MINE WATER – PRELIMINARY RESEARCH FOR BIOLOGICAL SULPHATE REMOVAL

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ABSTRACT

Mine water from closed sites throughout the main Romanian mining areas represents a significant vector for water pollution. Those mine water, especially from non-ferrous mines have a high variability of chemical-physical characteristics (pH, conductivity, ORP, heavy metals, alkaline and alkaline earth ions, sulphate and chloride).
There are significant challenges for the treatment of these types of water, including the removal of sulphate and alkaline-earth metals ions. For the sulphate removal, the biological reduction is one of the possible technical alternatives. This paper presents some results for a lab-scale trial for the evaluation of the potential of passive system for the biological sulphate reduction from mine waters.

Keywords*:* AMD waters, sulphate removal, SRB, passive treatment

INTRODUCTION

Passive systems for the mine water treatment have certain worldwide attention and there are studies on lab-scale or pilot scale and also on large scale. For the

sulphate removal, specifically, difficulties in starting and keeping in operation of the passive systems are often mentioned [1-5].
In Romania the passive technologies for the biological sulphate reduction (BSR) were not evaluated. The scale and the required operational period for processes are very significant. There are many drawbacks referring to the level of "passivity" of these systems, the level of necessary intervention and the real performances (costs and the quality of treated water, costs of other finishing treatment steps and the management of the solids formed by precipitation).
The start-up of a local exploratory level research for the sulphate passive biological reduction is presented here.

EXPERIMENTAL PART

This research had the following tasks:

- Inoculum production, specialized for the anaerobic biological reduction of sulphate
- Testing of an experimental model of a passive system for BSR
- Testing of a bioreactor with assisted substrate feeding

Inoculum production

The inoculum was obtained in an anaerobic type biofilter which reproduced at small scale a passive system for the BSR, using as innoculum sources like cow manure or similar, as cited by some papers failed [6,10]. Only using as innoculum samples from a mine site, from stagnant mine water areas, from N-W of Romania worked. The organic substrate was generated by the anaerobic decomposition of the organic filling. Mine water was supplied from a circum neutral AMD source, Boita Hateg, HD- Romania [7]. The structure of the inoculum growth biofilter is described in Table 1 (see also Figure 1-2)

Table 1 – Inoculum growth biofilter

Element	Characteristics
Biofilter	Column type, H= 1,5m, Φ80mm Flow: downwards
Inorganic filling	Gravel, d= 1-2cm; Hs = 0,38m; 1,6 dm^3; ε = 50%; Sand: d =1,6 mm; Hs=0,19m, Vs = 0,95 dm^3; ε = 16% Limestone - no
Organic filling and support	Beech chips: 450g, 1,8dm^3; Hay: 80g Inoculum seed, origin - Mestecanis
Ancillary	Recycle peristaltic pump Nitrogen cylinder, pressure regulator

Figure 1- The biofilter for the inoculum growth

Experimental model for the passive system for BSR

The experimental model for passive systems of type compost bioreactor (SRB200L) was dimensioned using the sulphate reduction rate observed at inoculum formation phase. Due to some difficulties during the previous phase, the sand filling was not used anymore, to prevent premature clogging of the biofilter (Table 2 & Figure 2). Also, the flow type was changed to up-wards.

Table 2 – Experimental model – compost bioreactor for the biological sulphate reduction

Element	Characteristics
Biofilter	Cylindrical tank, V=220L Flow: upwards
Inorganic filling	Gravel, d= 1-2cm; 47 dm3; 124 kg; ε = 50%; Sand: no; Limestone: no
Organic filling and support	Beech chips: 20 kg, 50 dm^3 Hay, layer 1: 8 kg; ≈ 40dm^3 ; Hay, layer 2: 10kg; ≈50dm^3 Compost: 1 kg Inoculum : 15kg, heterogeneous
Ancillary	Recycling pump: peristaltic 0-100 L/h, Pmax = 1,5 bar Feed pump: 0.1-0.5 L/h, Pmax = 1,5 bar N_2 gassing system
Others	Hydraulic closure; Valves, connectors

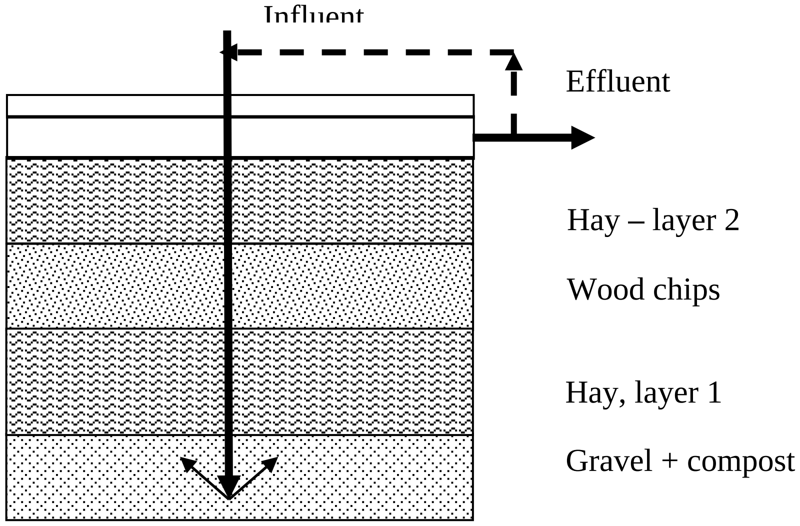


Figure 2 - Structure of the filing for the experimental model SRB200L

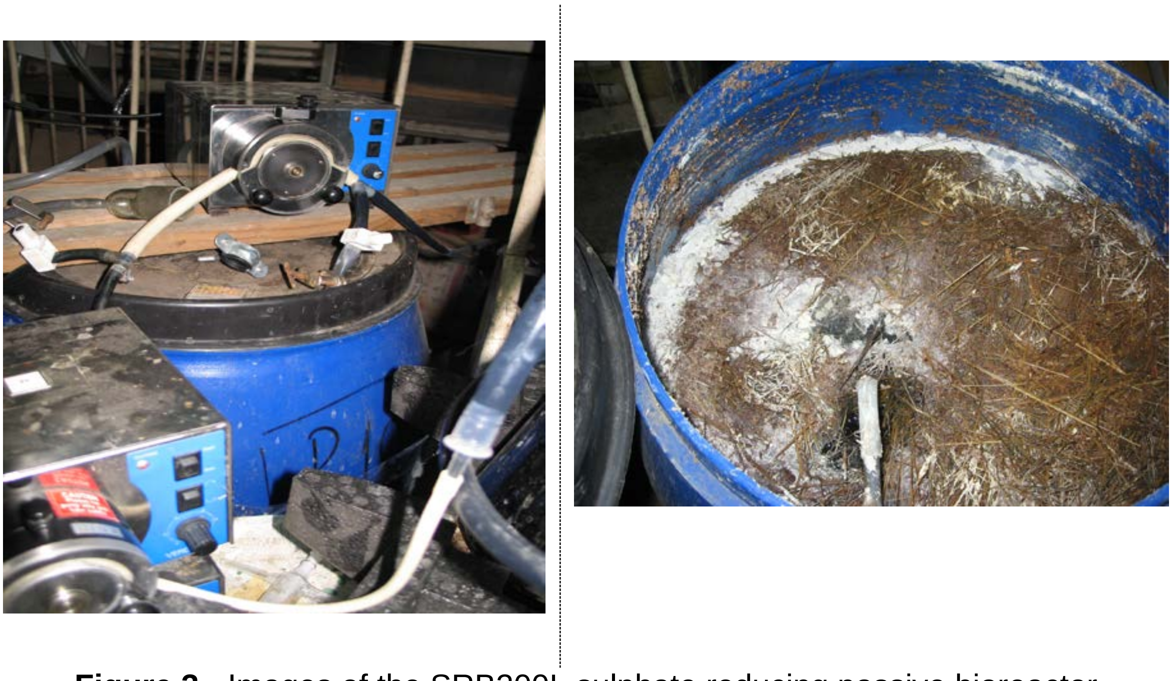


Figure 3 - Images of the SRB200L sulphate reducing passive bioreactor

The sulphate removal biofilter was loaded with mine water pre-treated with lime at pH approx 6.0 and fed further with other mine waters with lower pH (Table 3).

Table 3- Feed water composition for the SRB 200L bioreactor

pH	t	ORP	SO_4^{2-}	COD	Ca^{2+}	Mg^{2+}	Na^+	K^+	PO_4^{3-}	Cl^-
	^0C	*mV*	*mg/l*							
6.0	21	+205	1173	<5	521	85	43	7.9	4.7	17.5
5.0	21		1517	<5	317	80	80	88	0.8	18
4.0	21		2758	<5	341	59	56	75	<1	9.9

The various feed water samples had variable heavy metals compositions: Al (4,2-71,6 mg/l), Fe (7,3-79,1 mg/l), Mn (6,7-12,3 mg/l), Zn (6,7-35,9), Ni (0,1-0,31 mg/l), Cu (0,2-0,35 mg/l). Because copper is generally known as an inhibitor for such biological processes, even at low levels, the value of 1 mg/L was not exceeded for this research phase, focused on sulphate reducing process itself.

RESULTS AND DISCUSSION

Inoculum growth

The inoculum growth is a slow process, as mentioned in other few experimental works. This phase took about 4 months.
The aspect of waster in the biofilter changed soon after the inoculum grown, blackening due the sulphides formation. The progress of the seed biofilter is accompanied by the decreasing of the redox potential. The maximum sulphate reduction rate obtained in this phase was about 5g $SO_4^{2-}/(m^3 \cdot day)$.

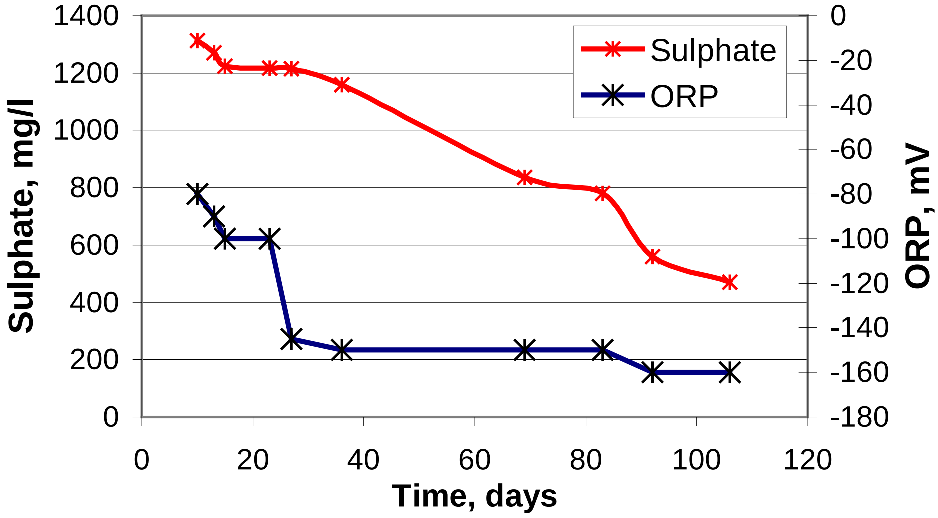


Figure 4 - Trend of the sulphate concentration and ORP – inoculum growth phase

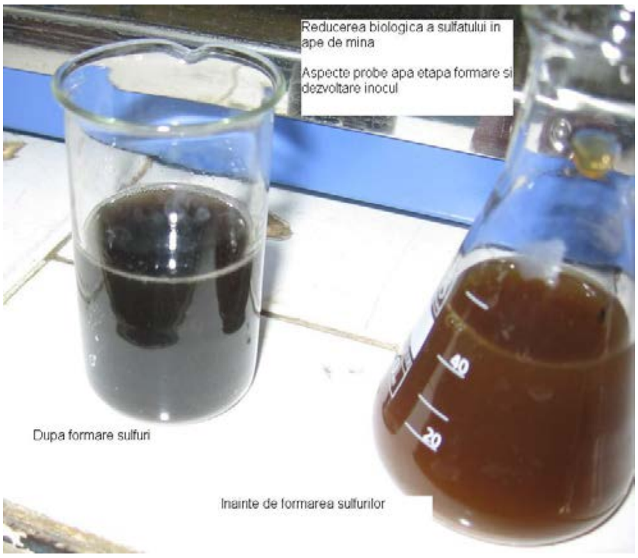


Figure 5 - Colour change of mine water during inoculum growth (sulphide formation)

Passive sulphate reducing bioreactor

The viability of the inoculum obtained in laboratory was proven at larger scale, in the model bioreactor. The anaerobic compost bioreactor successfully reduced sulphate to sulphides, with fair good reaction rates.
The main findings are (see also Figure 6-8):

- This type of bioreactor will work in a non-stationary regime, the capacity of generating organic substrate and nutrients (nitrogen, phosphorus species) is maximum and dependent of "recipe" and the operational parameters of the bioreactor (such as pH, heavy metals content in the mine water etc.).
- After inoculum transfer, the first phase is characterized by the high rate consumption of the most favourable organic substrate accompanied by the sulphate reduction. This phase is followed by a longer, quasi-stationary one.
- Starting with the first phase, the ammonium concentration in the effluent will decrease from high values (tens to hundreds ppm) to lower values, with a rate determined by the influent "recipe" and flow rate. Nutrients are used for the microorganisms, but also continuously washed-out, leaving the reactor with the effluent, generating a secondary pollution, which it is not specific to mine waters or ARD.
- The sulphate reducing process rate will decrease continuously, as the favourable organic substrate and nutrients quantities are diminishing. Long observation periods are necessary to assess the moment of a needed new human intervention.
- Due to the existence of ammonium, high organic load and sulphides in the effluent, some supplementary treatment steps are needed (e.g. biological aerobic treatment). Informatively, the effluent sulphide content (as H_2S and

S^{2-}/ HS^{-}) was 4.2-55 mg/L (not acceptable for discharge, not even in urban sewerage).

- The system generates alkalinity and tolerates influent AMD with pH > 3-4.
- The sulphate reducing process average rate is about 40 g SO_4^{2-}/(m^3▪day). This might be enhanced by assisting the process with more favourable substrate, as the maximum rate was indeed higher, about 135 g SO_4^{2-}/(m^3▪day), before depletion of the most appropriate substrate.

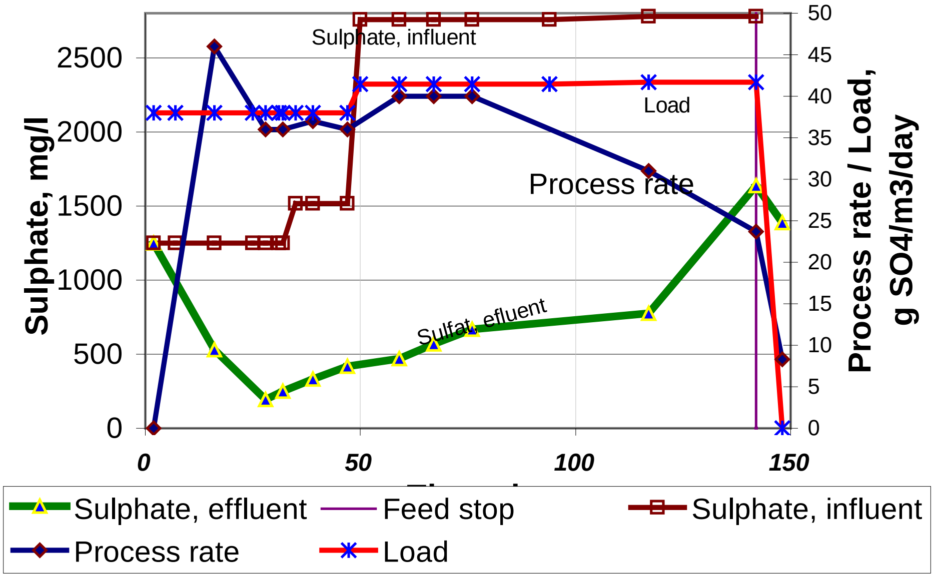


Figure 6 – Trends of main parameters for the SRB200L bioreactor

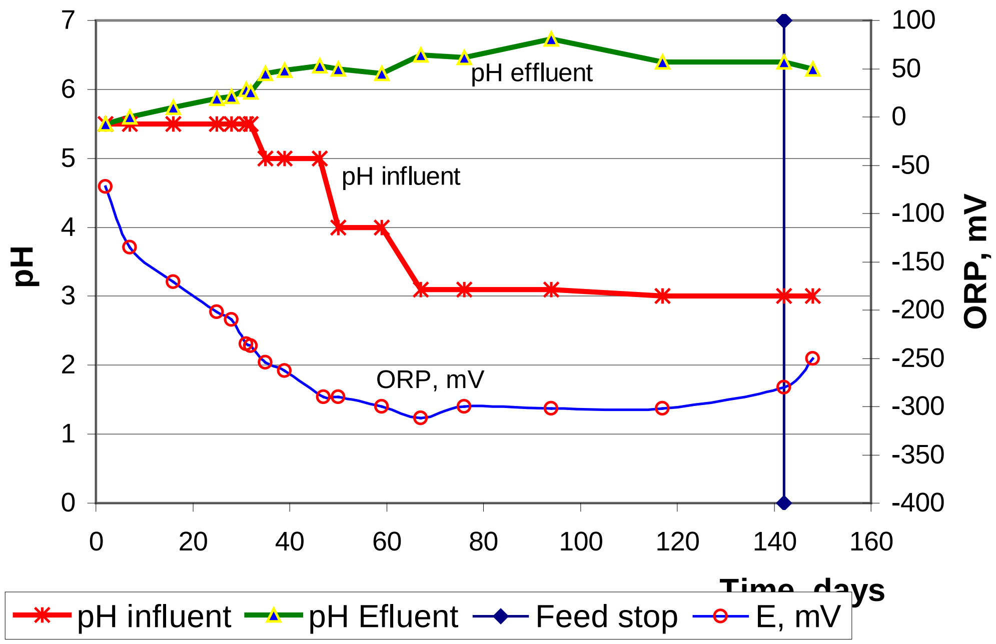


Figure 7 – Time evolution of pH and ORP for the SRB200L bioreactor

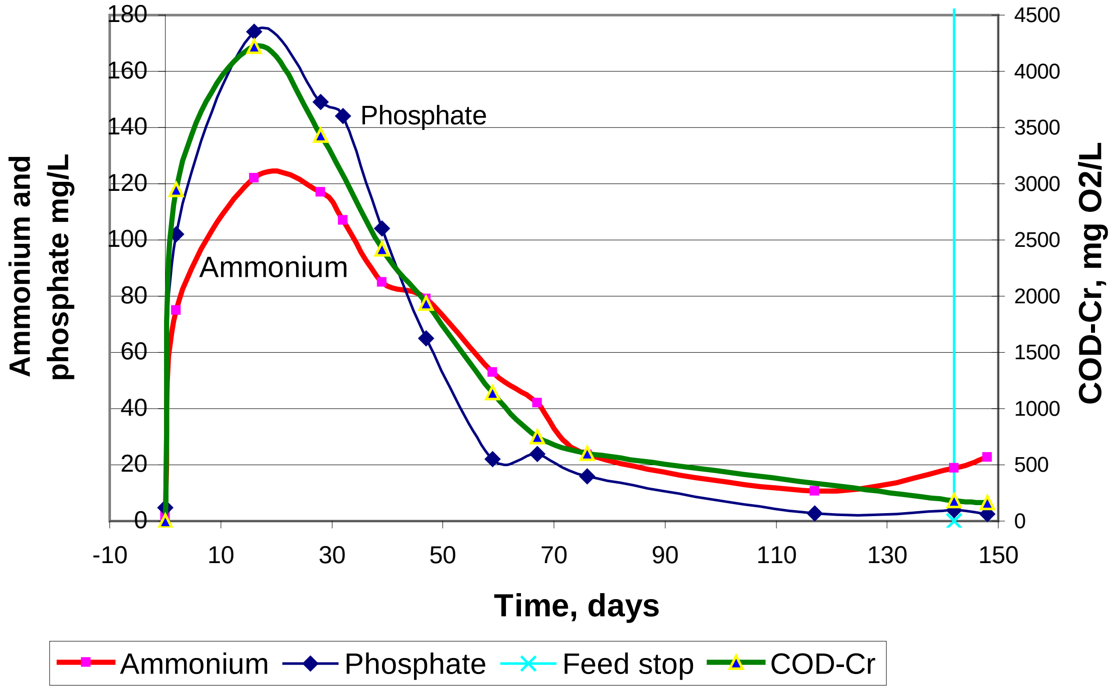
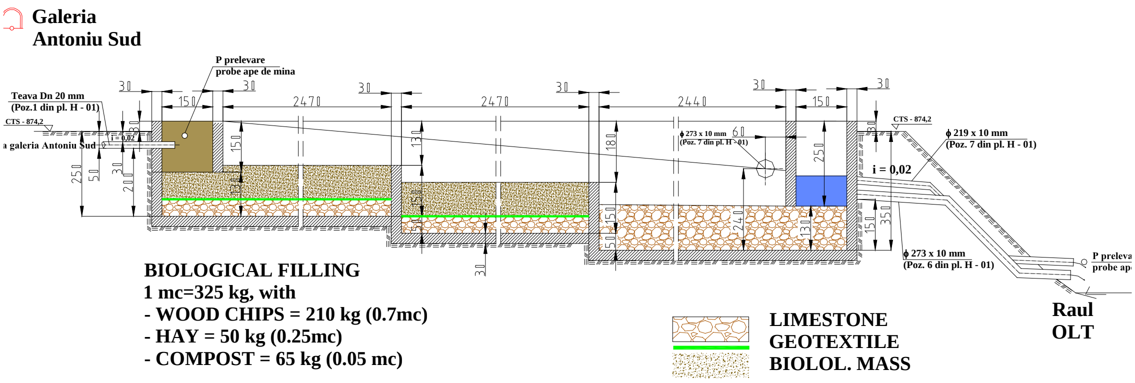


Figure 8 – Time evolution and washing out of nutrients for the SRB200L bioreactor

The results were used to check some guidance design parameters for passive sulphate reducing systems. In correlation, for assessing at larger scale the performances of the sulphate reducing bioreactors, it was designed a pilot plant for 3-5 m^3/day that uses an "out of order passive" limestone treatment system at Balan mine water treatment station [7].



CONCLUSION

This preliminary research indicates that the anaerobic sulphate reducing bioreactors of type wood chips – compost can achieve the 600 mg/l limit stipulated for discharge to surface water courses. The reaction rates are low, so the volumes needed are high.

The effluent of these bioreactors will exceed the discharge limits for organic load, phosphorous, ammonium, total nitrogen and sulphide, without proper supplementary treatment.

For assessing at larger scale the performances of the sulphate reducing bioreactors, it was designed a pilot plant that uses an "out of order passive" limestone treatment system.

Most probably the performance of sulphate reducing bioreactors can be improved by controlled dosing of proper organic substrate and nutrients, in correlation with less challenging tasks for finishing the effluent as required for discharging. Researches for assisted passive SBR were started at lab scale.

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