PERGAMON

Chemical Engineering Science 56 (2001) 1639–1645

Chemical Engineering Science

www.elsevier.nl/locate/ces

Treatment by sulfate-reducing bacteria of Chessy acid-mine drainage and metals recovery

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Abstract

Acid-mine drainage can contain high concentrations of heavy metals and release of these contaminants into the environment is generally avoided by lime neutralization. However, this classical treatment is expensive and generates large amounts of residual sludge. The selective precipitation of metals using H_2S produced biologically by sulfate-reducing bacteria has been proposed as an alternative process. Here, we report on experiments using real effluent from the disused Chessy-les-Mines mine-site at the laboratory pilot scale. A fixed-bed bioreactor, fed with an H_2/CO_2 mixture, was used in conjunction with a gas stripping column. The maximum rate of hydrogen transfer in the bioreactor was determined before inoculation. k_La was deduced from measurements of O_2 using Higbie and Danckwert's models which predict a dependence on diffusivity. The dynamic method of physical absorption and desorption was used. The maximum rate of H_2 transfer suggests that this step should not be a limiting factor. However, an increase in H_2 flow rate was observed to induce an increase in sulfate reduction rate. For the precipitation step, the gas mixture from the bioreactor was bubbled into a stirred reactor fed with the real effluent. Cu and Zn could be selectively recovered at pH = 2.8 and pH = 3.5, respectively. Other impurities such as Ni and Fe could also be removed at pH = 6 by sulfide precipitation. Part of the outlet stream from the bioreactor was used to regulate and maintain the pH during sulfide precipitation by feeding the outlet stream back into the bioreactor. The replacement of synthetic medium with real effluent had a positive effect on sulfate reduction rate which increased by 30–40%. This improvement in bacterial efficiency may be related to the large range of oligo-elements provided by the mine-water. The maximum sulfate reduction rate observed with the real effluent was 200 mg l^{-1} h^{-1}, corresponding to a residence time of 0.9 day. A preliminary cost estimation based on a treatment rate of 5 m^3 h^{-1} of a mine effluent containing 5 g l^{-1} SO_4^{2-} is presented.

Keywords: Acid mine drainage; Sulfate-reducing bacteria; Sulfide precipitation; Hydrogen transfer; Fixed bed column reactor

1. Introduction

The exploitation of sulfide ores and other sulfide-containing minerals, induces the in situ bacterial oxidation of iron and sulfur. This oxidation generates acid and metals-containing waters, which must be continually treated in order to avoid the spreading of toxic elements into the environment (Singer & Stumm, 1970). The classical lime neutralization method produces voluminous quantities of hydroxides that still contain metals (Zinck, 1997) and these wastes have to be dumped over large areas. The selective precipitation of metals with biologically produced H_2S has been proposed as an alternative process. Sulfate-reducing bacteria (SRB) use sulfate as a terminal electron acceptor; SO_4^{2-} being converted into H_2S. This method involves two stages: (1) the production of H_2S by SRB, and (2) the precipitation of metals by the biologically produced H_2S. This second step allows the selective recovery of some metals, such as copper or zinc, as pure sulfides (Hammack, Dvorak & Edenborn, 1993). The sulfate-containing solution that remains after metals precipitation is used to feed the SRB. Such processes have been developed, and even commercialized, with the aim of producing metal concentrates close to operating metallurgical sites (Scheeren, Koch & Buisman, 1993; De Vegt, Bayer & Buisman, 1997). However, improvements in the application of the basic principle must be achieved, in order to decrease the cost of this type of process and make it economically viable for use in the treatment of waste from disused mines. An SRB population able to use hydrogen as an electron donor was selected by BRGM in order to design and optimize a low-cost process. This treatment method would perform not only the

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0009-2509/01/$ - see front matter
PII: S0009-2509(00)00392-4

elimination of toxic metals, acidity and sulfate from acid mine drainage, but also enable the recovery of valuable metals as metallic sulfides. As an example, the real effluent from unused Chessy-les-Mines mine-site has been treated in this study at the laboratory pilot scale.

2. Material and methods

2.1. Experimental device

The experiments are carried out in the apparatus shown in Fig. 1.

The bioreactor consists of a fixed-bed column reactor ①(inner diameter of 0.1 m and total height of 2.75 m) used in conjunction with a distinct gas-stripping column ②(inner diameter of 0.04 m and total height of 1.75 m). The columns are made of glass and the bioreactor is maintained at 30°C by running water through its outer mantle. The special packing both provides a good gas–liquid mass transfer and ensures high bacterial concentrations. The recycle stream is pumped through the system by a metering pump ④, the liquid flow rate being measured with a rotameter ⑤. The gas used for the bioreactor is a mixture of H_2 and CO_2, with each partial flow rate regulated by a mass flow meter ⑦. A gas mixture of H_2, CO_2, H_2S flows out of the bioreactor ⑨, while residual H_2S is removed from the recirculating medium by N_2 pumped against the liquid stream in the stripping column. The N_2 flow rate is measured and regulated with a rotameter ⑧. The fresh solution fed into the reactor contains high concentrations of sulfate whereas the outlet stream has a sulfate concentration close to zero. Samples are analyzed from the bioreactor, the stripping, feed and outlet streams, while the pH and redox potential of platinum (mV/Ag–AgCl) are measured at the bioreactor outlet.

Precipitation takes place in a 10 l mechanically stirred reactor, a 10 l magnetically stirred reactor or a 2 l magnetically stirred reactor ③ into which the gas mixture from the bioreactor is bubbled. The pH is adjusted by the addition of a 10 N NaOH solution or by recirculating part of the outlet stream from the bioreactor in order to selectively recover metals.

2.2. Determination of mass transfer coefficient

Before inoculation experiments were performed to evaluate the maximum rate of hydrogen transfer in the bioreactor, as a function of different liquid and gas flow rates. As hydrogen has a very low solubility in water, only k_La (volumetric liquid-phase mass transfer coefficient) was experimentally calculated. k_La was deduced from measurement of oxygen according to Higbie (1935) and Danckwerts (1951) models which both predict a dependence on diffusivity. The dynamic method of physical absorption and desorption was used.

The hydrodynamic model for liquid phase is described in Fig. 2. The parameter γ is taken from measurements with LiCl used as tracer. The gas is supposed to run in a plug flow system. k_La for oxygen is determined by switching the gas feed from air to nitrogen and monitoring

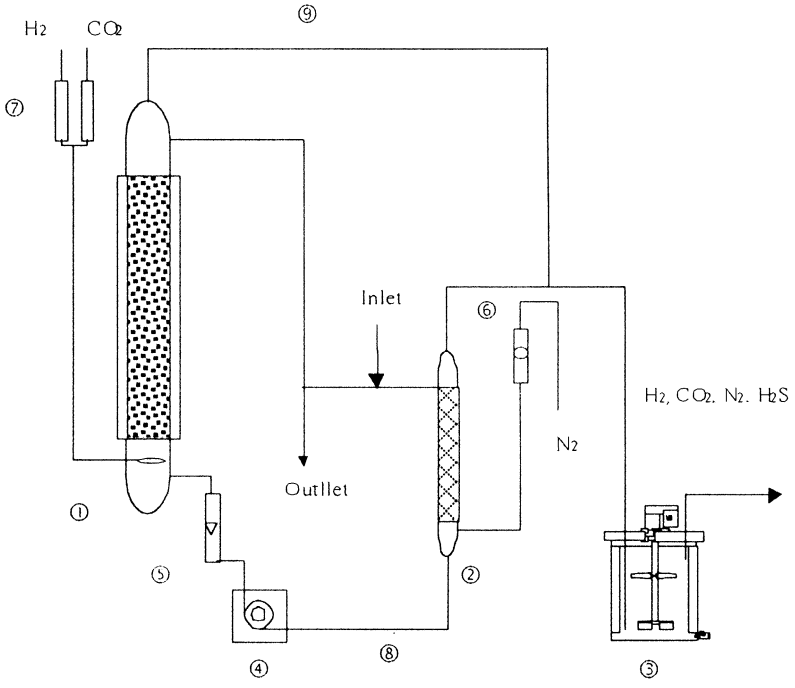

Fig. 1. Experimental apparatus.

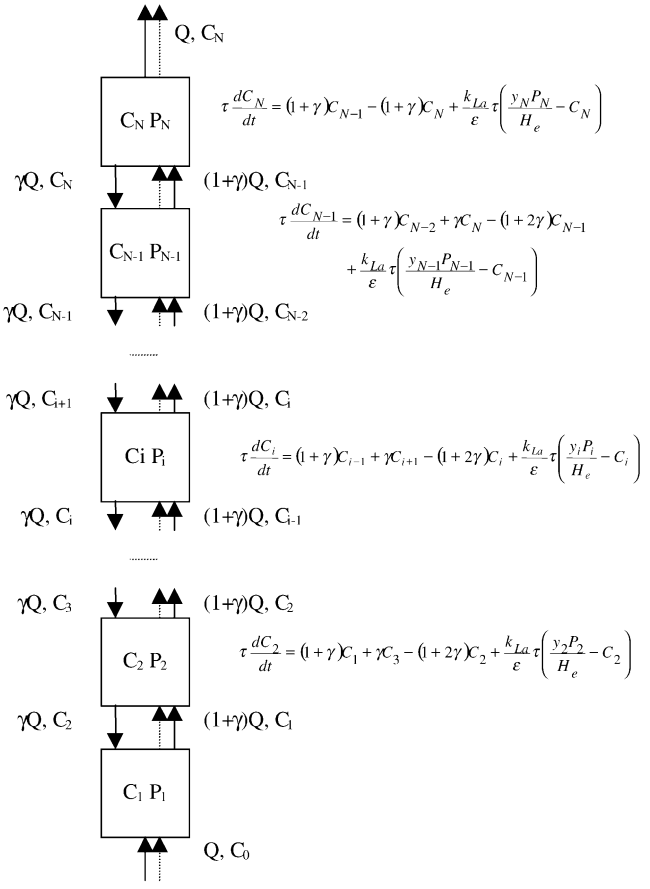

Fig. 2. Model used for k_La determination.

the dissolved oxygen concentration at the liquid inlet and outlet of the bioreactor with Clark probes. The oxygen concentration in the liquid phase is described by the equations in Fig. 2.

As for the gas phase, in a transitory state, the oxygen proportion is taken as the middle of the ith mixer and follows the equation:

$$y_i(t) = y_0\left(t - \left(i - \frac{1}{2}\right)\right)r_t\tau.$$

Simulink and Matlab software are used to solve the equations for $N = 32$ and the k_La for oxygen is determined by adjustment between experimental and calculated dissolved oxygen concentrations. k_La for hydrogen is then deduced using Danckwerts and Higbie theory for the values of gas diffusivities:

$$\frac{k_La,\ O_2}{k_La,\ H_2} = \left[\frac{D_{O_2}}{D_{H_2}}\right]^{1/2}.$$

2.3. Operating conditions

The operating conditions are presented in Table 1 for the determination of the mass transfer coefficient, which were obtained in the absence of reaction. Operating conditions for the bioreduction experiments and for the precipitation experiments respectively are presented in Tables 2 and 3.

Table 1
Operating conditions for the determination of k_La in the absence of reaction

Liquid ($l\,h^{-1}$)	Gas ($l\,h^{-1}$)
10–100	15–80

Table 2
Operating conditions for the bioreduction experiments

H_2 ($l\,h^{-1}$)	CO_2 ($l\,h^{-1}$)	N_2 ($l\,h^{-1}$)	Temperature (°C)
20–60	1–8.6	15–60	30
Feed rate ($l\,h^{-1}$)	$[SO_4^{2-}]$ inlet ($g\,l^{-1}$)	pH inlet	Recirculating rate ($l\,h^{-1}$)
0–0.4	5–10.5	6	50

Table 3
Operating conditions for the precipitation experiments

Experiment no	Volume (l)	Preliminary neutralization with pH adjustment at	pH regulation (at; with)
1	10	—	2.5–3.5–6
2–9	10	6	6
10	10	—	3–3.5–6
11	10	—	2.5–3.5–6
12	2	6	6: Biopulp
Experiment no	**Type of reactor**	**Agitation**	**Duration (h)**
1	batch	Mechanically	56
2–9	batch	Magnetically	2–3
10	batch	Magnetically	35
11	batch	Magnetically	50
12	continuous	Magnetically	—

2.4. Effluents compositions

Synthetic effluent (Table 4) was initially used to test the influence of gas flow rate.

Subsequently, a real effluent (Table 5) from the disused Chessy-Les-Mines site was treated in the laboratory pilot plant. The bioreactor feed is prepared with the real effluent obtained after sulfide precipitation, by adding urea, $MgCl_2 \cdot 6H_2O$; DAP; KOH and sodium acetate. No additional oligo-elements are added since traces of metals are already present in solution.

Table 4
Synthetic effluent composition

Urea ($g\,l^{-1}$)	$MgCl_2 \cdot 6H_2O$ ($g\,l^{-1}$)	Na_2SO_4 ($g\,l^{-1}$)	DAP ($g\,l^{-1}$)	KOH ($g\,l^{-1}$)
0.21	0.4	14.2	0.23	0.25
CH_3CO_2Na ($g\,l^{-1}$)	Oligo-elements ($ml\,l^{-1}$)	Rezazurin ($ml\,l^{-1}$)	pH	
0.5	1	0.5	6	

Table 5
Real effluent composition

pH	Density	$[SO_4^{2-}]$ ($g\,l^{-1}$)	$[Fe^{II}]$ ($mg\,l^{-1}$)	$[Fe^{III}]$ ($mg\,l^{-1}$)	[Zn] ($mg\,l^{-1}$)
2.55	1.006	5.8	1470	70	320
[Cu] ($mg\,l^{-1}$)	[Al] ($mg\,l^{-1}$)	[Mn] ($mg\,l^{-1}$)	[Co] ($mg\,l^{-1}$)	[Ni] ($mg\,l^{-1}$)	[Pb] ($mg\,l^{-1}$)
160	210	5.5	0.06	0.4	0.5

2.5. Analytical monitoring

Sulfate is determined by turbidimetry with barium chloride. The measurement is performed with an UV–visible spectrophotometer at 526 nm. Total dissolved sulfides are analyzed by potentiometric titration, using a sulfide-specific probe (Ag_2S–Ag) coupled to a reference probe (Ag–AgCl). The titrating solution is mercuric nitrate. The gaseous H_2S produced is quantified by gravimetry: the outlet gas is injected into a $50\,g\,l^{-1}$ zinc acetate solution.

3. Results and discussion

3.1. Mass transfer coefficient

A range of experiments were carried out before inoculation with variations in both gas and liquid flow rates. The results are presented in Fig. 3.

With the hypothesis that k_La is not dependent on liquid flow rate, the results can be described by the equation

$$k_La = 2 \times 10^{-3} u_G^{0.8}.$$

This correlation fits those based on the theories of Higbie and Kolmogorof:

$$k_La = bu_G^n.$$

Thus, for a $20\,l\,h^{-1}$ gas flow rate and $50\,l\,h^{-1}$ liquid flow rate, k_La for hydrogen was estimated at $2.6 \times 10^{-3}\,s^{-1}$ suggesting a maximum hydrogen transfer rate of $7 \times 10^{-3}\,mol\,l^{-1}\,h^{-1}$.

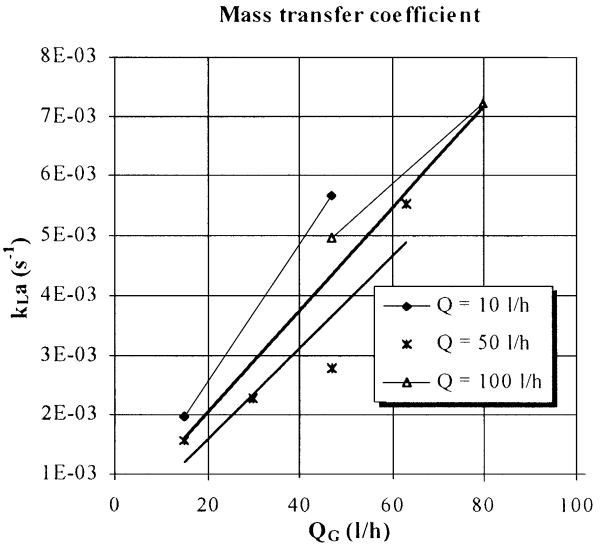

Fig. 3. Evolution of k_La with gas and liquid flow rates.

3.2. The kinetics of sulfate reduction

Influence of hydrogen flow-rate on the kinetics of sulfate reduction: The biological reduction of sulfate, when hydrogen is used as the electron source, is described by the following stoichiometry, verified by Herrera, Hernandes, Bravo and Vera (1997):

$$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O.$$

The availability of dissolved hydrogen is likely to limit the sulfate-reduction rate, as H_2 solubility in water is very low (3.5×10^{-4} M at 30°C). The evolution of the reaction rate with the synthetic effluent, relative to hydrogen flow rate, is provided in Fig. 4. The results obtained in batch and continuous conditions in the column reactor are compared with data from other batch experiments which have used H_2 as the energy source (Battaglia-Brunet, Foucher, Ignatiadis & Morin, 2000). The highest sulfate reduction rate obtained in the column bioreactor at $20\,l\,h^{-1}$ was $120\,mg\,l^{-1}\,h^{-1}$. This value is 3 times higher than the value obtained by culturing the same bacterial population in bottles. In the fixed-film column, the hydrogen bubbles are finely dispersed through the support, and a slight pressure at the bottom (0.25 bar) improves the gas–liquid transfer. In continuous flow conditions, the maximum reaction rate rises from 110 to $200\,mg\,l^{-1}\,h^{-1}$ when the hydrogen flow rate is increased from 20 to $60\,l\,h^{-1}$.

The data collected during this experiment are not sufficient to entirely describe the influence of hydrogen: it will be necessary to test higher flow rates in order to precisely determine the optimal operating conditions.

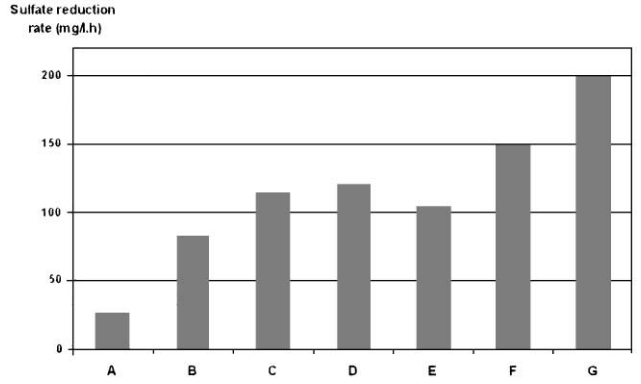

Fig. 4. Evolution of sulfate-reduction rate relative to hydrogen flow-rate and culture conditions. (A) bottle batch; (B) batch in mechanically agitated reactor. Herrera et al., 1997; (C) batch in column bioreactor with 4.6 g l^{-1} initial sulfate, H_2 20 l h^{-1}; (D) batch in column bioreactor with 7.1 g l^{-1} initial sulfate, H_2 20 l h^{-1}; (E) continuous culture in column bioreactor, H_2 20 l h^{-1}; (F) continuous culture in column bioreactor, H_2 40 l h^{-1}; (G) continuous culture in column bioreactor, H_2 60 l h^{-1}.

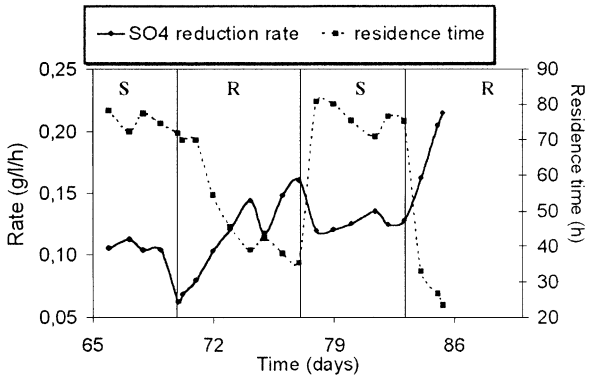

Fig. 5. Evolution of sulfate reduction rate and residence time in the column bioreactor with synthetic medium and real feeding from Chessy mine. (S) synthetic medium, 10 g l^{-1} SO_4^{2-} (R) real effluent, 5.5 g l^{-1} SO_4^{2-}.

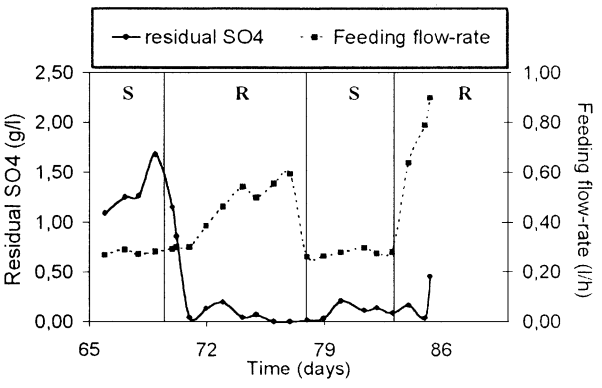

Fig. 6. Evolution of residual sulfate concentration in the column bioreactor and feeding flow rate with synthetic medium and real feeding from Chessy mine (S) synthetic medium, 10 g l^{-1} SO_4^{2-}; (R) real effluent 5.5 g l^{-1} SO_4^{2-}.

However, these results show that the biological sulfate reduction rate is limited by hydrogen availability up to 60 l h^{-1} H_2. Thus, for a 20 l h^{-1} gas flow rate and 50 l h^{-1} liquid flow rate, the k_La for hydrogen was estimated at 2.6×10^{-3} s^{-1}, indicating a maximum hydrogen transfer rate of 7×10^{-3} mol l^{-1} h^{-1}, under such operating conditions. The best hydrogen consumption rate for bacteria during sulfate reduction was 5×10^{-3} mol l^{-1} h^{-1}. According to the maximum rate of hydrogen transfer, this step should not be a limiting factor. The biological reaction rate may have been limited by the dissolved hydrogen concentration, which would be below the critical concentration. On the other hand, determination of k_La was based on several assumptions and did not take CO_2 co-absorption into account. Further investigations, including direct dissolved H_2 measurements with a hydrogen probe, are required to explain why the predicted and observed rates of sulfate reduction are different.

The maximum sulfate reduction rate obtained in the column reactor, 200 mg l^{-1} h^{-1} is 6 times higher than the rate obtained in batch bottles, and twice as high as the value reported by Herrera et al. (1997). These authors used a hydrogen-fed bacterial population in a fed-batch mechanically agitated reactor. The fixed-film column bioreactor appears to be more efficient, even during the initial batch phase, when the bacterial concentration is no higher than it would be in a free-cells system.

Treatment of the real effluent from Chessy mine: After several weeks of continuous experiment with the synthetic medium, the real effluent, cleared of most of its metals through precipitation, was used to feed the column bioreactor. The evolution of sulfate reduction rate and residence time in the bioreactor are provided in Fig. 5. The residual SO_4^{2-} concentration and feeding flow rate are provided in Fig. 6.

The Chessy effluent contains 5.5 g l^{-1} SO_4^{2-}, which is 50% of the SO_4^{2-} concentration in the synthetic medium. The residual sulfate concentration, remained between 1 and 2 g l^{-1} with the synthetic medium, but decreased to 0.1 g l^{-1} with the real effluent whereas the feeding flow rate was rapidly increased (Fig. 6). The sulfate reduction rate also increased using the real effluent, and in 4 days it exceeded the value obtained using the synthetic medium (Fig. 5). At the end of a week, the H_2S pre-treated effluent was entirely consumed, and a synthetic feeding was used. It is interesting to note that the rate using the synthetic effluent was higher during this period than it had been before the introduction of the real effluent. It seems that the bacterial affinity for sulfate was improved by the real effluent. When a new stock of H_2S pre-treated effluent was available, the flow rate of real effluent was rapidly increased. The maximum flow rate that could be applied was 900 ml h^{-1} which corresponds to a sulfate reduction

Table 6
Composition of synthetic medium, real effluent medium and outflow of the bioreactor

Nutrients	Synthetic medium	Real Chessy medium	Reactor outflow Chessy medium
N ($mg\,l^{-1}$)	104	107	46
P ($mg\,l^{-1}$)	46	47	18
K ($mg\,l^{-1}$)	175	191	166
Mg ($mg\,l^{-1}$)	48	97	70
Acetate ($mg\,l^{-1}$)	200	200	13
Fe ($\mu g\,l^{-1}$)	221	40	130
Zn ($\mu g\,l^{-1}$)	20	118	12
Ni ($\mu g\,l^{-1}$)	6	161	33
Cu ($\mu g\,l^{-1}$)	1	13	7
Co ($\mu g\,l^{-1}$)	27	11	8

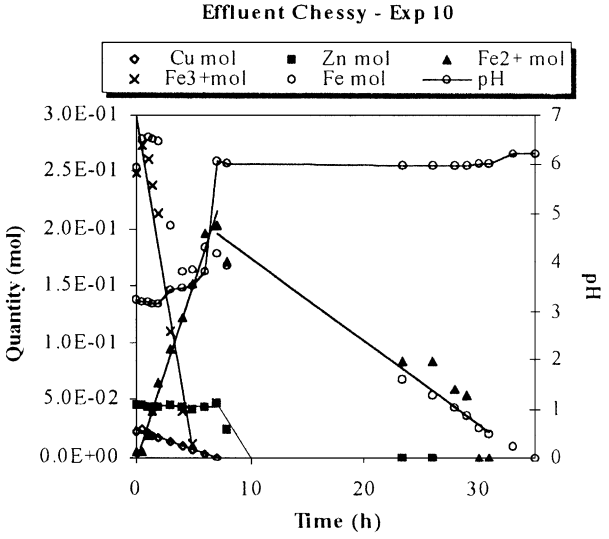

Fig. 7. Metals precipitation.

rate of $200\,mg\,l^{-1}$ and a residence time of 0.9 days. It would be interesting to know why the real effluent had a positive effect on bacterial activity. The feed medium is prepared by adding the major nutrients of the synthetic medium to the pre-treated effluent, excluding the oligo-element solution because the mine water already contains them. The composition of synthetic medium, real effluent medium, and outflow from the bioreactor fed with the real effluent are compared in Table 6.

The real effluent contains some metals, such as zinc, nickel and copper, in higher concentrations than the synthetic medium. The mine water also provides some of the major nutrients (N, P, K, Mg). In particular, it contains as much magnesium as the synthetic medium. However, the analysis of the bioreactor out-flow seems to indicate that the major nutrients (except acetate) are in excess in the medium. The improvement in bacterial efficiency associated with the use of the real effluent is most likely to have been induced by traces of metallic elements. Indeed, trace metals are used by micro-organisms for the production of cytochromes, which are key enzymes in the sulfate reduction process.

3.3. Precipitation results

With regard to sulfide precipitation, previous experiments were carried out in batch tests using different reactor configurations. They demonstrated that copper and zinc could be effectively and selectively recovered from the Chessy effluent at pH = 2.8 and 3.5, respectively, using H_2S provided by the bioreactor. Other impurities such as nickel and ferrous iron were also removed at pH = 6 by sulpfide precipitation. H_2S efficiency for metal precipitation depends not only on pH (dissociation constants) but also on the type of reactor (mass transfer limitation). Experiments that provided large amounts of fresh medium continuously to the bioreactor, showed that it was possible to regulate pH using part of the bioreactor outlet stream in the precipitation reactor without soda additions.

When effluent was not treated immediately, Fe^{2+} was oxidized in Fe^{3+} before the initiation of the experiments, with the rate of oxidation increasing with increasing temperature. Fe^{3+} was thus reduced to Fe^{2+} by H_2S at the same time that copper sulfide precipitates (Fig. 7).

4. Preliminary cost estimation

Investment costs mostly depend on the bioreduction reaction rate since the bioreactor size depends on the residence time. Operating costs are directly linked to the consumption of nutrients and the technology chosen to produce hydrogen. On the other hand, the magnitude of benefits associated with CuS and ZnS production are dependent on the Zn and Cu concentrations in the effluent. A coarse preliminary cost estimate based on the composition of Chessy mine effluent at a flow rate of $5\,m^3\,h^{-1}$ was carried out, and the results are as follows: 450,000 USD investment costs and 30,000 USD, operating costs without taking into account personal costs, partly offset by a 12,000 USD benefit associated with CuS and ZnS production. This means that the sale of sulfide products would not compensate for the operating costs. This seems to suggest that this process would not be financially viable. Further experiments can be performed in order to enhance the reaction rate and reduce investment costs. Moreover, some nutrients such as N, P and K, are probably delivered to the bioreactors in excess of requirements. Their concentrations have to be optimized in order to reduce operating costs. A further economic study has to be performed involving a cost comparison with other techniques available to treat this

type of pollution. The environment benefit will also have to be examined.

5. Conclusion

A process using sulfate-reducing bacteria to treat acid-mine drainage has been tested at the laboratory pilot scale. This process includes an H_2S biological production step using hydrogen followed by a chemical sulpfide precipitation step.

Two main parameters appear to influence the rate of biological H_2S production; the availability of hydrogen and the physiological state of the bacteria. The biological activity was particularly enhanced when the micro-organisms were fed with real effluent that had been pretreated through the precipitation of metal sulfides. This real effluent contains traces of metals that may enhance the bacterial affinity for sulfate. The highest kinetic rate of sulfate reduction obtained in this study is a little higher than 200 mg l^{-1} h^{-1} for hydrogen flow rate of 60 l h^{-1}.

With regard to sulfide precipitation, it was established that copper and zinc could be selectively recovered while other metals, commonly present in acid-mine drainage, under different pH conditions. One improvement is the use of part of the bioreactor outlet stream to maintain pH at operating levels.

A preliminary cost estimation for the case of the Chessy mine indicates that such a treatment would not be economically viable as a CuS and ZnS production unit. However, a further evaluation will be performed including not only technical improvements, but also an economic and environmental comparison with other treatment strategies.

Notation

C_0 bioreactor inlet oxygen concentration, mg l^{-1}
C_i oxygen concentration in the ith mixer, mg l^{-1}
C_N bioreactor outlet oxygen concentration, mg l^{-1}
D_{gas} gas diffusivity, cm^2 s^{-1}
He Henry's constant, atm/molar proportion
k_La volumetric liquid-phase mass transfer coefficient, s^{-1}
N number of mixers
$P_i(P_a)$ gas pressure in ith mixer
Q liquid flow rate, 1 h^{-1}
Q_G gas flow rate, 1 h^{-1}
r_τ gas residence time/liquid residence time in ith mixer
u_G superficial gas velocity, m s^{-1}
V mixer volume ($= V_t/N$), l
V_t bioreactor total volume, l
y_0 initial oxygen proportion in gas phase feeding reactor
y_i oxygen proportion in gas phase

Greek letters

ε liquid holdup
τ residence time in ith mixer, $(\varepsilon V/Q)$, s^{-1}
γ retromixing coefficient

Acknowledgements

This research was supported by BRGM (contribution 2000 N°6).

References

Battaglia-Brunet, F., Foucher, S., Ignatiadis I., & Morin, D. (2000). Production of H_2S by sulfate-reducing bacteria in a two-column gas/liquid reactor for the purification of metal-containing effluents *XXI IMPC.* Roma, 23–27 July 2000, pp. B12–9/17.

Danckwerts, P. V. (1951). Significance of liquid-film coefficients in gas absorption. *Industrial Engineering Chemistry*, *43*, 1460–1467.

De Vegt, A. L., Bayer, H. G., & Buisman, C. J. (1997). Biological sulfate removal and metal recovery from mine waters. *SME Annual Meeting*. Denver, Colorado.

Hammack, R. W., Dvorak, D. H., & Edenborn, H. M. (1993). The use of biogenic hydrogen sulfide to selectively recover copper and zinc from severely contaminated mine drainage. In A. E. Torma, J. E. Wey, & V. L. Lakshmanan (Eds.), Biohydrometallurgical technologies. Warrendale, PA: The Minerals, Metals & Materials Society. pp. 631–639.

Herrera, L., Hernandez, J., Bravo, L., & Vera, L. (1997). Biological process for sulfate and metals abatement for sulfate and metals abatement from mine effluents. *Environmental Toxicology and Water Quality*, *12*, 101–107.

Higbie, R. (1935). The rate of absorption of a pure gas into a still liquid short periods of exposure. *Transactions of the American Institution of Chemical Engineers*, *31*, 365–388.

Scheeren, P. J. H., Koch, R. O., & Buisman, C. J. N. (1993). Geohydrological containment system and microbial water treatment plant for metal-contaminated groundwater at Budelco. *International symposium — world zinc'93, Hobart*, 10–13 October, pp. 373–384.

Singer, P. C., & Stumm, W. (1970). Acidic mine drainage, the rate-limiting step. *Science*, *167*, 1121–1123.

Zinck, J. M. (1997). Acid mine drainage sludge in the Canadian mineral industry: Physical, chemical mineralogical and leaching characteristics. *Fourth international conference on acid rock drainage.* Vancouver. B. C., vol. IV. pp. 1693–1708.