

# **Synergetic Effect of Coal Flyash as a Scrubber to Acidic Wastes of the Phosphate Fertilizers Industry**

**Haim Cohen<sup>1</sup> Eli Lederman<sup>2,3</sup> , Mike Werner<sup>1b,4</sup>,  
Ithamar Pelly<sup>1</sup>, Mehmet Polat<sup>5</sup>**

1. a. NRCN and b. Ben-Gurion University of the Negev, Chemistry Department, Box 653 Beer-Sheva 84105, Israel.
2. Geological and Environmental Sciences Dept, Ben-Gurion University of the Negev, Box 653, Beer-Sheva 84105, Israel
- 3 Environmental Unit, Beer-Sheva Municipality, Box 15 Beer-Sheva 84105, Israel.
- 4 Bergakademie, Technische Universitat Freiberg, Freiberg, Germany.
- 5 Chemical Engineering Department., Izmir Institute of Technology, Urla 35430, Izmir, Turkey.

00972-8-6472170 00972-8-9200749 [hcohen@bgumail.bgu.ac.il](mailto:hcohen@bgumail.bgu.ac.il) or [ledermae@bgumail.bgu.ac.il](mailto:ledermae@bgumail.bgu.ac.il)

## Abstract:

Fly ash is produced in Israeli power stations via bituminous combustion. At present 1.5 million tons of fly ash are produced annually in 4 power stations and only ~50% of it is used as a cement additive. The rest is utilized in the construction industry.

Environmental regulations in Israel define fly ash as a non hazardous material but still the regulations impose that any potential utilization needs special permit from the Ministry of Environmental Affairs. Thus the regulations imply that the ash to be used will be in accordance with the CALWET or the improved EPA-TCLP1311 leaching methods.

The fly ash produced in Israel is very basic due to the low sulfur appreciable (up to 12%) mineral matter of the imported coals. Thus it is a good potential chemical scrubber to acidic wastes.

The fertilizer industry in Israel produces mainly phosphate based products. The production methods rely heavily on dissolution of phosphate rock in strong acids. Thus large quantities of acidic wastes are produced. These wastes have to be treated before final storage.

We have checked the possibility of using the fly ash to neutralize the acidity and fix the heavy toxic elements contained within the wastes.

The results show that the fly ash is an excellent scrubber and also that its large surface area serves as a very efficient absorber to the toxic heavy metals from

the waste. The final product is an aggregate substitute and as it passes the CAL WET leach test it can be used as a substitute for aggregates in the concrete industry.

Initial calculations show that the actual economic value of the ash is in the range of 3 to 5 times better than its present value in utilization as a cement additive or in the construction industry.

Thus using two wastes (fly ash and the acidic waste) can result in a green nonpolluting product with an appreciable economic value.

## 1. Introduction

Until the oil crisis in the 1970s, only heavy oil was used for generation of electricity. Only 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 [1]. Today four coal-fired power plants two in Hadera (Orot Rabin Power Plants) and two in Ashkelon (Rutenberg Power Plants) reside on the Mediterranean coast in Israel and burn annually more than 11 million tons of coal supplying ~71 % of Israel's electricity (~29200 GWH) [2].

The coal is imported from four continents to Israel whereas the current basket of suppliers is divided between South Africa (ca. 51 %), Colombia (ca. 20 %), Australia (ca. 16 %) and Indonesia (ca. 13 %) [3].

The amount of coal ash produced increased appreciably with the demand for supplied electricity in the last ten years, so that the total amount of ash generated by these power plants rose up from about 400,000 tons in 1990 to more than 1.3 million tons last year.

From the moment that coal has been used as fuel for power generation, the question of fly ash utilization has been under much discussion. Until few years ago fly ash had been handled in three main ways in Israel: (I) As an additive to cement (up to 10 wt%) as a pozzolanic admixture (II) Sea dumping 50 km from the coast by barges (~1.1 M tons, 1982-1999) and (III) Stockpiled in embankments around the power stations (~1.2 M tons 1982-1999). These methods have reached their maximum capacity, as sea dumping has been forbidden by the Ministry of the Environment because of environmental regulations while reclamation was restricted because of the risks of leaching of heavy metals into the aquifer [4].

### 1.1 Overview of coal fly ash utilization

Globally, less than 25 % of the total amount of fly ash (FA) produced in the world is utilized [5, 6]. However, in industrialized countries like Germany, Belgium and the Netherlands more than 95 % of the fly ash produced during 1996 was used [7]. In the United Kingdom, FA-utilization was ~50 % during 1998 [8]. In Israel, ~ 65 % of the fly ash generated so far were used for cement production [4]. On the other hand, in the USA and

China, huge quantities of fly ash are produced and its utilization levels were about 32 % and 40 %, respectively, in 1995 [7].

Fly ash from coal-fired power stations has an important potential as a component in cementations and other construction processes. 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 [8]. At this level it has been demonstrated that its properties are comparable to Portland cement concrete of equivalent strength. Thus the only other mean of utilization is in the construction industry.

## 1.2 Properties and classification of coal fly ash

Depending on the type of coal, particle size and combustion conditions, 5-15 % of the coal remains as ash, of which 3-10 % are unburnt organic material. The coal ash is subdivided into fly ash and bottom ash whereas the former accounts to ~ 90 % of the ash [9]. This lighter fraction is carried away from the boiler by the hot combustion gases and separated by the electrostatic precipitators. 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 [5]. Fly ash generally ranges in size from 0.5 to 200 microns, 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 is comprised of the clay minerals, illite ( $[\text{OH}]_4\text{K}_2[\text{Si}_6\text{Al}_2]\text{Al}_4\text{O}_{20}$ ) and kaolinite ( $[\text{OH}]_8\text{Si}_4\text{Al}_4\text{O}_{10}$ ); sulfides (such as pyrite cubic  $\text{FeS}_2$  and marcasite orthorhombic  $\text{FeS}_2$ ); carbonates like dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), ankerite ( $2\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot \text{FeCO}_3$ ), calcite ( $\text{CaCO}_3$ ) and siderite ( $\text{FeCO}_3$ ); quartz ( $\text{SiO}_2$ ) and apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) [8]. 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 the lightweight characteristic. Cenospheres vary in particle size from 20–200 microns and can compose up to 20 % by volume of the ash [5]. 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. The principal property of these spheres is that they are pozzolanic, whereas the silica reacts with the calcium hydroxide  $\text{Ca}(\text{OH})_2$  released by hydration of calcium silicate to produce calcium silicate hydrate [6]. 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 [5]. Granules of calcium oxide ( $\text{CaO}$ ) 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 [10].

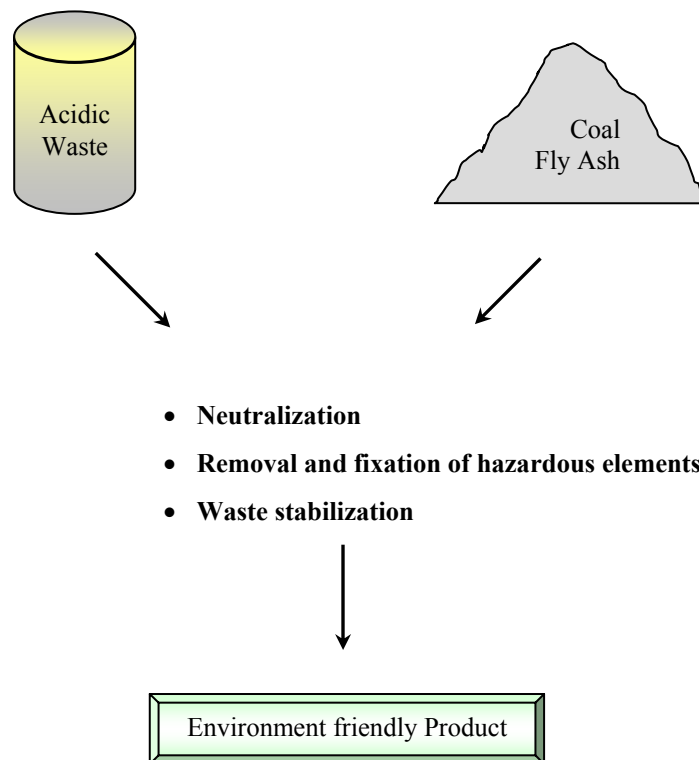
Coal is enriched with many elements such as B, Cr, Cu, Ni, Mo, S, V, etc. during and following its formation [11]. Therefore these elements may also occur in the fly ash, which can contain from 20 to 50 trace elements [5]. The distribution of each element within the fly ash structure is different from each other, however the smaller is the particle size the higher is trace elements content due to the increase in the surface/weight-ratio [9]. Some elements are found in the aluminosilicate matrix (Ti, Na, K, Mg, Hg, Fe), some are determined at the surface (As, Se, Mo, Zn, Cd, W, V, U) while others are discovered in an acid soluble phase (Ca, Sc, Sr, La, rare earth elements, and probably Ni). The elements Mn, Be, Cr, Cu, Co, Ga, Ba and Pb are dispersed between the matrix and the mineral matter [11]. The alkaline content depends on the concentration of the basic oxides and the amount of acidic substances such as SO<sub>2</sub>, SO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>, which are also presented in the coal fly ash.

### **1.3 Coal fly ash as a chemical scrubber for heavy metals**

Sludge handling and disposal is the most difficult and most costly aspect of wastewater treatment and up to 60 % of the total costs of operating and maintaining wastewater treatment plants is connected with the sludge management [12]. Increased population, industrialization and novel products have resulted in larger amounts of sludge and wastes from many different industrial activities in Israel [13] mostly classified as hazardous wastes because of the presence of heavy metals and the high acidity. The handling and transport of such a waste is not simple. 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). Most heavy metals have negative ecological significance due to their toxic, carcinogenic and accumulative behavior in animals and human beings. Cadmium, cobalt, chromium, arsenic, nickel and their compounds are considered highly toxic and even carcinogenic. Copper and zinc have been determined by the U.S. EPA as aquatic toxins whereas others such as lead, antimony and mercury are identified as poisons [14]. The adsorption of toxic metal ions by low cost adsorbents such as fly ash is supposed to be a versatile and widely used method [15] 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 [13, 15-18].

Coal fly ash may be a good potential material for the treatment of wastewater. In addition to the positive adsorption results it is reported [19] that the efficiency of fly ash in the removal of the toxic heavy metals depends on operating conditions. It has been found [19] 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 this study a scrubbing procedure, which is given in figure 1 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 in our previous studies could be confirmed [20]. The results show that indeed, FA can be an excellent and cheap way for neutralization of acidic wastes and also for the fixation of trace elements in the final product.



**Figure 1:** Basic procedure of fly ash utilization as a chemical scrubber for acidic sludge or waste.

## 2. Materials

### 2.1 Chemicals

All water used in the research were deionized water (distilled water passed through a MilliQ water purifier Millipore Co.) having resistance of  $>18\text{M}\Omega/\text{cm}$ . Chemicals used in the study were of AR grade of Aldrich-Sigma, Frutarom or Fluka.

### 2.2 Instrumentation

The pH of the solutions was determined by a pHmeter (model pH510 by EUTECH). The trace elements were analyzed by ICP AES spectrometer (VISTA by Varian). The scrubbing process was performed in a thermostated reactor built especially for the neutralization and fixation process (see below).

### 2.3 South African coal fly ash (SAFA)

The fly ash used was generated from South African coal combustion (13.9 % ash content) in Rutenberg A Power Plant in Ashkelon ( Israel Electric Corporation -IEC) and it represents ~61 % of all ash produced in Israel. Its composition with respect to the major compounds and trace elements is given in Tables 1,2. The ash can be classified as class F since the  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  fraction makes up almost 80% of the material. The ash is rich in calcium oxide (~10 wt %) and contains a small amount of sulfur. ( $\ll 1\%$ )

**Table 1:** Trace Elements content of the South African coal fly ash<sup>a</sup>

| Element | Conc. | Element | Conc. | Element | Conc. | Element | Conc. |
|---------|-------|---------|-------|---------|-------|---------|-------|
| Ag      | 13.6  | Cd      | <2    | Mo      | 11    | Sn      | <10   |
| As      | <10   | Co      | 40    | Ni      | 68    | Sr      | 2,500 |
| B       | 240   | Cr      | 150   | Pb      | 73    | Tl      | <50   |
| Ba      | 2,350 | Cu      | 77    | Sb      | <5    | V       | 180   |
| Be      | 9.43  | Mn      | 360   | Se      | <20   | Zn      | 160   |

<sup>a</sup> Concentrations are given by mg trace element in 1 Kg of ash.

**Table 2:** Analysis of South African (SA) coal fly ash for major components

| Compound                | wt%   | Compound              | wt%   |
|-------------------------|-------|-----------------------|-------|
| $\text{SiO}_2$          | 42.78 | $\text{TiO}_2$        | 1.83  |
| $\text{Al}_2\text{O}_3$ | 34.01 | $\text{Na}_2\text{O}$ | 0.43  |
| $\text{CaO}$            | 10.35 | $\text{K}_2\text{O}$  | 0.67  |
| $\text{Fe}_2\text{O}_3$ | 2.86  | $\text{SO}_3$         | 0.55  |
| $\text{MgO}$            | 2.40  | C                     | 4 – 5 |
| $\text{P}_2\text{O}_5$  | 1.65  |                       |       |

## 2.4 HAIFA Chemicals acidic waste (HC)

The process of HAIFA Chemicals is characterized by mixing phosphate rock with 22 % of hydrochloric acid (HCl). An organic solvent is used to extract the phosphoric acid ( $H_3PO_4$ ) formed from the mixture. The main components of the solvent are n-pentanol + 2-methyl butanol. Thus the waste produced is an acidic solution with low organic content (~0.1%). The material used in this study is the waste of the extraction process.

This acidic waste solution contains also small (<0.14%) of solid precipitate dispersion. It can be designated as a waste with low viscosity. The acidic content was determined via pH-meter to be 1.04. The trace element content of the solution is given, Table 3.

**Table 3:** *Composition of the HAIFA Chemicals acidic waste for trace elements<sup>a</sup>*

| Element | Concentration | Element | Concentration |
|---------|---------------|---------|---------------|
| Ag      | 5.3           | Mn      | 4.57          |
| As      | 2.39          | Na      | 1,195         |
| B       | 303           | Ni      | 6.29          |
| Ba      | 307           | P       | 12,410        |
| Be      | 0.147         | Pb      | 2             |
| Cd      | 2.74          | Se      | 5.19          |
| Co      | 0.84          | Si      | 4,520         |
| 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           |

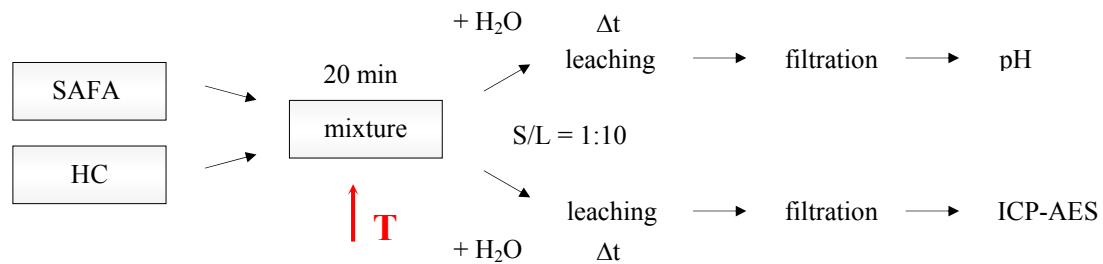
<sup>a</sup> Concentrations are given by mg trace element in 1 L of waste solution.

### 3. Experimental Methods and Procedures

#### 3.1 Experiments with fly ash and industrial waste

In this study South African fly ash (SAFA) was investigated in order to find a possibility to neutralize acidic wastes from industrial processes. Moreover it has been found that SAFA can be used as a fixation agent for trace elements and organic compounds.

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



**Figure 2:** General procedure of the experiments

The first step was 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 (1:1, 1:2, and 1:4) were chosen. The procedure was carried out in a temperature controlled reactor of 1.5 liter capacity specially designed and built for this study. During the scrubbing process (reaction time: 20 minutes) the mixture was stirred by a high torque-low speed stirrer. Thereby 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 deionized water. Each sample was agitated with 100ml deionized water (S/L = 1:10). The wetted samples were kept in an orbital shaker at 200 rpm. After a certain leaching period a liquid sample was taken from the container. The leaching tests were repeated at least twice in two different identical experiments. Following this procedure, 6 samples were used for pH-measurements (leaching periods: 0.5h, 1.5h, 6h, 1d, 4d, 16d) and 5 samples were taken for the determination of leached trace elements by

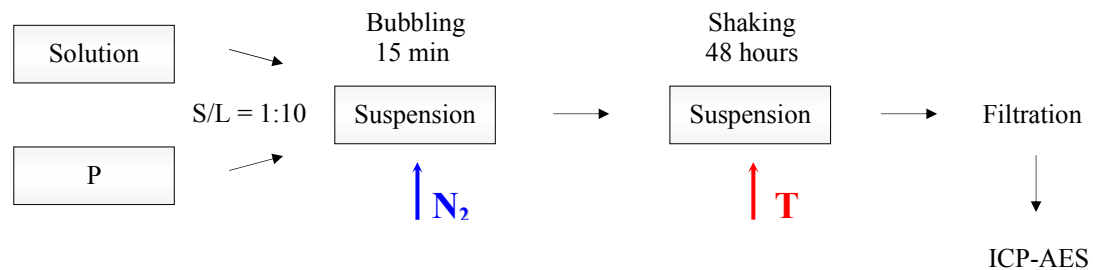


ICP-AES technique (leaching periods: 0.5h, 6h, 1d, 16d, 90d). In order to avoid precipitate presence the leaching samples were filtrated through a 0.2  $\mu\text{m}$  PTFE membrane filter. To the filtrate (40mls), 4 mls of concentrated nitric acid ( $\text{HNO}_3$ ) was added for the ICP-AES determination All filtrates were kept in polyethylene bottles. An identical procedure was followed by an extended reaction time of 3 days before leaching experiments have been performed, thus 3 days aging of the product have taken place.

### 3.2 The California waste extraction test (CALWET) procedure

In Israel the California Waste Extraction Test (CALWET), is used in order to classify hazardous waste. The CALWET procedure was developed in the USA, California 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 is very similar to the well known Toxicity Characteristic Leaching Procedure (TCLP) 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 grinded waste) and an extraction period of 48 h [21], Figure 3. In contrast to the CALWET, the TCLP uses acetic acid with pH of 5.0, a S/L ratio of 1:20 by a maximum particle size of 9.5 mm and an extraction time of 18 h [22].



**Figure 3:** Schematic procedure of the CALWET

This leaching solution makes the CALWET more aggressive towards certain wastes compared to the TCLP. That is why the Californian extraction is chosen in this study to determine the maximum level of leaching of trace elements from fly ash-waste products (P). The products from 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 which was mixed with 50 ml of sodium citrate solution in a cleaned polyethylene bottle. To prepare the extraction solution (sodium citrate) 1 liter of deionized water was mixed with 38.4 g of citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ). Afterwards this

solution was titrated by 4.0 N sodium hydroxide (NaOH) to reach a final pH of  $5.0 \pm 0.1$ . 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 immediately the plastic bottles were sealed. All samples were shaken for 48 hours in an orbital shaker incubator at a controlled temperature of 25C. The same procedure was also done for a blank sample without a fly ash-waste content. After the extraction of 48 hours the samples were filtrated through a 0.45  $\mu\text{m}$  membrane. The filtrates were analyzed by the ICP-AES to determine the trace element content in the leachate.

Thereby the regulatory limits for hazardous materials are given in two different threshold limit concentrations for several toxic elements:

- **Total Threshold Limit Concentration (TTLC):** “The TTLC is the maximum concentration allowed for a waste in solid or powdered form to be considered possibly non-hazardous. 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)” [22].
- **Soluble Threshold Limit Concentration (STLC):** “The STLC is the maximum concentration allowed for a waste in liquid form to be considered possibly non-hazardous. 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)” [22].

**Table 4 :** *List of inorganic persistent and bio-accumulative toxic substances and their Soluble Threshold Limit Concentration (STLC) and Total Threshold Limit Concentration (TTLC) [21]*

| element          | TTLC<br>mg/kg | STLC<br>mg/l | element | TTLC<br>mg/kg | STLC<br>ml/l | element | TTLC<br>mg/kg | STLC<br>mg/l |
|------------------|---------------|--------------|---------|---------------|--------------|---------|---------------|--------------|
| Ag               | 500           | 5.0          | Cr      | 2,500         | 5            | Ni      | 2,000         | 20           |
| As               | 500           | 5.0          | Co      | 8,000         | 80           | Sb      | 500           | 15           |
| Ba               | 10,000        | 100          | Cu      | 2,500         | 25           | Se      | 100           | 1.0          |
| Be               | 75            | 0.75         | Pb      | 1,000         | 5.0          | Tl      | 700           | 7.0          |
| Cd               | 100           | 1.0          | Hg      | 20            | 0.2          | V       | 2,400         | 24           |
| Cr <sup>6+</sup> | 500           | 5.0          | Mo      | 3,500         | 350          | Zn      | 5,000         | 250          |

## 4. Results and discussion

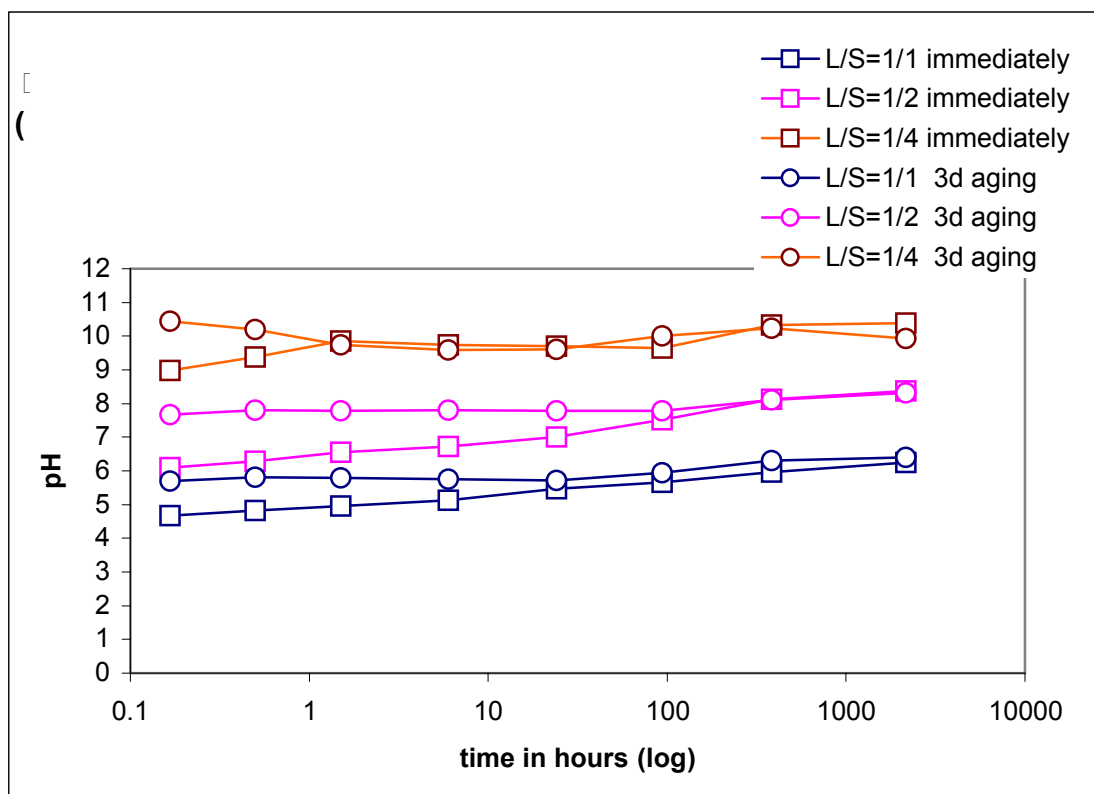
### 4.1 Influence of shaking time and aging period

The acidic/alkaline nature of the product P was determined by measuring the pH of a 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 waste (HC) to flyash (SAFA) is the main parameter which determines the acidity/alkalinity of the product. For product with HC/SAFA ratios of 1:1, 1:2 and 1:4 pHs of 4.8, 5.7 and 6.2 respectively were measured. Furthermore another important factor is the aging of the product. If the shaking is carried out with P which has aged for 3 days the acidity is raised appreciably: for HC/SAFA product ratios of 1:1, 1:2 and 1:4 pHs 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 do occur in the solid scrubbed product upon aging. This conclusion was corroborated by the trace elements leaching experiments (see below). Another parameter concerning the acidity/alkalinity nature 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 3 orders of magnitude (from 30 minutes to 1000 hours) almost does not affect the pH by more than 0.5 units. Furthermore, the aged product (3 days) is much less affected by the shaking period.

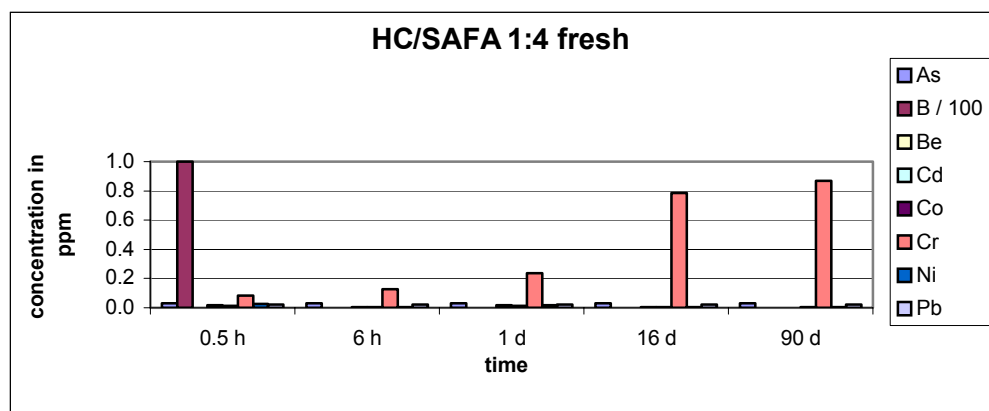
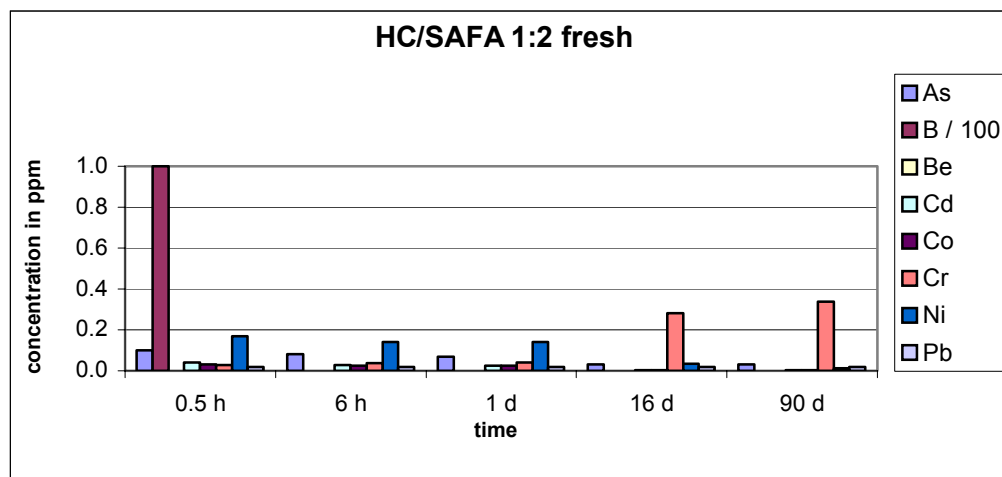
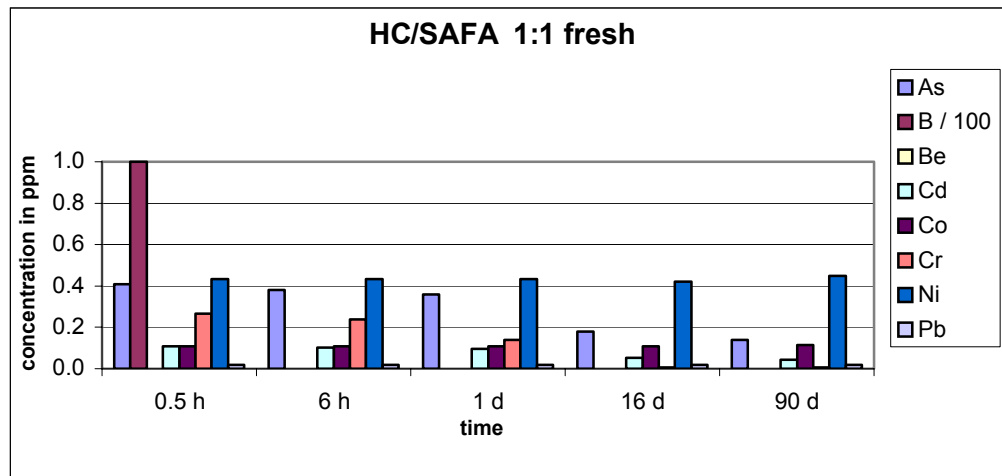
The leaching tests which have been performed with fresh product of the scrubbing process, Figure 5, do show for all trace elements measured, that there is a very good fixation of the products. The leaching experiments have been carried out with products formed via HC/SAFA ratios of 1:1, 1:2 and 1:4 and the leaching was studied for periods of up to 90 days. It shows that the 1:4 product has the best fixation properties for all trace elements but chromium. This is probably because (as has been checked in a previous studies in our group) the chromium that is dissolved is in the hexavalent form which is very soluble in basic conditions. Another observation is that most of the leaching process occurs within the first few hours of leaching, namely there is no difference in the concentration of all trace elements leached (again chromium is exceptional in this context). Another interesting conclusion is that the aging process of the solid product (which have been observed upon studies of the acidity/alkalinity of leaching) is also correlated to fixation of trace elements, Figure 6. In the 3 days aged samples the concentration of the leached trace elements is much lower than those determined for the fresh products. Hydrolysis of the metal ions, adsorption and precipitation at the surface of the flyash particles seems to be the process for the removal of the metals from the leach solutions. We recognize that the change in HC/SAFA ratio is very important due to 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 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

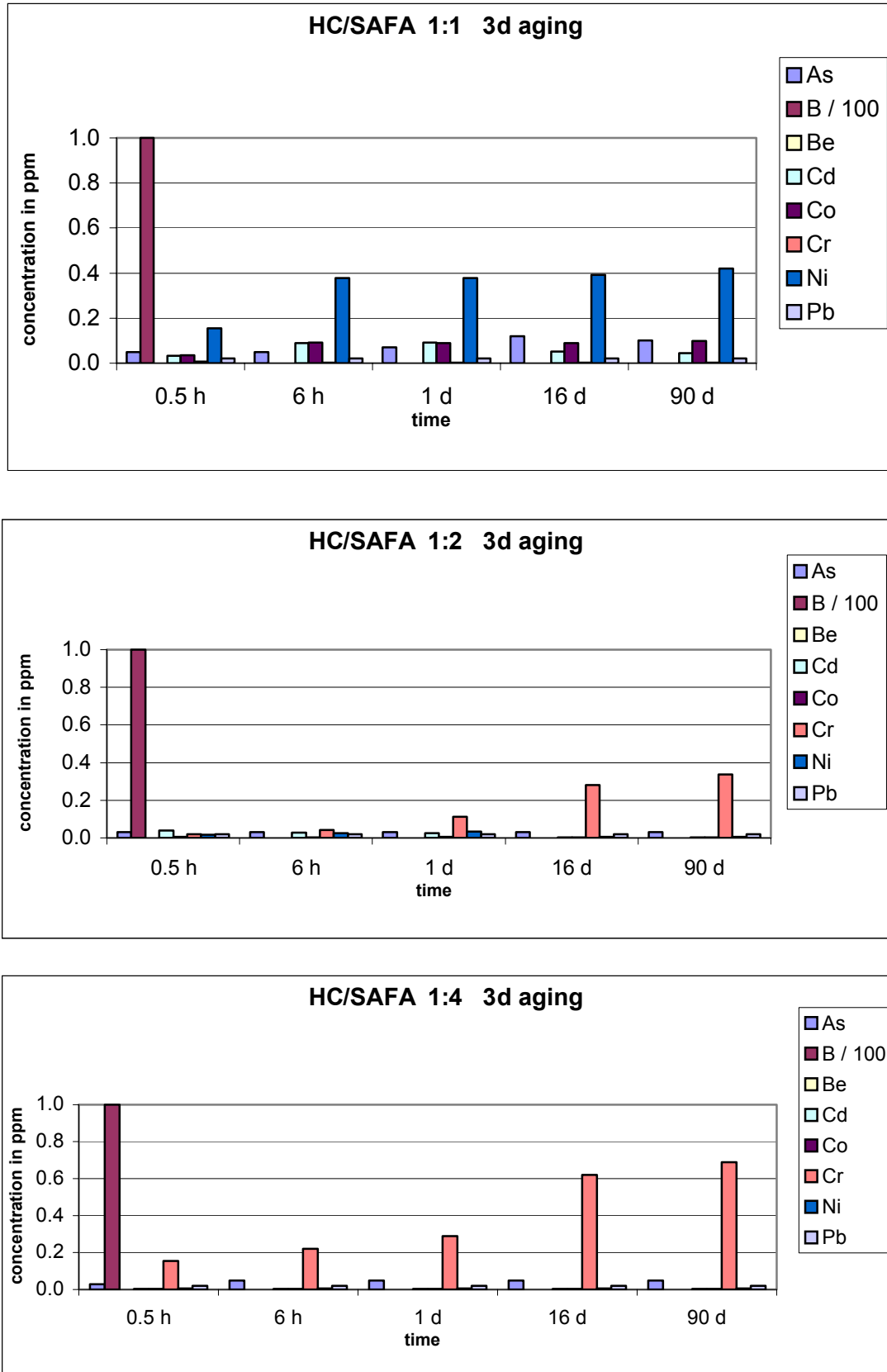
**Figure 4:** *Acidity/alkalinity of the leachates produced from the scrubbing product*



**Figure 5:** Leaching of trace elements from fresh HC/SAFA scrubbing product - effect of HC/SAFS ratio



**Figure 6:** Leaching of trace elements from aged HC/SAFA scrubbing product - effect of HC/SAFS ratio



## 4.2 The results of the CALWET extraction test

In order to assess the potential risk of the scrubbing product the CALWET extraction test was carried out. The optimal product with HC/SAFA ratio of 1:2 was tested. The results, Table 5 show that the product should be defined as a non-hazardous waste and thus can be used for any purpose. Definitely all the concentrations of the leached trace elements are much below the STLC limit. The concentrations of the metals which have been analyzed like 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, which also is presented in the CALWET procedure, was not checked because of sensitivity problems of the ICP-AES. However as the Hg content in the ash and the acidic waste is very low (<0.5ppm) there is no problem of leaching of mercury.

**Table 5:** Results of CALWET leaching test with HC/SAFA 1:2 scrubbing product<sup>a</sup>.

| ELEMENT | STLC | CAL WET 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                |

<sup>a</sup> concentration are given in mg element/liter leachate

Thus the determined contents of all toxic metals leached, which are given in table 5 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 is defined as non-hazardous and can be used for any utilization process. In a previous study it has been 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 flyash and the acidic waste of Haifa Chemicals is a green product which can be used in the construction industry in Israel.

## 5. Conclusions

Mixing hazardous waste with coal fly ash at the right conditions will result in a new environmentally friendly product. Mixing 1:2 ratio of HC/SAFA is optimal for the neutralization of those acidic materials. It has been found that the neutralization of this mixture depends on the reaction period and the aging process of the product.

The results of the metal content in the leachates show 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 cadmium, cobalt and nickel need more time for fixation compared to chromium, copper, zinc or arsenic. At pHs ~6.5-7.5 the largest content of toxic metals can be removed from a waste whereas the reaction period should be longer than 1 day. After this period fixation elements such as As, Cd, Co, Cr, Cu, Ni and Zn is almost absolute.

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, 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.

In order to estimate the potential economic value of the process some operating costs in controlling wastes in Israel should be taken into consideration. The price of flyash in Israel is 15\$/tons (including 150km transport costs). The price of the central facility in Ramat-Hovav, Israel for treatment of acidic wastes is ~300\$/ton waste. The HC/SAFA optimal product (1:2 ratio) can be produced relatively cheap: 30\$ for the flyash + operational costs of the mixing, probably not more than 10\$/ton product. Thus the overall cost will not exceed 60\$/ton. Furthermore the product can be used as a aggregate substitute in the construction industry, meaning that no other disposal costs are involved. Thus ab initio economic estimates show that the scrubbing process of acidic wastes by coal flyash can be a process with high economical added value.



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