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Fly Ash as a Potential Scrubber of Acidic Wastes from the Phosphate Industries in Israel

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A B S T R A C T

Fly ash (FA) is produced in Israeli utilities via bituminous coal combustion. It is used as a cement additive or in concrete production, and its economic value is low.

The FA produced in Israel is very basic (defined as class F) owing to ambient air quality standards that impose low sulfur content in the imported coals. Because the lime content is high (in the South African coal, ~10 wt%), it is a good potential chemical scrubber to acidic wastes.

The phosphate industry in Israel produces mainly phosphate fertilizers and water-treatment products as well as phosphoric acid. The production methods rely heavily on dissolution of phosphate rock in strong acids, either sulfuric acid (Rotem Amfart plant) or hydrochloric acid (Haifa Chemicals plant). Thus, large quantities of acidic wastes are produced. These wastes have to be treated and neutralized before final storage. The treatment is based upon the addition of lime or calcium carbonate to the liquid waste.

We have checked the possibility of using FA to neutralize the acidity and fix the trace elements contained within the wastes. The results show that FA is an excellent scrubber and a very efficient absorber to the trace elements from the waste. The final product is an aggregate substitute, and because it passes the California Waste Extraction Test leach test, it can be used as a partial substitute for aggregates in the concrete industry.

Initial calculations show that the actual economic value of the ash is in the range of 3-5 times better than its present value in utilizing it as a building material (cement additive or as aggregate in the construction industry). Thus, using two wastes (FA and the acidic waste) can result in a green nonpolluting product with an appreciable economic value.

1. Introduction

Traditionally, the electric power in Israel was produced from the burning of heavy fuel oil. This mode of power production changed after the oil crisis in the 1970s, when the Israeli government decided to diversify its fuel supplies. In 1982, the first coal-fired power plant began operation in Hadera site at the sea beach. Since then, all new power-generating facilities have been fueled by coal (Israeli National Coal Ash Board [INCAB], 2013). In the near future, Israel will switch to natural gas as a fuel, as large reserves have been found near the coast of the Mediterranean Sea. Today, four coal-fired power plants, two in Hadera (Orot Rabin Utility) and two in Ashkelon (Rutenberg Power Utility), reside on the Mediterranean

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coast in Israel and burn annually more than 12 Mt of coal, which supplies ~63% of Israel's electricity (~29,200 GWH in 2013; INCAB, 2013).

The coals imported to Israel are from several continents; the main coal suppliers are South Africa (~41%), Colombia (32%), and Russia (~21%). Other countries such as Australia (~6%) and Indonesia (~1%) also export some coal to Israel (European Coal Combustion Products Association [ECOBA], 2009).

The amount of coal ash produced has increased appreciably with the demand for supplied electricity in the last 24 years, so that the total amount of ash generated by these power plants has risen up from about 400,000 tons in 1990 to more than 1.3 Mt last year (2012; INCAB, 2013).

1.1. Overview of coal fly ash utilization

Globally, less than 35% of the total amount of fly ash (FA) produced in the world is utilized. However, in the 15 industrialized countries of the European Union (EU), such as Germany, Belgium, and The Netherlands, more than 95% of the fly ash produced during 2009 was used (ECOBA, 2009), where ~48% of the fly ash was used in the construction industry. Moreover, during 2010, China had used 60% of its fly ash, mostly as a building material, but also in other construction projects (Moon, 2013). On the other hand, in the United States, only ~45% of the fly ash was used during 2012 (American Coal Ash Association, 2012). In Israel, ~50% of the fly ash generated so far was used for cement production (INCAB, 2013), and the rest was used in the construction industry and other minor applications (e.g., agriculture; Iyer and Scott, 2001; Basu et al., 2009; Arivazhagan et al., 2011).

Fly ash from coal-fired power stations has an important potential as a component in cement production and other construction processes (Scheetz and Earle, 1998; Foner et al., 1999; Kayali, 2005; Arivazhagan et al., 2011). In many cases, these markets are close to saturation because of the fly ash limit in the concrete mix. Experiments with fly ash in structural concrete have generally proved that the material can be used up to levels of ~30 wt% of the cement (McCarthy and Dhir, 1999). At this level, it has been demonstrated that its properties are comparable to Portland cement concrete of equivalent strength. The only other means of utilization is in the construction industry as a substitute to aggregates and cement in concrete production. Another mode of utilization of basic fly ash (class F) is for acid mine drainage mitigation (Rios et al., 2008).

1.2. Properties and classification of coal fly ash in Israel

Depending on the type of coal, particle size, and combustion conditions, 5–15% of the coal imported to Israel remains as ash, of which 3–10% is unburnt organic material. The coal ash is subdivided into fly ash and bottom ash, and the former accounts for ~90% of the ash (Nathan et al., 1999). The pulverized coal particles undergo combustion in the boiler via two sequential processes: (1) pyrolysis at ~800°C, and combustion of the emitted flammable gases, where the bottom ash is formed, and (2) high-temperature combustion, ~1700°C, where the remaining char is burnt, and the fly ash particles are formed.

This lighter fraction is carried away from the boiler by the hot combustion gases and separated by electrostatic precipitators (in Israel, fabric filters are not used). The resulting physical properties of the coal fly ash, such as moisture content, particle mass, glass composition, and the portion of unburned carbon, are dependent on coal properties, the combustion temperature of the coal, the air flow/fuel ratio, coal pulverization size, and rate of combustion (Bailey et al., 1999). Fly ash generally ranges in size from 0.5 to 200 μm, has a hydrophilic surface, and is extremely porous. During combustion, the mineral matter forms fly ash and is thermally altered into different minerals. Many of these are by themselves chemically very reactive or can be chemically activated. The mineral constituents of the fired coal, which is responsible for this chemical composition, include the clay minerals illite ($K_2[Si_6Al_2]Al_4O_{20}[OH]_4$) and kaolinite ($Si_4Al_4O_{10}[OH]_8$); sulfides (such as pyrite [cubic FeS_2] and marcasite [orthorhombic FeS_2]); carbonates such as dolomite $(Ca,Mg)(CO_3)_2$, ankerite $(Ca,Mg,Fe)(CO_3)_2$, calcite ($CaCO_3$), and siderite ($FeCO_3$); quartz (SiO_2); and apatite ($Ca_5[PO_4]_3[F,Cl,OH]$) (Grossman and Nathan, 1988). An appreciable portion of the coal fly ash is composed of tiny glass "bubbles" called cenospheres, which are filled with carbon dioxide or nitrogen and give the fly ash a lightweight characteristic. Cenospheres vary in particle size from 20 to 200 μm and can compose up to 20% by volume of the ash (Grossman and Nathan, 1988). The rapid cooling of the molten mineral matter in the pulverized coal combustion at approximately 1450°C in the power-station boilers forms these glassy aluminosilicate spheres, which probably retain the refractory elements. The principal property of these spheres is that they are pozzolanic, whereas the silica reacts with the calcium hydroxide $Ca(OH)_2$ released by hydration of calcium silicate to produce calcium silicate hydrate (Grossman and Nathan, 1988). This pozzolanic character is responsible for its cementitious behavior, so that the pulverized coal fly ashes represent a chemical reactivity that is directly correlated to the calcium content of the ash (Bailey et al., 1999). Granules of calcium oxide (CaO) have been identified on the surface of the spherical glass particles. These small formations are dispersed on the surface of the melted silica particles as a consequence of superficial tension (Catalfamo et al., 1997).

Coal is enriched with many elements, such as B, Cr, Cu, Ni, Mo, S, V, etc., during and following its formation (Polat et al., 2007). Therefore, these elements may also occur in the fly ash, which can contain from 20 to 50 trace elements (Bailey et al., 1999). The distribution of each element within the fly ash structure is different, however; the smaller the particle size, the higher is the trace elements content due to the increase in the surface/weight ratio (Catalfamo et al., 1997). Some elements are found in the aluminosilicate matrix (Ti, Na, K, Mg, Hg, Fe), and some are determined at the surface (As, Se, Mo, Zn, Cd, W, V, U), while others are in an acid-soluble phase (Ca, Sc, Sr, La, rare earth elements, and probably Ni). Mercury, As, and Se are also associate with C. The elements Mn, Be, Cr, Cu, Co, Ga, Ba, and Pb are dispersed between the matrix and the mineral matter (Catalfamo et al., 1997). The alkaline content depends on the concentration of the basic oxides and the amount of acidic substances such as SO_2, SO_3, and P_2O_5, which are also present in the coal fly ash.

1.3. Coal fly ash as a chemical scrubber for trace elements

Sludge handling and disposal are the most difficult and most costly aspects of wastewater treatment, and up to 60% of the total costs of operating and maintaining wastewater treatment plants are connected with sludge management (Polat et al., 2007). Increased population, industrialization, and novel products have resulted in larger amounts of sludge and wastes from many
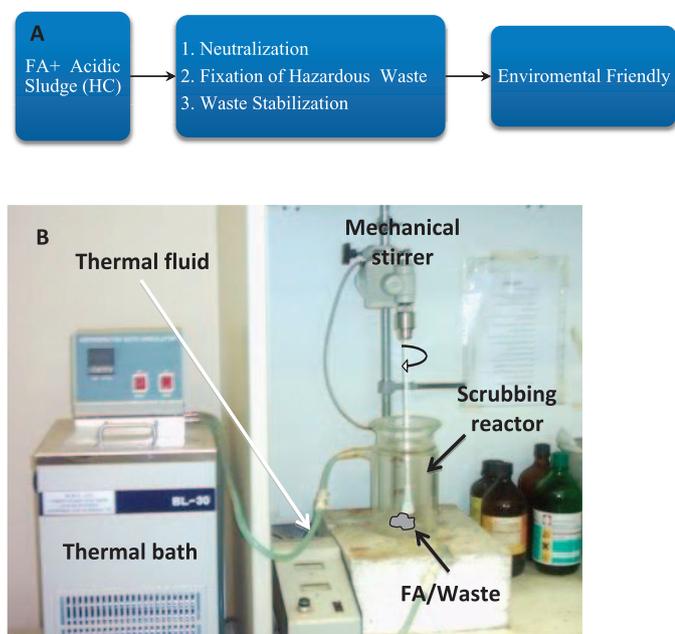
Fig. 1. (A) Procedure of fly ash (FA) utilization as a chemical scrubber of acidic wastes and (B) the experimental setup. HC = Haifa Chemicals.

different industrial activities in Israel (Viraraghavan and Wang, 1998), mostly classified as hazardous wastes because of the presence of heavy metals and high acidity. The handling and transport of such a waste are not simple issues. Due to the high costs of treatment methods for neutralization and removal of contained toxic metal ions, these sludges and wastes are currently transferred to the central hazardous waste treatment facility in Ramat Hovav (southern Israel). However, the acidic wastes of the phosphate industries are being neutralized at the production site using either lime or $CaCO_3$ in large settling ponds. Furthermore, after the pond is filled up, the neutralized wastes are covered with ~1 m of soil layer (for improved safe storage). Thus, the class F fly ashes produced in the Israeli coal combustion power plants can be an excellent potential neutralization reagent for these acidic wastes. Most heavy metals have negative ecological significance due to their toxic, carcinogenic, and accumulative behavior in animals and human beings. Cadmium, Co, Cr, As, Ni, and their compounds are considered highly toxic and even carcinogenic. Copper and Zn have been determined according to the U.S.

Environmental Protection Agency (US EPA) as aquatic toxins, whereas others such as Pb, Sb, and Hg are identified as poisons (Gupta and Torres, 1998; Gupta and Ali 2000). The adsorption of toxic metal ions by low-cost adsorbents such as fly ash is supposed to be a versatile and widely used method (Adriano, 1986; Ricou-Hoeffer et al., 2001) and has been studied extensively in the last decade. Most studies were carried out using an artificial waste solution, having an acidic character and predetermined amount of copper and zinc ions, and different fly ashes or fly ash/lime mixtures (Adriano, 1986; Viraraghavan and Wang, 1998).

Coal fly ash may be a good potential material for the treatment of wastewater. In addition to the positive adsorption results, Adriano (1986) reported that the efficiency of fly ash in the removal of toxic heavy metals depends on operating conditions. Lin and Chang (2001, 2002) found that when fly ash is mixed with wastewater, the final pH of the fly ash–waste mixture, the contact time, and the mineralogy of fly ash are the main factors in controlling the metal concentration in solution. Several experiments have been carried out to determine the optimal and best system for the removal of heavy metals from the solutions of treated water.

In the present study, a scrubbing procedure (Figure 1A) was used to investigate the neutralization behavior and the fixation of toxic heavy metals during the chemical reaction between basic coal fly ash and acidic waste. In that context, the fixation of hazardous elements in the product was checked, and other observations from our previous studies were confirmed (Peleg-Shepps, 2002). The results show that, indeed, fly ash can be an excellent and cheap way for neutralization of acidic wastes and also for the fixation of trace elements in the final product.

2. Materials and Methods

2.1. Chemicals

All water used in the research was MilliQ water (distilled water purified in a MilliQ system by Millipore Co.) having resistance of >18 MΩ/cm. Chemicals used throughout the study were of analytical reagent grade by Aldrich-Sigma, Frutarom, or Fluka.

2.2. Instrumentation

The pH of the solutions was determined by a pH meter (model pH510 by EUTECH). The trace elements were analyzed by

Table 1
Major and trace element contents of the South African coal fly ash

Major	Concentration (wt%)	Trace element	Concentration (mg/kg)	Trace element	Concentration (mg/kg)
SiO_2	42.78	Ag	13.6	Sb	<5
Al_2O_3	34.01	As	<10	Se	<20
CaO	10.35	B	240	Sn	<10
Fe_2O_3	2.86	Ba	2350	Sr	2500
MgO	2.40	Be	9.43	Tl	<50
P_2O_5	1.65	Cd	<2	V	180
TiO_2	1.83	Co	40	Zn	160
K_2O	0.67	Cr	150		
Na_2O	0.43	Cu	77		
SO_3	0.55	Mn	360		
LOI	4	Mo	11		
Total	~101	Ni	68		
		Pb	73		

Note: LOI = loss on ignition.

Table 2
Composition of the Haifa Chemicals acidic waste for trace elements

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Ag	5.3	Mn	4.57
As	2.39	Na	1.20×10^3
B	303	Ni	6.29
Ba	307	P	12.4×10^3
Be	0.147	Pb	2
Cd	2.74	Se	5.19
Co	0.84	Si	4.52×10^3
Cr	17.8	Sn	2
Cu	8.59	Sr	689
Fe	222	Ti	15.8
K	788	Tl	10
La	12.7	V	16
Mg	254	Zn	248

inductively coupled plasma–atomic emission spectrometer (ICP-AES; VISTA by Varian, detection limit of 0.1 ppm). The scrubbing process was performed with a temperature-controlled reactor built especially for the neutralization and fixation process (Figure 1B).

2.3. South African coal fly ash

The South African fly ash (SAFA) used in this study was produced via combustion of South African coal (14.7% ash content) in the Rutenberg Utility in Ashklon (The Israel Electric Corporation [IEC] utility). It represents ~41% of all fly ashes produced in Israel. Its composition with respect to the major compounds and trace elements is given in Table 1. The ash is very basic (high lime content ~10 wt%) and is classified as class F, since the $SiO_2 + Al_2O_3 + Fe_2O_3$ fraction makes up almost 80% of the material. The ash is rich in calcium oxide (~10 wt%) and contains a small amount of sulfur (<1%).

2.4. Haifa Chemicals acidic waste (HC)

The process of Haifa Chemicals is characterized by dissolving phosphate rock with solution of 22% hydrochloric acid (HCl). An organic solvent is used to extract the resulting phosphoric acid (H_3PO_4) from the mixture. The main components of the solvent are *n*-pentanol + 2-methyl butanol. As an excess of hydrochloric acid is used for the dissolution process, the waste produced is an acidic solution with low organic content (~0.1%). The material used in this study is the acidic waste of the extraction process and defined throughout the study as HC.

This acidic waste solution also contains small amounts of solid precipitate dispersion (<0.14%). It can be designated as a waste
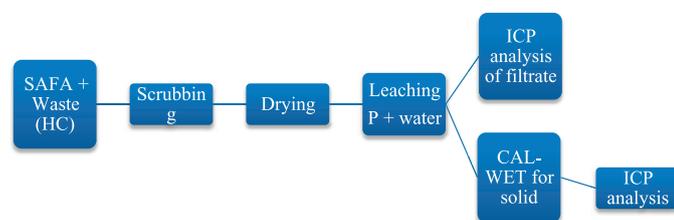
Fig. 2. General procedure of the experiments. SAFA = South African fly ash; HC = Haifa Chemicals; ICP = inductively coupled plasma; CALWET = California Waste Extraction Test.
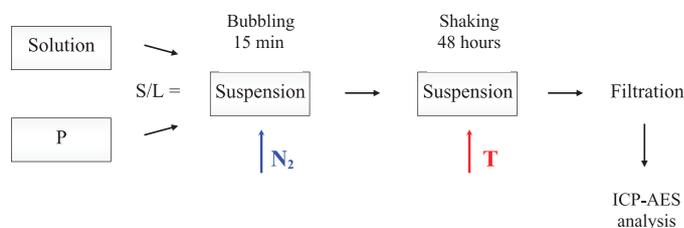
Fig. 3. Scheme of the California Waste Extraction Test procedure. ICP-AES = inductively coupled plasma–atomic emission spectrometer.

with low viscosity. The acidic content was determined via pH meter to be 1.04. The trace element content of the solution is given in Table 2.

2.5. Experiments with fly ash and acidic industrial waste

In this study, SAFA was investigated in order to determine its potential to neutralize acidic wastes from industrial processes (it has been reported that SAFA can be used as a fixation agent for trace elements and organic compounds; Polat et al., 2007; INCAB, 2013).

The general procedure followed in the experimental work is given in the scheme shown in Figure 2.

The first step is to mix the waste (HC) with SAFA. The process is exothermic, and heat is evolved. The evolution of heat is finished in 3–6 minutes after the beginning of the mixing. Six experiments were carried out using different fly ash waste liquid/solid (L/S) ratios. Thereby, proportions of HC/SAFA of 1:1, 1:2, and 1:4 were chosen. The procedure was carried out in a temperature-controlled reactor of 1.5-L capacity specially designed and built for this study (Figure 1B). During the scrubbing process (reaction time: 20 minutes), the mixture was stirred by a high-torque, low-speed stirrer; the stirring speed was 50 rpm, and the reactor temperature was maintained at 25°C. After 20 minutes, the product was taken from the reactor, and 11 samples (10 g) were transferred immediately into polyethylene vessels. These samples were used in leaching tests with MilliQ water. Each sample was agitated with 100 mL MilliQ water (S/L = 1:10). The wetted samples were kept in an orbital shaker at 200 rpm. After a certain leaching period (see below), a liquid sample was taken from the container. The leaching tests were repeated at least twice in two different identical experiments. Following this procedure, six samples were used for pH measurements (leaching periods: 0.5 hour, 1.5 hours, 6 hours, 1 day, 4 days, 16 days, 90 days), and five samples were taken for the determination of leached trace elements by ICP-AES technique (leaching periods: 0.5 hour, 6 hours, 1 day, 16 days, 90 days). In order to avoid precipitation in the solutions, the leached samples were filtrated through a 0.2-μm polytetrafluoroethylene (PTFE) membrane filter, and 4 mL aliquots of concentrated nitric acid (HNO_3) were added to the filtrate (40 mL) for the ICP-AES determination. The filtrates were kept in polyethylene bottles until analyzed. In addition, an identical procedure was followed using an extended reaction time of 3 days before leaching experiments were performed. The waste product (P) was analyzed for its fixation quality of the hazardous content via the California Waste Extraction Test (CALWET) leaching method.

Table 3

List of inorganic-persistent and bio-accumulative toxic substances and their soluble threshold limit concentration (STLC) and total threshold limit concentration (TTLC) (Lin and Chang, 2001, 2002)

| Element	TTLC (mg/kg)	STLC (mg/L)	Element	TTLC (mg/kg)	STLC (mg/L)	Element	TTLC (mg/kg)	STLC (mg/L)
Ag	500	5.0	Cr	2500	5	Ni	2000	20
As	500	5.0	Co	8000	80	Sb	500	15
Ba	10,000	100	Cu	2500	25	Se	100	1.0
Be	75	0.75	Pb	1000	5.0	Tl	700	7.0
Cd	100	1.0	Hg	20	0.2	V	2400	24
Cr^{6+}	500	5.0	Mo	3500	350	Zn	5000	250

2.6. The CALWET procedure

In Israel, the CALWET is used in order to classify hazardous waste. The CALWET procedure was developed in California, USA, for use in determining whether amounts of extractable constituents are available to leach to groundwater and, thereby, may have an impact on human health if the waste is discharged to landfill sites.

The CALWET (California Office of Administrative Law, 2005) is very similar to the well-known Toxicity Characteristic Leaching Procedure (TCLP 1311; US EPA, 1992) but differs in several parameters. It uses 0.2 M sodium citrate at pH 5.0 as the extraction solution, a solid/liquid (S/L) ratio of 1:10 (and maximal particle size of 1.0 mm in the grounded waste), and an extraction period of 48 hours (Figure 3). In contrast to the CALWET, the TCLP uses acetic acid with pH of 5.0, an S/L ratio of 1:20, a maximum particle size of 9.5 mm, and an extraction time of 18 hours.

This leaching solution makes the CALWET more aggressive toward certain wastes compared with the TCLP, the reason why the Californian extraction test was chosen in this study (in order to determine the maximum level of leaching of trace elements from fly ash waste products P). The waste products P from the neutralization fixation process of HC/SAFA in a ratio of 1:2 were chosen. Samples of 5 g of P were taken and crushed by a mortar to a fine powder, and these were mixed with 50 mL of sodium citrate solution in a cleaned polyethylene bottle. To prepare the extraction solution (sodium citrate), 1 L of MilliQ water was mixed with 38.4 g of citric acid ($C_6H_8O_7$). Afterward, this solution was titrated by 4.0 N sodium hydroxide (NaOH) to reach a final pH of 5.0 ± 0.1. After mixing the product sample into the extraction solution, the mixture was bubbled intensively by means of nitrogen (N_2). This step was carried out for a period of 15 minutes to remove and exclude the dissolved atmospheric oxygen from the extraction medium. Following this procedure, the plastic bottles were sealed. All samples were shaken for 48 hours in an orbital shaker incubator at a controlled temperature of 25°C. The same procedure was also done for a blank sample without the waste product P. After the extraction period of 48 hours, the samples were filtrated through a 0.45-μm membrane. The filtrates were analyzed by the ICP-AES to determine the trace element content in the leachate.

The regulatory limits for hazardous materials are given in two different threshold limit concentrations, TTLC and STLC, for several toxic elements (Table 3):
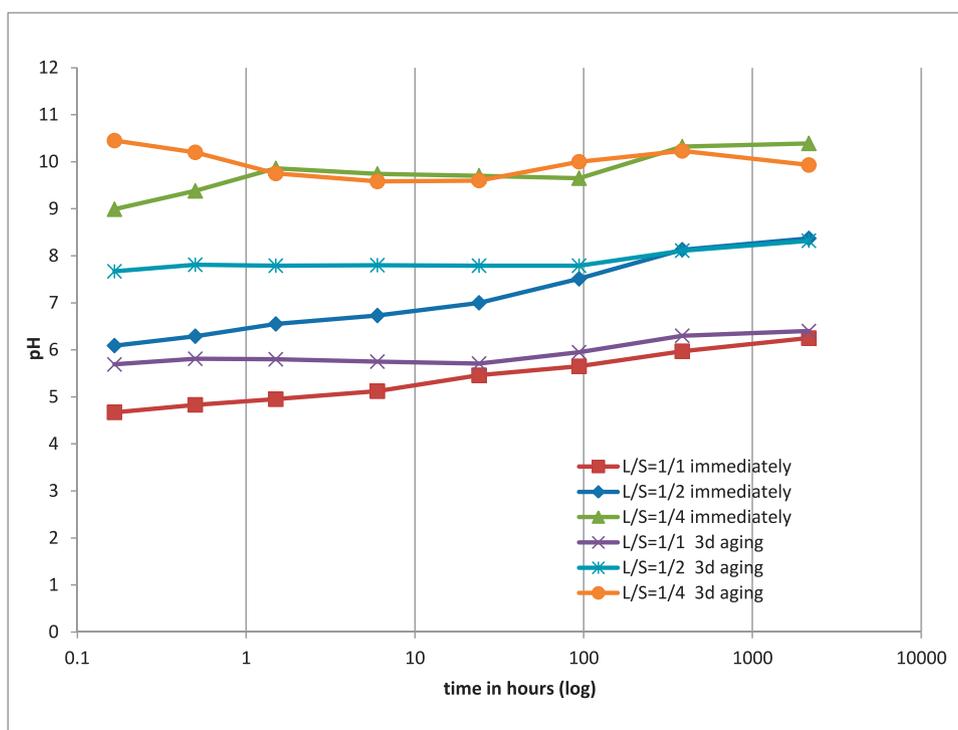
Fig. 4. Acidity/alkalinity of the leachates produced from the scrubbed product P. L/S = liquid/solid ratio.
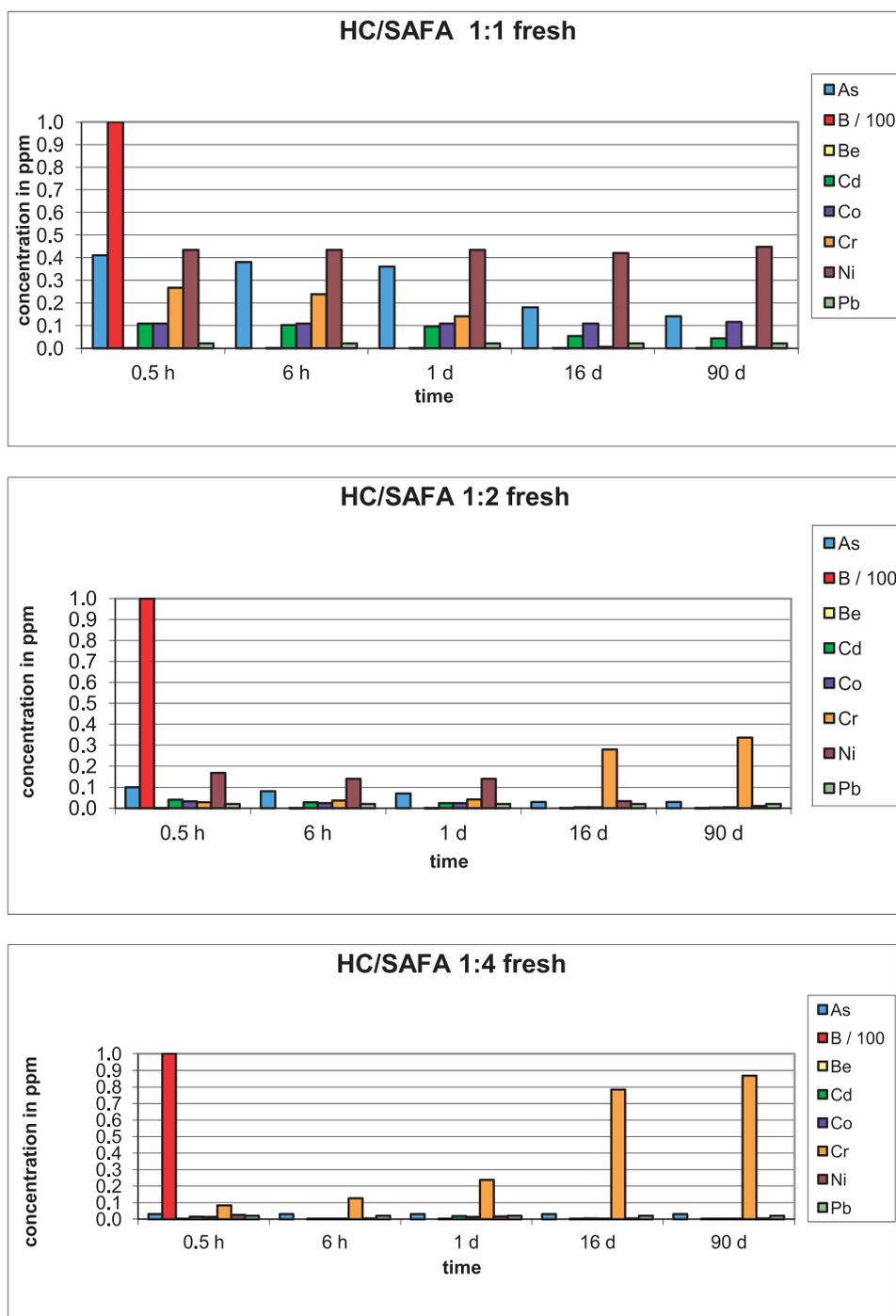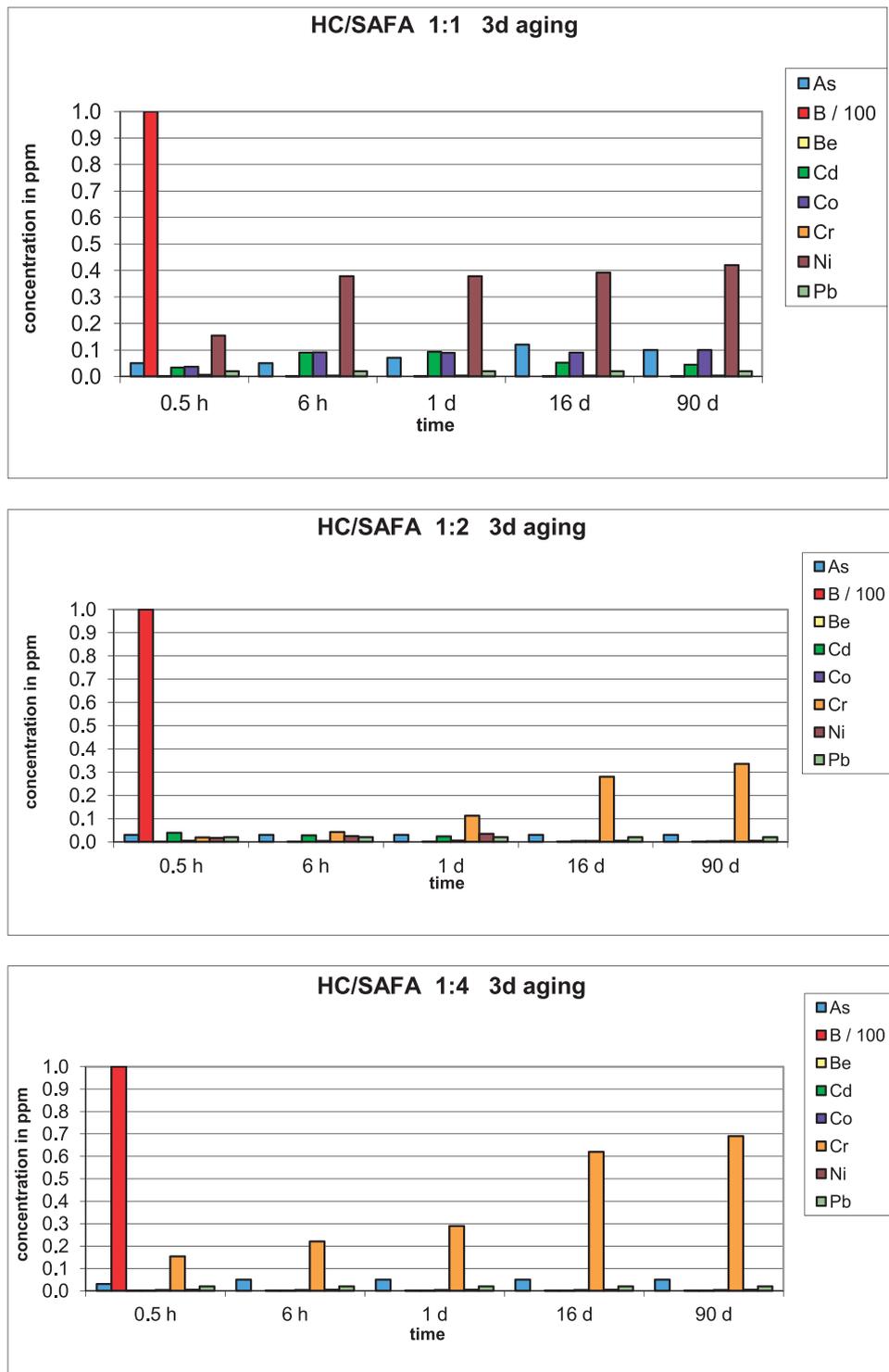
Fig. 5. Leaching of trace elements from fresh Haifa Chemicals acidic waste/South African coal fly ash (HC/SAFA) scrubbed product P and effect of HC/SAFA ratio.

- Total Threshold Limit Concentration (TTLC): "The TTLC is the maximum concentration allowed for a waste in solid or powdered form to be considered possibly nonhazardous. If the concentration of a waste is greater than the allowed TTLC value for that waste, the waste is toxic (and is thus hazardous waste)" (Peleg-Shepps, 2002).
- Soluble Threshold Limit Concentration (STLC): "The STLC is the maximum concentration allowed for a waste in liquid form to be considered possibly nonhazardous. If the concentration of a waste is greater than the allowed STLC value for that waste, the waste is toxic (and is thus hazardous waste)" (Peleg-Shepps, 2002).

3. Results and Discussion

3.1. Influence of shaking time and aging period

The acidic/alkaline nature of the product P was determined by measuring the pH of the leached solution of water shaken with P (L/S 1:10) for different shaking periods (Figure 2). As can be clearly seen (Figure 4), the ratio of the acidic waste (HC) to fly ash (SAFA) is the main parameter that determines the acidity/alkalinity of the product. For product with HC/SAFA ratios of 1:1, 1:2, and 1:4, pH values of 4.8, 5.7, and 6.2, respectively, were measured. Furthermore, another important factor is the aging of the fixation

Fig. 6. Leaching of trace elements from Haifa Chemicals acidic waste/South African coal fly ash (HC/SAFA) scrubbed product P aged 3 days and effect of HC/SAFA ratio.

waste product P. If the shaking is carried out with P that has aged for 3 days, the pH of the solution is raised appreciably (Figure 4): For HC/SAFA product ratios of 1:1, 1:2, and 1:4, pH values of 7.7, 9.2, and 10.7 were measured, respectively. This is an increase of more than 3–4 pH units. This result indicates that appreciable chemical/mineralogical changes occur in the solid scrubbed product P upon aging. This conclusion was corroborated by the trace elements leaching experiments (see below). Another parameter concerning the acidity/alkalinity of the product is the effect of

shaking time on the pH of the leached solution. It is observed that extending the shaking period by three orders of magnitude (from 30 minutes to 1000 hours) does not affect the pH by more than 0.5 unit. Furthermore, the aged product P (3 days) is much less affected by the shaking period.

The leaching tests, which were performed with fresh product of the scrubbing process (Figure 5), show that for all trace elements measured, there is a very good fixation of the products. The leaching experiments were carried out with products formed using

Table 4
Results of California Waste Extraction Test (CALWET) leaching test with Haifa Chemicals acidic waste/South African coal fly ash 1:2 scrubbing product P[1]

Element	STLC	CALWET leaching	% leaching of STLC
Ag	5	0.01	0.2
As	5	0.549	11
Ba	100	3.07	3
Be	0.75	0.086	11.5
Cd	1	<0.2	–
Co	80	0.205	0.25
Cr	5	2.08	41
Cu	25	0.61	2.5
Mo	350	0.436	0.12
Ni	20	0.441	2.2
Pb	5	0.028	0.5
Sb	15	0.052	0.3
Se	1	0.24	24
Tl	7	<0.1	–
V	24	3.69	15.4
Zn	250	1.79	0.7

[1] Concentrations are given in milligrams of element/liter of leachate. STLC = soluble threshold limit concentration.

HC/SAFA ratios of 1:1, 1:2, and 1:4, and the leaching was studied for periods of up to 90 days. The 1:4 product has the best fixation properties for all trace elements but Cr. This is probably because the chromium that is dissolved is in the hexavalent form (oxyanion CrO_4^{2-}), which is very soluble. As has been observed by Stam et al. (2001), ~5–10% of the total Cr present in the fly ash is in the hexavalent form, and the rest is insoluble trivalent chromium, as shown by Sheps et al. (1999). Most of the leaching occurs within the first few hours of the process; namely, there is no difference in the concentration of all trace elements leached (again Cr is exceptional in this context). The aging process of the solid product P (which has been observed in studies of the acidity/alkalinity of leaching) is also correlated to fixation of trace elements (Figure 6). In P samples aged for 3 days, the concentrations of the leached trace elements are much lower than those determined for the fresh products. Hydrolysis of the metal ions, adsorption, and precipitation at the surface of the fly ash particles seem to be the process for the fixation of the metals. Thus, the effect of HC/SAFA ratio is very important, stemming from the increase in the pH of the leached solution, which affects the fixation of the trace elements in the product.

Among the different HC/SAFA products P, the resulting product with the ratio of 1:2 is the one with the best fixation and neutralization properties. In order to test the leaching behavior of the aggregate product at more demanding leaching conditions, it was subjected to the CALWET procedure as was described in the Method section.

3.2. The results of the CALWET leaching test

In order to assess the potential risk of the scrubbing product, the CALWET leaching test was carried out. The optimal product with HC/SAFA ratio of 1:2 was tested. The results (Table 4) show that the product should be defined as a nonhazardous waste and thus can be used for any purpose. All the concentrations of the leached trace elements are definitely much below the STLC limit. The concentrations of the metals that were analyzed (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Pb, Mo, Ni, Sb, Se, Tl, V, and Zn) are less than the regulatory limits. Only Hg was not determined, because the Hg content in the ash and the acidic waste is very low (<0.5 ppm), and there is no problem of leaching of mercury.

Thus, the determined contents of all toxic metals leached (Table 4) are much lower than the STLC values. Even the chromium content is only 41% of the allowed STLC value. Consequently, the content of the leached elements from the product is within the regulatory limits. That means that the HAIFA-waste/SAFA scrubbing product P is defined as nonhazardous and can be used for any subsequent process. Polat et al. (2007) observed that the scrubbing product can be used as a good aggregate for concrete and brick production. This means that the product of mixing of two hazardous wastes, the coal fly ash and the acidic waste HC of Haifa Chemicals, is a green product, which can be used in the construction industry in Israel.

4. Conclusions

Scrubbing hazardous acidic waste with coal fly ash will result in a new environmentally friendly product. Mixing at a 1:2 ratio of Haifa Chemicals acidic waste from the phosphate plant with South African fly ash SAFA is optimal for the neutralization and fixation of environmental hazardous materials. It has been found that the neutralization of this mixture depends on the reaction period and the aging process of the scrubbed product.

The results of the metal content in the leachates show clearly that the fixation of toxic trace elements in the fly ash structure depends on the acid/alkaline properties of the product.

Depending on the toxic element, different pHs and reaction times are important parameters for their efficient fixation inside the fly ash structure. Therefore, elements like Cd, Co, and Ni need more time for fixation compared with Cr, Cu, Zn, or As. The largest content of toxic metals can be fixated in the product at pH values of ~6.5–7.5, and the reaction period should be longer than 1 day. After this period, fixation of elements such as, Cd, Co, Cr, Cu, Ni, and Zn is almost absolute.

Possible modes of fixation process are either cation exchange mechanism (probably via silicates and aluminates as the anionic groups, at the surface of the fly ash particles) or coordination bonding of trace elements (to the aluminate and silicate anions).

The official CALWET leaching procedure confirmed that the scrubbing products from the ash and the acidic waste can be used for landfill or as aggregate substitute in the cement industry, concrete production, etc. All contents of toxic metals inside the product and in the leachates from the CALWET are far less than the regulatory limits.

The expected operating costs for using coal fly ash as a neutralization and fixation reagent for acidic wastes from the phosphate industry in Israel show that the potential economic value of the process is appreciable. The price of coal fly ash in Israel is <$15/ton (including 150-km transport costs). The HC/SAFA optimal product (1:2 ratio) can be produced relatively cheaply: $30 for the fly ash + operational costs of the mixing = probably not more than $10/ton product. Thus, the overall cost will not exceed $60/ton of acidic waste. Furthermore, the product can be used as an aggregate substitute in the construction industry, meaning that no other disposal/storage costs are involved. The price of the present processes (neutralization of the acidic waste using lime or $CaCO_3$) is equivalent, however, the costs of heavy machinery to prepare the ponds for the neutralization is very expensive, not to mention that the scrubbed product has to be

covered by at least 1 m of soil after the pond is filled up. In the process studied here, the product is appropriate for utilization as a partial substitute of aggregates and cement for concrete production, and no storage is necessary. Thus, ab initio economic estimates show that the scrubbing process of acidic wastes by coal fly ash can be a process with high economical added value.

Acknowledgments

References

Adriano, D.C., 1986. Trace Elements in the Terrestrial Environment. Springer, New York.

American Coal Ash Association (ACAA), 2012. Coal combustion production & use statistics. http://www.acaa-usa.org/Portals/9/Files/PDFs/1966-2012_FlyAsh_Prod_and_Use_Charts.pdf, accessed 10 March 2014.

Arivazhagan, K., Ravichandran, M., Dube, S., Mathur, V., Khandakar, R., Yagnanarayana, K., Kamal Pasha, M., Sinha, A., Sarangi, B., Tripathi, V., 2011. Effect of coal fly ash on agricultural crops: showcase project on use of fly ash in agriculture in and around thermal power station areas of National Thermal Power Corporation Ltd., India. In: World of Coal Ash Conference WOCA, Denver, CO, 9–12 May 2011. http://www.flyash.info/2011/016-Arivazhagan-2011.pdf

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. Water Research 33, 2469–2479.

Basu, M., Pande, M., Bhadoria, P., Mahapatra, S., 2009. Potential fly-ash utilization in agriculture: a global review. Progress in Natural Science 19, 1173–1186.

California Office of Administrative Law, 2005. Code of Regulation. Title 22 Section 66261.126 Appendix II. Waste Extraction Test (WET) Procedures. http://ccr.oal.ca.gov, accessed 10 March 2014.

Catalfamo, P., Pasquale, S.D., Corigliano, F., Mavilia, L., 1997. Influence of the calcium content on the coal fly ash features in some innovative applications. Resources, Conservation and Recycling 20, 119–125.

European Coal Combustion Poducts Association e.V. (ECOBA), 2009. What are CCPs, Utilisation. http://www.ecoba.com/ecobaccputil.html, accessed 10 March 2014.

Foner, H.A., Robl, T.L, Hower, J.C., Graham, U.M., 1999. Characterization of fly ash from Israel with reference to its possible utilization. Fuel 78, 215–223.

Grossman, S.L., Nathan, Y., 1988. The mineralogy and chemistry of coal ash generated by the Hadera M.D. power station. Journal of Coal Quality 7, 22–26.

Gupta, K.V., Ali, I., 2000. Utilization of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. Separation and Purification Technology 18, 131–140.

Gupta, K.V., Torres, N., 1998. Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent. Hazardous Materials 57, 243–248.

Israeli National Coal Ash Board (INCAB), 2013. General info. http://www.coal-ash.co.il/english/info.html, accessed 10 March 2014.

Iyer, R.S., Scott, J.A., 2001. Power station fly ash—a review of value-added utilization outside of the construction industry. Resources, Conservation and Recycling 31, 217–228.

Kayali, O.A., 2005. High performance bricks from fly ash. In: World Coal Ash Conference WOCA, Lexington, KY, 11–15 April 2005.

Lin, C.J., Chang, J.E., 2001. Effect of fly ash characteristics on the removal of Cu(II) from aqueous solution. Chemosphere 44, 1185–1192.

Lin, C.J., Chang, J.E., 2002. EXAFS study of adsorbed Cu(II) on fly ashes with different residual carbon contents. Chemosphere 46, 115–121.

McCarthy, M.J., Dhir, R.K., 1999. Towards maximizing the use of fly ash as a binder. Fuel 78, 121–132.

Moon, S.T., 2013. World of Coal Ash (WOCA), Regulatory and Legal Applications: Fly Ash Use in Cement and Cementitious Products. http://energy.caer.uky.edu/AshSymposium/AshLibraryAgenda.asp#2013, accessed 10 March 2014.

Nathan, Y., Dvorachek, M., Pelly, I., Mimran, U., 1999. Characterization of coal fly ash from Israel. Fuel 78, 205–213.

Peleg-Shepps, S., 2002. Potential Risk of Leaching of Trace Elements from Coal Fly Ash. Ph.D. thesis, Ben-Gurion University of the Negev, Israel.

Polat, M., Guler, E., Lederman, E., Cohen, H., 2007. Neutralization of an extremely acidic sludge and stabilization of heavy metals in flyash aggregates. Waste Management 27, 482–489.

Ricou-Hoeffer, P., Lecuyer, I., Cloirec, P.L., 2001. Experimental design methodology applied to adsorption of metallic ions onto fly ash. Water Research 35, 965–976.

Rios, C.A., Williams, C.D., Roberts, C.L., 2008. Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. Hazardous Materials 156, 23–35.

Scheetz, B.E., Earle, R., 1998. Utilization of fly ash. Solid State & Material Science 3, 510–520.

Sheps, S., Finkelman, R.B., Councell, T.B., Cohen, H., 1999. Leaching of chromium from coal fly ash: European coal geology. In: Proceedings of the 3rd European Coal Conference (Nakoman, E., ed.). Dokuz Eylül University, Izmir, Turkey, pp. 475–480.

Stam, A.F., Meij, R., Winkel, H.T., Eijk, R.J.V., Huggins, F.E., Bram, G., 2001. Chromium speciation in coal and biomass co-combustion products. Environmental Science & Technology 45, 2450–2456.

U.S. Environmental Protection Agency (US EPA), 1992. Toxicity Characteristic Leaching Procedure (TCLP) – Method 1311. http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf, accessed 10 March 2014.

Viraraghavan, T., Wang, S., 1998. Wastewater sludge conditioning by fly ash. Waste Management 17, 443–450.