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Removal of heavy metals from leachates using organic/inorganic permeable reactive barriers

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ABSTRACT

In the present experimental study, the efficiency of permeable reactive barriers (PRBs) containing organic material mixed with zero-valent iron, fly ash or red mud to remove heavy metals from leachates was assessed. Upflow laboratory column experiments were carried out to assess system efficiency in terms of Cu, Zn, Ni and Mn removal. The initial concentration of each metal ion in the feed was 50 mg/L. X-ray diffraction as well as scanning electron microscopy and energy dispersive spectrometry were used to identify new mineral phases and to identify metal removal mechanisms. Results and analyses show that sorption and precipitation of metals as sulphides, hydroxides and other hydrated phases are the dominant metal removal mechanisms.

Keywords: Heavy metals; Permeable reactive barriers; Organic material

1. Introduction

Reactive materials are used for the cleanup of contaminated wastewaters, groundwater, industrial effluents and acidic leachates such as acid mine drainage (AMD) [1]. Inorganic reactive materials include, among others, zero-valent iron (ZVI), limestone, red mud (RM), activated carbon, zeolite, volcanic ash and coal fly ash (FA) [2–6]. Organic materials, used to induce sulphate reduction, may include agricultural by-products, sewage sludge and organic wastes [7–10]. Combined use of reactive organic and inorganic materials may be beneficial in terms of provision of alkalinity/buffering of pH and activation of more than one removal mechanisms (e.g. precipitation, co-precipitation and/or sorption) [11–13]. Organic material (CH_2O) is used as electron donor in the dissimilatory reduction of sulphates to sulphides and the alkalinity generated enables metal precipitation according to reactions (1) and (2).

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2CO_3 \qquad (1)$$

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$$Me^{2+} + H_2S \rightarrow MeS\downarrow + 2H^+ \quad (2)$$

Zero-valent iron has been widely used as reactive medium in PRBs for groundwater remediation and has demonstrated very good removal efficiency for several inorganic (e.g. Cr, Cu, Ni, As and Zn) and organic contaminants (e.g. TCE, PAHs and MTBE) [14–16]. It consumes oxygen according to reaction (3), establishing thus anaerobic conditions which favour growth of sulphate reducing bacteria (SRB), while the generated hydrogen can be used as electron donor by SRB according to reaction (4).

$$Fe^0 + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O \quad (3)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (4)$$

The volume of red mud produced in the Bayer process depends on the type of bauxite treated and can be as high as 2 t of mud per ton of alumina produced. It is disposed as slurry with solid concentration in the range of 10–30% w/v. It has pH 11–13, high ionic strength and high surface reactivity. So far red mud has scarcely been evaluated as reactive material for the removal of inorganic contaminants from AMD, contaminated plumes or industrial effluents [17,18]. Fly ash which is produced in thermal power plants has also been used for the removal of heavy metals such as Cd, Cr, Cu, Pb and Zn from solutions. However, its adsorption capacity is in general lower than that of other reactive media such as granular activated carbon and zeolite [19,20].

The efficiency of each reactive system is mainly affected by pH, surface area, contaminant concentration, flow rate, temperature and retention time and can be evaluated by predicting the fate of inorganic contaminants as well as by modelling the progress of the reaction front [21–24]. Optimum cleanup systems are characterized by increased reactivity, sufficient hydraulic conductivity, environmental compatibility and long-term stability [25–27].

The present paper aims to assess the efficiency of permeable reactive barriers containing organic/inorganic reactive media to remove Cu, Zn, Ni and Mn from synthetic sulphate solutions. Mineralogical studies were carried out in order to elucidate the main removal mechanisms involved.

2. Materials and methods

The reactive media used in the present study were goat manure (GOM), ZVI, RM and FA. GOM is a commercial organic fertilizer (pH ~ 7) containing 47% of organic matter, 21×10^{12} of total micro-organisms/g and traces of Ca, Mg, Fe, Mn, Cu, B, Mo and Zn. The main mineralogical phases identified in GOM were quartz, calcite, illite and albite since, during composting, manure was mixed with soil.

The ZVI (−12 mm, d_{50}: 0.5 mm) was purchased from Gotthart Maier, Germany. It contains (w/w) 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_2O 0.4% and has a specific surface area of 482 cm^2/g. The RM (−76 μm, d_{50}: 4 μm) was obtained from Aluminium of Greece S.A and has the following chemical composition (w/w): Al_2O_3 15.65%, SiO_2 6.96%, Fe_2O_3 45.58%, CaO 14.84%, MgO 0.19%, Na_2O 3.26%, K_2O 0.07%, TiO_2 7.07% and LOI 6.42%. The FA (−400 μm, d_{50}: 32 μm) was obtained from Ptolemais, Western Macedonia, thermal power station and is classified as type C according to ASTM. It consists of (w/w) $Fe_2O_{3(tot)}$ 5.6%, SiO_2 33.4%, Al_2O_3 13.1%, CaO 31.85%, MgO 3.67%, MnO 0.18%, Na_2O 0.46%, K_2O 0.76%, TiO_2 0.71% and SO_3 6.58% and LOI 2.7%.

Laboratory experiments were carried out at room temperature in plexiglas columns (45 cm length and 5 cm internal diameter). The GOM was mixed with silica sand (30% w/w) in order to optimize flow conditions within the fixed bed. No silica sand was added when ZVI, RM or FA were mixed (30% w/w) with GOM. The total dry weight of the reactive 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.

Feed solutions were prepared by dissolving the required amounts of sulphate salts ($CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}6H_2O$, $MnSO_4{\cdot}H_2O$ and $ZnSO_4{\cdot}7H_2O$) in distilled water. The pH of the feed solution was 5.5, while the initial concentration of each metal ion was 50 mg/L and the sulphate concentration was 320 mg/L. No nitrogen or phosphorus was added as nutrients for the micro-organisms due to their presence in GOM. The solutions were pumped in the columns from 20 L plastic vessels using PROMINENT GAMMA/4 peristaltic pumps with a Darcy velocity of 240 cm/day. Up-flow was applied to ensure the required retention time, eliminate channelling and allow optimum contact between solution and reactive media. The flow rate used was 1.3 ± 0.05 mL/min (approx. 80 mL/h), so that one pore volume (~350, 340, 310 and 320 mL for GOM, GOM + ZVI, GOM + RM and GOM + FA columns, respectively) was fed approximately every 4.4 h. The total empty bed contact time, defined as the ratio of the bed length to the approach velocity, was 4.5 h. The hydraulic loading rate, calculated by dividing the flow rate with the cross-sectional area, was 0.04 m/h.

The effluents were analysed immediately for pH, oxidation–reduction potential using a HANNA pH 211 combined pH/Eh metre and electric conductivity using a HANNA EC 215 EC metre, then filtered using 0.45 μm aero disc filters, acidified with concentrated hydrochloric acid to pH < 2 and stored at 4°C until metal analysis (using a Perkin Elmer Analyst 100 flame atomic absorption spectrophotometer). Sulphate analysis was performed using a LaMotte Smart2 colorimeter.

The XRD analysis was performed using a Siemens D500 diffractometer, with a Cu tube and a scanning range from 3° to 70° 2-theta, with a step 0.03° and 4 s/step measuring time. For the identification of the morphology of the newly formed mineral phases in the "exhausted" organic/inorganic reactive bed, a Scanning Electron Microscope JEOL 6380LV equipped with an EDS INCA microanalysis system were used with low vacuum, pressure 30 Pa, voltage 20 kV and sample distance from the detector (working distance) 10–12 mm.

3. Results and discussion

3.1. *Efficiency of reactive beds*

When GOM is used as sole reactive medium the pH of the effluent increases from the initial value of 5.5 to almost 8 just after a day and then drops gradually to 6.2 (Fig. 1(a)). When ZVI, RM or FA are mixed with GOM, pH after an initial increase to 8.5 drops gradually after 67 days to values around 6.0. The RM and FA due to inherent alkalinity exhibit higher pH buffering capacity than ZVI. The Eh values (Fig. 1(b)) vary in each column system between −60 mV and −20 mV at the start and only towards the end of the tests reach positive values (max. + 50 mV). This data indicates that, at least in the start of the tests, anaerobic conditions favouring SRB growth prevail in the columns.

Fig. 2 presents the evolution of Cu and Zn removal (%) vs. time. It is seen in Fig. 2(a) that when GOM was used as reactive medium, Cu removal was complete for a period of 10 days and then decreased gradually to 28% after 67 days. When GOM was mixed with FA, ZVI or RM, system efficiency improved and at the end of the test Cu removal ranged between 50 and 68%. As seen in Fig. 2(b), when GOM or GOM + FA was used as reactive media, Zn was completely removed over a period of 25 days; then system efficiency dropped sharply; and after 67 days the reactive bed was "exhausted". On the other hand, when GOM was mixed with ZVI, no Zn was detected in the column effluent for almost 40 days. Efficiency of GOM + RM column was slightly better in the long term and Zn removal attained after 67 days was almost 60%.

Fig. 3 shows the evolution of Ni and Mn removal (%) vs. time. As seen in Fig. 3(a), Ni is totally removed in the first 10 days when GOM is used as reactive medium, but system efficiency drops sharply and becomes zero after 26 days. Slightly better efficiency is seen when GOM is mixed with FA, RM or ZVI. Fig. 3(b) shows that all studied systems exhibit limited efficiency in terms of Mn removal due to the high mobility of this element over a broad pH range.

Reactions (5)–(11) show the standard reduction potential, E°, 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.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad (0.34V) \tag{5}$$

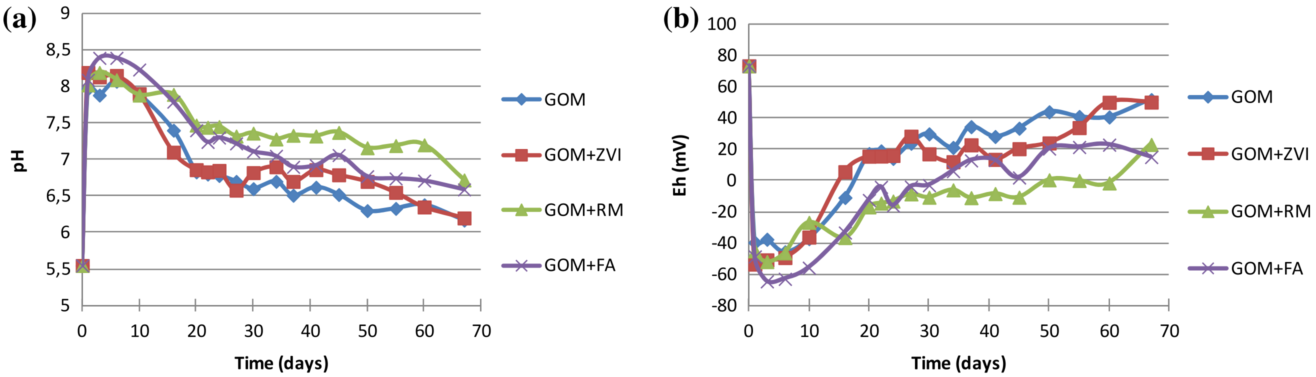

Fig. 1. Evolution of pH and Eh vs. time.

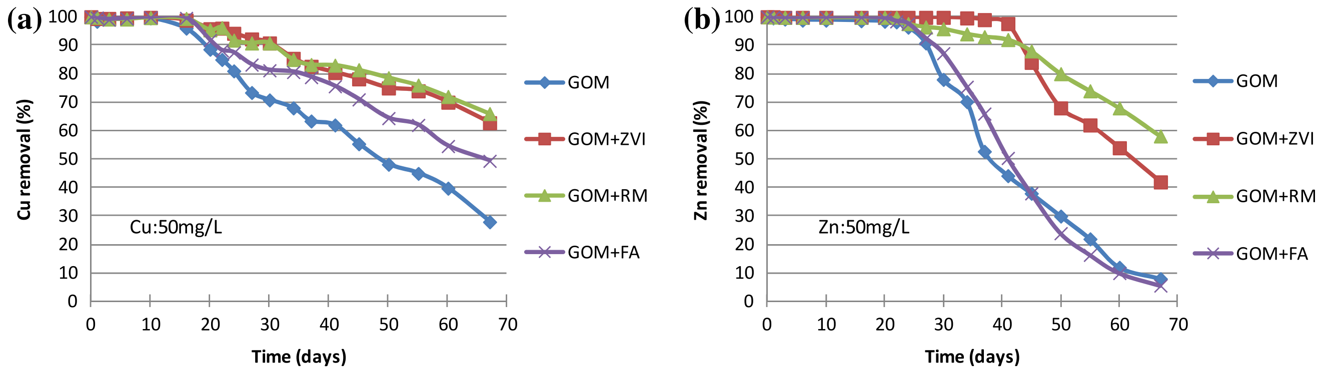

Fig. 2. Evolution of Cu and Zn removal (%) vs. time.

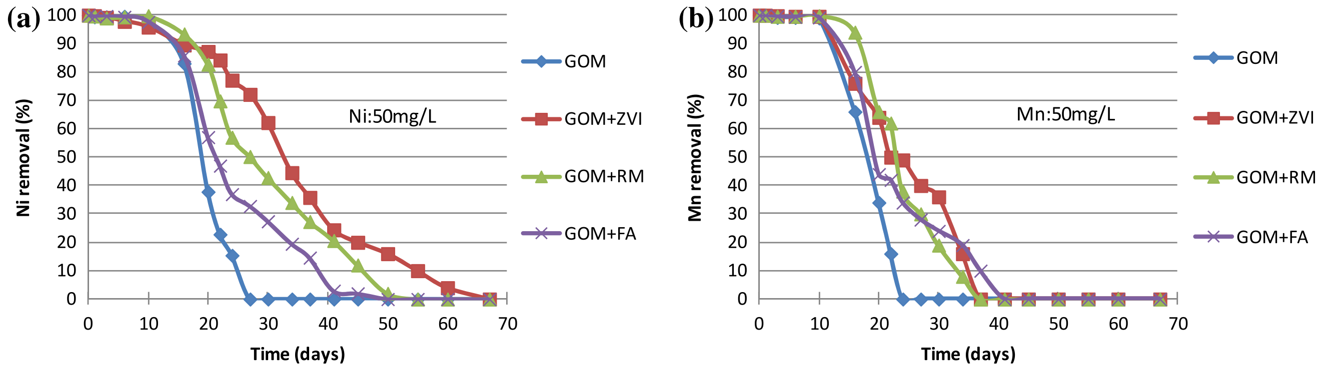

Fig. 3. Evolution of Ni and Mn removal (%) vs. time.

$$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+} \qquad (0.15V) \tag{6}$$

$$Fe^{3+}(aq) + 3e^{-} \rightarrow Fe(s) \qquad (-0.04V) \tag{7}$$

$$Ni^{2+}(aq) + e^{-} \rightarrow Ni(s) \qquad (-0.26V) \tag{8}$$

$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s) \qquad (-0.44V) \tag{9}$$

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s) \qquad (-0.76V) \tag{10}$$

$$Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s) \qquad (-1.18V) \tag{11}$$

The experimental results indicate that ZVI participates in reaction (12) which results in copper precipitation as well as in similar reactions for other metal ions studied. Due to the mild acidity of the incoming feed, iron corrosion is rather limited when ZVI is mixed with GOM and thus limited precipitation of metal hydroxides or metals is anticipated. The incoming solution reacts with ZVI, so that the Fe^{2+} ions are transferred in the solution and pH increases (reaction (13)). If the incoming feed was more acidic, Fe^{3+} ions would have been generated which would enhance iron corrosion according to reaction (14). It has to be mentioned that Fe^{3+} may also act as electron donor and decrease the reduction efficiency of sulphate. Reaction (15) causing precipitation of $Fe(OH)_2$ and potential co-precipitation of other metal hydroxides (e.g. $Mn(OH)_2$) may also take place [16,25].

$$Fe^{0} + Cu^{2+} \rightarrow Fe^{2+} + Cu^{0} \tag{12}$$

$$Fe^{0} + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^{-} \tag{13}$$

$$2Fe^{3+} + Fe^{0} \rightarrow 3Fe^{2+} \tag{14}$$

$$Fe^{0} + 2H_2O \rightarrow Fe(OH)_2 + 2H^{+} + 2e^{-} \tag{15}$$

The presence of FA and RM which exhibit complex mineralogy and higher inherent alkalinity involves dissolution of several phases affecting the

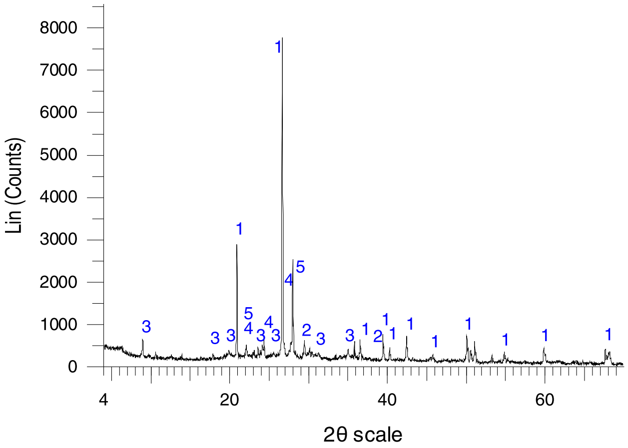

Fig. 4. X-ray pattern of “exhausted” GOM (1: quartz—SiO_2, 2: calcite—$CaCO_3$, 3: illite—$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, 4: albite—$NaAlSi_3O_8$ and 5: covellite—CuS.

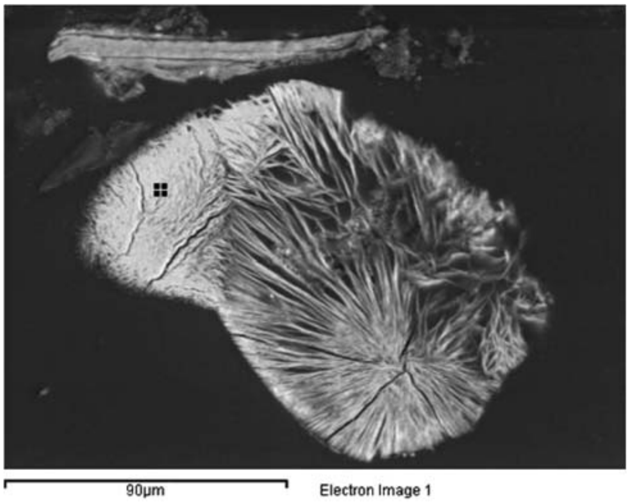

Fig. 6a. SEM-BSI of “exhausted” GOM, scale 90 µm.

overall solution chemistry and triggering other secondary removal mechanisms.

3.2. Mineralogical studies

The XRD pattern of the “exhausted” GOM confirms the formation of covellite (CuS) according to reaction (2), which is the only new phase detected (Fig. 4). Precipitation of metals as sulphides is also indicated by the drop in concentration of sulphates in column effluents from the initial value of 320 mg/L to less than 200 mg/L the first 20 days in all systems studied (Fig. 5).

The role of SRB is more dominant when system pH varies between 5 and 8 which is the optimum range for their growth [28,29]. The efficiency of GOM may had improved if a conditioning period of approximately 10 days was considered to allow for better adaptation of SRBs, resumption of their active metabolism and thus increased population growth [30,31].

Sorption on the organic material is also a main metal removal mechanism in the case when GOM is mixed with RM or FA. Similar results have been obtained from batch kinetic studies. Under the present pH conditions, limited dissolution of iron compounds found in RM or FA is anticipated. The XRD patterns of “exhausted” GOM + RM and GOM + FA mixtures (data not shown) show the presence of covellite and various calcium, sodium and manganese hydrated phases.

Fig. 6 shows a SEM back-scattered image of GOM (Fig. 6a) and the respective element spectrum (Fig. 6b). It is clearly seen from these data that GOM contains adsorbed Zn and Mn. The presence of P and Si is attributed to GOM and quartz, respectively. Similar images are seen when GOM is mixed with RM or FA.

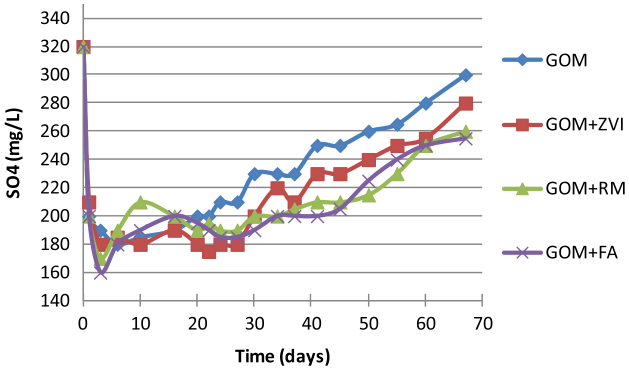

Fig. 5. Evolution of SO_4 concentration in effluents vs. time.

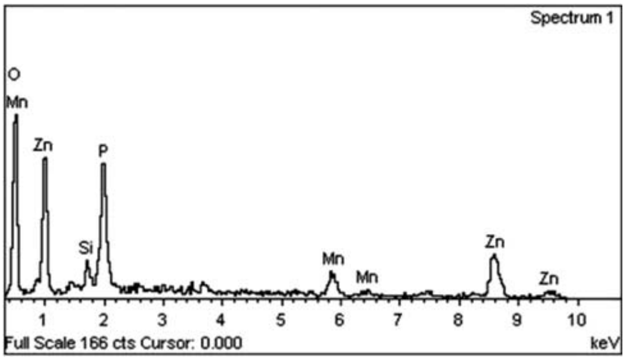

Fig. 6b. Element spectrum of “exhausted” GOM seen in Fig. 6a.

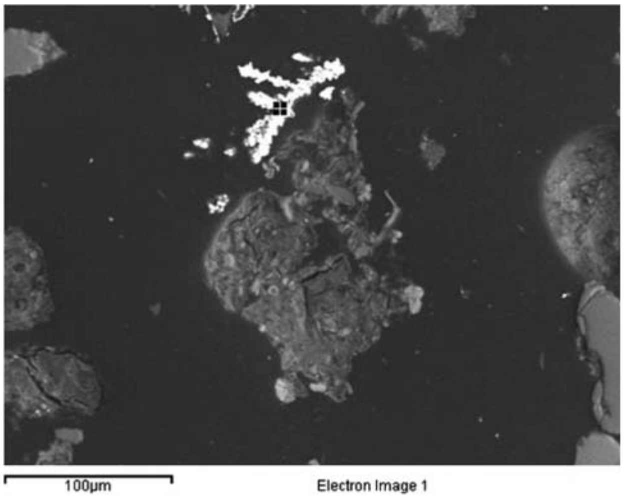

Fig. 7a. SEM-BSI of “exhausted” GOM + ZVI mixture, scale 100 μm.

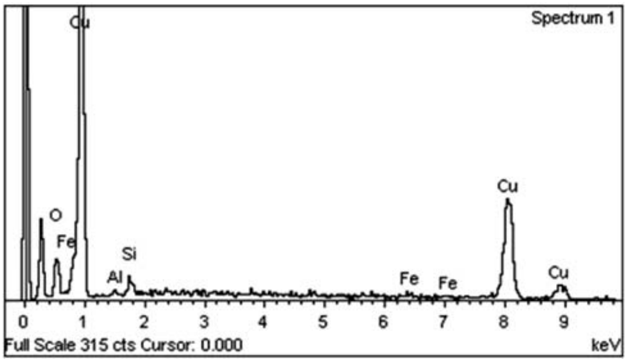

Fig. 7b. Element spectrum of “exhausted” GOM + ZVI mixture seen in Fig. 7a.

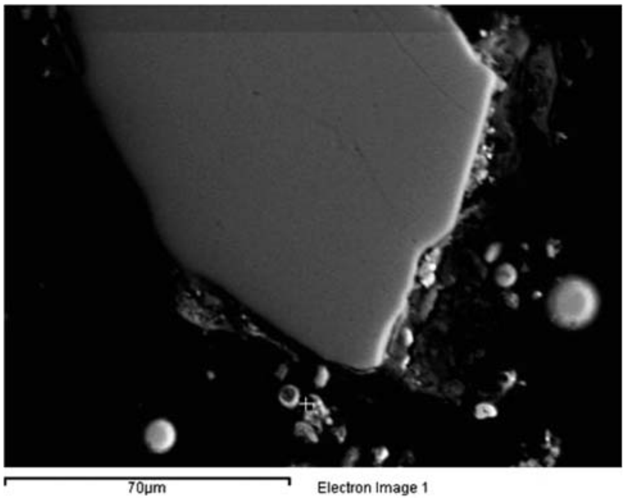

Fig. 8a. SEM-BSI of “exhausted” GOM + FA mixture, scale 70 μm.

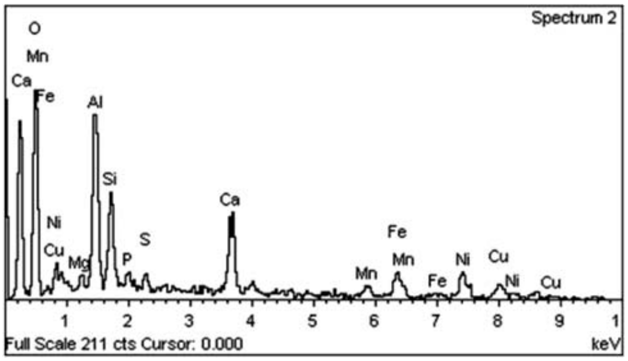

Fig. 8b. Element spectrum of “exhausted” GOM + FA mixture seen in Fig. 8a.

Fig. 7 shows a SEM back-scattered image of GOM + ZVI mixture (Fig. 7a) and the respective element spectrum (Fig. 7b). The formation of elemental copper (Cu^0), according to reaction (12), as well as Fe corrosion is clearly seen. Elemental copper is a redox-active phase formed by the reduction of dissolved copper and its subsequent deposition onto the corroded iron surface [26].

Fig. 8 shows a SEM back-scattered image of GOM + FA mixture (Fig. 8a) and the respective element spectrum (Fig. 8b). The presence of many elements is justified by the complex mineralogy of fly ash.

3.3. Issues for further consideration

It is seen from the experimental data that laboratory columns filled with organic and inorganic reactive media, by-products of other industrial/agricultural activities, provide useful data in terms of reactor design, fate of contaminants and identification of the main mechanisms involved. 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 in both cases, breakthrough curves are expected to be similar so that the degree of reliability of results is affected slightly [32]. Larger scale laboratory experiments are required in order to accurately assess the overall efficiency of the reactive media, the longevity of the system and finally simulate field PRB operation [33,34].

It has been proved that in order to prevent or eliminate channelling and wall effects in PRB laboratory studies, where relatively small columns are used, the ratio *column diameter (D): mean particle size (d)* should be greater than 50 [35]. In the case of ZVI, which is the material with the larger diameter in the reactive bed of the present study, this ratio is almost 100.

Another issue that has to be considered is the high anticipated head loss due to the high interstitial velocity of water in small column systems. This is why 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 [36].

Finally, it is known that geochemical modelling of systems containing reactive materials with complex mineralogy, such as fly ash or red mud, is an extremely difficult issue. Modelling of systems containing almost pure reactive media is more easy and reliable. Jeen et al. [23] provide extremely useful data regarding the long-term performance of granular iron PRBs. 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 and permeability reduction caused by mineral precipitation remains an important issue, reactivity loss of iron with respect to contaminant removal is often a determining factor for the longevity of PRBs. These two longevity issues are inter-related and should be evaluated simultaneously during the design stage.

4. Conclusions

Permeable reactive barriers containing organic material mixed with zero-valent iron, fly ash or red mud show quite good efficiency in decontaminating synthetic leachates containing 50 mg/L Cu, Zn, Ni and Mn. The present study shows that goat manure can be used as electron donor and carbon source for sulphate-reducing bacteria. Hence sulphate reduction for metal precipitation can be achieved with the use of cheap organic materials in permeable reactive barriers. Under the experimental conditions studied, sorption and precipitation of metals as sulphides, hydroxides and other hydrated phases seem to be the dominant metal removal mechanisms.

Additional experiments using more acidic feed as well as geochemical studies are required to assess more accurately the potential of each reactive material, to elucidate fully metal removal mechanisms and to predict the longevity of each system. Finally, toxicity studies are required in order to define proper management strategies for the exhausted mixtures.

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