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Evaluation of the Leaching Potential of Trace Elements from Coal Ash to the (Groundwater) Aquifer

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Abstract

Coal combustion in Israeli power plants (In 1998) produces more then 1,000,000 tones of ash annually. Most of the ash (60%) is used as cement additive. Since the expansion of coal combustion is much faster than the development of cement production, large amounts of fly ash are expected to accumulate in the next decade. Thus the environmental problem may be exacerbated if other means of utilization (e.g. embankments and marine reclamation or utilization as a chemical reagent) will not be possible in the future.

Unlike other countries overseas, coal ash is defined in Israel as hazardous material, thus any disposal or utilization scheme requires a special permit. The main concern is that pollution from the ash will leach out and contaminate the proximal ground water. We have decided to check the leaching behavior of South-African and Colombian fly ashes (the most abundant in Israel) using the following methods:

a. The improved EPA-TCLP 1311 (used in the US).

b.The EU-CEN/TC292/WG2 (declared recently as the method in the European Community).

c. The NVN2508 method.

The first two methods are batching methods and the third a flow through column method.

The main constituents of the ash (7-10% ash in the different coals) are: SiO_2 - 40-56%, Al_2O_3 - 20-33%, Fe, Ca, Na, K. Ti, Mn, Sr 0.1-1% and also traces of Co, Cu, B, V, Ba, Cd, Cr, Mo, Ni, Zn, Ag, As, Be, Hg, Pb, Se (up to 100ppm). Due to the low concentration of sulfur in the coal the ash's reaction in water is very basic (up to pH 13 in neutral water).

The effects of liquid to solid ratio L/S, leaching time and temperature on the concentration of the leachates have been investigated.

It has been observed that no appreciable amounts of most trace elements are dissolved from the ash except that of chromium which exceeds the drinking water limits. Furthermore most of the leached chromium is in the hexavalent form which is carcinogenic.

The effect of different parameters and the risk involved in leaching out of trace elements from the fly ash to the underground water aquifer will be discussed.

KEYWORDS: Leaching, Fly Ash, Trace Elements, Hexavalent Chromium, and Solid Wastes.

1. INTRODUCTION

Coal combustion in Israeli power plants produces 1,000,000 tones of ash annually[1]. Most of the ash (70%) is used as cement additive, the other 30% of the ash are marine disposed[2]. Since 1998 the Israel Electric Company is not allowed to dispose the ash at the sea. Moreover the expansion of coal combustion is much faster than the increase in cement consumption thus large amounts of fly ash are expected to accumulate in the next decade. The environmental problem may be worth if other means of utilization will not be available in the future.

The Israeli fly ash is very low in Hg, Cd and As[3]. This is due to strict environmental regulations concerning coal imports, as these elements are known for their toxicity. The fly ash has also low concentrations of sulfur thus the ash has a strong basic reaction (pH~13 at L/S=10) upon mixing with water[4].

Unlike most western countries overseas, coal ash is defined in Israel as a hazardous material; thus any disposal or utilization scheme requires a special permit. The main concern is that pollution from the ash will contaminate the proximal underground water.

The criteria for ash disposal are withstanding in leaching tests of trace elements. The results of the leaching tests do help to predict the risks toxic elements leaching to the aquifer.

We have characterized the most common two types of fly ashes (South-African and Colombian fly ashes) that are produced in Israeli power plants, table 1 (see below Results and Discussion).

Since in Israel there was no regulation of leaching test to asses the risks of disposal of fly ash it was decided to check the leaching behavior of the above two types of Israeli fly ash using the following three methods:

a. The improved EPA-TCLP 1311 (used in the US).[5]

b. The EU-CEN/TC292/WG2 (used in the European Community)[6].

c. The NVN2508 method (used in the Netherlands)[7].

The first two are batch methods and the third a column method.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Chemicals

All the chemicals and gases were analytical purity AR grade and were used without further purification.

The experiments were performed with distilled water were received by decontamination system of Milli Q model from Millipore company. The water have high conductivity >10 mΩ/cm

2.1.2 Type of Ash

The experiments were done with fly ash produce from coal combustion in Rutenburg Power Plant (Combustion Engineering Co.), Colombian or South-African which account for ~70% of the total sum of fly ash produced in Israel.

The ash content in Colombian Coal is 8.7% and in South-African coal is 13.9%.
The homogeneity of the ashes samples was measured by analyzing ash samples taken from 8 different containers (40kg per container) and the ashes were found to be homogeneous (>95% certainty, the experimental error is ±5%).

2.2 Methods

The leaching behavior of South-African and Colombian fly ashes was investigated using the three following methods:

* The improved EPA-TCLP 1311.
* The EU-CEN/TC292/WG2.
* The NVN2508.

2.2.1 TCLP (Toxicity Characteristic Leaching Procedure) Improved Method 1311 (Room Temperature 23±2°C)[5]

This method is used by Environmental Department of the Israeli Electric Co. and is used in the USA on all kinds of solid wastes (especially acidic wastes as it uses acidic solutions). This method predicts the leaching behavior of trace elements for long terms.

Procedure: Weight 100 gr. fly ash. Add 2 L of distilled water (L/S=20)+ 11.4 ml glacial CH_3COOH (pH 2.88).Place the capped bottle in a agitation device for 18±2 hours in 30±2 rpm shaker at 22±3°C. Filter the eluate through 0.6-0.8mm membrane.

2.2.2 CEN PROCEDURE (European Committee for Standardization)[6].

This method has been developed by the European Committee for Standardization in order to predict the leaching behavior of trace elements for long terms using demineralized water for the leaching test).

Procedure A: One stage batch test at L/S=2.

Place the sample100±5 gr of dry ash in a bottle. Add an amount of 200 ml distilled water and place the capped bottle in an agitation device for 24 ±0.5 hours (5-10 rpm) at room temperature 23±2 °C. Filter the eluent through a 0.45 mm membrane. Measure conductivity and pH of the eluate and analyze the trace elements of the eluate and Ca, Na, K.

Procedure B: One stage batch test at L/S=10.

The same procedure as procedure A but add an amount of 1000 ml distilled water as a leachant.

Procedure C: A two stage batch test at L/S=0-2 and L/S=2-10.

Follow the procedure described in A but the agitation period is only for 6±0.5 hours at 10±2 rpm. Add an amount of 800ml distilled water leachate. Place the capped bottle in agitation device for 18±0.5 hours at 10±2 rpm. Repeat the procedure described in procedure B.

This part gives a clue of a kinetic parameter to the leaching behavior of the fly ash.

2.2.3 COLUMN LEACHING METHOD (NVN2508)[7,8]

This method is a column method that is used in the Netherlands and predicts leaching of trace element for short terms ~ 50 years.

Procedure: Quantity of 30±0.01gr of fly ash is introduced into a 5cm-diameter*25cm-length column fitted with a glass wool plug to stop the ash from escaping. Various quantities of demineralized water containing HNO_3 at pH 4 were run through the ash (at room temperature) by gravitation until most of the liquid has passed through the column.

The effects of: liquid to solid ratio-L/S, agitation time and temperature on the leaching behavior of the leachates have been investigated also.

2.3 Analysis

The polluting toxic trace elements and Ca, Na, K have been analyzed using an ICP-AES spectrometer (Inductively Coupled Plasma – Atomic Emission Spectroscopy). model 48 JY of Jobin-Ivon Company. This method is very accurate ±2%, the detection limit is few ppbs

2.4 pH Measurements

The pH of the different solutions have been measured using a HI-8521 model Hanna instrument equipped with a calomel electrode.

2.5 Shakers

The TCLP and CEN method require two different types of shakers:

A table shaker (5-10 rpm) model N.J produced by New Brunswick Scientific and an end-over-end tumbler or rollertable rotating at about 28 rpm model 34R4BFCL-Z3 by Millipore.

2.6 Columns

The NVN method requires glass column with 5 cm diameter and 20 cm long, which was produced from Pyrex glass at the glassblower's shop.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Elements in the Fly Ash.

The different constituents of the fly ashes used have been determined, the results are given in table 1 (for the major constituents) and table 2 (for the trace elements).

Table 1: Characterization of major elements in the fly ashes used.

Elements	South-African [%Wt]	Colombian [%Wt]
SiO_2	**40.90**	**54.47**
Al_2O_3	**31.40**	**20.80**
TiO_2	**1.75**	**1.05**
Fe_2O_3	**3.05**	**6.18**
CaO	**8.35**	**4.65**
MgO	**2.45**	**2.05**
K_2O	**0.053**	**0.12**
Na_2O	**0.02**	**0.05**
P_2O_5	**1.95**	**0.75**
SO_3	**0.35**	**0.13**
C	**4-5**	**7-9**

The results show that both types of the fly ash are rich with calcium and have low sulfur content. This composition of the ash results in a very basic solution. When both ashes interact with water, the pH increases to higher then 12 at L/S larger then 10 due to dissolution of calcium oxides which is contained in the outer surface of the ash particle because of it's high volatility.

Other elements that mainly contribute to the resulting pH are sulfur, potassium and sodium, which present in lower concentrations, thus their influence is smaller. The South-African fly ash is the richest in calcium and the Colombian fly ash is the richest in iron oxides and unburned carbon.

Table 2: Characterization of trace elements in the fly ashes used

Elements	South-African [ppm]	Colombian [ppm]
Co	**60**	**40**
Cu	**70**	**60**
B	**240**	**240**
V	**160**	**200**
Ba	**2500**	**1300**
Cd	**<0.5**	**<0.5**
Cr	**160**	**130**
Mo	**<20**	**<20**
Zn	**110**	**110**
Mn	**340**	**340**
Ag	**<0.5**	**<0.5**
As	**7**	**12**
Be	**6**	**11**
Hg	**0.32**	**0.15**
Pb	**110**	**55**
Se	**5**	**17**

The results of trace element concentrations, table 2, show that both ashes are rich with barium, boron and manganese and poor in cadmium, mercury and arsenic, which are known as primary polluting trace elements. This observation is due to the strict environmental regulations, which prohibit coal imports rich in these trace elements.

3.2 Bulk Density of the Ash.

Since the density of the ash influences the leaching efficiency due to water movement through it we have decided to characterize the bulk density of the two ashes When the bulk density of the ashes is increased the solution is in contact with the ash for a longer period of time, therefore the leaching efficiency increases. The bulk density after compaction the intrinsic density of the ashes have been determined also, table 3.

Table 3: Intrinsic and bulk (before and after compaction) densities determinations

type	Intrinsic Density without [gr/cm^3]	Bulk Density	Bulk Density with compaction
Colombian	2.10	0.87	1.20
South-African	2.11	1.00	1.31

The intrinsic density is almost the same for both kinds of ashes but the bulk density of the South-African ash is appreciably higher higher than that of the Colombian ash. This means that the particle size is similar but the packing of South-African fly ash is much denser. The reason for that observation is probably caused by presence of high percentage of unburned carbon in the Colombian fly ash.

The shape of unburned carbon contained in the ash is angular with sharp edges and not spherical thus the packing of the Colombian ash is less denser, therefore movement of water through the ash is slower and the rate of leaching using the column method is higher

Since the three methods that we wanted to adopt in order to check the leaching behavior of the ashes produced in Israel have been developed in countries that have different climate conditions for ash storage (such as temperature, average rainfall etc.). It was decided to measure the effects of some parameters on the leaching rate of different elements. These parameters were:.

* Agitation time.
* L/S (liquid to solid) ratio.
* Temperature

3.3 The Effect of Agitation Time on Leaching

Agitation time can influence the pH and the concentration of the different elements leached into the solution, since different phases are dissolved at a different rate [such as silicates, iron oxide, alkaline]. The European and the American method were examined regarding agitation time. The results are given figures 1,2.

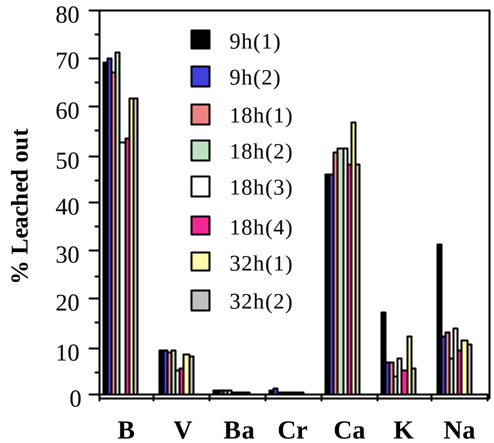

Figure 1: The effect of agitation time (9h,18h,32h) on Colombian fly ash. method. in TCLP method L/S=20

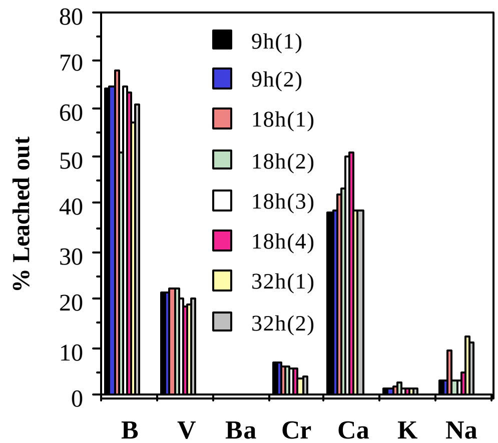

Figure 2: The effect of agitation time (9h,18h,32h) on South African fly ash TCLP TCLP method L/S=20.

The reproducibility of the results is in the range of 30% maximum and no trend was found. Observing the results using the TCLP method (figure 1,2) it was found that there is no significance influence of the agitation time on the leaching rate of toxic trace elements. These results prove that during a period of several hours most of the leachable concentrations of the elements are dissolved to the solution.

Therefore the agitation time recommended in the TCLP and CEN in order to determined the leaching behavior of the elements is relevance also for the conditions of fly ash storage in Israel.

3.4 The Effect of Agitation Time on Alkalinity in the CEN Method

The effect of agitation time on pH was measured in order to evaluate the time domain during which most of the basic constituents in the ash have leached/dissolved in the solution, which is in contact. This type of experiment was performed using the CEN method for both ashes.

The pH has been measured after 0.2, 1, 6, 20 and 24 hours difference times, the results are summarized in table 4.

Table 4: The effect of agitation time on pH in CEN method on both ashes.

	Agitation Time (hours)					
Ash Type	0.2	1	6	10	20	24
Colombian	11.50	11.49	11.45	11.46	11.69	11.54
Colombian	11.53	11.43	11.36	11.52	11.71	11.44
South-African	11.87	11.61	11.58	11.62	11.77	11.67
South-African	11.80	11.52	11.48	11.41	11.89	11.88

The results show clearly that already after 10 minutes the pH of both solutions is basic and has reached it’s maximum value. Thus proving that after a relatively short period (< 1 hour) most of the available concentrations of the basic elements are dissolved

3.5 The Effect of L/S (Liquid to Solid) Ratio on Leaching.

The volume of the liquid that is in contact with the ash is an important factor, which affects the amounts of leached materials to the solution.
The influence of the liquid volume to the weight of the solid over the release of the different elements was checked. The effect of liquid to solid ratio using the CEN method at L/S=2, 5, 10 and 20 has been investigated and the results are given, table 5.

Table 5: The average of the results is in mg/kg in CEN method.

Method	L/S	Type	pH	B	Ba	Cr	Ca	K	Na
CEN	10	C	11.47	39	10	2.0	4300	90	100
CEN	2	C	10.30	6	0.94	2.0	1500	60	100
CEN	10	S.A	11.84	1.35	29	2.4	8600	30	30
CEN	2	SA	9.60	0.44	2	1.3	1586	16	20

It is expected that the soluble elements will dissolve relatively fast and that when L/S is increased the element concentration in the solution will decrease via the dilution factor. This is indeed what occurs with the alkaline and alkaline earth elements (sodium, potassium and calcium) However when insoluble elements are dissolved, then only a minor percentage of the available concentration of them on the surface will dissolve and leach out to the solution. This is clearly observed with leaching of chromium.

3.6 The Effect of Temperature on Leaching

Since the average temperature in Europe and large parts of the USA is different from the average temperature in Israel, the effect of temperature on leaching has been checked. The temperature influences mainly the solubility of the insoluble salts.

Experiments have been carried out with all three leaching methods at the temperature range that is relevant in Israel. (Temperatures in the range 20-40°C). The results using the TCLP method are given figures 3 and 4.

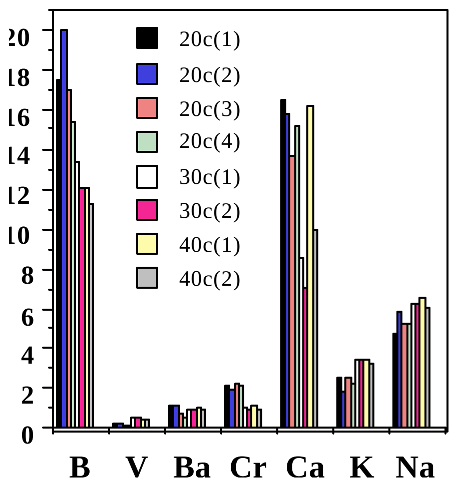

Figure 3: The effect of temperature at 21 ,23 and 34°C on Colombian fly ash with the TCLP method L/S=20

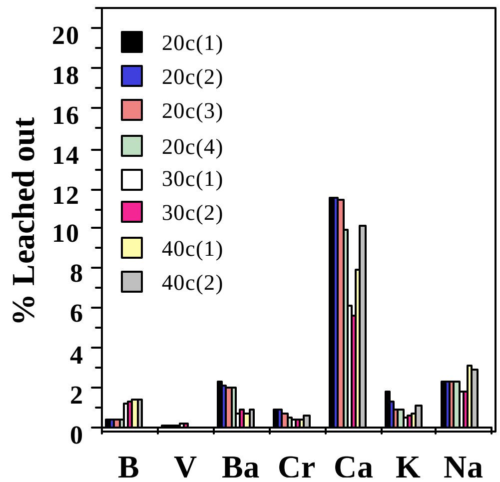

Figure 4: The effect of temperature at 21°C,23°C,34°C on South-African fly ash with the TCLP method L/S=20

Since the reproducibility of the results was 30% maximum, any change in concentration between these temperatures is included in the range of reproducibility of the results.
Thus the temperature in a range of 20-40°C. has no effect on the leaching rate of the trace elements or other elements into the solution.

Thus we recommend to adopt the temperature that is recommended by the three methods used.

3.7 Typical Leaching Results

The results of the leaching of different trace elements from the fly ashes produced in Israeli power plants have been obtained using the three methods. Typical results are given, table 6.

It has to be taken into account that these results are from leaching experiments with the typical ashes produced in the power plant in Israel and as such represent the situation which will occur upon storage of the ash for long periods. The criteria for the quality needed of the resulting solutions was taken as the D.L. (drinking water quality) of primary pollutants.

Table 6: Typical Results of Leaching Compared to the Standard Drinking Water Limits in Israel:

		CEN		NVN		TCLP		
Element	unit	C	S.A	C	S.A	C	S.A	D.L
L/S		10	10	10	10	20	20	
B	ppb	4200	110	5200	610	8200	7500	-----
V	ppb	<20	<20	<20	<20	910	1660	-----
Ba	ppb	1150	2925	973	1088	425	200	1000
Cr	ppb	278	95	182	219	28	480	50
Mn	ppb	<10	<10	<5	<5	920	1225	50
Zn	ppb	<50	<50	<20	<20	203	53	5000
Ca	ppm	445	713	409	977	735	1443	80
K	ppm	9	3	7	1.52	5.2	1.5	-----
Na	ppm	10	3	11	2.46	9.48	2.3	-----

The results are in μg/l but for Ca, Na, K in mg/l.
D.L- The maximum level of trace element that are allowed in Drinking Water in Israel.
C - Colombian S.A- South African

Definitely the concentrations observed for certain elements using the TCLP method are higher than those in the other methods. These results prove that acetic acid which is added at relative high concentrations using the TCLP induce leaching due to its compellation properties (of the acetate ions).

It is also observed that no appreciable amounts of most trace elements are dissolved from the ash except that of chromium, which exceeds the drinking water limit. Furthermore we have checked the oxidation state of the leached chromium and found out that most of the leached chromium is in the hexavalent form which is considered as carcinogenic[9].

4. CONCLUSION

(i) The results have shown that there is no appreciable effect temperature (at 20-40 °C), agitation time) and L/S ratio on the leaching behavior.
(ii) It is found that the CEN method is the most suitable test for Israel as the ash is very basic and thus acetic acid addition (in the TCLP method) affects appreciably the leaching behavior.
(iii) The TCLP method might be suitable but only for acidic ashes.
(iv) It is observed that no appreciable amounts of most trace elements are dissolved from the ash except that of chromium which exceeds the drinking water limit most of the leached chromium is in the hexavalent form which is the carcinogenic form.

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