

**Article II: Evaluation of Municipal Compost/Limestone/
Iron Mixtures as Filling Material for Permeable Reactive
Barriers for *in-situ* Acid Mine Drainage Treatment**

Journal of Chemical Technology and Biotechnology 78: 489-496 (2003)

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Evaluation of municipal compost/limestone/iron mixtures as filling material for permeable reactive barriers for *in-situ* acid mine drainage treatment

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Abstract: The aim of the present study was to assess the potential of municipal compost as a carbon source for sulfate-reducing bacteria for acid mine drainage bioremediation for use in permeable reactive barriers at high flow rates ($>0.1 \text{ m d}^{-1}$). Two different mixtures of municipal compost, limestone and zero-valent iron were assessed in two column experiments. The effluent solution was systematically analysed throughout the experiments. At the end of the experiments precipitates from both columns were withdrawn for scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffractometry examination and solid digestion and sequential extraction were carried out. Results showed that the effluent was free of metals and acidity. It seems that metal removal was not due to biogenic sulfide generation but to pH increase, ie metal (oxy)hydroxides precipitation. These precipitates can sorb other metals onto the surface. Sorption to organic matter could also contribute to metal removal. When zero-valent iron was present, cementation of copper also occurred. It can be concluded that municipal compost was a poor carbon source to support continuous bacterial activity under high flow rates.

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Keywords: acid mine drainage; passive remediation; permeable reactive barrier; sulfate-reducing bacteria

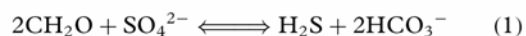
1 INTRODUCTION

Acid mine drainage (AMD) is one of the most serious environmental concerns associated with the mining industry around the world. It is generated by oxidation of pyrite and other metal sulfide minerals in rock wastes and tailing impoundments.

Metal sulfides other than pyrite may release Zn, Cu, Cd, As, Ni, Pb, etc. AMD is thus characterised by high acidity ($\text{pH} < 3$) and a high concentration of sulfates (up to 5000 mg dm^{-3}) and metals (Fe, Zn, Pb, Cd, Cu, etc). This acidic, metal-contaminated water adversely impacts on both surface and ground water, with the result that treatment is necessary to meet legislation standards.

Current techniques for AMD treatment consist of *ex-situ* chemical treatment, which conventionally involves the addition of an alkaline agent or sulfide in order to promote metal precipitation as hydroxides or sulfides. An alternative approach is metal precipitation

by bacterially *in-situ*-generated sulfides. This biological approach seeks to induce sulfate reduction by means of sulfate-reducing bacteria (SRB), which under favourable conditions convert sulfate to sulfide by the oxidation of organic carbon. This can be simplified by the following equation:^{1–4}



where CH_2O represents a simple organic carbon compound. Sulfate reduction reactions consume SO_4^{2-} , produce H_2S and result in an increase in alkalinity and pH. Toxic metal removal from the solution occurs via formation of metal sulfide precipitates.

Laboratory- and pilot-scale tests in bioreactors have shown that sulfate reduction is effective in increasing pH and removing metals and sulfate from mine wastes. However, these *ex-situ* treatments raise some

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Contract/grant sponsor: EU PIRAMID; contract/grant number: EVK1-1999-00061P

Contract/grant sponsor: CYCIT; contract/grant number: HID99-1147-C02

Contract/grant sponsor: MCYT; contract/grant number: REN-2002-04055-C02

(Received 30 July 2002; revised version received 2 December 2002; accepted 16 December 2002)

Table 1. Summary of key parameters in continuous systems based on natural complex organic sources reported in the literature

System	Material	SO ₄ ²⁻ (mg dm ⁻³)	t _R (days)	% SO ₄ ²⁻ removed ^a	Ref
Bioreactor	Mushroom compost (manure, hay straw, corn cobs, wood chips, gypsum, limestone)	1000	5–17	17–23	1
Bioreactor	Ryegrass, mollisol soil	2700	2–12	50	9
Column	Oak chips	2580	20	50	8
Column	Mushroom compost	2580	20	50	8
Column	Wood chips, leaf compost, poultry manure, urea, limestone, sand	1600	0.5	12	10
Full-scale barrier	Municipal compost, leaf compost, wood chips, limestone, silica sand	2000–4000	60–165 ^b	30–80	11

^a Rate values estimated from raw data.

^b The two different residence times correspond to the slow flow path at bottom and top of the barrier and fast flow path in the middle of the barrier.

problems because the equipment is expensive to build, to maintain and to operate, and the process generates a large amount of sludge. An inexpensive, *in-situ* treatment process is necessary owing to the large volumes of AMD that must be treated. Acid mine drainage *in-situ* bioremediation has in the last decades attracted the attention of biotechnologists. The most recent application is the permeable reactive barrier.^{5,6} A permeable reactive barrier (PRB) consists of digging a trench in the aquifer and filling it with an appropriate reactive material able to induce physico-chemical and/or biological processes that remediate contaminated groundwater. This treatment is passive so that once installed, low maintenance is required. Despite the fact that this technology has been widely used for chlorinated solvents, only few data exist for inorganic pollutants.⁵

PRB materials for AMD bioremediation include an SRB source (typically an environmental organic sample such a lake sediment) and an organic substrate to promote and maintain bacterial activity. The latter component is a determinant factor in the overall biotreatment performance. Additional proposed materials are limestone (to neutralise pH and facilitate bacterial activity),² iron (to induce reducing conditions and hydrogen generation, which appears to be a helpful electron donor for SRB)⁷ and silica sand or gravel (to enhance permeability).⁴

It is clear that development of large-scale biotechnologies such as PRB is inseparable from the supply and cost of raw materials, most of them being ideally wastes from agricultural and industrial activities and forestry. These wastes, which are mainly carbohydrates of varying chemical complexity, come in diverse types, but only very few of them can be utilised on a large-scale for economic and chemical reactivity reasons. The wide range of tested materials includes sewage sludge, leaf mulch, wood chips, animal manure, vegetal compost, sawdust,^{4,8} mushroom compost,^{1,2,8} whey,³ ryegrass,⁹ and other agricultural and food processing wastes.

Batch assays report sulfate removals of almost 100% and cite the production of biogenic sulfide as

being the main factor involved in the precipitation of metals as sulfides.^{3,4,10} However these data are not representative of continuously-fed systems operating, which imply long residence times needed for bacterial sulfate reduction to occur. Table 1 summarises the key parameters reported by researchers for experiments carried out under such conditions.^{1,8–11} As can be seen, residence time is commonly in the order of days and the amount of sulfate removal ranges between 12 and 50%. In field applications the full-scale barrier reported by Benner and co-workers¹¹ demonstrates that water flowing below 0.01 m d⁻¹ provided long residence times (60–165 days) with a reasonable barrier width (6 m). There are at present no reported experiments with scenarios at high water flows, which are common in gravel aquifers.

Literature descriptions of supported active sulfidogenesis in continuous systems on a laboratory scale involve only systems which were supplemented by easily assimilable electron donors like lactate,^{2,9} acetate, propionate, oxalate, glycerol,^{12,13} methanol,¹⁴ ethanol,^{13,15} and glucose.¹³ However, the addition of these compounds is not suitable for PRB due to its high cost.

The present paper investigates the potential use of municipal compost as a widely available organic mixture for use in *in-situ* permeable reactive barriers under high water velocity conditions (<0.1 m³ d⁻¹ m⁻²). This work forms part of the research on the mine accident at the Aznalcóllar Mine (Spain), which took place in 1998, when a tailing pond was breached. As a result 4 × 10⁹ m³ sludge and 2 × 10⁶ m³ acidic drainage flooded over the River Agrio valley. Although most of it was subsequently removed, pollution remaining in the soil resulted in acidic and metal-contaminated leachates draining into the groundwater. The threat of groundwater contamination demanded the setting up of water remediation systems. The installation of a PRB was postulated as a solution. It should be pointed out that high groundwater fluxes (0.1 m d⁻¹) were commonly measured in the Agrio alluvial aquifer.¹⁶

The main aim objective of this work was to ascertain whether a municipal compost (accompanied by calcite and optionally by iron) could remediate a metal-rich, acid water and could thus be a potential material for PRB under these high water flux conditions.

2 EXPERIMENTAL

2.1 Experimental set-up and methodology

Two reactive mixtures with different compositions were assessed in column experiments (id = 2.5 cm, l = 20 cm). Compositions (in vol %) are given in Table 2. Although only results pertaining to these two experiments are described in this article, unpublished preliminary and ongoing studies in very similar conditions have showed the same behaviour and comparable values from a chemical point of view.

Creek sediment acted as the SRB source and was collected from the anoxic zone of a local creek. The presence of SRB was indicated by a strong H₂S odour. No enrichment of SRB was carried out. Municipal compost was the provider of the carbon source. The favourable contribution of municipal compost has been reported by Benner and co-workers for the barrier at the Nickel Rim site.⁵ Furthermore, it was chosen since there is a composting facility close to the Aznalcóllar mine site and therefore it was a widely available organic substrate. Compost was provided by Aplicaciones de la Biomasa SA from Sevilla (Spain). A chemical analysis of the municipal compost revealed a C:N:P ratio of 29.8:1.38:1 and its contribution on the total alkalinity is negligible. Limestone (2–4 mm size) was used as the neutralising agent and it came from a quarry. The inclusion of iron aggregates in column 2 was postulated as a mechanism to promote bacterial activity via hydrogen production from water hydrolysis.⁷ It was supplied by Connelly-GPM, Chicago (Illinois) (8–80 mesh). Both mixtures had an estimated porosity of 0.5.

A synthetic acidic water was used to ensure the constant composition of water throughout the experiment. Its chemical composition was based on analysis of contaminated groundwater of the Agrio aquifer, Aznalcóllar, Spain (Table 3). Metals and anions were added to the dissolution as sulfates and chlorides, and pH was adjusted by addition of HCl.

The inflowing water, which was kept in a closed reservoir, to low oxygen being maintained by bubbling nitrogen, was pumped to the columns, from bottom to top, using a peristaltic pump. All tubings and fittings were made of Teflon, excluding the pump tubings which were made of Tygon. Joints were wrapped with

Table 2. Composition of column reactive mixtures (in vol %)

Component	Column 1	Column 2
Limestone	50	55
Compost	45	30
Creek sediment	5	10
Iron	-	5

Table 3. Simulated mine-drainage water

	Conc (mg dm ⁻³)
SO ₄ ²⁻	960
Fe(II)	10
Zn(II)	20
Al(III)	10
As(V)	2
Cu(II)	20
Cd(II)	2
pH	3

wax film to minimise air infiltration. The columns were covered with an opaque material to simulate light conditions encountered in the aquifer. Feed water was pumped to the base of the column at a flow rate of 0.075 cm³ min⁻¹, which taking into account the column section and the filling material porosity equals a flux of 0.44 m d⁻¹ (11 h average residence time). Both experiments were carried out at room temperature (23 ± 2 °C). No organic compounds were added to the water. The experiment lasted 123 days. The effluent from both columns was sampled and analysed to determine pH, and metal and sulfate concentrations. At the end of the experiments fractions of precipitate from both columns were retrieved to be visualised using scanning electron microscopy (SEM) and analysed by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Furthermore, solid fractions from different ports of column 2 were extracted and metal contents were determined by means of both total digestion and sequential extraction.

2.2 Water sampling and analysis

All pH and Eh measurements were made routinely in a sealed flow-through cell placed at the exit of the columns using a Hamilton combination pH electrode coupled to a Crison GLP22 pH meter. Effluent samples were collected periodically for metal and sulfate analyses. Samples were filtered (0.22 µm) and acidified with concentrated HCl. Zn, Fe, Cu, Cd and As were measured by inductively-coupled plasma mass spectroscopy (ICP-MS) (VG Plasma Quad PQ2), whereas Al was analysed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Spectra). Sulfate was measured by liquid ion chromatography (Alliance model Waters 2690) coupled to an electrical conductivity detector (Waters 996).

2.3 Solid analysis

On completion of the experiments, precipitates from both columns were sampled at different distances from the inlet and examined by scanning electron microscope (SEM) and analysed by energy-dispersive X-ray spectroscopy (EDS) (JEOL 6450, EDX-LINK-LZ5) and by X-ray diffractometry (XRD) (Siemens D-500) to characterise the precipitates.

Table 4. Three-step sequential extraction procedure for analysis of precipitate from column 2

Step	Extractant	Procedure	Target phase(s)
1	CH ₃ COOH (0.11 mol dm ⁻³)	1 g sample extracted with 40 cm ³ added and extraction for 16 h; centrifugation, and supernatant decanted for analysis	Carbonates, exchangeable metals
2	NH ₂ OH · HCl (0.5 mol dm ⁻³), pH 2	Residue from step 1 extracted with 40 cm ³ added, extraction for 16 h; centrifugation, and supernatant decanted for analysis	Fe/Mn (oxy)hydroxides
3	H ₂ O ₂ (31%) CH ₃ COONH ₄ (1.0 mol dm ⁻³), pH 2	Residue from step 2 treated twice with 10 cm ³ of H ₂ O ₂ (31%) and the dry residue extracted for 16 h with 50 cm ³ of CH ₃ COONH ₄ (1.0 mol dm ⁻³) adjusted to pH 5 with CH ₃ COOH; supernatant separated by centrifugation and analysed	Organic matter and sulfides

Precipitates from column 2 were sampled for chemical analysis of metal total contents. Samples of 1 g were digested in a microwave digester (Prolabo Microdigest A301) following a modified procedure described by Torres and co-workers.¹⁷ Contents of Zn, Fe, Al, Cu and Cd in the filtered extracts were measured by ICP as described above.

Sequential extraction was also run with samples from column 2. A number of sequential extraction schemes have been described in the literature, all of them consisting of the addition of reagents in an increasing reactivity order with the result that the extracted metal fraction could be associated with a specific chemical form. All these studies highlight the methodological limitations due to the restricted selectivity of extractants and operational factors. Therefore, sequential extraction must thus be regarded as an indication of chemical reactivity. The harmonisation and standardisation of a procedure is required and is currently being carried out. In this study a modified procedure proposed by the Community Bureau of Reference (BCR) was used. This protocol consists of a three-step procedure in which Zn, Pb, Ni, Cu, Cr, Cd are extracted into an acid soluble/exchangeable fraction (eg species associated with carbonates), a reducible fraction (eg species bound to Fe/Mn (oxy)hydroxides) and an oxidisable fraction (eg species bound to organic matter or sulfides) (Table 4).^{18,19}

3 RESULTS

3.1 Changes in water chemistry

Material effectiveness was indicated by the effluent's pH and metal and SO₄²⁻ concentrations. Both columns raised the pH from 3 to c pH 7 (Fig 1). The higher pH for column 2 decreased gradually and, after 2 months, it achieved pH values obtained for column 1 in the absence of iron. Effluent metal concentrations were in both cases below 0.2 mg dm⁻³ after the first 10 days (retention levels >99%) (Figs 2 and 3). Al and Cd concentrations were below detection limits (0.010 and 0.005 mg dm⁻³ respectively) and they remained unchanged throughout the experiment. Despite the

significant metal retention, net sulfate consumption was not detectable (Fig 4).

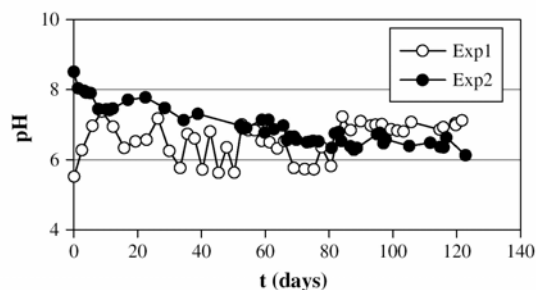


Figure 1. pH evolution for columns 1 and 2.

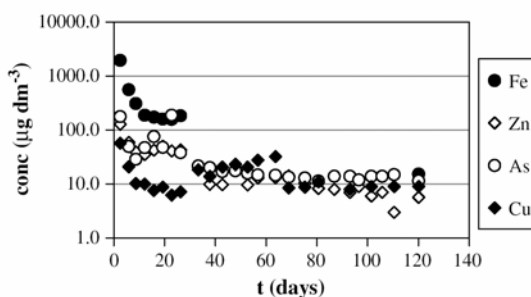


Figure 2. Metal concentration evolution for column 1.

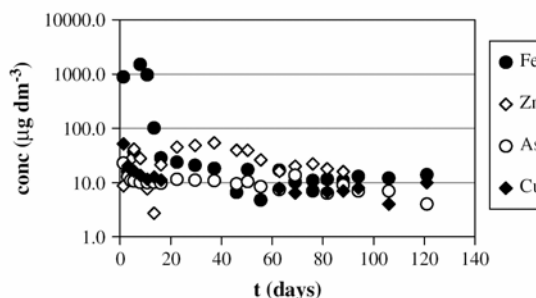


Figure 3. Metal concentration evolution for column 2.

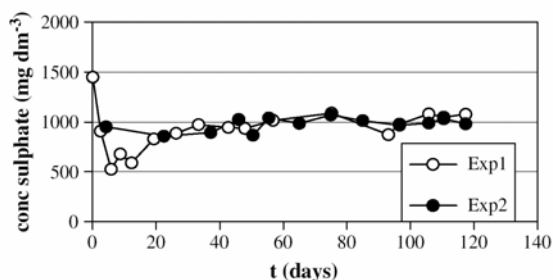


Figure 4. Sulfate concentration evolution for columns 1 and 2.

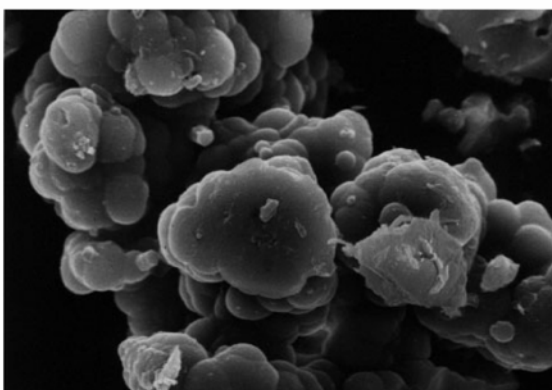


Figure 5. Aggregates of spherulites made up of Fe, Al, O, S and minor amounts of Zn, Cu and As observed in samples from column 2.

3.2 Mineralogy of precipitates

Brown and pale grey precipitates formed in the inlet port of both columns from the beginning of the experiment. These precipitates continued to form until the completion of the experiments. SEM examination of samples from the two columns showed a pervasive layer coating the surface of all the column material (Fig 5). This layer has no recognisable crystals and is made up of Al, Fe, S and O (H is not detectable) with minor amounts of Zn, Cu and As. The associated EDS mapping showed that these elements were distributed homogeneously. At the outlet of the column, spherical-shaped framboids averaging 5 μm in diameter were occasionally observed (Fig 6). They were constituted by Fe, S and minor amounts of Zn. Octahedral crystals of metallic Cu were also observed in column 2 (Fig 7). XRD identification of precipitates was not possible owing to their small quantities and poor crystallinity.

3.3 Determination of total metal content by chemical analysis

Once the experiments were concluded, three solid samples were collected at 5, 10 and 15 cm from the inlet of column 2, digested totally and analysed. As expected, the metal content decreased for all metals with increasing distance from the inflow port. Cu was the element most affected by distance (more than 97% was located at 5 cm from the inlet of the column). Similar trends were observed for the other metals (Table 5).

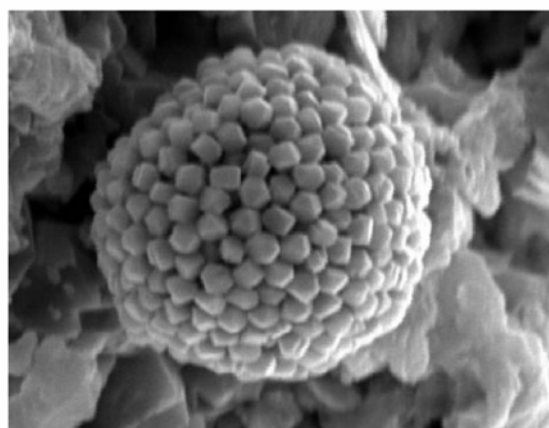


Figure 6. Spherical-shaped aggregates of Fe, S and minor amounts of Zn observed in samples from columns 1 and 2.

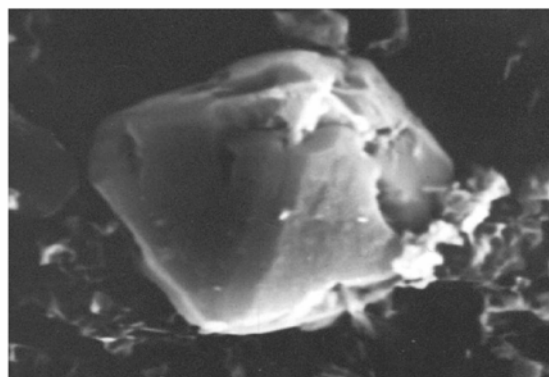


Figure 7. Octahedral crystals of metallic Cu formed by cementation in samples from column 2.

Table 5. Metal contents in precipitates from column 2

Sampling point (cm)	Metal content in sample (mg g^{-1})				
	Zn	Fe	Al	Cu	Cd
5	2.5	34.0	12.8	3.7	0.4
10	1.4	30.7	7.9	0.1	0.1
15	0.6	27.9	2.8	0.0	0.0

3.4 Solid selective sequential extraction

Four solid samples were collected at 5, 10, 15 and 20 cm from the inlet of column 2 and subjected to the sequential extraction described above. Given that the method of sequential extraction had been devised for metals, As was not measured.

Results presented in Table 6 show that Zn, Cu and Cd were mainly extracted in the first step, suggesting that they were present in an easily mobilised form. A significant proportion of Zn, Cu and Cd was also released within the reducible fraction, revealing associations of these metals with Fe and Mn (oxy)hydroxides. Cu was furthermore found in the oxidisable fraction, and was the most widely distributed between the three fractions.

Table 6. Contents of Zn, Cu and Cd associated with each of three sequential fractions for precipitate samples from column 2

	Port (cm)	Zn		Cu		Cd	
		mg g ⁻¹	% ^a	mg g ⁻¹	% ^a	mg g ⁻¹	% ^a
<i>Fraction 1</i>	5	2.927	87	1.882	70	0.662	94
(carbonates/	10	0.672	79	<0.030		<0.030	
exchangeable	15	0.505	83	<0.030		<0.030	
metals)	20	0.061	100	<0.030		<0.030	
<i>Fraction 2</i>	5	0.453	13	0.520	19	0.039	6
(Fe/Mn	10	0.184	21	<0.030		<0.030	
(oxy)hydroxides)	15	0.101	16	<0.030		<0.030	
	20	<0.030		<0.030		<0.030	
<i>Fraction 3</i>	5	<0.030		0.284	11	<0.030	
(organic matter/	10	<0.030		<0.030		<0.030	
sulfides)	15	<0.030		<0.030		<0.030	
	20	<0.030		<0.030		<0.030	

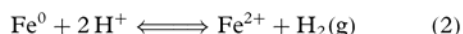
^a Percentage of metal in a given fraction over the total metal content extracted at a given port of the column.

The distribution of the three metals in the different fractions confirms their differences in speciation. However, it must be taken into account, as stated above, that the results from the sequential extraction analysis must be regarded as an indication of chemical speciation rather than a precise quantitative analysis.

4 Discussion and Conclusions

The results of this study indicate that the treatment based on the proposed municipal compost achieved part of the objectives of an AMD remediation, ie pH neutralisation and metal removal.

Limestone was demonstrated to be an efficient neutralising agent. Carbonate dissolution was able to raise an influent pH of 3 to around 6.5, within the range of 5–9.5, which is suitable for sulfate-reducing bacteria.⁹ During the first 2 months the pH in column 2 was higher than in column 1 (Fig 1). This can be attributed to corrosion of zero-valent iron, which reacts under anaerobic conditions, consuming acidity and producing H₂ in accordance with the following net reaction.^{7,20,21}



The higher pH for column 2 decreased gradually and, after 2 months, it achieved the pH values obtained for column 1 in the absence of iron. This pH decrease can be attributed to the precipitation of (oxy)hydroxides, which formed a film on the Fe⁰ surface coating the reaction sites and thus reduced the reactivity of the zero-valent iron.^{7,21–23} After iron passivation pH was controlled by limestone dissolution in both columns.

As regards the metals, the treatment in both columns removed more than 99% of the initial concentrations of Fe, Zn, Al, Cu, Cd and As. However most metal removal did not take place as a result of biogenically mediated sulfide precipitation since no appreciable sulfate removal was detected. Nevertheless, SEM analysis detected occasional Fe(Zn)S spherical framboids, indicating that bacterial activity had occurred.

Mechanisms whereby metal removal took place may be more related to the pH increase than to the biogenic sulfide generation. At neutral pH, an amorphous iron (oxy)hydroxide precipitate with crystals constituted by Fe, Al, S and O was formed as a coating layer. This precipitate acted as a strong secondary adsorption phase for metals and arsenic. These results are in part corroborated by the metal sequential extraction analysis carried out for column 2, whereby Zn, Cu and Cd were found to be present predominantly in the more mobile form (exchangeable and/or carbonate). It can be speculated that metal release in this fraction is attributable to the desorption from the iron (oxy)hydroxide layer rather than from carbonates, which were not observed in SEM analysis. Zn and Cu were also extracted, in a lesser proportion, by the reducible fraction, revealing associations of these metals with Fe and Mn (oxy)hydroxides. A number of other studies have reported Zn to be strongly associated with Fe and Mn (oxy)hydroxides.^{24,25}

As expected from the negligible net sulfate consumption and SEM observations, metal sulfides were only occasionally observed by SEM in samples retrieved from the outlet end of the column. These observations are consistent with sequential extraction analysis, where metal contents in the oxidisable fraction revealing the presence of sulfides were negligible. One exception was Cu, which was present in the sample collected at 5 cm from the inlet port with a content of up to 11% weight. Cu in this fraction was probably associated with organic matter rather than precipitated as sulfides, as suggested by the high stability of copper complexes with organic matter.^{24,26} Iron sulfide precipitation has been observed in previous laboratory batch experiments²⁷ and in field applications in permeable reactive barriers^{5,28} and artificial wetlands.²⁹

Metal ions like Cu, Ni and Cd can also be removed by cementation. In column 2, where zero-valent iron was present, octahedral crystals of reduced Cu were observed, providing evidence that more reducing conditions were achieved.

Metal adsorption onto organic matter could be another removal process, as reported in the literature.^{30,31} Although this process cannot be completely ruled out, we have not considered it in our interpretation, with the exception of Cu referred above.

With regard to the total metal content profile along column 2, large spatial differences were detected. The results showed that most precipitation took place at the entrance of the column. The metal most retained at the inlet was Cu (97%), followed by Cd (80%) and Zn (55%). Metal contents in samples retrieved at the outlet end of the column were less than 15%. Since both Fe and Al were present in the initial packing column material, only small differences with distance were found.

It can be concluded that there are multiple poorly understood variables that affect the efficiency of the biological treatment. Both the nature of the organic substrate and hydrodynamic conditions are acknowledged to be the main determinant factors. Among the organic substrate characteristics, the complexity and thus the digestibility of the carbon compounds, the available carbon content, the C:N:P ratios (as an important nutritional parameter for SRB) and the level of stabilisation must be mentioned. A rigorous and methodical test to predict the biodegradability of organic substrates by SRB still needs to be investigated. Concerning the hydrodynamic requirements, several studies have shown that a sufficient residence time must be given to the system in order to allow SRB to develop and support a continuous activity. Judging by these laboratory results, the tested municipal compost, assessed under high-flow conditions, was not an effective carbon source. Only framboidal sulfide precipitates were occasionally formed near the outlet of the column. The residence time in the present study was, on average, 17 h, which was much shorter than those reported in the literature. The short residence time and/or the slow degradability of some municipal compost must be taken into consideration when planning passive systems based on bacterial sulfidogenesis.

ACKNOWLEDGEMENTS

We gratefully acknowledge J Sastre (Analytical Chemistry Department, Universitat de Barcelona) for assistance in sample digestions for chemical analysis, and M Marsal (Laboratory of Electronic Microscopy, Universitat Politècnica de Catalunya) for the SEM analysis. We also thank Connelly-GPM, Chicago (Illinois), for providing iron aggregates. This work was funded by the EU PIRAMID project (EVK1-1999-00061P) and by the Spanish CYCIT programme (HID99-1147-C02) and the MCYT programme (REN-2002-04055-C02).

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