

## **PREVENTION OF GROUNDWATER CONTAMINATION IN WASTE DISPOSAL SITES USING COMPOSITE REACTIVE BARRIERS**

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### **ABSTRACT**

The high risk of groundwater contamination in wider mining and waste disposal sites is due to the production of acidic leachates over long periods of time even after cease of activities. The present paper explores the potential of composite permeable reactive barriers containing mixtures of organic and inorganic materials, mainly by-products of other industrial operations, for the treatment of leachates and the prevention of groundwater contamination.

Upflow lab column experiments simulating permeable reactive barriers operation were carried out to assess the efficiency of organic and inorganic reactive media for the cleanup of synthetic acidic solutions (pH ~3) containing Cu, Zn, Mn, Ni (50 mg/L) and sulphates. The columns were filled up with each reactive mixture and packed slightly to simulate field conditions in terms of groundwater or leachate flow. Leachates were collected periodically and analyzed for pH, oxidation-reduction potential, metal ion and sulphate concentration. The effect of each reactive medium was assessed and the most important mechanisms contributing to leachates clean up were identified and discussed.

X-Ray Diffraction as well as Scanning Electron Microscopy and Energy Dispersive Spectrometry were used to identify new mineral phases and elucidate the main mechanisms involved in metal removal and leachates cleanup for each system studied. Finally the main issues affecting reliability of laboratory tests for the design of field PRB systems are briefly discussed.

### **Keywords**

heavy metals; permeable reactive barriers; organic material, zero valent iron, acidic leachates

## 1. INTRODUCTION

Several reactive materials have been tested for the cleanup of contaminated wastewaters, effluents such as acid mine drainage (AMD) and groundwater using permeable reactive barriers (PRBs). Reactive inorganic materials include among others zero valent iron (ZVI), limestone and red mud (RM), activated carbon, zeolite, volcanic ash and lignite-based fly ash (FA) (Komnitsas et al, 2004; Bartzas et al, 2006; Woinarski et al, 2006; Hong et al, 2009; Yang et al, 2010). Organic materials include agricultural products and by-products, sewage sludge and several organic wastes (Boni et al, 2008; Gupta et al, 2010). In the last years, emphasis is given in utilization of industrial by-products or wastes as reaction media in order to reduce clean-up cost. Combined use of organic and inorganic reactive materials may be beneficial in terms of provision of alkalinity / buffering of pH and activation of more than one cleanup mechanisms (e.g. precipitation and sorption) (Pagnanelli et al, 2009).

Adsorption, and/or (co)precipitation, and/or cementation are the major mechanisms involved in cleanup processes. Organic material (CH<sub>2</sub>O) is used as electron donors in the dissimilatory reduction of sulphates to sulphides, which generates alkalinity and enables metal precipitation according to reactions 1 and 2:



ZVI PRBs are widely used for groundwater remediation and they have demonstrated very good removal efficiency in terms of inorganic and organic contaminants (Bartzas et al, 2006; Komnitsas et al, 2006a and 2007; Moraci et al, 2010). ZVI consumes oxygen, establishing thus anaerobic conditions which favour Sulphate Reducing Bacteria (SRB) growth, and generates hydrogen that is used as electron donor by SRBs (reactions 3 and 4). Potential removal mechanisms include sorption onto its surface and corrosion products or reaction between the target contaminant and ZVI that is oxidized to ferrous or ferric state.



Red mud (RM) is a waste material produced during digestion of bauxite for the production of alumina. Due to its texture and composition, it is characterized by high surface reactivity, but as yet it has scarcely been evaluated for the removal of inorganic contaminants from AMD, contaminated plumes or industrial effluents (Li et al, 2010). Fly ash (FA), produced from burning of lignite in fired power plants, may be also used for the removal of various heavy metals (e.g. Cd, Cr, Cu, Pb, and Zn) from industrial solutions and effluents (Komnitsas et al, 2006b; Cetin et al, 2007).

The most important parameters affecting the efficiency of a PRB include pH, contaminant concentration, flow rate, temperature and retention time. The efficiency of each system can be evaluated by predicting the fate of each contaminant as well as by modelling the progress of the reaction front. Optimum systems are characterized by increased reactivity, sufficient hydraulic conductivity, environmental compatibility, low cost and long-term stability (Bartzas et al, 2010). The present paper attempts to assess the efficiency of an organic/inorganic fixed bed containing low-cost reactive materials such as goat manure, ZVI, RM or FA for the removal of Cu, Mn, Zn and Ni from synthetic acidic sulphate solutions.

## 2. MATERIALS AND METHODS

GOM is an organic fertilizer (pH~7) consisting of 47% organic matter, total microorganisms of  $16 \cdot 10^7$  colonies/g and traces of N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, Ca, Mg, Fe, Mn, Cu, B, Mo, Zn. ZVI (-12 mm, d<sub>50</sub>: -

0.5 mm) was purchased from Gotthart Maier, Germany. It contains Fe 92.03%, C 3.31%, Si 2.04%, Mn 0.63%, Al 0.16%, S 0.09%, Ni 0.06%, Cr 0.05%, P 0.04% and H<sub>2</sub>O 0.4%. ZVI has specific gravity 2.8 g/cm<sup>3</sup> and specific surface area 482 cm<sup>2</sup>/g. RM (-76 µm, d<sub>50</sub>: -4 µm) was obtained from Aluminium of Greece S.A and has the following mineralogical and trace element composition: Al<sub>2</sub>O<sub>3</sub> 15.65%, SiO<sub>2</sub> 6.96%, Fe<sub>2</sub>O<sub>3</sub> 45.58%, CaO 14.84%, MgO 0.19%, Na<sub>2</sub>O 3.26%, K<sub>2</sub>O 0.07%, TiO<sub>2</sub> 7.07%, LOI 6.42%, As 147 mg/kg, Cd 0.4 mg/kg, Cr 600 mg/kg, Cu 54 mg/kg, Mn 222 mg/kg, Ni 1055 mg/kg, Pb 24 mg/kg and Zn 94 mg/kg. FA (-400 µm, d<sub>50</sub>: -32 µm) was obtained from Ptolemais thermal power station and is classified as type C according to ASTM; the annual production of fly ash in Greece exceeds 10<sup>7</sup> tons. It consists of Fe<sub>2</sub>O<sub>3(tot)</sub> 5.6%, SiO<sub>2</sub> 33.4%, Al<sub>2</sub>O<sub>3</sub> 13.1%, CaO 31.85%, MgO 3.67%, MnO 0.18%, Na<sub>2</sub>O 0.46%, K<sub>2</sub>O 0.76%, TiO<sub>2</sub> 0.71% and SO<sub>3</sub> 6.58% (LOI 2.7%) (Komnitsas et al, 2004; Bartzas et al, 2006).

Laboratory experiments were carried out in plexiglas columns (45 cm length and 5 cm internal diameter). GOM was mixed with silica sand (30% w/w) in order to optimize flow conditions within the fixed bed. No silica sand was added in case when ZVI or RM (20% w/w) were mixed with GOM. The total dry weight of the bed was 650 g. Two 2.5 cm thick silica sand layers were placed at the base and the top of each column in order to ensure optimum flow distribution and prevent loss of fine particles. Up-flow was applied in order to eliminate channeling, maintain optimum contact between solution and reactive materials and increase retention time. Feed solutions were prepared by dissolving sulphate salts (CuSO<sub>4</sub>·5H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O, MnSO<sub>4</sub>·H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O) in distilled water, so that the initial concentration of each metal ion was 50 mg/L. The solution was then acidified with concentrated sulfuric acid to pH~3 and pumped in the columns from 20 L plastic vessels using PROMINENT GAMMA/4 peristaltic pumps at a Darcy velocity of 100 cm/day. The flow rate used was 1.3 ± 0.05 mL/min so that one pore (bed)volume (~320, 315, 300 and 290 mL for GOM, GOM+ZVI, GOM+RM and GOM+FA columns respectively) was fed every 4.10, 4.04, 3.85 and 3.72 hours, respectively. The total empty bed contact time, defined as the ratio bed length : approach velocity was 10.8 h. The hydraulic loading rate, calculated by dividing the flow rate with the cross-sectional area, was 0.04 m/h.

Column effluents were analyzed immediately for pH, oxidation-reduction potential and electrical conductivity. Solutions were filtered using 0.45 µm acro disk filters, acidified with concentrated HCl to pH < 2 and stored at 4 °C prior to measurements (using a Perkin Elmer Analyst 100 flame atomic absorption spectrophotometer). Sulphate analysis was done by a LaMotte Smart2 colorimeter. Representative samples of the “exhausted” reactive media were air-dried and then analysed by XRD using a Siemens D500 Diffractometer at 30kV and 15mA. SEM analyses were also carried out using a JEOL 6380LV Scanning Electron Microscope equipped with an EDS INCA microanalysis system, under low vacuum, to study the morphology of the formed phases.

### 3. RESULTS AND DISCUSSION

#### 3.1 Column studies

Figure 1 shows the evolution of metal ion concentration in the effluents of the GOM and GOM+ZVI beds as well as pH vs. time. The pH of the feed in the GOM system increases from the initial value of 3 to almost 8.1; then drops gradually and reaches 6.6 at the end of the run. It is seen that when GOM is used as reactive medium, complete Zn and Cu removal is attained for a period of 15 and 9 days respectively; then system efficiency drops gradually and the concentration of Zn and Cu reaches 28 and 50 mg/L after 56 days, respectively. On the other hand, removal of Mn and Ni is limited and the system gets “exhausted” after almost 15 days.

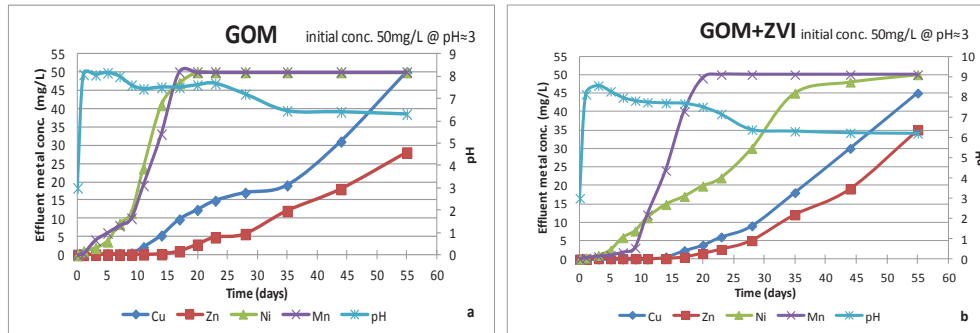


Figure 1. Evolution of metal concentration and effluent pH vs. time in GOM and GOM+ZVI systems

When GOM is mixed with ZVI (Figure 1b) system efficiency improves slightly and no Zn or Cu are detected over a period of 17 and 15 days respectively. Ni is completely removed the first 3 days and then its concentration in the effluent increases gradually and reaches 50 mg/L after 56 days. Mn is almost completely removed the first 3 days but the system becomes inefficient after 20 days. Fe dissolution (data not shown) increases slightly with time and reaches at the end of the run 26 mg/L. Feed pH increases from the initial value of 3 to 8.5 just after a day, then drops gradually and after 30 days is stabilized to 6.2

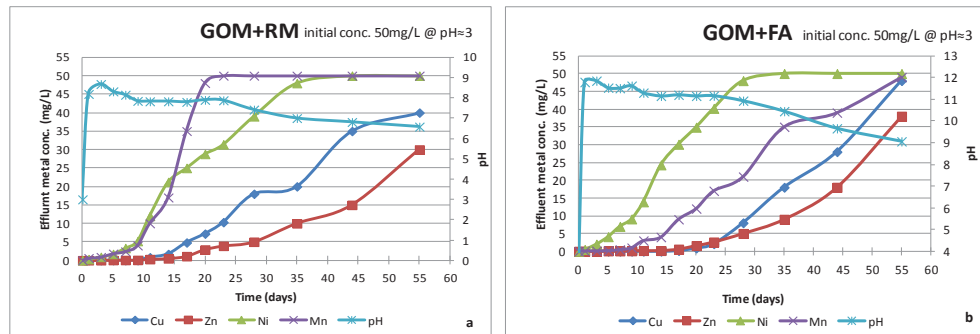


Figure 2. Evolution of metal concentration and effluent pH vs. time in GOM+RM and GOM+FA systems

Figure 2 shows the evolution of metal ion concentration in GOM+RM and GOM+FA PRB systems as well as pH vs. time. RM and FA due to their inherent alkalinity, exhibit better pH buffering capacity than ZVI; pH in GOM+RM system after an initial increase to 8.7 drops gradually and after 56 days reaches 6.6 (Figure 2a). On the other hand, in the GOM+FA system due to the dissolution of FA oxides (mainly CaO and MgO) by the acidic feed and the addition of alkalinity, pH is around 11.5 the first 25 days and then drops gradually to 9 (Figure 2b). As seen in Figure 2a, when GOM is mixed with RM, Cu and Zn are efficiently removed the first 10 and 15 days, respectively. Then removal efficiency drops continuously and after 56 days Zn and Cu concentration in the effluent is 30 and 40 mg/L respectively. Mn removal is almost complete the first 5 days, then drops sharply and the system becomes inefficient after 20 days. Ni removal trend is slightly better than Mn.

When GOM is mixed with FA (Figure 2b), the efficiency of the system improves clearly. No Zn or Cu are detected in the effluent the first 18 days while after 56 days their concentration in the effluent is 37 and 47 mg/L respectively. Mn is completely removed the first 7 days and the system

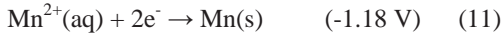
becomes inefficient after 56 days. Finally, in terms of Ni removal, the reactive medium is “exhausted” after 35 days.

Table 1 shows the rate of metal ion removal (in mg of metal ion/g of reactive mixture) for all systems studied over the entire experimental period. It is seen from this data that in terms of Zn and Cu, GOM acts better while the addition of ZVI, RM or FA does not improve in general system performance. On the other hand in terms of Ni and Mn system performance improves substantially when these industrial by-products are mixed with GOM. The experimental data indicate that sorption and/or reductive precipitation are the major metal removal mechanisms; domination of one mechanism over the other depends on the type of the reactive medium, the metal ion present in solution and system pH. It is foreseen than in systems containing GOM sorption is the dominant mechanism since metal ion removal mechanism.

TABLE 1. Rate of metal ion removal in each system

| System  | mg/g of reactive material |      |      |      |
|---------|---------------------------|------|------|------|
|         | Zn                        | Cu   | Ni   | Mn   |
| GOM     | 7.20                      | 5.70 | 1.77 | 1.84 |
| GOM+ZVI | 7.18                      | 6.33 | 3.71 | 2.23 |
| GOM+RM  | 7.40                      | 5.90 | 3.08 | 2.36 |
| GOM+FA  | 7.23                      | 6.46 | 2.51 | 4.94 |

Reactions (5)-(11) show the standard reduction potential  $E^0$ , for half reactions of the involved metal ions at 25°C, 1 atm and 1 mol/L concentration. It is known that standard reduction potential provides a quantitative measure of a metal ion’s tendency to accept electrons while ions with greater reduction potential show greater tendency for reduction.



ZVI may be also involved in reaction (12) that results in copper and other metal ions precipitation. The presence of FA and RM which exhibit complex mineralogy and higher inherent alkalinity may involve dissolution of other phases affecting thus the overall solution chemistry and triggering secondary reactions.



The acidic feed, as the one used in this study, accelerates iron corrosion so that  $\text{Fe}^{2+}$  and eventually  $\text{Fe}^{3+}$  ions are transferred in solution and pH increases (reaction 13).  $\text{Fe}^{3+}$  ions accelerate iron corrosion according to reaction (14). Reaction (15) results in precipitation of  $\text{Fe}(\text{OH})_2$  and potential co-precipitation of other metal hydroxides (Komnitsas et al, 2006a). In the case of GOM precipitation of metal sulphides may be anticipated (reactions 2 and 16)



### 3.2 Mineralogical studies

The XRD pattern of “exhausted” GOM indicates the formation of covellite (CuS) (Figure 3). Precipitation of metals as sulphides is also confirmed by the decrease in concentration of sulphates in column effluents from the initial value of 600 to less than 360 mg/L (Figure 4). The activity of SRB increases when system pH varies between 5 and 8 which is the optimum range for their growth (Komnitsas et al, 2007).

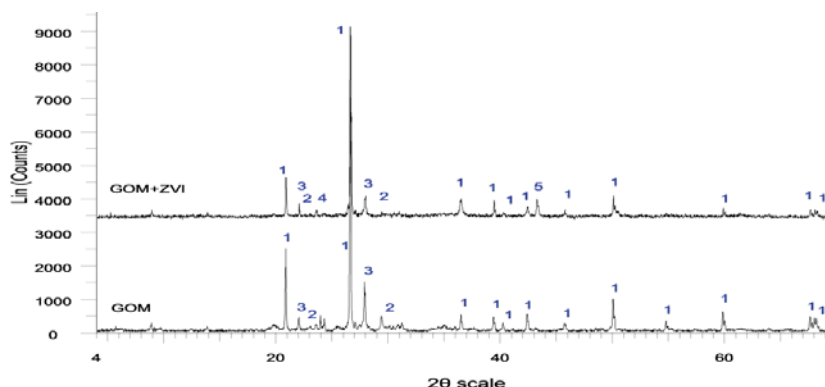


Figure 3. X-ray diffraction pattern of “exhausted” GOM and GOM+ZVI (1: quartz SiO<sub>2</sub>, 2: calcite CaCO<sub>3</sub>, 3: covellite CuS, 4: Fe(OH)<sub>3</sub>, 5: metastable iron sulfide FeS)

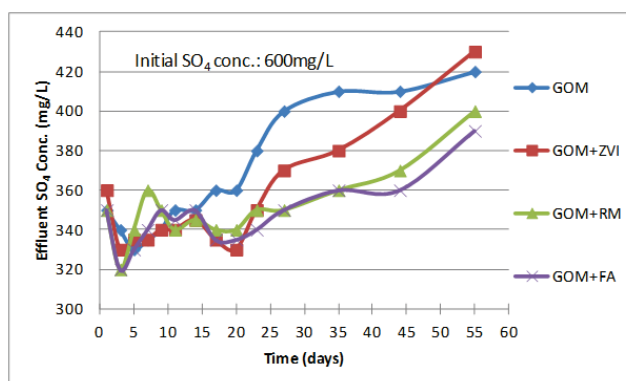


Figure 4. Evolution of effluent SO<sub>4</sub> concentration vs. time in all studied systems

On the other hand, the XRD pattern of exhausted GOM+ZVI shows the precipitation of Fe(OH)<sub>3</sub>. Metastable iron sulfide may be also formed in systems containing Fe<sup>2+</sup> (due to iron corrosion) and H<sub>2</sub>S (reaction 16). XRD patterns of “exhausted” GOM+RM and GOM+FA mixtures (data not shown) reveal the presence of covellite, tenorite (CuO) and various calcium, sodium and manganese hydrated phases.

SEM and EDS analyses were also carried out to examine the morphology of the newly formed phases as well as their elemental composition and elucidate the main removal mechanisms involved. Figure 5 shows a SEM back scattered image of GOM (Figure 5a) and the respective element spectrum (Figure 5b). It is clearly seen from these data that GOM contains adsorbed Zn and Mn. The presence of P and Si is due to GOM and quartz, respectively. Similar SEM images are seen when GOM is mixed with RM or FA.

SEM and EDS analyses of “exhausted” GOM+ZVI and GOM+RM mixtures (Figures 6 and 7, respectively) confirm the formation of elemental copper ( $\text{Cu}^0$ ), according to reaction (12). Elemental copper is a redox-active phase formed by the reduction of dissolved copper and subsequently deposited onto the corroded iron surface. SEM and EDS analyses of “exhausted” GOM+FA are rather complex due to the mineralogy of FA and indicate new phases formed as well as inherent phases initially present in FA (Figure 8).

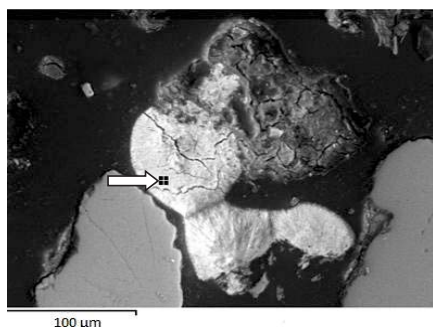


Figure 5a. SEM-BSI of “exhausted” GOM, scale 100 μm

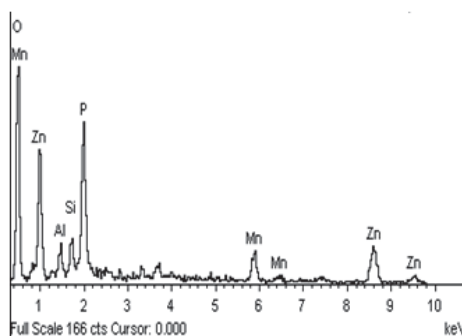


Figure 5b. Element spectrum of “exhausted” GOM seen in Figure 5a

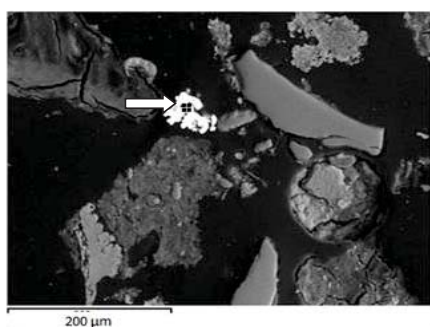


Figure 6a. SEM-BSI of “exhausted” GOM+ZVI mixture, scale 200 μm

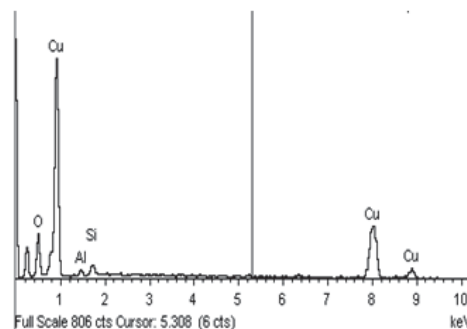


Figure 6b. Element spectrum of “exhausted” GOM+ZVI mixture seen in Figure 6a

### 3.3. Issues affecting the reliability of laboratory tests for the design of field PRB systems

An issue that needs to be taken into consideration in laboratory studies is the degree of reliability of results when they are used for the design of larger PRB treatment systems, since reproduction of field hydrodynamic conditions is not always easy in laboratory scale (Crittenden et al, 1991; Westerhoff et al, 2006). In small scale systems, as the one used in the present study, a fraction of time and water volume is required compared to pilot or large scale systems. It is assumed that due to the similarity of mass transfer processes and hydrodynamic characteristics between the two systems, the breakthrough curves are expected to be similar. A good approach to achieve this, is to keep experimental flow rates and Peclet numbers close to field values. The Peclet number quantifies the relative importance of advection, molecular diffusion, and dispersion for solute transport and it is therefore important in order to define laboratory test hydrodynamic conditions (Ahmad et al, 2007). It is defined as  $Pe=v \cdot L/D$  where:  $v$  is the groundwater velocity in the longitudinal direction (m/s),  $L$  is the length scale of the flow system (m), and  $D$  is the axial dispersion coefficient of a contaminant in a field ZVI PRB for which a literature value of  $1,5 \cdot 10^{-9} \text{ m}^2/\text{s}$  is considered (Zhang et al, 2001). In the present study the flow rate used (100 cm/d) is comparable to groundwater velocity



which depending on the type of the aquifer may vary between 0.1 to 45 m per day; the highest values are recorded in sandy or gravelly aquifers (Li et al, 2005; Jin suk et al, 2009; Jeen et al, 2011).

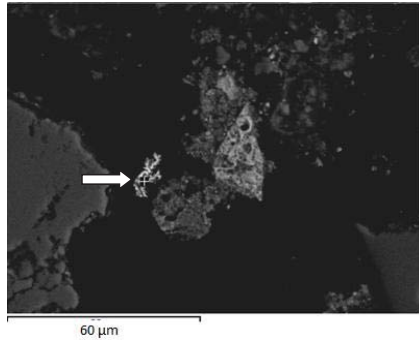


Figure 7a. SEM-BSI of “exhausted” GOM+RM mixture, scale 60  $\mu\text{m}$

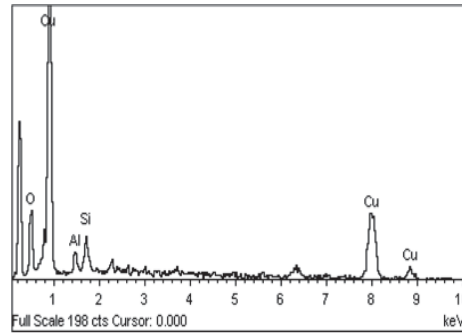


Figure 7b. Element spectrum of “exhausted” GOM+RM mixture seen in Figure 7a

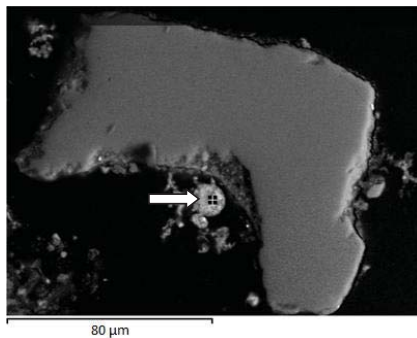


Figure 8a. SEM-BSI of “exhausted” GOM+FA mixture, scale 80  $\mu\text{m}$

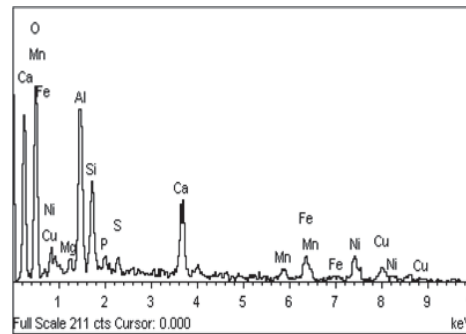


Figure 8b. Element spectrum of “exhausted” GOM+FA mixture seen in Figure 8a

A Peclet number smaller than 0.4 indicates that solute transport is diffusion controlled, a number between 0.4 and 6 suggests a transition between diffusion control and dispersion and advection mechanisms, while a Pe greater than 6 indicates dominance of dispersion and advection over molecular diffusion (Fetter, 1999). In the present study, the estimated Peclet number for the GOM+ZVI system is 34.7, meaning that advection dominates column mass transport. As a result, diffusion does not seem to be a significant factor at the applied upflow velocity.

It is obvious that in small column systems interstitial water velocity is high and therefore high head loss is anticipated. Therefore, lower velocities are recommended in small scale laboratory systems as long as the effect of dispersion does not become dominant over other mass transport processes (Westerhoff et al, 2005). This limitation requires that the  $Re \cdot Sc$  value should remain in the range of 200- 200,000, which is the mechanical dispersion range ( $Re$  is the Reynolds number and  $Sc$  is the Schmidt number). The Reynolds and Schmidt numbers are defined as  $Re = d \cdot v / \nu$  and  $Sc = \nu / D$ , respectively, where  $v = 1 \text{ m/d}$  is the average Darcy velocity,  $d = 5 \cdot 10^{-4} \text{ m}$  is the characteristic length and  $\nu = 1 \cdot 10^{-6} \text{ m}^2/\text{s}$  is the kinematic viscosity of water at 25 °C. The value of  $Re \cdot Sc = 3.7$  calculated



for the present study indicates that contaminant removal mechanisms were not significantly affected by mass transfer mechanisms.

Jeen et al (2011) provide extremely useful data regarding the long term performance of granular iron permeable reactive barriers. Simulation results and column reactivity tests clearly show that the declining reactivity of iron should be incorporated into predictive models in order to adequately represent long-term performance of iron PRBs. With regard to PRB design, it has been demonstrated that while porosity loss and permeability reduction caused by mineral precipitation remain important issues, loss of iron reactivity with respect to contaminant removal is often a determining factor for the longevity of PRBs (Bartzas and Komnitsas, 2010). These two longevity issues are inter-related and should be evaluated simultaneously during the field design stage.

#### **4. CONCLUSIONS**

Composite permeable reactive barriers, containing goat manure and limited quantities of ZVI, RM or FA can be used for the clean up of acidic leachates and contaminated groundwater, containing elevated concentrations of Cu, Mn, Zn and Ni, in wider mining and waste disposal sites. Their efficiency is higher in terms of Zn and Cu removal, whereas Mn and Ni removal is limited.

Under the experimental conditions studied, sorption and precipitation of metals as sulphides and hydroxides are the dominant metal removal mechanisms. The use of analytical characterization techniques including XRD and SEM provides useful information in terms of identification of new phases and elucidation of the main clean up mechanisms.

Additional experiments are under way to accurately assess the efficiency of the organic-inorganic reactive beds, determine the contribution of each reactive material, assess the optimum retention time, elucidate removal mechanisms and define a geochemical model in each case.

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