

REMOVAL OF METAL IONS FROM MINE EFFLUENTS USING BACTERIAL REACTIONS BY SULFATE REDUCING BACTERIA¹

A. Choudhury², S. Bandopadhyay, S. Schiewer, T. E. Wilson

Abstract : Metals in mine effluents, especially metal mines, have been a major environmental concern. High mobility of the metals in solution and the subsequent lowering of discharge limits by the EPA have necessitated expensive chemical treatment of the effluent. Bacteriological reactions, particularly by Sulfate Reducing Bacteria, have been known to reduce metals content in water by precipitating them as metal sulfides. The technique was used on samples of untreated mine plant water (prior to treatment for disposal) from the Teck-Cominco Red Dog Mine in northern Alaska. Further experiments were conducted to determine bioreactor design parameters. Bioreactor lab tests revealed that metal content was reduced by over a hundred fold. Pilot scale test cells were established in the Red Dog mining area and their performance was monitored.

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² A. Choudhury, Graduate Student, Dept. of Mining & Geological Eng., University of Alaska Fairbanks, Fairbanks Alaska 99775, Dr. S. Bandopadhyay – Professor, Dept. of Mining & Geological Eng., University of Alaska Fairbanks. Dr. S. Schiewer – Asst. Professor, Dept. of Civil and Environmental Eng., University of Alaska Fairbanks., Dr. T.E. Wilson – Adjunct Asst. Professor, Dept. of Mining and Geological Eng., University of Arizona, Tucson, Arizona 85721.

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Introduction

In recent years environmental concerns have come to the forefront for all industries. Mining, an industry where the exploitation of natural resources inevitably causes the dislocation of the environment from its natural state, has been under much scrutiny. Mining may result deforestation of previously virgin forest land, subsidence in the case of underground mining, and large cavities in the land in the case of surface mining. Mining also has the potential to cause significant air and water pollution. In this paper, remediation of polluted water is the primary focus. The contribution of mining to pollution of local water bodies is primarily by intermixing of local water resources with the mine runoff water, which transports contaminants, both metallic and non-metallic, from the mining area into the aquatic environment. The research this paper describes was conducted with funding from the U.S. Department of Interior – Minerals Management Service, and with valuable help from Teck-Cominco Red Dog Mine in northern Alaska. The focus of the research was the remediation of the aqueous phase of mine tailings by bacteriological action, also called bioremediation. Emphasis was upon the reduction of metal concentrations in such water. The metals chosen for remediation were Pb, Zn Cd, Fe and Mn.

Brief Literature Review

Bioremediation primarily proceeds through anaerobic bacterial action, aerobic bacterial action and sorption (Seyler *et al.* 2003; Unten *et al.*, 1998). The anaerobic process is explained by Unten *et al.* (1998). The set of reactions most important to Bioremediation by an anaerobic process using Sulfate Reducing Bacteria (SRB) are given as:

i) Hydrolysis of cellulose



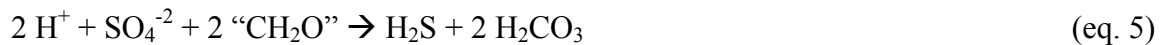
ii) Fermentation



iii) Methanogenesis



iv) Sulfate Reduction



v) Metal Reduction (Iron)



Metal reaction can be also expressed (Lintern, 1994) as



Eq. 7 is possible because H₂S is a very strong reducing agent.

Bioremediation has been widely reported in literature as a viable means of reducing metal concentrations in water. Christensen *et al.* (1996) used a bench scale setup to investigate bioremediation by SRB and achieved high removal rates for Cu, Zn, Fe, and Al. Unten *et al.* (1998) also reported similar removal of metals like Cd, Cr, Se, Zn, Fe, and As. Performance of field scale bioreactors at the West Fork Lead Mine in Missouri were assessed by Gusek *et al.* (2000). It was noted by the authors that the system was quite effective in removing metals, but was not entirely maintenance-free. Canty (2000) reported encouraging results for bioremediation of effluent water from Lilly/Orphan Boy Mine, located at the Elliston mining district of Powell County, Montana. Metals like Al, Cd, Cu and Zn were removed very efficiently in general, but the performance of the reactors was noted to be seasonally variable.

Experimental Procedures

Laboratory scale and field scale experiments were conducted to investigate various aspects of bioremediation. Field scale bioreactors were set up on the Red Dog Mine property. The designed residence time of the reactors was seven days. Samples of the concentrating plant effluent prior to treatment for release from the mine property were collected by Red Dog Environmental department personnel, and were analyzed at UAF using the ICP mass spectrography. These experiments will be discussed in a separate report. These experiments helped establish the viability of bioremediation for removing metals from mine effluents in a northern Alaskan environment.

Laboratory scale experiments were conducted to determine various parameters related to the performance of bioremediation, including efficiency of removal of contaminants, residence time, and sorption vs. chemical change. Experiments were conducted in eight ounce mason jars which were loaded with the required amount of biomass and with 125 ml of mine effluent water. The setup was left undisturbed for between seven and one days (as the experiments required). In the case of the sorption experiments, the jars were loaded on to a shaker table and were left in agitation for three hours. Samples were collected, strained and the metal concentrations were measured by ICPMS. Digestion experiments were also conducted to determine whether there was a difference in metal content in the compost being used for bioremediation before and after the bioremediation reaction. The aliquots of dried and pulverized biomass were treated with one liter 70% HNO₃, 200 ml of concentrated H₂SO₄ and 400 ml 60% HClO₄. This mixture was then boiled first at 300 °C for 15 minutes and then at 600 °C for 45 minutes. The metal content of the digested samples was determined using ICP-MS. The metal precipitates were not separated from the biomass.

Results

The following Table 1 summarizes the results for the bioremediation replication experiments that were conducted in the laboratory.

Figure 1 illustrates an example of the results received from the experiments conducted to determine the efficiency of the biomass. Here the X – axis contains the number of grams of compost loaded in the test jars. The highest amount was 20 grams, and it was brought down in steps of 4 grams to the minimum of 4 grams. The Y – axis contains the concentrations of the metal Pb in ppm and the Z – axis marks the two replicates.

Table 1: Effluent Concentrations for Basic Bioremediation Process

Metal	Influent Concentration (ppm)	Effluent Concentration Range (ppm)
Lead	56.7	0.10 - 0.39
Zinc	4259.8	31.45 - 410.54
Cadmium	322.6	0.66 - 2.05
Iron	1020.5	53.09 - 247.88
Manganese	77.8	36.30 - 142.07

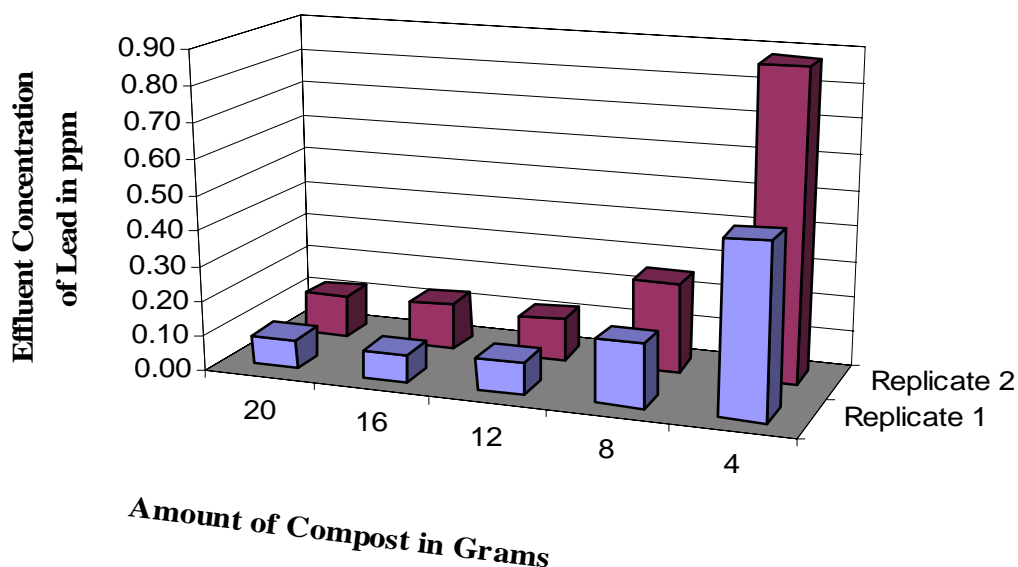


Fig – 1: Effect of Quantity of Biomass on Removal of Lead (influent concentration 56.7 ppm)

Table 2 enumerates the results from the sorption experiments, conducted to find the percentage removal of metals by pure sorption. Data for Pb and MN are not available.

Table 2: Summary of Reduction of Metals in Sorption Experiments

Metals	Influent (ppm)	Effluent		Percent Removed
		Mean (ppm)	St. Dev. (ppm)	
Zn	1027.88	587.77	184.35	42.82
Cd	1.03	0.59	0.18	42.82
Fe	39240.00	1613.38	507.71	95.89

Digestion experiments showed that, as expected, there was an increase in the concentration of the metals in the reacted biomass as compared to the unreacted samples of biomass. There was, unfortunately, no clear trend available from the residence time experiments.

Discussions

We can see from Table 1 that there is several orders of magnitude (1 to 3) removal of metals from the influent, through bioremediation in bench scale experiments. Also, the influent pH, which was usually in the range 3 – 3.5 was raised to nearly neutral (6.5 – 6.8). As pH is raised, some heavy metals might form insoluble oxides or hydroxides and precipitate out of solution. This process complements bioremediation. Experiments for efficiency of biomass metal removal, however, yielded mixed results. In the case of Pb, Zn and Cd, an anticipated trend is seen, that of concentrations of metals slowly decreasing as the amount of biomass is increased. Iron and Mn, however, do not conform to this trend. In case of Fe, the biomass may not have been homogeneous in composition. This may have introduced spiked concentrations of Fe in some samples. In the case of Mn, it is known that the metal is primarily removed by sorption (Seyler *et al.* 2003). This fact may explain insensitivity displayed by Mn towards varying amounts of compost. In Table 2, it can be observed that Fe is almost entirely removed by sorption, while more than 40 % of Zn and Cd are removed by the same process. Sorption of Zn and Cd may have been suppressed by competition with other ions, e.g., Fe. It may also be that Zn and Cd may have reached their full potential for sorption under the laboratory conditions, and any further removal would invoke bacterial remediation. Lead and Mn do not this trend. The lack of such a trend may indicate that the formation of Zn and Cd sulfides, characteristic of bioremediation, may not be happening in the cases of Pb and Mn.

Conclusions

It is possible to conclude from the experiments that the bioremediation process described can effectively treat heavy-metal-contaminated water. We can also conclude that the mode of removal of a specific metal may differ from that of another. The primary goal in an industrial bioremediation operation would be to steer the process towards removing the maximum quantity of metals from the influent, and not maximize a particular sub-process of metal removal (say, sorption or anaerobic removal). One important aspect of applying the technology to the industry is prediction of performance at the field. Scaling up of the laboratory results to predict the performance of the process in the field will require further work.

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