

# **Scrubbing Hazardous Wastes of the Spanish Phosphate Industry and Used Tires Ash *via* Coal Fly Ash and Incorporation of the Product in Concrete for Civil Engineering Purposes**

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## **Abstract**

Coal fly ash (FA) is an abundant commodity in countries using steam coal for power production. This results in the production of large amount of FA, from which less than 50% of it is being used. As this FA is considered as Class F FA (<20% CaO) it may act as an excellent scrubber and fixation reagent for acidic wastes containing many toxic trace elements.

This paper studies the potential use of FA, categorized as Class F, as a neutralization and fixation reagent for both the hazardous sludge waste of the phosphate industry and the used tires ash formed during the fire in Seseña (near Toledo, May 13<sup>th</sup>, 2016) of 5M tires. Several analytical techniques (ICP, SEM, XRD, leaching experiments – EN12457-2) were used to this end. These results allowed identifying the best ratios between FA/waste in order to reach full neutralization and fixation. As investigated in previous studies, addition of Ca-species source prevents excessive leaching of As, Mo, and Se, and allows achieving full neutralization and fixation. The final aggregate product compound was used as a partial substitute in concrete that can be used in civil engineering projects, as an environmental safe product.

## 1. Introduction

Coal fly ash (FA) is produced *via* firing of coal in pulverized coal combustion (PCC) facilities worldwide. The pulverized coal particle (average size 30 $\mu$ m), which contains ~10% mineral matter, is injected into the boiler and undergoes 2 processes during the ~15s residence time. A pyrolysis step, at ~800<sup>0</sup>C, where the light hydrocarbon gases and molecular hydrogen are released and ignited <sup>1</sup>. During this stage some inorganic material melts, and solidifies down in the bottom of the boilers, to yield bottom ash (BA). In the second stage, the coal particle which is transformed into char and heats up to ~1700<sup>0</sup>C, is burnt and small solid particles (1-17 $\mu$ m) - the FA are formed <sup>2</sup>. The FA accounts for ~90% of the total ash formed during the coal combustion process <sup>3</sup>.

Spain utilizes both imported (50%) and local (anthracite and bituminous) coals, which is considered as one of the primary fossil fuel for electricity production (12.6% of fossil fuel used), with a total energy production of ~280 billion kWh (in 2012) <sup>4,5</sup>. The use of coals supply is up to ~9% (~12Mt annually) of the total energy demand <sup>5</sup>. Moreover, high ash content in local coals (~20%) requires to combust coals mix (mostly with Colombian and South African coals) to increase the calorific value. Coal combustion of these mixes generates large amounts of FA - ~1.5Mt annually.<sup>6</sup>

The possibility of using FA as an effective neutralization and fixation reagent for acidic wastes has been explored and suggested as a more significant economic value added as a utilization method <sup>2, 7-9</sup>. The high content of lime and large specific surface area (compared to other non-porous materials) are what makes the FA a potential chemical scrubber <sup>10-13</sup>. Moreover, the scrubbing end products can serve as an aggregate or clinker substitutes in the construction industries <sup>7, 10, 14-19</sup>. The aggregate products formed (AP) <sup>20-22</sup> were sand-like aggregates with a low leaching rate for the pollution elements (according to TCLP1311 and EN12457-2 analysis). Mechanical strength and ion resistivity test on concrete bricks containing the APs as partial substitute indicated on improve properties of the final product.

Tires industry is considered as one of the largest industries in the world with a turnover of >170M €a year <sup>23</sup>. ~400,000 t/annually of used tires are recycled in the UK and over 2.5M t/annually in the US <sup>24</sup>. Moreover, as tires are considered toxic and add to the global warming and environmental pollution, several tires recycling

sites are built in order to reduce the environmental impact of tires. In nature, it takes the tire more than 500 years to decompose; hence, in 2003 environmental law requirements required that all wheels, which are out of use, must be recycled under strict environmental controls, to prevent any contamination.

The largest dump center for used tires in Europe is located in Seseña (near Toledo), center Spain. The tires are being stored there prior to being recycled. Unfortunately, on May 13<sup>th</sup>, 2016, a fire started in this tire dump burning more than 5M tires (>100,000 tons), causing toxic clouds of black smoke into the sky, and formation of high ash amount, resulted in the evacuation of 9,000 people from their homes.

Phosphate industry is considered also as one of the largest industries. The procedure of dissolution of the phosphate rock to form phosphoric acid and fertilizers is by using either sulfuric acid ( $H_2SO_4$ ) or hydrochloric acid (HCl). However, the following by-products are also formed:

(1) *Via*  $H_2SO_4$

- $CaSO_4 \cdot 2H_2O$ , HF

(2) *Via* HCl

- $CaCl_2$ , HF,  $CaH_4(PO_4)_2$

Overall, on a global level, the phosphoric acid market is expected to grow annually by 2% per year. As indicated in the dissolution formula of phosphate rock *via*  $H_2SO_4$  for every 3t of phosphoric acid ( $H_3PO_4$ ), formation of 5t phosphogypsum (PG) occurs. The formation of PG, and associated recirculated solution (HU) as by-products is considered problematic as it contains many toxic trace elements (e.g. U, Hg, As).

In South-west Spain (Huelva), large phosphate industry facilities were established during the 1960s. As no regulations upon treatment of the PG or HU were used, it was only stored in large deposits (Figure 1), adding 2-3Mt annually (120Mt of PG in total). These deposits cause several environmental problems, such as leaching, radioactive elements, and potential transport of airborne pollutants from the ponds to the surrounding area (only 500m from the city of Huelva).

As FA was found to be a good scrubber for acidic and also toxic waste, the possibility of using it as a potential fixation reagent was investigated in this study. The two wastes chosen were the acidic green solution arising from the recirculated process solution of the phosphate, and the toxic waste of the ash formed during the fire of 5M tires in Seseña, in center Spain.

## 2. Materials & Methods

### 2.1 Experimental samples

The LBFA, HU recirculated solution waste, Bivalve shells (CA), Seseña tire ash (SE) were selected for the study.

**The fly ash selected** was produced from the combustion of two pulverized bituminous Colombian coal in the Los Barrios coal combustion facility. The ratios of the coals in the combustion procedure were 45% of B-446 MV XIN Jin Hai and 55% of B-447 MV Pleiades Dream. The coals have ash content 5.8% and 11.6%, and moisture of 13.7% and 10.1% respectively. Thus, the ash is enriched with alkali and alkali earth elements, resulting as a Class F FA, with pozzolanic behavior. Also, SEM analysis has shown that the FA morphology is mostly of a small <sup>12, 13, 25, 26</sup> glassy particles (some as cenospheres and pleuospheres), and also larger unburned carbon particles. XRD bulk analysis of the FA samples shows that the primary minerals presented are the mullite ( $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ) and quartz ( $\text{SiO}_2$ ). Moreover, traces of hematite ( $\text{Fe}_2\text{O}_3$ ) and gypsum ( $\text{CaSO}_4, 2\text{H}_2\text{O}$ ) were detected. This is in line with the average chemical composition of the FA (Table 2), which indicates a high content of aluminosilicate (>73%), Fe (8.9%), and CaO (3.5%).

**The HU recirculate solution** was green solution stored in the evaporation ponds (Eps) and arising from the recirculated process solutions of the phosphate production plants.

**The CA shells** were collected from Mazagon (near Huelva) shore as a calcite source for the fixation process. In the area, there are numerous factories produced canned sea-food that produce this material as a byproduct.

**Seseña ash** (denoted as SE) was collected from the burnt used tires field in Seseña (near Toledo, Spain).

Composition patterns of these wastes are shown in Table 2.

### 2.2 Characterization methods

The elemental composition was determined, using a two-step digestion method (developed by Querol et al. <sup>27</sup>) for the analysis of the major and trace elements in the material by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ThermoFisher Scientific model ICAP6500 Radial, and Inductively

Coupled Plasma Mass Spectrometry (ICP-MS), Thermo model X-SeriesII. An international reference material NBS1633b was also digested to determine the accuracy of the methods. Mercury concentration in the solid samples was analyzed using LECO AMA 254 gold-amalgam atomic-absorption spectrometer. The mineralogy of samples was determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer (monochromatic Cu K $\alpha$ <sub>1,2</sub> radiation;  $\lambda=1,5405$  at 40kV; and 40mA). The primary parallel X-ray beam was generated by a Göbbel mirror and the scattered beam was analyzed by a Sol-X detector (scanning parameters: from 4 at 60° of 2 $\theta$ , a step size of 0.05°, 3s time per step). The particle composition and morphology of samples were investigated by a MK2 Quanta 200 SEM with energy dispersive X-ray analyzer (SEM-EDX). Grain size distribution of <63 $\mu$ m fraction was determined by a laser light-scattering-based particle sizer, MALVERN Hydro 2000MU, working range 0.1-1,000  $\mu$ m. The European Standard leaching test EN-12457 (Council decision 2003/33/EC) was applied to FA, HU, SE, CA, and AP to determine the leaching potential of major and trace elements using an overhead shaker, Heidolph model REAX 2. The pH and ionic conductivity were determined by conventional methods. The leachates were analyzed by means of ICP-AES, ICP-MS and High Performance Liquid Chromatography (HPLC).

### **2.3 Fly ash/waste fixation tests**

Then APs were prepared (LBFA/waste mix or LBFA/waste/CA) with different ratios using a temperature-controlled batch reactor with mechanical stirrer (Hslangtai Machinery Industry Co. LTD model).

Homogenization was obtained by mixing the AP for 20 minutes at 250rpm, while adding 25% of Ultra Pure Deionized Water (UPDI – 18M $\Omega$ m/cm) to the mixture. The resulting APs were dried at 45°C overnight (in oven). In order to evaluate the efficiency of metal immobilization the European Decision protocol of the above was applied to the APs. This protocol dictates an agitation of 24h $\pm$ 30min with a 1/10 Solid/Liquid mixing ratio in an overhead shaker at rotating frequency of 5-10rpm.

Similar to the characterization of the raw materials, grain size, mineralogy, bulk chemistry, and leaching properties of all AP samples were evaluated in order to study the environmental features of the products.

Moreover, APs formed from the LBFA/HU/CA were used as sand substitute in concrete in two content ratios (48 and 80 kg/m<sup>3</sup> concrete). Compressive stress and chloride ion penetration tests (according to ASTM 1202-12) were used for testing the properties of the APs-concretes.

## 2.4 Concrete preparation

Concrete mixtures were prepared and tested to evaluate LBFA, and a LBFA/HU/CA mixture effect on the concrete properties. The mixture design is described in Table 1.

To test the effect of LBFA and LBFA/HU/CA partial amount of the sand was replaced with 80kg/m<sup>3</sup> of FA and partial replacement of sand with a combination of 7kg/m<sup>3</sup> HU + 28kg/m<sup>3</sup> LBFA + 85kg/m<sup>3</sup> CA.

The concrete blend was mixed while adding the same amount of water (w/c=0.65), and the slump of the concrete mixtures was measured according to IS 26/2.1, after mixing all the concrete components for 10 min.

The properties of the harden concrete were tested; compressive strengths after 1 day and 28 days from casting. The compressive strength was measured according to IS 26/4.1 by a press (controls). The chloride penetration was tested according to ASTM C1202<sup>28</sup>.

Once the hardened concretes were formed, final compressive strengths (after 28 days from casting) were carried out following the IS 26/4.1 by a press (controls). Furthermore, chloride penetration tests, according to ASTM C1202, were performed on each concrete sample<sup>28</sup>, and their environmental behavior (e.g. leaching) have been tested according to the European Directive<sup>20</sup>, the USEPA TCLP 1311<sup>22</sup>, and the CALWET<sup>21</sup> methods.

## 3. Results & Discussion

### 3.1 Chemical Characterization

Table 2 indicates the bulk elemental contents of the starting materials (LBFA, HU, SE, CA). The raw-LBFA is characterized by high Si, Al, Fe, Na, Ca, and S being their oxide weight fractions of 53.4, 20.5, 8.92, 4.48, 3.51, and 0.3wt.% respectively, with LOI yield of 2%. Concentrations of several trace elements such as Ba, Cr, Mn, Mo, Se, and V are found in higher concentration compared to both previous studies and also the EU average of fly ash<sup>10-12, 26, 29-31</sup>.

Major and trace element concentration determined by ICP-AES, and ICP-MS of the phosphogypsum solution sludge (HU) were definitely dominated by P (4.45wt.% as  $P_2O_5$ ), S (0.5wt.% as  $SO_3$ ), Ca (0.3wt.% as CaO) and water (92wt.%). Uranium (56.4 $\mu$ g/g), V (57 $\mu$ g/g), Cr (52.5 $\mu$ g/g), Zn (121 $\mu$ g/g), As (47 $\mu$ g/g), and Sr (48.4 $\mu$ g/g) are also present in significant concentration.

The tire ash waste (SE) particles used in the research were filtered in a mechanical filter (<500 $\mu$ m) to efficiently remove stone, Fe-fibers, and other pollutions. The Bulk sample received indicated that high enrichment of elements such as Fe (18.7wt.%), Ca (9.12wt.%), S(4.78wt.%), Zn(3.18%), and Al (1.24%). Moreover, trace elements, such as Mn (1030 $\mu$ g/g) and Cu (478 $\mu$ g/g) are found in high concentration. As expected CA was characterized by high Ca contents and a high LOI yield (20%). The impact of the Rio Tinto (Reddish in Spanish) River metal supply to the ocean water of this area resulted probably in contamination of the shells; thus, they were enriched with Mn (~139 $\mu$ g/g), Zn (~83 $\mu$ g/g), Sr (>750 $\mu$ g/g), Pb (10 $\mu$ g/g), and As (~12 $\mu$ g/g).

### 3.2 Physical & Mineral Characterization of starting materials

XRD of the starting materials is shown in Figure 2. The diffraction pattern of raw-LBFA indicates that the main minerals are similar to most Class F FA as mullite ( $3Al_2O_3-2SiO_2$ ), quartz ( $SiO_2$ ), hematite ( $Fe_2O_3$ ) and gypsum ( $CaSO_4-2H_2O$ ) were detected by XRD (Figure 2A).

XRD analysis evidenced that the main minerals in CA (Figure 2B) are calcite, aragonite (another  $CaCO_3$  polymorph), quartz, with traces of Ca-rich albite ( $(Na, Ca)Al(Si, Al)_3O_8$ ), microcline, and gypsum.

XRD pattern from SE bulk pattern (Figure 2C) showed a relatively high background between 20°-30° of 2 $\theta$ , which indicated either, a relative high amorphous content in the sample, or microcrystalline species. The Bulk content of the SE sample is characterized in major proportion by calcium sulphate mineral phases such as anhydrite ( $CaSO_4$ ), gypsum and basanite ( $CaSO_4-0.5H_2O$ ). Also, analysis evidenced iron oxides (as hematite,  $Fe_2O_3$  and magnetite,  $Fe_3O_4$ , 7.5% and 5% respectively), calcite ( $CaCO_3$ ) and quartz in high amounts. Trace amounts of illite ( $(K, H_3O)Al_2Si_3AlO_{10}(OH)_2$ ), microcline ( $KAlSi_3O_8$ ) and graphite (C) (5%, 5%, and 4%, respectively), and relatively high proportions of Zn mineral as zincite (ZnO), willemite ( $Zn_2SiO_4$ ), and sphalerite (ZnS). Moreover, additional test was carried out using a known concentration of  $CaF_2$  as an internal

pattern in Seseña bulk sample, the content of amorphous matrix in this sample was determined (54.3%, Table 4).

SEM-EDX evaluation of the starting materials is shown in Figure 3. High content of free lime (CaO) was evidenced in most LBFA particles. Also, Ti, and Fe oxides and considerable amounts of K, S, Na and Mg were detected as well.

The grain morphology of SE and CA was examined also by SEM-EDX. The micro-distribution of the components in both the SE and CA were in line with the chemical composition described in Table 2. It was observed that SE particle surfaces are covered with high content of Ca, Zn, S, Na, Fe and Al. However, it was observed that the grains are divided into two types:

(1) Seseña tire ash

- a. Ca, Si, Al-rich particles containing high amount of S, and K with traces of Fe, Zn, Mg, and Na.
- b. Zn – rich particles containing traces of Na, Si, S, Ca, Fe, Mg

(2) Bivalve shell

- a. Ca- rich particles containing traces of Na, Mg, P, S, and K
- b. Si- rich particles with traces of Al, Na, P, S, Cl, Ca and P.

### 3.3 Environmental patterns of the starting materials

In order to assess the leachability of the starting materials the European Directive leaching test (EN12457-2) was applied. Previous studies<sup>10, 26, 30-32</sup> indicated that FA originating in Colombia tends to have very high leaching yield for Mo, Se (1.5-2.3, and >45 times higher than the non-hazardous limit) according to the European Council Decision (2003/33/EC) for Land-Filling. These results are in line with the LBFA, which is produced by combustion of Colombian coals. Leaching tests carried out on SE and CA samples conclude no environmental leachable risk (Table 3) as no trace elements exceeded the non-hazardous limit of the European Directive. However, leaching tests under different pH conditions (acid rain) can result in massive yielding of S from SE sample (4 times higher). Moreover, SE ash contains fine particles, which are considered as airborne, resulting in another health issue.



### 3.4 Fixation capability of the LBFA/waste mixture

LBFA/HU ratios 1/1, 2/1, 4/1, and 6/1, and LBFA/SE ratios 1/1, 2/1 and 1/2, 4/1 and 1/4, and 6/1 and 1/6 were tested in order to neutralize and fixate the toxic trace elements of the waste and FA. Evaluation of the fixation quality was studied by applying the European Directive leaching test (EN12457-2). Tables 5-6 indicate that most of the hazardous trace elements in HU or SE wastes, according to 2003/33/EC Council Decision, were fixed. Neutralization of HU waste was achieved only at ratios of 2/1 to 6/1 kg/kg. However, several toxic trace elements in both APs (LBFA/HU and LBFA/SE) still exceed the non-hazardous limit, and even the hazardous one. The Trace elements, which exceeded the limit of the European Directive, were:

1. HU waste
  - a. Selenium and As
2. SE waste
  - a. Molybdenum, Se, and  $\text{SO}_4^{2-}$

In the case of the HU AP higher dose of LBFA was found to decrease the levels of Se and As. However, increase of LBFA dose resulted in an increased of the Mo in the leachate exceeding the non-hazardous limit according to the European Directive.

LBFA was found to decrease the levels of  $\text{SO}_4^{2-}$  in the SE APs, however, it resulted in an increase of both Mo and Se in the leachate.

Previous studies reported that addition of calcite form an AP, which is covered with fine carbonate particles that were adsorb at the AP surface, reducing the leaching potential of S, As, Ni, Se, B, and P. Moreover, addition APs covered with these fine carbonate particles resulted in a better and also environmentally safer concrete product. Thus, the use of CA as calcite source was tested.

As shown in Table 7 indeed the addition of calcite results in reducing of leachable yielding of the hazardous elements, producing a neutralized and fixed product. The optimal ratio found between the LBFA/HU/CA was 4/1/12 kg/kg/kg, and between the LBFA/SE/CA was 1/4/12 kg/kg/kg

Additionally, leaching test using the concrete products prepared with LBFA/HU/CA end product determine full neutralization, and fixation. Moreover, most of the hazardous trace elements were below the inert levels, hence no additional environmental problems are expected rise by adding the AP end product to the concrete.

### 3.5 Concrete properties

Concrete mixtures were produced without fly ash and with partial replacement of the sand with LBFA or LBFA/HU/CA end product according to the methodology described above. The performances of the concretes were tested by several tests: Compressive strengths, specific weight, and resistance of  $\text{Cl}^-$ .

Compressive strengths result after 1 day and 28 days (from casting) determined that after 28 days from casting, 15% higher strength was obtained in concrete sample containing the AP end product as partial replacement of sand. The higher strength was obtained because of a reaction between the FA particles-calcium hydroxide to C-S-H<sup>33-35</sup>. The better strength achieved with the concrete containing the AP end product compared with LBFA only can be explained by the increased specific weight of the concrete, as can be seen in Figure 4. The specific weight of the concrete having only LBFA was increased compared to the mixture without FA, and the specific weight was even greater by partial replacement of the sand with the combination of LBFA/HU/CA. Moreover, ion penetration test carried out on all samples, according to ASTM C1202, determined a significant  $\text{Cl}^-$  penetration in both the LBFA and AP (as partial substitutes of sand) concrete mixes.

## 4. Conclusions

A number of conclusions may be drawn from the finding of this study:

- Phosphogypsum recirculated solution waste (HU) and tire ash are considered hazardous as it can result in leaching of toxic trace elements to the aquifer and surroundings.
- LBFA can serve as an efficient scrubber for toxic byproducts of the phosphate and tire ash.
- Addition of Ca-rich source material can reduce the leachability of Mo, and Se by the adsorption of the fine carbonate at the AP surface, reducing the leaching potential and forming an environmental friendly material.
- Concrete tests (Strength, Ion penetration, slump, and specific weight) suggest that improved properties can be obtained by partial replacement of the sand with the mixed AP formed.
- Leaching yield potential of elements of environmental concern (i.e. As, Se, Mo, Sb) in the produced concrete conclude no environmental risk as no trace elements exceeded the inert limit according to 2003/33/EC decision.

- A Method to increase the ecological, economic and technological benefits is suggested by using the FA as a fixation reagent for hazardous waste and their incorporation in concrete.

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**Tables**Table 1. Mix design of the concrete (m<sup>3</sup>)

<b>Material</b>	<b>kg m<sup>-3</sup></b>
<b>Cement CEM II AM 42.5 N</b>	270
<b>Coarse aggregate</b>	850
<b>Fine aggregate</b>	600
<b>Sand</b>	450
<b>Water</b>	180
<b>Chemical admixture</b>	2.7

**Table 2.** Chemical composition of LBFA, HU sludge, SE tire ash, and CA (Ca-rich source) starting products

<i>Compound –wt. %</i>	<i>LBFA</i>	<i>HU</i>	<i>SE</i>	<i>CA</i>	<i>EU average of fly ash</i>
<i>SiO<sub>2</sub></i>	53.4	0.11	30.1	30.1	N.A
<i>Al<sub>2</sub>O<sub>3</sub></i>	20.5	0.03	2.3	0.42	24.6
<i>TiO<sub>2</sub></i>	0.79	<0.01	0.13	0.02	5.9
<i>Fe<sub>2</sub>O<sub>3</sub></i>	8.92	0.03	26.7	0.70	7.9
<i>CaO</i>	3.51	0.3	12.8	47.4	2.3
<i>MgO</i>	1.91	0.27	1.09	0.26	1.82
<i>K<sub>2</sub>O</i>	1.91	0.06	0.58	0.18	0.54
<i>Na<sub>2</sub>O</i>	4.48	1.0	0.50	0.36	0.69
<i>P<sub>2</sub>O<sub>5</sub></i>	0.17	4.45	0.14	0.02	1.00
<i>SO<sub>3</sub></i>	0.72	0.5	12.0	0.24	1.17
<i>ZnO</i>	0.01	0.01	3.18	0.01	0.02
<i>Water</i>	N.A.	92	0.10	0.10	0.2
<i>LOI</i>	2.03	N.A.	20.2	20.2	5
<i>Element- µg/g</i>					
<i>Li</i>	76	0.73	13	4.1	185
<i>Be</i>	5.6	0.41	<0.001	<0.01	8
<i>B</i>	419	7.0	<0.001	23	259
<i>Sc</i>	34	0.78	12	<0.1	15
<i>V</i>	4880	57	44	7.9	228
<i>Cr</i>	259	53	1030	3.1	148
<i>Hg</i>	0.07	N.A.	303	0.006	NA
<i>Mn</i>	331	27	38	139	35
<i>Co</i>	23	1.13	478	1.91	96
<i>Ni</i>	92	12	4.0	3.2	86
<i>Cu</i>	81	19	13	48	154
<i>Ga</i>	32	0.17	<0.001	<0.01	NA
<i>As</i>	63	47	9.5	12	7
<i>Se</i>	41	0.16	1.67	<0.01	55
<i>Rb</i>	90	0.54	27	4.7	7
<i>Sr</i>	1180	48	714	754	108
<i>Y</i>	47	3.1	4.2	1.68	757
<i>Zr</i>	222	0.75	21	5.3	NA
<i>Nb</i>	18	0.03	2.7	<0.01	NA
<i>Mo</i>	45	0.41	4.1	9.2	NA
<i>Cd</i>	3.2	19	2.7	<0.01	11
<i>Sn</i>	3.1	0.01	5.9	3.9	2
<i>Sb</i>	15	0.63	9.5	0.5	8
<i>Cs</i>	7.6	0.03	1.61	<0.01	4
<i>Ba</i>	3767	0.10	94	29	NA
<i>La</i>	46	1.11	19	2.2	1350
<i>Ce</i>	84	0.66	18	4.3	NA
<i>Pr</i>	10	0.17	2.22	<0.01	NA
<i>Nd</i>	37	0.80	16.2	2.3	NA
<i>Sm</i>	7.6	0.20	1.65	<0.01	NA
<i>Gd</i>	7.5	0.29	1.44	<0.01	NA
<i>Dy</i>	9.0	0.38	1.08	<0.01	NA
<i>Er</i>	5.5	0.33	1.00	<0.01	NA
<i>Yb</i>	4.1	0.31	<0.87	<0.01	NA
<i>Ta</i>	2.2	0.003	2.14	<0.01	NA
<i>W</i>	6.2	0.02	2.03	<0.01	NA
<i>Pb</i>	31	0.75	56	10	80
<i>Th</i>	14	0.03	4.2	<0.01	30
<i>U</i>	6.8	56	1.29	<0.01	12

**Table 3.** Leaching test according to EN12457-2 for LBFA, CA, and SE starting materials compared with the non-hazardous limit of the European Directive 2003/33/EC

µg/g	LBFA	CA	SE	SE (acid rain)	Non-hazardous limit
pH			10.3	10.6	
Al	187	1.53	<0.1	<0.1	
Ca	2490	76.1	7620	8,530	
Fe	<0.1	0.1	<0.01	<0.01	
K	99	15.3	287	292	
Mg	<0.1	36.4	68	25.8	
Na	1486	202	447	407	
P	<0.1	<0.1	<0.01	<0.01	
SO <sub>4</sub> <sup>2-</sup>	7060	163	5250	24300	20,000
Si	<0.1	9.8	60	45	
Li	3.5	0.02	0.80	0.85	
Be	<0.01	<0.01	<0.01	<0.01	
B	62.8	0.62	0.69	0.79	
Sc	<0.1	<0.1	<0.01	<0.01	
Ti	<0.1	<0.1	<0.01	<0.01	
V	3.3	0.03	0.09	0.08	
Cr	2.3	<0.01	<0.01	<0.01	10
Mn	<0.01	<0.01	<0.01	0.01	
Co	<0.01	<0.01	0.02	0.02	
Ni	<0.01	<0.01	0.08	0.10	10
Cu	<0.01	0.16	0.12	0.09	50
Zn	0.06	0.03	0.47	0.91	50
Hg	0.07	<0.001	0.2	0.2	0.2
Ga	0.71	<0.01	<0.01	<0.01	
Ge	0.07	<0.01	<0.01	<0.01	
As	0.39	0.04	0.03	0.04	2
Se	23	<0.1	0.03	0.04	<b>0.5</b>
Rb	0.3	0.01	0.47	0.48	
Sr	66.9	0.37	69	88	
Y	<0.1	<0.1	<0.01	<0.01	
Zr	<0.1	<0.1	<0.01	<0.01	
Nb	<0.1	<0.1	<0.01	<0.01	
Mo	23	0.02	0.10	0.13	<b>10</b>
Cd	0.05	<0.1	<0.01	<0.01	1
Sn	<0.1	<0.1	<0.01	<0.01	
Sb	0.1	<0.1	0.09	0.08	0.7
Cs	0.02	<0.1	<0.01	<0.01	
Ba	15	<0.1	0.87	1.02	100
La	<0.1	0.01	<0.01	<0.01	
Ce	<0.1	<0.1	<0.01	<0.01	
Pr	<0.1	<0.1	<0.01	<0.01	
Nd	<0.1	<0.1	<0.01	<0.01	
Sm	<0.1	<0.1	<0.01	<0.01	
W	3.6	<0.1	0.03	0.05	
Tl	<0.01	<0.01	<0.01	<0.01	
Pb	<0.01	<0.01	<0.01	<0.01	10
Bi	<0.01	<0.01	<0.01	<0.01	
Th	<0.01	<0.01	<0.01	<0.01	
U	<0.01	<0.01	<0.01	<0.01	
Cl	<0.01	<0.01	N.A.	N.A.	15,000
F	<0.01	<0.01	N.A.	N.A.	150



**Table 4:** Mineralogical composition (%wt.) determined by XRD in Seseña bulk content including the amorphous content.

	Formula	bulk
Anhydrite	$\text{CaSO}_4$	15.3
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.7
Bassanite	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	0.5
Quartz	$\text{SiO}_2$	5.6
Calcite	$\text{CaCO}_3$	5.8
Zincite	$\text{ZnO}$	0.6
Sphalerite	$\text{ZnS}$	0.3
Albite	$\text{NaAlSi}_3\text{O}_8$	<0.5
Microcline	$\text{KAlSi}_3\text{O}_8$	2
Willemite	$\text{Zn}_2\text{SiO}_4$	0.5
Spinel-Zn	$\text{Zn}(\text{Zn}_{0.913}\text{Ti}_{0.087})(\text{Zn}_{0.087}\text{Ti}_{0.913})\text{O}_4$	<0.5
Illite	$(\text{K},\text{H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	1.8
Hematite	$\text{Fe}_2\text{O}_3$	5.7
Magnetite	$\text{Fe}_3\text{O}_4$	3.1
Grafito	$\text{C}$	1.8
Amorphous content		54.3

**Table 5: Leaching yield tests according to EN12457-2 for the aggregate products for LBFA/HU blends with comparison to the non-hazardous limit of the Directive 2003/33/EC**

mg/kg	AP1	AP2	AP3	AP4	Non-hazardous limit
<b>pH</b>	<b>5.5</b>	<b>6.3</b>	<b>7.3</b>	<b>8.3</b>	<b>&lt;6</b>
Al	<0.01	<0.01	<0.01	<0.01	
Ca	281	175	165	152	
Fe	<0.01	<0.01	<0.01	<0.01	
K	24	15	10	9.4	
Mg	222	101	45	33	
Na	656	377	251	195	
P	472	972	22.2	2.8	
S	386	316	275	251	
SO <sub>4</sub> <sup>2-</sup>	160	950	825	753	20000
Si	46	34	20	12	
<b>Li</b>	<b>5.5</b>	<b>4.1</b>	<b>3.6</b>	<b>3.2</b>	
<b>Be</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>B</b>	<b>87</b>	<b>73</b>	<b>61</b>	<b>57</b>	
<b>Sc</b>	<b>0.2</b>	<b>0.1</b>	<b>0.1</b>	<b>0.0</b>	
<b>Ti</b>	<b>0.2</b>	<b>0.2</b>	<b>0.1</b>	<b>0.1</b>	
<b>V</b>	<b>1.8</b>	<b>6.0</b>	<b>6.9</b>	<b>6.8</b>	
<b>Cr</b>	<b>0.1</b>	<b>0.5</b>	<b>0.8</b>	<b>1.1</b>	<b>10</b>
<b>Mn</b>	<b>2.9</b>	<b>0.8</b>	<b>0.1</b>	<b>0.0</b>	
<b>Co</b>	<b>0.6</b>	<b>0.1</b>	<b>0.0</b>	<b>&lt;0.01</b>	
<b>Ni</b>	<b>8.2</b>	<b>1.7</b>	<b>0.2</b>	<b>0.1</b>	<b>10</b>
<b>Cu</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>50</b>
<b>Zn</b>	<b>0.4</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>50</b>
<b>Ga</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Ge</b>	<b>1.4</b>	<b>1.6</b>	<b>1.3</b>	<b>0.9</b>	
<b>As</b>	<b>43</b>	<b>32</b>	<b>17</b>	<b>7.2</b>	<b>2</b>
<b>Se</b>	<b>19</b>	<b>15</b>	<b>11</b>	<b>5.3</b>	<b>0.5</b>
<b>Rb</b>	<b>0.6</b>	<b>0.4</b>	<b>0.3</b>	<b>0.3</b>	
<b>Sr</b>	<b>18</b>	<b>12</b>	<b>11</b>	<b>14</b>	
<b>Y</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Zr</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Nb</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Mo</b>	<b>2.9</b>	<b>4.6</b>	<b>7.0</b>	<b>9.9</b>	<b>10</b>
<b>Cd</b>	<b>0.6</b>	<b>0.1</b>	<b>0.0</b>	<b>0.0</b>	<b>1</b>
<b>Sn</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Sb</b>	<b>0.2</b>	<b>0.3</b>	<b>0.3</b>	<b>0.3</b>	<b>0.7</b>
<b>Cs</b>	<b>0.1</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	
<b>Ba</b>	<b>0.3</b>	<b>0.3</b>	<b>0.2</b>	<b>0.6</b>	<b>100</b>
<b>La</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Ce</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Pr</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Nd</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Sm</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Eu</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Er</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Tm</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>W</b>	<b>&lt;0.01</b>	<b>0.2</b>	<b>0.4</b>	<b>0.7</b>	
<b>Tl</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Pb</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>10</b>
<b>Bi</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>Th</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	
<b>U</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	





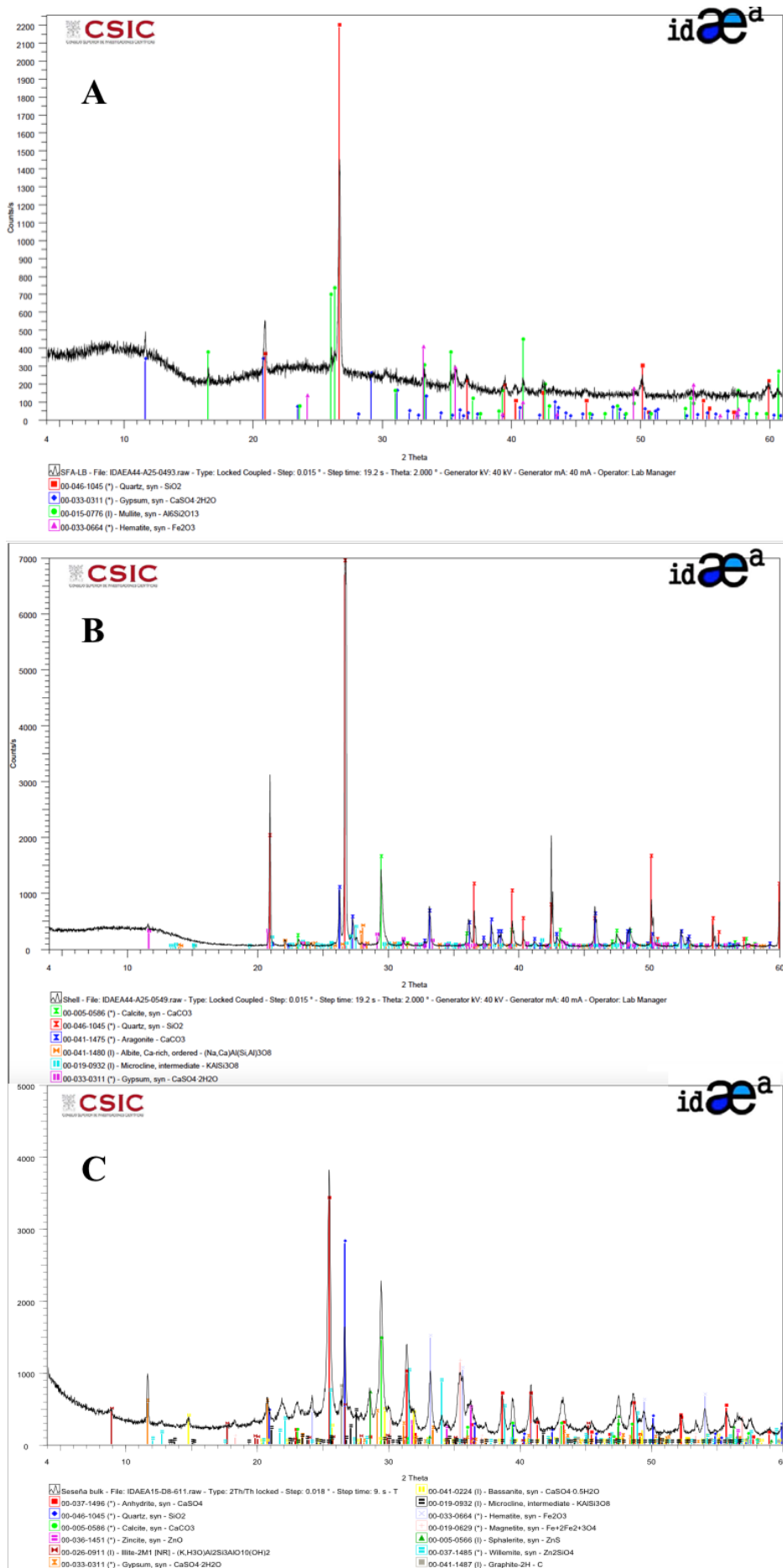
## Figures

Figure 1. Huelva satellite image of Huelva City and phosphogypsum deposits site (Google 2016)

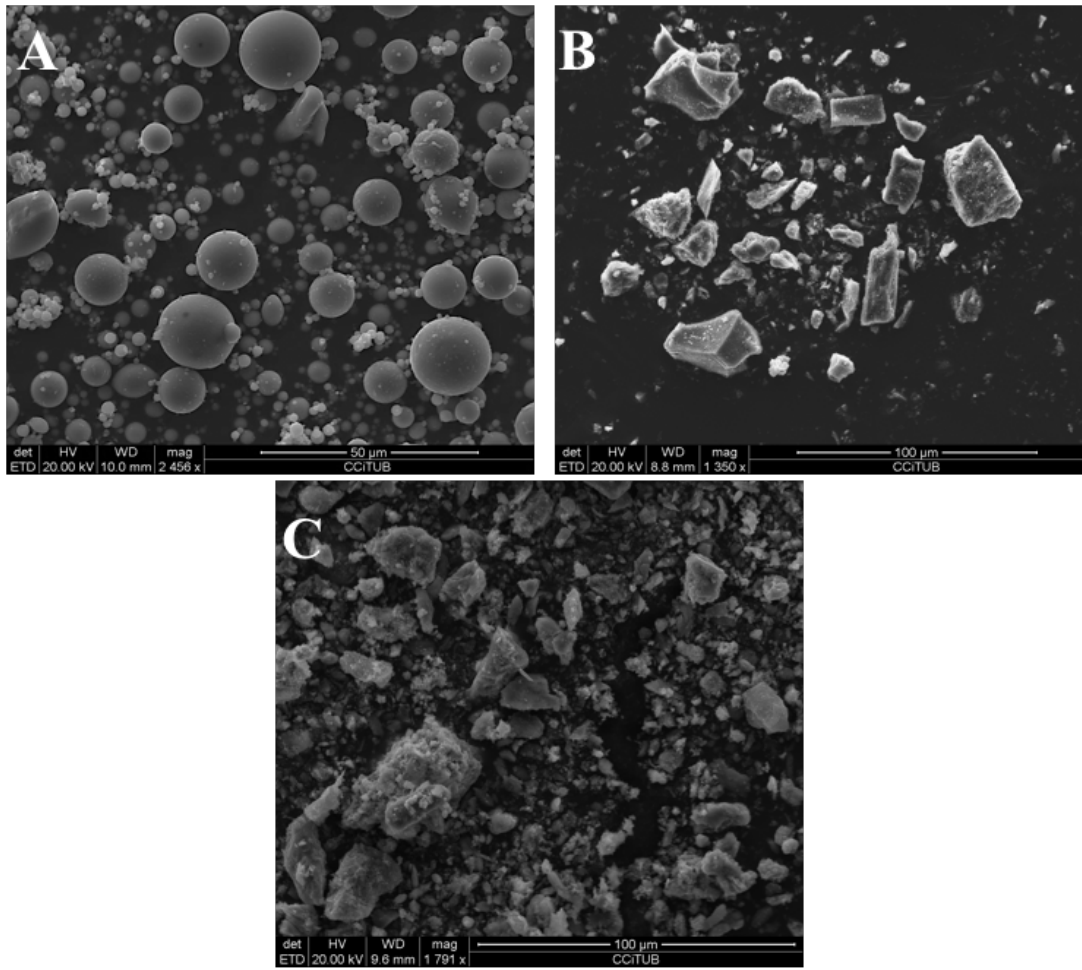


Picture taken from Google map

Figure 2. XRD spectra of the LBFA (A), CA (B), and SE (C) starting materials



**Figure 3.** Morphology and particle composition of LBFA (A), CA (B), and SE (C)



Averaged wt.% - EDX	Si	Al	Fe	Ti	Ca	K	S	Na	Mg	P	Cl	Mn	Zn
Image A - LBFA	46.4	19.2	14.0	1.7	7.0	5.3	2.2	2.5	1.7	N.A.	N.A.	N.A.	N.A.
Image B - CA	15.5	0.8	N.A.	N.A.	72.0	1.9	N.A.	3.3	2.4	1.8	2.3	N.A.	N.A.
Image C - SE	11.7	3.91	3.84	N.A.	32.6	1.74	19.0	5.71	1.75	0.55	N.A.	1.06	18.1

Figure 4. Physical and chemical properties of the concretes produced. Compressive tests after 1 day and 28 days after casting (A), Specific weight (B), and Ion penetration (C). All results are compared to standard concrete.

