Coal Ash as a Potential Scrubber for Wastes from the Quarry and Phosphate industries in Israel

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ABSTRACT

Israel imports ~13Mtons of Bituminous coal annually. The pulverized coal is fired in 4 power plants and produce ~1.3Mtons of coal Fly Ash (FA) and ~180kton of bottom ash (in 2013) as residues. As a result of strict environmental regulations in Israel, the coal undergoes beneficiation before transport to reduce its mineral content including sulfur. Therefore, the fly ashes produced (Class F) are very basic upon immersion in water (liquid/solid ratio 10/1, South African Fly Ash, SAFA, pH>12.5, Colombian Fly Ash, COFA, pH>10.5).

Recently, it has been found that class F FAs show excellent scrubbing and fixation properties for acidic wastes, mainly from phosphate and oil regeneration industries, which contain also variety of toxic trace elements. In this study we have investigated (1) scrubbing of very fine wastes from quarries in Israel and the Palestinian Authority (QS). These wastes are composed of very fine particles, and therefore could not be used in the concrete industry. (2) Utilization of the Aggregate products formed as a partial substitute for sand or aggregates in concrete mixture has been studied.

The results have shown that class F FAs have the ability to act as an efficient encapsulation reagent also for the QS. Moreover, leaching experiments, *via* the European Directive (EN12457-2), have proved that the aggregate product and the concrete produced are in accord with the compliance test for leaching and the leached water is within the D.L. standards in Israel and also under the hazardous limits of the European Directive.

1. Introduction

The Israeli electric utilities are using bituminous coal as the main source for energy production (~63% in 2013[1]). Coals imported were from South Africa, Colombia, Russia, and Australia[2, 3], and contain ~10% of inorganic mineral content. Ashes are formed as residues, ~1.3Mt of Class F Fly Ash (FA), and ~0.2Mt of Bottom Ash (BA). Moreover, Israel has strict environmental regulation regarding emission of different pollutants during the combustion process [4]. Thus, the coal, undergoes a beneficiation procedure to reduce its pollutants mineral, such as Sulfur (S), Phosphorous (P) and several toxic trace elements (e.g. Hg, As)[5], prior to the transportation to Israel by ships. Thus, the FA that is formed is enriched with alkali and alkali earth elements (as shown in Figure 1), and has a pozzolanic properties.

The enrichment of alkali and alkali earth elements, which classify the FA as Class F, results in a highly basic Class F FA (South African Fly Ash (SAFA) – pH>12.5, Colombian Fly Ash (COFA) – pH>10.5, at Solid/Liquid (S/L) ratio of 1/10). In recent years (2000-2014), 100% of the FA, and BA produced, are used, mostly in the construction industry as a partial substitute to sand or as a cement additive [6-9] . There are some minor utilization as road structural filler, and in agriculture [10, 11].

Recent studies have shown that the FA can be used as an effective neutralization and fixation reagent for several acidic wastes[7-9]. These wastes are produced from regeneration processes of used motor oil (*via* Oleum extraction), or the phosphate industry (dissolution of the phosphate rock with sulfuric or hydrochloric acids). The FA was found to be an excellent neutralization and fixation reagent for these wastes and also, the Aggregate Product (AP) formed could be used as a partial substitute to sand in concrete production. The AP and the concrete produce are non hazardous material as determined by using three leaching procedures: [1] TCLP 1311[12] [2] CAL-WET[13], and [3] European Directive (EN 12457-2)[14].

Another Industry that produces large amount of environmentally hazardous waste is the quarrying industry. Due to the fact that the anticipated demand for quarry product both in Israel and the world is increasing (~45 million tons today to ~90 million tons in 2040 in Israel)[15], there is an increase in the byproducts of the industry. During the cutting of the limestone and dolomite plates in the Palestinian Authority and in Israel, the fine dust is accumulated under water as a sludge, which may cause a major environmental problem, of disposed in rivers[16].

Also Quarry Sludge (QS) is formed during the stone cutting process and aggregate size storing under water, which forms a hazardous material. The QS is a fine mineral material residues (smaller than 2mm), and considered as sub-economic material[17]. Nonetheless, these residues are used in the cement industry, as clinker additive, for production of molded bricks, and also in the construction industry, where it is used in material such as red ceramic bricks and tiles [15-17].However, due to the fact that the consumption of these materials is much lower than the production, it creates a negative environmental impact, because the unused material is piled up in abandoned piled around the quarries area[18].

The fact the materials are considered as Particle Matter (PM) 10_{micron} or less, it must be kept moist or in submerged conditions.

This study deals with 3 different hazardous wastes: (1) the first, fine sludge (QS) produced from cutting limestone in Palestinian Authority, and the Northern Negev area in Israel (2) the second, QS from 2 quarries, Modi'in quarries, and Rosh-Ha'ain in Israel (denoted as MO and RH), and (3) a hazardous waste derived from the dissolution of phosphate industry *via* hydrochloric acid (denoted as HCW). The aims of this study are to determine the leaching potential of the wastes, to test scrubbing capability of the FA with the wastes, and to evaluate the potential utilization of the Aggregate Product (AP) formed as a partial substitute for sand during the concrete production.

2. Materials and Methods

2.1 Materials

Haifa Chemicals supplied wastes formed from the dissolution of the Phosphate rock in Hydrochloric acid. Two of the most common Fly Ash (FA) samples in Israel, namely South African Fly Ash (a.k.a. SAFA), and Colombian Fly Ash (a.k.a. COFA), Limestone QS (a.k.a HB) from the quarries near Hebron (in the Palestinian Authority), and quarries wastes from Rosh Ha'ain QS (a.k.a. RH) and Modi'in QS (a.k.a MO) were used.

The HB includes samples from three stages of the storage procedure. Both FAs are produced from firing of pulverized bituminous coal in the power facilities in Israel. The RH and MO were collected from Rosh Ha'ain and Modi'in quarries. The experimental procedure is outlined in Figure 2.

2.2 Characterization of the fly ash, and the wastes

The mineralogy of samples was determined by X-ray powder diffraction (XRD). XRD patterns were collected using a Bruker D8 Advance diffractometer with monochromatic Cu Kα1,2 radiation (λ=1,5405) operated 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 with the following scanning parameters: from 4 at 60° of 2θ , a step size of 0.05° and time per step of 3s. Content of 57 major and trace elements in solid samples were determined *via* Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), respectively. A special two steps sample digestion method which was developed by Querol et al. [19] to study the of potentially volatile elements in coals and FAs was used to dissolve the samples prior to the analysis. An international reference material NBS1633b was digested as a reference to determine the accuracy of the analytical and digestion methods. Mercury analyses were analyzed using LECO AMA 254 gold amalgam atomic absorption spectrometer. The particle resolved composition and morphology of samples were investigated by a MK2 Quanta 200 Scanning Electron Microscope with energy dispersive X-ray analyzer (SEM-EDX). The grain size distribution of <63µm fraction was determined by means of a laser light-scattering-based particle sizer, MALVERN Hydro 2000MU, with a working range from 0.1 to 1,000 µm.

The European Standard leaching test EN-12457 (according to Council decision 2003/33/EC) was applied to FA, wastes and AP mixtures to determine the leaching potential of major and trace elements using an overhead shaker from Heidolph model REAX 2. The pH and ionic conductivity were determined by conventional methods.

2.3 Fixation tests and study of aggregate product formed concretes

The aggregate formation was preformed with a temperature-controlled reactor built especially for the fixation process, with Hslangtai Machinery Industry Co. LTD model, mechanical stirrer. Prior to the fixation process all samples were dried and homogenized. The duration of the fixation procedure was 20 minutes at 250 rpm. Moreover, in order to prevent formation of non-homogenous solid mixture, an addition of ultra pure water was needed. The Aggregate Products (AP) formed was air-dried, and also examined for physical, chemical, and leach ability properties.

The leaching test was preformed with the aim to study the fixation quality of the APs formed. It was carried *via* the European Directive (EN 12457-2, 5g of AP were mixed with Ultra Pure Deionized water (UPDI) with a 1/10 AP/UPDI ratio). According to EN 12457-2 the mixture was agitated for 24h±30min in an overhead shaker at rotation frequency of 5-10rpm. Finally, the slurry was filtered and analyzed *via* ICP (AES and MS).

It was found [9] that the optimal FA/Waste ratios, for full neutralization and fixation, are as following:

1. FA/HB: with SAFA (1/1, and 1/2), with COFA (1/4).
2. FA/HCW: with SAFA (1/1), with COFA (1/1)
3. FA/RH: with both SAFA and COFA (2/1)
4. FA/MO: with both SAFA and COFA (2/1)

The APs (in a ratio of 2/1 and 4/1 FA/Waste) were used as a partial substitute to sand in concrete. In the preparation of the concrete, two replacements contents were used, 50 and 100kg/m^3. The prepared APs concrete were tested for compressive strength and resistant to chloride ion penetration according to ASTM 1202-12, and compared to concrete reference (denoted as standard). The concrete samples were aged for 1-90 days.

3. Results and Discussion

3.1 Physical and chemical characterization of the FAs and the wastes

Particle size distribution analyses () were preformed with a solution of ethanol, preventing dissolution and aggregation. The results indicate that the FAs and HB particles are very fine (average of 3-21 μm).

Digestion analyses of the FAs (Figure 1A) show that both the SAFA and the COFA contain more the 70% of Al-Si content (This is in line with what reported in previous studies [20]). Moreover, the ashes contained appreciable amounts of soluble salts of Ca, Ba and Sr, and SO_4^{2-} and PO_4^{3-} ions. It can be noticed that several trace elements like B, As, Se, Mo, and Sb are also observed. HB (Figure 1A) indicated that the moisture content is ~25-27%, and also the occurrence of ankerite results in high contents of Mg (1.4%), and Fe (0.15%). Furthermore, as expected from the limestone nature of the HB, the material show low leach ability for most of the elements with only Se exceeding the non-hazardous values according to EC/33/2003/decision (Figure 4A). HCWs digestion (Figure 1B) analyses of the 5 HCWs show that the wastes are enriched with Ca, P, Cl, and also contain large amount of organic compounds (~20-34% of the total composition). Moreover, noticeable concentration of U, As, Cr, Mo, Se and several other toxic trace elements are shown. Leachable levels of the phosphate wastes were measured and indicated that the concentration levels of Sb, Se, and Mo are exceeding the non-hazardous levels (Figure 4B).

3.2 The results of the EN 12457-2 test for the aggregate products

In order to assess the potential risk of the scrubbed product the European Directive leaching test (EN 12457-2) was carried out. Fixation products were prepared with each one of the wastes, results for HB aggregate product (Figure 5A), and results of the HCWs aggregate product (Figure 5B) are given. Figure 5B shows that the product fixated with SAFA should be defined as a non-hazardous waste; therefore, it can be used for any purpose. However, HCWs aggregate product mixed with COFA (Figure 5C) results in leaching above the non-hazardous limit of Mo. Thus, only the SAFA-HCW APs were used in the concrete preparation.

Leaching results of the fixation products are shown in Figures 4-5. It is clear that the APs formed during the fixation procedure are considered as environmental safe materials. Comparison between the raw material and the APs leaching tests determine that the concentration that the concentrations of Ba, Cr, Mo, SO_4, Sb, Se and Zn in the leached solution decrease compared to that of the raw FAs, or the raw wastes. The decrease in leaching occurs as a result of the increased fixation of the concrete by itself. Moreover, from the SEM images it is clear that the small waste particles are adsorb onto the FA surface reducing the leach ability of most of the toxic trace elements.

3.3 Potential utilization of APs in concrete

As discussed previously, recent studies have shown that the APs formed *via* the fixation of hazardous wastes by the FA can be used as a partial substitute to sand in concrete. The potential utilization of the fixation products of hazardous wastes in concrete, was tested in two fixation products (2/1 (FA/Waste), and 4/1 (FA/waste). The types of APs were used as a partial substitute in concrete, in two replacement content, 50 and 100kg/m^3 concrete, and tested for compressive strengths and chloride ion penetration after 1-90 days of aging, (Figure 6). The results indicate that the final strength of the APs concrete, according to concrete standards, was stronger (up to 30% stronger) than regular concrete. Also, ion penetration test performed (Figure 7) according to ASTM 1202-12 indicate showed a decrease of the chlorides penetration compared to that of standard concrete. Leaching analyses of the concrete mixtures were performed in order to study the leach ability of toxic trace elements from the concrete. As can be seen in Table 1, it is clear that all elements leached out are below the non-hazardous limit according to the EN 12457-2, thus proving that it is an environmental safe concrete.

4. Conclusions

In this study we have examined the possibility of using SAFA and COFA as a scrubber for hazardous material from the phosphate and quarry industries. The conclusions that can be drawn from this study are as follows:

1) Both the SAFA and COFA can be used as efficient fixation reagents for different hazardous waste from the phosphate and quarry industries.
2) Small particles of the APs are adsorbed on the FA surface, whereas the lime and carbonate particles are preventing leaching of trace elements to the environment.
3) The potential economic value of the process would save very high operating costs of treatment, transporting, and storing of the hazardous wastes.
4) Utilization of the APs as a partial substitute to sand results in an environmental safe concrete and improved mechanical properties compared to regular concrete.

Finally, this study showed a better procedure of treating hazardous waste, which is highly economical and also forms environmental safe materials that can be used in the industry.

5. Acknowledgements

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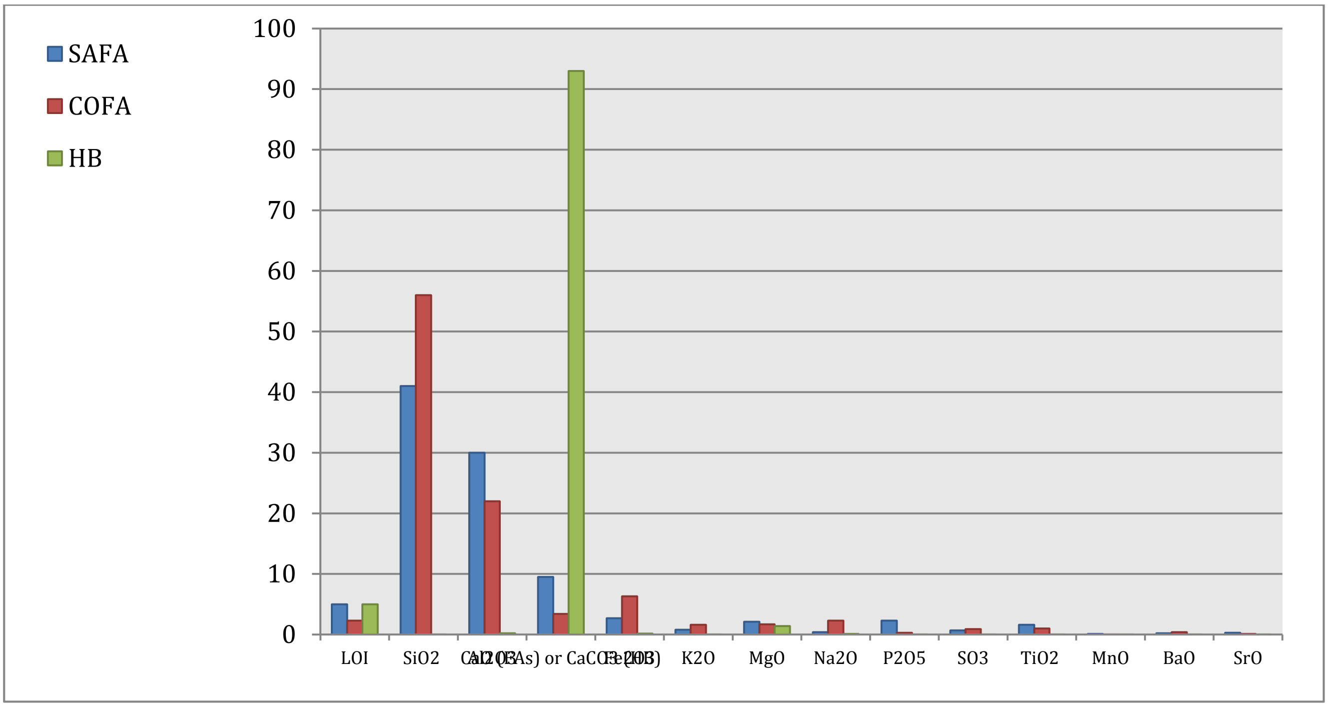
Tables

	S6 28days	S7 28days	S8 28days	S9 28days	S6 90days	S7 90days	S8 90days	S9 90days	Inert	Non hazardous	Hazardous
pH	14	14	14	14	13.3	13.9	14	14			
mg/kg											
SO_4	54.9	58.4	50	55.3	285	89.8	49.5	61.3	1000	20000	50000
Li	8.33	<0.001	<0.001	7.88	<0.001	<0.001	<0.001	<0.001			
Be	<0.001	0.08	0.04	<0.001	<0.001	<0.001	<0.001	<0.001			
Ti	<0.001	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
V	<0.001	0.02	0.02	<0.001	0.16	<0.001	<0.001	0.90			
Cr	0.23	<0.001	<0.001	0.31	2.4	1.50	1.20	<0.001	0.5	10	70
Mn	<0.001	<0.001	<0.001	0.00	<0.001	<0.001	<0.001	<0.001			
Co	0.01	0.07	0.07	0.01	<0.001	<0.001	<0.001	<0.001			
Ni	0.13	0.01	0.01	0.14	<0.001	<0.001	<0.001	<0.001	0.4	10	40
Cu	0.09	<0.001	<0.001	0.02	<0.001	<0.001	<0.001	<0.001			
Zn	0.09	0.06	0.06	<0.001	0.04	0.05	0.04	0.03	4	50	200
Ga	0.05	<0.001	<0.001	0.06	<0.001	<0.001	<0.001	<0.001			
Ge	<0.001	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
As	0.56	0.02	0.02	<0.001	<0.001	<0.001	<0.001	<0.001	0.5	2	25
Se	0.04	1.48	1.15	0.02	0.02	0.04	0.02	0.02	0.1	0.5	7
Rb	0.97	49.95	54.87	2.61	N.A	N.A	N.A	N.A			
Sr	130.60	<0.001	<0.001	86.33	N.A	N.A	N.A	N.A			
Zr	0.03	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
Nb	<0.001	0.28	0.28	<0.001	N.A	N.A	N.A	N.A			
Mo	0.40	<0.001	<0.001	0.24	0.2	0.20	0.10	0.20	0.3	10	30
Cd	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.04	1	5
Sn	0.08	0.08	0.07	<0.001	0.004	0.001	0.001	0.001			
Sb	0.12	15.95	18.97	0.25	N.A	N.A	N.A	N.A	0.02	0.7	5
Cs	44.62	<0.001	<0.001	31.61	0.4	3.2	4.9	11.6			
Ba	<0.001	0.02	0.02	<0.001	<0.001	<0.001	<0.001	<0.001	20	100	300
Tl	0.06	<0.001	<0.001	0.02	0.01	0.002	0.01	0.01			
Pb	0.03	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.5	10	50
Th	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
U	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			

Figures

Figure 1: Major compounds of the fly ashes, Hebron waste, and Haifa Chemical wastes



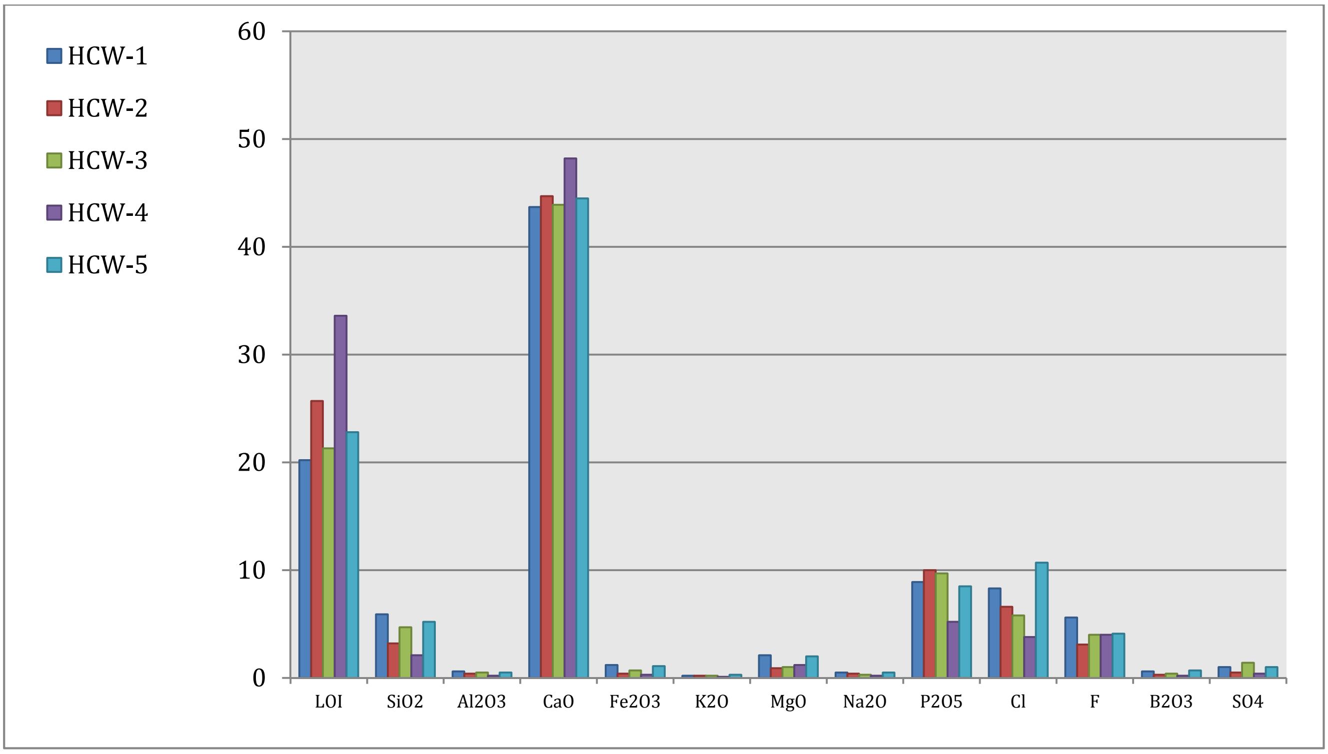


Figure 2: Experiments procedure of the fly ashes, wastes, and aggregate product

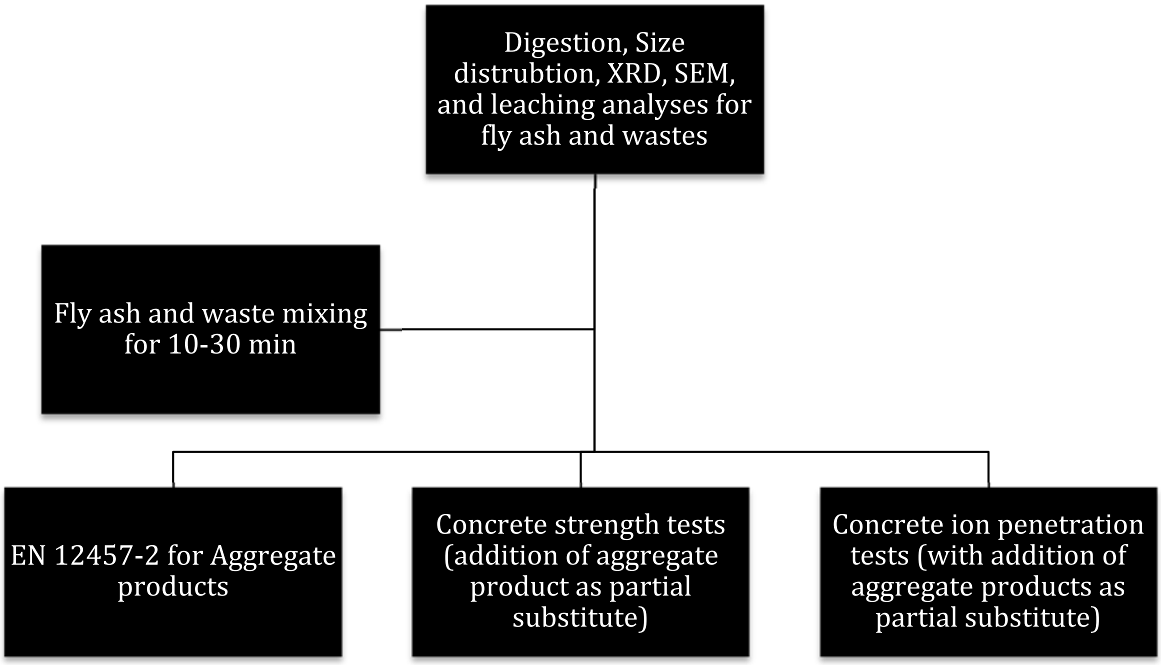


Figure 3: FA and wastes particles size

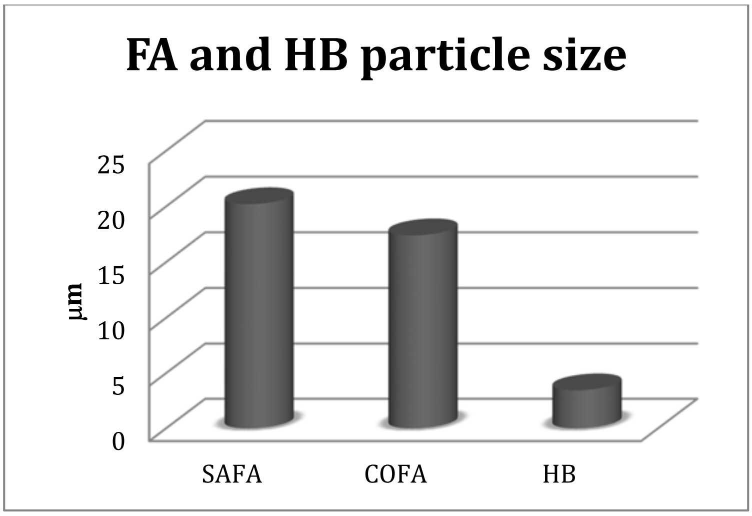
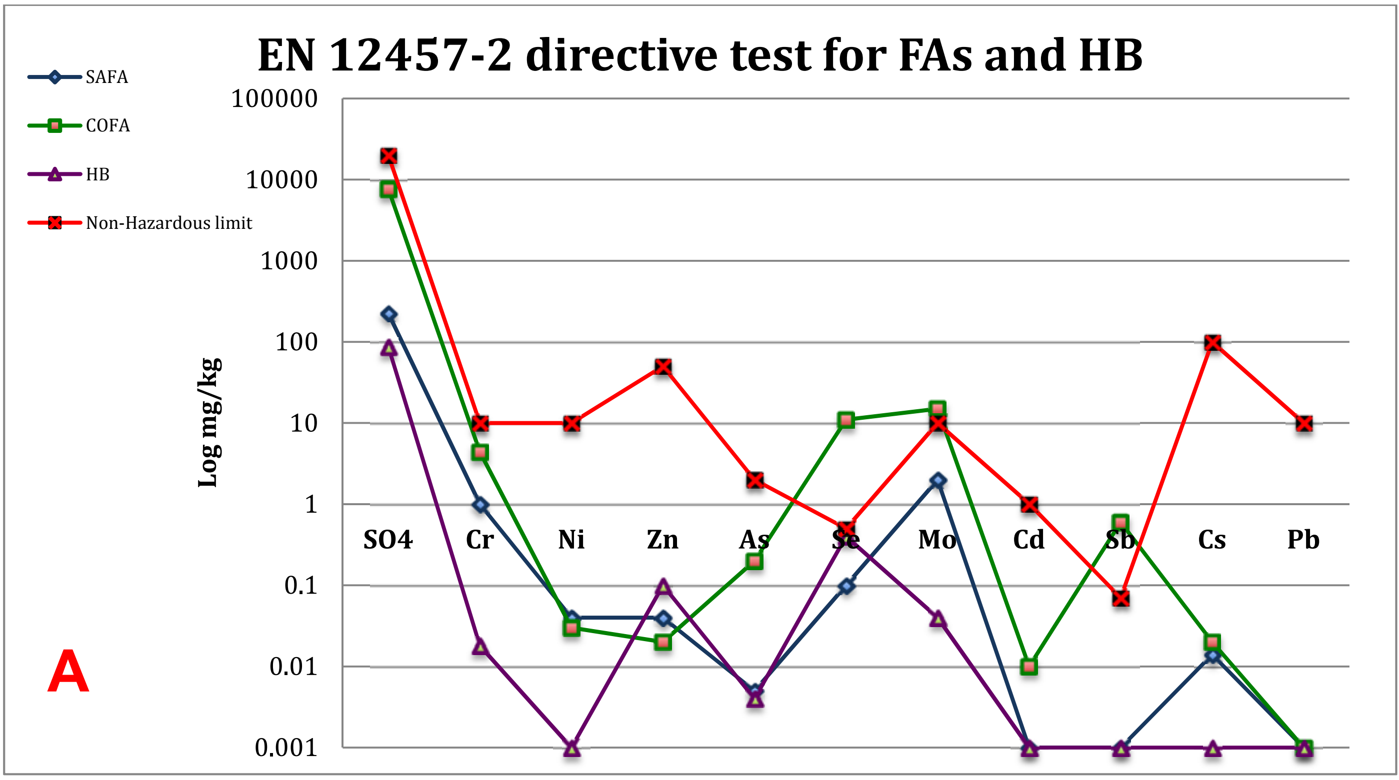


Figure 4: Leaching test according to the European Directive (EN 12457-2)



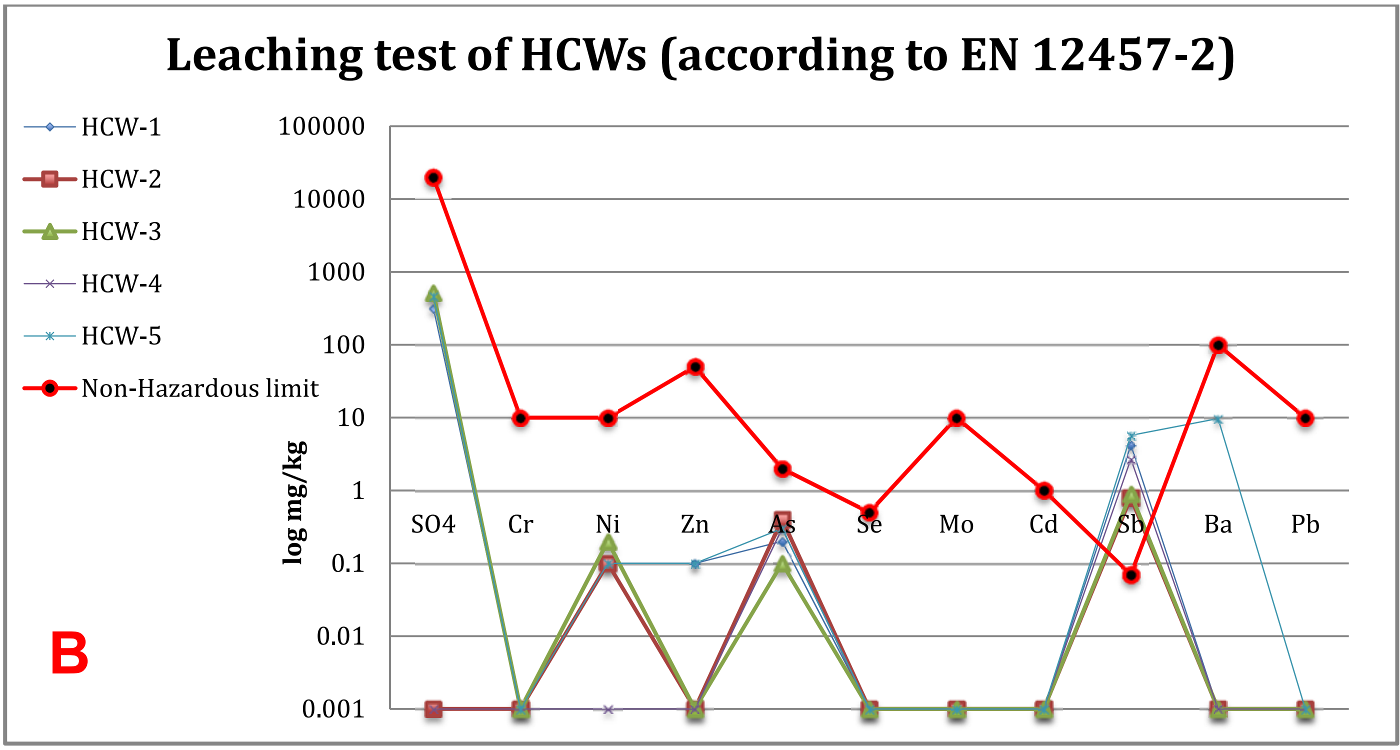
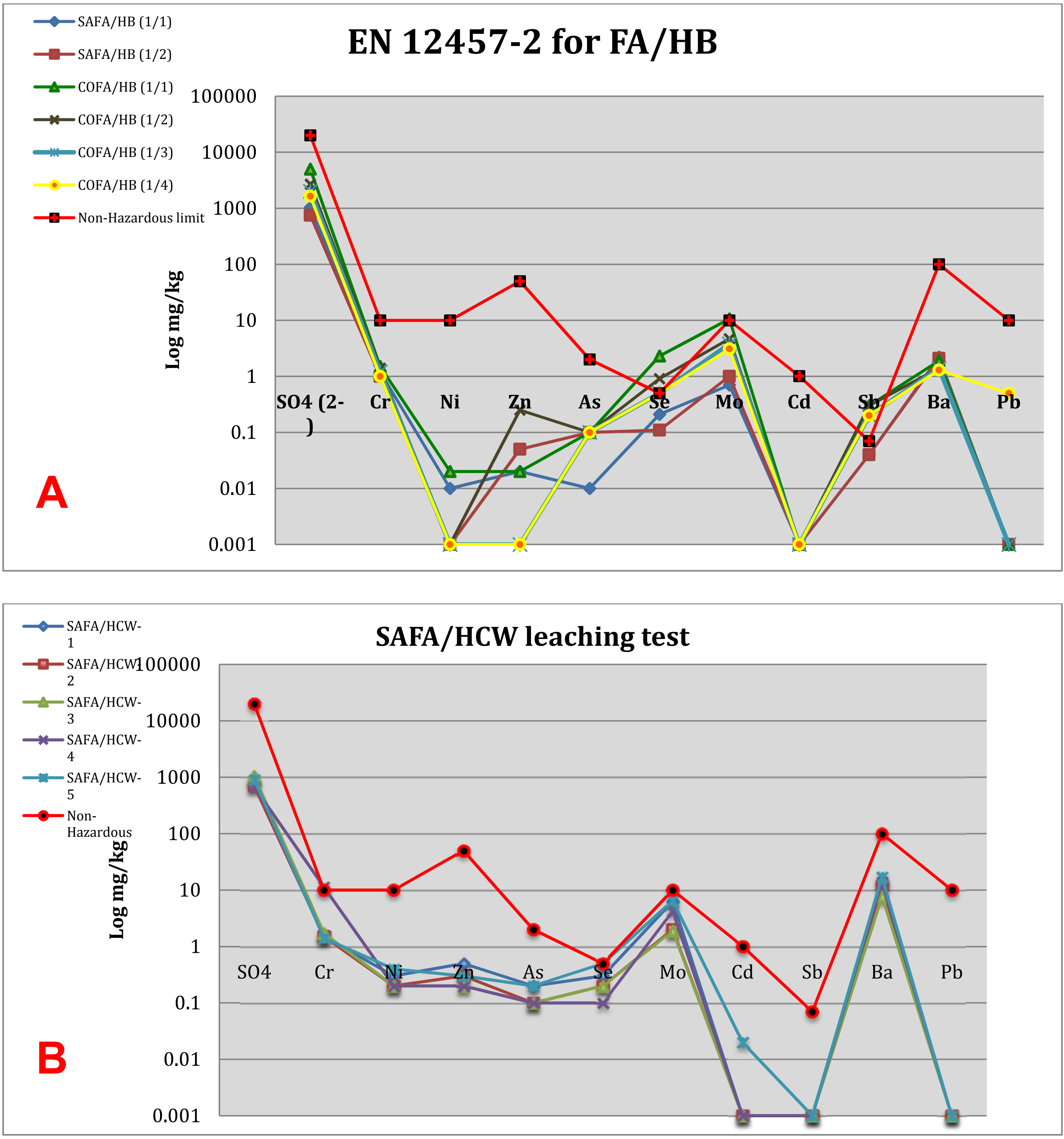
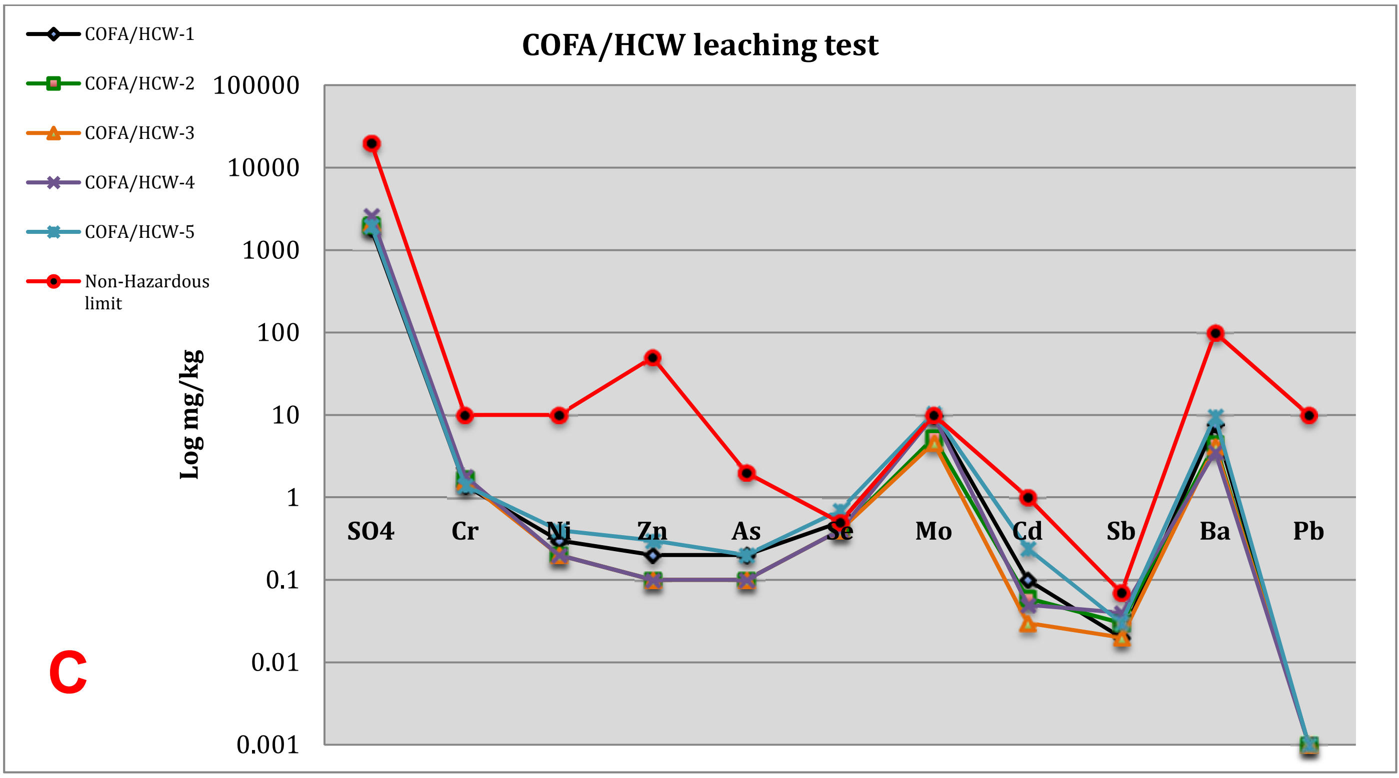


Figure 5: Leaching test according to the EN 12457-2 for aggregate products





COFA/HCW leaching test
COFA/HCW-1
COFA/HCW-2
COFA/HCW-3
COFA/HCW-4
COFA/HCW-5
Non-Hazardous limit
Log mg/kg
100000
10000
1000
100
10
1
0.1
0.01
0.001
SO4
Cr
Ni
Zn
As
Se
Mo
Cd
Sb
Ba
Pb
C

Figure 6: Strength tests of the concrete and the paste contain the aggregate product: (A) for HCW with South African fly ash, and (B) for HB with South African fly ash

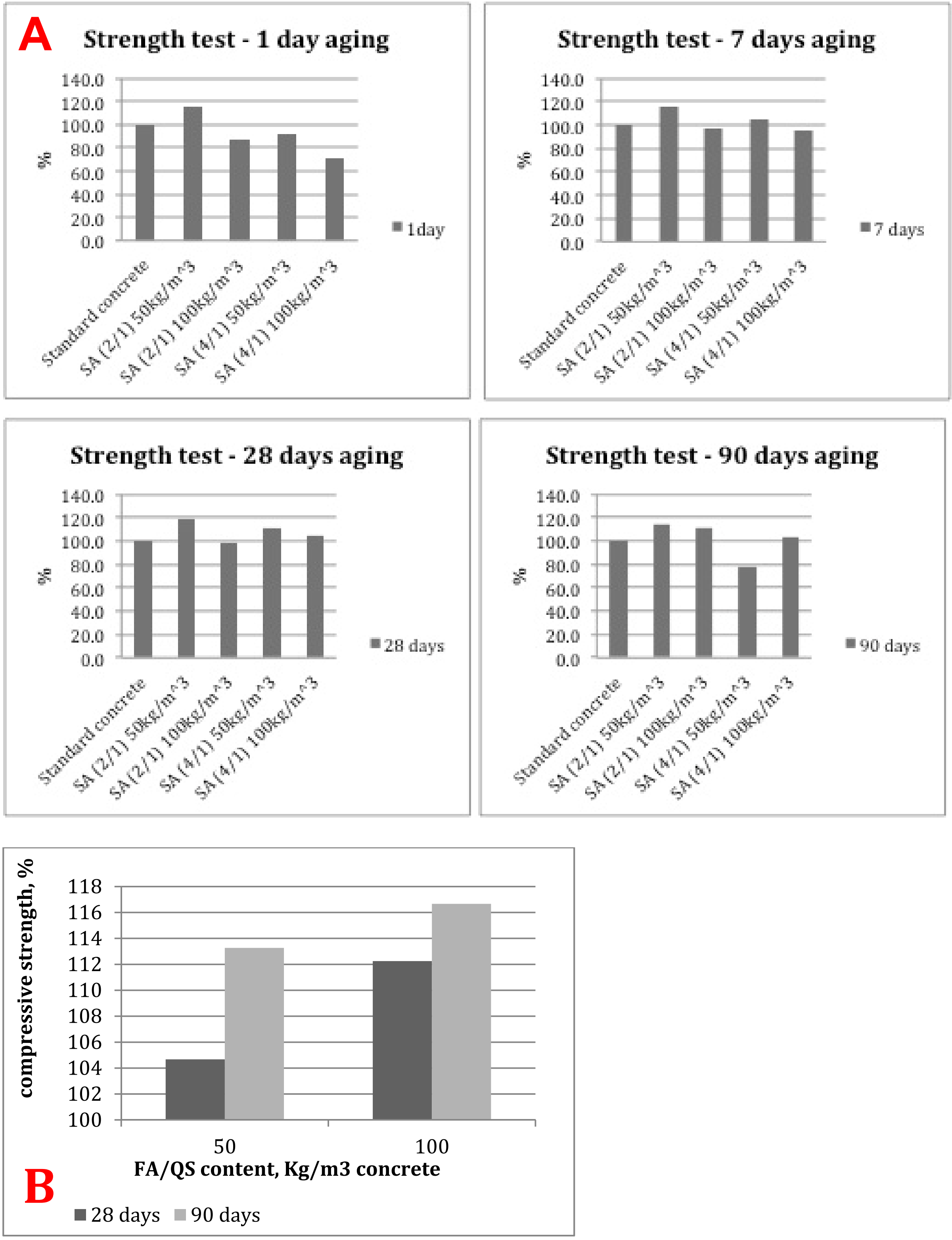


Figure 7: Ion penetration test for concrete and paste, contain the aggregate product, compared to standard concrete: (A) Paste composed of HCW with South African fly ash, and (B) Concrete composed of HB with South African fly ash