2003 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #51.
http://www.flyash.info

Fly Ash: A Potential Excellent Scrubber for Acidic Wastes in Israel

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Abstract

Bituminous coal combustion in large utility plants is the main source (78% in 2001) of power generation in Israel and the annual coal consumption is 12.5 Mtons in four power stations. Coal ash is a byproduct resulting in ~1.5 Mtons per year (90% accounts for fly ash) that should be utilized or disposed off properly in order to avoid environmental problems. At present ~43% of the fly ash is used as cement additive to clinker (10%w in the product) and the rest as construction material for embankments and road basements.

The Israeli fly ash is highly basic when exposed to water, due to the very low sulfur content of feed coals (because of strict environmental regulations in respect to SOx emissions).

Thus, the fly ash is a potential chemical scrubber for acidic wastes. In this study, coal fly ash has been examined as a scrubber for acidic wastes produced from the regeneration process of used motor car oil and the phosphate fertilizers industry. The results show that the fly ash can be used as a very efficient scrubber of the sludge. Furthermore the trace elements and the organic components are fixed within the fly ash particles efficiently. The product leaching limits are within the CAL WET leaching test, thus it can serve as a good aggregate in concrete production. Bricks produced using the aggregate as sand substitute, have proved to be hard enough according to the concrete standards in Israel and the leaching of the trace elements from the bricks is within the environmental regulations (the CAL WET test). The neutralization and fixation processes will be discussed in detail.

Keywords: fly ash, acidic wastes, chemical scrubber, trace elements

1. Introduction

Israel is relying today on coal combustion for production of electricity. The bituminous coal which is used as fuel in large utility plants is the main source (more than 80% in 2002) of power generation in Israel. This results in annual coal consumption of 12.5 Mtons in four power stations. The coal is imported by sea in large ships from different sources but the majority is arriving from South Africa (~50% in 2002). Due to strict environmental regulations the imported coal is low in toxic trace elements like mercury, arsenic, cadmium, selenium, chromium etc. Furthermore in order to reduce sulfur emissions it is also low in sulfur content (<1w%). The coals contain 6-12w% of ash. The ash production is at present at an annual rate of ~1.4 Mtones of fly ash and ~150,000 tones of bottom ash. The separation of the fly ash in the power stations is captured by electrostatic separators (efficiency>99.98%) and it's accumulation is a major problem for future trends in power generation via coal combustion. In the early stages of coal combustion the major utilization processes were in the construction industry. All the fly ash was used for two needs: (i) The cement industry- All the cement produced in Israel contains 10W% of fly ash. (ii) Embankments around the power stations. All the excess of fly ash was dumped into the Mediterenian Sea ~50km from the coast using large barges. The bottom ash was accumulated in open storage sites near the power stations (two storage facilities).

This was the situation until 1999. Upon signing the Mediterenian Basin Treaty all nations have agreed to stop dumping wastes into the sea and since then sea dumping is prohibited. Also the embankments buildup around the two sites where the power stations reside was finished. Thus the only available method for utilization left was as a cement additive. The production of cements during 1999 in Israel was 4,500,000 tones using 450,000 tones of fly ash and the excess of ~500,000 tons of fly ash had to be disposed. Thus new methods for fly ash utilization or construction of new storage facilities. As the construction of storage sites is expensive, new utilization methods were adapted oriented at the construction industries.

The bottom ash available has been used for basement layers for road construction. The fly ash is used mainly for landfill applications and as aggregate substitute for special concrete production. The economic value of the ash is rather low, 5-10$/ton which is equal to the price of it's transportation to the consumer's site. These facts dictate looking for better economic applications for fly ash, in order to lower the costs of power production using coal as the fossil fuel.

The main deterent in Israel for using fly ash is the risks which are involved to the underground aquifer in Israel. The average rainfall in the country is low and the quality of drinking water is already in danger of possible contamination from industrialization. In order to asses the leaching potential of trace elements from the fly ash or the concrete products, two leaching methods have been adapted by the Israeli authorities: The improved 1311TCLP method* (for the fly ash) and the CAL WET method for the concrete products. Also several monitoring systems have been established for sampling of water from the aquifer near the roads or sites where flyash has been utilized. The main concern was from leaching of chromates-Cr^{6+} and boron and from change in the acidity (basic pHs) of the aquifer. So far, 3 years, the monitoring proves that there is no appreciable leaching of trace elements or change in acidity to the aquifer at these sites.

As stated (see above), the bituminous coals used in the power plants in Israel have low sulfur content and contain ~10w% mineral matter. Therefore the fly ash has very basic reaction upon it's contact with water, the main basic element is calcium but also iron, magnesium, and the alkali elements sodium and potassium do occur in the ash in appreciable concentrations. Naturally, this property- high basicity raise the question if it can serve as a scrubber to acidic wastes. We have decided to check the possibility of using the Israeli Class F flyash as a potential scrubber for acidic wastes. It is found that indeed

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It is recognized that the improved 1311TCLP method is not the ideal method as it uses strong ligands (acetic acid) which might induce increased leaching, thus when the European method will be validating, probably it will substitute the 1311TCLP method.

it is an excellent potential chemical reagent and furthermore that the scrubbed product is an environmentally friendly green product.

2. Acidic Wastes in Israel

Two major types of acidic wastes do occur in Israel: (i) Liquid wastes from the phosphate industry and (ii) Sludge from the motor oil regeneration processes. The most abundant are the liquid acidic wastes from the phosphate industry in Israel.

(i) Liquid waste from the phosphate industry

The production process in this industry is characterized by mixing phosphate rock with concentrated hydrochloric acid- HCl or sulfuric acid- H_2SO_4 (both acids are used). In the second stage an organic solvent is used to extract the phosphoric acid (H_3PO_4) formed. Thus the waste produced is an acidic aqueous solution with low organic content (~0.1w%), pH~1 (~0.1M acidity) and low viscosity. It contains also small amount (<0.1-0.2w%) of dispersed solid precipitate. Elemental composition of the solution consists of ~1% P, ~0.4%Si and 100-1000ppm Fe, B, Sr, Ba, Mg, Zn, Na and K 1000ppm and low content (sub to few ppm range) of Ag, As, Be, Cd, Co, Cr, Cu, Rare elements, Mn, Ni, Pb, Se, Sn, Ti, Tl, and V.

Most of these acidic liquid wastes are treated within the plants facility and the solid suspension is left to precipitate and for water evaporation in large ponds (the plants are in a remote desert areas without any urban population). Usually, lime is used for the scrubbing process.

(ii) Sludge from motor oil regeneration processes

This process uses sulphonic hydrogenation processes to regenerate motor oil (Oleum: 100% sulfuric acid- H_2SO_4+ 30%SO_3 is used). A high viscosity black organic homogeneous sludge is formed as a waste, It contains ~4-5w% H, ~17w% C and ~27w% S (mostly as -SO_3H groups) chemically bonded to the organic macromolecule backbone). It is very acidic (1 liter sludge is titrated by ~19 moles of NaOH!!), high density, ~1.6g/cc and it has very unpleasant sharp odor as it emits toxic gases (such as SOx). The trace element content of the solution is Fe, B, Si and Ca in the 100-1000ppm range, Al, Ni, Cr, Mg, Na, Cu, Tl, Mn, K, and Zn in the 5-40 ppm range and P, Ag, As, La, Mo, Se, Pb, Sr, Sn, V, Ti in the 0.1-4 ppm level

These highly acidic sludges cannot be treated at the regenaration plant and have to be transferred to the central hazardous waste treatment facility in Ramat Hovav (the Southern part of Israel). The current situation is that the wastes are stored in large ponds and so far no efficient method was found for treatment of these toxic wastes. The estimates are that the storage costs are at least 500$/ton sludge, not including the transportation costs.

3. Israeli Fly Ash Characterization

The largest amount of fly ash produced in Israel is the result of South African coal combustion which has high mineral content (~12w%) (it accounts for ~65% of the ashes which are produced) thus we have decided to use it for the scrubbing experiments. It is classified as class F ash since the SiO_2 + Al_2O_3 + Fe_2O_3 fractions make up almost 80% of the material. It is rich in calcium oxide (~10w%) and contains a small amount of sulfur, Table 1.

Table 1: South African coal fly ash content:major and trace elements

Major components, %		Trace elements, ppm			
SiO_2	42.78	Ag	13.6	Mo	11
Al_2O_3	34.01	As	bdl	Ni	68
CaO	10.35	B	240	Pb	73
Fe_2O_3	2.86	Ba	2350	Sb	bdl
MgO	2.40	Be	9	Se	5
P_2O_5	1.65	Cd	<0.5	Sn	bdl
TiO_2	1.83	Co	40	Sr	2500
Na_2O	0.43	Cr	150	Tl	bdl
K_2O	0.67	Cu	77	V	180
SO_3	0.55	Mn	360	Zn	160
C	4 – 5				

bdl: below detection limit

The average particle size of the fly ash is 5-30 μm and it contains also 3-6w% LOI (unburnt carbon).

Potentially this is an excellent chemical reagent for neutralization of acidic wastes. Furthermore, due to the small particle size it has a large surface area (high percentage of cenospheres and palerospheres) and it can serve as an excellent adsorption surface to the trace and heavy toxic elements of the mixture.

4. Scrubbing Methods

The general experimental flow sheet used in the experiments is outlined in Figure 1. It is based on mixing the liquid waste or the sludge with the fly ash in a thermally controlled reactor under different conditions such as ash/wa**S**te (A/S) and water/wa**S**te (W/S) ratios. The product obtained in all cases is in the form of an aggregate. In some cases (with the liquid waste when large amounts of waste solutions were used) had to be separated from the solution by filtration. The product aggregate P is then subjected to leaching tests in an aggregate/water (P/W) ratio of 1/10 as a function of time up to 90 days. Solids are filtered using 0.45 membrane filters at a predetermined times of leaching (0.5, 6 and 24 hrs, 16 and 90 days) and the leachate is checked for pH and is sent to elemental analysis (ICP) for trace elements. The solids may be subjected to washing or to the California Wet Extraction test (CALWET) or to the 1311TCLP leaching procedure (TCLP), whose leach solutions are again analyzed using ICP.

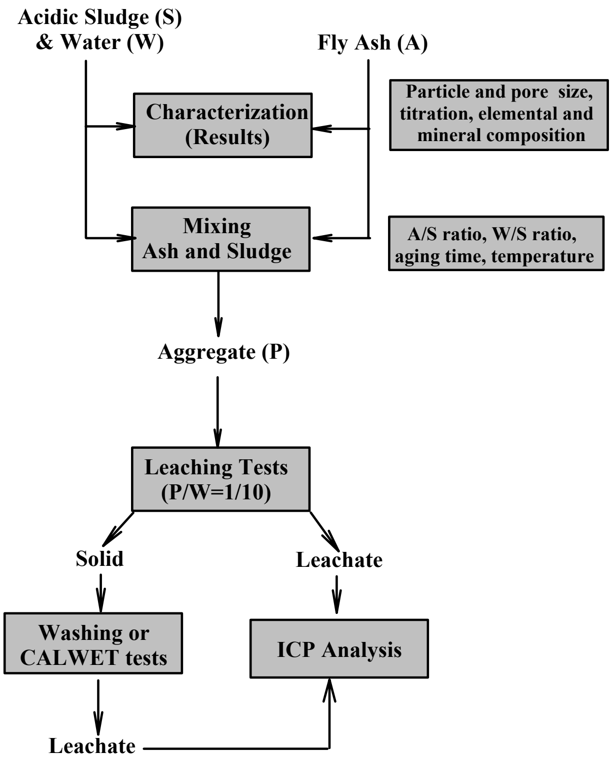


Figure 1: General flow sheet used for scrubbing experiments

5. Scrubbing Processes and Products

The two major representative types of acidic waste were selected and tested for scrubbing with South African fly ash produced in Ruthenburg Power Station in Ashklon of the Israel Electric Corporation (IEC), (denoted as SAFA in the text). The acidic liquid waste was from the process of Haifa Chemicals South (denoted as HC in the text) which is a fertilizer producer using hydrochloric acid for dissolution of the phosphate rock. The acidic sludge used was the effluent material of the PAZ-Schmanim recycling plant in Haifa (denoted as PAZ in the text.

Enclosed is a sum up of the results obtained with these two types of acidic wastes (which represent more than 90% of the quantity of acidic wastes produced in Israel) using SAFA as the scrubbing chemical reagent.

(i) Haifa Chemicals Liquid Acidic Waste

Different L/S (liquid waste volume to solid fly ash weight) were used in the ranges 1/1-1/8. The most optimal product was 1/2 in which the best neutralization occurs, namely 1 liter of waste solution is scrubbed optimally by 2 kg of fly ash. The solid product precipitates and the clear neutral solution is either to stand for evaporation of the water or the solid can be filtrated (both processes can be used). There is an appreciable aging process on the product which affects the neutralization of the acid in the waste: it is improved with aging time.

It was also very satisfying and promising to recognize the fact that another optimal positive process has occurred. It is observed that excellent fixation of the toxic heavy metals and trace elements has been achieved. The CALWET (as well as the TCLP) used to evaluate the leaching rate has shown that the amounts of leaching of trace elements is much below the STLC values (Soluble Threshold Limit Concentrations), Figure 2. as can be clearly seen from the figure all the trace elements are leached at a very low level much lower than the STLC. Thus defining the product as a non-hazardous product that can be used as an aggregate substitute in concrete production!!. Also correlation with aging of the product is observed: the fixation is improved with aging time.

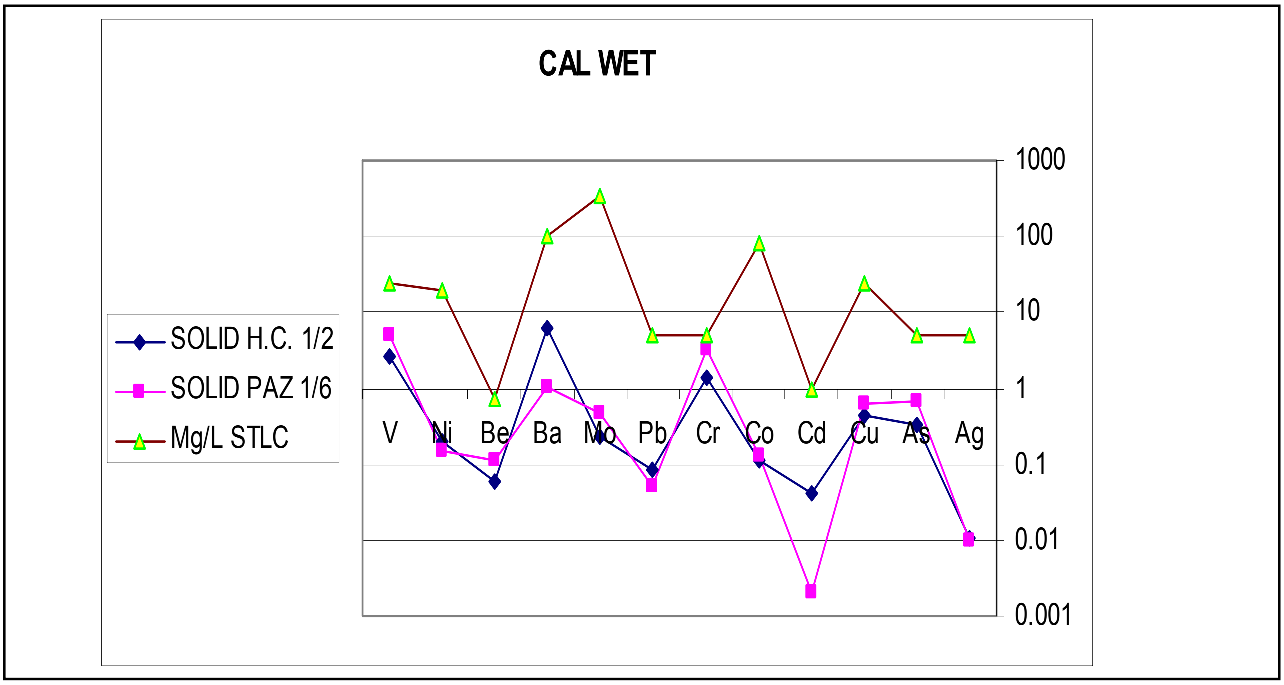


Figure 2: Leaching tests of the 1/2 ratio HC/SAFA and 1/6 ratio of PAZ/SAFA using the CALWET method

The effect of aging on the neutralization and fixation properties of the scrubbed product/aggregate indicates that apart from the fast processes occurring in the first 20-30 minutes time range, there is a slower process which last for days in which probably basic oxides under the surface of the fly ash particle undergo slow diffusion towards the surface to contribute to the neutralization process and also that different minerals are formed in which the fixation of the different trace elements is improved.

(i) Paz Scmanim Acidic Sludge

As the sludge is very viscose and is composed of organic substance, which is not soluble in water we were concerned about the possibility that the fly ash will neutralize the acid content of the sludge. We thought that the scrubbing process might require addition of appreciable quantities of water to the reaction mixture. However the results have clearly demonstrated (see below that water addition is not needed (Still water can be added and improve the quality of the scrubbed product but the effect of water addition wouldn’t be discussed here). Also in this case different L/S (liquid sludge volume to solid fly ash weight) were used in the ranges 1/1-1/8. As the acid content of the sludge is much higher, larger amounts of ash were needed in order to achieve acid neutralization. The most optimal product was 1/6 in which the best neutralization occurs, namely 1 liter of waste solution is scrubbed optimally by 6 kg of fly ash. The product is a solid gray aggregate with unpleasant odor which fades out after few weeks. This odor fading is due to aging processes occurring in the scrubbed product. As in the case with the Phosphate Industries liquid waste, there is an appreciable aging process of the product, which affects the neutralization of the acid in the waste: it is improved with aging time.

Also in this case, it was very satisfying and promising that the toxic contents are trapped within the matrix. The trace elements and toxic elements undergo efficient fixation within the product aggregate matrix. The CALWET (as well as the TCLP) used to evaluate the leaching rate has shown that the amounts of leached elements, is much below the STLC values, Figure 2. As can be clearly seen from the figure all the trace elements are leached at a very low level much lower than the STLC except for the chromium. Still the chromium amount which is leached is 30% below the STLC. This observation indicates that the product is defined as a non-hazardous product and that it can also be used as an aggregate substitute in concrete production!!. Likewise the case with the phosphate industry acidic waste an aging effect of the product is observed: the fixation is improved with aging time.

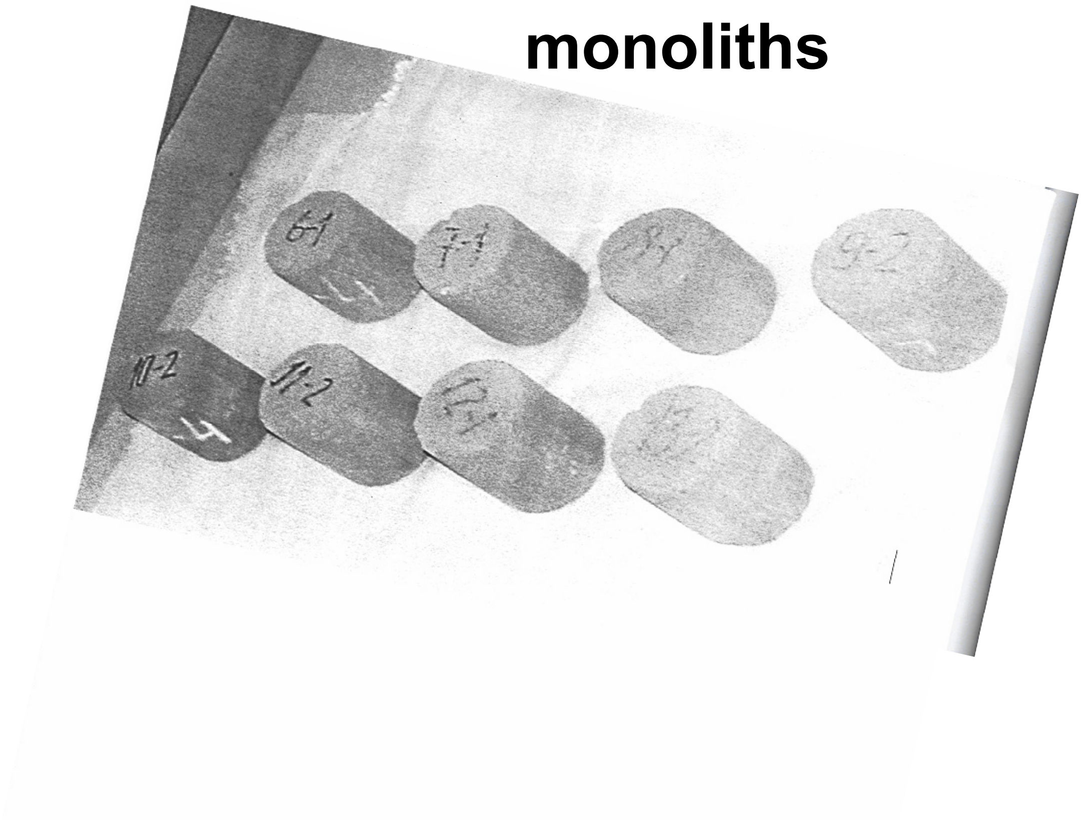
These results are quite impressive. Though the sludge contains high percentage of organic constituents and large numbers of anionic species together with appreciable concentrations of toxic heavy metals and trace elements, the basic fly ash not only neutralizes the acid content but also fix the organic species and the toxic elements to a level that essentially the results indicate that it is an environmentally green wastes!!.

5. Utilization of PAZ/SAFA 1/6 Product as an Aggregate Substitutes

As the scrubbing product has aggregate like properties and is defined as a non-hazardous material (see above, CALWET test, Figure 2), we have decided to check if PAZ/SAFA 1/6 product can be used as an aggregate substitute (assuming that if the answer is positive than probably also the HC/SAFA 1/2 can also be used as such). Thus the product was transferred to the Desert Research Institute of the Ben-Gurion U. to use it as partial sand substitute in monolit production, in the range of 5-20% sand replacement. The monolits were measured for mechanical strength compared to 100% sand products. Also the monolits were grinded and checked for leaching via the CALWET test. The photographs of the monolits as well as the leaching tests result are given, Figure 3.

In the two processes where PAZ/SAFA ratios were 1/6 and 1/8 and the sand substitution level was 5% there was no difference between the mechanical strength of the monolits with the aggregate product and the blank samples which contained only sand as an the aggregate.

Furthermore in all the monolits (not only those which had sufficient mechanical strength) the leaching of all the trace elements was much below the STLC according to the CALWET test. This observation indicates that the bricks that will be produced from the same mixture can be used for any construction purposes.



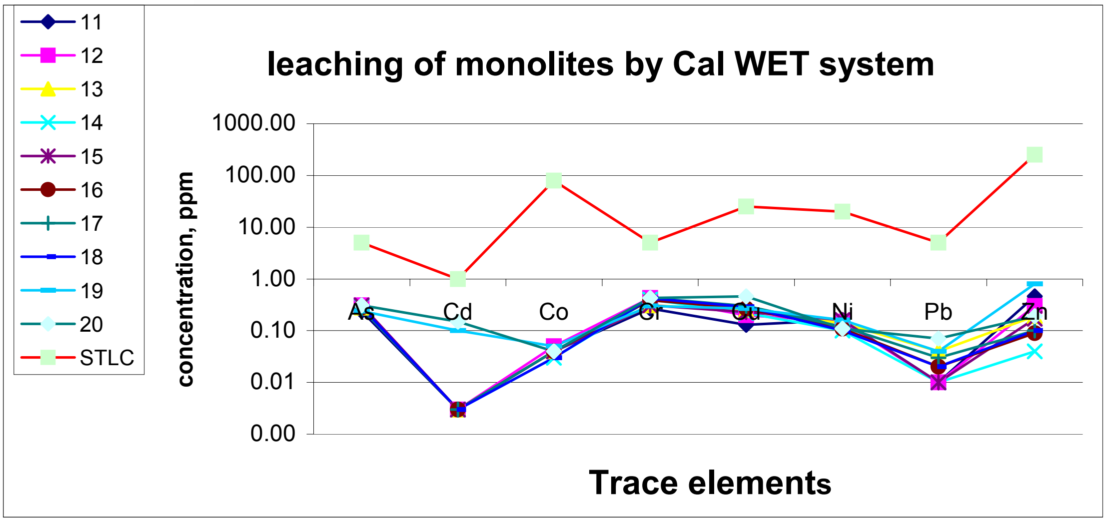


Figure 3: Photographs of the Monolits and the CALWET test results for the grinded monolits* (in brackets- the % of sand substitution)

*** samples 6-1 (5%), 7-1(10%), 8-1(15%), 9-2(20%)-PAZ/SAFA 1/4**

10-2 (5%), 11-2(10%), 12-1(15%), 13-2(20%)-PAZ/SAFA 1/4

Of course the experiments carried so far can be assigned only as a feasibility studies and in order to have confirmation to use the scrubbed product many more compliance tests should be carried out. However it does show that using the bituminous coal Class F fly ash as a chemical reagent for scrubbing toxic acidic wastes might result in production of environmental friendly product that can further be used in the construction industry.

6. Some Preliminary Economical Evaluations

In order to asses the economical potential of utilization of the fly ash as a chemical reagent for scrubbing acidic wastes it should be able to compete commercially with existing processes.

At present the price of cement in Israel is 55$/ton and this is the actual maximum value that might be put as the consumer value for the fly ash (as the 10% additive to the clinker).

The sticker price for treatment of the acidic sludge is set to be 500$/ton sludge. As the estimates of the **sludge/fly ash** ratio is **1/6**, 6 tons of fly ash will be needed for the treatment of each ton of sludge. This marks up the value of the fly ash to ~84$/ton which is much higher than the value of the cement. We didn’t include the price of the ash transportation and scrubbing of the sludge but the rough estimates are that this will cost 10-20$/ton sludge. Thus the preliminary evaluations indicate that the process might be economically much more valuable than existing utilization methods for the fly ash. Of course much more experimental work should be carried out before a good economic assessment can estimate it’s commercial value.

However there is one point, which should be taken into account and has big advantage over many other aspects to be considered. The process in which fly ash is used as a chemical scrubber to acidic wastes uses a toxic acidic waste (that should be treated or taken care of) mix it with another waste-the coal fly ash and produces a product which is environmentally green, safe product that can be used as an aggregate in the construction industry.

6. Conclusions

1. Fly ash produced from bituminous coal combustion can be used as an efficient chemical reagent for scrubbing toxic acidic wastes from the phosphate industry and the motor oil regeneration processes.
2. The scrubbing product is a non hazardous material (withstands the CALWET test and the improved TCLP1311 leaching procedure).
3. The scrubbed product can serve as an aggregate substitute to sand in concrete production and the product has the same mechanical strength and does not leach toxic trace elements upon contact with water.
4. Preliminary economical evaluations show that using fly ash as a chemical reagent has much higher added value than using it in the cement or the construction industry.

Acnowledgements- The author would like to acknowledge the work carried out by Mr. Eli Lederman from the Ben-Gurion, Dr Constantin Fridin from The Desert Reearch Institute-BGU, U. Of the Negev, Prof. Mehmet Polat from IATEK, Izmir-Turkey, Prof. Ithamar Pelly from Ben-Gurion U. Of the Negev, and Mr. Mike Werner from the Technische U. Freiberg-Germany and helpful discussions with Prof. Fari Goodarzi from the Geological Survey-Calgary, Canada. Also to acknowledge Paz Schmanim Co. and Haifa Chemicals for supply of the waste samples and the Israel Electricity Co. (IEC) for the supply of the fly ash. The author would like to acknowledge financial support by the Israeli Coal Supply Co, and the Israeli Ash Administration Authority.