

Proactive Prevention of Acid Generation: Reduction/Inhibition of Sulphide Oxidation

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Abstract The effects of adding phosphate mining wastes (NPR) to acid-generating mining waste rocks are described after experiments which included: 1) a 2.7 year experiment outdoors, 2) a further storage indoors for 4.5 years, 3) a re-exposure outdoors without NPR for a year, 4) indoor storage for a further 8 years. Analyses of the waste rock surfaces revealed mainly gypsum, frequent Fe, Si and S precipitates, but only traces of P as precipitates embedded into an organic matrix, a biofilm. The organic coatings on the waste rocks exposed with and without NPR were distinctly different. The persistence of these coatings over a period of 17 years suggests that these coatings are robust and long-lasting.

Key Words biofilm, sulphide oxidation, acid rock drainage, natural phosphate rock

Introduction

Practical and economic means to reduce sulphide oxidation in mining wastes are currently not available. Different strategies have been proposed, based on laboratory tests, which generate a physical oxidation barrier on mining waste rock and on tailings by precipitating or complexing ferric iron in sulphidic mineral oxidation products in situ. These oxidation barriers prevent the dissolution into, and transport with, atmospheric precipitation generating acid rock (ARD) or mine drainage (AMD). Iron-phosphate and silicate coatings on sulphidic mineral surfaces are reported by several authors (Belzile et al. 1997; Georgopoulou et al. 1996; Kargbo 2005; Khummalai and Boonamnuayvitaya 2005; Lan et al. 2002) and coating on pyrite by lipids having two hydrophobic tails by Elsetinow et al. (2003) and Kargbo et al. (2004). To take these approaches from the bench to full scale up would require the delivery of the reactant in a solution to the mineral wastes. Considering the magnitude of most mine waste deposits, the delivery of a solution poses a serious, practical delivery problem, which to date, has been a serious block to scale up and further development of a workable technology.

Phosphate mining wastes (NPR) are an oxidation/reduction reactant which is economic and easy to apply. NPR is only soluble under acidic conditions. Granular (<0.04 to > 4mm) NPR was tested in plots on tailings from uranium, polymetallic mines and fresh pyrrhoite from nickel mine. All test resulted in much lower pore-water acidity compared to no NPR being ploughed into the test plot (Kalin et al. 2003; Kalin 2004).

To test the effects of NPR on waste rock, 3 t of sulphidic waste rock samples (0.01–0.25m) were collected from piles in northern Quebec and exposed in 70 L drums outdoors in Toronto, Ontario. Shortly after the first winter, Fyson et al. (1995) reported improved effluents and coatings on the rocks with only traces of phosphate. Further, precipitates of Fe, Si and S were found embedded in a biofilm by Kalin et al (1997). Monitoring of the effluent from the drum continued for 2.7 years then the rocks were stored indoors (Kalin et al 1998). The involvement of microbial activity in the formation of biofilms was confirmed by Ueshima et al. (2003, 2004). A second outdoor exposure of the stored rocks, was intended to destroy the coatings and generate acidic effluent. No further NPR was added. The rocks experienced wetting and drying in the summer and freezing in the winter (Kalin and Harris 2005).

Waste rock samples from the first outdoor exposure with and without NPR were supplied to R. Smart, U of Western Australia for surface investigations. Under the AMIRA project P933 in 2006, the coating was confirmed, containing similar inorganic precipitates as those reported by Kalin et al. (1997). The presence of the coating, which had developed simply by adding NPR on top of waste rock, had persisted in storage 11 years, independently observed encouraged further investigations into the conditions of the surfaces, as rocks from the same experiment were still stored by 2009 now for 17 years. This paper supplies selected SEM/EDX observations made in: a) 2006

on rocks stored indoors for 11 years and exposed outdoors between 1992 and 1995 (first outdoor exposure) and b) 2009 on rocks stored indoors for 17 years and never exposed outdoors, and c) 2009 on rocks stored for 8 years after the second outdoor exposure between 2000 and 2001.

Methods and Materials

Storage conditions

Prior to the experiment, a subset of the rocks was stored in plastic bags in 5 gallon buckets covered tightly with lids, producing a set of rocks which never took part in the experiment, but reflected storage conditions. Details of the drum setup and dismantling are given in Kalin and Harris (2005). After the second exposure the rocks were stored in 5 gallon buckets with lids outdoors (sheltered) between 2001 and 2004. The buckets were then moved to a room ($>40^{\circ}\text{C}$) behind an SEM for about 1 year. Thereafter, the buckets were stored in a metal garden shed, experiencing cold winters and hot summers, typical for Toronto. The buckets were finally moved to a cool basement at the University of Toronto in 2009 when further surface investigations were made.

Rock selection for SEM/EDX

Rocks for SEM surface investigations were selected randomly. The first SEM/EDX scans in 1996 focused on finding a phosphate signal on the surface of the minerals, representing iron-phosphate precipitates. Only one phosphate signal was found on low pyrite removed from the pit < 1 year (type A2 with NPR) from the many rocks investigated at that time (Fig. 1b and Kalin et al. 1997). SEM/EDX investigations in 2009 selected rocks randomly from the same rock type A2.

SEM/EDX sample preparation

To observe the surfaces, a small section of each sample was cut (approximately 1 cm^3) and coated with a conducting metal (gold-palladium or carbon) for SEM observations. Gold coating was only applied on rocks from A2 2nd exposure because of its intense interference with the sulphur peaks. All other samples were coated 4 times with carbon. SEM/EDX scans were made in 2009 with a JSM-840 Scanning Microscope at the Geology Department of the University of Toronto.

Results

The scans in Figure 1 differ in storage time after the 1st outdoor exposure with NPR (year 11 [a and b] and year 14 as identified in the AMIRA P933 assessment [d]). These surfaces are stunningly similar, with a knob like pattern and drying cracks. The younger coating one year after storage 1 [c] showing a smoother coat with microbes visible at arrows in larger view. Likely the organic coating

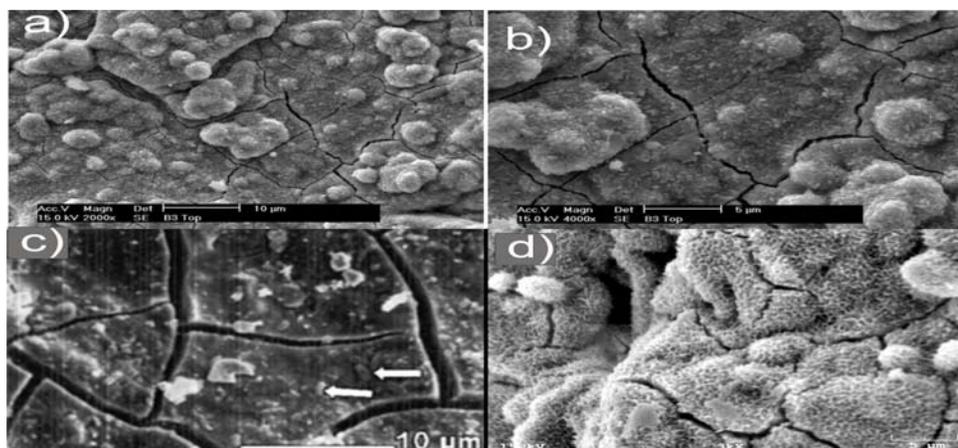


Figure 1 Low pyrite $< 1\text{y}$ after 1st exposure with NPR: (a, b) AMIRA P933 observed in 2006 after 11 years in storage at mag. (10 and 5 μm); (c) Kalin et al. 1997 observed in 1996 after 1 year of storage at g. (10 μm); (d) observed in 2009 after 14 years of storage at mag. (5 μm)

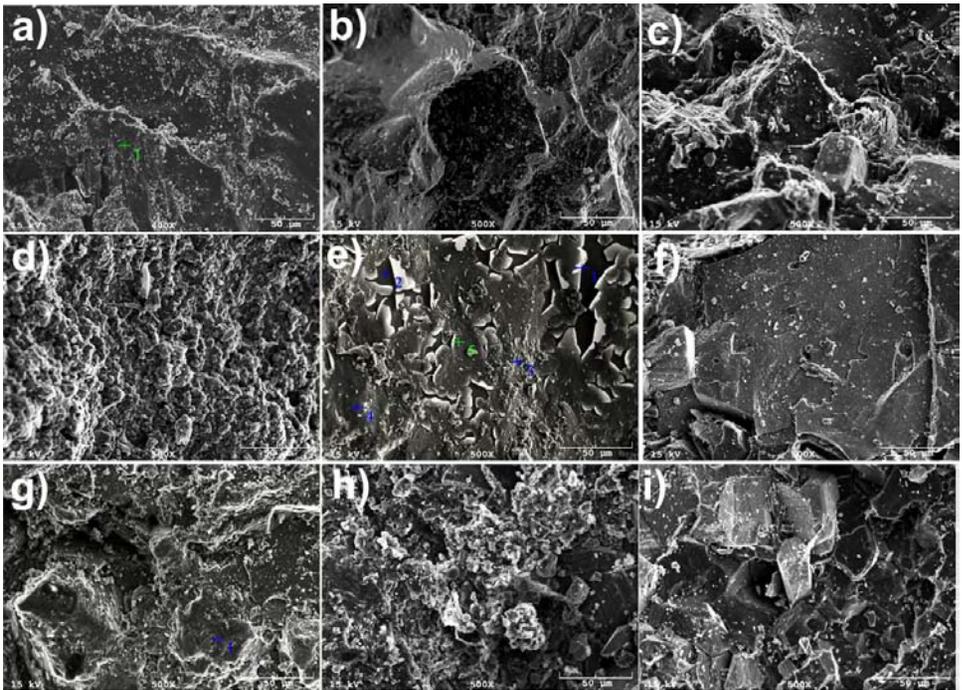


Figure 2 All observations in 2009 at magnification of 50 μm (a) never exposed outdoors stored for 17 years (b,c) No NPR added 2nd exposure stored for 8 years after 2nd exposure. Fig 2 d,e,f,h,i are NPR added in 1st exposure only; exposed in 2nd outdoor exposure with no NPR and stored for 8 years.

provided a medium for further colonisation while in storage. Figure 2 (a) are surfaces never exposed 17 years show little difference to Fig 2 b and c. A more flaky surface can be noted after 2nd exposure without NPR and stored for 8 are depicted in Fig's 2 d – i.

Conclusions

The simple application of the NPR in field or outdoor tests led to the formation of an inorganic/organic coating or biofilm on mineral surfaces which reduced sulphide oxidation. The NPR gravel was simply dumped on top of open experimental drums mimicking a truck distributing the gravel onto benches of a waste rock pile. The NPR was therefore allowed to pass through the wastes in the same way that rain and snowmelt would take through a waste rock pile. The coatings persisted during storage under hot and freezing conditions, even after the exposures for more than 10 years. The SEM/EDX investigations of the mineral surface 17 years after the start of the waste rock experiment should dispel the general belief that biofilms are fragile, and unstable and thus cannot contribute to the long-term reduction of sulphide oxidation

References

- Belzile N, Maki S, Chen Y, Goldsack D (1997) Inhibition of pyrite oxidation by surface treatment. *Sci Total Environ* 196(2):177–186
- Elsetinow A; Bordab M; Schoonen M; Strongin D (2003) Suppression of pyrite oxidation in acidic aqueous environments using lipids having two hydrophobic tails. *Adv Environ Res* 7(4):969–974
- Fyson A, Kalin M, Smith MP (1995) Reduction of acidity in effluent from pyritic waste rock using natural phosphate rock. In: *Proceedings of the 27th Annual Meeting of Canadian Mineral Processors*, Ottawa, Ontario, p 270–277
- Georgopoulou ZJ, Fytas K, Soto H, Evangelou B (1996) Feasibility and cost of creating an iron-phosphate coating on pyrrhotite to prevent oxidation. *Environ Geol* 28(2):61–69

- Kargbo D; Atallah G, Chatterjee S (2004) Inhibition of pyrite oxidation by a phospholipid in the presence of silicate. *Environ Sci Technol* 38(12):3432–3441
- Kargbo D (2005) Stability of silicate coatings on pyrite surfaces in a low pH environment”. *J Environ Eng* 131(9):1340–1349
- Kalin M; Harris B. (2005) Chemical precipitation within pyritic waste rock. *Hydrometallurgy* 78:209–225
- Kalin M (2004) Improving pore water quality in reactive tailings with phosphate mining wastes. In: Rao SR, Kozinski JA, Cheng TC, Harrison FW, Amaratunga LM, Richards GG (Eds), Fifth International Symposium on Waste Processing and Recycling in Mineral and Metallurgical Industries, Hamilton, Ontario, p 427–437
- Kalin, M, Ferris, G, Paulo C (2009) Reducing sulphide oxidation in pyritic mining wastes – phosphate mining wastes stimulate biofilm formation on mineral surfaces. In: Eighth International Conference on Acid Rock Drainage, Skelleftea, Sweden (in press).
- Kalin M, Fyson A; Smith MP; Werker A (2003) Tailings surface cover development through integration of reactive phosphate and organic matter. In: Proceedings of the Mining and Environment III and Annual Meeting of CLRA (CD), Sudbury, Ontario., PDF #80, 10 p
- Kalin M, Smith MP, Fyson A (1997) The use of natural phosphate rock to reduce acidic drainage from pyritic waste rock” ICARD Conference, Vancouver, BC, P-07, 13 p
- Kalin M, Smith MP; Fyson A (1998) The role of phosphate in applied biotechnology in mine waste management: reduction in AMD from pyritic waste rock. In: Proceedings of the Intl Symposium of the Metallurgical Society of the Canadian Institute for Mining, Calgary, Alberta, p 15–29
- Khummalai N, Boonamnuyvitaya V (2005) Suppression of arsenopyrite surface oxidation by sol-gel coatings. *J Biosci Bioeng* 99(3):277–284
- Lan Y, Huang X, Deng B (2002) Suppression of pyrite oxidation by iron 8-hydroxyquinoline. *Arch Environ Con Tox* 43(2):168–174
- Ueshima M, Kalin M, Fortin D (2003) Microbial effects of natural phosphate rock (NPR): addition to mining wastes. In: Proceedings of the 20th Annual National Meetings of ASMR and the 9th Billings Land Reclamation Symposium, Billings, Montana, p 1294–1303
- Ueshima M; Fortin D, Kalin M (2004) Development of iron-phosphate biofilms on pyritic mine waste rock surfaces previously treated with natural phosphate rocks. *Geomicrobiol J* 21(5):313–323
- Williamson, MA; Rimstidt JD (1994) The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochim Cosmochim Ac* 58(24):5443–5454