

# Biogeochemical Analysis of Hydrogen Sulfide Removal by a Lava-Rock Packed Biofilter

Hebi Li, Donald R. Lueking, James R. Mihelcic, Karl Peterson

**ABSTRACT:** Although lava-rock-based biofilters have demonstrated their efficiencies for hydrogen sulfide (H<sub>2</sub>S) removal found in odorous air emissions, the biogeochemical basis for this removal is unclear. In this study, samples of lava rock and rinse water from biofilters at Cedar Rapids Water Pollution Control Facilities (Iowa) were used to study the structure and chemical composition of lava rock and to identify the predominant microorganism(s) present in lava-rock-based biofilters. It was found that iron, in the form of Fe<sup>2+</sup> and Fe<sup>3+</sup>, was present in lava rock. Although literature suggests that *Acidithiobacillus thiooxidans* are primarily responsible for gaseous H<sub>2</sub>S removal in biofilters, our study showed that *Acidithiobacillus ferrooxidans* was the dominant microorganism in the lava-rock-based biofilters. A novel mechanism for H<sub>2</sub>S removal in a lava-rock-based biofilter is proposed based on the biogeochemical analysis of lava rock. *Water Environ. Res.*, 77, 179 (2005).

**KEYWORDS:** biofiltration, hydrogen sulfide, lava rock, odor.

## Introduction

Hydrogen sulfide (H<sub>2</sub>S) is an odorous, toxic, and corrosive air pollutant. Emissions of H<sub>2</sub>S from the municipal wastewater treatment and industrial processes (e.g., petrochemical refining, paper and pulp manufacturing, animal operation, food processing, and treatment of "sour" natural gas) are a growing concern in the recent years. Biofiltration has been found to be an ecologically and economically favorable technology for H<sub>2</sub>S removal, especially for treating offgases at low concentrations (Li et al., 2003; Martin et al., 2002).

The selection of a proper packing medium is an important step toward developing a successful biofiltration operation. Materials that are commonly used for biofilter packing media include organic materials (e.g., compost, peat, bark mulch, or a mixture of these), natural inorganic solids (e.g., perlite, mearl, and lava rock), and synthetic materials (e.g., ceramic rings). The inorganic media generally have structural integrity and can resist bed compaction, but the use of a solely inorganic medium requires proper seeding with nutrients and organisms. The organic media offer an advantage of having nutrients present in the media, but they have a main drawback of undergoing mineralization as a result of resident microbial activities and eventually suffering from bed compaction (Swanson and Loehr, 1997), and it is possible that the rate of nutrients release is too slow (Deviny et al., 1999) and organic materials are exhausted of nutrients during long-term operation.

Lava-rock-based biofilters have been used to treat H<sub>2</sub>S or a mixture of H<sub>2</sub>S and volatile organic compounds (VOCs) and have demonstrated high H<sub>2</sub>S removal efficiencies (Chitwood et al., 1999; Chitwood and Deviny, 2001; Martin et al., 2002; Morton and Caballero, 1996). These beds are generally inoculated with

microorganisms before operation. For example, in one study, the beds were inoculated with recirculation water containing sulfur-oxidizing microorganisms obtained from the crowns of inlet sewers to wastewater treatment plants (Morton and Caballero, 1996) and, in another study, with influent wastewater (Chitwood et al., 1999). Water and nutrients are also added periodically by sprinklers installed in the headspace above the media. Lava-rock-based biofilters have also demonstrated removal of VOCs and organic sulfides (Chitwood and Deviny, 2001; Martin et al., 2002).

However, the biochemical basis of H<sub>2</sub>S removal in lava-rock-based biofilters remains unclear. Several species of *Acidithiobacillus* have been reported to oxidize H<sub>2</sub>S as a sole energy source and fix carbon dioxide (CO<sub>2</sub>) as its carbon source (Jensen and Webb, 1995). In a study conducted with a ceramic carrier-packed biofilter treating H<sub>2</sub>S, a strain of *Acidithiobacillus thiooxidans* was isolated from the packing medium (Shinabe et al., 1995). However, no study has been conducted to isolate predominant microorganism(s) from a biofilter packed with lava rock, and it is currently believed that the organisms responsible for gaseous H<sub>2</sub>S removal in biofilters are *Acidithiobacillus thiooxidans*. Based on pilot- and full-scale lava rock-based biofilters that have been studied previously (Li et al., 2002; Martin et al., 2002), the main objective of this paper is to identify the predominant microorganism(s) present in the lava-rock-based biofilters and to investigate the biogeochemical mechanisms responsible for H<sub>2</sub>S removal. This includes studying the physical and chemical properties of lava rock, which could promote the growth of microorganism(s) responsible for H<sub>2</sub>S removal.

## Materials and Methods

**Lava-Rock-Based Biofilters and Sample Collection.** Cedar Rapids Water Pollution Control Facilities (Cedar Rapids, Iowa) owns two parallel full-scale, lava-rock-based biofilters for treatment of odorous emissions produced during the wastewater treatment process and a pilot-scale, lava-rock-based biofilter for research purposes. Both the full- and pilot-scale biofilters were packed with lava rock to a depth of 0.5 m (1.8 ft). A polyvinyl chloride peg board, with 6.4-mm holes that were 76 mm apart, supported the lava rock above the gas feed and provided uniform air distribution through the beds. Before operation, the beds were inoculated with water containing sulfur-reducing microorganisms obtained from the inside of the roughing filter ducts. To provide moisture and nutrients for microbial growth and to wash away oxidation products, secondary effluent is sprayed on the top of the lava-rock beds through spray nozzles for five minutes every hour. The secondary effluent contains 30 mg/L carbonaceous biochemical oxygen demand (CBOD),

50 mg/L total suspended solids (TSS) (some spikes above this), 1 mg/L ammonium ( $\text{NH}_4^+$ ) (highly variable), and some basic micronutrients (e.g., phosphorus and potassium). A more detailed description of these biofilters is provided elsewhere (Martin et al., 2002).

The inlet  $\text{H}_2\text{S}$  concentration to the full-scale biofilters ranges from 50 to 300 ppm, and the treatment objective of 0.5 ppm, is achieved at the outlets most of the time. Lava-rock and rinse-water samples were taken from the pilot-scale biofilter for the following microbial studies. The samples were stored at 4°C before use.

**Microbial Strains, Media, and Enrichments.** *Acidithiobacillus ferrooxidans* (ATCC 19859) and *Acidithiobacillus thiooxidans* (ATCC 19377) (Kelly and Wood, 2000), obtained from the American Type Culture Collection (ATCC), were used as control microorganisms. *A. ferrooxidans* was routinely grown on a ferrous iron ( $\text{Fe}^{2+}$ )-based minimal medium and maintained in liquid culture at 4°C, or at -70°C on ProLab biobeads (Pro-Lab Diagnostics, Austin, Texas) (LaCombe-Barron and Lueking, 1999). *A. thiooxidans* was grown in an elemental sulfur-based minimal medium and maintained in liquid culture at 4°C.

Enrichments for *A. thiooxidans* (sulfur oxidizers) were conducted in Medium 125 (Starkey's medium, pH 4.1) (Starkey, 1925). Incubations were conducted under both static and dynamic (shaking) conditions at 30°C. Growth was monitored by direct cell counting using a Petroff-Hausser (Hausser Scientific, Blue Bell, Pennsylvania) counting chamber and by measuring decreases in culture pH. Growth on  $\text{H}_2\text{S}$  was evaluated on solidified Starkey's medium lacking elemental sulfur. Incubations were conducted in Brewer jars (Becton Dickinson and Co., Sparks, Maryland) at room temperature under an atmosphere of  $\text{H}_2\text{S}$  in air. Enrichments for *A. ferrooxidans* (iron oxidizers) were conducted in a  $\text{Fe}^{2+}$  (15 g/L)-based minimal medium (pH 1.9) at 30°C under an atmosphere of 7.5%  $\text{CO}_2$  and 92.5% air (Kelly and Wood, 2000).

Growth was monitored by observing medium color changes (ferric iron [ $\text{Fe}^{3+}$ ] production), direct cell counting, and by monitoring the change in optical density at 500 nm ( $\text{OD}_{500\text{nm}}$ ) (Kelly and Wood, 2000). Growth of iron oxidizers on solidified medium was conducted by the agarose overlay procedure (Yates and Holmes, 1987). Rinse-water and lava-rock samples obtained from the pilot-scale biofilter were used as inoculum sources for the enrichment of sulfur or iron oxidizing microorganisms. Inocula consisted of either cells that had been concentrated from the water samples by centrifugation (12 100 × g, 10 min) or by directly placing lava-rock samples into the medium.

Extraction of DNA from cells contained in rinse-water samples and enrichment cultures was conducted by the filtration method of Somerville et al. (1989). Cells were concentrated using a Millipore Sterivex-GS (Millipore Corp., Bedford, Massachusetts) filtration unit equipped with a 0.22- $\mu\text{m}$  cellulose filter and the DNA was extracted by sequential treatment of the filtered cells with lysozyme, sodium dodecyl sulfate, and proteinase K as previously described (Somerville et al., 1989). The resulting ethanol-precipitated DNA was resolubilized in 50-mM Tris-HCl buffer (pH 7.6) for further studies.

Small subunit ribosomal RNA (rRNA) sequences were amplified from isolated target DNA by polymerase chain reaction (PCR) using primers based on 16S rRNA sequences that were specific for *A. ferrooxidans* and *A. thiooxidans*, as described by De Wulf-Durand et al. (1997). The complete sequences of these primers have been previously published (De Wulf-Durand et al., 1997). Primers were obtained from Integrated DNA Technologies (Integrated DNA Technologies, Coraville, Iowa). The PCR incubation mixtures (25  $\mu\text{L}$ ) contained 100 ng target DNA, 0.5  $\mu\text{M}$  each of the forward

and reverse primers 3 mM magnesium chloride ( $\text{MgCl}_2$ ), 0.2 mM deoxynucleotide triphosphate (dNTP) mix, and 0.6 units of enzyme activity (U) of thermus aquaticus polymerase (Taq) polymerase, added last. Thermal cycling involved a hot start (94°C, 30 sec) followed by incubation at 50°C for 30 sec and 72°C for 1.5 min. The regimen was continued for 25 cycles.

The PCR products were analyzed by agarose (1%) gel electrophoresis and were recovered and cloned into a pGEM-T plasmid vector (Promega Corporation, Madison, Wisconsin) in preparation for automated DNA sequencing. DNA sequencing of the PCR products was conducted using an ABI Prism 310 Genetic Analyzer (PE Applied Biosystems, Foster City, California), with the ABI Prism bigdye terminator cycle sequencing-ready reaction kit containing AmpliTaq DNA polymerase. Final sequences obtained by this procedure were then subjected to basic local alignment search tool (BLAST) analysis using the standard National Center for Biotechnology Information (NCBI) nucleotide-nucleotide (nr) database (Blastn program).

**Lava Rock Analysis.** To understand the mechanism of  $\text{H}_2\text{S}$  removal in lava rock biofilters, it is important to know the key physical and chemical properties of lava rock in addition to the predominant microorganism(s) in lava rock biofilters. A few pieces of lava rock randomly taken from the upper 0.3 m (1 ft) of the full-scale biofilter were used to analyze the particle density (ratio of the weight of dry rock to the total volume of the particle, which includes the pore volume), material density (ratio of the weight of dry rock to the volume of the material only), and porosity (ratio of the pore volume to the total volume of the particle), according to the methods provided by Sontheimer et al. (1988).

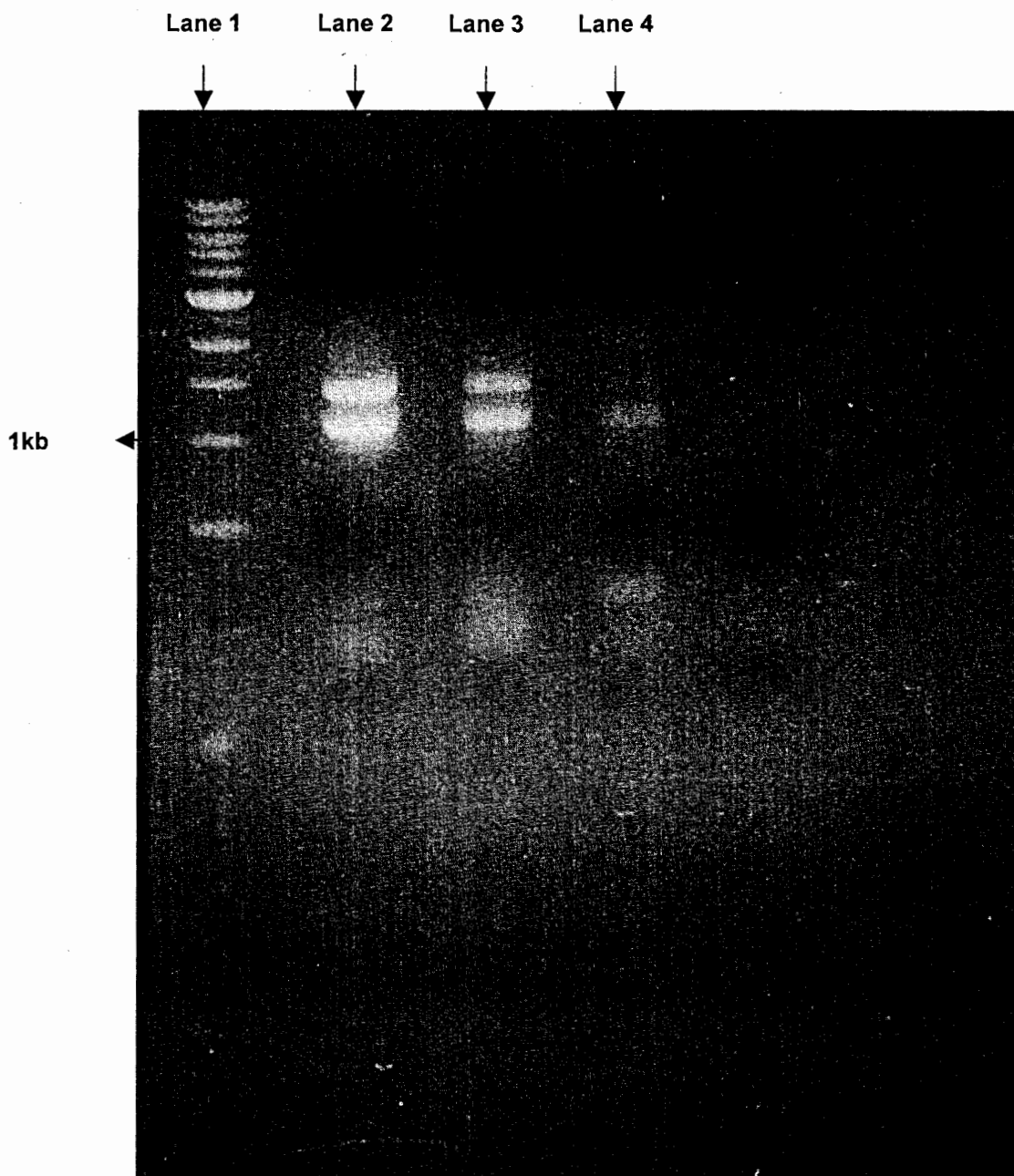
The lava rock was also analyzed for pore structure, mineralogy, and chemical composition using an optical zoom stereo microscope (Olympus SZH10 [Olympus Corporation, Tokyo, Japan]), an optical petrographic microscope (Olympus BX-60), and a microprobe (Japan Electron Optics Laboratory Co., Ltd. [JEOL] JXA-8600 [Tokyo, Japan]), which essentially consists of a scanning electron microscope equipped with an x-ray energy dispersive spectrometer.

Several pieces of rock were placed in a vacuum, immersed in a fluorescent-dyed epoxy, and brought back to atmospheric pressure to force the epoxy into the pore structure. After the epoxy had cured, the rocks were cut into 2-mm-thick slices with a precision low-speed diamond saw. Kerosene was used as a cutting, grinding, and polishing medium throughout the process. Some of the slices were set aside to study the pore structure using the optical zoom stereo microscope, while other slices were prepared in thin section according to methods described by Walker and Marshall (1979).

## Results and Discussion

**Microbial Study.** Based on the previous studies on the removal of  $\text{H}_2\text{S}$  in biofilters (Chitwood et al., 1999; Shinabe et al., 1995), a strain of *A. thiooxidans* had been expected to be present in lava-rock and rinse-water samples. However, repeated attempts to demonstrate the growth of *A. thiooxidans* in a sulfur-based growth medium were unsuccessful. Growth in Medium 125 was non-existent after seven weeks of incubation when either concentrated cells from the water sample or lava rock were used as inocula. In contrast, significant growth was observed with the control organism (ATCC 19377) in the same medium.

Surprisingly, similar enrichments conducted in a  $\text{Fe}^{2+}$ -based medium yielded significant growth in 48 hours when lava rock was used as the inoculum source. These gram-negative, rod-shaped  $\text{Fe}^{2+}$ -oxidizing organisms were repeatedly subcultured in the  $\text{Fe}^{2+}$ -



**Figure 1**—Polymerase chain reaction products showing that DNA from the rinse-water and lava-rock isolates yields the expected ~1 kb PCR fragment produced by the *A. ferrooxidans* control DNA (ATCC 19859); Lane 1—Standards, Lane 2—DNA from *A. ferrooxidans* control (ATCC 19859), Lane 3—DNA from the rinse water isolate, and Lane 4—DNA from lava rock isolate.

based minimal medium and were shown to produce small white colonies with a developing yellow-orange precipitate when grown on ferrous agarose overlay plates. In addition, these organisms displayed growth on a solidified minimal salts medium under an atmosphere of  $H_2S$  where they produced white, circular, non-shiny, convex colonies approximately 2 mm in diameter. These data strongly suggested that the organism was a species of *Acidithiobacillus* and possibly *A. ferrooxidans*.

To examine this possibility, DNA from the rinse-water and lava-rock isolates was extracted as described in the Materials and Methods

section, and PCR was conducted on the DNA using a 16S-rDNA primer developed for *A. ferrooxidans*. As shown in Figure 1, this primer yielded the expected ~1-kilobase (kb) fragment using the DNA from either the rinse water (lane 3), *A. ferrooxidans* control (lane 2), or lava-rock isolate (lane 4). Following cloning and sequencing of these fragments (described in the Materials and Methods section), evaluation of these sequences using a BLAST search virtually confirmed that the isolated organisms were *A. ferrooxidans*. Identical studies using 16S rDNA primers (De Wulf-Durand et al., 1997) developed for *A. thiooxidans* yielded no response. These results

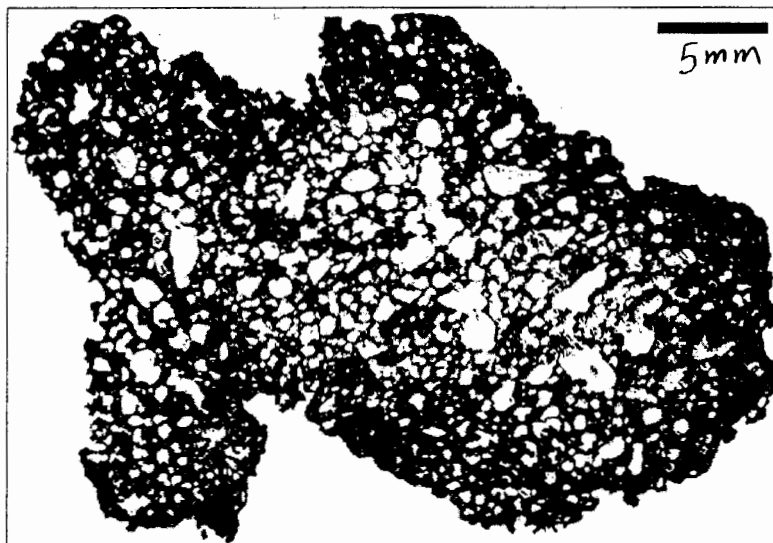


Figure 2—Binary image of cross-section through lava rock where rock appears black and the entire pore structure appears white.

provided additional confirmation that the organism(s) isolated from the rinse water and lava rock is *A. ferrooxidans*.

**Physical Properties and Pore Structure of Lava Rock.** The particle density, material density, and porosity of lava rock were determined to be 1.13 g/mL, 1.41 g/mL, and 0.20, respectively. These values indicate that lava rock is a porous material. The pore structure was further illustrated by the microscopic analysis.

The rock slice that was set aside after the first vacuum impregnation with fluorescent epoxy was illuminated with UV light, and digital images were recorded with the optical zoom stereo microscope. The epoxy did not fully penetrate the rock. To assist in the identification of the pore structure not filled with epoxy, a white powder (2- $\mu$ m wollastonite) was pressed into the pore structure of the rock slice. Figure 2 shows a binary image where the rock appears black, and the entire pore structure appears white. The size of the pores is up to 5 mm. Assuming 20°C and a wetting angle of zero degrees, the capillary rise in a cylindrical pore with a diameter of 5 mm is 6 mm, according to the capillarity equation (Franzini et al., 1997), which is comparable to the largest pore size (5 mm). Although it may be difficult for water to penetrate the rock to reach the pores located away from the surface, it is believed that the pores close to the rock surface are able to hold water and make it available for microbial growth. The porous structure also demonstrates a large specific surface area for microbial attachment, but the inner pores may not be accessible.

**Mineralogy of Lava Rock.** The thin sections were examined with the optical petrographic microscope, and the lava rock was found to consist of olivine and plagioclase phenocrysts in a matrix of hematite and plagioclase laths. Figure 3 shows a large olivine phenocryst surrounded by plagioclase laths of varying size and fine-grained hematite. Figure 4 shows a closeup of plates of hematite enclosed in a large plagioclase lath.

The minerals were further examined with the microprobe to determine their composition. The hematite was found to contain small amounts of titanium, suggesting that the hematite belonged to a solid-

solution series between ilmenite ( $\text{FeTiO}_3$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). The plagioclase composition was found to be 30% albite ( $\text{NaAlSi}_3\text{O}_8$ ) and 70% anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_7$ ). The olivine phenocrysts were unusual. Although the exterior of the crystals appeared very euhedral, the interior of the crystals tended to be more skeletal. Furthermore, four different olivine compositions ( $\text{Mg}_2\text{SiO}_4 \sim \text{Fe}_2\text{SiO}_4$ ) were found within an individual phenocryst, suggesting that the temperature of the melt was changing as the phenocryst was forming. The reduced form of iron,  $\text{Fe}^{2+}$ , is present in olivine.

The results of microscopic analysis also demonstrate that lava rock has an integral structure. Unlike organic packing media, lava rock has demonstrated its ability to resist bed compaction in the field. At the full-scale lava-rock biofilters at Cedar Rapids Water Pollution Control Facilities, the lava rock has not been replaced since the startup in 1998, and the pressure drop is only 0.2 to 0.5 in.  $\text{H}_2\text{O}$ .

**Proposed Mechanism for Hydrogen Sulfide Removal.** Previously reported studies have implicated *A. thiooxidans* in the biological removal of  $\text{H}_2\text{S}$  in biofilters (Chitwood et al., 1999; Shinabe et al., 1995). In the present study, no evidence was obtained for the presence of *A. thiooxidans* or its involvement in the removal of  $\text{H}_2\text{S}$ . In contrast, cells of *A. ferrooxidans* were readily isolated from both rinse-water and lava-rock samples. Importantly, this is the first time that a strain of *A. ferrooxidans* has been isolated from a lava-rock-based biofilter.

In a separate study, we conducted at a two-stage biofilter that was packed with wood chips and compost and treated a mixture of  $\text{H}_2\text{S}$  and organic sulfur compounds (Li et al., 2003) *A. ferrooxidans* was not found. However, other species of sulfur oxidizing microorganisms, *Chryseobacterium* and *Sinorhizobium*, were identified after detailed microbial evaluation (data not shown). The abundance of *A. ferrooxidans* relative to other sulfur-oxidizing microorganisms in the lava-rock-based biofilter strongly suggests that it significantly contributes to biofilter function. Although the possible function of *A. ferrooxidans* in the removal of  $\text{H}_2\text{S}$  in a lava-rock biofilter has not previously been studied, several possibilities exist for the organism's involvement.

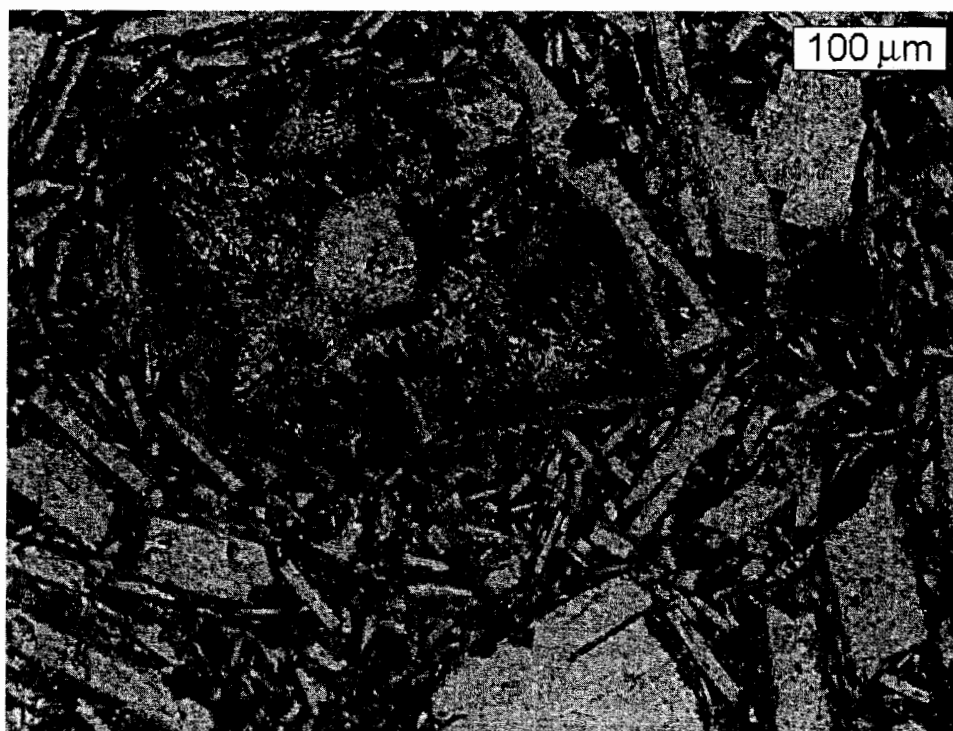
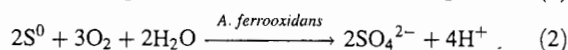
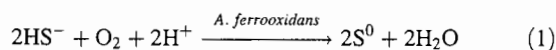


Figure 3—Lava-rock samples examined with an optical petrographic microscope showed olivine phenocryst (large hexagonal feature) in a matrix of plagioclase laths and hematite.

First, the organism could use  $\text{H}_2\text{S}$  as the sole energy source. In this scenario, *A. ferrooxidans* oxidizes  $\text{H}_2\text{S}$  in the presence of  $\text{O}_2$  (Buisman et al., 1991; Jassen et al., 1995).



In biofilters treating  $\text{H}_2\text{S}$ , the oxidation of  $\text{H}_2\text{S}$  produces sulfuric acid. Under acidic conditions and/or the attack of *A. ferrooxidans*, lava rock could release  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  ions—a process similar to the bacterial leaching of ores (Sand et al., 1995; Schippers and Sand, 1999).

In the second scenario, *A. ferrooxidans* could use  $\text{Fe}^{2+}$  as an energy source and oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (Asai et al., 1990; Halfmeier et al., 1993). The  $\text{Fe}^{3+}$  ions produced by this oxidation, together with those released from lava rock, could then spontaneously oxidize  $\text{H}_2\text{S}$  via pure chemical reactions (Asai et al., 1990; Halfmeier et al., 1993), or via biological reactions in which *A. ferrooxidans* uses  $\text{Fe}^{3+}$  as an electron acceptor (Sugio et al., 1985, 1987, and 1988). However, under aerobic conditions, this latter biological oxidation would not be expected to be favored. As shown in Figure 5, the iron ions could then be recycled in the system to continue the oxidation of  $\text{H}_2\text{S}$ .

In the second scenario, there exist the following two critical questions:

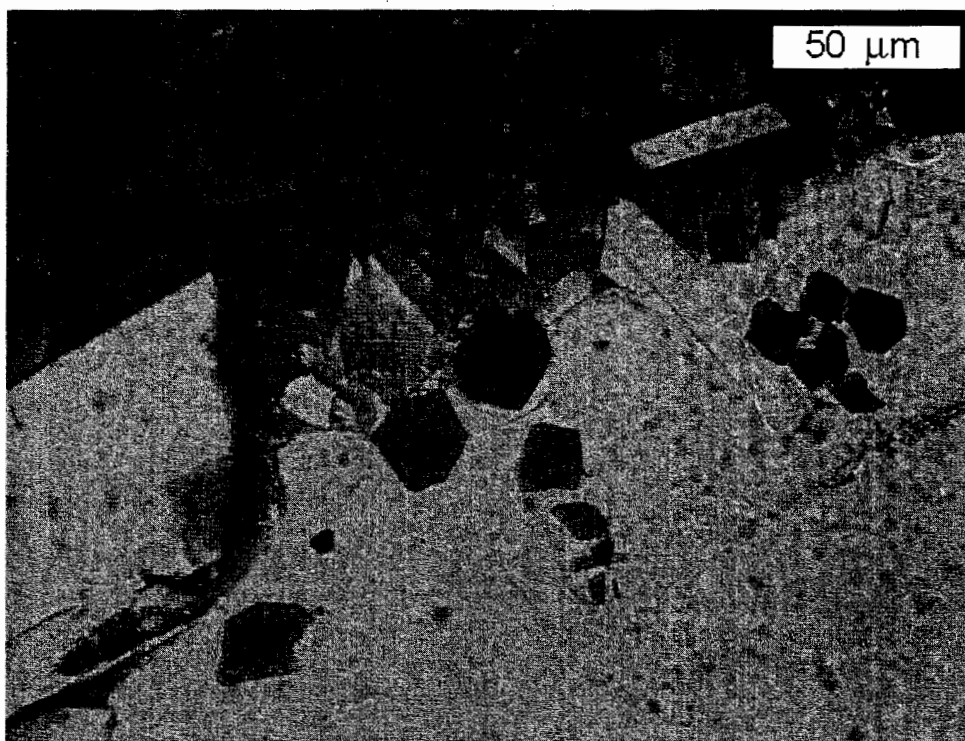
- (1) Does lava rock in the biofilter release  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$ ?
- (2) Are the  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  ions available for the use of microorganisms instead of forming complexes and/or precipitates in the biofilter?

The first question was answered by the observed low pH in the biofilter (pH 2.0 to 3.0), brownish color of the effluent rinse water, and increased total dissolved iron in the effluent rinse water (10.3 mg/L) compared to that in the influent rinse water (0.27 mg/L) after several years of operation. These data seem to clearly indicate that the low pH contributes to an active lava-rock surface chemistry where  $\text{Fe}^{3+}$  and/or  $\text{Fe}^{2+}$  is released.

The second question was studied by modeling the water chemistry of the effluent rinse water from the lava-rock biofilter. The chemical components of our concern (not all possible chemical components) include  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$ , hydrogen ( $\text{H}^+$ ), hydroxide ( $\text{OH}^-$ ), hydrosulfide ( $\text{HS}^-$ ) (from dissociation of  $\text{H}_2\text{S}$ ), bicarbonate ( $\text{CO}_3^{2-}$ ) (from dissociation of dissolved  $\text{CO}_2$ ), and sulfate ( $\text{SO}_4^{2-}$ ) (from oxidation of  $\text{H}_2\text{S}$ ). Table 1 provides the measured or estimated concentrations of these chemical components, which were determined based on the following assumptions:

- (1) pH of the aqueous system is 3.0 and the total dissolved iron is 10.3 mg/L, based on the field measurements;
- (2) The average concentration of  $\text{H}_2\text{S}$  in the influent air to the biofilter is 100 ppm<sub>v</sub>, and  $\text{H}_2\text{S}$  in the effluent rinse water is in equilibrium with the influent air (because water and air are flowing in opposite directions);
- (3)  $\text{CO}_2$  in the effluent rinse water is in equilibrium with the atmosphere ( $P_{\text{CO}_2} = 3.5 \times 10^{-4}$  bar); and
- (4) The acidification of the rinse water is caused by the accumulation of sulfuric acid.

The complexes and solids of our concerns that can be formed from the simplest chemical species and the corresponding equilibrium constants are provided in Table 2 (eqs 8 to 23).



**Figure 4**—Lava rock samples examined with an optical petrographic microscope showed plates of hematite (dark) enclosed in a plagioclase lath.

Chemical equilibrium calculations were performed for two extreme cases. The first case assumed that all the iron was present as  $\text{Fe}^{2+}$ , and the second case assumed that all the iron was present as  $\text{Fe}^{3+}$ . For both cases, it was found that no significant amount of precipitate or complex would form, and that the percentage of free ions ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) was greater than 99%. The  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  ions released from lava rock, therefore, are believed to be available for the use of *A. ferrooxidans* in the biofilter.

Because the iron ions released from lava rock could be recycled in the system (see Figure 5), a small amount of iron release could be capable of oxidizing much more  $\text{H}_2\text{S}$  than would be predicted on a stoichiometric basis. This mechanism actually proposes a possible synergy between iron ions and  $\text{H}_2\text{S}$ . Therefore, the presence of *A. ferrooxidans* and release of iron ions from lava rock could enhance the removal rate of  $\text{H}_2\text{S}$  considerably.

In our previous work (Li et al., 2002; Martin et al., 2002), the maximum specific biomass growth rate ( $\mu_{\text{max}}$ ) obtained from the model calibration with the  $\text{H}_2\text{S}$  data from lava-rock biofilters at Cedar Rapids Water Pollution Control Facilities ( $0.27 \text{ h}^{-1}$ ) was slightly higher when compared to the value provided by the study conducted with *A. thiooxidans* at the same temperature ( $0.18 \text{ h}^{-1}$ ; Shinabe et al., 1995). A possible explanation is that a different, but more efficient, mechanism was responsible for the removal of  $\text{H}_2\text{S}$  in the lava-rock based biofilters. This mechanism could be supported by the use of iron in the biofiltration of odorous air emissions in the literature. For example, an iron-sponge medium, which consisted of hydrated iron oxide, soda ash, and limestone on wood shavings and chips that served as carriers, was used to effectively control odor emissions from a wastewater treatment plant in a pilot study (Zappi, 2001).

### Summary

Although further studies are still required to prove the specific mechanism(s) of  $\text{H}_2\text{S}$  oxidation in lava-rock biofiltration systems, it is believed that the presence of *A. ferrooxidans* and the release of  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  ions from the lava rock may contribute to the high removal rate of  $\text{H}_2\text{S}$  in a lava rock biofiltration system. This finding has direct benefit on the biofiltration of odorous air emissions in municipal, manufacturing, and agricultural settings.

Because of its porous structure and resistance to bed compaction, a biofilter packed with lava rock has a lower pressure drop and, thus, can typically be operated for a longer period of time before the packing material needs to be replaced, when compared to a biofilter packed with organic material. For existing biofilters seeking to improve removal efficiency, it may help to periodically spray an iron solution on the bed if bed compaction from the additional moisture does not pose a problem. If the biofilter bed suffers from compaction, it may be useful to replace the packing material with lava rock. A biofilter packed with lava rock has also been shown to remove significant quantities of reduced organic sulfur compounds (Martin et al., 2002).

A biofilter model (called Biofilter [Michigan Technological University, Houghton, Michigan]), which simulates the mass transport and biological reaction of odor-causing compounds (or VOCs) in a biofilter, has been calibrated and validated with  $\text{H}_2\text{S}$  and reduced organic sulfur compound data obtained from several biofilters that contained different packing media. It has also been incorporated to an easy-to-use software package (Li et al., 2002 and 2003; Martin et al., 2002 and 2004). The usefulness of the model in designing and improving operation of biofilters has been recently shown by Martin et al. (2004).

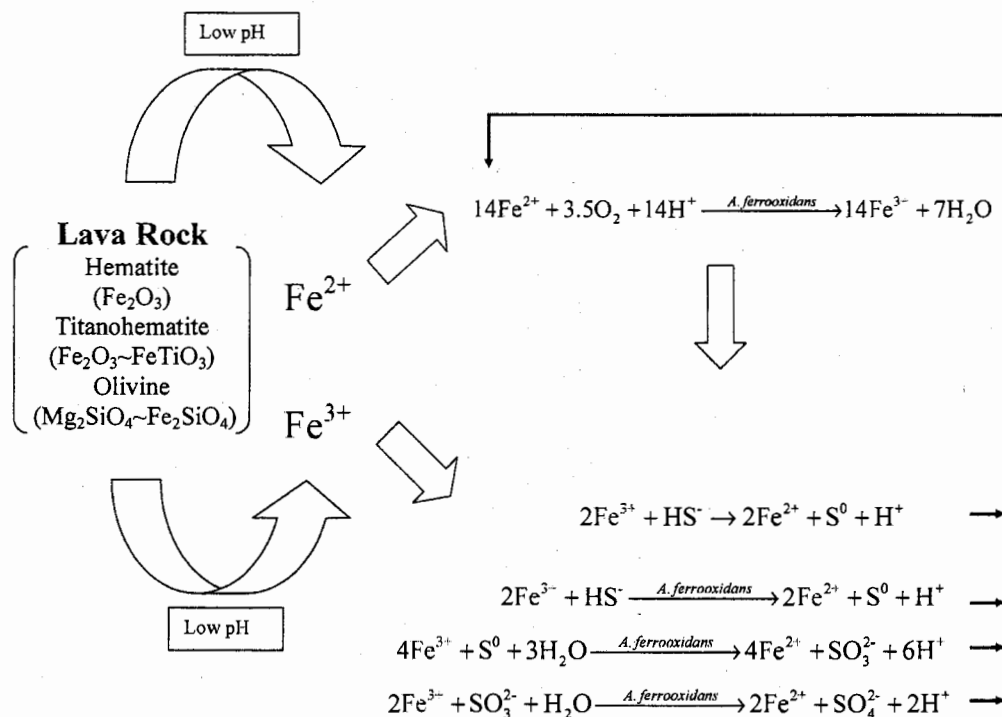


Figure 5—A proposed hydrogen sulfide removal mechanism in lava-rock-based biofilters.

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a similar position at Michigan Technological University. Donald Lueking is an associate professor in the Department of Biological Sciences at Michigan Technological University. James Mihelcic is a professor in the Department of Civil and Environmental Engineering at Michigan Technological University. Karl Peterson

Table 2—Reactions and equilibrium constants (25°C) selected for modeling the chemistry of the effluent rinse water from a lava-rock biofilter (equilibrium constants obtained from Benjamin, 2002).

Reaction	Equilibrium constant
$\text{H}_2\text{S}(\text{g}) \leftrightarrow \text{H}_2\text{S}(\text{aq})$ (3)	$H = 0.38$ (dimensionless)
$\text{H}_2\text{S}(\text{aq}) \leftrightarrow \text{H}^+ + \text{HS}^-$ (4)	$K_{a1} = 10^{-6.99}$
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$ (5)	$H = 30.2$ bar-L/mol
$\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ (6)	$K_{a1} = 10^{-6.35}$
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ (7)	$K_{a2} = 10^{-10.33}$
$\text{Fe}^{2+} + \text{OH}^- \leftrightarrow \text{Fe}(\text{OH})^+$ (8)	$\beta_1 = 10^{-9.50}$
$\text{Fe}^{2+} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_2^0$ (9)	$\beta_2 = 10^{-20.57}$
$\text{Fe}^{2+} + 3\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_3^-$ (10)	$\beta_3 = 10^{-31.00}$
$\text{Fe}^{2+} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_2^+$ (11)	$K = 10^{15.90}$
$\text{Fe}^{2+} + \text{HS}^- \leftrightarrow \text{H}^+ + \text{FeS}(\text{s})$ (12)	$K = 10^{3.92}$
$\text{Fe}^{2+} + 2\text{HS}^- \leftrightarrow \text{Fe}(\text{HS})_2^0$ (13)	$\beta_2 = 10^{8.95}$
$\text{Fe}^{2+} + 3\text{HS}^- \leftrightarrow \text{Fe}(\text{HS})_3^-$ (14)	$\beta_3 = 10^{10.99}$
$\text{Fe}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{FeSO}_4^0$ (15)	$\beta = 10^{2.25}$
$\text{Fe}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{FeCO}_3(\text{s})$ (16)	$K = 10^{-10.55}$
$\text{Fe}^{3+} + \text{OH}^- \leftrightarrow \text{Fe}(\text{OH})^{2+}$ (17)	$\beta_1 = 10^{-2.19}$
$\text{Fe}^{3+} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_2^+$ (18)	$\beta_2 = 10^{-5.67}$
$\text{Fe}^{3+} + 3\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_3^0$ (19)	$\beta_3 = 10^{-13.60}$
$\text{Fe}^{3+} + 4\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_4^-$ (20)	$\beta_4 = 10^{-21.60}$
$\text{Fe}^{3+} + 3\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_3(\text{s})$ (21)	$K = 10^{37.11}$
$\text{Fe}^{3+} + \text{SO}_4^{2-} \leftrightarrow \text{Fe}(\text{SO}_4)^+$ (22)	$\beta_1 = 10^{3.92}$
$\text{Fe}^{3+} + 2\text{SO}_4^{2-} \leftrightarrow \text{Fe}(\text{SO}_4)_2^-$ (23)	$\beta_2 = 10^{5.42}$

Table 1—Concentrations of concerned chemical species in the effluent rinse water from a biofilter packed with lava rock. The iron concentration was measured and the concentrations for the remaining ions were estimated.

Species	Concentration (M)
Fe <sup>2+</sup> and/or Fe <sup>3+</sup>	$1.84 \times 10^{-4}$
H <sup>+</sup>	$1.00 \times 10^{-3}$
OH <sup>-</sup>	$1.00 \times 10^{-11}$
HS <sup>-</sup>	$1.10 \times 10^{-9}$
CO <sub>3</sub> <sup>2-</sup>	$4.17 \times 10^{-15}$
SO <sub>4</sub> <sup>2-</sup>	$1.00 \times 10^{-6}$

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