CHALLENGES OF PASSIVE TREATMENT OF METAL MINE DRAINAGE IN THE IBERIAN PYRITE BELT (SOUTHERN SPAIN): PRELIMINARY STUDIES ¹

Tobias S. Rötting, Robert C. Thomas, Carlos Ayora, Jesus Carrera²

Abstract. AMD in the Iberian Pyrite Belt is a problem of global scale. Successful implementation of passive treatment systems could remediate at least part of this problem at reasonable costs. However, initial trials with ALD and RAPS based on gravel size limestone failed due to rapid loss of chemical reactivity and plugging. Limestone buffered organic substrate (LBOS), which employs fine-grained limestone in an organic matrix, is an attractive alternative to conventional RAPS or ALD substrates, because it combines high reactivity with low plugging. However, LBOS has only been tested on ferric-iron waters, while our target AMD is mainly ferrous-iron. Due to the high ferrous to ferric iron ratio, we envision a LBOS treatment system that relies on sulfate reducing bacteria (SRB) in addition to the fine-grained limestone in the substrate. This study presents preliminary batch and column trials on reactivity and hydraulic properties. Other challenges include finding appropriate and locally available LBOS components. Tested substrates include compost, wood chips, limestone screenings and sugar beet lime.

Results show that only some SRB types tolerate the high metal concentrations. Reactors with SRB activity produce higher alkalinity, but support lower flow rates than reactors based on limestone dissolution only.

Additional Key Words: Limestone buffered organic substrate, LBOS, plugging, armoring.

¹ Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502

² Tobias S. Rötting is PhD student at the Institute of Earth Sciences "Jaume Almera" of the Spanish Superior Council of Scientific Investigations (CSIC), 08028 Barcelona, Spain. Robert C. Thomas is Federal Post Doctoral Associate at US EPA - NERL/ERD, Athens, GA 30605-2700, USA. Carlos Ayora is Professor at the Institute of Earth Sciences "Jaume Almera" (CSIC). Jesus Carrera is Professor at the Department of Geotechnical Engineering and Geosciences of the Technical University of Catalonia (UPC), 08034 Barcelona, Spain.

Introduction

During the last two decades, passive systems have become a widely used option for the treatment of acid mine drainage (AMD) in Northern America and increasingly in Europe (e.g. Younger et al., 2002, Ziemkiewicz et al., 2003). Nevertheless, these systems have mainly been applied at coal mines and other sites with relatively low metal concentrations, while experience is scarce for waters with higher metal loads. The abandoned mines of the Iberian Pyrite Belt (SW Spain) discharge acid waters with high heavy metal concentrations to the Rio Tinto and Rio Odiel river basins (e.g. Olias et al., 2004). Passive treatment systems, which only require naturally available energy sources and infrequent maintenance, may be an economical option to improve water quality in this region.

Anoxic limestone drains (ALD, Turner and McCoy, 1990) and Reducing and Alkalinity Producing Systems (RAPS, Kepler and McCleary, 1994) are employed frequently for the passive treatment of AMD. ALD are used to treat reduced, Fe^{+2} iron-dominated ARD (i.e. <1 mg·L⁻¹ $A1^{+3}$, Fe^{+3} , or O_2). They usually consist of a trench filled with limestone isolated from atmospheric O_2 through which AMD flows. The main alkalinity producing process in ALDs is the reaction of calcite with carbonic acid $H_2(CO_3)$ (Hedin et al., 1994), which under field conditions produces up to 350 mg·L⁻¹ CaCO₃ equivalents net alkalinity (i.e., the sum of influent acidity neutralized + measured effluent alkalinity: Hedin et al., 1994; Watzlaf and Hyman, 1995; Watzlaf et al., 2000) due to elevated pCO₂ inside the ALD. When exposed to >1 mg·L⁻¹ of Al, an ALD will usually clog due to precipitation of Al-hydroxides in the pore space of the system; when exposed to >1 mg·L⁻¹ of Fe^{3+} , it will usually lose reactivity due to precipitation of Fehydroxides and -hydroxysulphates on the surface of the limestone grains (passivation).

RAPS were designed to overcome the limitation of >1 mg·L⁻¹ of Fe⁺³ in the inflowing water. They consist of an ALD overlain by an organic layer (e.g. compost or manure). Inside the organic layer, bacterial activity is supposed to reduce Fe⁺³ to Fe⁺² so that it does not precipitate inside the underlying limestone drain. Sulphate reducing bacteria (SRB) also generate additional alkalinity, so that RAPS have been described to generate up to approximately 450 mg·L⁻¹ net alkalinity as CaCO₃ (Watzlaf, 2000).

Both ALD and RAPS are designed to produce alkalinity but not to precipitate metals inside the reactor. The generated alkalinity is used outside the ALD to precipitate the iron load of the water by subsequent oxidation and precipitation steps (usually sedimentation ponds aerated with cascades between the ponds).

Nevertheless, Watzlaf (1997) found that Fe and Al can be removed within a RAPS type system without critically compromising reactivity or permeability. Based on this observation, Thomas (2002; see also Thomas and Romanek, 2002a and 2002b) used a novel Limestone Buffered Organic Substrate (LBOS) consisting of 75 % vol. composted stable waste (mainly horse manure mixed with wood chips) and 25 % vol. limestone screenings. They found that precipitation of Al- and Fe-compounds within the LBOS did not negatively affect either reactivity or permeability. During the two years of their study, they observed a mean alkalinity production of 1800 mg·L⁻¹ net alkalinity as CaCO₃, and a mean outflow alkalinity of 620 mg·L⁻¹ as CaCO₃. They concluded that the high performance of their system was based on the inorganic conversion of mineral acidity (i.e. Al⁺³ and Fe⁺³) to proton acidity. The precipitation of Al- and Fe-hydroxides liberates protons that then dissolve calcite which neutralizes acidity and produces

additional alkalinity. This indicates that it may even be advantageous to precipitate metals inside the reactive substrate as long as it as it is possible to maintain reactivity and permeability. LBOS seems to meet these requirements.

Acid mine drainage from metal mines in the Iberian Pyrite Belt often has both high Al and Fe concentrations. LBOS could be an attractive option for passive treatment of these waters. Yet, LBOS has been tested only on Fe⁺³ iron waters, while our target AMD has mainly Fe⁺² iron. Therefore, one of our goals is to evaluate LBOS performance in high Fe⁺² iron AMD.

Also, Thomas (2002) suggested that the system performance was not dependent on SRB activity. Nevertheless, this hypothesis had not been tested specifically, so in the present study we also investigate how a substrate with SRB activity performs in comparison with a substrate without SRB activity. An additional challenge is finding appropriate materials for the mixing of LBOS. Ideally, waste materials will be employed to keep costs low.

This study presents preliminary batch and column trials on reactivity and hydraulic properties of different mixtures of materials.

Materials and Methods

Target site

The study presented here was carried out to design a field pilot plant at the abandoned "Monte Romero" mine in Southern Spain (Huelva province). The Monte Romero mine is situated within a massive pyrite deposit with minor amounts of Zn, Pb and Cu sulfides. The enclosing rocks are siliclastic schists with no carbonate beds present. The AMD emerging from the adit (Table 1) has a mean flow rate of around 2 L/s. Reactive Materials

LBOS can be regarded as a mixture of two components:

- 1. a fine-grained alkaline material (typically calcite) that produces mineral alkalinity abiotically.
- 2. an organic material that serves two purposes:
 - a. to promote bacterial activity.
 - b. to provide a large pore space where metals can precipitate without effecting permeability.

One purpose of the present study was to find suitable substrates for manufacturing the LBOS material.

Two alkaline substrates were tested:

- 1. Calcite sand. It must be purchased, and the nearest quarry is about 210 km from Monte Romero mine. In our study, we used a grain size ranging from 0.05-5 mm, with a size distribution very similar to that used by Thomas (2002).
- 2. Sugar beet lime. It is a waste material from sugar production with a high calcite content. It can be obtained for free, and the nearest sugar factory is about 150 km

from Monte Romero mine, so it might be an attractive alternative to limestone sand. Nevertheless, is has a very small grain size (<0.2 mm).

Table 1. Mean dissolved composition of target AMD.

target AMD.	
рН	3.3
Acidity (mg·L ⁻¹ as CaCO ₃)	2340
Acidity (meq·L ⁻¹)	47
$Al (mg \cdot L^{-1})$	134
Ca (mg·L ⁻¹)	213
Cd (mg·L ⁻¹)	0.6
Co (mg·L ⁻¹)	0.8
Cu (mg·L ⁻¹)	11
Fe (mg·L ⁻¹)	347
% Fe(II)	83 %
$K (mg \cdot L^{-1})$	1.8
Mg (mg·L ⁻¹)	256
Mn (mg·L ⁻¹)	18
Na (mg·L ⁻¹)	19
Ni (mg·L ⁻¹)	0.9
$P (mg \cdot L^{-1})$	0.6
Pb (mg·L ⁻¹)	0.2
S (mg·L ⁻¹)	1180
Si (mg·L ⁻¹)	37
Zn (mg·L ⁻¹)	396

Organic substrates investigated included the following materials:

- 1. Composted branches and leaves of the rockrose bush (*Cistus ladaniferus L.*) which grows abundantly in Southern Spain and is used to produce cistus essential oil for the perfume industry. The sample was collected at a local rubbish dump and contained traces of underlying soil.
- 2. Extracted branches and leaves of the rockrose bush. This was a residue from a local cistus oil extraction plant.
- 3. Municipal compost from a local composting plant.
- 4. Composted sludge from a local municipal wastewater treatment plant.
- 5. Wood chips from a local wood processing plant.
- 6. Horse manure. We used fresh horse manure as a major substrate, and some old manure that had been stored anaerobically during one year as SRB source.
- 7. For comparison, we also used a sample of the original stable waste (horse manure and wood chips) that had been used in the study of Thomas (2002).

Batch tests

Batch tests were carried out first to determine which mixtures of alkaline and organic material were able to produce bacterial sulfate reduction. Here, we present three sets of batch tests which were performed iteratively in order to narrow the set of substrates. Glass vessels (125 mL bottles for the first set, 300 mL jars for the second and third set) were filled to two thirds of the total volume with the substrate mix, and then were filled up to top with either AMD from Monte Romero Mine or with mineral water saturated with gypsum. The latter was used as a blank test to investigate whether SRB activity is reduced by the high metal concentrations of Monte Romero AMD (cf. Table 1). The combinations of substrates and waters are specified in the Results section. The vessels were stored in the dark at room temperature. After one week and three weeks, the vessels were opened and sulfide (S⁻²) concentration was measured using a Macherey-Nagel "visocolor" test kit (range 0.05-1.0 mg·L⁻¹ S⁻²). If S⁻² concentration was below detection limit and neither smell of H₂S nor black coloration of the substrate was noticed, it was concluded that SRB activity was absent or very low.

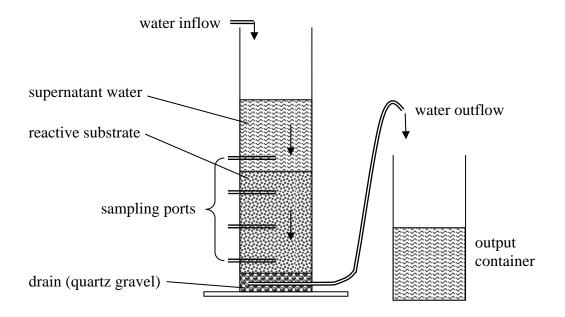
Column study

Once suitable reactive mixtures were found, laboratory columns were set up to investigate the hydraulic and long-term treatment performance of the mixture. The columns were made from clear plexiglass (9.4 cm inner diameter, 35 cm high; Fig. 1 A+B) and are equipped with Eijkelkamp "Macro Rhizom" sampling ports (0.1 µm pore size) at 5 cm depths intervals.

The columns were filled (from bottom to top) with 2.5 cm quartz gravel as a drain and 17.5 cm reactive substrate. Columns were first saturated with water from the bottom to expulse air trapped in the substrate. During the experiment, input water (AMD from Monte Romero Mine) was fed from the top of the column using a Gilson "Minipuls 3" peristaltic pump. The water flows down through the column and out of the overflow pipe into an output container that acts as an aeration and sedimentation tank. The input water was changed at least weekly in order to replenish ferrous iron which was oxidized gradually upon contact with air.

Water samples were taken weekly from the input container, from the supernatant water, and from the drain pipe. Samples from the intermediate sampling ports were taken monthly. The pH was measured using a Crison glass electrode. For samples with pH > 5.6, total alkalinity was measured using CHEMetrics "Titrets" test kits (range 10-100 or 100-1000 mg·L⁻¹ as CaCO₃). Filtered samples (0.1 μ m) were acidified with HNO₃ for analysis of cations and total S by ICP-AES and with HCl for analysis of Fe⁺² and total Fe by spectrophotometer (method modified after To, 1999). Sulfide (S⁻²) concentration was measured using a Macherey-Nagel "visocolor" test kit (range 0.05-1.0 mg·L⁻¹ S⁻²).

A)



B)



Figure 1. A) Design of laboratory columns, B) Column #1 at the start of the experiment with input container (right), output container with overflow pipe (middle) and peristaltic pump (left).

Results

Batch tests

In the first set of batch tests (Table 2), the different organic materials were tested for suitability as a substrate in sulphate reducing treatment systems. Seventy-five percent by volume of organic material were mixed with 25% of limestone sand or (in some cases) sugar beet lime. For most materials, a second bottle with an additional SRB source (anaerobically stored horse manure) was set up. Most bottles were filled with Monte Romero AMD, and a few with mineral water saturated with gypsum. After one week, all bottles were opened and sulfide concentration of the supernatant was measured, but no sulfide was detected in any batch. After the third week, all bottles were opened again, and this time sulfide was detected in four batches (Table 2):

- Both bottles with the composted rockrose, limestone sand and AMD (with and without additional SRB source, ID 1.1 and 1.2).
- For the wood chips, only the bottle filled with gypsum-amended water showed SRB activity (ID 1.13).
- Also for the stable waste, only the bottle filled with gypsum-amended mineral water showed SRB activity (ID 1.17).

The bottles with sugar beet lime instead of limestone sand had shown no SRB activity, and it was found that this substrate was so fine-grained that most of it ended up at the bottom of the bottle. Therefore, it was concluded that sugar beet lime was not suitable as a component for LBOS, and it was excluded from further studies.

The only substrate capable of generating SRB activity in contact with AMD was the composted rockrose. Nevertheless, this material consists mainly of rather coarse branches (approx. diameter 0.5 cm) which are not very suitable for mixing with limestone sand as most of the sand falls to the bottom of the vessel. So it was discarded for textural reasons.

Wood chips and stable waste had shown SRB activity when in contact with gypsum-amended mineral water and seemed to give a better pore structure. Therefore, a second set of batch tests (Table 3) was carried out to first trigger SRB activity by starting the batch trial with mineral water, and then change the water to AMD. Three jars were filled with 75 % vol. stable waste and 25 % vol. limestone sand. One batch was set up with AMD; one with a mix of 50% AMD with 50% gypsum-amended mineral water; and one with gypsum-amended mineral water.

Only batch 2.3 showed SRB activity after three weeks. In this jar, the mineral water was drained and replaced by AMD. But after four more weeks, sulfide concentration was much lower. We concluded that SRB found in fresh horse manure do not tolerate the high metal concentrations found in AMD very well.

Table 2. Substrate combinations (in % vol.) and water type (Monte Romero AMD or mineral water saturated with gypsum) used in the first set of batch tests, and sulfide concentration (mg·L⁻¹ S⁻²) measured after three weeks.

	O	mate	rial			aline erial	SRB source			
Batch trial ID	Composted rockrose Extracted rockrose	Municipal compost	Wastewater sludge	Wood chips	Stable waste	Limestone sand	Sugar beet lime	"Old" horse manure	Water type	S ²⁻ concentration
1.1	75%					25%			AMD	0.4
1.2	75%					25%		5%	AMD	0.2
1.3	75%					25%			AMD	0
1.4	70%					25%		5%	AMD	0
1.5	75%						25%		AMD	0
1.6	70%						25%	5%	AMD	0
1.7	75%					25%			mineral	0
1.8	70%					25%		5%	mineral	0
1.9				75%		25%			AMD	0
1.10				70%		25%		5%	AMD	0
1.11				75%			25%		AMD	0
1.12				70%			25%	5%	AMD	0
1.13				70%		25%		5%	mineral	0.2
1.14		75%				25%			AMD	0
1.15			75%			25%			AMD	0
1.16					75%	25%			AMD	0
1.17					70%	25%			mineral	0.7

So after the second set of batch trials, the only substrate capable of generating SRB activity upon immediate contact with AMD still was the composted rockrose. In order to improve hydraulic and mixing properties, we tried four combinations containing 25-70 % vol. of wood chips, together with either 5 or 25 % vol. of fine-cut composted rockrose as SRB source (Table 4). In one case (ID 3.5), we alternatively tried a higher fraction of "old" manure in order to see whether SRB activity in contact with AMD could be stimulated that way. We also added fresh horse manure to two batches in order to see if additional nutrients and organic carbon would stimulate SRB activity.

Table 3. Substrate combinations (in % vol.) and water type (Monte Romero AMD or mineral water saturated with gypsum) used in the second set of batch tests, and sulfide concentration (mg·L⁻¹ S⁻²) measured after three weeks and after 7 weeks.

Batch trial ID	Stable waste	Wood chips	Fresh manure	Limestone sand	Water type during first 3 weeks	S ²⁻ concentration (mg·L ⁻¹) after 3 weeks	Water type dutring next 4 weeks	S ²⁻ concentration (mg·L ⁻¹) after 7 weeks
2.1	75%			25%	AMD	0	AMD	0
2.2	75%			25%	50% AMD + 50% mineral	0	50% AMD + 50% mineral	0.1
2.3	75%			25%	mineral	>1.0	AMD	0.2

Table 4. Substrate combinations (in % vol.) and water type (Monte Romero AMD or mineral water saturated with gypsum) used in the third set of batch tests, and sulfide concentration (mg·L⁻¹ S⁻²) measured after three weeks.

Batch trial ID	Composted rockrose	"Old" manure	Fresh manure	Wood chips	Limestone sand	Water type	S ²⁻ concentration
3.1 3.2 3.3 3.4 3.5	25% 25% 5% 5%	15%	25%25%10%	25% 50% 45% 70% 50%	25% 25% 25% 25% 25%	AMD AMD AMD AMD AMD	>1.0 [†] 0.4 0 0 0 0

[†]triplicate trials gave the same result.

[‡]duplicate trials gave the same result.

Results show that from the substrates tested here, only the composted rockrose substrate bears SRB capable of living in contact with Monte Romero AMD. A relatively high fraction of this substrate (>25% vol.) is necessary to produce SRB activity. The mixture of equal volumes of composted rockrose cuttings, fresh horse manure, wood chips and limestone sand gave the highest sulfide production.

Column studies

Column #1. This column was designed to have no SRB activity, and therefore contained a mixture of 75 % vol. wood chips and 25 % vol. limestone sand. Mean flow rate was 0.41 mL·min⁻¹. Assuming a porosity of 0.5, this yields a residence time of 28 hours. The pH in the AMD source container was usually slightly below 3 (Fig. 2) but fluctuated due to Fe-precipitation in the container (see below). Output pH was above 6 during the first nine weeks of the experiment, but slightly below 6 afterwards. Outflow alkalinity started around 320 mg·L⁻¹ as CaCO₃, but dropped steadily to below 200 mg·L⁻¹ as CaCO₃ by week 8.

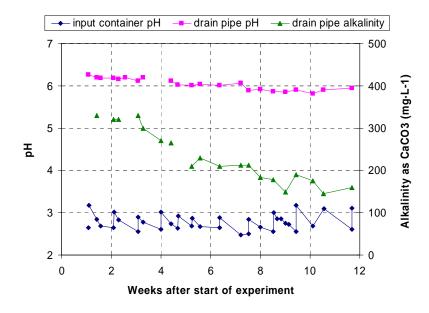


Figure 2. Input container pH and drain pipe pH and alkalinity in column #1.

Total and ferrous iron concentrations (Figures 3 and 4) fluctuated greatly due to oxidation of Fe^{+2} iron and precipitation of Fe^{+3} iron both in the input container that was replenished weekly and in the larger AMD storage container. In order to obtain higher ferrous iron concentrations in the input water, from week 6 on extra Fe^{+2} iron as $FeSO_4 \cdot 7H_2O$ was added. Both the total Fe and Fe^{+2} iron fluctuated less in the supernatant water. Supernatant Fe^{+2} iron concentration was about half the concentration in the input container; while drainage pipe Fe^{+2} iron concentration was very high, considerable iron concentrations (mostly Fe^{+2} iron) were detected in the drain pipe. Both Fe^{+2} and total iron decreased to below 0.1 mg·L⁻¹ in the outflow container, except during the last two weeks when in the drain pipe pH was below 6 and Fe^{+2} iron very high.

Al concentrations were more constant (Fig. 5). Supernatant concentrations were slightly higher than input container concentrations, probably due to evaporation, because S and Si concentrations showed the same trend (not shown). The Al concentration decreased to around $10~\text{mg}\cdot\text{L}^{-1}$ (90% removal) in the drain pipe and to around $5~\text{mg}\cdot\text{L}^{-1}$ (95% removal) in the output container.

Zn concentrations were not lowered by column #1. In- and outflow concentrations were not significantly distinct (not shown).

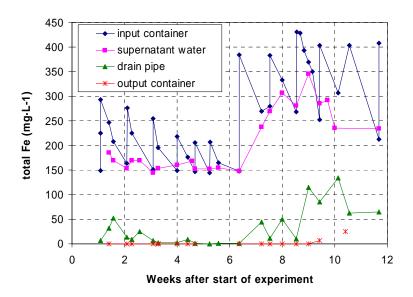


Figure 3. Total iron concentration in input container, supernatant water, drain pipe and output container of column #1.

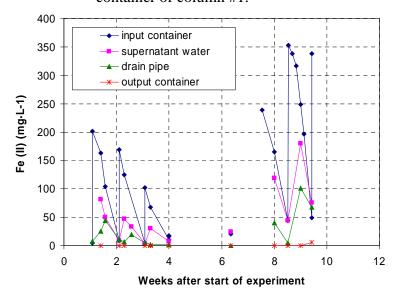


Figure 4. Ferrous iron concentration in input container, supernatant water, drain pipe and output container of column #1.

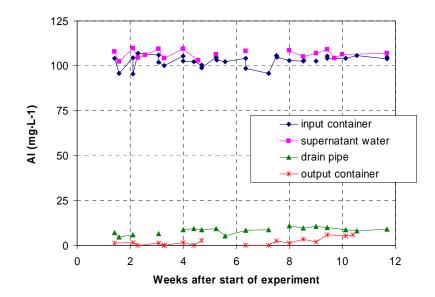


Figure 5. Al concentration in input container, supernatant water, drain pipe and output container of column #1.

Column #2. Column #2 was designed to have SRB activity, and therefore was set up once the batch trials had concluded. It contained a mixture of equal volumes of composted rockrose cuttings, fresh horse manure, wood chips and limestone sand that had given the highest sulfide production with AMD. Mean flow rate was 0.08 mL·min⁻¹. Assuming a porosity of 0.5, this yields a residence time of 5.5 days. By the time of writing, only chemical analysis of the first two weeks and pH, sulfide and alkalinity data of the first eight weeks of operation were available for column #2.

The pH rose from 2.6-3.0 in the input container to 6.5-7.1 in the drain pipe (Fig. 6). Outflow alkalinity was between 450 and 1000 mg·L⁻¹ as CaCO₃. Total Fe decreased from 160-270 mg·L⁻¹ in the input container to 1 mg·L⁻¹ in the drain pipe, Al and Zn were completely eliminated (Al from 101-108 mg·L⁻¹ in the input container to below 1 mg·L⁻¹ in the drain pipe, Zn from 357-377 mg·L⁻¹ in the input container to below 0.25 mg·L⁻; not shown). Sulfide concentrations in the outflow were between 0.8 and 1 mg·L⁻¹ (not shown).

Column #3. A third column, as column #1 designed to have no SRB activity, was set up together with column #2. It has a low flow rate (mean 0.07 mL•min⁻¹) in order to be directly comparable to column #2. Supposing a porosity of 0.5, it yields a residence time of 6.5 days.

<u>Column #3 performance.</u> As for column #2, only pH and alkalinity data of the first eight weeks and chemical analysis of the first two weeks of operation were available for column #3.

The pH rose from 2.6-3.0 in the input container to 6.5-6.7 in the drain pipe (Fig. 7). Outflow alkalinity was between 240 and 300 mg·L⁻¹ as CaCO₃. Al decreased from 101-108 mg·L⁻¹ in the input container to below quantification limit (>1 mg·L⁻¹) in the drain pipe, total iron from 160-270 mg·L⁻¹ to 16 mg·L⁻¹, but Zn concentrations did not change significantly (not shown). Sulfide concentrations in the outflow were below detection limit (not shown).

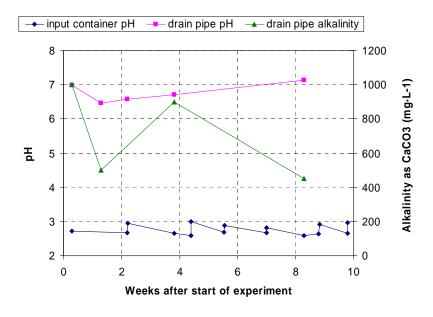


Figure 6. Input container pH and drain pipe pH and alkalinity in column #2.

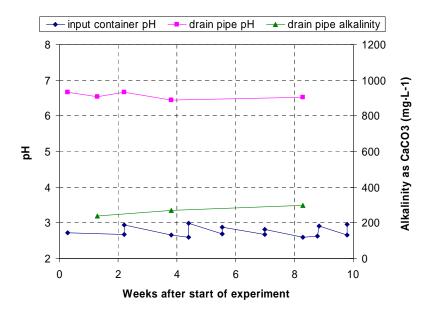


Figure 7. Input container pH and drain pipe pH and alkalinity in column #3.

Conclusions

- An appropriate SRB source with bacteria tolerant to AMD composition needs to be introduced into the substrate. It seems insufficient to assume that suitable bacteria will establish themselves automatically; SRB from horse manure seem not to tolerate our AMD composition.
- Column #1 shows good removal of Fe and Al, but outflow pH and alkalinity decrease within a few months, and no Zn is eliminated.
- Column #2 shows higher initial performance than columns #1 and #3. SRB activity and/or sorption of metals onto the organic substrates seem to enhance performance of column #2. Nevertheless, a longer observation period is necessary to draw robust conclusions.
- Column #3 performs comparably to column #1 despite the lower flow rate.

Acknowledgements

We are grateful to E. Pelegri (University of Barcelona) for technical assistance. This study was funded by the Spanish Government projects REN-2002-04055-C02 and REN-2003-09590-C04.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Literature Cited

- Hedin, R.S., Watzlaf, G.R. and Narin, R.W., 1994. Passive treatment of acid mine drainage with limestone. J. Environ. Qual., 23: 1338-1345.
- Kepler, D.A. and McCleary, E.C., 1994. Successive alkalinity-producing systems (SAPS) for the treatment of acidic mine drainage, Proc. Int. Land Reclamation and Mine Drainage Conference and Third Int. Conference on the Abatement of Acidic Drainage. USDI, Bur. of Mines Spec. Publ. SP06A-94, Pittsburgh, PA, pp. 195-204.
- Olias, M. et al. 2004. Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain). Science of the Total Environment, Vol. 333 (1-3), 267-281.
- Thomas, R.C., 2002. Constructed treatment wetlands in the remediation of acid rock drainage: Mechanisms of metal removal and acid neutralization, microbial ecology, and design innovations. Ph.D. Thesis, University of Georgia, Athens, GA.
- Thomas, R.C. and Romanek, C.S., 2002a. Passive treatment of low-pH, ferric iron-dominated acid rock drainage in a vertical flow wetland I: Acidity neutralization and alkalinity generation, Proceedings of the 19th Annual National Meeting of the American Society of Surface Mining and Reclamation. ASMR, Lexington, KY.

- Thomas, R.C. and Romanek, C.S., 2002b. Passive treatment of low-pH, ferric iron-dominated acid rock drainage in a vertical flow wetland II: Metal removal, Proceedings of the 19th Annual National Meeting of the American Society of Surface Mining and Reclamation. ASMR, Lexington, KY.
- To, T.B., Nordstrom, D.K., Cunningham, K.M., Ball, J.W. and McCleskey, R.B., 1999. New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. Environmental Science & Technology, Vol. 33 (5), 807-813.
- Turner, D. and McCoy, D., 1990. Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. In: D.H. Graves and R.W. DeVore (Editors), Proc. 1990 Nat. Symp. on Mining, Univ. of Kentucky, Lexington, KY, pp. 73-75.
- Watzlaf, G.R., 1997. Passive treatment of acid mine drainage in down-flow limestone systems. In: J.E. Brandt (Editor), Proceedings of the 14th Annual National Meeting of the American Society of Surface Mining and Reclamation., Austin, TX, pp. 611-622.
- Watzlaf, G. et al. 2000. Long term performance of anoxic limestone drains for the treatment of coal mine drainage. Mine Water and the Environment, Vol. 19 (2), 98-110.
- Watzlaf, G.R. and Hyman, D.M., 1995. Limitations of Passive Systems for the Treatment of Mine Drainage, 17th Annual Association of Abandoned Mine Lands Conference, French Lick, Indiana, pp. 186-199.
- Younger, P.L. et. al. 2002. Minewater: Hydrology Pollution and Remediation, Kluwer Academic, Dordrecht.
- Ziemkiewicz, P.F. et al. 2003. Long-term Performance of Passive Acid Mine Drainage Treatment Systems. Mine Water and the Environment, Vol. 22 (3), 118–129.