Mineralogy and granulometry of biogenic sulphidic sludge

P. Kousi, E. Remoundaki, A. Hatzikioseyian and M. Tsezos

Laboratory of Environmental Science and Engineering, School of Mining and Metallurgical Engineering, National Technical University of Athens, 9, Iroon Polytechniou str., 15780 Zografou, Greece.
Keywords: sulphate-reducing bioreactors, sulphidic sludge, pyrite, vivianite
Presenting author email: remound@metal.ntua.gr

Industrial wastewater, such as wastewater originating from mining and metallurgical industries, is often acidic and typically characterized by a significant content of sulphate and soluble metals, such as Fe, Zn, Cu, Ni, Pb and Cd. A viable bioremediation process involves Sulphate-Reducing Bacteria (SRB) which obtain energy for cell synthesis and growth by coupling the oxidation of organic substrates or molecular hydrogen (H_2), under anaerobic conditions, to the reduction of sulphate (SO_4^{2-}) to sulphide (H_2S, HS^-) (Rabus *et al.*, 2007). The generated sulphide may then react, either in situ or ex situ (Kaksonen *et al.*, 2007), with divalent metal ions, which are then sequestered from wastewater as insoluble metal sulphides, in the form of various mineral phases (Herbert *et al.*, 1998), producing sludge which is, generally, more dense and stable and exhibits better thickening and dewatering characteristics compared to conventional chemical treatment (Huisman *et al.*, 2006). Therefore, a key aspect of the sustainability of the process is the management of the generated sludge. In order to address this issue and propose specific alternatives, a detailed characterisation of the produced solid waste is essential.

The present work involves the characterisation of the biogenic sulphidic sludge generated in a laboratory-scale, upflow packed-bed sulphate-reducing bioreactor system in terms of mineralogy and granulometry. The system had already operated for six years in batch mode. The bioreactor was fed with a modified variation of Postgate's medium (DSMZ, 2005) with ethanol as carbon/electron source to treat acidic sulphate- and metal-bearing synthetic solutions of divalent iron, zinc, nickel and copper, simulating an anaerobic treatment scheme for industrial wastewater (Kousi *et al.*, 2011). The initial pH of the feeding solution was 3.5-4.0. Sludge samples were collected from the bottom of the reactor column (low redox and neutral pH conditions) and from the bottom of the feeding vessel (higher redox and lower pH conditions) where the solid precipitates, which were not retained within the reactor column, were allowed to accumulate. The sludge samples are compared in terms of mineralogy and particle size distribution.

To avoid any oxidation of the solid material and remobilisation, or redistribution among fractions, of the metals contained therein, the sludge samples were collected anaerobically and immediately stored in a desiccator, under nitrogen atmosphere, at room temperature (approx. 25 °C) until dryness. The particle size distribution was determined by Laser Diffraction Method – Low Angle Laser Light Scattering (Malvern Mastersizer Micro-P). The XRD analysis was performed on a Bruker D8 Focus X-Ray Diffractometer, operating with Ni-filtered CuKα radiation (λ=1.5405 Å). The samples were step-scanned from 5° to 70° (2θ), at a step rate of 0.02°/5 s. The major peaks of the XRD pattern were identified based on reference patterns calculated from crystal structure data (Crystallography Open Database, COD (Grazulis *et al.*, 2009)).

X-ray diffraction analysis (Figure 1) of the dehydrated sludge which was collected from the bottom of the reactor column demonstrated the presence of pyrite as the main iron sulphide, covellite as the main copper sulphide, wurtzite and sphalerite as the main zinc sulphide and millerite and heazlewoodite as the main nickel sulphide. Most of these biogenically produced minerals, along with some mixed metal sulphides (i.e. haycockite, cubanite and chalcopyrite) were identified in the 25° to 35° range, where the XRD analysis revealed a broad diffraction band, confirming the presence of amorphous or poorly crystalline phases (Gramp *et al.*, 2006; Gramp *et al.*, 2007; Karnachuk *et al.*, 2008; Remoundaki *et al.*, 2008). However, the dominant crystalline ferrous phase in the diffractogram of the sludge collected from the bottom of the feeding vessel is vivianite ($Fe_3(PO_4)_2.8H_2O$, identified at 13.2°).

In higher redox and lower pH conditions (feeding vessel), ferrous sulphide becomes unstable and the released Fe(II) is abiotically precipitated as phosphate (Jencarova *et al.*, 2014; Roussel, 2012). The absence of dominant Fe(III) (hydr)oxides indicates that the change in the sludge mineralogy may be mainly attributed to the E_h-pH effect on the stability of Fe(II) sulphides rather than the oxidation of the sulphidic phases due to contact with air. This redissolution and reprecipitation mechanism leads to the formation of particles of larger size as it is demonstrated by the results of the PSD analysis (Table 1).

Table 1. Characteristic PSD values

	D10 (μm)	**D50** (μm)	**D90** (μm)
Feeding vessel sludge	0.45	13.46	61.10
Reactor column sludge	0.20	8.31	45.73

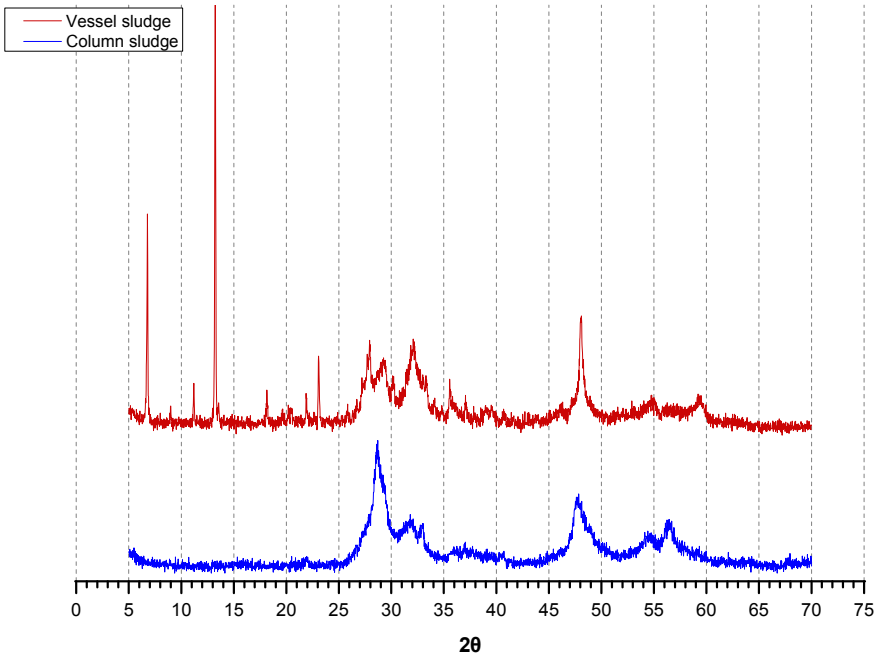

Figure 1. X-ray diffractograms acquired for the sludge sample collected from the bottom of the feeding vessel (top) and from the bottom of the reactor column (bottom)

Acknowledgments
The authors would like to express their gratitude to the School of Mining and Metallurgical Engineering (NTUA, Greece) and the Laboratory of Metallurgy (NTUA, Greece) for facilitating access to all the analytical instrumentation required for the completion of the present work.

References

DSMZ, Germany: Medium 63 - *Desulfovibrio* medium. www.dsmz.de, Feb. 2005.

Gramp, J.P., Sasaki, K., Bigham, J.M., Karnachuk, O.V. & Tuovinen, O.H. (2006). Formation of covellite (CuS) under biological sulfate-reducing conditions. *Geomicrobiology Journal* 23(8): 613-619.

Gramp, J.P., Bigham, J.M., Sasaki, K. & Tuovinen, O.H. (2007). Formation of Ni- and Zn-sulfides in cultures of sulfate-reducing bacteria. *Geomicrobiology Journal* 24(7): 609-614.

Grazulis, S., Chateigner, D., Downs, R.T., Yokochi, A.F.T., Quiros, M., Lutterotti, L., Manakova, E., Butkus, J., Moeck, P. & Le Bail, A. (2009). Crystallography Open Database - an open-access collection of crystal structures. *Journal of Applied Crystallography* 42(4): 726-729.

Herbert, R.B., Benner, S.G., Pratt, A.R. & Blowes, D.W. (1998). Surface chemistry and morphology of poorly crystalline iron sulfides precipitated in media containing sulfate-reducing bacteria. *Chemical Geology* 144(1-2): 87-97.

Huisman, J.L., Schouten, G. & Schultz, C. (2006). Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. *Hydrometallurgy* 83(1-4): 106-113.

Jencarova, J., Luptakova, A., Jandacka, P. & Matysek, D. (2014). The examination of biogenic and non-biogenic iron precipitates created by hydrogen sulphide. *Journal of the Polish Mineral Engineering Society* 34(2): 281-286.

Kaksonen, A.H. & Puhakka, J.A. (2007). Sulfate reduction based bioprocesses for the treatment of acid mine drainage and the recovery of metals. *Engineering in Life Sciences* 7(6): 541-564.

Karnachuk, O.V., Sasaki, K., Gerasimchuk, A.L., Sukhanova, O., Ivasenko, D.A., Kaksonen, A.H., Puhakka, J.A. & Tuovinen, O.H. (2008). Precipitation of Cu-sulfides by copper-tolerant *Desulfovibrio* isolates. *Geomicrobiology Journal* 25(5): 219-227.

Kousi, P., Remoundaki, E., Hatzikioseyian, A. & Tsezos, M. (2011). Sulphate-reducing fixed-bed bioreactors fed with different organic substrates for metal precipitation. in: Qiu, G., Jiang, T., Qin, W., Liu, X., Yang, Y. & Wang, H. (Eds.), *Biohydrometallurgy: Biotech key to unlock mineral resources value, Proceedings of the 19th International Biohydrometallurgy Symposium (IBS 2011)*, Changsha, China. Central South University Press: pp. 1078-1084.

Rabus, R., Hansen, T.A. & Widdel, F. (2007). Dissimilatory sulfate- and sulfur-reducing prokaryotes. in: Dworkin, M., Falkow, S., Rosenberg, E., Schleifer, K.-H. & Stackebrandt, E. (Eds.), *The Prokaryotes: Ecophysiology and Biochemistry*, 3rd ed. New York: Springer, pp. 659-768.

Remoundaki, E., Kousi, P., Joulian, C., Battaglia-Brunet, F., Hatzikioseyian, A. & Tsezos, M. (2008). Characterization, morphology and composition of biofilm and precipitates from a sulphate-reducing fixed-bed reactor. *Journal of Hazardous Materials* 153(1-2): 514-524.

Roussel, J. (2012). Metal behaviour in anaerobic sludge digesters supplemented with trace nutrients, Ph.D. thesis. Birmingham: Department of Civil Engineering, University of Birmingham.