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THERMAL POWER ASH: REMEDY FOR SULPHUR CONTAMINATED SOIL

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Abstract- Contaminants such as Iron, Sulphur etc are present in high concentrations in acidic leachate produced in coal mining and coal waste disposal sites. Laboratory column tests were conducted to study the chemical impact of coal mine drainage on soil. An assessment of the changes in contaminants in soil induced by the addition of fly ash was performed by a batch test. The experimental configuration comprised a 40 cm long glass continuous flow column. The experimental results underline the leaching over a long period, high loads of contaminants from acidic leachate. The main mechanisms involved in contaminants removal is adsorption at the surface of fly ash and the produced hydrous iron oxides, precipitation and co-precipitation. With addition of fly ash lower leaching of contaminants is observed during the experiment.

Keywords- Fly Ash, Coal Mine Drainages, Soil, Contamination, Leachates.

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Introduction

Acid mine drainage (AMD) is caused by the oxidation of residual sulphide minerals in the vadose zone of mine tailings and waste rock. The generated effluents are usually extremely acidic and contain elevated concentrations of sulfates, ferrous iron and dissolved hazardous trace elements. Although buffering of the pH to near neutral conditions may occur in groundwater, oxidation of Fe (II) to Fe(III) takes place when AMD is discharged to receiving surface waters. This generates additional acidity, causes mainly the precipitation of ferric oxy-hydroxides and has adverse impacts on aquatic ecosystems by lowering the pH and enhancing mobility of hazardous trace elements (Komnitsas et al., 1995). Permeable Reactive Barriers (PRBs) are an emerging technology used for the remediation of acidic leachates and contaminated groundwater. They are defined as "an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a preferential flow path through the reactive media and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals at points of compliance" (US EPA, 1997). Currently, two basic designs are being used in full scale applications: (1) the funnel and gate and (2) the continuous trench, while other designs are being investigated. Both configurations require information on contaminant concentration, contaminant degradation rate in the presence of the reactive subsurface and groundwater flow rate through the barrier. Reactive media used for the construction of PRBs should be fully characterized prior to their use so that they have low cost, maintain their reactivity over long periods of time, are compatible with the subsurface environment, do not cause any adverse chemical reactions with the constituents of the contaminated plume and do not deplete serving as source of contaminants themselves (Powell et al., 1998). Furthermore, they should promote geochemical reactions resulting in the removal of the hazardous ions from contaminated plumes in stable forms (Blowes et al., 2000). PRBs are installed along the path of the contaminating plume, therefore they should maintain their permeability as secondary precipitates accumulate and result in the attenuation of inorganic species over long periods varying from years to decades. PRBs are able to remove multiple contaminants depending on the reactive medium used for their construction (Snow, 1999). Zero-valent iron, limestone, fly ash, phosphate, ferrous salts and other compounds (e.g. $Mg(OH)_2$, $Mg(CO)_3$, $BaCl_2$, $CaCl_2$) are some of the most common reagents that raise pH to alkaline values and cause the precipitation of heavy metals as stable phases (Morrison, 1998; Ott, 1998). Zero-valent iron has been proven very efficient in reducing chlorinated organic solvents such as trichloroethylene (TCE) while limestone can be used for the clean up of AMD and the subsequent prevention of groundwater contamination. Research efforts on fly ash barriers to date have focused on the study of mechanisms involved in contaminant uptake. The most important characteristics of fly ash are the calcium content that provides alkalinity in the system raising pH to strongly alkaline values (~12) and the {$SiO_2+Al_2O_3+Fe_2O_3$} content. Alkali Fly Ash - Permeable Reactive Barriers (AFA-PRBs), constructed from fly ash that otherwise would have been disposed of or landfilled are an emerging and innovative technology that can be effective in removing heavy metals from acidic leachates or contaminated groundwater in an economically feasible manner. The removal of heavy metals from effluents and wastewaters by adsorption and precipitation on fly ash has been studied by a number of researchers. Bayat (2000, a and b), examined the effectiveness of fly ash for the removal of Ni, Cu, Zn, Cr and Cd while Mavros et al. (1993) used two different types of fly ash (from the coal fields of Kardia and Megalopolis in Greece) to remove Ni from wastewater. Weng and Huang (1994) pointed out that fly ash can be used as an effective adsorbent for Zn and Cd to clean up dilute industrial wastewaters. Héquet et al. (2001) studied the removal of Cu, Zn and Pb by fly ash and lime mixtures underlining that the most important parameters are fly ash properties, leachates pH, concentration of contaminants and fly ash/lime ratio. The properties of fly ash, which is in many countries a readily available and cheaper reactive material compared to zero-valent iron or activated carbon and the quality of the leachates, in terms of load and toxicity, define the efficiency of fly ash PRBs (Gavaskar, 1999). Another key issue is the residence time of leachates or the contaminated groundwater; this can be determined by taking into account the permeability of the selected media, the reaction rates or half-lives and the initial concentration of the contaminants. It has to be mentioned that after a long treatment period the reactive surface will be coated with metal hydroxides and other precipitates resulting in partial or total loss of porosity and hydraulic conductivity (NATO/CCMS Report, 2002). These disadvantages though can be overcome by careful design and control during construction and operation. In the present work, column experiments have been carried out to study the efficiency of lignite fly ash barriers for the removal of inorganic contaminants and the subsequent clean up of extremely acidic leachates generated at mining and waste disposal sites.

Column studies offer the following advantages (Gavaskar et al., 1998):

1. Design parameters are determined under dynamic flow conditions. The concentration of contaminants that changes with the distance traveled within the reactive cell can be monitored by installing sampling ports along the column walls.
2. Contaminant half-lives are generally more reliable than those determined through batch
3. tests.
4. Nonlinear sorption is simulated more precisely.
5. Since in a batch system reaction products formed tend to accumulate, continuous flow through columns may force partial re-solubilization for some of them and subsequent deposition in longer distances; this approach is more realistic in actual field conditions.

Experimental

The AMD contaminated soil, Demineralized Water & Bituminous Coal Fly Ash is used in this study

Laboratory experiments were carried out in duplicate at room temperature using two 40 cm long and 5 cm inner diameter Plexiglas columns. These dimensions are considered as standard and have been used in many research studies. They offer several advantages regarding maintenance of the desired flow rate, study of contaminants degradation profile and modeling of the process. The reactive media in each column contained 50% w/w of fly ash 50% w/w of Soil. Fly ash is composed of spherical, amorphous ferro-aluminosilicate minerals and has low permeability, low bulk density and high specific surface area. (Xenidis et al., 2002). Due to its higher than 90% $SiO_2+Al_2O_3+Fe_2O_3$ content (91 %) it is characterized as Class F along with Oxides of Alkali & Alkaline earth metals, IA & IIA period of periodic table of elements.

Mixing of fly ash with contaminated soil was carried out to minimize potential clogging and cementation problems during the later stages of operation. Each column was packed with the reactive media in such a way as to ensure a homogeneous matrix. The experimental set up shown in figure No.1.

Fig. 1-

Results & Discussion

The most important experimental data derived from leachate analysis at each sampled volume part as a function of the number of pore volumes passed through the columns. The chemical analysis is shown in Table No.1. From the table it is evidenced that the Sulphate & Iron concentration was drastically decreased from the leachates

It is well studied that the all hazardous ions of contaminated soil will leached in acidic condition. From the column experiments carried out it is seen that Bituminous fly ash exhibit a noticeable potential for the clean up of acidic leachates containing high loads of Sulphur & Iron. By taking into account this experimental work, it is strongly believed that this efficiency will substantially increase in real AMD contaminated sites. Even better results are expected if such barriers are used for groundwater remediation.

The main clean up mechanisms are precipitation and/or surface adsorption. Hydroxides, oxyhydroxides and sulfates are the major compounds formed. Sulfate concentration was decreased from the initial value of 7574 mg/Kg to 667 mg/Kg i.e. 91.19 % at the end of the runs.

Fly ash has the potential to neutralize this acidity and precipitate most ions very quickly. The results showed that the concentration / toxicity of the resulting precipitates, regarding all hazardous ions in concern, is well below compliance limits, therefore the operation of fly ash barriers is not expected to cause any environmental problems.

Table 1-

Minerals in form of Oxides in FLY ASH	
Minerals	(%)
Silica as SiO2	62.1
Aluminium as Al2O3	24.43
Iron as Fe2O3	4.2
Titanium as TiO2	2.77
Calcium as CaO	2.2
Magnesium as MgO	1.03
Sodium as Na2O	0.22
Potassium as K2O	0.77
Sulphite as SO3	1.1
Phosphorous Pentaoxide	0.3

Table 2-

Parameters	Farming Soil	Contaminated Soil	Contaminated Soil after Leaching
pH	7.20	2.30	6.63
Chlorides	91.00	655.00	144.00
Sulphates	146.00	7574.00	667.00
Iron	2.70	13.70	1.28
Nitrogen	0.04	0.10	0.12
Water Retaining Capacity	26.40	40.80	53.70
Moisture Content	1.90	19.00	31.08
Organic Content	6.80	10.30	5.61
Fixed Residue	91.30	70.70	63.30

Conclusion

Fly ash is efficient in decontaminating extremely acidic leachates, loaded with high concentrations of Sulphate & Iron. Experimental column studies showed that all contaminants can be completely removed. It is very much useful for the treatment of acidic leachates and remediation of the AMD contaminated soil.

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