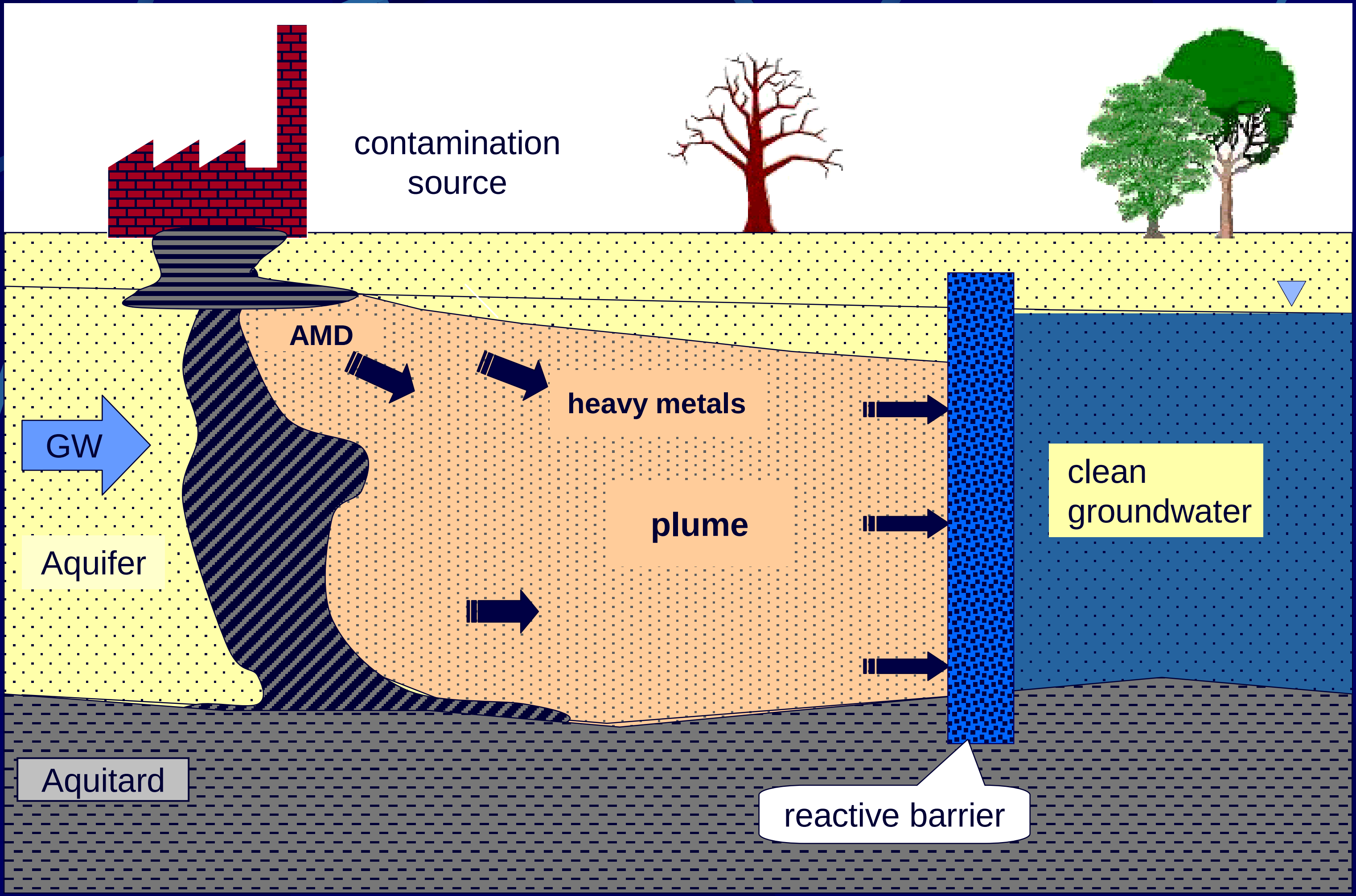
EVALUATION OF LOW-COST MATERIALS FOR THE DECONTAMINATION OF ACIDIC LEACHATES USING PERMEABLE REACTIVE BARRIERS

K. Komnitsas[1], G. Bartzas[2] and I. Paspaliaris[2]

[1]Technical University of Crete
Department of Mineral Resources Engineering
Laboratory of Waste Management

[2]National Technical University of Athens
School of Mining Engineering and Metallurgy
Laboratory of Metallurgy

A typical PRB system



Objective

To study the efficiency of PRBs for treatment of AMD and clean up of contaminated groundwater

In situ PRBs installed in the path of contaminated plume are alternative technologies to traditional pump and treat systems

Methodology

Literature Review	Column Tests	Geo-chemical Modeling
– Permeable Reactive Barriers (PRBs) – Reactive materials (low cost, commonly used) – Modeling (column chemistry, simulation)	– Characterization of the reactive materials (also at the end of the experiments) – Column tests design and results	– PHREEQC (geochemical speciation/mass transfer computer code) – MINTEQ Database – Determine ionic forms in the aqueous phase and calculate saturation indices – Reveal clean-up mechanisms

Why column studies?

- **Design parameters are determined under dynamic flow conditions**
- **Measured half-lives of contaminants are more reliable than those measured in batch tests**
- **Nonlinear sorption is better simulated**
- **Column profile offers data which can be used in an in situ geochemical barrier**

Desirable characteristics of reactive materials

- effective in removing contaminants of concern
- readily available
- active over long periods of time
- no adverse geochemical reactions or byproducts
- compatible with subsurface environment
- low O & M costs

Type of materials used

Reactive Materials

Lignite fly ash - Class C
(SiO_2+Al_2O_3+Fe_2O_3: 53%)

Quarry quality Limestone

Column Tests Design

Main Components and Characteristics

Reactive Mixtures

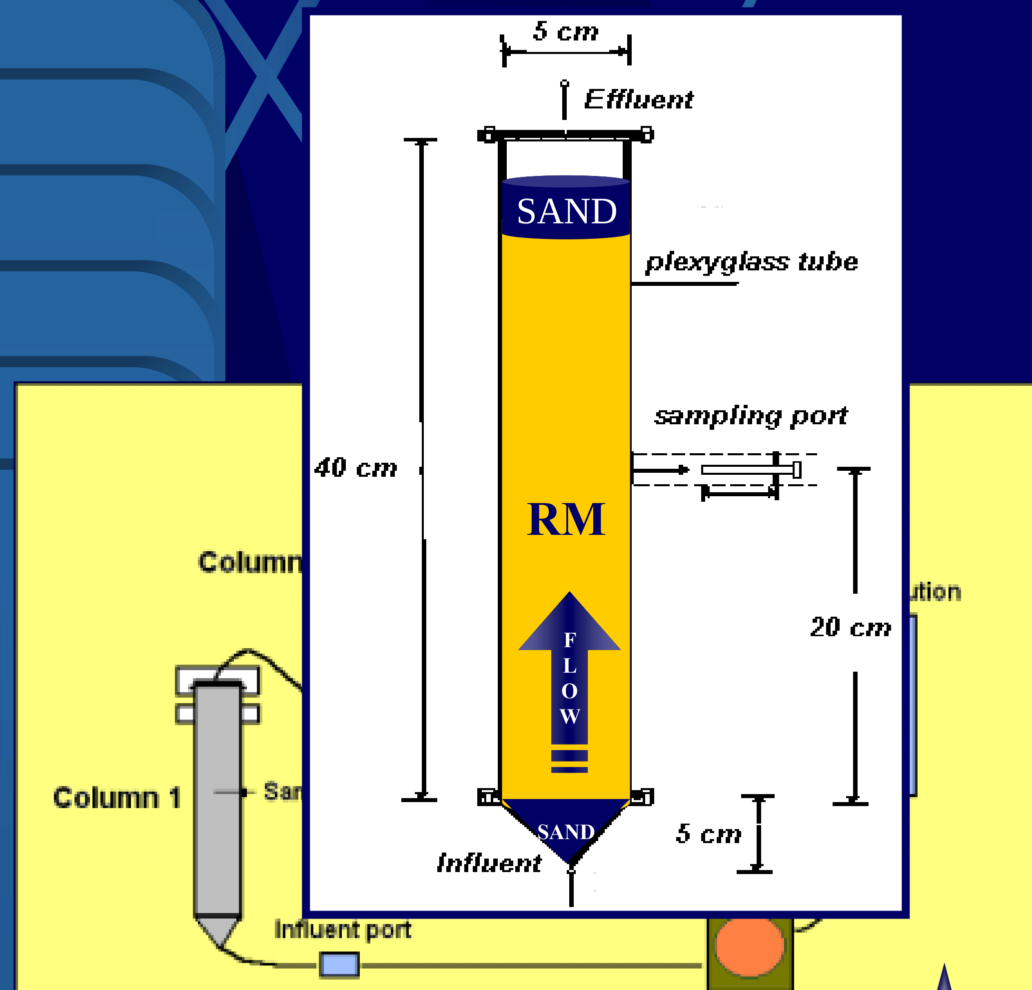
Flow

Volume

Porosity

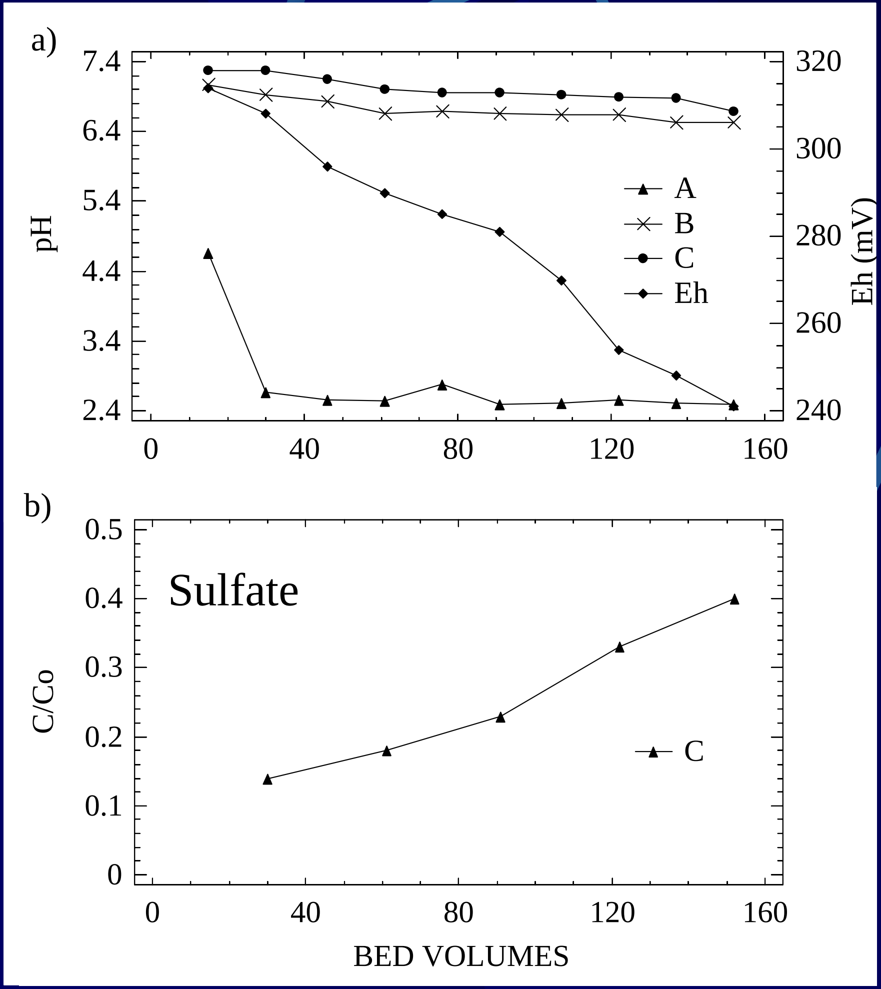
Metal-uptake mechanisms

- Precipitation
- Co-Precipitation
- Surface Adsorption

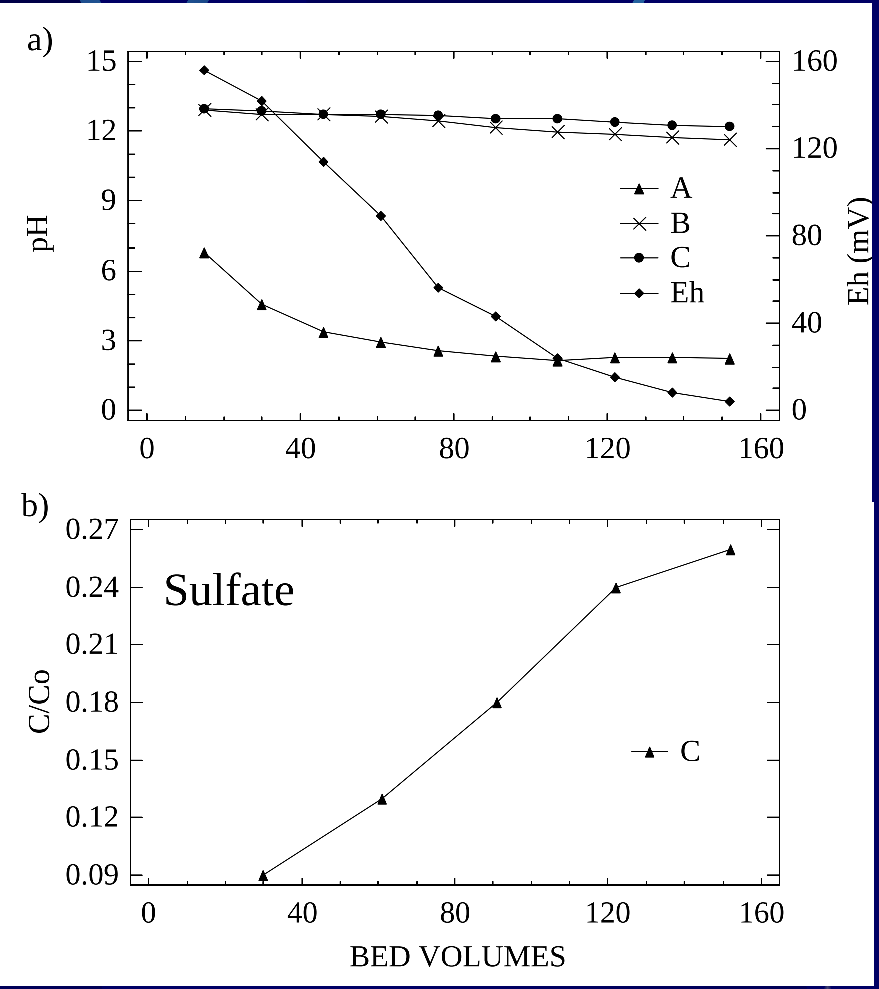


Column Tests Plots

Limestone



Lignite-based fly ash

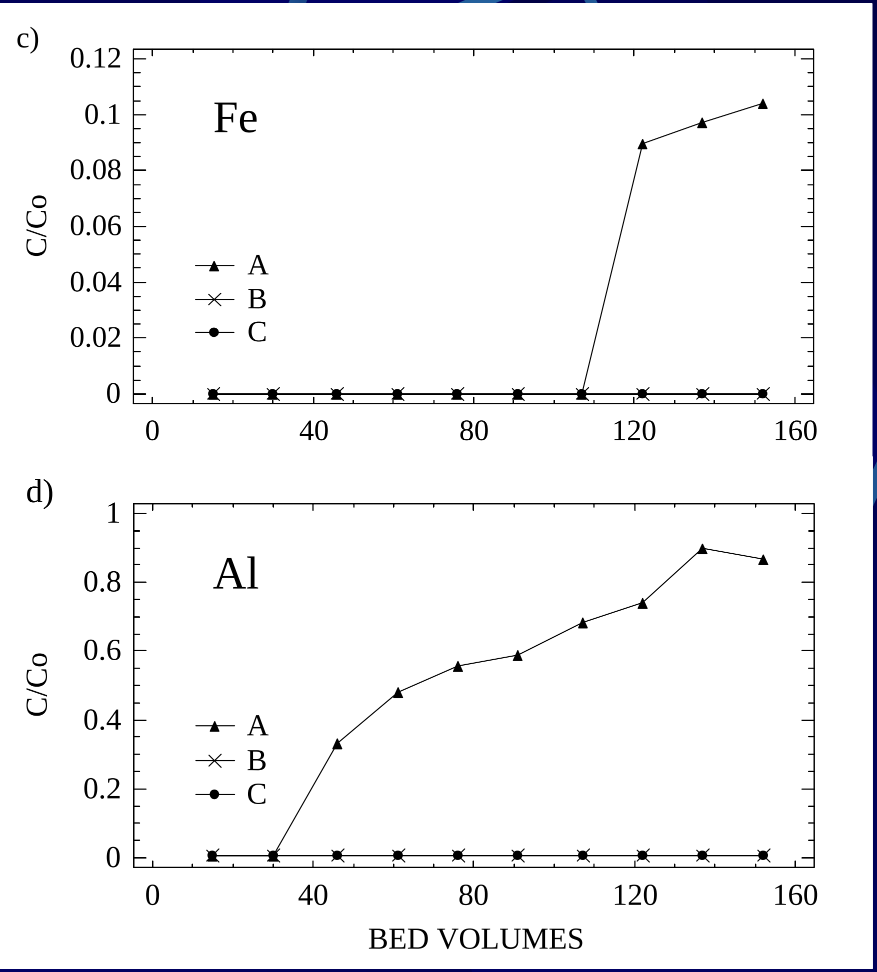


Initial pH=~2.2, Initial Conc.Sulfate=6400 mg/l

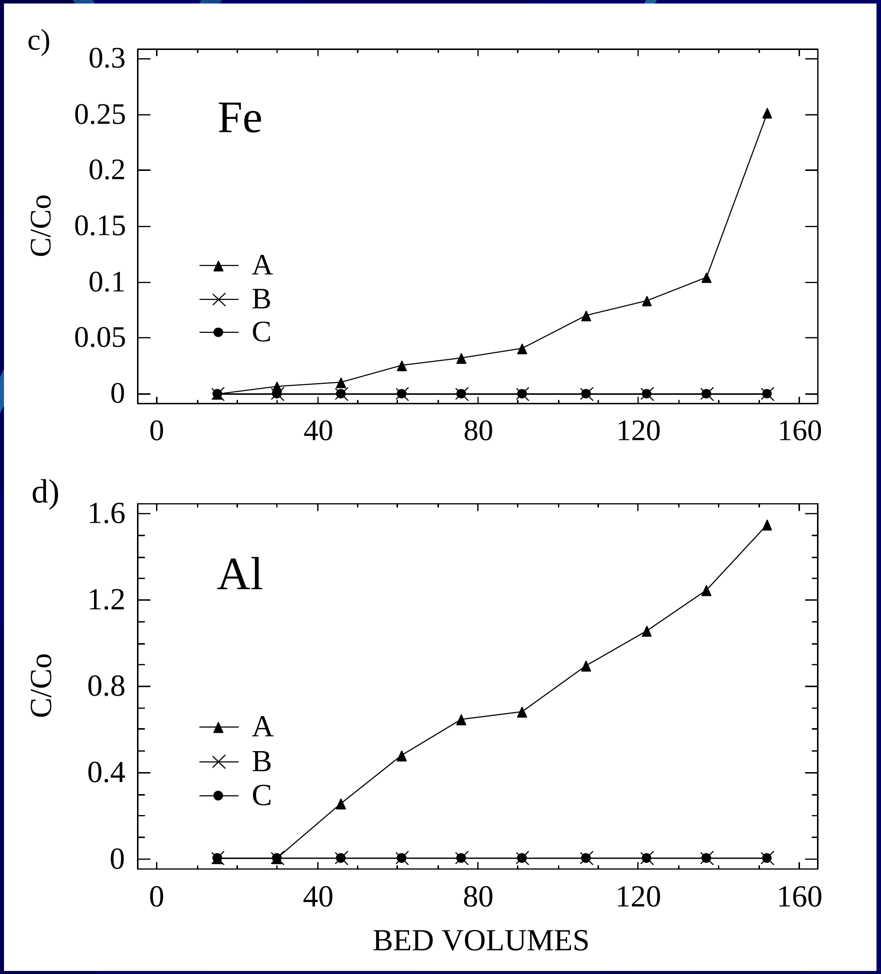
152 Bed Volumes = 5 weeks

Column Tests Plots

Limestone



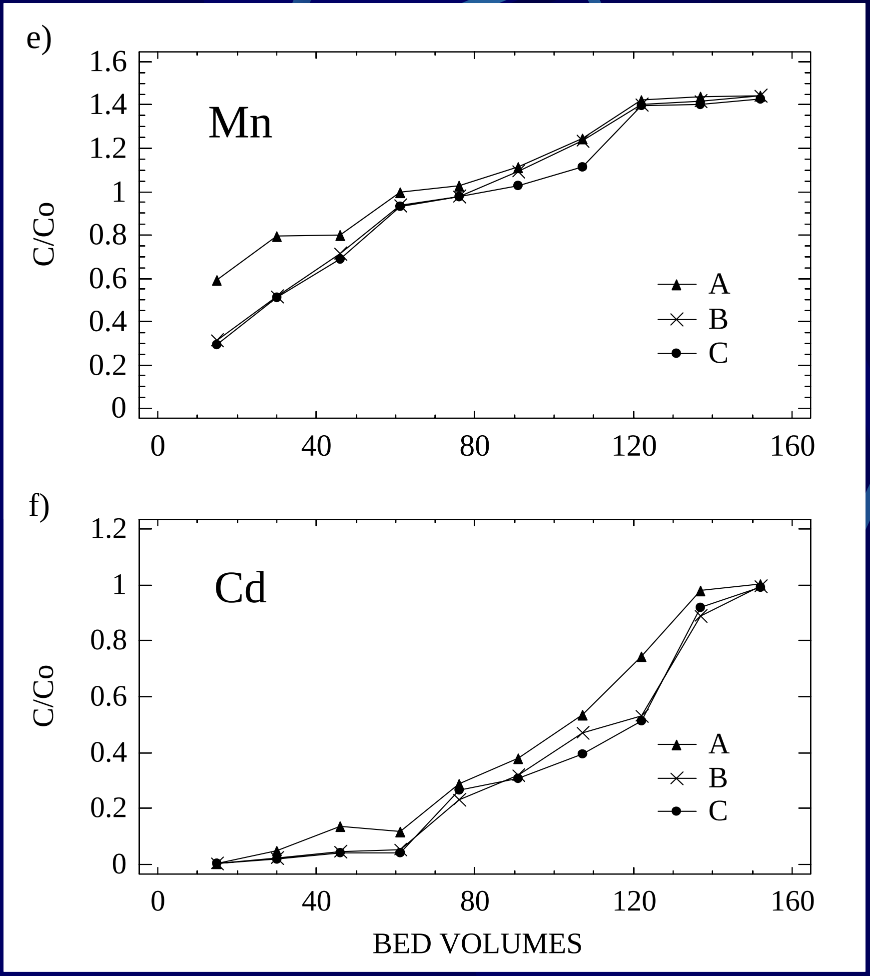
Lignite-based fly ash



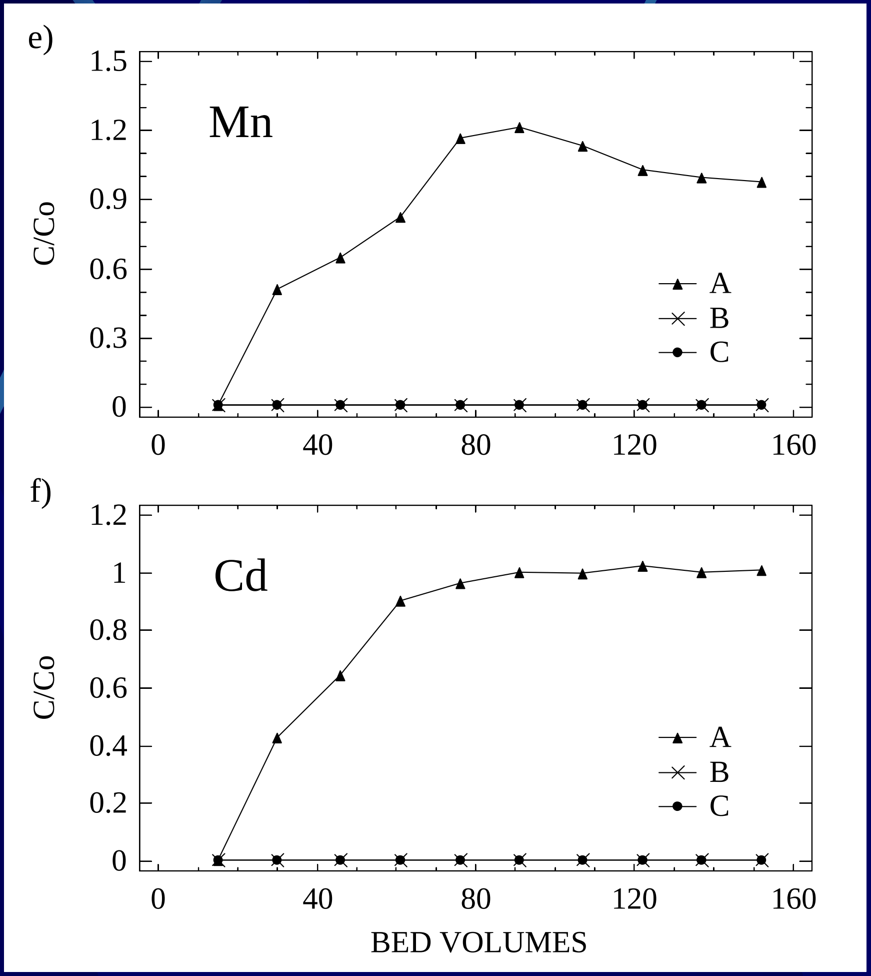
Initial Conc. Fe=1500 mg/l, Al=100 mg/l

Column Tests Plots

Limestone



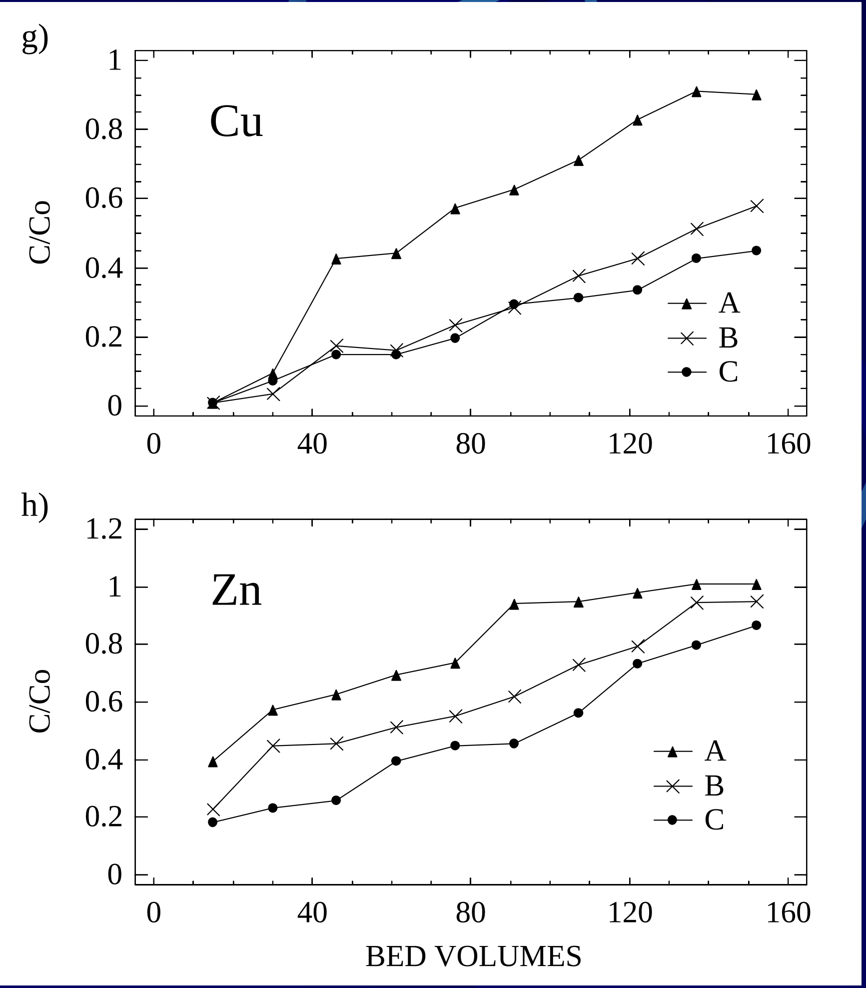
Lignite-based fly ash



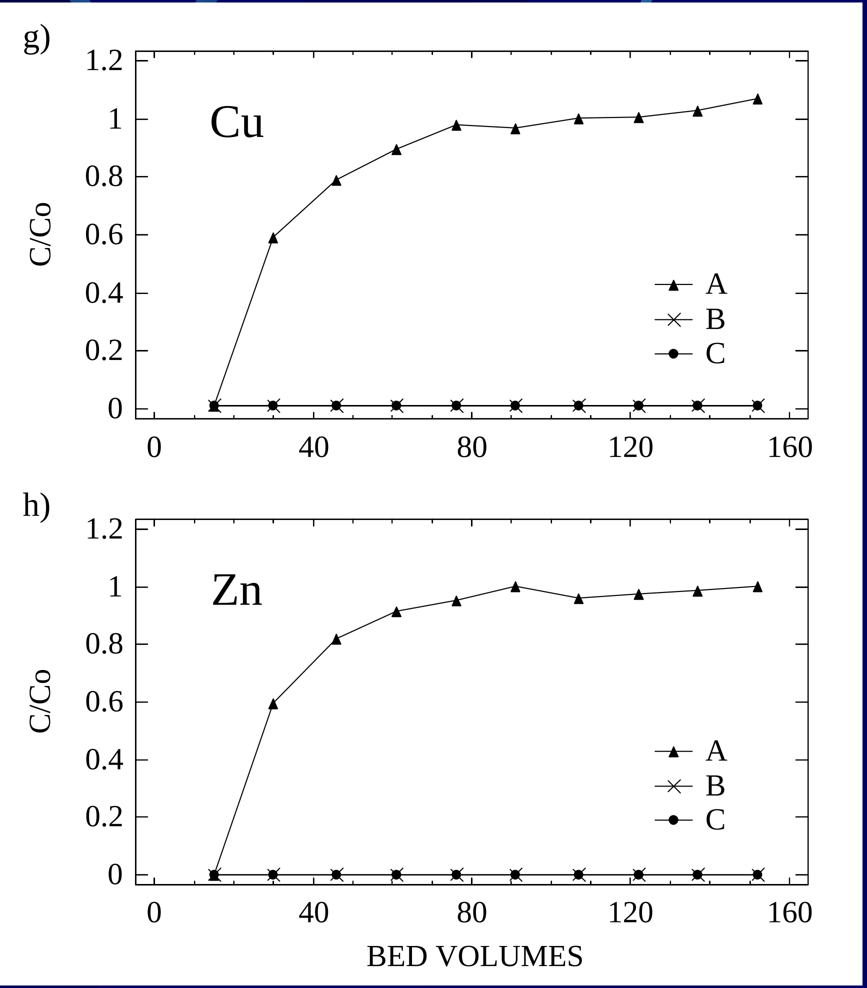
Initial Conc. Mn=5 mg/l, Cd=5 mg/l

Column Tests Plots

Limestone



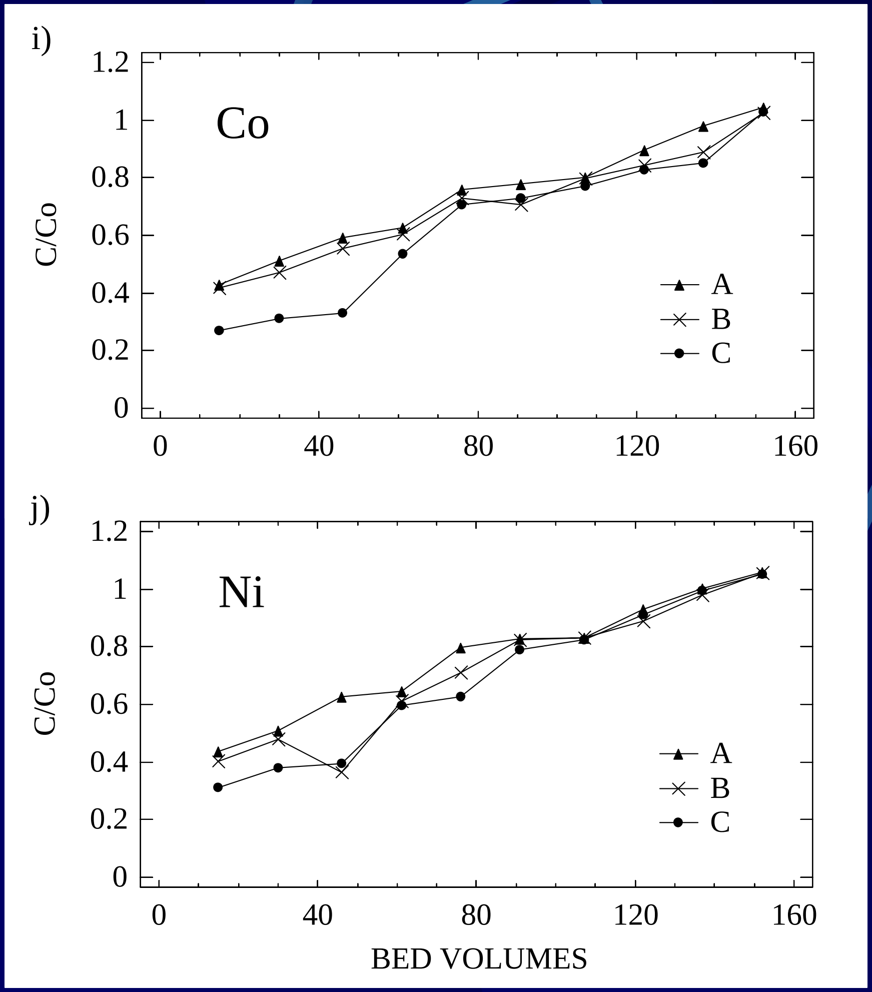
Lignite-based fly ash



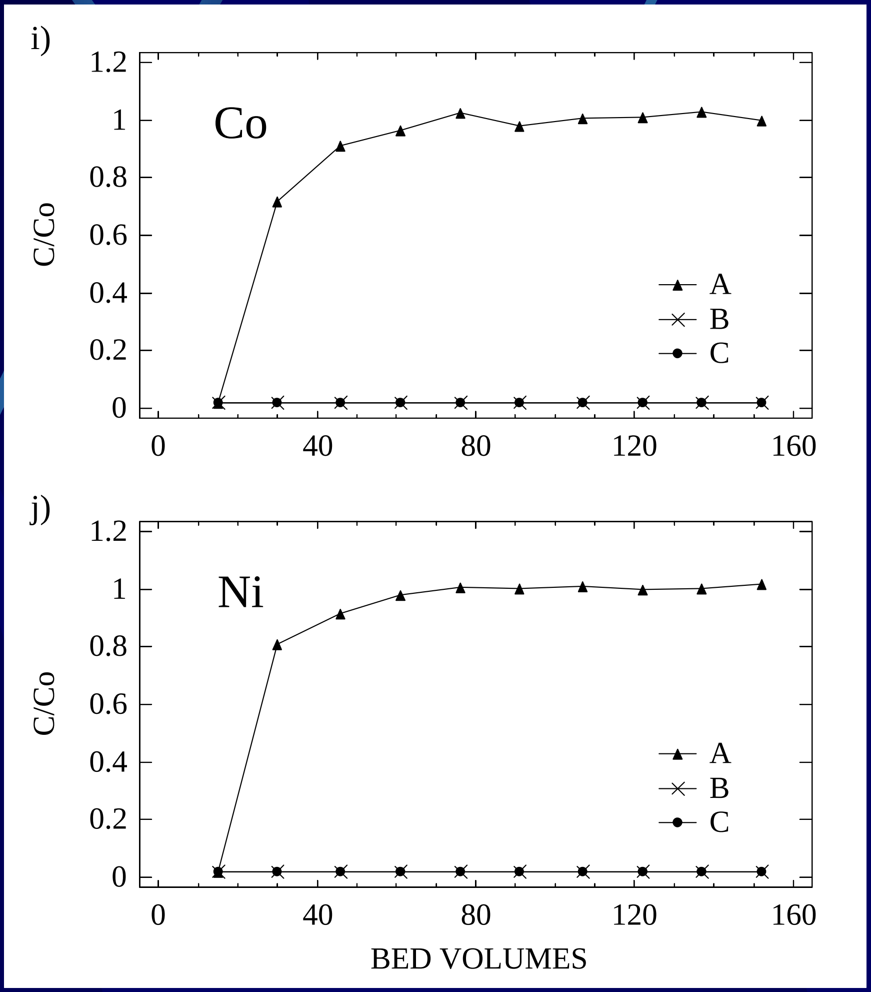
Initial Conc. Cu=5 mg/l, Zn=20 mg/l

Column Tests Plots

Limestone



Lignite-based fly ash



Initial Conc. Co=5 mg/l, Ni=5 mg/l

Results

Limestone

- Column tests with fly ash were run for 152 Bed Volumes (about 32,5 l) for high flow rate until heavy metal concentration in the effluent reached its initial value

- Limestone provides less alkalinity in the system and therefore can not clean up contaminated plumes over long periods (except for Fe and Al)

- The effective life time of an actual field PRB system can be easily predicted

- Efficiency is expected to increase substantially under field conditions, where lower flow rates are expected

Results

Lignite based fly ash

- Column tests with fly ash were run for 152 Bed Volumes (about 37,8 l) for high flow rate until heavy metal concentration in the effluent reached its initial value

- The concentration of all heavy metal ions in the effluents was below discharge values over a long period (5 weeks)

- Fly ash provides sufficient alkalinity in the system and therefore can clean up contaminated leachates

- The effective life time of an actual field PRB system can be easily predicted

- Efficiency is expected to increase substantially under field conditions, where lower flow rates are expected.

Results

Lignite based fly ash

- The pH dependent sequence of metal hydroxides solubility, formed with the action of lignite based fly ash is Mn>Co≈Ni>Cd>Zn>Cu>Al>Fe (in accordance with the order of solubility for the corresponding metal hydroxides)

- XRD and SEM indicate that iron precipitates as goethite, hematite and ferrihydrite as well as the presence of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} - 26H_2O$)

- Increased Al and Mn concentrations may be due to re-dissolution of previously formed precipitates or leaching of the relevant ions from the reactive material (Mn content in fly ash: 339 mg/kg)

Geochemical Modelling PHREEQC

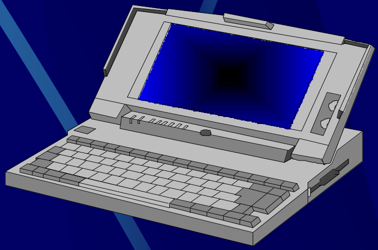
Limestone

Iron precipitates

- Ferrihydrite
- Hematite
- Goethite

Al precipitates

- Mainly as $Al(OH)_3$ (am) at pH values higher than 5.0
- Jurbanite



Lignite based fly ash

Iron precipitates

- Ferrihydrite at pH 3-8
- Hematite at pH 8-9
- Goethite at pH 9-12

Al precipitates

- Mainly as $Al(OH)_3$ (am) at pH values higher than 5.0
- Ettringite

Conclusions

- Limestone and especially Lignite based fly ash permeable reactive barriers are efficient in decontaminating acidic leachates generated at mining sites and containing a large number of hazardous heavy metal ions

- The main clean up mechanisms for both materials are (i) precipitation as a separate phase, mainly as hydroxides and sulfates for Fe, Al, Mn, Zn, Cu, Co and Ni and (iii) co-precipitation/sorption mainly for Cd

- Careful reactive and control is required though to optimize performance and avoid inefficiencies under field conditions (relatively fast consumption of alkalinity, decrease of permeability, re-solubilisation due to previously formed precipitates and desorption of heavy metal ions)

- The efficiency of lignite based fly ash used can be compared with that of other potential materials such as zero valent iron or activated carbon

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the European Commission, in the Framework of the Copernicus II ENVIMAN project (ended Dec. 2003) Contract No. ICA2-CT-2000-10010, entitled:
"Environmental management of hazardous mining wastes and effluents"

and "Alexander S. Onassis" Foundation in the framework of the project entitled:
"Prevention of groundwater contamination from effluents generated at mining and metallurgical sites with the use of PRBs"

Any Questions?

Kostas A. Komnitsas
Associate Professor
Department of Mineral Resources Engineering
Technical University of Crete
E-mail: komni@mred.tuc.gr