<u>Coal Fly Ash as a Chemical Reagent for Scrubbing Industrial Acidic Wastes</u>

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The use of coal as an energy source to produce electricity in Israel, entails the production of more than 3,000 tons of coal fly ash (CFA) a day. Fly ash is a reusable material, that must be under environmental control, which makes it ideal for building and infrastructure applications. To prevent ecological damage to the environment, the imported coal must be relatively free of sulfur compounds. Coal cleaned of sulfur produces an ash, rich in compounds that undergo basic reactions with water (especially when the coal is also rich in calcium and alkali metals). The primary goal of this research was to test the capacity of fly ash (Class F compound) as a neutralizer of highly acidic industrial wastes. Another goal was to test if its chemical properties and its large surface area can be used to fix the toxic elements in industrial wastes. The fixation quality is defined according to the extent of leaching of toxic elements to water. An equally important goal is to gain a full understanding of the mechanisms behind the neutralization and fixation/adsorption processes of toxic trace elements. An additional goal of this research was to test how the organic component of the industrial waste affects fixation quality. We also wanted to test the efficacy of using the product of fly ash-based industrial sludge fixation as a replacement for sand in producing concrete, while testing its fixation ability within monoliths. To investigate these issues, we prepared the fixation products via the reaction between fly ash with a highly acidic organic sludge from the factory of the Paz Oil Company in Haifa (PAZ). The sludge, which is a by-product of the used engine oil recycling process, is highly acidic, with a significant organic component. Likewise, the neutralization and fixation process of the acidic sewage from the Haifa Chemicals Company Ltd. (HC), a waste product of the phosphoric acid production process, was examined. Additional experiments were undertaken to deepen out understanding and to compare the different processes studied in the research. Most experiments were carried out using fly ash from the combustion of South African coal – SAFA (comprises the majority of fly ash produced by coal burning power plants in Israel), but a minority of experiments employed fly ash from the burning of Columbian coal – COFA. The research revealed that the potential for the fly ash to release its basic/alkaline component to water, is a function of time. Release of the hydroxide groups into solution depends on removing the appreciable part of the insoluble components from the fly ash. The shaking period in an aqueous solution must be of a long enough duration for the water to deeply penetrate the matrix of the fly ash particle (the structure of which is not uniform and whose particles reflect a wide range of shapes and cavities). Optimal neutralization of the highly acidic organic sludge defined as (PAZ) [H^+ concentration exceeded 20M] occurred for mixtures at a weight ratio of one part sludge to six parts fly ash. Optimal neutralization of the acidic sewage (HC) [H^+ concentration about 3M] was for weight ratio of one part sewage to two parts fly ash. Likewise, we tested fly ash capacity to fix toxic metals, because the toxic wastes discussed above contain substantial levels of environmentally dangerous elements (e.g., nickel, chromium, and lead). The stability of their fixation in the product under conditions of washing with water, was investigated for periods lasting from a half an hour and up to three months (for each time period a filtered sample of the solution was taken for a chemical analysis of the element present). The results of these experiments provided a picture of fly ash metal fixation quality. The effects on fixation quality of adding water to the PAZ sludge before its reaction with SAFA and at different temperatures (25-65C) was examined. The effect of ageing on the fixation product was also investigated. Elucidation of the mechanism of metal–fly ash binding (fixation/adsorption – sorption) was done via experiments in which a solution containing a bivalent metal cation was added to South African Fly Ash – (SAFA) raw material (untreated), SAFA prerinsed with water, or SAFA pretreated with acid. Based on previous experiments we found that the fly ash loses about 4% of its weight to rinsing with water and about 16% of its weight after rinsing with diluted hydrochloric acid. Bivalent cations M^{2+} (e.g., Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}) fixation was examined for cation size dependence. For example, clearly the electric field induced by Cu^{2+} (radius 0.69 Å) is larger than that of Pb^{2+} (radius 1.20 Å). It was expected that the electrostatic interaction between the cation and fly ash surface area, would increase with decreasing ionic radius, and indeed the experiments revealed that copper was adsorbed in an electrostatic binding mechanism in which the fly ash functioned as an ion exchanger, while the lead ion underwent fixation via strong chemical coordination, that utilized a small number of binding sites. The effect of organic material on the fixation process was examined with two organic oils and it was found that the quality of fly ash binding was not affected by the addition of organic materials. The fixation product was tested as a partial substitute for sand, in the production of concrete, and it was revealed that the mechanical strength of the monoliths produced was good up to a level of 15% exchange of the sand. The quality of fixation between the fly ash and the different waste products and within the monoliths, was determined via two standard leaching procedures (CAL-WET and TCLP, accepted by the Ministry of Environmental Protection), which showed that the concentration of toxic metals that leached from the compounds, was much below the soluble threshold limit concentration (STLC). In other words, fixation quality for such metals is excellent. The fixation of toxic metals in the acidic sewage (HC) was more effective in basic solutions (as long as the acidity was neutralized and more hydroxide groups were present to form insoluble compounds [$M(OH)_2$]). Hydroxide precipitates undergo excellent fixation in ash via strong electrostatic interaction with the charged surface of the ash particles. Measurements done using a scanning electron microscope (SEM) revealed overall ash character before and after washing with water or wuth dilute hydrochloric acid. Also, an analysis was performed on the primary elements, such as calcium, magnesium, sodium, potassium, sulfur, phosphate, silicon and aluminum, present on the surface of fly ash particles. The fly ash comprised particles of a variety of shapes, including closed and open spheres and some amorphous particles covered in pockmarks (within which are small beads that constitute the overall matrix). Likewise, SEM was used to examine the products of PAZ/SAFA fixation at ratios of 1/2 and 1/8 showing the dissipation of the different elements at the surface of the fixation product.

Based on the research, our main conclusions are:

A. Fly ash produced in Israel from the combustion of low sulfur bituminous coal has chemical reagent qualities effective in neutralizing highly acidic waste. Neutralization efficiency is not affected by the presence of very high levels of organic material.

B. Some of the basic elements (about 50% of fly ash potential) are located deep within the fly ash particle structure, and as such their full potential is not exploited during washing with water.

C. Fly ash is the most efficient chemical reagent for binding the toxic metals (those investigated in this research) found in the different industrial wastes tested in this study. Fixation quality meets the officially accepted standards for the cleansing of toxic materials. In other words, an environmentally friendly by-product was produced that can be used as one of the raw materials needed for various infrastructure projects and that can partially replace the sand required to make concrete. Fly ash fixation quality is the result of its pozzolanic properties, since the surface of fly ash particles are electrically charged. Under the experimental conditions for ageing the fixation product and after washing with water while shaking for periods of up to 16 days, close to 100% binding was achieved for the toxic metals tested.

D. The research was based on understanding the three fixation/adsorption mechanisms of bivalent cations on fly ash. These mechanisms depend on the characteristics of the double layer of charge at the surface of the fly ash and of the solution around the fly ash. These values depend on solution pH and on the zeta potential that characterizes the behavior of a substance under different pH conditions, of which three ranges were identified. In the basic pH range, the insoluble hydroxide compounds formed adsorb to the fly ash surface. Coordinated covalent bonds with specific sites on fly ash particles occur at neutral pH values. And in the acidic pH range the elements undergo electrostatic interaction with the fly ash particles in an ionic exchange manner.

E. The organic componenet of the waste does not affect the fixation quality of the fly ash.

F. Initial economic estimates of the cost of waste treatment (PAZ) when comparing toxic waste treatment at a central facility with treatment at a factory showed that local treatment, based on our procedure, may save about 50% using the fly ash. That figure does not include using the fixation product for other, environmentally friendly applications.

G. In its role as an alternative aggregate to sand, the fixation product can be used to partially replace sand in the production of concrete monoliths, which can be used in the construction industry without any environmental limits (as shown by the tests done in this research according to the regulations currently accepted by the Ministry of Environmental Protection in Israel).