Passive treatment of acid mine drainage: repeatability for sulphate reducing passive bioreactor column efficiency testing

Thomas Genty[1], Bruno Bussière[1], Carmen M. Neculita[2], Mostafa Benzaazoua[3], Gérald J. Zagury[4]

[1]*Industrial Chair CRSNG Polytechnique-UQAT: Environment and mining wastes management, University of Québec in Abitibi-Témiscamingue, 445 boulevard de l'Université J9X 5E4 Rouyn-Noranda, Québec, Canada, thomas.genty@uqat.ca, bruno.bussière@uqat.ca*

[2]*Division of Environmental Engineering and Sustainability, Department of Civil and Environmental Engineering, KAIST (Korea Advanced Institute of Science and Technology), 335 Gwahak-ro, Yuseong-gu, Daejeon 305—701, Republic of Korea, cmn@kaist.edu*

[3] *Laboratoire de Génie Civil et d'Ingénierie Environnementale, INSA de Lyon, Bât. Sadi Carnot, 9, rue de la physique, 69621 Villeurbanne Cedex, France, mostafa.benzaazoua@insa-lyon.fr*

[4]*Industrial Chair CRSNG Polytechnique-UQAT : Environment and mining wastes management, École Polytechnique, 2900 boulevard Édouard Montpetit H3T 1J4 Montréal, Québec, Canada, gerald.zagury@polymtl.ca*

Abstract This work presents an experimental method developed over the years to design, set-up, and operate columns that test sulphate reducing passive bioreactors (SRPBs) for acid mine drainage (AMD) treatment. Results obtained from identical columns with this experimental approach are presented and interpreted for their statistical validity. The statistical analysis was based on the "paired-difference test" which allows comparing two sets of data in pairs by looking at the difference between the two sets of data. The three series of data showed a good repeatability (data within a confidence interval of 95%) for pH, oxydoreduction potential, alkalinity, total iron and sulphate concentrations. Hence, duplicate or triplicate column tests are not systematically required for assessing the performance of SRPBs, if the columns are designed, set-up, and operated as proposed by the authors.

Key Words passive treatment, sulphate-reducing passive bioreactor, statistical analysis, repeatability

Introduction

Preventing the formation of AMD is generally the preferred option for mine sites rehabilitation (Aubertin *et al.* 2002). In many cases, especially when the weathering process of metal sulphide minerals is already entailed, prevention alone is not sufficient and the collection and temporary treatment of contaminated mine water is also required. There are numerous available options to treat the AMD, which can be classified into chemical and biological systems that both mainly aim at increasing pH, neutralising acidity, and removing metals. Another classification differentiates the active systems, which require continuous input of resources to sustain the process, from passive systems, which in exchange, require relatively minimal maintenance during operation (Neculita *et al.* 2008, Potvin 2009). Passive systems, together with an AMD control method, are the best option to rehabilitate abandoned mine sites. The present study focuses on SRPBs as sustainable biotechnology for AMD treatment. SRPBs permit to increase the pH, generate alkalinity and remove metals from contaminated water (Neculita *et al.* 2007, Potvin 2009).

Passive systems for AMD treatment are often designed on the basis of column efficiency testing. However, the repeatability of these tests could be questionable due to the inherent heterogeneity of solid materials be used in the reactors and to differences in laboratory experimental test procedures. Performing duplicate or even triplicate column tests are often requested to obtain statistically valid results. The number of scenarios that could be tested for AMD treatment is limited by the high costs involved (Demers *et al.* 2011). This study presents a laboratory methodology which was developed in order to set-up and to operate SRPBs laboratory columns, and to evaluate the repeatability of column tests.

Columns set-up and operation

SRPB duplicate (or triplicate) tests were performed under similar conditions (14 cm diameter × 70 cm height in Genty 2007 and 2011, 10 cm diameter × 45 cm height in Neculita *et al.* 2008). Column reactors were built with transparent Plexiglas and equipped at the bottom side with a perforated plastic plate, which was covered with a geotextile to avoid the leaching of fine particles in the effluent. In addition, to prevent clogging and/or to allow a uniform flow distribution at the influent and effluent ports, column ends were filled with 5 cm heights of gravel (≈ 1 cm diameter) in both the upper and bottom areas. SRPB mixture materials were firstly mixed and homogenized, and then packed in columns in 10 cm height layers (each layers should have similar weights and water content). Layer was slightly compacted before the addition of the next one. Then, an aluminum foil was laid around the column to prevent chemolithotrophic and phototrophic bacteria development. After the set-up, the bioreactors were saturated with Postgate B medium (Postgate 1984), which was prepared using distilled water and had the following composition: 3.5 g/L sodium lactate; 2.0 g/L $MgSO_4{\cdot}7H_2O$; 1.0 g/L NH_4Cl; 1.27 g/L $CaSO_4{\cdot}2H_2O$; 1.0 g/L yeast extract; 0.5 g/L KH_2PO_4; 0.5 g/L $FeSO_4{\cdot}7H_2O$; 0.1 g/L thioglycolic acid, and 0.1 g/L ascorbic acid. Columns were then incubated for four weeks (acclimation period) before starting their operation. The individual volume of Postgate B medium was used to calculate the porosity of each column. Theoretically, the estimated porosity should be as close as possible for the duplicate (or triplicate) columns. AMD fed was started after the acclimation period; the column was considered ready for AMD treatment when the oxydoreduction potential decreased to values below -150 mV (Neculita *et al.* 2008). The AMD was pumped at selected flow rates to insure the reaching of the targeted hydraulic retention time (HRT). The flow direction was upward or downward, depending on the study. A schematic representation of an upward flow column design is presented in figure 1.

Slight differences existed between the three sets of experiments, which were used for the present statistical analysis. The first series of SRPB tests (Genty 2011) was performed in four 10.7 L columns. The composition of two SRPB mixtures (#4 and #7), which were tested in duplicates columns, is given in table 1, previously optimized (Genty 2011). The porosity was estimated at 0.41, for both columns filled with mixture #4, and at 0.40 and 0.39, for the duplicate columns filed with mixture #7. Artificial AMD 1 (see table 2) was pumped in upward flow, for 64 days, at an HRT of 5 days (0.6 mL/min).

The second series of tests (Genty 2007) was performed using a similar design and set-up procedure, but the HRT was set at 10 days. The compositions of the filling mixture (#1) and of the artificial AMD 2 tested in these columns are presented in table 1 and table 2, respectively. Finally, the third series of tests used three 3.5 L columns filled with the same filling mixture #1 in triplicate and operated in downward flow at an HRT of 10 days for the treatment of the artificial AMD 3 (see table 2). More details about this last study are available in Neculita *et al.* (2008).

To assess the performance of all the tested columns, influent and effluent were weakly measured for pH, oxydoreduction potential (called ORP, and Eh if the ORP is corrected relative to the standard hydrogen electrode), sulphates concentration, acidity, alkalinity, and metals concentrations.

Repeatability evaluation

The aim of statistical analysis performed in the present study was to ascertain whether two sets of data from two similar column tests set-up and operated as proposed in this study, come from the same population. The statistical approach is similar to the one detailed in the work of Demers *et al.* (2011). The use of student's t distribution was justified by the relatively limited available data. To compare two series of data, the "Paired-difference test" and a two-tailed test at 95% confidence interval were used (Demers *et al.* 2011). The method hypothesis was that the difference between the two means (μ) of two series of data from two columns (1 and 2) was null.

$$\mu_1 - \mu_2 = 0 \qquad [1]$$

The t test notation became:

$$t = \frac{\bar{d}}{s_d / \sqrt{n}} \qquad [2]$$

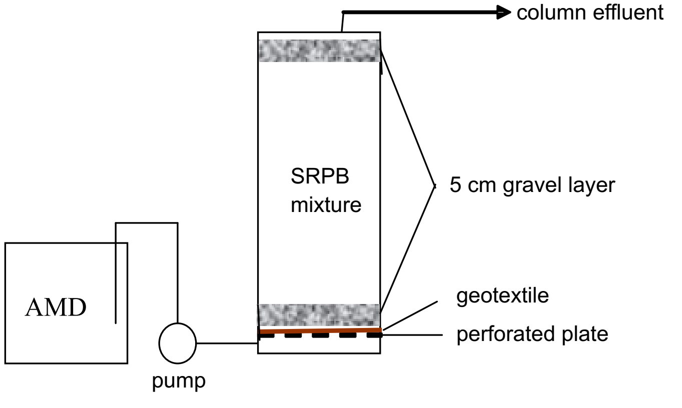

***Figure 1** Upflow column design.*

***Table 1** Composition of SRPB mixtures (%, dry).*

Mixture	#1	#4	#7
Celullosic wastes			
Maple chips	10	5	6
Sawdust	20	10	11
Organic wastes			
Chiken manure	10	5	8
Leaf compost	20	10	12
Inoculum			
Sediment	15	8	8
Inert structural agent			
Sand	20	10	50
Nutriment (Nitrogen)			
Urea	3	2	3
Neutralizing agent			
Calcium carbonate	2		2
Calcite		50	

***Table 2** AMD composition (mg/L, except for pH).*

Elements	AMD 1	AMD 2	AMD 3
Al	7	7	0
Cd	0.5	1	9.8
Cr	1	2	1
Fe	4000	1600	1066 to 504
Mg	10	100	85.8
Mn	10	21	10.1
Ni	2	7	13.7
Pb	0.5	1	0.5
SO_4^{2-}	9000	4200	4022
Zn	0.5	2	14.5
pH	3.5	3.5	2.8 to 5.7

Where $\overline{d}$ was the mean of the paired differences, n was the number of paired differences and s_d was the standard deviation of the paired differences. For the calculation of s_d the following equation was used :

$$s_d = \sqrt{\frac{\sum_{i=1}^{n}(d_i - \overline{d})^2}{n-1}} \quad [3]$$

The hypothesis (data come from the same population) was rejected when the t value obtained with the equation [2] was above a pre-determined value (determinated in statistical tables for a two-tailed test at 95% confidence interval, n-1 was the degree of freedom).

Selected results

First experiment set: Genty (2011)

Effluent quality (pH, ORP, alkalinity and total iron concentration) at the exit of duplicate SRPB columns with mixture #4 and #7 are presented in figure 2.

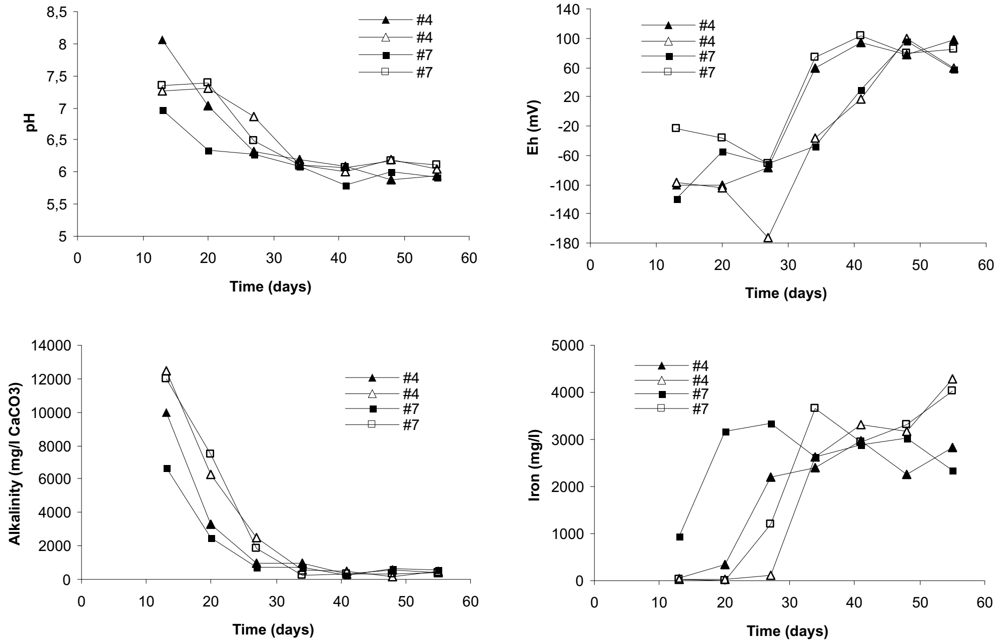

***Figure 2** Evolution of pH, Eh, alkalinity and iron concentration in treated effluent using mixtures #4 and #7.*

The pH of treated effluent steadily decreased during the first 30 days from values above 8 to between approximately 6 and 6.5 and then stabilized, without significant difference between duplicate columns. Consistently, alkalinity values decreased from 11250 mg/L $CaCO_3$ or 9333 mg/L $CaCO_3$ to 504 mg/L $CaCO_3$ or 450mg/L $CaCO_3$, respectively for mixture #4 and mixture #7. During the same period, Eh increased constantly from negative values (as low as -120 mV) to 74—75 mV, regardless the mixture or duplicate reactors. Similar trend was recorded for the evolution of acidity (not presented here) and total iron, which concentration increased values up to 3500 mg/L (mixture #4) or to 3200 mg/L (mixture #7). Standard deviation of iron concentration (both mixtures) exceeded 1000 mg/L and indicated relatively high variability. Finally, sulphate concentrations (not shown in figure 2) ranged from 6811 mg/L to 10054 mg/L (for mixture #4) and from 6270 mg/L to 11837 mg/L (for mixture #7).

Apparently, results from duplicate columns seemed comparable. However, a simple visual comparison of the data on effluent quality is not accurate enough to evaluate the repeatability of the tests and statistical calculations are required. Table 3 presents results on repeatability calculation for the two tested columns: mixture #4 and #7.

During the first 64 days, calculated t values were below the t test value (2.45 or 4.3, depending on the parameter) for a confidence interval of 95 %, except for the pH of column #7, for which the calculated t is very close to the t test value (2.46 vs. 2.45). This statistical analysis allowed the interpretation that the data could come from the same population, and thus from almost identical tests. Therefore, physicochemical parameters such as pH, Eh, alkalinity, iron and sulphate concentrations were repeatable for the two columns filled with the same mixture and treating the same AMD quality.

Second experiment set: Genty (2007)

Figure 3 presents the main quality parameters of the treated effluent of the two duplicate columns tested in the second study. The pH values continuously decreased from around 8 to 6.5, at the end of the experiments. However, Eh remained relatively low during the testing period with values between -80 and -130 mV; similar variations were recorded in the two columns. Iron concentrations decreased from approximately 1600 mg/L in influent AMD to values usually below 3 mg/L in treated water. Duplicate columns showed slightly different alkalinity, with final values of 1584 and 1676 mg/L of $CaCO_3$. Small differences were recorded between values measured at the same sampling time. Similarly to the first study, the results presented here seem, at least visually, comparable.

Table 4 presents the statistical results for these last two column tests. As it can be seen, statistical interpretation of the data on pH, Eh, alkalinity,

Table 3 *T-test statistics for physicochemical parameters for treated effluents using mixtures #4 and #7.*

Parameters	column	Average $\bar{d}$	Standard deviation s_d	degrees of freedom	calculated t	t test value	within 95% confidence interval
pH	# 4	0.040	0.43	6	0.23	2.45	yes
	# 7	0.33	0.328	6	2.46	2.45	no
Eh	# 4	40.93	49.30	6	2.03	2.45	yes
	# 7	45.16	51.83	6	2.13	2.45	yes
Alcalinity	# 4	912.00	1384.00	6	1.61	2.45	yes
	# 7	1508.43	2555.37	6	1.45	2.45	yes
Total iron	# 4	76.74	1124.19	6	0.17	2.45	yes
	# 7	448.76	1724.29	6	0.64	2.45	yes
Sulphate	# 4	178.70	2300.93	2	0.11	4.30	yes
	# 7	1705.46	3352.52	2	0.72	4.30	yes

Table 4 *T-test statistics for physicochemical parameters for treated effluent using mixture #1 (source of original data: Genty 2007).*

Parameters	Average $\bar{d}$	Standard deviation s_d	degrees of freedom	calculated t	t test value	within 95% confidence interval
pH	0.12	0.098	10	0.38	2.23	yes
Eh	18.02	11.65	10	0.47	2.23	yes
Alcalinity	2.53	5.35	5	0.19	2.57	yes
Total iron	428.00	353.18	8	0.40	2.31	yes

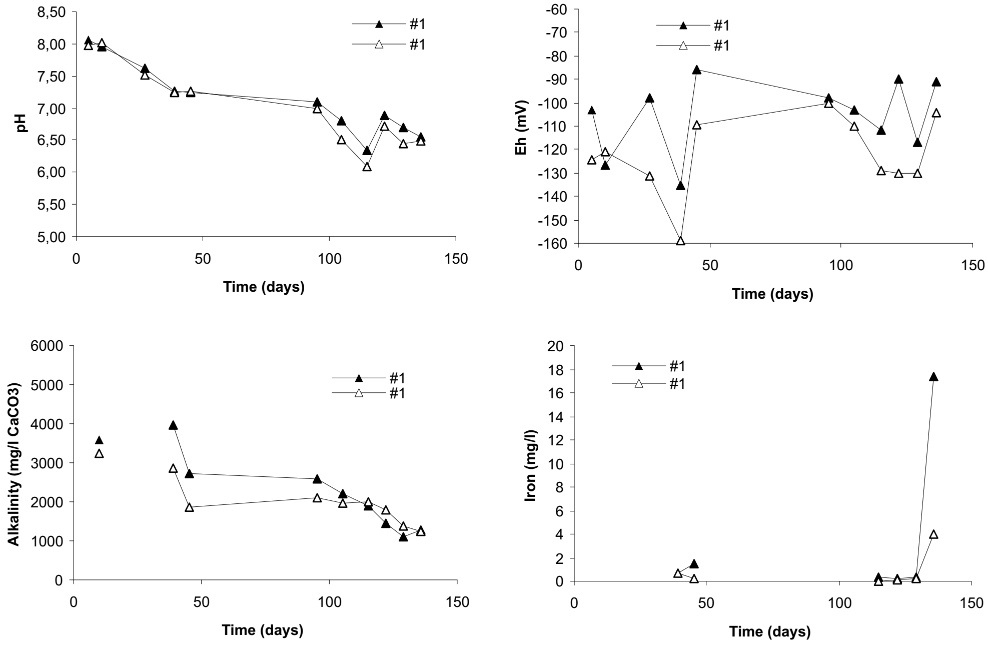

***Figure 3** Evolution of pH, Eh, alkalinity and total iron concentration in treated effluent using mixture #1.*

iron concentrations from Genty (2007) proved that the two column tests were repeatable within 95% confidence interval.

Third experiment set: Neculita et al. (2008)

Table 5 presents statistical results of column tests performed with mixture #1 and AMD 3 (Neculita *et al.* 2008). Triplicate columns were compared two by two (columns 1 and 2, columns 2 and 3, and columns 1 and 3) for their repeatability. If each pair of columns was found repeatable, thus the three columns were repeatable too. Once again, the statistical analysis showed good repeatability for all selected parameters (pH, ORP, total iron and sulphate concentrations) with all data within the 95% confidence interval.

Conclusions

Results from three independent studies, which tested the performance of 9 SRPBs for the treatment of three qualities of artificial AMD were compared to evaluate the repeatability of the experimental procedure. Indeed, numerous factors (like analytical instruments, operator, sampling,

***Table 5** T-test statistics for physicochemical parameters treated effluent using mixture #1 (source of original data: Neculita et al. 2008).*

Parameters	Columns tested	Average $\bar{d}$	Standard deviation s_d	degrees of freedom	calculated t	t test value	within 95% confidence interval
pH	1 and 2	0.15	0.20	43	0.11	2.02	yes
	2 and 3	0.18	0.30	43	0.09	2.02	yes
	3 and 1	0.19	0.28	43	0.10	2.02	yes
ORP	1 and 2	16.93	18.08	43	0.14	2.02	yes
	2 and 3	23.18	22.56	43	0.15	2.02	yes
	3 and 1	22.73	20.09	43	0.17	2.02	yes
Total iron	1 and 2	44.49	89.51	43	0.07	2.02	yes
	2 and 3	53.48	75.68	43	0.11	2.02	yes
	3 and 1	46.69	94.39	43	0.07	2.02	yes
Sulphate	1 and 2	211.93	185.87	43	0.17	2.02	yes
	2 and 3	260.80	200.03	43	0.20	2.02	yes
	3 and 1	273.86	219.47	43	0.19	2.02	yes

material set up procedure, etc.) could affect the result of an experiment. Statistical analyses of the treated effluent quality showed good repeatability (within a confidence interval of 95%) for selected parameters (pH, ORP or Eh, alkalinity, total iron and sulphate concentrations). Based on these results, duplicate or triplicate column tests are not systematically required for assessing the performance of passive treatment systems such as SRPBs, providing that the columns are designed, set-up, and operated with a good methodology and a rigorous control of the boundary conditions.

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