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Research article

Biogeochemical oxidation of calcium sulfite hemihydrate to gypsum in flue gas desulfurization byproduct using sulfur-oxidizing bacteria

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ABSTRACT

Flue gas desulfurization (FGD) is a well-established air treatment technology for coal and oil combustion gases that commonly uses lime or pulverized limestone aqueous slurries to precipitate sulfur dioxide (SO_2) as crystalline calcium salts. Under forced oxidation (excess oxygen) conditions, FGD byproduct contains almost entirely (>92%) gypsum ($CaSO_4 \cdot 2H_2O$), a useful and marketable commodity. In contrast, FGD byproduct formed in oxygen deficient oxidation systems contains a high percentage of hannebachite ($CaSO_3 \cdot 0.5H_2O$) to yield a material with no commercial value, poor dewatering characteristics, and that is typically disposed in landfills. Hannebachite in FGD byproduct can be chemically converted to gypsum; however, the conditions that support rapid formation of gypsum require large quantities of acids or oxidizers. This work describes a novel, patent pending application of microbial physiology where a natural consortium of sulfur-oxidizing bacteria (SOB) was used to convert hannebachite-enriched FGD byproduct into a commercially valuable, gypsum-enriched product (US Patent Assignment 503373611). To optimize the conversion of hannebachite into gypsum, physiological studies on the SOB were performed to define their growth characteristics. The SOB were found to be aerobic, mesophilic, neutrophilic, and dependent on a ready supply of ammonia. They were capable of converting hannebachite to gypsum at a rate of approximately five percent per day when the culture was applied to a 20 percent FGD byproduct slurry and SOB growth medium. 16S rDNA sequencing revealed that the SOB consortium contained a variety of different bacterial genera including both SOB and sulfate-reducing bacteria. *Halothiobacillus*, *Thiovirga* and *Thiomonas* were the dominant sulfur-oxidizing genera.

1. Introduction

Approximately 560 coal-fired electricity generators operate in the USA (USEIA, 2014). Byproducts of fossil fuel combustion present in the flue gas include sulfur dioxide gas (SO_2) which is both a contributor to acid rain and an indirect greenhouse gas (Srivastava and Jozewicz, 2001). Discharge levels of SO_2 into the atmosphere have been governed by the Clean Air Act Amendments since November 1990 and regulated by the United States Environmental Protection Agency due to the reaction of SO_2 with water vapor in the atmosphere to form sulfuric acid (Nolan, 2000). To remove SO_2 prior to discharge, the flue gas is treated using a process known as flue gas desulfurization (FGD). The most common FGD processes pass the flue gas through a crushed limestone-water or lime slurry to oxidize SO_2 to either sulfite or sulfate that further reacts with excess calcium from the limestone or lime to form hannebachite ($CaSO_3 \cdot 0.5H_2O$) or gypsum ($CaSO_4 \cdot 2H_2O$) depending on the availability of oxygen. Although various FGD scrubber systems are available, wet FGD scrubbing systems as described above have proven SO_2 removal efficacies of between 95 and 99% (Poullikkas, 2015). During the flue gas and limestone slurry interaction under natural atmospheric conditions, SO_2 dissolves in the water as sulfite (SO_3^{2-}) and is subsequently precipitated by Ca^{2+} to form calcium sulfite ($CaSO_3$) (Brown et al., 2012). When excess air (21 percent oxygen) is forced into the system during SO_2 scrubbing, the resultant $CaSO_3$ reacts with the oxygen in the presence of water to form calcium sulfate ($CaSO_4$) (Brown et al., 2012). The resultant sludge of

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natural oxidation wet FGD systems consists of $CaSO_3 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$ crystals, some fly ash carried over from combustion, and unreacted calcium carbonate (limestone). Where oxygen is limiting, $CaSO_3 \cdot 0.5H_2O$ forms in a much higher proportion compared to $CaSO_4 \cdot 2H_2O$ resulting in a byproduct with no commercial value. Conversely, when excess air is supplied to the FGD process, known as forced oxidation, nearly complete oxidation of sulfur dioxide to sulfate occurs with the result being high purity gypsum, a marketable byproduct. One of the highest value uses of gypsum is for manufacturing wallboard which consumed 7.4 million tons in 2013 (ACAA, 2013). Other uses for gypsum include admixture in cement where it acts as a set retarder (Tzouvalas et al., 2004), agricultural uses as soil amendments to diminish soil acidity and make nutrients more bioavailable (Clark et al., 2001), and as fire resistant coating (Leiva et al., 2010).

FGD byproduct containing excessive $CaSO_3 \cdot 0.5H_2O$ is typically landfilled, however, it can be converted at a cost to $CaSO_4 \cdot 2H_2O$. Chemical conversion processes include the addition of H_2O_2 (Bhatt, 1995) or acid, preferably H_2SO_4 (Hudson, 1980). Hydrogen peroxide oxidizes sulfite whereas sulfuric acid can be used to acidify the pH which allows auto-oxidation. The lower the pH, the faster the auto-oxidation (Lee et al., 2007). Both of these chemical reactions involve the addition of substantial amounts of oxidant or acid. An alternative to these chemical reactions exploits the biogeochemical oxidation of reduced sulfur (sulfite) to sulfate.

Bacteria characterized as sulfur-oxidizing include a wide variety of genera, display broad habitat diversity, and may be heterotrophic, mixotrophic, chemolithotrophic, or photoautotrophic (Ehrlich and Newman, 2009). Sulfur-oxidizing bacteria (SOB) fulfill an important role in the conversion of reduced sulfur (sulfide) and partially oxidized forms of sulfur (e.g., elemental sulfur, thiosulfate, and sulfite) into sulfate. SOB produce various enzymes including, sulfite oxidase, adenosine phosphosulfate reductase (APS reductase) and quinone oxidoreductase to mediate oxidation of both sulfide and partially oxidized sulfur compounds (Hell et al., 2008). Utilizing the ability of bacteria to manipulate the oxidation states of sulfur is not a novel concept. Plumb et al. (1990) proposed the use of sulfur reducing bacteria (SRB) to eliminate SO_2 emissions from coal-fired exhaust gas to eliminate wet or dry calcium-based treatments. Parshina et al. (2010) focused on the removal of sulfate from waste water using sulfate-reducing bacteria. However, investigations on converting $CaSO_3 \cdot 0.5H_2O$ rich FGD byproduct into marketable $CaSO_4 \cdot 2H_2O$ using SOB have not been conducted previously.

2. Materials & methods

2.1. Media and cultures

Reagent grade chemicals for culture medium originated from Thermphos International (Flushing, Netherlands), Thermo FisherScientific (Waltham, MA), and Acros (Geel, Belgium). Continuous culturing of the sulfur-oxidizing consortium and all physiological experiments on SOB were performed using SOB culture medium (Charles and Suzuki, 1966). The SOB consortium was isolated from the FGD byproduct and was maintained through serial dilution in liquid SOB medium weekly for 24 months under constant agitation and aeration. The continuously grown SOB consortium (seed reactor) provided biomass for physiology characterization, next generation sequencing, and FGD byproduct treatment tests. When treating FGD byproduct in reactors, the mixed liquor from the seed reactor was added as 5% [v/v] of the working volume of the FGD treatment reactor. During typical operation, reactors converting hannebachite to gypsum were amended with NH_4Cl (0.1 g/L), $Na_2HPO_4 \cdot 7H_2O$ (0.3 g/L) and $MgCl_2 \cdot 6H_2O$ (0.1 g/L). Thiosulfate was not added to the reactors to force the SOB to oxidize sulfite. For all experiments the SOB consortium was diluted to a starting optical density at 595 nm (OD_{595}) of 0.03 or equivalent of $2.5–4 \times 10^5$ cells/mL.

2.2. Cell density measurements

Several methods were evaluated for routine use in making reliable and practical measurements of SOB cell density in cultures and slurry reactors. OD_{595} was measured in solids-free cultures using a Hach spectrophotometer, Model DR 5000 (Loveland, CO). Plate counts and most probable numbers (MPN) tests were modified for use of the SOB medium in agar solidified medium in petri dishes or liquid medium in MPN tubes. ATP levels were measured using the Quench-Gone™Aqueous Test Kit (LuminUltra®, New Brunswick, Canada). Physical cell counts were performed using disposable Cellometer® counting chambers (Nexcelom Bioscience, Lawrence, MA) viewed using an Omax phase contrast microscope (Omax, Korea) at 1000 × magnification. Bacteria observed in the central square of the chamber were tallied and multiplied by the appropriate dilution factor to estimate cells per ml.

2.3. Growth temperature testing

The optimal growth temperature for the consortium was evaluated as a process control parameter that affected the gypsum formation rate. The SOB consortium, maintained at room temperature, was grown at temperatures ranging between 15 ± 1 °C and 45 ± 1 °C to identify the temperature that would yield the fastest SOB growth rate in SOB medium. The SOB medium components were prone to precipitate at lower temperatures (15–22 °C); therefore, to verify the accuracy of cell density measurements, cell counts were performed in parallel with optical density readings. To achieve incubation conditions above or below room temperature (22 ± 1 °C) the SOB consortium was either warmed in a Precision 2835 water bath (ThermoFusherScientific, Waltham, MA) or cooled in a refrigerated unit (Draghetto, Greenaby, WI), using a magnetic stirrer (VWR®, Arlington Heights, IL) and an immersible magnetic stirrer (Electrothermal, Burlington, NJ), respectively. The temperature was monitored with a thermometer (Thermo FisherScientific, Waltham, MA). Cell growth experiments continued with monitoring twice daily until the cells/mL started to decline.

2.4. pH sensitivity

The SOB medium had an unadjusted pH of 7.1. The pH was adjusted by altering the molar ratio of KH_2PO_4 and K_2HPO_4 and where necessary by adding H_2SO_4 or NaOH to yield batches of SOB medium with a pH of 3.5, 5.0, 6.0, 7.0, 8.0 and 9.5. Stirred batch growth experiments conducted at room temperature using the pH adjusted media and performed in a Phipps & Bird jar tester (PB 700, Richmond, VA) mixing at 85 RPM provided data to evaluate the effect of pH on cell growth. The OD_{595} and the pH of each pH treatment were measured daily. Medium pH was measured with an Accumet XL15 pH meter with a combination electrode (Thermo FisherScientific, Waltham, MA). The pH of each treatment was adjusted with either H_2SO_4 or NaOH during testing to maintain the initial pH of the medium.

2.5. Oxygen requirements

The oxygen requirement of the SOB consortium was assessed by culturing in SOB medium at various dissolved oxygen (DO)