Purity and Poison Gas: Investigating the Relationship between Gypsum Purity and Hydrogen Sulfide Production under Anaerobic Conditions

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Abstract

Gypsum is a naturally occurring crystalline mineral that can also be generated synthetically. Gypsum dihydrate ($CaSO_4 \cdot 2H_2O$) is most widely known for its use in wallboard in the construction industry. As residential and commercial construction waste is produced, wallboard is deposited along with other materials in construction and demolition (C&D) landfills where anaerobic (low oxygen) conditions and the presence of sulfate-reducing bacteria promote the decomposition of wallboard/gypsum into hydrogen sulfide gas (H_2S). Due to local and state regulations on odor control, these C&D sites are required to routinely monitor their fill for hydrogen sulfide gas. One method of detection is by surveying the air around the site using a portable H_2S-sensitive gold-film instrument, such as Arizona Instrument's Jerome® 605 Hydrogen Sulfide Gas Analyzer (J605®). In this paper, we demonstrate that as gypsum decomposes in the presence of sulfate-reducing agents, hydrogen sulfide is produced and gypsum purity degrades. Gypsum purity can be determined from the amount of chemically bound water that is available within a sample of gypsum. Measuring this bound moisture via loss-on-drying analysis (MAX® 5000XL) gives a reliable measurement of gypsum purity and can offer a way to predict the amount of H_2S that will be produced under anaerobic conditions.

Introduction

Calcium Sulfate ($CaSO_4$) more commonly known as gypsum is a naturally occurring white crystalline mineral that has many different uses and applications.[1] When water is added to gypsum, the resulting gypsum paste can be molded and shaped into various forms and dried to maintain its shape. The word 'gypsum' is derived from the Greek word for plaster, which is telling of its initial use as wall plaster during the ancient Greek and Roman empires.[2] In the late 1800's gypsum paste was molded between two sheets of paper board and dried to create the first functional wallboard.[3] Gypsum in its hydrated form ($CaSO_4 \cdot 2H_2O$) is used in the construction industry for fire resistance in buildings. Outside of the construction industry, gypsum is used in the food and fertilizer industry for calcium and sulfate fortification respectively.

Although gypsum has many applications in various fields, when it is eventually deemed unusable, it ends up in a landfill along with other construction debris. These construction and demolition (C&D) landfills promote a low oxygen environment (anaerobic) for any product buried deep within the fill.[4] When gypsum is buried within the pile it is metabolized by specialized sulfate-reducing bacteria via fermentation. Coupled with various carbon sources found within a C&D landfill (paper, adhesives, organic debris) the bacteria begin producing hydrogen sulfide according to the equation below.[4] For every 4 grams of gypsum that decompose, 1 gram of hydrogen sulfide is produced.[5]

Equation 1

$$Organic\ Matter + [SO_4]^{2-}_{(aq)} + H_2O_{(l)} \rightarrow H_2S_{(g)} + CO_{2(g)}$$

Hydrogen sulfide (H_2S) is a hazardous, colorless gas notorious for its 'rotten egg' odor that is detectable even at low levels.[6] A number of instruments are available that measure toxic gas in the part per million (ppm) range, but there is a need to detect and quantify hydrogen sulfide in the much lower parts per billion (ppb) concentrations because the human odor threshold of detection of H_2S is 8 ppb.[7] To control this problem many state and local regulations limit the amount of detectable H_2S in the environment, especially if a C&D landfill is nearby. The Jerome® 605 Hydrogen Sulfide Gas Analyzer is a portable gold-film sensing instrument which is used to survey C&D sites where H_2S odors are suspected.

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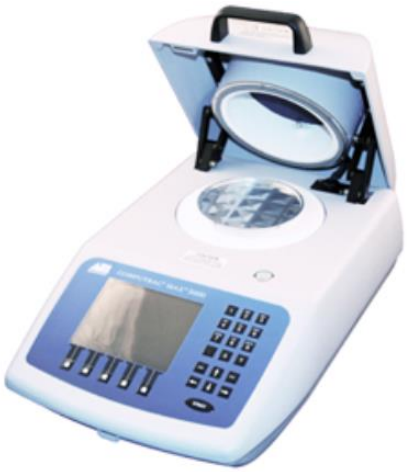
Jerome® 605 Hydrogen Sulfide Gas Analyzer

Although there are various forms of Gypsum (Anhydrous, Hemihydrate, Dihydrate,) with varying levels of purities, this paper focuses on pure synthetic gypsum dihydrate ($CaSO_4 \cdot 2H_2O$). Focusing on pure synthetic gypsum eliminates extraneous variables that may interfere with the results of this study. Variables such as glue & paper content, variable purity samples of gypsum and non-homogenous sampling could be potential sources of error that could be analyzed in a future study. When discussing the byproducts of gypsum it is important to address the starting concentration of the sulfate anion available to sulfate-reducing bacteria, which can be inferred from the purity value of gypsum.[4] Although there are several wet chemical methods for determining gypsum quality, one fast and reliable method utilizes a rapid loss-on-drying instrument.[8] Gypsum dihydrate has two levels of hydration. One level of hydration is 'free' moisture which describes the water that is adsorbed to the surface of the gypsum sample. This level of moisture may fluctuate drastically if the sample is a powder or slurry. This free moisture will evolve at temperatures between 40 - 80°C.[9] The second level of hydration is 'bound' moisture. This moisture describes the chemical association of the dihydrate water molecules to the sulfate anion of the calcium sulfate. This moisture level is directly proportional to the concentration of calcium sulfate and does not fluctuate based on environmental moisture. This bound water evolves at 240°C and the resulting percent moisture content can be multiplied by 4.778 to determine the % purity of gypsum.[9]



Computrac® MAX® 5000XL Rapid Loss-on-Drying Analyzer

The Computrac® MAX® 5000XL is a rapid loss-on-drying analyzer that is widely used in the gypsum industry to determine gypsum purity. The MAX® 5000XL is capable of heating samples to 600°C, and can start testing at room temperature, making it an ideal candidate for testing gypsum for free and bound moisture. Additionally, the analyzer provides real time measurements during analysis, and testing criteria can be optimized. The MAX® 5000XL also can test for free and bound moisture simultaneously, and can output the purity of the gypsum following the test, preventing manual calculation error by technicians conducting the analysis.

The objective of this research paper is to couple both methods of analysis to observe the relationship between the purity of gypsum (calcium sulfate dihydrate) and hydrogen sulfide concentration as a sample is fermented by sulfate-reducing agents (e.g. bacteria). The scope of this research may be beneficial for industrial hygienists concerned with C&D landfill H_2S levels or for incoming gypsum processing plants who suspect poor quality gypsum.

Methods/Results

See 'Appendix A' for sulfate-reducing culturing methods.

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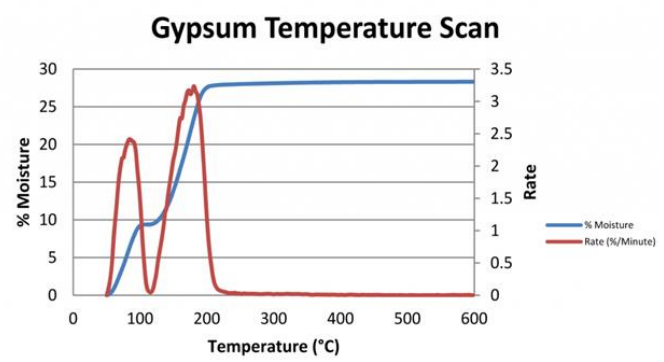
Measuring Gypsum Purity

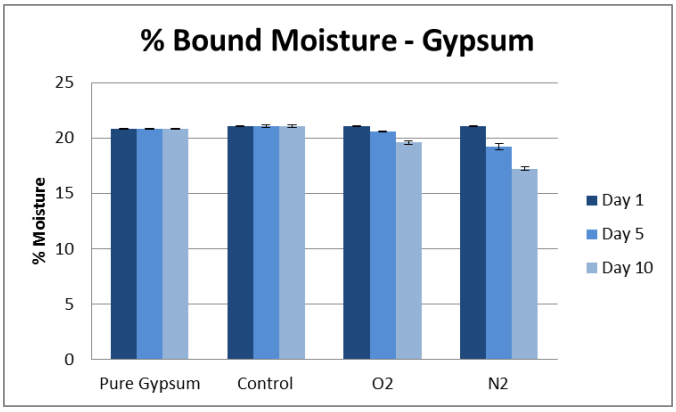
The MAX® 5000XL has the ability to perform a slow temperature ramp allowing for different levels of hydration to evolve from a sample. The graph shown below is an example of the pure synthetic gypsum ($CaSO_4 \cdot 2H_2O$) during a temperature scan to 600°C.[10]



The red line demonstrates the rate (%/min) of weight loss during the temperature scan (10°C/min). From this temperature scan, it becomes evident that the bulk of the free moisture evolves at approximately 80 °C, while the bound moisture (which is indicative of the gypsum purity) evolves at 240°C. The MAX® 5000XL allows the user to have two separate but linked tests on the same sample. Therefore, when pure synthetic gypsum was run in triplicate, an average of 20.84% moisture was detected from the second bound moisture peak indicating a gypsum purity of 99.6%. This purity value does not represent a true composition of gypsum within a landfill.

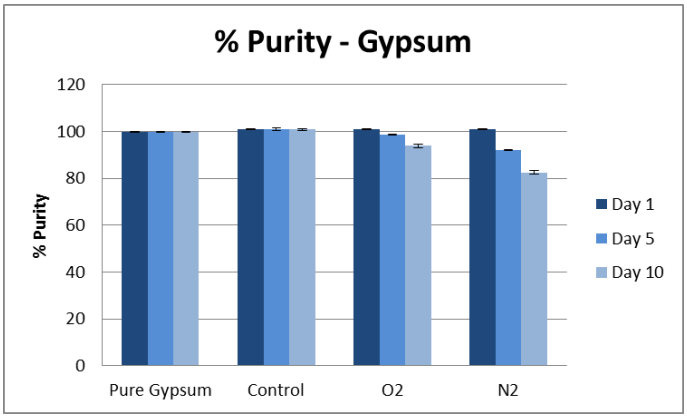
In order for fermentation to occur, there must also be a carbon source. Carbon within a C&D landfill usually comes from paper, adhesives or other organic debris mixed in with discarded wallboard. To simulate a carbon source found in a landfill, 10% calcium citrate was added and homogenized with the 99.6% synthetic gypsum powder (30g calcium citrate, 270 g gypsum) and used as the control stock for the rest of the experiment. Citrate is commonly used as a simple carbon source for anaerobic bacteria to utilize during fermentation.[11]

Figure 1



For the 'control', 10 mL of sterile media A was added to 100 g of the control gypsum stock (gypsum + citrate) in a 500 mL Erlenmeyer vacuum flask. The headspace of the vial was displaced with pure nitrogen gas for 10 minutes then securely capped. This control vessel has all theoretical components for anaerobic fermentation of gypsum (sulfate source, carbon source, low oxygen environment) but is void of any active sulfate-reducing agents. Two other vessels were generated from the same control stock but with 10mL of incubated 'media A' soil extract.

Figure 2



These two vessels were labeled 'O_2' & 'N_2' corresponding to the composition of the headspace above the inoculated slurry. The 'O_2' vessel contains

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all components for gypsum fermentation (including sulfate-reducing agents) but in atmospheric conditions (oxygen rich). The 'N_2' contains all components for gypsum fermentation without the presence of oxygen (nitrogen purge). All experimental vessels were stored in the incubator at 45°C in-between testing and re-purged (if necessary) with nitrogen gas as sample was taken.[12] Out of the ~100g sample from each vessel, ~7-8g was removed for loss-on-drying analysis on the MAX® 5000XL and run at 240 °C.

Figures 1 & 2 show the percent bound moisture and percent purity respectively for these variable conditions at day 1, 5 & 10. It becomes clear that the 'Pure Gypsum' (simply powdered gypsum no citrate, no liquid media A, left in atmospheric conditions) as well as the 'Control' remain unchanged after 10 days. The two vessels with active sulfate-reducing agents decrease in sulfate purity over time. The 'N_2' is markedly lower than its oxygen counterpart in which by day 10 the percent purity drops from ~101% down to ~82%. All tests were performed in triplicate. Error bars represent +/- the standard deviation of each individual data set at each time point.

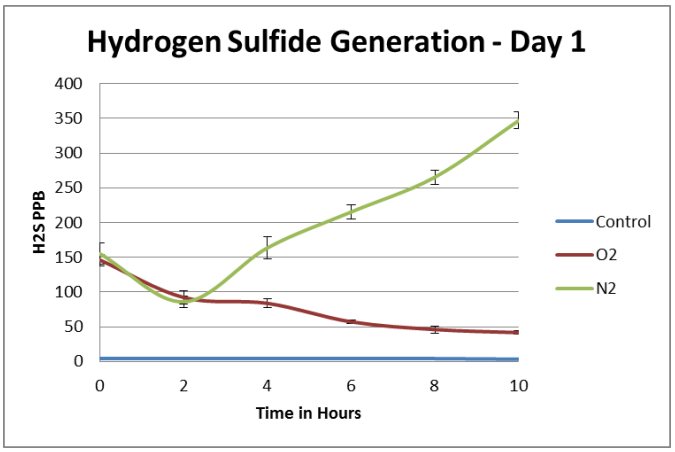
The results of this loss-on-drying purity assay suggest that the sulfate-reducing agents present in the soil extract are decreasing the purity of the gypsum. Moreover, when anaerobic (N_2) conditions are met, a greater rate of decomposition is observed.

Detecting hydrogen sulfide gas

As the sulfate-reducing bacteria use calcium sulfate in their metabolic cycle, hydrogen sulfide gas generated as a by-product.[11] The Jerome® 605 was utilized to periodically measure the headspace of each vessel condition (control, O_2, and N_2). This experiment was not designed to measure total H_2S produced in each vessel, as the extensive sampling required to do so would potentially disrupt the incubation of the sample as well as introduce oxygen from atmospheric conditions into the vessel.

On 'Day 1' of incubation, 2-hour increment testing was performed by the same J605 on all three conditions during a 10-hour period. The J605 was set to 'auto' range since the concentration of hydrogen sulfide was unknown. All data points were performed in triplicate. Figure 3 presents the with the error bars +/- one standard deviation of triplicate testing at each 2-hour time point.

Figure 3



At time point '0' (when the 10 mL of media/soil extract was added to vessels), ~150 ppb of hydrogen sulfide was detected for both the O_2 & N_2 vessels. This initially elevated concentration in hydrogen sulfide is most likely derived from the media A fermentation itself. Media A contains sulfate ions intended for anaerobic growth in bacteria. As time proceeds, a tapering effect of the O_2 vessel is observed from ~150 ppb to ~48 ppb while an increase in concentration occurs with N_2 vessel (~350 ppb) in the same 10 hour timespan as compared to the control vessel maintaining a level of ~3-4 ppb.

Figure 4

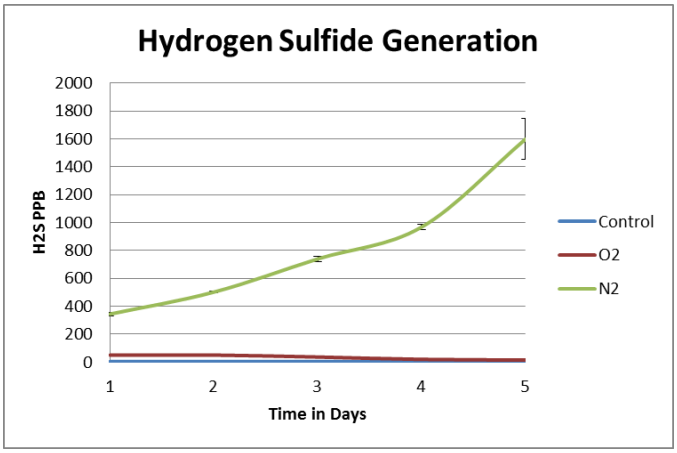


Figure 4 followed the same process as figure 3 but over a 5 day period in which sampling occurred once per day. The N_2 vessel (anaerobic conditions) increases from ~350 ppb on the first day to ~1600 ppb on the day 5. Further data was collected at Day 10 not shown on Figure 4 which indicated a concentration of ~2100 ppb. As time proceedes it appears that hydrogen sulfide production might plataeu between day 5 and 10. Further investigation is necessary to elucidate trend.

Chart 4

Day	Control	Control	O_2	O_2	N_2	N_2
	H_2S	Purity	H_2S	Purity	H_2S	Purity
	ppb	%	ppb	%	ppb	%
1	4.34	100.90	50.31	100.89	344.33	101.05
5	3.39	100.88	15.24	98.66	1598.33	91.95
10	3.11	100.79	13.54	93.81	2132.84	82.47

Chart 4 presents the mean values for hydrogen sulfide gas sampling and gypsum purity for Day 1, 5, & 10. As hydrogen sulfide gas emissions increase, gypsum purity values decrease especially under anaerobic conditions where sulfate-reducing agents are present. Under anaerobic conditions the purity value dropped from 101.05% to 82.47%, a nearly 18.6% loss of purity. Coupling the rapid loss-on-drying analysis from the MAX® 5000XL with the hydrogen sulfide specific Jerome® 605 demonstrates the inverse relationship between Gypsum purity and hydrogen sulfide generation due to anaerobic fermentation.

Figure 5

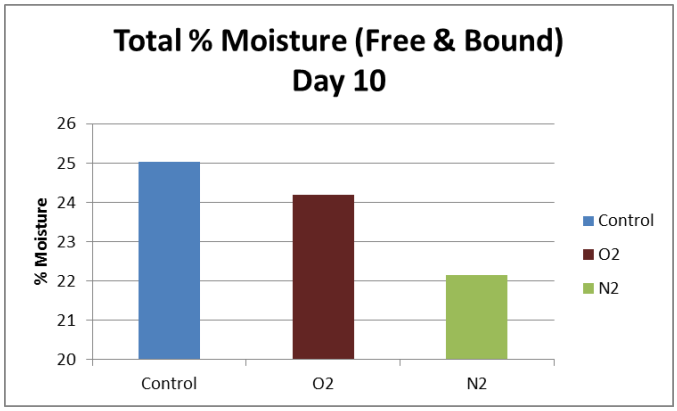
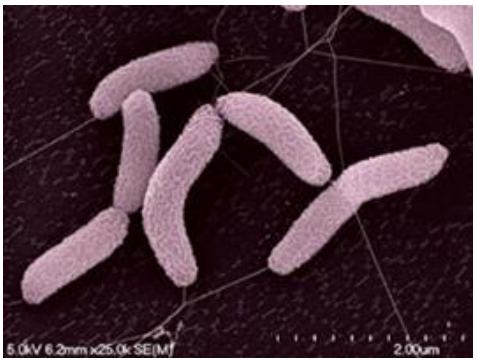


Figure 5 demonstrates the Total % Moisture at Day 10 (after all other anaylsis were performed). These samples were poured out of their corresponding vessels (Control, O_2, N_2), and placed into labelled aluminum pans. These pans were then placed in a forced air oven and dried for 1 hr at 80°C. These samples were then cooled at room temperature in atmospheric conditions and re-pulverized into a powder and left on the counter top for 48 hours in ambient conditions. These samples were then subjected to steadily increasing temperature from 50°C to 300°C with a temperature rate of 10°C/min. This test shows that even if the slurry is dried and brought back to normal atmospheric conditions, the gypsum purity will remain altered after anaerobic fermentation occurs.

Discussion

Hydrogen sulfide generation due to anaerobic fermentation of gypsum is a problem in many different industries. Construction & demolition landfills (C&D) sites in particular must monitor the hydrogen sulfide emisions from decaying gypsum-based wallboard. Anaerobic fermentation occurs when sulfate-reducing bacteria such as the type

shown below (*Desulfovibrio vugaris*) are present in a low oxygen environment.



Assuming these forms of bacteria have a sufficent carbon source and sulfate source (both found in wallboard), they will begin to grow and multiply. In the process they will reduce the sulfates found in gypsum and produce hydrogen sulfide gas. Hydrogen sulfide gas has many health risks along with having a corrosive effect on metals. Monitoring for odor control for nearby residential areas is strictly governed by state and city regulations. Understanding the relationship between gypsum purity and hydrogen sulfide gas is important in predicting the amount of hydrogen sulfide gas produced from fermenting gypsum.

Using a rapid loss-on-drying assay can quickly and reliably produce a measurement of gypsum quality. This occurs because of the unique chemical association between water molecules and the sulfates of synthetic gypsum. The Computrac® MAX® 5000XL is useful in this process because it provides a pre-linked test that removes adsorbed free moisture and subsequently tests for the bound moisture at 240°C. Coupling this method of gypsum purity analysis with the Jerome® 605 hydrogen sulfide gas analyzer makes it possible to track the inverse trend between gypsum and H_2S.

The results of this research indicate that if there is a sufficient amount of sulfate-reducing bacteria present on gypsum, then there will be a decrease in gypsum purity. This occurs at high and low oxygen levels; however, it is dramatically increased in anaerobic environments. Furthermore, as the gypsum purity diminishes, an increase in concentration of hydrogen sulfide is observed. This study follows a fermentation process of 10 days; further investigation is warranted to determine the effects of longer fermentation periods.

This research was conducted under very strict laboratory controls (Temperature, oxygen environments, and pure gypsum). These variables were selected to simulate the real-world conditions of gypsum in a C&D landfill. Future studies may include more types of gypsum type (anhydrous and hemihydrate) as well as including real wallboard and other construction debris. In this study, fermenting gypsum was periodically sampled for hydrogen sulfide gas concentrations. Due to a large volume of headspace in the vial, it was impractical to quantify the total concentration of hydrogen sulfide at each time point. Future studies may include a smaller vessel with less headspace to get a more accurate quantification of hydrogen sulfide concentration.

References

1. Cornelis Klein & Cornelius S. Hurlbut, Jr. (1985) Manual of Mineralogy, John Wiley, 20th ed,. Pp. 352-253.
2. "Compact Oxford English Dictionary: gypsum"
3. http://www.gypsum.org/mediaguide.html Gypsum Association History of Gypsum Board
4. Agency for Toxic Substances and Disease Registry. 2006. ToxFAQs™ for Hydrogen Sulfide, U.S. Department of Health and Human Services, Public Health Service.
5. Maine Department of Health & Human Services, Maine Center for Disease Control & Prevention, Division of Environmental Health, Environmental & Occupational Health Program. 2006. Ambient Air Guidelines for Hydrogen Sulfide.
6. "Hydrogen Sulfide – PubChem Public Chemical Database". The PubChem Project. USA: National Center for Biotechnology Information.
7. Hydrogen Sulfide (also known as H2S, sewer gas, swamp gas, stink damp, and sour damp) Hole". OSHA. 12 February 2013. Retrieved 23 July 2014.
8. Garrett Rowe, LOD vs. Thermogravimetric Analysis. http://www.azic.com/downloads/white_papers/LOD%20vs%20Thermogravimetric%20Analysis.pdf
9. ASTM International C471M-01 "Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products.
10. James Moore, Moisture Analysis of Gypsum. http://www.azic.com/blog/?p=131
11. Eric N. Kaufman et.al, A biological Process of the Reclamation of Flue Gas Desulfurization Gypsum Using Mixed Sulfate-Reducing Bacteria with Inexpensive Carbon Sources. Applied Biochemistry and Biotechnology Volume 63-65, 1997, pp 677-693
12. K.R. Butlin et. al., The Isolation and Cultivation of Sulphate-Reducing Bacteria. http://mic.sgmjournals.org/content/3/1/46.short
13. American Society for Microbiology. Sulfur-Indole-Motility Agar Recipe (modified w/o indole & with Media A as broth) http://www.microbelibrary.org/library/laboratory-test/3658-motility-test-medium-protocol

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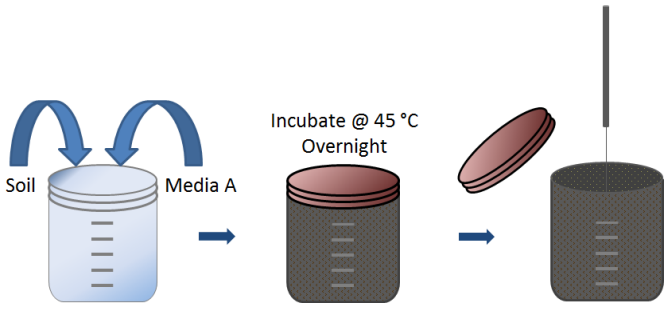
Appendix A

Culturing Sulfate-Reducing Agents

Before hydrogen sulfide gas could be measured from a pure source of fermenting gypsum, a sulfate-reducing agent had to be cultured. In this context an 'agent' will be synonymous with bacteria, even though there was no direct assay conducted to test for the organismal domain. The source of the sulfate-reducing agent came from 1 cup of potting soil from an outdoor herb box. Sample was placed in a 250 mL screw top container and approximately 50 mL of liquid 'Media A' was added to the potting soil making sure that there was little to no headspace. The container was then sealed with a screw top lid and sealed with a strip of Parafilm®. The container was then placed in the 45°C incubator overnight.[12] Having a good seal with no headspace promotes the low oxygen environment that is required for the sulfate-reducing agents to grow. See Figure 6 below.

Figure 6



After the overnight incubation, the lid was removed and a strong 'sulfur' odor was noted. The J605 was set to 'auto' and allowed to run above the soil suspension which yielded a reading of ~90 ppb. Although hydrogen sulfide byproduct was detected (indicating sulfate-reducing agents), a second culturing technique was utilized to ensure sulfate-reducing agents were present. Several Sulfur-Motility (SM) agar slants were aseptically poured from the Medium A mixed with 0.5% Agar and allowed to cool.[13] A sterile needle was dipped into the overnight incubation soil suspension and was stabbed into the agar slant. These agar slants were then incubated at 45°C for 48 hours.[12] Because there is soluble iron (II) in the media (from the ferrous ammonium sulfate) any dissolved hydrogen sulfide gas produced by an organism at the site of the needle inoculation will complex with the iron and precipitate out as black iron sulfide. The medium will change from an opaque beige color to a dark black if a sulfate-reducing agent (e.g. bacteria) is present in the media. This media also offers insight on the agent's level of motility due to the softness of the agar media. See Figure 7 for schematic.

Figure 7

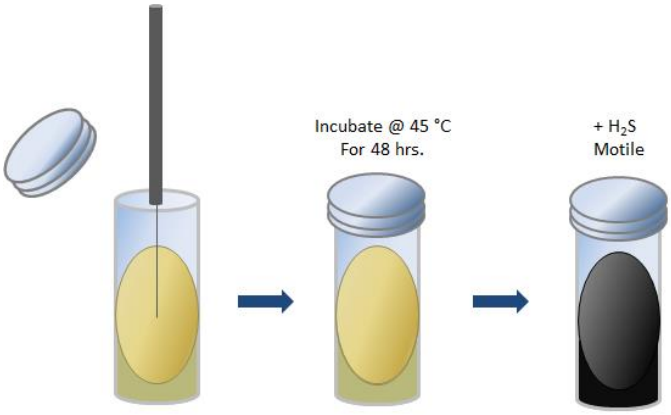
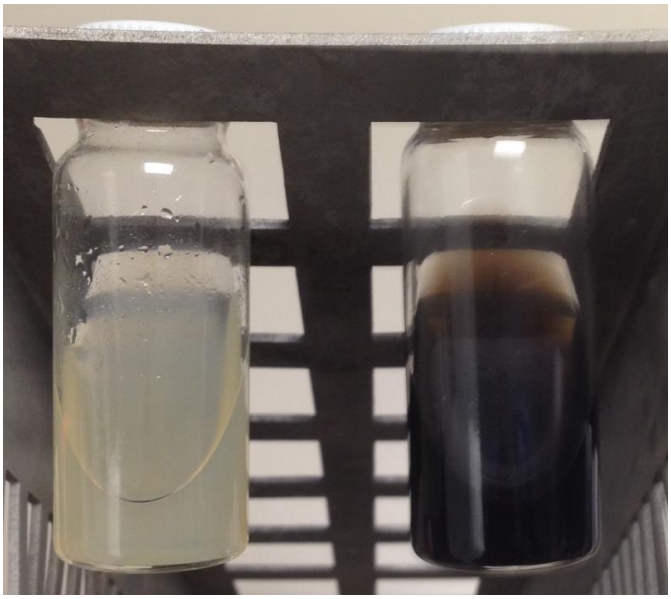


Figure 8 is a photograph of the SM agar slants. The vial/agar slant on the left is the control vial in which a sterile needle was used (no active organism). The vial/agar slant on the right is the vial inoculated with the suspected sulfate-reducing agents from incubated soil suspension. The vial on the right demonstrates the presence of hydrogen sulfide production (black precipitate) as well as motility since the the entire agar is black and not just at the sight on inoculation.

Figure 8



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