

# Coal Residues: The new Golden Treasure

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## Abstract

At present, coal is the major fossil fuel used for power production in utilities and it will stay as an important source for several decades to come. A major environmental problem associated with coal combustion is the ash residues. Most of the ashes produced are stored or dumped in ponds. The main utilization mode of the ashes is as a partial substitute to cement, sand or aggregates in concrete for civil engineering projects.

As appreciable percent of the ashes produced, contain large amounts of basic elements (mainly aluminosilicate with appreciable lime- CaO content) it can be used for neutralization of acidic wastes. The small ash particles (1-35 $\mu$ m) have also a relatively large surface area and contain aluminate ( $-\text{AlO}_2^-$ ) and silicate ( $-\text{SiO}_3^-$ ) anionic groups at the surface. Thus, it has excellent adsorption properties.

Several studies have shown that the ashes are excellent neutralization and fixation reagents to acidic industrial wastes and trap efficiently toxic trace elements and organic contaminants. Thus, the scrubbed product is defined as a nonhazardous waste according to the improved TCLP 1311 method and the European Compliance test 12457.

Furthermore, it can be used as a partial substitute to cement or sand in concrete to be used for industrial projects. Thus, the coal fly ash is a valued commodity with an actual added value that can reduce costs of treatment of toxic industrial wastes and solve storage problems of the ash and the waste upon its incorporation in industrial concrete as a green product.

**KEYWORDS:** Coal Fly Ash, Waste Fixation, Toxic Trace Elements, Concrete

### 1. Introduction

Coal is considered as one of the main fuels for electricity generation worldwide. As coal is abundant, easy to transport and store, and the least expensive of all fossil-fuel

sources (considering the energy content) it is fueling >40% of the global electricity, even though in 2015 the global coal consumption fell by 1.8%<sup>1</sup>. Moreover, the coal reserves in 2015 were sufficient for 114 years of global products, which is the highest for any fossil fuel<sup>1</sup>. In pulverized coal combustion (PCC) plants, the pulverized coal particle (average size of 30 $\mu$ m) is injected into the boiler and undergoes 2 processes: (1) pyrolysis, (2) burning of the char. The total process yields several byproducts, in which the main byproduct is coal fly ash (FA, ~90% of the mineral content). The FA is rich in alkali and alkali earth elements, with pozzolanic and cementitious properties. Thus, the main use of FA, is in the construction industry as an additive to concrete and cement. Thus, its' economic value is relatively poor ( $\leq 15$ \$/ton).

In order to increase FA economic value several studies evaluating the possibility of using the FA as an effective neutralization and fixation reagent have been carried out<sup>2-9</sup>. The wastes studies were:

- (1) Acidic waste from the phosphate industry, which is a byproduct of phosphate rock treatment with either sulfuric or hydrochloric acid (0.1-1M acidity of the solution).
- (2) Extremely acidic waste (~10M acidity) formed from the regeneration processes of used motor oil with Oleum.

Results have indicated that FA can act as an efficient acid neutralization, and also as an excellent fixation reagent to trace elements and organic components, according to TCLP1311<sup>10</sup>, CAL-WET<sup>11</sup>, and European Directive EN12457-2<sup>12</sup>).

The mechanisms suggested for the fixation of metal ions at the FA surface were<sup>5</sup>:

- (1) Cation-exchange mode– in which the anionic functional groups- mainly aluminates-O-AlO<sup>-</sup>, and silicates-O-SiO<sub>2</sub><sup>-</sup> at the surface of the FA particles are the fixation sites.

- (2) Coordinative bonding – fixation occurs via a chemical bond formation between the non-bonding electrons of one of the oxygen atoms of the functional groups at the surface of the FA with trace elements in the waste. Thus the FA acts as a Lewis base and the trace element as a Lewis acid.
- (3) Electrostatic interactions – of fine ionic precipitates with FA negative electrostatic field of the FA surface.

Furthermore, several studies to evaluate the potential of the scrubbed product (AP) to be used as an aggregate as a partial substitute for sand and cement in concrete were carried out. The results prove that indeed AP can serve as a partial substitute for sand and aggregates in concrete, yielding concrete with improved properties compared to regular concrete.

This study aims to determine the potential utilization of FA as a fixation reagent and also the use of the end fixed product as a partial substitute for sand in concrete.

## 2. Materials & Methods

### 2.1 Experimental samples

FA of two origins (South-Africa, Colombia) were chosen, limestone quarry fines (quarries near Hebron, in the Palestinian Authority), dolomite quarry fines from two quarries in Israel, and phosphate waste (HC)

**The fly ashes selected** were produced from the combustion of either of South Africa coal (SAFA), or Colombian coal (COFA) and supplied by the Israel Electric Company. The ash contents in the coals were 13.9% and 8.7% respectively with a specific density of  $1.25\text{g/cm}^3$  and  $1.14\text{g/cm}^3$ , respectively<sup>13-15</sup>. The ashes were enriched with alkali and alkali earth elements, resulting as a Class F FA, with pozzolanic behavior. XRD bulk analysis of the FA samples shows that the primary minerals presented are the mullite ( $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ) and quartz ( $\text{SiO}_2$ ). Moreover, traces of hematite ( $\text{Fe}_2\text{O}_3$ ), calcite

(CaCO<sub>3</sub>), and lime (CaO) were detected in SAFA, and magnetite (Fe<sub>3</sub>O<sub>4</sub>), hematite and anhydrite (CaSO<sub>4</sub>) were detected in COFA (Figure 1). This is in line with the average chemical composition of the FA (Table 1), which indicates a high content of aluminosilicate (>70%), Fe (8.9%), and CaO (3.5%).

### **The quarry wastes selected were**

- (1) Limestone rich - Quarry fines (QF) of limestone were taken from quarries near Habron (HB) in the Palestinian Authority with moisture content of 25-27%
- (2) Dolomite rich QF from quarries of the center of Israel
  - a. One sample from Rosh Ha'ayin (RH) quarry – moisture content of 5.4%
  - b. Two samples from Modi'in quarry
    - i. MO 40-75 – moisture content of 3.1%
    - ii. MO>75 – moisture content of 8.7%

### **Phosphate industry wastes selected in this study were**

- (1) Liquid sludge formed from dissolution of phosphate rock (PS)
- (2) 5 samples arise from the neutralization of phosphate sludge combined with CaO (HC1-HC5)

Composition patterns of the FA and wastes are shown in Tables 1-2.

## **2.2 Characterization methods**

The elemental composition was determined, using a two-step digestion method <sup>16</sup> for the analysis of the major and trace elements in the material, *via* Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). 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  $60^\circ$  of  $2\theta$ , a step size of  $0.05^\circ$ , 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  $<63\mu\text{m}$  fraction was determined by a laser light-scattering-based particle sizer, MALVERN Hydro 2000MU, working range 0.1-1,000  $\mu\text{m}$ .

The European Standard leaching test EN-12457 (Council decision 2003/33/EC) was applied to FA, QF, 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

The APs were prepared with different ratios (FA/QF) 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 – 18MOhm/cm) to the mixture. The resulting APs were dried at  $45^\circ\text{C}$  overnight (in oven). In order to evaluate the efficiency of metal immobilization the European Decision protocol of the above was carried onto the APs. This protocol dictates an agitation of  $24\text{h}\pm 30\text{min}$  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 FA/QF were used as sand substitute in concrete in different content ratios (50 and 100 kg/m<sup>3</sup> concrete for HB, and 40kg/m<sup>3</sup> QF with 80 kg/m<sup>3</sup> FA for RH and MO). 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 FA, and a FA/QF mixture effect on the concrete properties.

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>17</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>17</sup>, and their environmental behavior (e.g. leaching) have been tested according to the European Directive <sup>12</sup>, the USEPA TCLP 1311 <sup>18</sup>, and the CALWET <sup>11</sup> methods.

## 3. Results

### 3.1 Characterization of starting materials

#### 3.1.1 Size Distribution

Ethanol solutions with each one of the starting materials were prepared to analyze the size distribution of the particles.

QF samples of Israeli quarries (RH, MO40-75, and MO>75) showed similar grain size patterns with a lognormal and unimodal grain size distribution. However, particle size measurement indicated that RH and the MO>75 are coarser than MO40-75, with a median of 29, and 49  $\mu\text{m}$  respectively, compared to 12  $\mu\text{m}$  of the MO40-75.

QF sample of Hebron quarry shows a lognormal and unimodal grain size distribution (around 2-3  $\mu\text{m}$ ), a median of 3.5  $\mu\text{m}$  (below the breathable size fraction, 4.5  $\mu\text{m}$ ). Thus, this very fine size of QS classifies it as a hazardous material by Israeli regulations<sup>19</sup>.

The FA shows a relatively fine particle size (median of 20  $\mu\text{m}$  for SAFA, and 13  $\mu\text{m}$  for COFA).

HC size distribution measurements indicated of a relatively large average particle size. HC1 had a median of 483  $\mu\text{m}$ , HC2 518  $\mu\text{m}$ , HC3 497  $\mu\text{m}$ , HC4 627  $\mu\text{m}$ , and HC5 264  $\mu\text{m}$ .

### *3.1.2 Analysis and characterization of starting materials*

SAFA and COFA composition patterns indicates high concentration of water soluble species enriched in Ca, Fe, S, P, Ba, and Sr (Table 1). Moreover, both the SAFA and COFA are composed mainly (>70%) of aluminosilicates. Overall, both FAs show similar properties, such as high surface area ( $2.42 \pm 0.01 \text{ m}^2/\text{g}$  and  $1.59 \pm 0.02 \text{ m}^2/\text{g}$  respectively), pH (>10.5), and morphology. Also, water-soluble trace elements – mainly oxyanions (e.g. As, Se, and Mo) are detected in considerable concentration.

As expected all QFs contribute mainly Ca- and Mg- species, with typical impurities in the limestone and dolomite.

XRD analysis of the Israeli QFs (MO or RH) indicated that the dolomite and calcite are the main mineral phases (Figure 2). Trace of anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) were also detected. Moreover, quartz was also determined in the RH samples.

As the Ca mineralogy between the FAs and the QFs is different, the pH values are different as well. The FA was yielding leachates with higher pH (>10.5).

Leachable levels of Se, Mo, and Sb from COFA, due to their high mobility exceed the limits established in the 2003/33/EC decision for landfilling, thus considered as hazardous material (Table 3). This is the result of low pH values in COFA resulting in higher yielding of these elements<sup>20</sup>. For SAFA leachates, no additional environmental risk is noticed as most of the elements are within the inert limits of the European Directive (EN12457-2) with exception of Cr, and Mo which are below the non-hazardous limits.

As expected from limestone and dolomite QFs, only low yielding potential is noticed as most elements (except Se), fall within the inert limits of the European Directive (Table 3).

XRD bulk analysis of the HC samples (Figure 3) indicates that the primary minerals presented are the calcite ( $\text{CaCO}_3$ ) and quartz. Traces of chlorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ), apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{X}$ ), and aluminum phosphide (AlP), and Fluoroapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ).

Yielding leaching tests according to the European Directive (EN12457-2) were carried out for all 5 HC samples (Table 4). Antimony showed high mobility exceed the limits established in the 2003/33/EC decision.

### 3.2 Fixation tests and characterization of end fixed product

All fixation products (APs) were tested by the European Decision leaching test for landfilling (EN12457-2, 2003/33/EC). The test was performed on the fixed end product of FA/waste. As expected different optimized ratios were needed in order to fixate hazardous trace elements from all starting materials. Tables 5-6 and figures 4-5 indicate that a full fixation was achieved. Results of these studies evidenced that (1) leaching of As, Se, and Mo from the AP decreased drastically when calcite was added, (2) full neutralization and fixation of PS was achieved as a result of the free lime leached to the

solution and the presence of  $-\text{AlO}_2^-$  and  $-\text{SiO}_3^-$  at the aluminosilicate glassy phase. Furthermore, nonhazardous APs were produced, according to the European Council Decision (2003/33/EC), which can be used for any purpose. The optimal ratios for FA/wastes were:

- (1) SAFA/PS – 2/1
- (2) (SAFA/COFA)/HC – 1/1
- (3) FA/QF
  - a. SAFA/HB – 1/1
  - b. COFA/HB – 1/4
  - c. SAFA/RH – 1/1
  - d. SAFA/MO – 1/1

### 3.3 Utilization potential of APs in concrete production

The performances of the concrete mixture of the concrete mixture without FA and with partial substitute of the sand with FA and mix of FA/waste were tested. All final concretes that were obtain showed higher strength compared to the strength obtained without the replacement of the sand. The higher strength of the mixtures having the FA was obtained as a result of the reaction between the FA particles and the calcium hydroxide to form C-S-H<sup>21-23</sup>. Moreover, resistance of  $\text{Cl}^-$  penetration was tested according to ASTM C1202 (Figures 6-7). As can be seen a  $\text{Cl}^-$  reduced penetration was obtained in all FA/waste samples. These tests suggest that AP formed during the fixation process of FA with either hazardous waste from the phosphate industry, or quarry fine by-product can serve as a partial substitute for sand in concrete, yielding concrete with improved properties.

#### 4. Conclusions

The results of this study demonstrated that Class F fly ash from the combustion of coal power plants can serve as an excellent potential economic, and environmental safe material for several types of hazardous wastes. Both SAFA and COFA are Ca-rich FAs (also enriched with several toxic elements, e.g. Se, Mo, As, Sb), which are easily soluble as the oxy-anionic form. The high mobility of these elements classifies the COFA as a hazardous material, and the SAFA as non-hazardous material according to 2003/33/EC Decision for land filling.

Fine carbonate from the QF adsorbed at the surface of the FA, thus decreasing the pH of the end products, and also reducing the leachability of toxic trace elements.

Concrete tests carried out with AP formed by mixing of FA/waste resulted in improved properties. Therefore, a method to increase the ecological, economic and technological benefits is suggested by using combination of FA as a scrubber for hazardous industrial wastes.

Thus Class F coal fly ash is an excellent and very commodity that can be used as an very good neutralization and fixation reagent for toxic acidic wastes and the scrubbed product can be used as partial substitute to sand and aggregates in industrial concrete for civil engineering projects. Namely coal fly ash is a GOLDEN TREASURE and not an environmental burden if it is used properly!!!.

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## Tables

**Table 1.** Composition patterns of the FA and solid wastes

%	SAFA	COFA	Dry QS	HC1	HC2	HC3	HC4	HC5	MO40-75	MO>75	RH
LOI	5.0	2.3	5.0	20.2	25.7	21.3	33.6	22.8	4-6	1	4-6
SiO <sub>2</sub>	41	56	<0.01	5.9	3.2	4.7	2.1	5.2	<0.01	<0.01	<0.01
Al <sub>2</sub> O <sub>3</sub>	30	22	0.2	0.6	0.4	0.5	0.2	0.5	1.6	0.4	1.7
CaO	9.5	3.4	CaCO <sub>3</sub> = 93	43.7	44.7	43.9	48.2	44.5	61.1	61.0	60.9
Fe <sub>2</sub> O <sub>3</sub>	2.7	6.3	0.15	1.2	0.4	0.7	0.3	1.1	0.7	0.1	0.7
K <sub>2</sub> O	0.8	1.6	<0.01	0.2	0.2	0.2	0.1	0.3	0.6	0.6	0.6
MgO	2.1	1.7	1.4	2.1	0.9	1.0	1.2	2.0	30.7	37.1	30.3
Na <sub>2</sub> O	0.4	2.3	0.1	0.5	0.4	0.3	0.2	0.5	<0.01	<0.01	<0.01
P <sub>2</sub> O <sub>5</sub>	2.3	0.3	<0.01	8.9	10.0	9.7	5.2	8.5	<0.01	<0.01	<0.01
SO <sub>3</sub>	0.7	0.9	<0.01	1.0	0.5	1.4	0.4	1.0	<0.01	<0.01	<0.01
TiO <sub>2</sub>	1.6	1.0	<0.01	0.03	0.03	0.03	0.02	0.03	<0.01	<0.01	<0.01
MnO	0.1	0.04	<0.01	0.03	0.03	0.03	0.02	0.03	<0.01	<0.01	<0.01
BaO	0.2	0.4	<0.01	<0.01	0.02	0.02	0.02	0.02	<0.01	<0.01	<0.01
SrO	0.3	0.1	0.02	0.07	0.07	0.07	0.07	0.07	0.02	0.02	0.02
mg/kg											
Li	387	102	1.5	2.2	1.2	<0.01	<0.01	1.7	4.3	1.6	5.3
Be	9.2	10	<0.001	4.0	3.3	4.0	2.3	3.7	<0.001	<0.001	<0.001
B	161	322	277	1,860	932	1240	621	2170	63.6	54.0	74.4
Sc	26	35	<0.001	15.2	6.2	7.1	5.0	14.9	1.2	<0.001	1.3
V	143	272	13	516	219	196	264	480	355	103	464
Cr	153	119	5.7	226	167	165	104	209	11.1	3.7	12.0
Hg	0.40	0.22	0.002	0,044	0.030	0.026	0.047	0.025	<0.001	0.003	0.004
Mn	436	331	20	124	320	349	68.5	118	96.9	33.1	1167
Co	30	38	3.1	3.0	2.1	2.3	1.6	2.7	3.3	0.8	2.4
Ni	48	99	7.7	144	42.7	31.5	67.0	131	16.2	7.6	13.5
Cu	88	82	7.2	106	35.7	27.4	43.3	97.4	8.4	4.6	7.7
Zn	148	175	53	2050	617	468	784	1990	23.7	12.4	21.3
Ga	57	43	<0.001	2.8	2.0	3.0	1.2	2.5	1.8	<0.001	1.9
Ge	11	26	<0.001	1.2	<0.01	<0.01	<0.01	1.1	001	<0.001	001
As	16	27	1.2	45.7	16.8	19.7	17.9	49.6	2.6	<0.001	1.9
Se	10	27	2.9	17.3	13.0	7.4	9.8	16.9	<0.001	<0.001	<0.001
Rb	34	63	1.5	2.5	1.3	1.6	<0.01	2.5	8.1	2.2	8.0
Y	85	54	1.0	218	88.6	112	75.9	203	1.4	<0.001	1.9
Zr	279	235	2.0	60.8	27.3	35.0	18.6	53.1	12.5	3.3	15.6
Nb	76	50	1.3	8.6	1.8	3.1	0.9	4.0	1.9	<0.001	2.1
Mo	10	25	13	83.1	19.0	17.4	33.1	77.2	<0.001	<0.001	<0.001
Cd	0.01	2.1	<0.001	94.8	15.5	19.8	35.6	89.9	<0.001	<0.001	<0.001
Sn	<0.001	4	1.0	0.9	<0.01	<0.01	<0.01	1.8	<0.001	<0.001	<0.001
Sb	0.9	15	<0.001	10.9	1.9	2.5	1.6	8.5	<0.001	<0.001	<0.001
Cs	4.7	5.7	<0.001	N.A.	N.A.	N.A.	N.A.	N.A.	<0.001	<0.001	<0.001
La	121	52	7.1	79.7	44.0	65.8	30.6	72.2	2.1	<0.001	3.0
Ce	225	98	0.9	45.8	43.0	74.8	23.0	41.3	4.9	1.4	7.2
Pr	27	12	1.3	10.8	7.5	11.4	4.3	9.9	<0.001	<0.001	<0.001
Nd	89	43	<0.001	44.4	29.8	43.8	17.2	40.4	1.7	<0.001	2.3
Sm	18	9.5	<0.001	9.6	6.2	8.9	3.6	8.7	<0.001	<0.001	<0.001
Eu	2.7	2.0	<0.001	2.0	1.2	1.7	<0.01	1.8	<0.001	<0.001	<0.001
Gd	17	9.4	<0.001	13.1	7.3	10.0	4.8	11.9	<0.001	<0.001	<0.001
Tb	2.5	1.4	<0.001	2.0	1.1	1.4	<0.01	1.9	<0.001	<0.001	<0.001

Dy	16	9.4	<0.001	15.0	7.0	9.1	5.3	13.7	<0.001	<0.001	<0.001
Ho	3.1	1.9	<0.001	3.8	1.6	2.1	1.3	3.5	<0.001	<0.001	<0.001
Er	8.6	5.3	<0.001	12.4	5.0	6.3	4.2	11.1	<0.001	<0.001	<0.001
Yb	8.4	5.2	<0.001	11.4	4.3	5.6	4.0	10.3	<0.001	<0.001	<0.001
Lu	1.2	<0.001	<0.001	1.9	<0.01	0.9	<0.01	1.7	<0.001	<0.001	<0.001
Hf	6.4	5.5	<0.001	3.5	0.4	1.0	<0.01	1.2	<0.001	<0.001	<0.001
Ta	10	5.0	<0.001	7.8	3.0	4.9	1.8	7.5	<0.001	<0.001	<0.001
W	18	15	14	2.2	<0.01	<0.01	<0.01	1.0	<0.001	<0.001	<0.001
Tl	0.9	1.9	<0.001	N.A.	N.A.	N.A.	N.A.	N.A.	<0.001	<0.001	<0.001
Pb	80	44	5.2	11.8	2.9	0.8	2.6	8.9	1.6	0.8	1.9
Bi	3.5	1.6	<0.001	N.A.	N.A.	N.A.	N.A.	N.A.	<0.001	<0.001	<0.001
Th	47	19	<0.001	1.9	2.0	3.1	0.7	1.3	<0.001	<0.001	1.6
U	17	8	1.3	473	174	170	187	386	1.6	1.9	1.9

**Table 2. Composition of Haifa Chemical acidic waste**

mg/kg	PS (mg/kg)
LOI	N.A.
Si	4520
Fe	222
K	788
Mg	254
Na	1200
P	12400
Ti	15.8
Mn	4.57
Ba	307
Sr	689
Be	0.147
B	303
V	16
Cr	17.8
Mn	4.57
Co	0.84
Ni	6.29
Cu	8.59
Zn	248
As	2.39
Se	5.19
Ag	5.3
Cd	2.74
Sn	2
La	12.7
Tl	10
Pb	2

**Table 3.** Major and trace elements leaching yields during European leaching test

(EN12457-2) for SAFA, COFA and quarry fines

mg/kg	SAFA	COFA	MO40-75	MO>75	RH	HB	Inert	Non-Hazardous limit	Hazardous
pH	11.9	9.9	9.0	8.4	8.6	7.81		6	
Al	7.2	286	<0.01	<0.01	1.8	<0.001			
Ca	3440	2940	52.3	50.0	46.1	78			
Fe	<0.01	<0.01	<0.01	<0.01	<0.01	<0.001			
K	34	68	8.5	17.3	18.3	40			
Mg	<0.01	<0.01	41.4	54.1	49.7	17			
Na	57	1102	25.3	31.5	46.4	106			
P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.001			
Si	16	<0.01	8.0	25.0	22.5	18			
Cl <sup>-</sup>	N.A.	N.A.	68.3	63.8	18.8	N.A.	800	15,000	25,000
NO <sub>3</sub> <sup>-</sup>	N.A.	N.A.	18.4	14.5	13.9	N.A.			
SO <sub>4</sub> <sup>2-</sup>	225	7680	27.5	44.3	30.4	87	1,000	20,000	50,000
F <sup>-</sup>	N.A.	N.A.	3.2	3.8	10.3	N.A.	10	150	500
Li	15.8	5.2	<0.01	<0.01	<0.01	0.01			
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
B	0.3	116	0.06	0.16	0.07	0.2			
Sc	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
Ti	0.004	<0.01	<0.01	<0.01	<0.01	<0.01			
V	0.04	3.4	0.03	0.09	0.13	0.1			
Cr	1.0	4.4	<0.01	0.01	0.01	0.018	0.5	10	70
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	0.003			
Co	0.005	0.004	<0.01	<0.01	<0.01	<0.01			
Ni	0.04	0.03	<0.01	<0.01	0.01	<0.01	0.4	10	40
Cu	0.02	0.02	<0.01	<0.01	<0.01	0.03	2	50	100
Zn	0.04	0.02	0.04	0.04	0.04	0.1	4	50	200
Ga	0.2	1.5	<0.01	<0.01	<0.01	<0.01			
Ge	<0.01	0.1	<0.01	<0.01	<0.01	0.003			
As	0.005	0.2	<0.01	0.01	0.02	0.004	0.5	2	25
Se	0.1	<b>11</b>	<0.01	<0.01	<0.01	0.4	0.1	0.5	7
Rb	0.1	0.2	<0.01	<0.01	<0.01	0.02			
Sr	82	48	0.16	0.21	0.15	0.5			
Y	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
Nb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
Mo	2.0	<b>15</b>	0.03	0.04	0.02	0.04	0.3	10	30
Cd	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.04	1	5
Sn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
Sb	<0.01	0.6	<0.01	<0.01	<0.01	0.00	0.02	0.7	5
Cs	0.014	0.02	<0.01	<0.01	<0.01	<0.01			
Ba	20	10	0.01	0.03	0.06	0.01	20	100	300
W	1.3	6.9	<0.01	<0.01	<0.01	0.01			
Tl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			
Pb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.5	10	50
Bi	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01			

Th	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
U	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

**Table 4.** Major and trace elements leaching yields during European leaching test (EN12457-2) for HC1-HC5

mg/kg	HC1	HC2	HC3	HC4	HC5	Inert	Non-hazardous	Hazardous
pH	6.95	7.00	6.64	6.85	6.56	6		
Si	<0.01	<0.01	<0.01	<0.01	<0.01			
Al	<0.01	<0.01	<0.01	<0.01	<0.01			
Ca	41000	24000	28000	17900	54000			
Fe	<0.01	<0.01	<0.01	<0.01	<0.01			
K	1500	1400	880	516	2010			
Mg	476	1200	525	1170	1240			
Na	1680	1420	984	1170	2290			
P	<0.01	<0.01	<0.01	<0.01	<0.01			
SO <sub>4</sub> <sup>2-</sup>	316	<0.01	522	<0.001	465	1000	20000	50000
mg/kg								
Li	<0.01	<0.01	<0.01	<0.01	<0.01			
Be	<0.01	<0.01	<0.01	<0.01	<0.01			
B	<0.01	<0.01	<0.01	<0.01	<0.01			
Sc	0.1	<0.01	<0.01	<0.01	0.1			
Ti	<0.01	<0.01	<0.01	<0.01	<0.01			
V	0.6	1.9	0.3	0.9	0.8			
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	0.5	10	70
Mn	<0.01	<0.01	<0.01	<0.01	<0.01			
Co	0.2	0.2	0.2	0.2	0.4			
Ni	0.1	0.1	0.2	<0.001	0.1	0.4	10	40
Cu	<0.01	2.5	0.2	0.1	0.1			
Zn	0.1	<0.01	<0.01	<0.01	0.1	4	50	200
Ga	0.6	0.4	0.4	0.3	0.9			
Ge	0.1	0.1	0.1	0.1	0.1			
As	0.2	0.4	0.1	0.3	0.3	0.5	2	25
Se	<0.01	<0.01	<0.01	<0.01	<0.01	0.1	0.5	7
Rb	<0.01	<0.01	<0.01	<0.01	<0.01			
Sr	180	92	78	84	238			
Y	0.6	0.3	0.4	0.3	0.9			
Zr	1.0	0.5	0.6	0.4	1.4			
Nb	190	94	83	85	254			
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	0.3	10	30
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	1	5
Sn	<0.01	<0.01	<0.01	<0.01	<0.01			
Sb	4.2	0.8	0.9	2.7	5.7	0.02	0.07	5
Ba	<0.01	<0.01	<0.01	<0.01	9.7	20	100	300
La	0.04	<0.01	<0.01	<0.01	<0.01			
Ce	<0.01	<0.01	<0.01	<0.01	<0.01			
Pr	<0.01	<0.01	<0.01	<0.01	<0.01			
Nd	<0.01	<0.01	<0.01	<0.01	<0.01			
Sm	<0.01	<0.01	<0.01	<0.01	<0.01			
Eu	<0.01	<0.01	<0.01	<0.01	<0.01			
Gd	<0.01	<0.01	<0.01	<0.01	<0.01			
Tb	<0.01	<0.01	<0.01	<0.01	<0.01			
Dy	<0.01	<0.01	<0.01	<0.01	<0.01			
Ho	<0.01	<0.01	<0.01	<0.01	<0.01			
Er	<0.01	<0.01	<0.01	<0.01	<0.01			
Tm	<0.01	<0.01	<0.01	<0.01	<0.01			



Sn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Sb	0.1	0.2	0.04	0.04	0.04	0.04	0.7
Cs	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Ba	2.6	1.3	1.9	2.4	2.2	1.3	100
W	1.7	1.0	0.40	0.37	0.37	0.32	
Tl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Pb	<0.01	0.5	<0.01	<0.01	<0.01	<0.01	10
Bi	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Th	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
U	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	

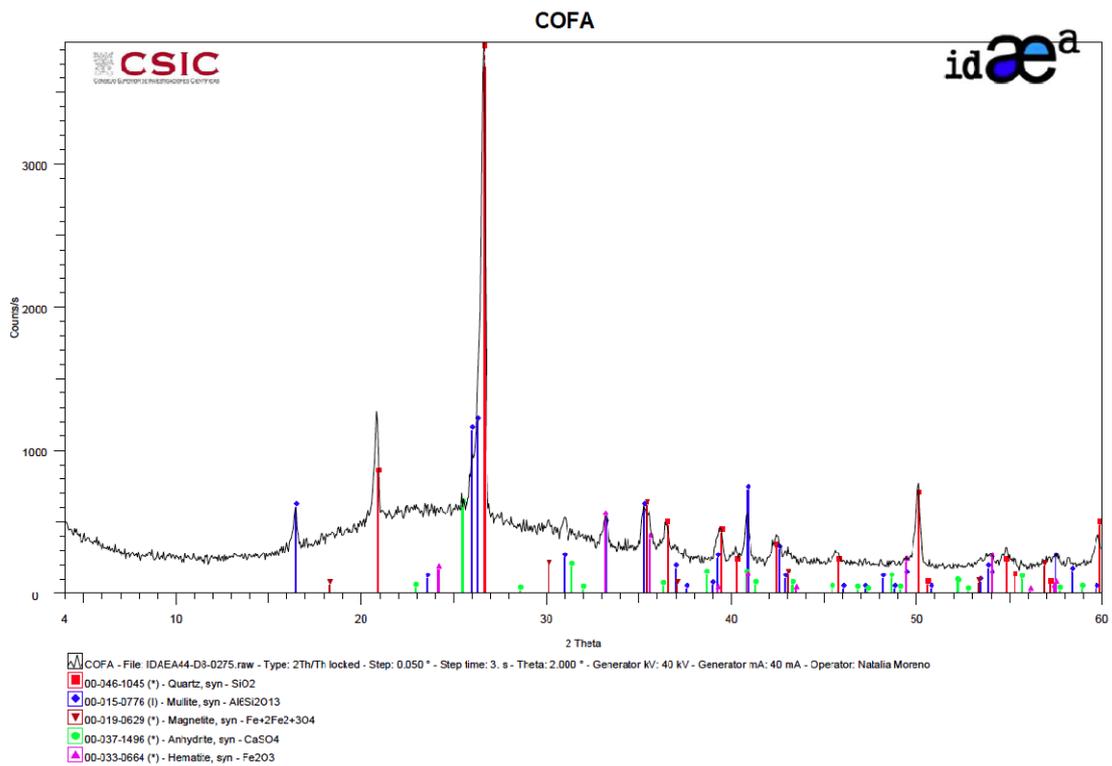
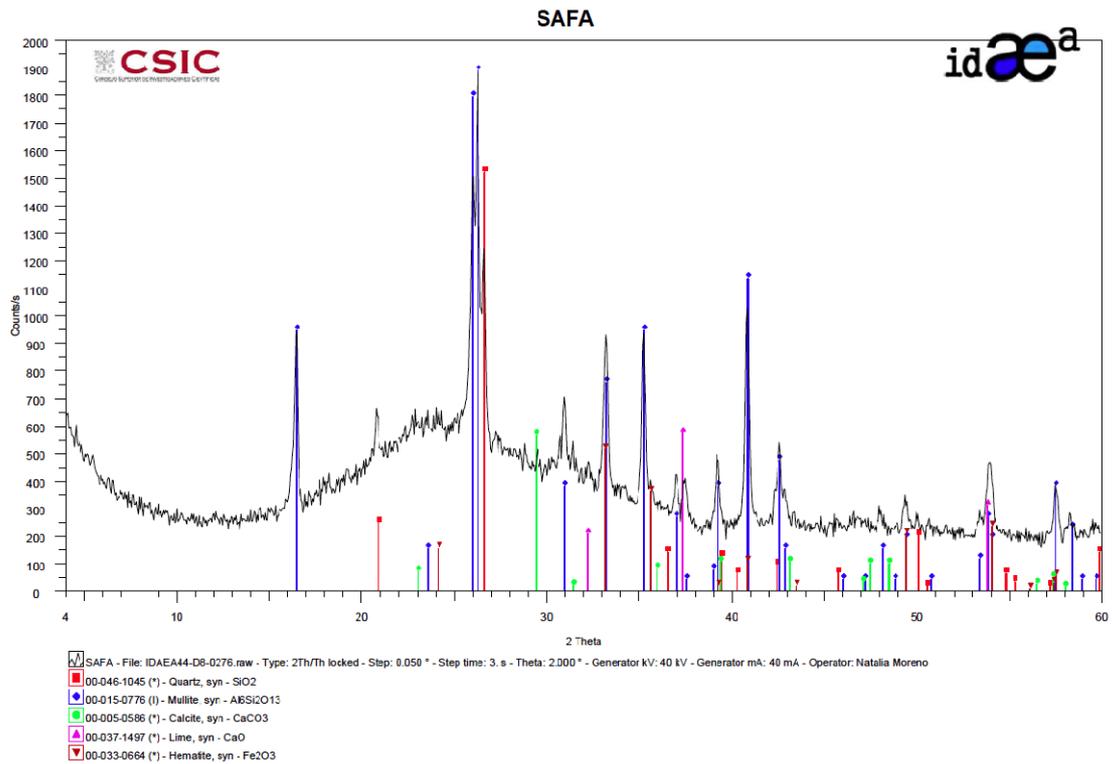
**Table 6.** Major and trace elements leaching yields during European leaching test (EN12457-2) for end fixed product produced with FA combined with solid phosphate waste (HC)

mg/kg	AP <sub>SAFA-HC1</sub> 1/1	AP <sub>SAFA-HC2</sub> 1/1	AP <sub>SAFA-HC3</sub> 1/1	AP <sub>SAFA-HC4</sub> 1/1	AP <sub>SAFA-HC5</sub> 1/1
pH	8.6	9.2	8.8	9.9	8.7
Si	<0.01	<0.01	<0.01	<0.01	<0.01
Al	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	20100	11700	13900	9600	27100
Fe	<0.01	<0.01	<0.01	<0.01	<0.01
K	765	672	449	259	984
Mg	69	25	51	<0.01	89.0
Na	857	657	480	443	1130
P	<0.01	<0.01	<0.01	<0.01	<0.01
SO <sub>4</sub>	822	707	1040	679	911
mg/kg					
Li	7.7	6.4	7.5	7.8	7.3
Be	<0.01	<0.01	<0.01	<0.01	<0.01
B	<0.01	<0.01	<0.01	<0.01	<0.01
Sc	<0.01	<0.01	<0.01	<0.01	<0.01
Ti	0.03	<0.01	<0.01	<0.01	0.03
V	0.2	0.1	0.1	0.1	0.2
Cr	1.5	1.5	1.7	11.3	1.4
Mn	<0.01	<0.01	<0.01	<0.01	<0.01
Co	0.03	<0.01	<0.01	<0.01	0.04
Ni	0.3	0.2	0.2	0.2	0.4
Cu	0.04	0.03	0.03	0.02	0.05
Zn	0.5	0.3	0.2	0.2	0.3
Ga	0.2	0.3	0.3	0.5	0.2
Ge	<0.01	<0.01	<0.01	<0.01	<0.01
As	0.2	0.1	0.1	0.1	0.2
Se	0.3	0.2	0.2	0.1	0.5
Rb	0.6	0.4	0.4	0.3	0.7
Sr	173	114	102	117	205
Y	<0.01	<0.01	<0.01	<0.01	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01
Nb	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	6.3	2.0	1.9	4.2	6.5
Cd	<0.01	<0.01	<0.01	<0.01	0.02
Sn	<0.01	<0.01	<0.01	<0.01	<0.01
Sb	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	14.4	12.0	7.7	13.9	17.1
La	<0.01	<0.01	<0.01	<0.01	<0.01
Ce	<0.01	<0.01	<0.01	<0.01	<0.01
Pr	<0.01	<0.01	<0.01	<0.01	<0.01
Nd	<0.01	<0.01	<0.01	<0.01	<0.01
Sm	<0.01	<0.01	<0.01	<0.01	<0.01
Eu	<0.01	<0.01	<0.01	<0.01	<0.01
Gd	<0.01	<0.01	<0.01	<0.01	<0.01

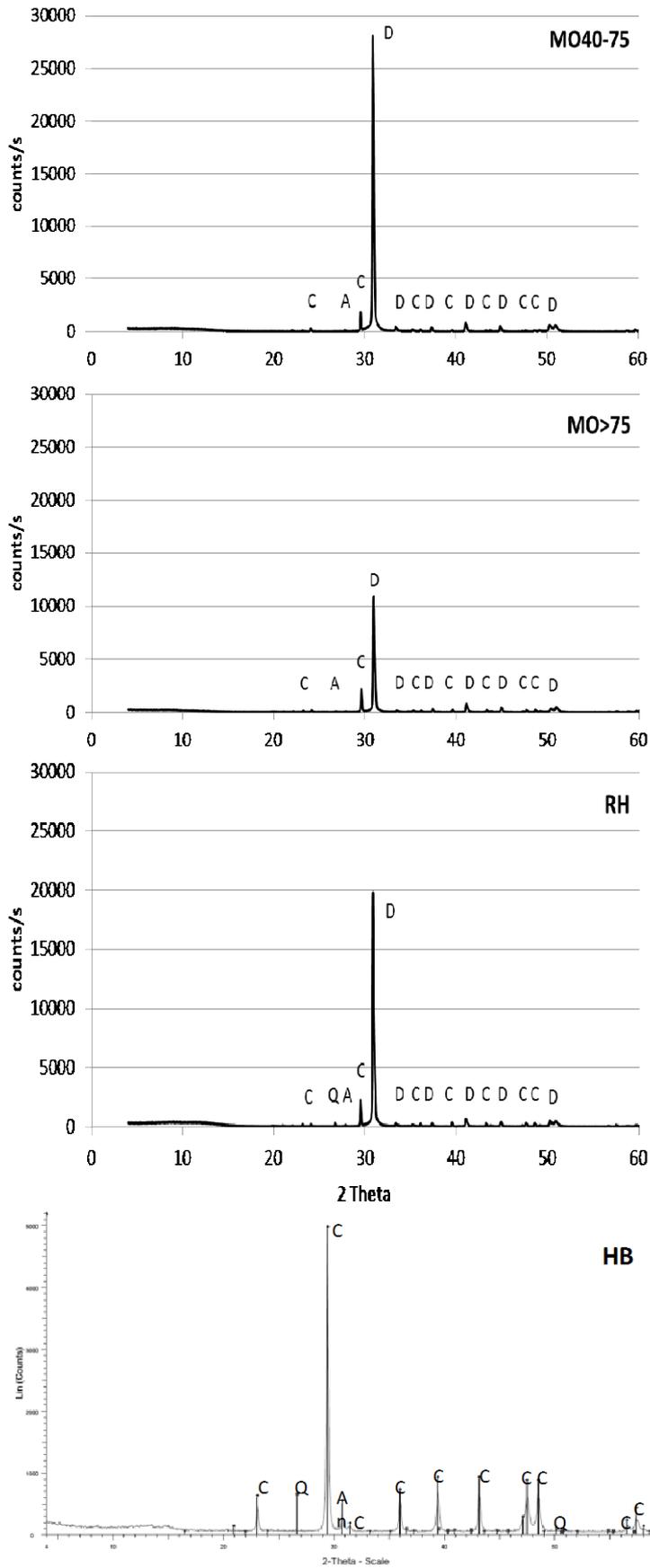
Tb	<0.01	<0.01	<0.01	<0.01	<0.01
Dy	<0.01	<0.01	<0.01	<0.01	<0.01
Ho	<0.01	<0.01	<0.01	<0.01	<0.01
Er	<0.01	<0.01	<0.01	<0.01	<0.01
Tm	<0.01	<0.01	<0.01	<0.01	<0.01
Yb	<0.01	<0.01	<0.01	<0.01	<0.01
Lu	<0.01	<0.01	<0.01	<0.01	<0.01
Hf	<0.01	<0.01	<0.01	<0.01	<0.01
Ta	<0.01	<0.01	<0.01	<0.01	<0.01
W	0.5	0.7	0.5	0.8	0.6
Pb	<0.01	<0.01	<0.01	<0.01	<0.01
Th	<0.01	<0.01	<0.01	<0.01	<0.01
U	<0.01	<0.01	<0.01	<0.01	<0.01

## Figures

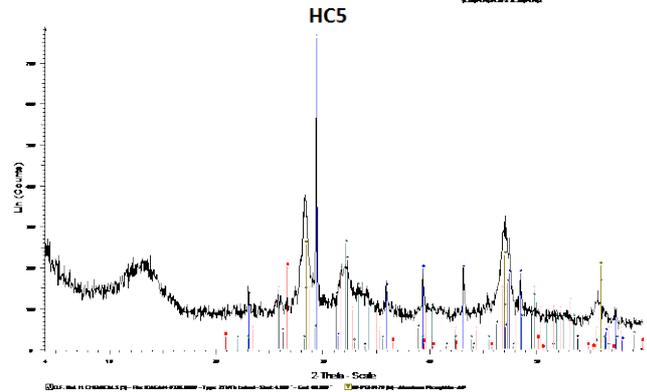
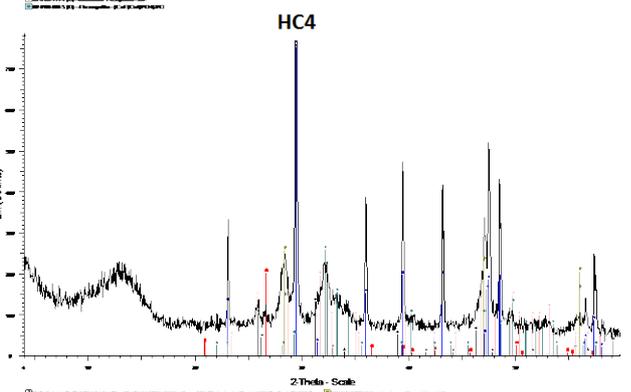
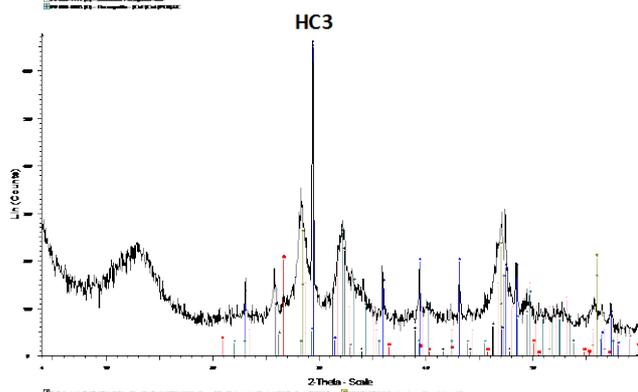
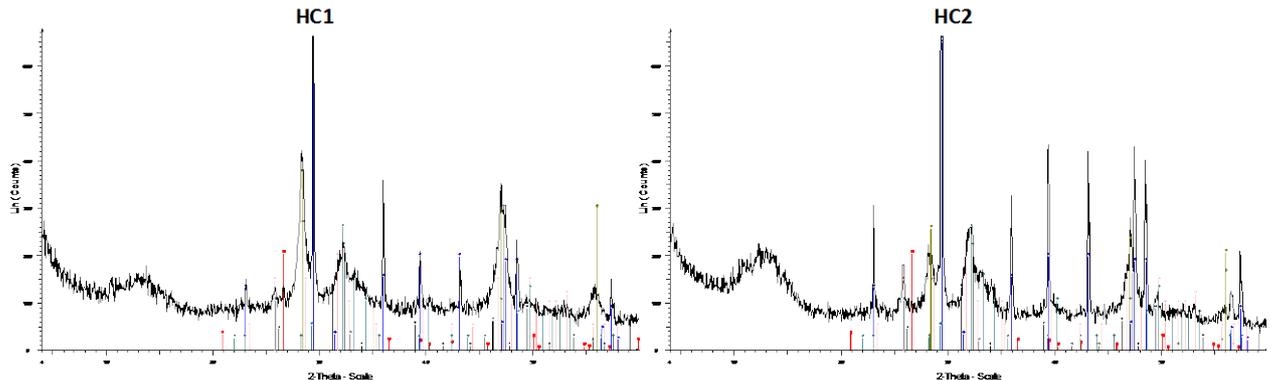
**Figure 1.** XRD spectra showing the mineral crystallization of the SAFA and COFA



**Figure 2.** XRD spectra showing the mineral crystallization of the QFs MO40-75, MO>75, RH, and HB. C indicates calcite, D: dolomite, Q: quartz, A: anorthite, and An: Ankerite.



**Figure 3.** XRD spectra showing the mineral crystallization of the phosphate solid waste (HC).



**Figure 4.** SEM images showing the aggregate product composed with the FA and the quarry fines (A,B) SAFA/COFA with HB respectively, (C) SAFA/RH, (D) SAFA/MO 40-75, and (E) SAFA/MO>75

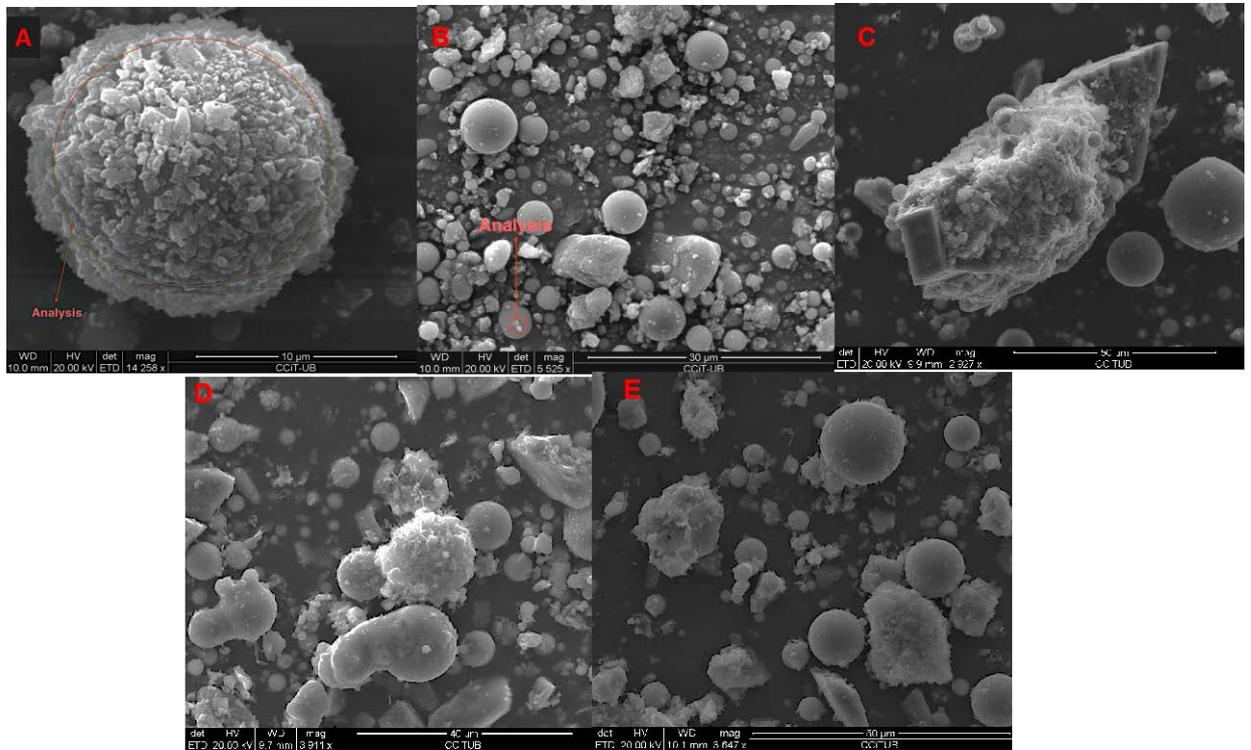
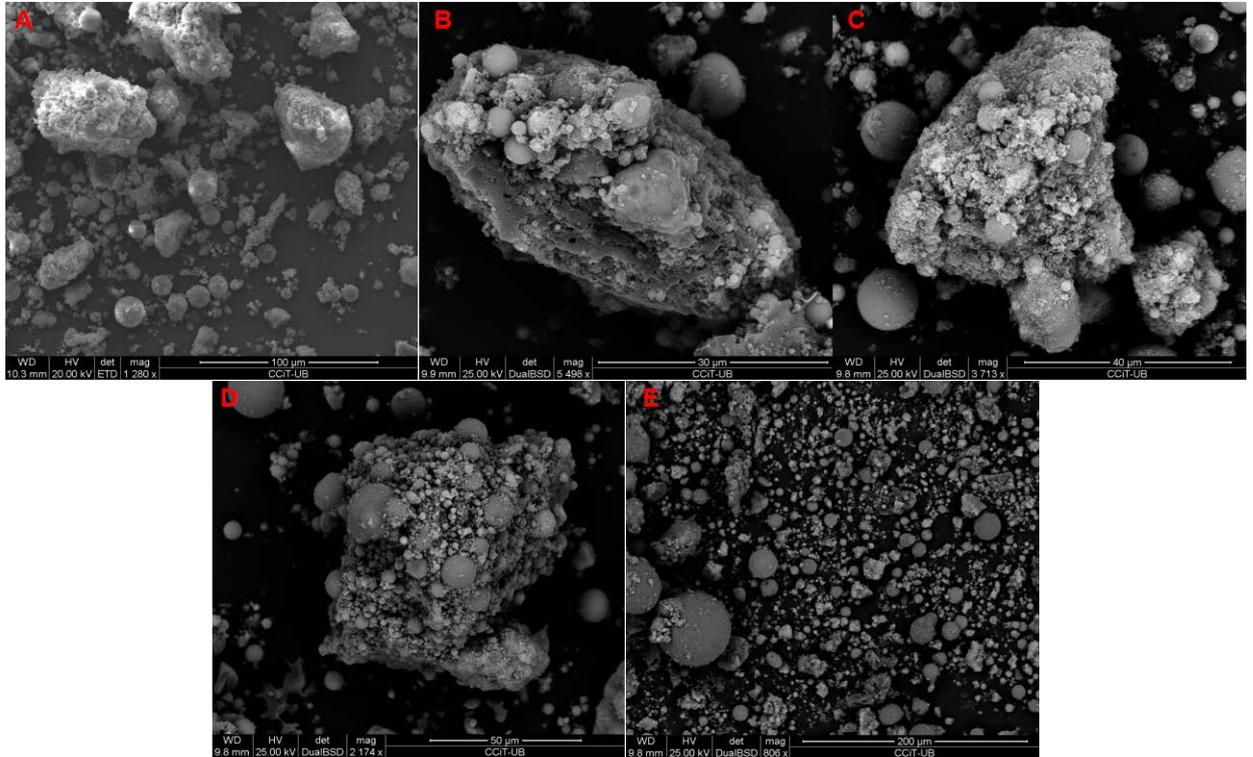


Figure 5. SEM images showing the aggregate product composed with the FA and the phosphate solid wastes (A-E) HC1, HC2, HC3, HC4, and HC5 respectively



**Figure 6.** The compressive strengths of the concrete containing the aggregate product as partial substitute for sand (A-FA/HB, B-FA/RH, FA/MO), and The ion penetration in the concrete of aggregate product compared to concrete reference, AP free (B-FA/HB, D-FA/RH, FA/MO)

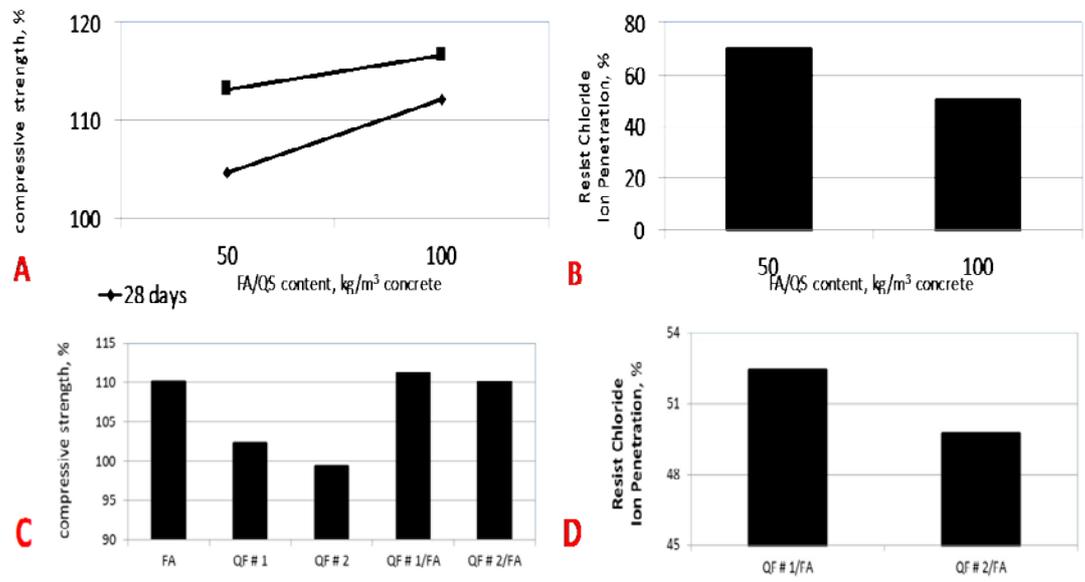


Figure 7. Strength days of concrete with addition of aggregate product composed with SAFA and phosphate waste (HC) compared to concrete with no aggregate substitute addition

