Journal of Industrial Microbiology, 6 (1990) 49–52
Elsevier

SIM 00261

Bioleaching of cobalt from smelter wastes by *Thiobacillus ferrooxidans*

Gregory J. Olson [1], Craig K. Sakai [2], E.J. Parks [1] and F.E. Brinckman [1]

[1] *Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD and* [2] *Department of Chemical Engineering, University of Maryland, College Park, MD, U.S.A.*

(Received 14 January 1989; revised 22 October 1989; accepted 3 November 1989)

Key words: Leaching; Metal recovery; Strategic metal; Cobalt; Smelter waste; *Thiobacillus ferrooxidans*

SUMMARY

The bioleaching of cobalt from domestic, industrial smelter wastes was studied. *Thiobacillus ferrooxidans* solubilized Co from sulfidic dross furnace mattes. At pulp densities of 4% (w/v) up to 600 mg of Co per liter of leaching solution was released from nickel matte, corresponding to removal of about two-thirds of the original amount of Co in the matte. Bioleaching methods may be useful as a component of a process for solubilization and recovery of Co from sulfidic smelter mattes.

INTRODUCTION

Cobalt is among the strategic and critical materials important to industrial economies [3]. However, the United States has produced no Co since 1971 because domestic ores contain cobalt in low concentrations and the processing of such low grade ores is not economically feasible at present [11]. A potential domestic source of Co exists in the residues and by-products from lead mining and smelting in the state of Missouri, where commercial smelting and refining of lead produces smelter mattes and slags in which metallic impurities are concentrated as sulfides [10]. The St. Joe Lead Company smelter produces in one year residues containing about 9×10^4 kg of Co [10].

Hydrometallurgical approaches to the recovery of Co from smelter wastes (e.g., chemical leaching using ferric chloride brines) have been reported [10]. Given the sulfidic nature of the material, leaching of these wastes with metal sulfide-oxidizing bacteria is also an attractive potential route for solubilization and recovery of the Co. Microbial leaching of sulfidic ores contributes strongly to the recovery of copper and uranium from commercial leaching operations in the United States, Canada and elsewhere [9]. There is considerable world-wide interest in applying bioleaching techniques to the large scale recovery of other metals from ores and wastes.

A candidate microorganism is the iron- and sulfur-oxidizing bacterium *Thiobacillus ferrooxidans*, which has been studied extensively for its ability to oxidize metal sulfide ores. This bacterium is active in metal sulfide weathering and mining environments around the world [9]. *T. ferrooxidans* has been shown to oxidize synthetic cobalt sulfide, producing soluble Co and sulfate [16]. While cobalt sulfide leaching (and sulfur oxidation) by *T. ferrooxidans* strain AP19-3 is strongly inhibited by 0.1 mM Co^{2+}, this inhibition is relieved by ferrous iron [15].

Industrial wastes generated from smelting and roasting of Pb and Zn ores have been subjected to bioleaching for evaluation of metal recovery [7]. In 30 days, *T. ferrooxidans* and *T. thiooxidans* leached 33–69% of Cu and Zn from such wastes.

The purpose of this investigation was to determine whether *T. ferrooxidans* could release Co into solution from sulfidic smelter wastes, indicating that microorganisms might be considered as part of a process for Co recovery from these materials.

Correspondence (Present address): G.J. Olson, Pittsburgh Energy Technology Center, P.O. Box 10940, Pittsburgh, PA 15236, U.S.A.

MATERIALS AND METHODS

Nickel matte. Dross furnace mattes in dry powder form were obtained from the St. Joe Lead Company, Herculaneum, MO. The composition of the nickel matte is given in Table 1. The material was sieved and −200 mesh (<74 μm) and −50 + 100 mesh (150–300 μm) fractions were used for subsequent study. The sulfur content of the two fractions varied only slightly, 8.5% for −200 mesh and 9.7% for −50 + 100 mesh, as determined by a high temperature combustion method with iodimetric titration [2]. Infrared spectra of the matte material were taken with an Analect (Utica, NY) AQS-20 Fourier transform infrared (FT-IR) spectrometer with a diffuse reflectance accessory. Prior to FT-IR analysis, the nickel matte was diluted 1 : 100 in KBr and shaken 10 s in a wig-l-bug mixer (Crescent Dental Manufacturing Co., Lyons, IL).

Organisms and culture conditions. Three strains of *T. ferrooxidans* were used in this study. Strain BA-4 was originally isolated from coal mine sediments in Wyoming [13]. Strain SW9K1 was isolated from cinnabar mines in Italy [4]. Strain 13661 (American Type Culture Collection designation) was obtained from R.M. Kelly, The Johns Hopkins University. All three strains were tested for the presence of heterotrophic contaminants as described by Harrison [8] and shown to be free of such organisms.

The organisms were maintained on 9K liquid medium basal salts [14] with pyrite added (4%, w/v) as the energy source. The basal salts solution consists of $(NH_4)_2SO_4$, 3.0 g; KCl, 0.1 g; K_2HPO_4, 0.5 g; $MgSO_4 \cdot 7H_2O$, 0.5 g; $Ca(NO_3)_2$, 0.01 g; 10 N H_2SO_4, 1.0 ml; and deionized water, 700 ml. The basal salts were autoclaved at 121 °C for 15 min, and the solid substrates (pyrites, smelter mattes) were sterilized by heating them at 160 °C for 1 h. Cells were grown at 25 °C with aeration on a rotary shaker at 120 rpm. Samples were removed occasionally for monitoring cell growth as determined by solution cell numbers (Petroff-Hausser bacteria counter with phase contrast microscopy) and soluble iron [1] measurements. Inocula for leaching experiments were prepared by centrifugation of active cultures (4000 × *g* for 15 min) and washing (twice) and resuspending cells in 0.01 M H_2SO_4. Flasks containing basal salts and furnace matte were inoculated to give a starting cell concentration of approximately 10^7/ml.

Bioleaching studies. Leaching studies of nickel matte were conducted using 100 ml of basal salts plus 4.0 g of matte in 250-ml conical flasks inoculated with *T. ferrooxidans*. The pH of the solutions was adjusted to 2.5 with H_2SO_4. Pyrite (−50 mesh, <297 μm) (Matheson, Coleman and Bell, Norwood, OH) was added to certain flasks to determine if microbial oxidation of pyrite would accelerate Co leaching. The pyrite was 44.1% Fe, as determined by a colorimetric procedure [1] following peroxide fusion, and 53.8% S as determined by a combustion-titration procedure [2]. Periodically, 1.0-ml samples were removed for counting cell numbers and for determination of Co in solution by graphite furnace atomic absorption spectroscopy (GFAAS).

TABLE 1

Composition of nickel matte

Element	Weight %
Pb	23.0
Cu	22.8
Ni	20.0
As	7.2
S	6.6
Zn	5.5
FeO	4.0
Co	2.0
Na	0.7
Ag	0.03
Cd	0.02

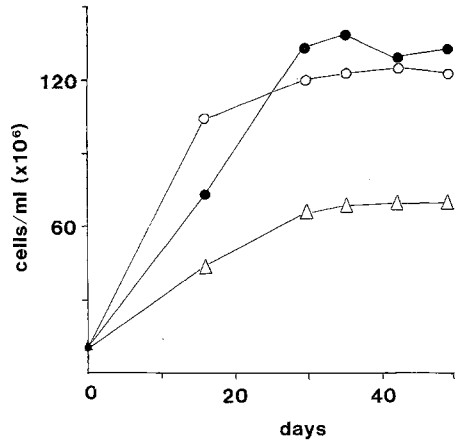

Fig. 1. Growth of *T. ferrooxidans* strain 13661 on smelter matte (4 g in 100 ml of basal salts) as monitored by solution cell counts. △, −200 mesh; ●, −50 + 100 mesh; ○, −50 + 100 mesh plus 2 g pyrite. No cells were detected in uninoculated control flasks.

Cobalt determinations. Leaching solutions were centrifuged at 12000 × *g* for 2 min in plastic centrifuge tubes. Cobalt in the resulting solution was determined with a Perkin Elmer model 460 atomic absorption spectrophotometer equipped with an HGA 2100 graphite furnace atomizer. A Perkin Elmer hollow cathode cobalt lamp was used at a wavelength of 240.7 nm. Cobalt in nickel matte was determined also by GFAAS after dissolution of the matte in a mixture of hot hydrochloric, nitric, hydrofluoric and perchloric acids [12].

RESULTS AND DISCUSSION

The matte material contained alkaline components as evidenced by the rise in pH of the basal salts medium on addition of the matte. Additional H_2SO_4 was added to adjust the pH of the medium to about 2.5. At 4% pulp density, 3.1 mEq of acid (as H_2SO_4) per g of nickel matte were required to maintain the pH in the region of 2.5–3.0. Infrared spectra of the nickel matte showed loss of a prominent peak at 1420 cm^{-1} upon acid treatment. This peak was assigned to carbonate functionality.

The three strains of *T. ferrooxidans* were maintainable on the smelter matte, which contains metal sulfides, as the sole source of energy. Solution cell counts with strain 13661 increased from an initial 10^7 cells/ml to 7.2–13.5 × 10^7 cells/ml when grown on nickel matte (Fig. 1). We did not attempt to count cells attached to particles in this heterogeneous system. The increase in cell numbers in solution with time is a reflection of growth in the medium. However, much of the growth may occur on particle surfaces with cells being shed into solution.

Preliminary experiments with the three strains of *T. ferrooxidans* showed that all three released Co into solution from the nickel matte (Table 2). After 14 days of incubation in shake flasks, the culture solutions contained 66–122 mg/l of Co compared to 0.01 mg/l Co in a sterile control. Nickel was also detected in solution at relatively high concentrations in both uninoculated and inoculated flasks, indicating that acidification alone solubilized nickel.

TABLE 2

Dissolution of Co and Ni from nickel matte (after 14 days) by strains of *T. ferrooxidans*

Strain	Soluble Co (mg/l)	Soluble Ni (mg/l)
BA-4	66	653
SW9K1	80	497
13661	122	449
sterile	0.01	361

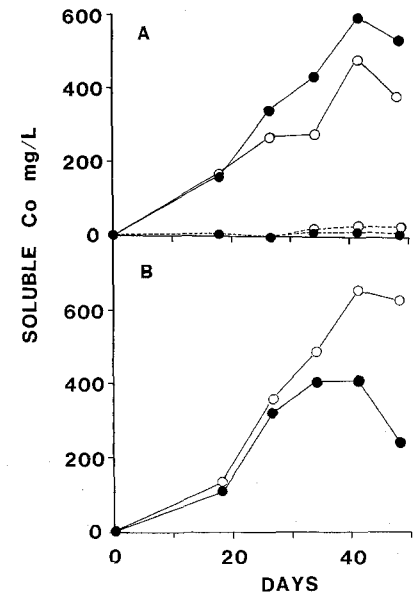

Fig. 2. Dissolution of Co from nickel matte (4% pulp density in 9K basal salts) by *T. ferrooxidans* strain 13661. (A) – 200 mesh matte; (B) – 50 + 100 mesh matte. Open circles denote flasks with pyrite (2.0 g) amendment. Dotted lines represent sterile controls.

Strain 13661 was chosen for time course experiments of Co bioleaching. In the presence of this organism, Co in solution increased with time to concentrations of several hundred mg of soluble Co/l after 6 weeks of incubation (Fig. 2A). The addition of pyrite did not increase the rate or extent of Co dissolution with the – 200 mesh nickel matte sample. However, the addition of pyrite to the – 50 + 100 mesh material (Fig. 2B) increased the total Co in solution after 6 weeks. Sterile controls showed very little Co dissolution, nor was soluble Co detected in flasks containing cells and pyrite but no smelter matte. Cell numbers in solution after 6 weeks were about 10^8 cells/ml. No cells were seen microscopically in the sterile controls.

The extent of Co removal from the spent nickel matte by *T. ferrooxidans* after 6 weeks incubation was about 65% for – 200 mesh and 43% for – 50 + 100 mesh samples. These values were calculated based on the concentration of soluble Co, the volume of solution and the amount of Co in the starting material. To confirm these findings, the processed material was digested in acid and

analyzed by AAS for residual Co. These results showed that 30% of the Co remained in the −200 mesh material and 40% remained in the −50 + 100 mesh material. Thus, a reasonable mass balance for Co was obtained.

Hydrometallurgical processes have been applied to smelter wastes in attempts to develop cost-effective Co recovery technology. Metals in finely ground smelter wastes were dissolved by hot ferric chloride brines. Metal separation steps follow, including the use of chelating resins to achieve separation of Co from Fe and Pb in acidic solutions [10]. Ferric chloride leach liquors from chemical leaching of copper mattes (0.9% Co, pulp density 2.5%) typically contain 0.2 g/l of Co, representing about 90% recovery of the starting Co. We found that *T. ferrooxidans* could generate solutions containing 0.6 g/l Co from −200 mesh nickel mattes (2.0% Co, pulp density 4.0%), representing about 65–70% recovery. However, several weeks were required to achieve Co dissolution. Ebner [7] also found several weeks were necessary for significant enhancement of bioleaching of Cd, Cu and Zn from smelter and roasting wastes. Improvements in bioleaching rate may be possible through manipulation of leaching conditions, or through the use of mixed cultures or thermophilic metal sulfide leaching bacteria [9]. The presence of pyrite did not significantly stimulate Co release except, perhaps, after 5 weeks of incubation with +50 − 100 mesh matte. *T. ferrooxidans* oxidizes pyrite to generate ferric sulfate-rich solutions which are good chemical oxidants of metal sulfide minerals. This process contributes to copper and uranium recovery in commercial bioleaching operations [9].

This study showed that substantial amounts of Co can be released from sulfidic smelter wastes by pure cultures of *T. ferrooxidans*. However, bioleaching rates are relatively slow. Additional work is necessary to determine the conditions under which bioleaching might be effective in heap leaching of smelter wastes. Such a process might be coupled to a subsequent treatment step for selective Co recovery from solution, perhaps involving ion exchange techniques [10] or the use of microbial metal recovery agents [5,6].

ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research.

REFERENCES

1 American Society for Testing and Materials. 1986. Standard test methods for iron in water. Volume 11.01–Water, pp. 523–538, ASTM, Philadelphia, PA.

2 American Society for Testing and Materials. 1988. Standard test methods for sulfur in the analysis sample of coal and coke using high temperature tube furnace combustion methods. Volume 5.05–Gaseous Fuels, Coals and Coke, pp. 366–367, ASTM, Philadelphia, PA.

3 Anonymous. 1985. Strategic Materials: Technologies to Reduce U.S. Import Vulnerability. Report by U.S. Office of Technology Assessment, Washington, DC.

4 Baldi, F. and G.J. Olson. 1987. Effects of cinnabar on pyrite oxidation by *Thiobacillus ferrooxidans* and cinnabar mobilization by a mercury-resistant strain. Appl. Environ. Microbiol. 53: 772–776.

5 Brierley, J.A., C.L. Brierley and G.M. Goyak. 1986. AMT-BIOCLAIM: a new wastewater treatment and metal recovery technology. Proc. 6th Internat. Symp. Biohydrometal., Vancouver, BC., August, 1985.

6 Darnall, D.W., B. Greene, M.T. Henzi, J.M. Hosea, R.A. McPherson, J. Sneddon and M.D. Alexander. 1986. Selective recovery of gold and other metal ions from an algal biomass. Environ. Sci. Technol. 20: 206–208.

7 Ebner, H.G. 1978. Metal recovery and environmental protection by bacterial leaching of inorganic waste materials. In: Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena (Murr, L.E., A.E. Torma and J.A. Brierley, eds.), pp. 195–206, Academic Press, NY.

8 Harrison, A.P. Jr. 1984. The acidophilic thiobacili and other acidophilic bacteria that share their habitat. Ann. Rev. Microbiol. 38: 265–292.

9 Hutchins, S.R., M.S. Davidson, J.A. Brierley and C.L. Brierley. 1986. Microorganisms in reclamation of metals. Ann. Rev. Microbiol. 40: 311–336.

10 Kennedy, D.C., A.P. Backer III and A.A. Worcester. 1987. Development of an ion-exchange process to recover cobalt and nickel from primary lead smelter residues. In: Metals Speciation, Separation and Recovery (Patterson, J.W. and R. Passino, eds.), pp. 593–618, Lewis Publishers, Inc. Chelsea, MI.

11 Kirk, W.S. 1985. Cobalt. In: Mineral Facts and Problems, Bureau of Mines Bulletin 675, pp. 171–183, U.S. Bureau of Mines, Washington, DC.

12 Lewis, C.L. and W.L. Ott. 1970. Analytical Chemistry of Nickel, p. 172, Pergamon Press, Oxford.

13 Olson, G.J., S.C. Turbak and G.A. McFeters. 1979. Impact of western coal mining. II. Microbiological studies. Water Res. 13: 1033–1041.

14 Silverman, M.P. and D.G. Lundgren. 1959. Studies on the chemoautotrophic iron bacterium *Ferrobacillus ferrooxidans*. I. An improved medium and harvesting procedure for securing high cell yields. J. Bacteriol. 77: 642–647.

15 Sugio, T., C. Domatsu, T. Tano and K. Imai. 1984. Role of ferrous ions in synthetic cobaltous sulfide leaching of *Thiobacillus ferrooxidans*. Appl. Environ. Microbiol. 48: 461–467.

16 Torma, A.E. 1971. Microbiological oxidation of synthetic cobalt, nickel and zinc sulfides by *Thiobacillus ferrooxidans*. Rev. Can. Biol. 30: 209–216.