

## CLEAN UP OF ACIDIC LEACHATES USING FLY ASH BARRIERS: LABORATORY COLUMN STUDIES

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### ABSTRACT

Laboratory column tests were conducted to study the efficiency of lignite fly ash barriers in removing heavy metal ions, such as Fe, Zn, Mn, Ni, Cd, Co, Al and Cu, present in high concentrations in acidic leachates produced in mining and waste disposal sites. The experimental configuration comprised two 40 cm long plexiglas continuous flow columns installed in series. An upward flow of synthetic acidic solutions spiked with high concentrations of contaminants was maintained in order to simulate field flow rates and residence times. Sampling ports fitted along the column walls allowed sampling and provided information on geochemical mechanisms within the barrier and contaminant degradation rates in the presence of the reactive material.

The geochemical speciation/mass transfer computer code PHREEQC and the MINTEQ database were used for geochemical modeling of the process.

The experimental results underline the potential of lignite fly ash permeable reactive barriers to remove almost completely, over a long period, high loads of inorganic contaminants from very acidic leachates. The main mechanisms involved in contaminants removal are adsorption at the surface of fly ash and the produced hydrous iron oxides, precipitation and co-precipitation. The toxicity of the reactive material at the end of the treatment period, regarding all heavy metals studied, is limited.

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**KEYWORDS:** permeable reactive barriers, fly ash, geochemical modeling.

### 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, fer-

rous 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 precipi-

tation 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 ( $\sim 12$ ) 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 Kardias 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 tests.
3. Nonlinear sorption is simulated more precisely.
4. 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.

## MATERIALS AND METHODS

### Materials and methodology

Laboratory experiments were carried out in duplicate at room temperature using two 40 cm long and 5 cm inner diameter plexiglas columns in series. 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 Greek fly ash obtained from Kardias thermal power plant and 50% w/w of silica sand 20-30 mesh (0.84-0.60 mm). Fly ash is composed of spherical, amorphous ferro-aluminosilicate minerals and has low permeability, low bulk density and high specific surface area. Due to its higher than 50%  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  content (53%) it is characterized as Class C and possesses cementitious and pozzolanic properties (Xenidis *et al.*, 2002). Its grain size distribution, evaluated using a Malvern mastersizer microplus laser apparatus with a capability of tracing particles between 0.05 and 556 microns, was -500+100 microns: 22%, -100+50 microns: 20%, -50+10 microns: 33% and -10 microns: 25%. The fly ash used in this study has an almost identical particle

size distribution with the fly ashes produced from Agios Demetrios and Ptolemais, Greece, thermal power plants (20-23 % >105 microns, 16-25% < 63 microns), but it is finer than the fly ash produced from the Amyntaion - Filotas plant (45% > 105 microns, 10% < 63 microns) (Arditsoglou *et al.*, 2004). Mixing of fly ash with silica sand was carried out to minimize potential clogging and cementation problems during the later stages of operation. The mixture was placed in the middle section of the column between a 3 cm silica sand layer at the bottom and a 5 cm layer at the top. Each column was packed with the reactive media in such a way as to ensure a homogeneous matrix. The average total porosity was 0.33 (total pore volume was 568  $\text{cm}^3$ ), while the average flow rate used to simulate real field conditions was  $30 \pm 0.25$  cm per day. Therefore, the calculated leachates flow rate, based on total pore volume, was  $1.15 \pm 0.05$  pore volumes per day and the residence time  $0.4 \pm 0.05$  days. The porosity was determined by dividing the total pore volume by the volume of the columns while the total pore volume was determined by weighting the columns dry and fully saturated.

The synthetic aqueous solutions used in this study as simulated severe AMD were prepared by adding appropriate concentrations of the target contaminants in deionized water in HCl-cleaned glassware. Initial ion concentration was  $1.5 \text{ g l}^{-1}$  Fe(III),  $100 \text{ mg l}^{-1}$  Al(III),  $5 \text{ mg l}^{-1}$  Co(II),  $5 \text{ mg l}^{-1}$  Ni(II),  $5 \text{ mg l}^{-1}$  Cu(II),  $5 \text{ mg l}^{-1}$  Mn(II) and  $20 \text{ mg l}^{-1}$  Zn(II). The concentrations used are considerably higher than most of those tested in literature in order to allow in a relatively short experimental period the study of the efficiency of lignite fly ash in removing heavy metal ions, the calculation of the optimum residence time and the design of a PRB system. The analytical grade reagents used were iron sulfate monohydrate,  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ , aluminum sulfate 18-hydrate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , cadmium trisulfate octahydrate,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , copper sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , manganese sulfate monohydrate,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , zinc sulfate heptahydrate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , nickel sulphate hexahydrate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and cobalt sulfate heptahydrate,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . The pH of this simulated leachate was  $\sim 2.2$  while the Eh was  $\sim 325$  mV. An upward flow of the synthetic solution was maintained through the columns using a peristaltic pump Gala/4W in order to simulate

precisely actual field flow rates. The actual experimental flow rate was monitored daily by collecting timed volumes of solutions.

Sampling ports installed along the column walls, at a distance of 20 cm (sampling port A) and 60 cm from the inlet (sampling port B), allowed sampling and analysis of the leachates quality during column operation. Samples were collected from each sampling port using glass syringes to avoid disturbance and analyzed for pH and redox potential (Eh) immediately after sampling with a pH/Conductivity meter (Metrohm 691 pH meter). Solutions were filtered through 0.45 $\mu$ m filters (Gelman Science sterile aerodisc) and analyzed for total Fe, Zn, Mn, Al, Ni, Cu, Co and Cd using Flame Atomic Absorption Spectrophotometry (Perkin Elmer 2100). Sulfate concentration was measured gravimetrically by adding saturated BaCl<sub>2</sub> solution to form BaSO<sub>4</sub> precipitate. Concentration profiles were generated periodically for all sampling ports and elements of concern. Solid samples of the reactive material were collected at the end of each experiment and analyzed by X-ray diffraction analysis (XRD) using a Siemens 500X Diffractometer to determine all mineralogical phases formed. Toxicity of the used reactive material was determined by the Toxicity Characteristics Leaching Procedure (TCLP, EPA Method 1311) (US EPA, 1986).

### Geochemical Modeling

Geochemical modeling, using the equilibrium computer code PHREEQC (Parkhurst, 1995) and the MINTEQA database (Allison *et al.*, 1991), was performed to determine the ionic forms present in the aqueous phase and to calculate saturation indices.

PHREEQC is a software developed by the US Geological Survey able to perform aqueous geochemical calculations and modeling including

- Speciation and saturation-index calculations
- Reaction-path and advective-transport calculations, involving specified irreversible reactions, mixing of solutions, mineral and gas equilibria, surface complexation reactions, ion-exchange reactions and
- Inverse modeling to determine sets of mineral and gas mole transfers that account for composition changes in solutions within specified compositional uncertainties.

Input parameters were Al, Cd, Cu, Fe (III), Mn,

Ni, Si, and SO<sub>4</sub><sup>2-</sup> for the simulation of the leachates quality and Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CaO for the interpretation of the geochemical reactions taking place between lignite fly ash and the contaminants. Co was not taken into account since it does not exist in the MINTEQA database. Calculations show that Cu, Cd, Mn, Ni and Zn are mainly present in the leachates (feed) as free ions; 32-40% of Cu, Cd, Ni and Zn are present as dissolved MSO<sub>4</sub> (aq) species. Al is present as AlSO<sub>4</sub><sup>+</sup>, while Fe as FeSO<sub>4</sub><sup>+</sup>. The simulated AMD feed is supersaturated with respect to goethite, hematite, jarosite-H, lepidocrocite, maghemite, cupric and cuprous ferrites.

### RESULTS AND DISCUSSION

The most important experimental data derived from leachate analysis at each sampling port as a function of the number of pore volumes passed through the columns are seen below.

The effluent pH decreased slowly from 12.86 to 11.02 when 37 pore volumes passed through the columns. The pH at sampling port A decreased more quickly and after 12 pore volumes reached 2.62 while the decrease of pH at sampling port B was actually initiated after 32 pore volumes (Figure 1). This indicates that although the lower parts of the PRB, coated with formed precipitates, lose part of their efficiency to buffer pH, the upper parts retain their reactivity for a long period. Over the same period redox potential was maintained at low values and varied between 200 and 350 mV, indicating that poor oxidation conditions prevail within the entire reactive materials profile.

Iron was completely removed from the leachates, as seen from measurements at sampling ports B and C, after 37 pore volumes have passed through the columns. It was again detected at sampling port A after 22 pore volumes but precipitated again before reaching sampling port B due to reaction with "fresh" lignite fly ash (Figure 2a). Iron precipitation was clearly seen by observing the color changes of the reactive material; the initial light, sandy-brown color before the start of the tests turned to a dark yellowish-orange at the end. XRD analysis of the fly ash at the end of the tests revealed that the main iron precipitates were hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), goethite ( $\alpha$ -FeOOH) and in lesser amounts ferrihydrite (Fe<sub>5</sub>HO<sub>8</sub>·4H<sub>2</sub>O) or iron hydroxide (Fe(OH)<sub>3</sub>) (Allison *et al.*, 1991 and Baltpurvins *et al.*, 1997). Geochemical modeling indicates that iron precipi-

tates as goethite, hematite and ferrihydrite when pH ranges between 9-12, 8-9 and 3-8 respectively. Aluminium shows similar to iron behavior. The final effluent concentration was below detection limit and therefore meets remediation concentration goals, but the concentration at sampling ports B and A after 37 pore volumes was 85.6 and 589.3 mg l<sup>-1</sup> respectively (Figure 2b). The high concentration measured at sampling port A is due to re-solubilization of Al precipitates when fresh acidic leachate flows through the column; partial dissolution of aluminium from fly ash may be also considered. While most of the precipitates were amorphous and therefore could not be detected by XRD analysis, calculation of saturation indices (SI) indicates that Al(OH)<sub>3</sub> (am) can precipitate at pH values higher than 5. This conclusion is supported by the pH values recorded at the upper parts of the experimental configuration; these values were well above 5 at sampling port B after 32

pore volumes passed through the system. Copper concentration remains below analytical detection limits at sampling ports A, B and C after 18, 32 and 37 pore volumes have passed (Figure 3a). Geochemical speciation calculations suggest that at pH values between 5 and 6 copper precipitates as cupric and cuprous ferrite and can be adsorbed on the surface of fly ash, as indicated in previous studies (Manceau *et al.*, 2000). Zinc concentration in again noticeable in the leachates at sampling ports A and B only after 16 and 32 pore volumes have passed through the columns, whereas it remains below detection limit at sampling port C at the end of the runs (Figure 3b). Zn immobilization seems to be combined with sulphate reduction. MINTEQC indicates that Zn co-precipitates mainly with Si that is slowly solubilized either from the fly ash or the silica sand at pH 6-7 and forms willemite (Zn<sub>2</sub>SiO<sub>4</sub>) (Héquet *et al.*, 2001, Manceau *et al.*, 2000). Nickel and cobalt show, as expected, similar behavior and are detected in the leachates at sampling ports A and B only after 16 and 32 pore volumes have passed through the columns (Figures 3c,d). Concentration at sampling port C remains for both elements well below detection limit after 37 pore volumes. PHREEQC calculations indicate that nickel precipitates as Ni(OH)<sub>2</sub> or co-precipitates as NiSiO<sub>4</sub> (Rao *et al.*, 2002). Cadmium removal trend was similar to copper. Cadmium concentration remained below analytical detection limits for 19, 32 and 37 pore volumes at sampling ports A, B and C respectively (Figure 4a). Modeling and previous studies (Yadawa *et al.*, 1987) indicate that removal of Cd from leachates is accom-

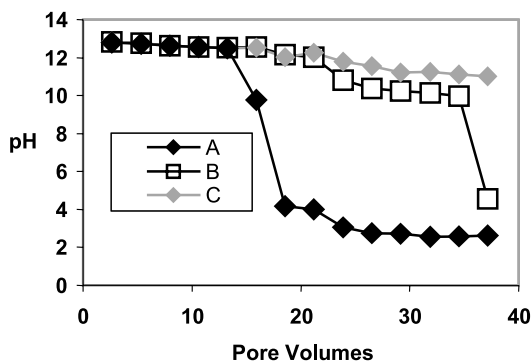


Figure 1. pH values at sampling ports A,B and C versus pore volumes

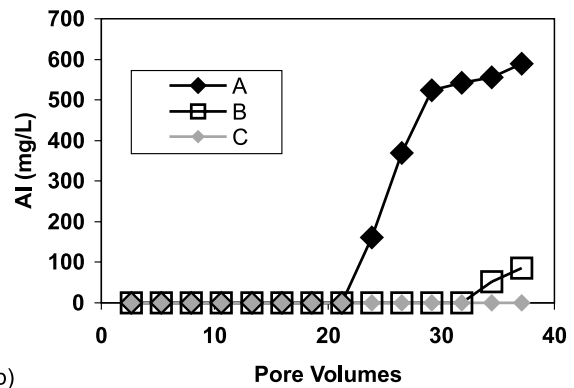
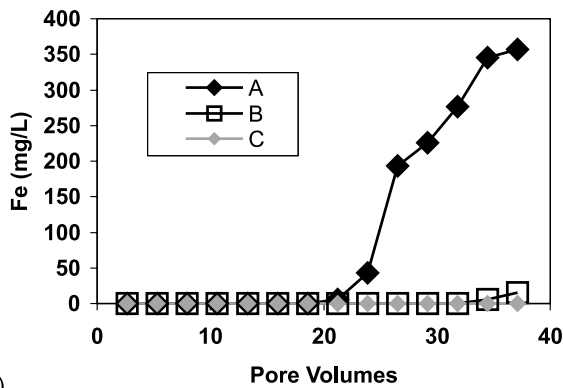


Figure 2 a,b. Fe and Al concentrations at sampling ports A, B and C versus pore volumes (Initial concentrations: 1.5 g l<sup>-1</sup> Fe and 100 mg l<sup>-1</sup> Al)

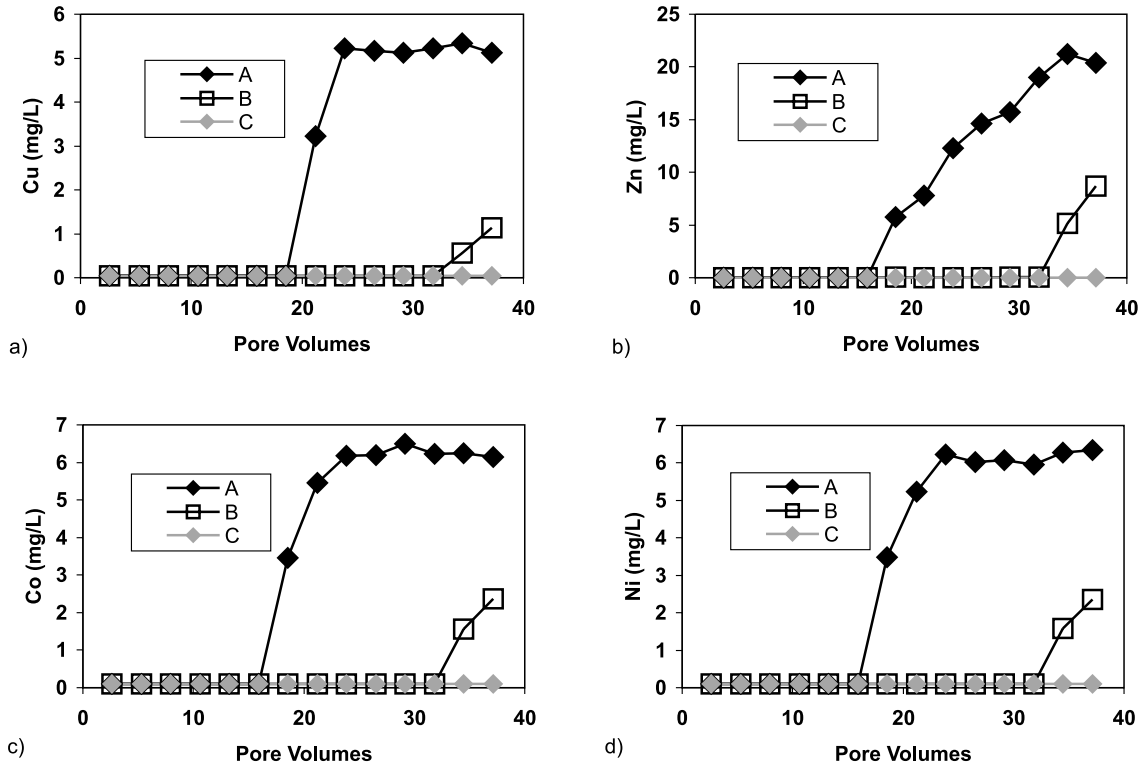


Figure 3 a,b,c,d. Cu, Zn, Co and Ni concentrations at sampling ports A, B and C versus pore volumes (Initial concentration 5 mg l<sup>-1</sup> except for zinc 20 mg l<sup>-1</sup>)

plished by co-precipitation/adsorption as CdSiO<sub>3</sub>. Experimental results indicate that the stability of this phase is quite high since its re-solubilization by fresh acidic solutions is limited and does not cause any increased Cd concentrations at sampling port A after 37 pore volumes; maximum Cd concentration at this point remains stable at 5 mg l<sup>-1</sup>.

Manganese is an extremely mobile ion and its removal from leachates is in most cases an extremely difficult task. Study of the Pourbaix diagrams shows that under mild oxidizing conditions manganese is in a +4 valence state and forms an insoluble precipitate, MnO<sub>2</sub>, while under reducing conditions is converted to the +2 valence state and is present as soluble Mn<sup>2+</sup> cation. Manganese reached the initial feed concentration at sampling port A after 21 pore volumes and exceeded that by three times after 37 pore volumes have passed through the system (Figure 4b). The concentration at sampling port B started to increase after 32 pore volumes, while no Mn was reported at the effluent (port C) after the end of the runs.

Increased Mn concentrations at sampling port A

are due to re-dissolution of previously formed unstable precipitates or desorption from the surface of hydrous iron oxides or fly ash by the action of the low pH fresh AMD or due to leaching of manganese from fly ash (Mn content in fly ash: 310 mg kg<sup>-1</sup>).

From the column experiments carried out it is seen that lignite fly ash PRBs exhibit a noticeable potential for the clean up of acidic leachates containing high loads of various heavy metals, at a rate of 27 m<sup>3</sup> per ton of fly ash. By taking into account that this volume includes all hazardous ions studied in this experimental work it is strongly believed that this efficiency will substantially increase in real conditions where less and in lower concentration ions are usually present. 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 4640 mg l<sup>-1</sup> to 2300 mg l<sup>-1</sup>

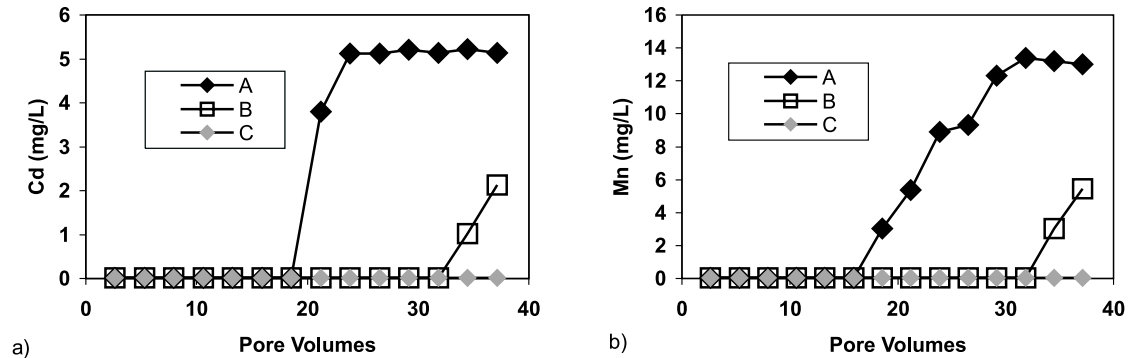


Figure 4 a,b. Cadmium and manganese concentrations at sampling ports A, B and C versus total pore volumes (Initial concentrations 5 mg l<sup>-1</sup>)

at the end of the runs. It has to be underlined though that the formation of hydrated oxide-type sorbents may hinder precipitation of metal hydroxides in a saturated solution as for example happens in suspensions containing silica sorbents that bind copper ions and prevent copper precipitation (Park *et al.*, 1995).

Even though in some cases re-solubilization of some hazardous ions is seen in the first parts of a fly ash PRB due to the flow of "fresh" highly acidic solution, the reactive material has the potential to neutralize this acidity and precipitate most ions very quickly. The pH dependent sequence of metal hydroxides solubility in the leachates, as determined in this study, Mn>Co≈Ni>Cd>Zn>Cu>Al>Fe, is in accordance with that reported in other experimental studies (Stumm and Morgan, 1981).

TCLP tests (US EPA, 1986) performed at the end of the runs show that the 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, provided that the local chemical and hydro-geological conditions at the construction site do not alter dramatically with time. Care should be taken though during operation in real field conditions to avoid cementation and clogging by mixing fly ash with inert materials such as silica sand at ratios varying between 1:1 and 1:3 and by maintaining saturated conditions within the fly ash barrier. Cementation is caused due to the pozzolanic properties of fly ash and the formation of calcium-silicate hydrates. Similar problems were encountered in the present experimental study towards the end of the runs due to power cuts for a couple of days.

## CONCLUSIONS

Lignite fly ash permeable reactive barriers are efficient in decontaminating extremely acidic leachates, loaded with high concentrations of hazardous heavy metal ions. Experimental column studies show that all contaminants can be completely removed for a long period and provide useful information for the design of PRBs installed in the field for the treatment of such leachates and the prevention of groundwater contamination. The main clean up mechanisms are (i) adsorption at the surface of fly ash particles for Ni, Cu and Cd (ii) precipitation as a separate phase, coating fly ash particles for Fe, Al and Ni and (iii) co-precipitation for Cu, Zn and Cd.

Monitoring of the leachates quality along the flow path, by sampling at a number of ports fitted along the column walls, allows the estimation of the optimum residence time required, within the reactive zone, to achieve remediation goals, enabling thus calculation of the required thickness of the permeable reactive barrier. Careful design and control is required though to optimize its performance and avoid operational difficulties under field conditions. In addition, the seasonal anticipated changes of groundwater table should be seriously taken into consideration. Finally, the solubilisation of fly ash elements as well as the re-solubilisation of previously formed unstable precipitates should be also considered in order to optimize the effectiveness of similar PRB systems. It is believed though that the latter factors will not influence to a great extent field applications due to the significantly lower acidity and hazardous load seen in leachates produced in mining and waste disposal areas and in contaminated groundwater.

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