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A Biological Process for the Reclamation of Flue Gas Desulfurization Gypsum Using Mixed Sulfate-Reducing Bacteria with Inexpensive Carbon Sources

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ABSTRACT

A combined chemical and biological process for the recycling of flue gas desulfurization (FGD) gypsum into calcium carbonate and elemental sulfur is demonstrated. In this process, a mixed culture of sulfate-reducing bacteria (SRB) utilizes inexpensive carbon sources, such as sewage digest or synthesis gas, to reduce FGD gypsum to hydrogen sulfide. The sulfide is then oxidized to elemental sulfur via reaction with ferric sulfate, and accumulating calcium ions are precipitated as calcium carbonate using carbon dioxide. Employing anaerobically digested municipal sewage sludge (AD-MSS) medium as a carbon source, SRBs in serum bottles demonstrated an FGD gypsum reduction rate of 8 mg/L/h $(10^9 \text{ cells})^{-1}$. A chemostat with continuous addition of both AD-MSS media and gypsum exhibited sulfate reduction rates as high as 1.3 kg FGD gypsum/m^3·d. The increased biocatalyst density afforded by cell immobilization in a columnar reactor allowed a productivity of 152 mg SO_4^{-2}/L·h or 6.6 kg FGD gypsum/m^3·d. Both reactors demonstrated 100% conversion of sulfate, with 75–100% recovery of elemental sulfur and chemical oxygen demand utilization as high as 70%. Calcium carbonate was recovered from the reactor effluent on precipitation using carbon dioxide. It was demonstrated that SRBs may also use synthesis gas (CO, H_2, and CO_2) in the reduction of gypsum, further decreasing process costs. The formation of two marketable products—elemental sulfur and calcium carbonate—from FGD gypsum sludge, combined with the use of a low-cost carbon source and further

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improvements in reactor design, promises to offer an attractive alternative to the landfilling of FGD gypsum.

Index Entries: Gypsum sludge; sulfate-reducing bacteria; synthesis gas; sulfur; calcium carbonate; flue gas desulfurization.

INTRODUCTION

The burning of coal at power plants produces sulfur dioxide (SO_2), which causes acid rain. Although regenerable sorbents for SO_2 capture at power plants are gaining popularity, they are frequently economical only at newly constructed facilities. Disposable sorbents, such as limestone, are utilized in many of today's flue gas desulfurization (FGD) systems. As of 1991, 80% of FGD capacity (over 120 GW) consisted of wet limestone scrubbing *(1)*. Limestone processes are also a common choice for retrofitting FGD capacity in pre-existing plants (*see*, for example, Bove et al. *[2]*). The absorption of SO_2 onto limestone produces calcium sulfite and carbon dioxide. Forced oxidation of the resulting sulfite sludge yields a residue rich in calcium sulfate (gypsum). Although other countries utilize gypsum for wallboard or cement, only three plants in the US find this process economical *(3)*. Transportation costs, low purity, and regulations regarding ash constituents in building material do not allow FGD gypsum to compete with the natural gypsum mined in the US. This country utilizes <5% of its FGD gypsum and disposes the remaining 15–20 million t/yr, thus requiring a massive landfill volume *(1,3,4)*. In 1992, the US landfilled more than 12 million t of FGD residue and ponded an additional 8.6 million t *(1)*. The amount of FGD residue a given plant produces is dependent on the size of the plant, the sulfur content of the coal, and the FGD technology employed. A 1000 MW steam plant burning 0.5% sulfur coal (a low-sulfur coal) with a spray dry scrubber removal efficiency of 70% may be expected to produce about 350 kt of FGD residue/yr *(1)*.

It is difficult to determine the actual cost of FGD gypsum disposal, since these numbers are rarely included in the literature, and when published, may not include construction and maintenance costs for the facility. Disposal costs are generally quoted to range between 3 and $12/t *(5,6)*. Some utility companies are able to take advantage of readily available land and lenient regulatory laws that permit them to stack or "rim ditch," their gypsum in an unlined area for much lower operating costs *(5,7)*. Other utility companies are forced to utilize expensive, lower-sulfur-content coal in order to avoid desulfurization entirely. An economically viable process capable of recycling FGD gypsum to reclaim the calcium carbonate sorbent and recover marketable elemental sulfur could dramatically decrease the operating costs for a limestone FGD system. Recycling of the waste product would decrease the land requirements for a limestone facility, and reclamation of calcium carbonate would decrease both the required inventory and the material costs of the sorbent.

The ability of bacteria to reduce sulfates and sulfites to sulfides was first reported in 1864, and a wealth of information has been accumulated regarding sulfate-reducing bacteria (SRB), their environmental and nutritional requirements, and their enzymatic pathways (*see* Barton *[8]* and Widdel and Hansen *[9]* for reviews). Their role in oil well souring has been of particular interest *(10,11)*. SRB oxidize organic acids or hydrogen while reducing sulfates and sulfites into sulfides. Various investigators have suggested that SRB may be utilized to treat FGD gypsum biologically, however, a commercially viable process has not been realized. Apel and Barnes *(12)* demonstrated that SRB may utilize carbon sources, such as lactate, pyruvate, citrate, alanine, cysteine, glycerol, and ethanol to reduce FGD gypsum to hydrogen sulfide. These investigators concluded that commercial viability of the process could not be achieved until expensive carbon sources could be eliminated and an effective reactor design could be achieved. Uphaus et al. *(13)* seemingly decreased the cost of a carbon source by utilizing two reactors in series. A photosynthetic green sulfur bacterium, *Chlorobium*, utilized the H_2S and CO_2 evolved from SRB to form elemental sulfur and organic acids. The organic acids were in turn utilized as a "free" carbon source for the SRB. The hidden cost of this process was the 10,000-foot-candles of light required as the energy source for the *Chlorobium*.

Synthesis gas (syn-gas) and sewage digest have been investigated as inexpensive carbon and energy sources for SRB reactors. Syn-gas (40–65%, CO, 25–35% H_2, 1–20% CO_2, and 0–7% CH_4, H_2S, and COS *[14]*) would be the most desirable feedstock for an SRB process owing to its wide availability particularly at the utility plant and its zero chemical oxygen demand (COD) discharge. Various groups *(15–17)* have demonstrated that SRB could be supported by carbon dioxide as the sole carbon source and hydrogen as the electron donor. Du Preez et al. *(18)* operated a sulfate-reducing reactor with a mixed SRB population, which was fed 30% H_2, 59% CO, 8% CO_2, and 3% N_2, demonstrating the feasibility of using whole syn-gas as the feed source for SRB. Recently, van Houten et al. *(19)* reported the operation of a gas lift sulfate-reducing reactor fed up to 20% CO with the balance being H_2. They reported a slight decrease in productivity owing to the use of CO (12 to 6 $kg/m^3{\cdot}d$). Sublette and Gwodzdz *(20)* assessed the economic viability of a microbial process to reduce the effluent SO_2 from a regenerable FGD process as compared with conventional hydrotreating. This study concluded that although fixed capital investment costs for the two processes were identical, the high cost of the carbon source (corn hydrolysate) rendered the biological process uneconomical. Selvaraj and Sublette *(21)* demonstrated that sewage digest (anaerobically digested municipal sewage sludge; AD-MSS media) may be utilized as the carbon and energy source for SRB. They defined the targets for necessary organic

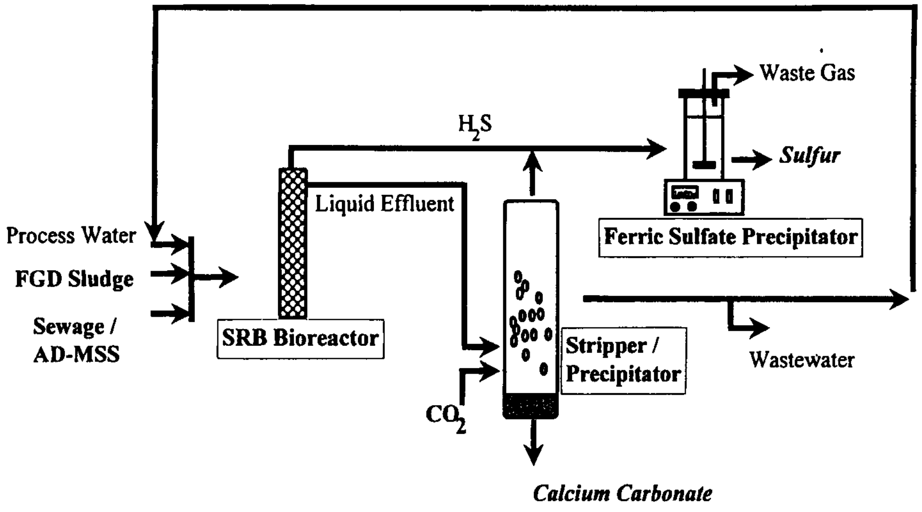

Fig. 1. Reclaiming of sulfur and calcium carbonate from FGD gypsum. A culture of SRB utilizes sewage digest as its carbon and energy source, and reduces the sulfates and sulfites in FGD gypsum sludge to hydrogen sulfide. The sulfide is oxidized by ferric sulfate to form elemental sulfur. The resulting ferrous sulfate may be reoxidized chemically or biologically. Calcium ions accumulating in the liquid of the SRB reactor are precipitated using carbon dioxide to form calcium carbonate, which may be reused as an FGD adsorbent. This process diagram is intended to be generic in nature. Alternative carbon and energy sources, means of sulfide reoxidation, and methods for carbonate precipitation may also be employed.

acid content of the AD-MSS media as well as the biocatalyst density necessary to achieve an economically viable process. Significant progress has been made in achieving higher utilization of COD and organic acids in the AD-MSS, media as well as in improving the biocatalyst density through cell immobilization *(22)*.

Recently, a process has been proposed for recycling FGD gypsum or waste sludge into calcium carbonate and elemental sulfur *(23)*. This process (*see* Fig. 1) incorporates biological and chemical transformations into an economical method with tremendous capital and environmental impact. Although some of the technologies have been utilized in other applications, a combined system for FGD gypsum recycling has not been addressed. In this process, waste sulfate and sulfite in the form of a gypsum slurry are transformed to hydrogen sulfide by a mixed culture of SRB. The bacteria utilize sewage or syn-gas as their carbon source *(20–22,24,25)*, thus eliminating prohibitive nutrient costs that exist in other reported SRB processes. Hydrogen sulfide is then further processed by ferric sulfate oxidation *(26,27)* into marketable elemental sulfur. The ferric sulfate may be regenerated using *Thiobacillus* species *(28,29)*. Excess biocatalyst from both the SRB culture and the *Thiobacillus* culture may be removed using a gravity settler in an overall process. Calcium ions that accumulate in the bioreactor owing to the reduction of sulfite and sulfate from the $CaSO_3$ and $CaSO_4$ are combined with the waste gas carbon dioxide under alkaline conditions to re-form $CaCO_3$ *see*, for example, Wachi and Jones *[30]*, which may then be reused as an SO_2 adsorber at the power plant. Elemental sulfur is a valuable industrial chemical with an annual US market of 13 million t/yr and a selling price of about $50/t *(31)*. The regenerated limestone may be reused as an FGD adsorber at the steam plant, minimizing further purchase of FGD scrubbing materials, which are between 5 and $15/t *(5,6)*.

In this study, many aspects of a biochemical process for the recycling of FGD gypsum to elemental sulfur and calcium carbonate have been demonstrated. The results show that:

1. AD-MSS media or syn-gas can serve as the carbon and electron source for SRBs performing gypsum reduction at rates competitive with cells fed rich media;
2. AD-MSS media can be used in a well-mixed reactor system with continuous, sustained gypsum reduction;
3. An immobilized-cell reactor can be operated with a continuous gypsum feed to achieve improved volumetric productivity;
4. Sulfur can be continuously recovered via ferric sulfate precipitation; and
5. Calcium can be recovered as calcium carbonate.

METHODS

Microbial Culture and Media

The preparation and optimization of AD-MSS media have been discussed in detail previously *(22)*. Municipal sewage solids were obtained from the diffused air flotation (DAF) unit of the Oak Ridge, TN, municipal sewage treatment plant and were fed continuously as a 15% wet wt solid suspension into a 15-L vessel at 37°C. The hydraulic retention time of the sewage solids in this digester was 5.2 d: Chloroform was added at a concentration of 50 ppm to the DAF feed solution during the course of the operation as an inhibiting agent for methanogenesis. Note that unlike previous studies *(32)*, no additional salts or nutrients were added to the sewage solids to promote digestion into organic acids. The supernatant of the effluent from this 15-L digester was used as AD-MSS medium for the gypsum recycling experiments. The pH of this media was 6.9. Effluent samples were analyzed for soluble COD and organic acids as described below.

SRB were isolated from the DAF sewage solids. The cells were incubated at 30°C in serum bottles containing 50 mL AD-MSS media and 0.15 g of gypsum sludge as the terminal electron acceptor. The culture was maintained by weekly repassaging into identical media under aseptic conditions.

FGD Gypsum

FGD gypsum sludge from the Dalman plant of the Springfield Illinois City Water, Light, and Power Company was generously supplied by Y. P. Chugh at the Southern Illinois University at Carbondale. On receipt, the sludge was oven-dried at 100°C to remove free moisture. The resulting powder yielded 551 mg/L sulfate when 0.1 g of sludge was dissolved in 100 mL distilled water at room temperature. Typically, 500 mg/L sulfate resulted when 1 g of sludge was dissolved in 1 L AD-MSS media at room temperature. The maximum solubility of sulfate in AD-MSS media was 1200 mg/L.

Analytical Techniques

Sulfate concentrations were analyzed by either ion chromatography or tubidimetrically. For ion-chromatography analysis, a Dionex 4500i (Dionex, Sunnyvale, CA) with an IonPac AS4A-SC 4-mm column was utilized with a 2 mL/min flow and isocratic elution using HCO_3^-. Turbidimetric sulfate analysis was performed using premeasured Sulfaver IV reagent powder (Hach Chemical, Loveland, CA). Spectrophotometric determination of the analyte was performed at 450 nm using a Spectronic 21 D (Milton-Roy Instruments, Rochester, NY). Organic acids were quantified by gas chromatography using a Hewlett Packard 5890 II gas chromatograph equipped with a flame ionization detector. A 30-m HP-INNOWax column (19091N-133, Hewlett Packard) was used with a helium carrier flow of 1.5 mL/min through a ramped temperature profile from 120°C (1 min) to 240°C (1 min) at 10°C/min. The injector was operated at 250°C, and the detector was operated at 300°C. Hydrogen sulfide, CO, H_2, and CH_4 were determined using a Hewlett-Packard 5890 II gas chromatograph equipped with a thermal conductivity detector. A helium carrier flow of 25 mL/min was passed through a 6 ft × 1/8 in. Teflon column using a Super Q 80/100 mesh stationary phase (Ohio Valley Specialty Chemical, Marietta, OH). The oven temperature was held at 50°C; both the detector and the injector were set at 125°C. The COD was determined spectrophotometrically at 620 nm using Hach premeasured COD reagent vials (0–1500 ppm). Counts of SRB were made using the most probable number (MPN) method (Bioindustrial Technologies, Georgetown, TX).

Serum Bottle Trials

Initial trials to assess the potential use of AD-MSS media in a gypsum reduction process were carried out in 150-mL serum bottles. Three separate series were prepared. The first series contained 55 mL AD-MSS media, 0.15 g dried gypsum sludge, and 5 mL SRB inoculum from the stock culture described above. The second contained the same media and inoculum amounts, but no gypsum was added. Both series were prepared aseptically. The third series (an abiotic control) contained 60 mL of autoclaved media and 0.15 g gypsum sludge. Each series was tested daily for H_2S by withdrawing 500 µL of headspace and injecting onto the gas chromatograph. The headspaces were then evacuated for 1 min by passing nitrogen through each bottle (~500 mL/min) using syringe needles as both injector and vent. Once the gas injector was removed, the vent was left in place for 5 s to ensure that the headspace pressure decreased to ambient. Measured liquid samples were removed every other day, centrifuged at 11,750*g* for 10 min, and analyzed for sulfate, organic acids, COD, and pH. At d 14, the bottle with SRB and gypsum was sampled for an MPN determination. All other analyses were continued until H_2S evolution ceased.

Mixed Reactor System

Once it was established that the cells could reduce the gypsum sludge to sulfide using the AD-MSS media, a reactor system was constructed the could operate using FGD gypsum in a batch, fed-batch, or continuous mode. The primary reactor consisted of a Virtis OmniCulture chemostat with a 1-L reactor vessel (Virtis, Gardiner, NY). The vessel headplate was fitted for acid and base addition as well as gas and liquid influents and effluents. The pH was regulated at 7.0 with a Chemcadet controller (Cole-Parmer Instrument, Niles, IL); 6*N* NaOH were used as base, and 6*N* H_3PO_4 were used for acid addition. Influent and effluent flows (0.2–0.4 mL/min.) were regulated by peristaltic pumps. The reactor was maintained at 30°C and was continuously stirred at 150 rpm. A feed reservoir was constructed that allowed an adjustable nitrogen flow over the AD-MSS media to help prevent contaminant growth. The reactor was continuously sparged with nitrogen to remove the resulting H_2S and carry it to the sulfur-precipitating unit. Sulfate, organic acid, and COD levels were measured daily. The effluent from the reactor was centrifuged daily; the cells were returned to the reactor, and the supernatant was stored for use in calcium precipitation experiments.

To establish biomass in the reactor, a working culture of SRB was grown in a fed-batch mode over a 10-d period with gypsum sludge added to the AD-MSS media. Cells were centrifuged and resuspended in fresh media prior to each gypsum addition, and this cycle continued until a suitable biomass population was established. At this point, the reactor was converted to have continuous AD-MSS feed (0.2 mL/min, 3.5-d residence time) with gypsum manually supplied in a fed-batch mode. Organic acid and COD levels of the influent and effluent AD-MSS media were monitored, as was the sulfate level in the reactor. Gypsum was manually added (typically 1–2 g when the sulfate level fell to near zero).

After the well-mixed reactor had been operated in a fed-batch mode for a period of 34 days, the gypsum feed was made continuous by adding it directly to the AD-MSS feed vessel. FGD gypsum (1–3 g) was added to 1 L of AD-MSS media, which was subsequently autoclaved to ensure that no SRB activity existed outside the reactor. The resulting solution was decanted to remove residual solids, and was then used to feed AD-MSS media and gypsum simultaneously to the reactor at a rate of 0.2–0.4 mL/min.

Immobilized-Cell Reactor

An immobilized-cell reactor was constructed in order to achieve higher reactor productivity owing to the higher biomass density afforded per unit volume. A fully jacketed glass columnar reactor (5821-24, Ace Glass, Vineland, NJ) of internal dimensions 2.5 × 30 cm was filled with BIO-SEP™ beads (Dupont, Glasgow, DE). The resulting fixed-bed reactor had a total volume of 181 mL and a liquid volume in the active portion of the reactor of 81 mL. The porous beads were inoculated using effluent biomass from the above well-mixed reactor, resuspended in fresh AD-MSS media. The liquid stood stagnant over the beads at 30°C for 12 h. At this point, operation was initiated with a continuous and simultaneous gypsum/AD-MSS media feed of 0.17 mL/min (7.9-h liquid residence time). The prolific reduction of sulfate in the columnar reactor resulted in a pH gradient being established within the column. The pH at the column inlet was 6.9, and sulfate reduction increased the pH at the column outlet to 8.3 (above the optimal pH for SRB). To correct this, further trials were performed using a recycle stream (Fig. 2) in which the liquid feed was more rapidly circulated (1 mL/min) through the column, and the effluent was collected in a holding vessel (200 mL) where the pH was adjusted to 7.0 using 6*N* H_3PO_4 before re-entering the reactor. Liquid from the gypsum feed bottle and the holding vessel was introduced into the reactor at a "tee" junction so that the sum of their flow rates equaled 1 mL/min. Liquid was removed from the holding vessel at the same rate as liquid was fed from the gypsum feed bottle. Sulfide was stripped from the reactor and precipitated as sulfur. Analyses of sulfate, organic acids, and COD were performed daily by sampling liquid at the reactor apex.

Sulfur Precipitation and Analysis

In the continuous reactor systems for FGD gypsum reduction, the resulting sulfide was oxidized to elemental sulfur both as an analytical tool to complete the sulfur mass balance and also to demonstrate the formation of a salable product. Hydrogen sulfide was sparged from the reactor units using a continuous flow of nitrogen gas (30 mL/min). The resulting gas stream was contacted with a 0.1*M* ferric sulfate (FX0235-1, EM Science, Gibbstown, NJ) solution with a 0.3-s gas residence time to form elemental sulfur by the reaction.

$$H_2S + Fe_2(SO_4)_3 \rightarrow S^0\downarrow + 2FeSO_4 + H_2SO_4 \qquad (1)$$

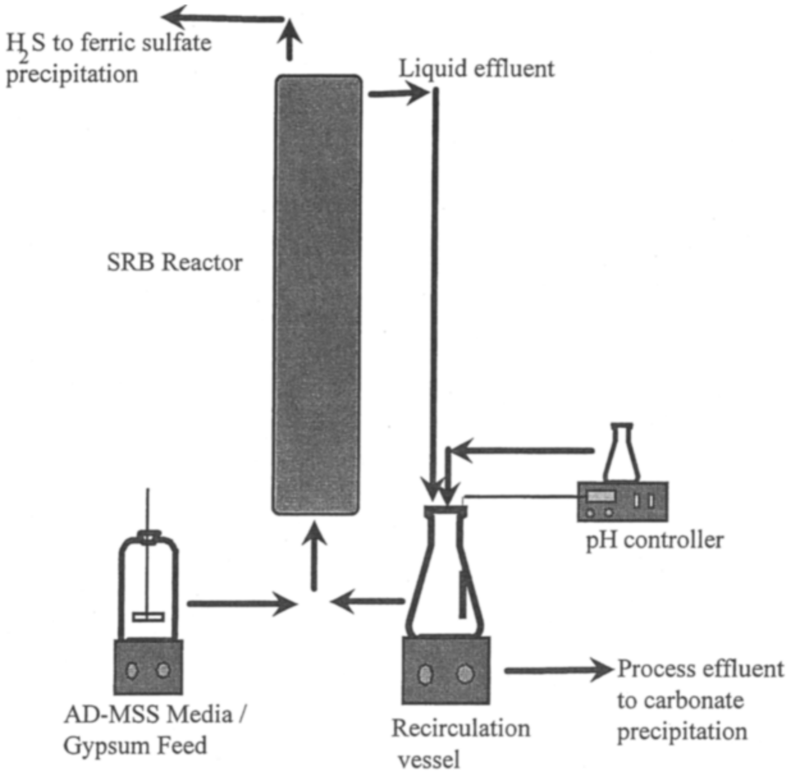

Fig. 2. Immobilized-cell recycle reactor. To regulate the pH within the immobilized-cell reactor, the total liquid flow rate through the reactor was increased to 1 mL min., and the process effluent was adjusted to pH 7.0 before being recirculated to the reactor. The feed rate of fresh AD-MSS media containing FGD gypsum was balanced with the rate of liquid discharge from the recirculation vessel in order to maintain a constant liquid volume. The residence time of the gypsum solution in the reactor was calculated as the liquid volume of the reactor divided by the fresh AD-MSS media/gypsum feed rate.

The method utilized was based on the patented BIO-SR process, *(26–28)* which further reoxidizes the ferrous sulfate back into ferric sulfate using *Thiobacillus* via:

$$2FeSO_4 + H_2SO_4 + 0.5\ O_2 \rightarrow Fe(SO_4)_3 + H_2O \qquad (2)$$

The amount of sulfur precipitate was determined gravimetrically by filtration through Whatman 541 grade filter paper and drying at 100°C. When operating reactors in a fed-batch manner, the sulfur was usually collected when a new batch of gypsum was added. During operation of continuous feed reactors, sulfur was collected when the gypsum feed bottles were replenished.

Calcium Carbonate Precipitation and Analysis

To demonstrate the ability to regenerate calcium carbonate, effluent from the well-mixed reactor was brought to pH 11.0 through the addition of 50% w/v NaOH. Carbon dioxide was then bubbled through the vessel resulting in a white precipitate. This precipitate was filtered and dried as above, and was analyzed by X-ray diffraction. The X-ray diffraction sample was prepared by powdering the dried precipitate, dispersing it in toluene, and depositing a thin portion on an Si substrate. A Phillips Model XRG3100 diffractometer with Cu Kα radiation was used to perform the X-ray analysis. The peaks were then identified using search/match software of the International Center for Diffraction Data (ICDD) files for various organic/inorganic phases known in the literature.

Synthesis Gas Experiments

Initial trials to assess the potential use of synthesis gas as the carbon and energy sources in a gypsum reduction process were carried out under anaerobic conditions in a 2-L Schott bottle (Ace Glass Co., Vineland, NJ) fitted with a headplate, which facilitates gaseous influent sparging, and liquid and headspace sampling. A minimal salts media (1.2 g/L Na_2HPO_4, 1.8 g/L KH_2PO_4, 0.7 g/L $MgCl_2$, 0.2 g/L NH_4Cl, 0.2 g/L $FeCl_2$; batch vitamin solution 2 mL/L [24], and heavy metal solution 15 mL/L [24]) containing 1.5 g/L gypsum sludge was prepared anoxically within the bottle by boiling 10 min under a continuous nitrogen sparge. Thirty milliliters of concentrated SRB culture were inoculated into 970 mL media and sparged 10 min with synthesis gas (47% CO, 36% H_2, 10% CO_2, 2% N_2, 0.03% Ar, balance CH_4, Air Liquide, La Porte, TX). Methane and N_2 served as internal standards owing to their inert nature in the reactions under consideration. The pH was readjusted to 6.5 (with 6.5*N* NaOH), and the bottle incubated at 30°C with gentle shaking.

The bottle headspace was sampled daily by withdrawing 350 µL and injecting onto the gas chromatograph. Liquid samples of 3 mL were removed following gas withdrawal, filtered through 0.2-µ*M* filters, and analyzed for sulfate, organic acids, and pH. Three mL of nonsulfate-containing makeup media was injected immediately after liquid withdrawal so as not to cause a vacuum within the bottle.

RESULTS AND DISCUSSION

Serum Bottle Experiments

Batch experiments conducted in serum bottles demonstrated that a mixed strain of SRB was capable of utilizing organic acids in AD-MSS media to reduce FGD gypsum to hydrogen sulfide (Figs. 3 and 4). The results show that this sulfide production was biological, rather than chem-

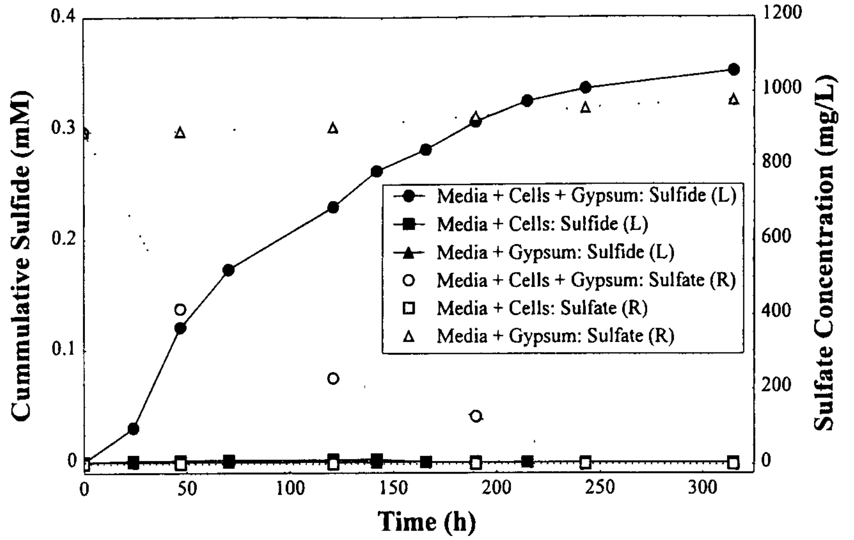

Fig. 3. Sulfate reduction and sulfide production from FGD gypsum sludge by SRBs. Serum bottles were established with (a) media, SRB, and gypsum, (b) media and SRB, and (c) media and gypsum. Sulfate was rapidly depleted in the bottle with media, SRB, and gypsum at the rate of 8 mg/L/h (10^9 cells)$^{-1}$. No sulfide was detected in either the abiotic control or the control bottle without gypsum, indicating that sulfide production was owing to the biological reduction of FGD gypsum.

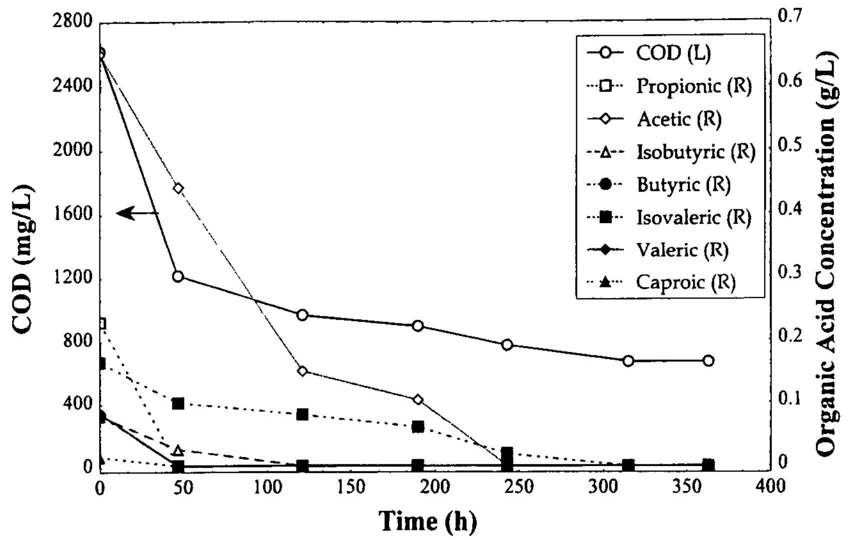

Fig. 4. COD reduction and organic acid utilization by SRB that utilize sewage digest as their carbon and energy sources. Serum bottles were established as described in Fig. 3. SRB utilized short-chain organic acids present in the AD-MSS media as their carbon and energy sources in the reduction of FGD gypsum to hydrogen sulfide. Organic acid utilization reduced the COD of the media from 2617 to 672 mg/L in 13 d.

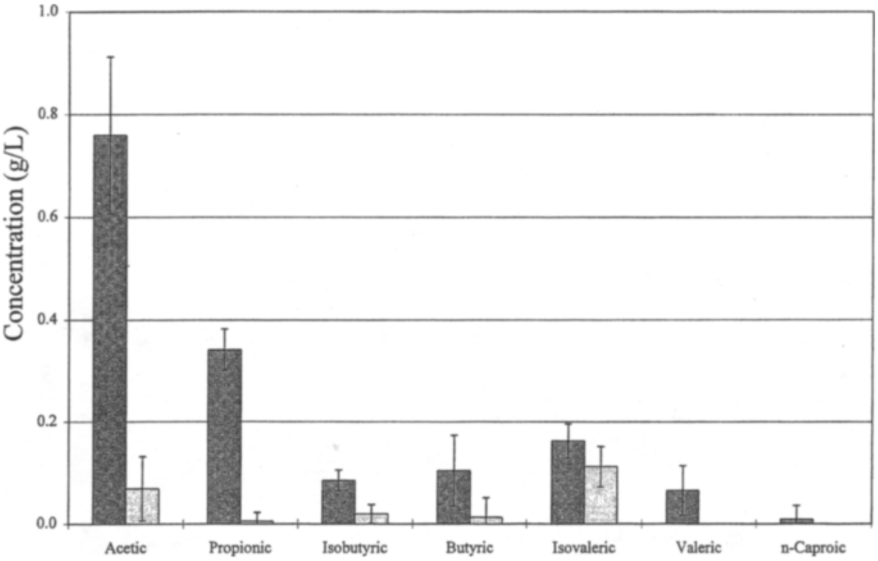

Fig. 5. Utilization of organic acids in the fed-batch well-mixed reactor. Both the AD-MSS media feeding the reactor ($n = 11$) and the reactor effluent ($n = 18$) were monitored during the course of the reactor run to determine which organic acids were utilized by the mixed SRB population. Paired bars denote the influent (dark) and effluent (light) concentrations of the organic acids assayed. Error bars represent the standard deviation of the pooled data. Acetic acid was the most prevalent acid in the feed and was also the product of the utilization of larger organic acids. The influent COD to the reactor was typically 3000 mg/L, whereas the effluent was 1500 mg/L.

ical, in that no sulfide was produced from the abiotic control. The COD was reduced from 2617 to 672 mg/L in 13 d, indicating the utilization of organic acids in the AD-MSS media. Individual organic acids fell below detection limits after 10 d. The sulfate reduction rate in these serum bottle experiments was 8.0 mg/L/h (10^9 cells)$^{-1}$ when calculated for the first 48 h. This compares favorably with the 18.5 mg/L/h (10^9 cells)$^{-1}$ reported by Apel and Barnes *(12)*, considering that they utilized pure *Desulfovibrio desulfuricans* with a rich media formulation with lactate as a carbon source, and reported the initial rate for a 20-h period.

Organic Acid Utilization in Reactor Systems

The AD-MSS media contains a variety of short-chain organic acids, including acetic, propionic, butyric, isobutyric, valeric, isovaleric, and caproic, which may be utilized by the mixed culture of SRBs *(22)*. Influent and effluent COD and organic acid concentrations were routinely measured in the continuous reactors to optimize AD-MSS media residence time and demonstrate organic acid utilization by the SRB culture. Such utilization by the well-mixed fed-batch reactor is illustrated in Fig. 5. It is seen that all of the assayed acids were utilized by the culture. In actual process

Table 1
Results of Gypsum Recycling Trials in Continuous Reactors

Inlet SO_4 (mg/L)	SO_4 Conversion (%)	Residence Time (h) /Recycle Ratio[a]	% S Recovered[b]	% COD Reduced	Productivity[c] (kg/m^3•d)
Mixed					
488	100	83/na	100	48	0.25
1,003	100	83/na	78	54	0.52
1,148	100	83/na	74	49	0.59
1,227	100	42/na	80	71	1.27
Column					
578	100	8/na	93	40	1.40
928	100	8/na	98	5	2.25
1107	100	8/na	73	19	2.68
896	100	4/2.8	73	62	4.59
1,000	100	3/2.2	92	64	6.55

[a] Residence times were calculated by dividing the working liquid volume of the reactor by the gypsum feed influent rate. For the well-mixed reactor, the working liquid volume was 1 L. The immobilized-cell reactor had a liquid working volume of 81 mL. When operated in the recycle mode, the recycle ratio for the immobilized-cell reactor was calculated by dividing the total liquid flow to the reactor by the gypsum influent flow rate.

[b] The theoretically possible recoverable sulfur was calculated based on the concentration of sulfate in the feed solution and the duration of the experiment.

[c] The productivity is reported as kg of dried FGD gypsum sludge reduced/m^3 of reactor volume/d. It assumes that the FGD gypsum exists solely as $CaSO_4{\cdot}2H_2O$.

operation, the effluent water would be recycled for preparation of AD-MSS media. Any discharged water would have a reduced COD owing to the biological oxidation of the organic acids present. Allowable COD ranges for discharged water are between 300 and 2000 *(33)*. Although maximum reduction of COD is desired from the point of view of process water treatment, this is not feasible in a well-mixed reactor because such low levels of organic acids would adversely affect culture viability. In the well-mixed reactor, a media residence time of 3.5 d resulted in a typical reduction of COD from 3000 to 1500 mg/L. The columnar reactor with media recycle and an influent flow rate of 0.35 mL/min demonstrated a COD reduction from 3000 to 1100 mg/L.

Reactor Trials

Results from continuous gypsum recycling trials in the well-mixed reactor are summarized in Table 1. The duration for each test was 70–92 h. Trials were first conducted at a liquid residence time of 3.5 d with an increasing gypsum concentration until saturation was reached in the feed solution. At this point, further gypsum loading to the reactor was achieved by increasing the feed rate of saturated solution to the reactor, thus decreasing the liquid residence time. Total conversion of sulfate was realized in each case; however, further increases in gypsum loading were not possible beyond the 42-h residence time trial owing to extensive cell washout in the well-mixed reactor. Between 75 and 100% of the sulfur in the gypsum sludge was recovered as elemental sulfur through ferric sulfate precipitation, and the COD of the process water was typically reduced by 50%. The maximum productivity achieved in the well-mixed reactor was 1.3 kg/m^3/d, being limited by biomass washout. As with the well-mixed reactor, trials in the immobilized-cell reactor were first conducted at a set liquid residence time with increasing gypsum concentration until saturation was reached in the feed solution. With a saturating concentration of gypsum and a one-pass influent flow rate of 0.17 mL/min. however, an appreciable pH gradient was established in the reactor. The pH at the reactor inlet was 7.0, whereas the pH reached 8.3 at the reactor apex, beyond the optimal pH for SRB activity. At this point, further gypsum loading to the reactor was achieved by operating the reactor in a "recycle" mode in which the total flow rate of liquid through the reactor was increased to 1.0 mL/min, and the reactor effluent was returned to a holding vessel where the pH of the liquid was adjusted to 7.0 before re-entering the reactor. Addition of gypsum to the reactor was controlled by altering the influent and effluent flow rates from the holding vessel while keeping the total flow of liquid through the reactor constant at 1 mL/min. In this manner, the gypsum loading to the reactor could be increased, the biomass in the reactor was more effectively utilized, and reactor productivity increased while maintaining 100% conversion of gypsum into sulfide. A maximal reactor productivity of 6.6 kg/m^3/d was achieved with complete sulfate conversion and >60% reduction in the COD of the process liquid. This corresponded to a hydraulic loading rate of 1349 L/m^2/d. To date, the capacity of the immobilized-cell reactor has not been exceeded, and further increases in productivity are expected.

Sulfur and Calcium Carbonate Recovery

Elemental sulfur was recovered from the FGD gypsum by oxidizing the sulfide gas formed through bacterial conversion of sulfate. The theoretically possible amount of recoverable sulfur was calculated based on the known sulfate concentration in the input media and its rate and duration of addition to the reactor. As seen in Table 1, >70% sulfur recovery was achieved in all of the reactor trials. Loss of sulfur could be owing due to the formation of insoluble sulfides with metal constituents of the FGD gypsum or AD-MSS media, the incomplete dissolution of hydrogen sulfide into the ferric sulfate solution, or loss on filtering the resulting sulfur precipitate. Improvements in sulfur recovery efficiency will obviate the need to treat

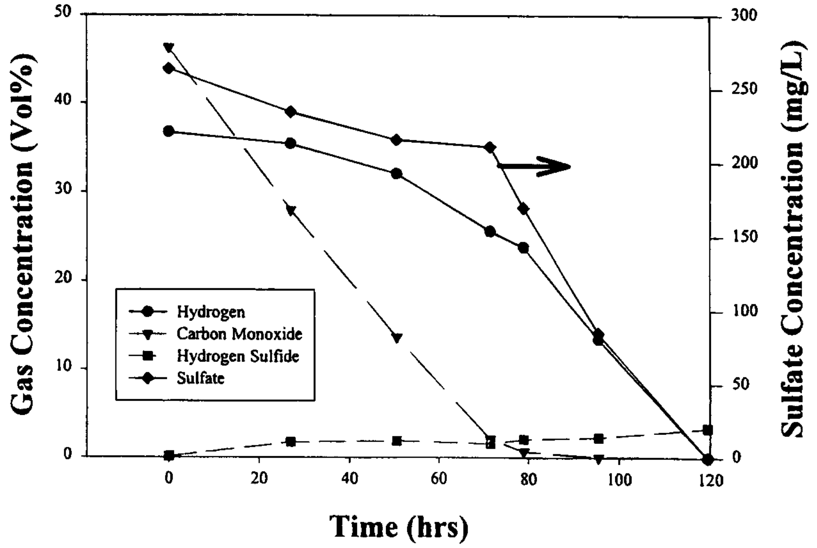

Fig. 6. Synthesis gas as a carbon and energy source for SRB in the reduction of FGD gypsum to hydrogen sulfide. Although reduction rates were not as rapid as those seen in experiments utilizing AD-MSS media, these preliminary studies indicate that synthesis gas may also serve as an inexpensive energy source for gypsum bioconversion.

the liquid effluent further in the overall process. The melting point of the yellow powder resulting from ferric sulfate oxidation was 121°C, consistent with that of elemental sulfur.

Spent process solution was precipitated using carbon dioxide in an alkaline solution in order to recover calcium ions as calcium carbonate—which could be reutilized as an adsorbent for sulfur dioxide in flue gases. X-ray diffraction analysis of the resulting precipitate revealed that major signals were attributable to calcium carbonate and other calcium salts. Additional peaks were attributable to residual organic matter that could be burned off at the coal plant through sorbent injection.

Synthesis Gas Experiments

Batch experiments demonstrated that a mixed strain of SRB was capable of utilizing CO and H_2 to reduce FGD gypsum to H_2S (Fig. 6). Sulfate concentrations were reduced from 263 to 0 mg/L in 120 h, much more slowly than that seen in the AD-MSS media trials. Although results are preliminary and the exact stoichiometry of the reactions are not understood, multiple experiments have demonstrated that sulfide production and sulfate elimination are concomitant with decreases in CO and H_2 levels in the headspace gas. Du Preez et al. *(18)* proposed that the stoichiometry for SO_4^{2-} reduction using H_2 is:

$$4H_2 + SO_4^{2-} \rightarrow H_2S + 2OH^- + 2H_2O \qquad (3)$$

with CO being utilized to produce additional H_2 by:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (4)$$

van Houten et al. *(19)* suggested that H_2 may also be utilized in the synthesis of organic acids. In our preliminary investigations, without a mass balance closure on CO_2 or the amount of biomass, we are unable to determine the extent to which Eq. (4) enters into the observed sulfate reduction. Like van Houten et al. *(19)*, we observe the production of organic acids (up to 0.5 g/L acetic acid and 0.1 g/L propionic acid) and more H_2 being utilized than is stoichiometrically needed for the reduction of sulfate. Although more research is needed to elucidate the mechanisms of synthesis gas utilization by SRB, it is clear that this inexpensive energy source may be utilized in the bioconversion of FGD gypsum.

CONCLUSIONS

The components of a closed-loop biochemical process for the conversion of FGD gypsum into elemental sulfur and calcium carbonate have been demonstrated at the bench scale, and offer an attractive alternative to the landfilling of waste gypsum. Although an economic assessment of the proposed process has not been completed, this study has established a low-cost carbon source and an efficient reactor design, which improve process economics and move this technology toward economic viability.

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