Worldwide phosphogypsum production is estimated to be around 280 Mt per year (Yang et al., 2009). However, only 15% of the phosphogypsum is recycled (Kim, 2010) because of existing contaminants, such as organic substances, metals and other potentially toxic elements and natural radionuclides from the ^{238}U decay series (Mas et al., 2006; Pérez-López et al., 2007). The remaining 85% is often stored in large stacks in areas close to fertiliser plants (Tayibi et al., 2009). Spanish phosphoric acid production began in the city of Huelva (SW Spain) in 1968, and since then the *PG* waste has been slurried with water, pumped out of the fertiliser plant by a pipe system and then dumped on a nearby disposal site in the salt-marshes of the Tinto River (1200 ha containing about 120 Mt) without any commercial application (Bolívar et al., 2009a, 1995). The proximity of the waste to Huelva, less than 1 km away, is an important concern because of its alleged implications for the health of the local population of roughly 150,000 inhabitants. After looking unsuccessfully for sustainable solutions to the stockpiling of wastes, the fertiliser plant ceased dumping phosphogypsum in December 2010. However, the waste piles still remain in the area without an apparent solution. The urgent need to perform the current study is related to the great social interest in an action plan proposing solutions to the problem of the phosphogypsum stacks.

The main restrictions on reusing *PG* are related to its relatively high content of radionuclides and metallic elements, and evidence

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[*] Corresponding author.
E-mail address: bolivar@uhu.es (J.P. Bolívar).

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Annex II

INFORME SOBRE APORTACIONES CIENTÍFICAS DERIVADAS DE LA TESIS DOCTORAL Y FACTOR DE IMPACTO DE LAS REVISTAS CIENTÍFICAS (JOURNAL CITATION REPORTS)

1-. Publicaciones en revistas científicas (Capítulos de la Tesis)

Manuel Contreras, Manuel Jesús Gázquez, Irene García-Díaz, Francisco. J. Alguacil, Félix. A. López, Juan Pedro Bolívar. Valorisation of waste ilmenite mud in the manufacture of sulphur polymer cement. Journal of Environmental Management (J ENVIRO MANAGE). 128 (2013) 625-630. **(CAPÍTULO 3.1 de la Tesis)**

IF-3.188. Posición de la revista en relación a su categoría específica: 39/216; primer cuartil (Q1), primer tercil (T1)

M. Contreras, M.I. Martín, M.J. Gázquez, M. Romero, Juan Pedro Bolívar. Valorisation of ilmenite mud waste in the manufacture of commercial ceramic. Construction and Building Materials (COM BUIL MAT). 72 (2014) 31–40. **(CAPÍTULO 3.2 de la Tesis)**

IF-2.421. Posición de la revista en relación a su categoría específica: 9/61; primer cuartil (Q1), primer tercil (T1)

M. Contreras, S.R. Teixeira, R.S. Magalhães, G.T.A. Santos, M.J. Gázquez, M. Romero, Juan Pedro Bolívar. Construction and Building Materials (COM BUIL MAT). Under Review. **(CAPÍTULO 3.3 de la Tesis)**

IF-2.421. Posición de la revista en relación a su categoría específica: 9/61; primer cuartil (Q1), primer tercil (T1)

M. Contreras, S.R. Teixeira, M.C. Lucas, L.C.N. Lima, D.S.L. Cardoso, G.A.C. da Silva, G.C. Gregório, A.E. de Souza, A. dos Santos. Recycling of construction and demolition waste for producing new construction material (Brazil case-study). Construction and Building Materials (COM BUIL MAT). 123 (2016) 594–600. **(CAPÍTULO 3.4 de la Tesis)**

IF-2.421. Posición de la revista en relación a su categoría específica: 9/61; primer cuartil (Q1), primer tercil (T1)

M. Contreras, R. Pérez-López, M.J. Gázquez, V. Morales-Flórez, A. Santos, L. Esquivias, J.P. Bolívar. Fractionation and fluxes of metals and radionuclides during the recycling process of phosphogypsum wastes applied to mineral CO_2 sequestration. Waste Management (WASTE MANAGE). 45 (2015) 412–419. **(CAPÍTULO 3.5 de la Tesis)**

IF-3.829. Posición de la revista en relación a su categoría específica: 34/225; primer cuartil (Q1), primer tercil (T1)

2-. Publicaciones en revistas científicas (Otras publicaciones derivadas)

M. Contreras, M.J. Gázquez, J.P. Bolívar. Valorisation of ilmenite mud in commercial cements manufacturing. Construction and Building Materials (COM BUIL MAT). Under review.

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IF-1.056. Posición de la revista en relación a su categoría específica: 161/223; tercer cuartil (Q3), tercer tercil (T3)

M. Contreras, M.I. Martín, M.J. Gázquez, M. Romero, J.P. Bolívar. Valorisation of ilmenite mud waste in the manufacture of commercial ceramic. Key Engineering Materials (KEY ENG MAT). 663 (2014) 75-85.

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3-. Comunicaciones presentadas en congresos internacionales

J.P. Bolívar, M.J. Gázquez, I. García-Díaz, **M. Contreras**, F.A. López, F.J. Alguacil. Valorization of waste coming from titanium dioxide and phosphate fertilizer NORM industries in sulfur polymer concrete. EU-NORM 1st International Symposium 2012, Tallín (Estonia). Comunicación oral.

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F. Mosqueda, M.J. Gázquez, **M. Contreras**, S. Pérez-Moreno, R. Garcia-Tenorio, J.P. Bolivar, J. Mantero, E. Rodríguez. Radioactive characterization of leachates and efflorescences in a phosphogypsum disposal site as a preliminary step before its restoration. International Conference Environmental Radioactivity ENVIRA 2015, Thessaloniki (Grecia). Póster.

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M. Contreras. NORM4BUILDING TU1301 COST Action, Training school on NORM in Building Materials 2015, Hasselt (Bélgica). Mesa redonda.

J.P. Bolivar, **M. Contreras**, M.J. Gázquez. Valorización de residuos industriales inorgánicos; el caso de la industria de producción de TiO_2. I Encuentro Internacional Virtual Académico de Ciencias Ambientales 20, Bogotá (Colombia).

4-. Comunicaciones presentadas en congresos nacionales

S.M. Pérez-Moreno, **M. Contreras**, M.J. Gázquez, J.P. Bolívar. Balances de radionucleidos en la valorización de residuos ricos en yeso mediante un proceso de captura de CO_2. III Congreso Conjunto SEFM-SEPRl 2013, Cáceres (España). Poster.

M. Contreras. VIII Jornadas sobre calidad en el control de la radiactividad 2014, Huelva (España). Organizador.

5-. Capítulos de libros

Contraras, M.; Gázquez, M.J.; Bolívar, J.P. Chapter 2: Waste Incorporation in Traditional Materials. Processing Ceramics from Waste: A New Raw Material Source for a Global Change. Trans Tech Publications Inc. (2016). ISBN: 78-3-03835-590-8.

6-. Estancias en centros extranjeros

Universidade Estadual Paulista “Julio de Mosquita Filho”. Presidente Prudente, Sao Paulo (Brasil). Duración: 3 meses. Fecha inicio: 15 de marzo fecha fin: 15 de junio. Programa para el fortalecimiento de las capacidades de I+D+i de la universidad de Huelva.

7-. Formación complementaria

IX Jornadas de la Industria Cementera Andaluza (JICA). La problemática de la Gestión de los Residuos. Niebla, Huelva (España). 5 horas (0.5 créditos ECTS). 2016

Café con la Industria. Mesa I+D+i. Universidad de Huelva (España). 5 horas (0.5 créditos ECTS). 2016

Introducción a los reglamentos Europeos sobre sustancias y mezclas químicas: REACH y CLP. Universidad de Huelva (España). 10 horas (1 créditos ECTS). 2016

Jornadas técnicas suelos contaminados. Universidad de Huelva (España). 25 horas (2.5 créditos ECTS). 2015

Workshop de extensao universitaria, inovaçao tecnologica e desenvolvimiento regional. Presidente Prudente (Brasil). 16 horas (1.6 créditos ECTS). 2015

Protección radiológicas en las industrias NORM. Universidad de Sevilla. 30 horas (3 créditos ECTS). 2014

Curso de formación residuos y reciclajes: gestión y educación ambiental. Prográma de educación ambiental sobre residuos y reciclaje. Universidad de Huelva. 15 horas (1.5 créditos ECTS). 2014

Tratamientos de datos experimentales. Universidad de Huelva-UNIA. 40 horas (4 créditos ECTS). Curso 2013-14

Seminario técnico: la aplicación de la directiva marco de aguas ante el horizonte 2015. Universidad de Huelva- proyecto “campus EAgUa". 10 horas (1 créditos ECTS). 2013

Training network courses 2013: técnicas avanzadas para la medida de radionucleidos en agroalimentación. Universidad de Huelva- CEIA3. 25 horas (2.5 créditos ECTS). 2013

Los residuos en nuestra sociedad: gestión y educación ambiental. Prográma de educación ambiental sobre residuos y reciclaje. Universidad de Huelva. 12 horas (1.2 créditos ECTS). 2013

UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
Câmpus de Presidente Prudente

Presidente Prudente, 12 de junho 2015.

DECLARAÇÃO

Declaro que o Doutorando **Manuel Contreras Llanes**, bolsista de Pós-Graduação do Departamento de Física Aplicada, na Universidade de Huelva, Espanha, fez um estágio de três meses (15 de março a 15 de junho de 2015) em nosso laboratório (LaMaC), na Faculdade de Ciências e Tecnologia – FCT da Universidade Estadual Paulista – UNESP, campus de Presidente Prudente. Durante este período o Sr. Llanes desenvolveu as seguintes atividades:

- Calibração e Operação do equipamento de Análise Térmica (DSC/TG/DTA), marca TA Instruments, modelo SDT Q600;
- Operação e utilização do software para análise e identificação de fases cristalinas, no equipamento de Difração de Raios –X, marca Shimadzu modelo XRD-6000;
- Preparação e sinterização de corpos de provas cerâmicos CPs para ensaios físicos e determinação da retração linear de queima;
- Caracterização dos CPs utilizando máquina de ensaio de resistência mecânica à flexão e método de Arquimedes para determinação de: Porosidade Aparente, Massa Específica Aparente e Absorção de Água;
- Participou do Workshop de Extensão Universitária, Inovação Tecnológica e Desenvolvimento Regional;

- Participou, com apresentação de um trabalho, do 2° Fórum Nacional de Meio Ambiente: Recursos Naturais e Sociedade de Consumo;
- Apresentou uma palestra para alunos e professores da UNESP/FCT, sobre os trabalhos desenvolvidos por ele e pelo Grupo de Pesquisas em Física, Radiação e Meio Ambiente, da Universidade de Huelva, Espanha;
- Iniciou uma revisão e estruturação de um artigo científico sobre utilização de resíduo de construção e demolição para produção de tijolos modulares.

Teixeira

Professor Dr. Silvio Rainho Teixeira

Laboratório de Materiais Cerâmicos – LaMaC

Departamento de Física, Química e Biologia – DFQB

Silvio Rainho Teixeira

R.G.: 6.661.430 – SSP/SP

CPF: 097.317.091-34

Rua Hortêncio Ferreira do Nascimento 77

Damha – I, 19053-714 - Presidente Prudente - SP

Fone: (18) 3229-5741 e (18) 99775-8817