Inhibition of hydrogen sulfide generation from disposed gypsum drywall using chemical inhibitors

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ABSTRACT

Disposal of gypsum drywall in landfills has been demonstrated to elevate hydrogen sulfide (H_2S) concentrations in landfill gas, a problem with respect to odor, worker safety, and deleterious effect on gas-to-energy systems. Since H_2S production in landfills results from biological activity, the concept of inhibiting H_2S production through the application of chemical agents to drywall during disposal was studied. Three possible inhibition agents – sodium molybdate (Na_2MoO_4), ferric chloride ($FeCl_3$), and hydrated lime ($Ca(OH)_2$) – were evaluated using flask and column experiments. All three agents inhibited H_2S generation, with Na_2MoO_4 reducing H_2S generation by interrupting the biological sulfate reduction process and $Ca(OH)_2$ providing an unfavorable pH for biological growth. Although $FeCl_3$ was intended to provide an electron acceptor for a competing group of bacteria, the mechanism found responsible for inhibiting H_2S production in the column experiment was a reduction in pH. Application of both Na_2MoO_4 and $FeCl_3$ inhibited H_2S generation over a long period (over 180 days), but the impact of $Ca(OH)_2$ decreased with time as the alkalinity it contributed was neutralized by the generated H_2S. Practical application and potential environmental implications need additional exploration.

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1. Introduction

Elevated hydrogen sulfide (H_2S) levels in biogas from landfills that accept construction and demolition (C&D) debris have created environmental and operational problems for operators of these facilities [1]. The H_2S results from the biological reduction of sulfate from disposed gypsum drywall ($CaSO_4 \cdot 2H_2O$), one of the major components of C&D debris [2,3]. Landfills provide an ideal environment for H_2S generation: the drywall provides sulfate, which is used as an electron acceptor by sulfate reducing bacteria (SRB); the environment tends to be anaerobic, moist, and warm; and wood, vegetation, and paper provide a carbon source. High concentrations of H_2S in the gas from C&D debris landfills have been reported in previous studies. Lee et al. [1], in a study of ten C&D debris landfills in Florida, measured H_2S concentrations in the range of less than 0.003–12,000 ppm in the surface soil vapor and from less than 0.003 ppm to over 50 ppm in ambient air above the landfill [1]. In laboratory experiments simulating C&D debris landfills, concentrations as high as 150,000 ppm have been measured [4].

Problems resulting from elevated H_2S concentrations in landfill gas are manifested in several manners. The concentrations in the gas are great enough to pose an acute health threat to workers exposed to the gas in confined spaces. Release of landfill gas to the atmosphere is expected to sufficiently dilute H_2S so not to pose an acute health risk due to ambient exposure, but these concentrations can result in strong odors and possibly contribute to chronic health issues [5]. Elevated H_2S concentrations are also problematic for landfills attempting to utilize biogas for energy production, as H_2S can contribute to rapid corrosion of gas handling equipment, hence necessitating sulfur removal. Hydrogen sulfide present in landfill gas also proves challenging when flared since H_2S coverts to SO_2 in the atmosphere, an air pollutant with its own regulatory and environmental issues.

The research reported here explored whether the addition of a chemical agent to gypsum drywall upon disposal could inhibit future H_2S production. Chemicals such as molybdate and ferric minerals are known to reduce biological H_2S production by suppressing SRB activity; accordingly, several researchers have investigated these chemicals for preventing H_2S generation in marine sediments, anaerobic digesters, and the petroleum industry [6,7]. The inhibition of H_2S generation from gypsum drywall using three separate chemical additives under simulated landfill conditions was investigated using both flask and column experiments, where flask experiments provided a quick evaluation of the effect of chemical inhibitors at different doses and the column experiments provided a longer-term assessment more comparable to landfill conditions. The chemical addition would be performed as part of landfill operations (e.g., spreading a chemical on drywall-rich loads of waste prior to burial), though a potential consideration

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is the direct incorporation of inhibiting agents into drywall products themselves.
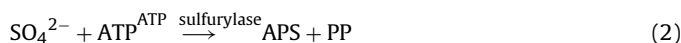
2. Mechanisms for inhibition of H₂S generation

Under anaerobic conditions such as those in a landfill, SRB utilize leached sulfate from gypsum drywall as an electron acceptor resulting in the production of sulfide Eq. (1) [8,9]. The biodegradable organic matter consumed by the SRB, represented in Eq. (1) as CH₂O, originate from organic wastes in the landfill (e.g., paper products, woody waste, food waste) as well as the drywall product (e.g., paper facing and backing, organic additives such as starch).

$$SO_4^{2-} + 2 \langle CH_2O \rangle \xrightarrow{SRB} H_2S + 2HCO_3^- \qquad (1)$$

Since this process is biological, H₂S generation can be minimized or prevented if the growth of SRB are slowed or stopped. SRB are anaerobic bacteria, widespread in anaerobic environments, and have been observed to occur in soil, water, sewage, oil and natural gas wells [9]. Postgate [8] reported that in order to cultivate SRB, the redox potential of the environment should be −100 mV or less and that the most effective and inexpensive inhibitor of SRB is oxygen. However, addition of air or aerated water is likely not practical at most landfills.

SRB prefer a neutral pH environment and are usually inhibited at pH values lower than 5.5 or higher than 9 [9]. Altering environmental pH by adding acid or alkali has been reported as a method of SRB control in industrial plants [8]. In simulated landfills, H₂S generation was reported to be reduced when drywall was co-disposed with alkaline concrete debris [10]. In terms of temperature, the optimal temperature range for SRB growth is between 30 °C and 37 °C [9] and most species of SRB die rapidly at temperatures above 45 °C [8,9]. However, landfills with large amounts of municipal solid waste (MSW) often reach temperatures greater than this, and H₂S production often remains an issue when large amounts of drywall are disposed.

As an alternative to providing an unfavorable environment for SRB growth, researchers have investigated SRB suppression through chemical contact. Chemical inhibitors of SRB activity have been reviewed and summarized by Saleh et al. [11], including antibiotics, detergents, dyes, mercurials, metal ions, complexes, nitrocompounds, phenolic substances, sulfate analogues, sulfoamides, and other miscellaneous substrates. The most common chemical inhibitor of SRB has been molybdate (MoO_4^{2-}) in the form of sodium molybdate (Na_2MoO_4); it has been extensively used as a selective inhibitor in lake, marine sediments, and anaerobic digesters [6,7]. Biological sulfate reduction by SRB includes three major steps: sulfate activation Eq. (2), sulfate reduction to sulfite Eq. (3), and sulfide formation Eq. (4) [12]. Since sulfate ion is very stable, it cannot be reduced without first being activated by adenosine triphosphate (ATP) Eq. (2). This reaction is catalyzed by the enzyme ATP sulfurylase, which catalyzes the attachment of the sulfate ion to a phosphate of ATP to form adenosine phosphosulfate (APS). As a stereo chemical analog of sulfate (SO_4^{2-}), molybdate (MoO_4^{2-}) can inhibit the ATP sulfurylase, resulting in the interruption of sulfate reduction [8].

$$SO_4^{2-} + ATP \xrightarrow[\text{sulfurylase}]{ATP} APS + PP \qquad (2)$$

$$SO_4^{2-} + APS + H_2 \rightarrow HSO_3^- + AMP + H^+ \qquad (3)$$

$$HSO_3^- + 3H_2 \rightarrow HS^- + 3H_2O \qquad (4)$$

Another SRB inhibition method involves stimulating growth of a competing group of anaerobic bacteria that utilize an electron acceptor other than sulfate; the addition of chemicals, such as ferric iron and nitrate, can stimulate the growth of iron reducing bacteria (IRB) and nitrate reducing bacteria (NRB) which can outcompete

SRB as these reactions are more favored thermodynamically [13]. Lovley and Phillips [13] found that the addition of ferric iron to sediment inhibited sulfate reduction by 86–100%. Ferric iron has the added benefit of helping control H₂S odor since its reduced form reacts with sulfide to form a low solubility iron sulfide mineral (this technique has been reported in use at wastewater treatment plants to control odor) [14]. Similarly, nitrate reduction has a large thermodynamic advantage over SRB for use of the same substrates [15], can increase redox potential, and has been used to prevent H₂S generation in the oil industry [16]. Some biocides (e.g., glutaraldehyde) have been used to prevent H₂S generation, but they tend to be costly and less effective because of the growth of SRB in protected niches [15,17].

3. Materials and methods

The H₂S generation inhibition potential of three different chemical agents was assessed in two different experiments, laboratory flasks and columns, each using size-reduced drywall. Multiple chemical doses were evaluated in the flask experiments, with the results used to select a dose for the column experiment.

3.1. Chemical inhibitor selection

The three chemical agents tested were sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), and hydrated lime ($Ca(OH)_2$). Sodium molybdate was selected because it is known to interrupt the sulfate reduction process. Ferric chloride was selected to provide an electron acceptor source for a more thermodynamically favored, competing bacterial population. Nitrate was not selected because iron was viewed as safer with respect to possible groundwater contamination. Hydrated lime was selected as a chemical to increase pH outside the range optimal for SRB activity.

For each inhibitor, four different solution concentrations were evaluated using laboratory flasks (Table 1). The chemical solutions were prepared by dissolving an appropriate amount of the solid chemicals into 1 L of deionized water. Based on previous research [18], the concentrations of Na_2MoO_4 solutions selected ranged from 2 mM (484 mg/L) to 20 mM (4,840 mg/L). No similar range of $FeCl_3$ concentrations was found in the literature, so a range of 5 mM (1,350 mg/L) to 500 mM (135,000 mg/L) was tested. A previous study by Xu et al. [3] found that 1% $Ca(OH)_2$ amended to sandy soils reduced H₂S generation in a field study. In the current study, four lower percentages (0.01%, 0.1%, 0.3%, and 0.5%) of $Ca(OH)_2$ were used to make different $Ca(OH)_2$ solutions (100, 1,000, 3,000, and 5,000 mg/L). Based on the flask test results, one concentration of each chemical was tested using laboratory-scale simulated landfill columns.

3.2. Preparation of drywall

The gypsum drywall was purchased from local hardware stores. First, the drywall was size reduced to square pieces (5 cm × 5 cm) using a power saw. For the flask experiments, the size-reduced drywall blocks (with backing and facing paper) were then ground into fine powder to improve the surface area using an Urschell mill (Fritsch, Germany). For the column experiments, the size-reduced drywall blocks were directly loaded into the columns.

3.3. Flask experiment

Each flask experiment was monitored over a 30-day period. As shown in Fig. 1, the experimental apparatus consisted of a 1-L glass flask (Cole-Parmer Inc.), a #9 rubber stopper (FisherSci. Inc.), two different lengths of glass tube, and two plastic valves (model 30600-01, Cole-Parmer). The glass tubes penetrated through the rubber

Table 1
Concentrations of chemical inhibitors in the flask experiment.

Chemical inhibitors	Amount of chemicals	
	Concentration (mM)	mg (chemical)/kg drywall
Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$)	2; 4; 10; 20	484; 968; 2,420; 4,840
Ferric chloride ($FeCl_3 \cdot 6H_2O$)	5; 10; 100; 500	1,350; 2,700; 27,000; 1,35,000
Hydrated lime ($Ca(OH)_2$)	1.3; 13.5; 40.4; 67.5	100; 1,000; 3,000; 5,000

stopper into the flask at different depths. Two plastic valves were connected to the tubes for flushing nitrogen and taking samples.

One hundred grams of the drywall powder was placed in each flask and 100 mL of inhibitor solution was added to the drywall powder to reach a moisture content of 50%. The rubber stopper was tightly capped and pure nitrogen gas was flushed into the flask for a minimum of 5 min to remove air; the valves were immediately closed to keep the flask under anaerobic conditions. The flask was placed into an incubator (FisherSci. Inc.) with a constant temperature of 35 °C. Gas samples were collected using a glass syringe from the gas sampling port and transferred into Tedlar bags for gas dilution and H_2S concentration analysis. No seed was added in the experiments as SRB are expected to be widespread in the environment.

3.4. Column experiment

Column experiments were used to evaluate the longer-term inhibition resulting from each chemical using a dose selected from the results of the flask experiments. Similar laboratory column experiments were previously conducted and reported in research on the effect of co-disposed C&D debris on H_2S generation and

to evaluate H_2S removal by cover materials in simulated landfill conditions [4,10]

In the present study, eight columns were constructed from PVC pipe; all of the columns had a height of 50 cm and a diameter of 10 cm. As shown in Fig. 2, a 10-cm slip cap was fitted on the end of each column and a MPT hose labcock valve (Asahi-America) was installed in the slip cap for leachate drainage. A 10-cm deep layer of gravel was placed in each column to serve as a leachate reservoir. A geotextile was then placed over the gravel layer to separate it from the waste layer. The drywall blocks were pretreated by immersing them in the inhibitor solutions over night. Approximately 750 g of pretreated wet gypsum drywall blocks were loaded into each column, forming a 30 cm waste layer with a bulk density of 318 kg/m³. Four hundred milliliter of deionized water was added to each column to reach a moisture content of approximately 50%. The only carbon source available was the paper facing and backing from the
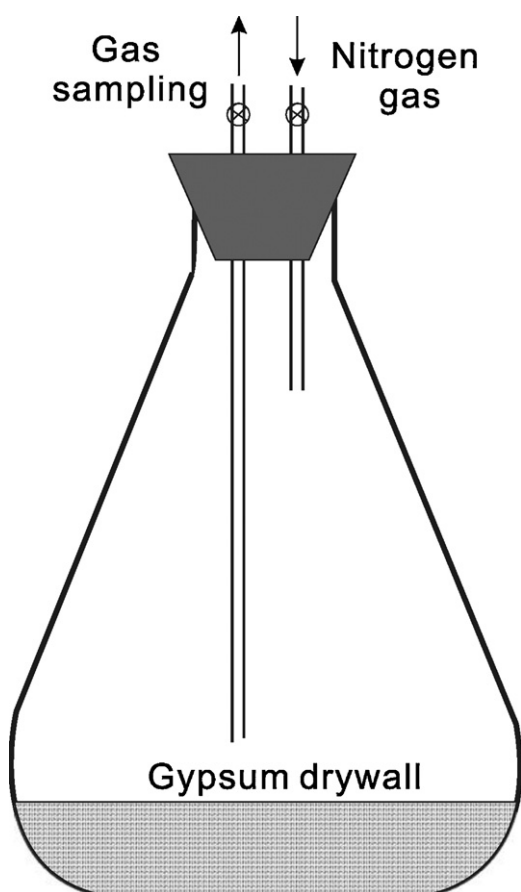

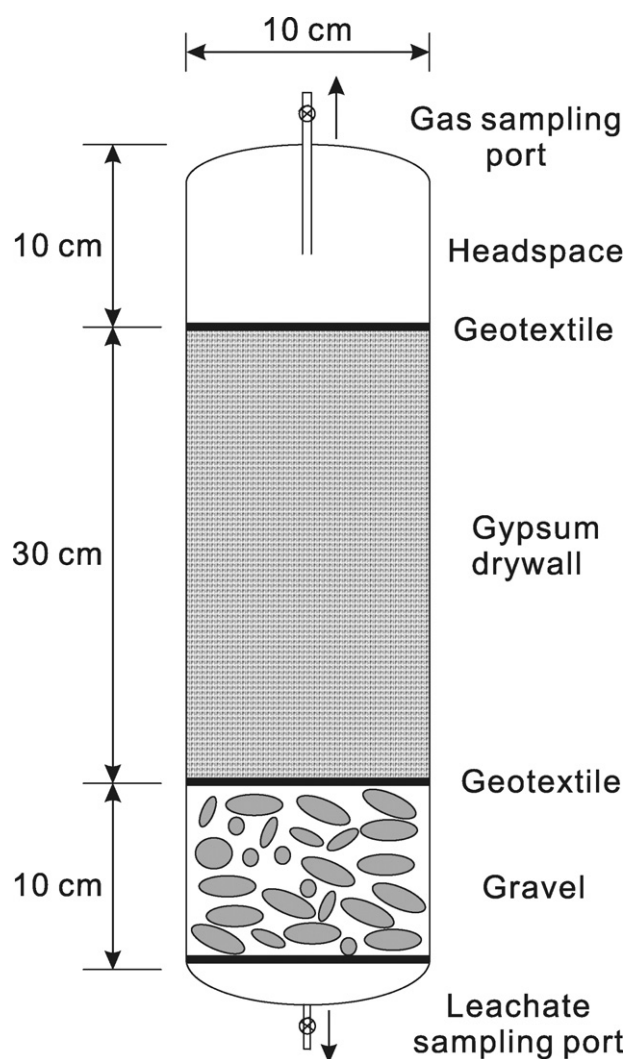**Fig. 1.** Schematic of flask experiment apparatus.

Fig. 2. Schematic of laboratory inhibition column experiment.

gypsum drywall. A 10-cm slip cap was fitted on the top of each column with a final headspace height of 10 cm. Similar to the flask experiment, no seed was added.

Gas samples were collected from the headspace using another MPT hose labcock valve (Asahi-America) installed on the top slip cap of each column. Nitrogen gas was flushed for 10 min from the bottom to remove air and all of the valves were closed to maintain the columns under anaerobic conditions. The columns were monitored for six months. To avoid changing the inhibitor concentration, no water was added during the experiment.

3.5. Sample collection and analysis

In the flask experiment, gas samples were collected three times per week over the 30-day period. In the column experiment, gas samples were collected from the columns twice per week over six months. Gas samples were analyzed for H_2S using a Jerome 631-X H_2S analyzer (Arizona Instruments, AZ). The Jerome meter's internal pump pulls gas samples over a gold film sensor whose electrical resistance is proportional to the concentration of H_2S in the sampled gas. The Jerome meter has a detection range of 0.003–50 ppm and is factory calibrated annually using National Institute of Standards and Technology (NIST) methods. Before analyzing the gas samples, the Jerome meter was checked using a 25 ppm H_2S standard (Air Liquid America Corp.) and laboratory air.

In the column experiment, leachate samples were collected monthly by gravity draining the leachate from the bottom of the columns. Six samples were collected over the experimental period for leachate analysis. Sulfate was analyzed using a Dionex DX 500 ion chromatograph according to EPA SW-846 Method 9056. Molybdenum (Mo) was measured using EPA method 6010B by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The method used for pH was equivalent to Standard Method 4500-H. Blanks, replicates, and calibration check samples were performed as appropriate. Both flask and column experiments were conducted in duplicate; average concentrations are presented in the following sections.

4. Results and discussion

H_2S generation from gypsum drywall with no amendments is discussed first, followed by the inhibition of H_2S generation by each chemical agent. The environmental implications of these inhibitors are then discussed.

4.1. Hydrogen sulfide generation from gypsum drywall

Fig. 3 presents the change of average H_2S concentration over a 30-day period from flask versus column experiments, demonstrating the H_2S generation occurred more rapidly in the flask than in columns. Average concentrations in the flask experiment increased from 1.1 ppm at day 1 to 11,550 ppm at day 8 and continued to increase throughout the experimental period, reaching a maximum concentration 67,500 ppm at day 28. In the column experiment, gas sampling began on day 6 with a concentration of 0.5 ppm; by day 30, the H_2S concentration reached 11,300 ppm and fluctuated near 20,000 ppm at the end of the experiment (about 180 days). The more rapid generation and greater concentrations of H_2S in the flask experiment are believed to have resulted from the warmer temperature (35 °C) and finer gypsum drywall particle size, which stimulated SRB to rapidly grow in a short period (the column temperatures were not controlled); biological sulfate reduction rates are reported to depend on temperature [9]. The maximum H_2S concentrations in the columns (20,000 ppm) are comparable, though somewhat lower, than those measured in previous laboratory column experiments (approximately 30,000 ppm in Yang et al. [10]
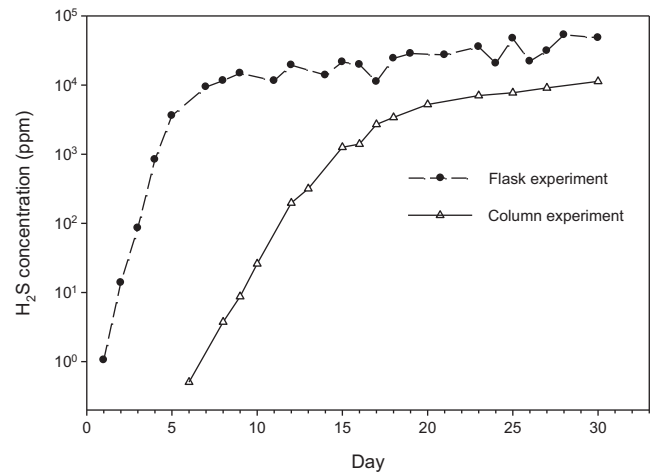

Fig. 3. Comparison of the average H_2S concentration from gypsum drywall in the flask and column experiments.

and 80,000 in Plaza et al. [4]); these differences likely result from variations in experimental conditions among the studies.

Both the flask and column tests demonstrate that gypsum drywall alone can, with the activity of SRB, result in large concentrations of H_2S. Although biological sulfate reduction requires an organic carbon source, the paper facing and backing from the gypsum drywall (approximately 10% the mass of the drywall) provides enough organic carbon to produce large H_2S concentrations [4]. Since H_2S concentrations in the range of 500–1000 ppm can be lethal to humans, these concentrations are certainly of environmental significance.

4.2. Effect of Na_2MoO_4 on H_2S generation

Average H_2S concentrations with time resulting from the application of Na_2MoO_4 are presented in Fig. 4A and B, for the flask and column experiments, respectively. Compared to H_2S concentrations observed with untreated gypsum drywall, concentrations in flasks where drywall was exposed to Na_2MoO_4 were low, on the order of approximately 10 ppm over most of the experimental period, three orders of magnitude lower than the control flask. The highest H_2S concentration measured was 26.3 ppm, detected in the 2 mM (484 mg/L) Na_2MoO_4 flask at day 30 (the lowest molybdate dose). Average H_2S concentrations in the 2 mM (484 mg/L), 4 mM (968 mg/L), 10 mM (2,420 mg/L), and 20 mM (4,840 mg/L) Na_2MoO_4 flask were 8.6 ppm, 5,5 ppm, 2.9 ppm, and 4.8 ppm, respectively (Table 2). Statistical analysis found that the average H_2S concentration in the 10 mM (2,420 mg/L) flask experiment was significantly less than the other flasks, thus the 10 mM (2,420 mg/L) Na_2MoO_4 solution was selected for the column experiment. It was determined that there was no significant benefit to increase to the 20 mM (4,840 mg/L) concentration.

In the column experiment, gypsum drywall was treated by immersing the pieces in a 10 mM (2,420 mg/L) Na_2MoO_4 solution over night. The generation of H_2S from the treated drywall was effectively inhibited, resulting in an average H_2S concentration of 0.27 ppm (Fig. 4B). In the control columns, the H_2S concentration was approximately 20,000 ppm after the first month, four to five orders of magnitude higher than the inhibition columns. The average leachate pH and sulfate concentrations from the control and the inhibition columns were similar. Sulfate concentrations in the control columns averaged 1,300 mg/L with a corresponding pH of 6.7; sulfate concentrations in the inhibition columns averaged 1,260 mg/L with a corresponding pH of 6.6. The sulfate concentrations were at the solubility limit of sulfate from gypsum

Table 2
H_2S concentrations in the flasks with addition of sodium molybdate.

H_2S concentration (ppm)	Sodium molybdate concentrations				
	0 mM	2 mM	4 mM	10 mM	20 mM
Average	$27,304 \pm 21,365$	8.6 ± 7.2	5.5 ± 3.7	2.9 ± 1.6	4.8 ± 2.7
Minimum	0.6	0.9	0.7	0.5	0.4
Maximum	67,500	26.3	11.1	4.3	10.4

(approximately 1,300 mg/L [1]). The average leachate Mo concentration was 23.6 mg/L in the inhibition columns and 0.07 mg/L in the control columns. Inhibition of H_2S generation from gypsum drywall resulted from the Na_2MoO_4, not from the leachate pH. Possible environmental implications from the elevated Mo concentrations are discussed later.

4.3. Effect of $FeCl_3$ on H_2S generation

Fig. 5A and B presents the average H_2S concentrations versus time for the flask and column experiments where $FeCl_3$ solution was used. All $FeCl_3$ solutions resulted in a decrease in H_2S concentration, but the resulting concentration trends differed (more so than observed with the Mo experiments). At day 14, the H_2S concentration was 2,900 ppm in the 5 mM (1,350 mg/L) $FeCl_3$ flask and 110 ppm at the 10 mM (2,700 mg/L) $FeCl_3$ flask, while the concentrations were only 6.65 ppm and 0.21 ppm in the 100 mM (27,000 mg/L) and 500 mM (1,35,000 mg/L) $FeCl_3$ flasks, respectively. In the flasks with lower doses of $FeCl_3$, 5 and 10 mM (1,350 and 2,700 mg/L), H_2S concentrations initially lagged behind those in the control flask, but reached similar levels at the end of the experiment. The flasks with higher $FeCl_3$ doses, 100 and 500 mM (27,000 and 1,35,000 mg/L), resulted in very low H_2S concentrations throughout the 30-day period, with concentrations fluctuating near 1 ppm. Since higher $FeCl_3$ concentrations resulted in more inhibition, the 500 mM (1,35,000 mg/L) solution was selected for the column experiment.

Drywall treatment with the 500 mM (135,000 mg/L) $FeCl_3$ solution resulted in a nearly complete inhibition of H_2S production. The average H_2S concentration was only 0.08 ppm in the inhibition columns compared to approximately 20,000 ppm in the control columns. The average leachate sulfate concentration in the $FeCl_3$ columns was 1,500 mg/L, slightly higher than the control columns. The leachate pH, however, was much lower (pH 1.9) than the control columns (pH 6.7). The 500 mM (1,35,000 mg/L) $FeCl_3$ solution was acidic (pH 0.84). The pH of the environment resulting from the mixture of drywall with a $FeCl_3$ solution will depend on the relative amount of solution retained, the buffering capacity of the drywall, and any additional water added. The environment in the
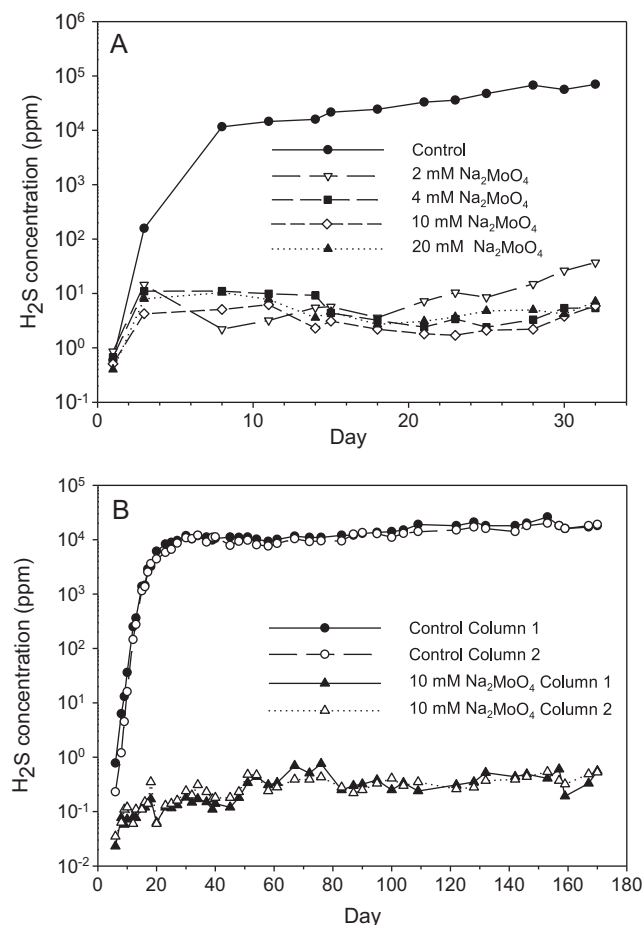

Fig. 4. The inhibition effect of Na_2MoO_4 on H_2S generation. (A) The flask experiment results. (B) The column experiment results.
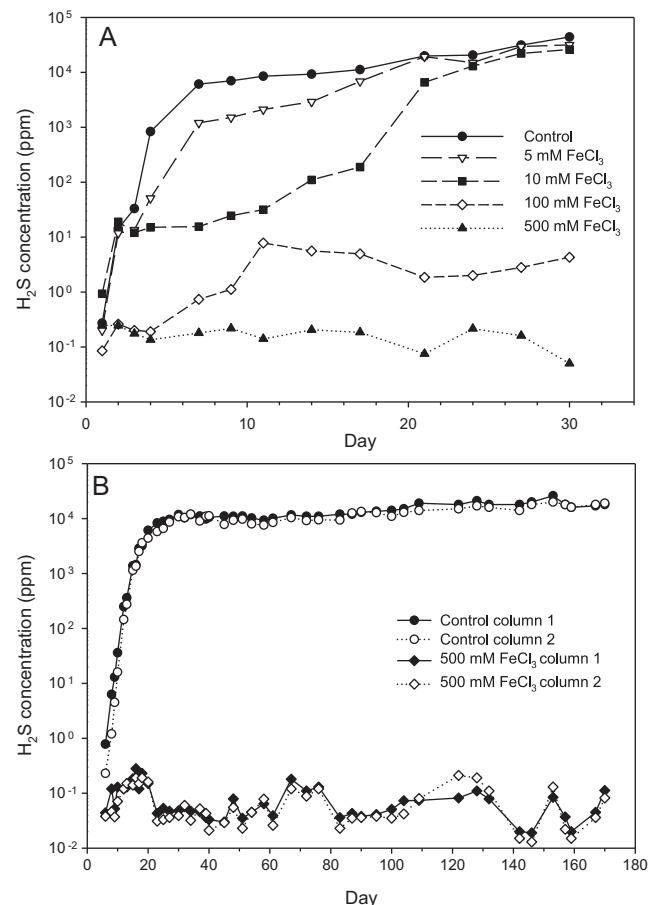
Fig. 5. The inhibition effect of $FeCl_3$ on H_2S generation. (A) The flask experiment results. (B) The column experiment results.

columns created by the 500 mM (1,35,000 mg/L) solution in this experimental setup remained acidic throughout.

Ferric iron was selected as a candidate inhibitory agent because of its potential to affect biological sulfate reduction by stimulating growth of IRB. The iron reduction process is more thermodynamically favorable than the sulfate reduction process, and thus under some environmental conditions, IRB should outcompete SRB by consuming concentrations of organic substrates at a greater rate. However, in the column experiment, SRB inhibition by $FeCl_3$ addition is not attributed to this mechanism, but rather to the low pH. The pH range for IRB growth has been reported from 4.8 to 8.2 (optimum 6.3–6.5 [19]) and for SRB growth from 5.5 to 9.0 [9]. SRB and IRB activity should both have been suppressed by the acidic column environment. In addition, $FeCl_3$ is also an oxidant for oxidation dehydrogenation, which may increase the redox potential to the level unfavorable for SRB growth [20,21].

To determine whether the competition of IRB might have played a role at lower $FeCl_3$ doses, the results of the flask experiment were examined in more detail. Although all four concentrations of $FeCl_3$ solution used in this study were acidic, after contact with the ground drywall, the pH of the mixtures increased (Table 3). For example, the pH of 5 mM (1,350 mg/L) $FeCl_3$ solution was 2.6, while the pH of the drywall and 5 mM (1,350 mg/L) $FeCl_3$ mixture was 6.9. Under this pH condition, both IRB and SRB can grow and compete for the same organic carbon. The IRB can outcompete the SRB, thus the H_2S generation was initially inhibited (Fig. 5A). After the ferric iron was reduced to ferrous iron by IRB, the activity of SRB dominated, increasing H_2S concentrations in the flask (Fig. 5A). Based on these results, although lower concentrations of $FeCl_3$ may inhibit H_2S generation by stimulating IRB growth, H_2S generation resumes after ferric iron is consumed.

4.4. Effect of Ca(OH)$_2$ on H$_2$S generation

Average H_2S concentrations versus time are presented in Fig. 6A and B for tests using $Ca(OH)_2$. Hydrogen sulfide concentrations inside the flasks with lower $Ca(OH)_2$ doses, 1.3 and 13.5 mM (100 and 1,000 mg/L), were only slightly lower than in the control flasks. At day 16, average H_2S concentrations were 19,800, 18,100, and 16,900 ppm in the control, 1.3 mM $Ca(OH)_2$, and 13.5 mM $Ca(OH)_2$ flasks, respectively. However, higher concentrations of $Ca(OH)_2$ – 40.4 and 67.5 mM (3,000 and 5,000 mg/L) – did result in reduced H_2S concentrations. At day 16, H_2S concentrations were 44 ppm and 1.1 ppm in the 40.4 mM (3,000 mg/L) and 67.5 mM (5,000 mg/L) $Ca(OH)_2$ flasks, respectively. Hydrogen sulfide concentrations started to increase in the 40.4 mM (3,000 mg/L) $Ca(OH)_2$ flask with time, increasing from 48 ppm at day 21 to 420 ppm at day 30; the inhibition effect became weaker as the experiment progressed. Based on these results, the 67.5 mM (5,000 mg/L) $Ca(OH)_2$ solution (0.5% $Ca(OH)_2$) was selected for the column experiment.

Hydrogen sulfide concentrations from columns containing drywall treated with $Ca(OH)_2$ varied over the experimental period (Fig. 6B). The average H_2S concentration was 0.2 ppm during the first 40 days, but increased to 5,300 ppm during the period from day 61 to day 170. Similar to the flasks, SRB activity was initially suppressed, but over time increased. Average leachate sulfate concentrations from the control and the $Ca(OH)_2$ columns were similar, 1,300 and 1,250 mg/L, respectively. Leachate pH in the $Ca(OH)_2$ columns decreased throughout the experimental period (Fig. 7). With the decreasing leachate pH from 12.0 at day 6 to 6.9 at day 171, H_2S concentration increased from 0.071 to 9,350 ppm.

The initial high pH environment suppressed SRB activity, resulting in low H_2S concentrations in the first month. However, since
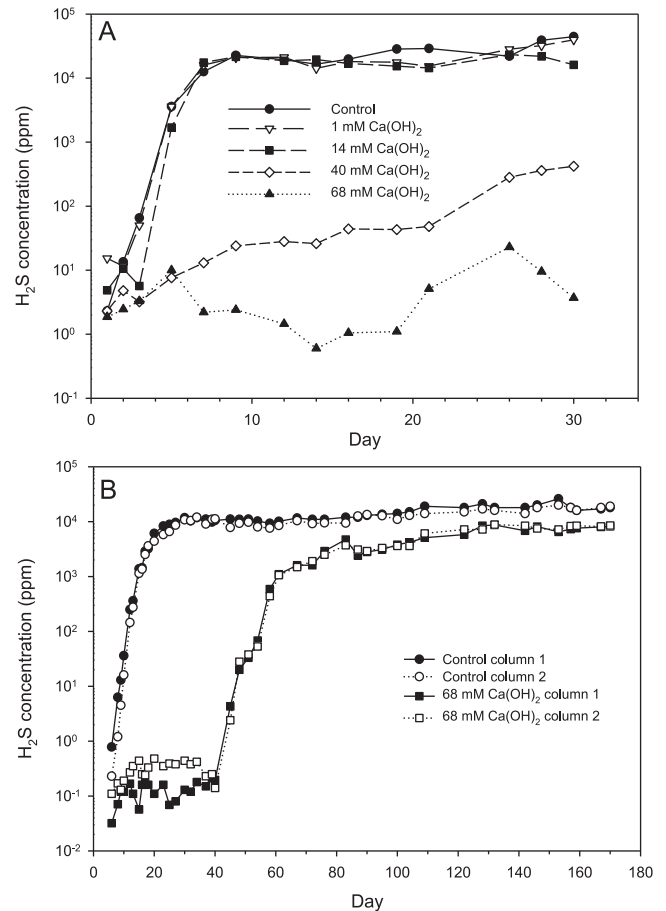

Fig. 6. The inhibition effect of $Ca(OH)_2$ on H_2S generation. (A) The flask experiment results. (B) The column experiment results.

some of the generated H_2S dissolves into the column leachate, the pH decreases. As pH in the columns decreased, SRB activity responded and more H_2S was generated, furthering the pH decrease and the increase in H_2S generation (Fig. 7). At the end of the experiment, column leachate pH became neutral and the H_2S concentrations correspondingly increased to over 10,000 ppm. The results showed that $Ca(OH)_2$ could be used to inhibit H_2S generation from gypsum drywall, but the inhibition effect decreases over time as the $Ca(OH)_2$ is neutralized.
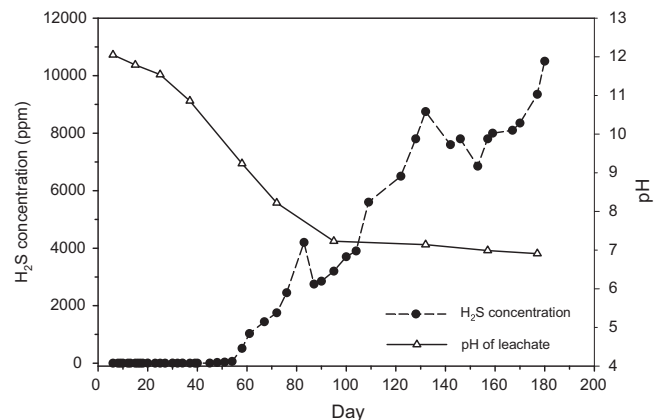

Fig. 7. Change of average H_2S concentrations and average leachate pH in the lime columns.

Table 3
pH change of ferric chloride solutions after mixing with gypsum drywall.

FeCl$_3$ concentration	5 mM	10 mM	100 mM	500 mM
pH of FeCl$_3$ solution	2.58	2.34	1.62	0.84
pH of the mixture of FeCl$_3$ and drywall	6.91	6.84	5.53	1.77

4.5. Examination of environmental implications

All three chemical agents demonstrated an ability to inhibit biological H$_2$S generation from gypsum drywall. This suggests that they may provide a useful tool for landfill operators to reduce H$_2$S concentrations that might otherwise occur in landfill gas. However, in addition to considering the efficacy and duration of the inhibition, other issues, such as cost-effectiveness and environmental impacts, would need to be weighed when considering whether to apply a chemical inhibitor agent.

The addition of lime to loads of drywall disposed in landfills has previously been suggested as a tool to control H$_2$S odor [22]. While the column experiment showed that the inhibition effect of Ca(OH)$_2$ might diminish with time, lime represents the agent with the least probable environmental impact. Several common waste materials placed in landfills have alkaline characteristics similar to lime (e.g., concrete, fly ash, lime sludge, lime rock). Elevated groundwater pH could conceivably be a concern at unlined landfills, but in most cases the overall landfill pH would tend to neutralize sources of high pH leachate.

Ferric chloride addition at low levels only suppressed SRB activity temporarily. Higher concentrations decreased H$_2$S more effectively because of the low pH environment created (not IRB outcompeting SRB). The application of high concentrations of FeCl$_3$ solutions is probably not practical to implement at landfill operations because of its corrosive characteristics. Further research to investigate the inhibition effect of other ferric chemicals on H$_2$S generation, agents that would not have such a dramatic impact on pH, may be worthwhile. Nevertheless, given the large amount of sulfate in drywall, it might not be feasible to reduce H$_2$S by fostering a competing group of bacteria.

Sodium molybdate was very effective at inhibiting SRB activity. Molybdenum does have potentially toxic properties at elevated concentrations, however, so landfill application must be assessed from the perspective of possible environmental contamination. One simple measure of potential Mo risk is to compare the Mo concentration in the drywall to typical human health risk thresholds. For example, based on the amount of Na$_2$MoO$_4$ solution sorbed to the drywall in the column experiment, the Mo concentration in the treated drywall was approximately 450 mg/kg. This compares to Florida's residential direct exposure risk threshold for Mo in soil of 440 mg/kg. From this perspective, the added Mo concentrations do not suggest a great risk. The leachate from the columns possessed an average Mo concentration of approximately 24 mg/L, much greater than the groundwater standard of 0.035 mg/L. While leachate Mo concentrations would be expected to become diluted in an actual landfill and attenuated by underlying soils [23], the potential for environmental contamination, particularly for unlined landfills, demands thought and additional investigation.

A final consideration is the method in which a chemical agent would be applied. This research utilized an aqueous solution containing the agents as the addition mechanism. A landfill could implement this using standard water spraying or spreading equipment. Alternatively, dry materials could be added and mixed to loads as they are disposed, perhaps in a manner similar to common practices for cover soil application. Finally, an intriguing possibility is the incorporation of inhibitory agents directly into the drywall; clearly many other factors would need to be evaluated in assessing the feasibility of this approach.

5. Summary and conclusions

In this study, three chemical agents were evaluated to assess their potential for inhibiting H$_2$S generation from landfilled gypsum drywall. Flask experiments provided an assessment of a range of chemical doses over a limited duration, and column experiments allowed a longer-term assessment of H$_2$S inhibition under conditions more representative of landfill conditions.

All three chemical agents resulted in reduced H$_2$S production. Assuming that the molybdate effect followed the inhibitory mechanisms previously described in the literature, Na$_2$MoO$_4$ reduced H$_2$S generation by inhibiting ATP sulfurylase to interrupt the sulfate reduction process. Ferric chloride and Ca(OH)$_2$ affected H$_2$S generation by creating a pH environment outside the suitable range for SRB growth. Inhibition due to increased pH by lime addition was expected. The low pH impact of FeCl$_3$ was not the originally targeted mechanism for this agent. The ferric iron target mechanism was to provide an alternative electron acceptor to sulfate so that a competing group of bacteria could grow. When conditions in the flask experiments did provide a suitable pH for SRB and IRB activity in the presence of added ferric iron, SRB activity was suppressed initially by IRB competition, but became dominant when the added ferric iron was used up.

Lime addition, though it exhibited a decrease in effectiveness with time, posed the least potential environmental concerns. Molybdate addition was very effective, but concerns regarding possible impact on groundwater quality demand additional consideration and analysis. The addition of a FeCl$_3$ solution successfully suppressed H$_2$S generation, but this occurred because of a reduced pH, not by fostering competitive bacteria. The use of other forms of ferric iron (those that do not impact pH to the same extent) warrants additional exploration. Overall, the results justify additional exploration of this technique, particularly in field-scale applications (in controlled settings). The potential of incorporating inhibitory agents into the original drywall products also merits further consideration.

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