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THERMAL TREATMENT, CARBON SEQUESTRATION, AND METHANE GENERATION THROUGH DEEP-WELL INJECTION OF BIOSOLIDS

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INTRODUCTION

Almost 10 million wet tons of municipal sewage sludge (biosolids) are generated each year in the United States. The volume and the costs associated with disposal and recycling of this material are steadily increasing nationwide. For example, most sanitation districts in Southern California are forced to truck their biosolids more than 100 miles to rural areas in Kern County and Riverside County at processing and transport costs of $40 per wet ton or more.

The prevailing methods for biosolids management include land applications (to, rangeland, forests, or public parks), composting (mixing biosolids with other organic wastes such as wood chips), and landfill disposal. Most biosolids generated in Southern California are currently applied to the surface or placed in landfills, where they degrade and are released into the atmosphere each year as several hundred thousand tons of carbon dioxide. A primary obstacle confronting biosolids land application is public perception and nuisances such as odor and wind-blown dust. Severe weather conditions can hamper land application for indefinite periods, leaving districts scrambling for alternative disposal techniques. Trucks hauling large volumes of waste on public roads and highways create additional risks and nuisance. In areas where biosolid material is disposed into municipal waste landfills, the capacities of these limited resources are

also stretched. Greenhouse gas generation (primarily CO_2 and CH_4), surface land impairment, and potential groundwater impacts are also byproducts of land application and landfill practices.

Occasional local opposition to landspreading, combined with increasing volume and costs, have pressured sanitation districts nationwide to investigate alternative management options for biosolids. Terralog Technologies and the City of Los Angeles have therefore proposed a new and innovative technology for biosolids management through deep-injection disposal. The ideal geologic target for such a disposal method would be a high porosity and high permeability sand formation with an effective overburden seal, such as a depleted oil and gas formation or similar geologic trap. In the elevated temperature environment of the subsurface, the biosolids should undergo a natural process of anaerobic biodegradation, which could fully sterilize the material within days, and within months, convert a significant portion the organic mass to methane and carbon dioxide. The carbon dioxide, which would otherwise be released into the atmosphere during land application, would preferentially dissolve into the formation fluid, because it is about ten times more soluble than methane at the pressure and temperature conditions typical of the subsurface. Through a combination of solubility trapping and mineralization, the CO_2 would be sequestered while relatively pure methane would accumulate for possible recovery and use as an energy source.

PROPOSED TECHNOLOGY

Terralog Technologies and The City of Los Angeles, working in coordination with the U.S. Environmental Protection Agency Region 9, propose to demonstrate the technology of biosolids injection through a four-year pilot project in Los Angeles County. New wells for the project would be drilled to a depth of about 1,700 m in an isolated fault block near the Wilmington Oil Field in Long Beach. The injection-reservoir targets will be the Ranger and Upper Terminal zones, where the reservoir temperatures are on the order of 125 to 145°F. Extensive monitoring, sampling, and parallel laboratory research would be conducted to better quantify biodegradation rates, long-term carbon sequestration, and optimum injection parameters for enhanced methane generation.

This technology holds a number of very significant environmental advantages over current long-distance transportation and land application options. These advantages include:

- More rapid and more thorough thermal treatment (sterilization,
- Greater protection for surface and groundwater,
- Reduced truck traffic and associated emissions,
- Reduced greenhouse gas (CH_4 and CO_2) release to atmosphere, and
- Potential recovery and beneficial use of generated methane as a clean fuel.

Placing material at least 1,500 m below any usable source of groundwater, with thick and clearly defined permeability barriers that block upward flow, is inherently more protective of groundwater than placing material directly on the surface, where it can percolate unimpeded to groundwater only tens of feet below. Furthermore, the high-temperature (≈55°C) saline environment (on the order of 20,000 ppm TDS) existing at depth is extremely hostile to

pathogens. Deep-well injection of biosolids therefore substantially reduces any potential impact to the surface water and groundwater when compared with surface application.

Deep-well injection would substantially decrease the current truck traffic associated with biosolids transport, and allow biosolids to be managed within Los Angeles County. After successful conclusion of the demonstration phase, new injection sites could be constructed adjacent to the current Hyperion and Terminal Island sewage treatment plants, both of which are situated near existing oil and gas reservoirs.

A permit application for an experimental demonstration project titled "Converting Biosolids to Methane through Deep Injection and Biodegradation," was submitted to the U.S. EPA in June 2001. The proposed experimental program includes both field measurements (monitoring and fluid and gas sampling) and supporting laboratory experiments to better interpret and optimize the field observations.

The objectives of the laboratory experiments are to demonstrate and measure to what extent:

- The high temperature in the deep subsurface (about 55°C or 130°F) will thermally treat (sterilize) the biosolids;
- The extent to which biodegradation in the subsurface will convert the biomass to methane and carbon dioxide;
- The potential for carbon dioxide to be permanently sequestered through solubility trapping in the formation brine; and
- Whether methane could be generated that might eventually be recovered for beneficial use.

Although a definitive technical validation can come only from field demonstration and measurement, we believe there is a strong likelihood of success, because full-scale digestion studies have been completed by the City of Los Angeles at the Hyperion treatment plant, El Segundo, California, demonstrating sterilization and biodegradation at high-temperature conditions consistent with the deep subsurface. Small-scale laboratory experiments at the University of California at Los Angeles also clearly demonstrate that biodegradation and methane generation will occur under high temperature and high pressure conditions expected in the subsurface. The remainder of this chapter is devoted to a review of both the Hyperion digester tests and the high temperature, high pressure, biosolids-degradation tests. The chapter concludes with a discussion of the feasibility of biosolids waste disposal through deep-injection disposal in the subsurface.

HYPERION ANAEROBIC MESOPHILIC AND THERMOPHILIC DIGESTION PILOT TEST

The pilot test to evaluate treatment levels and gas generation under mesophilic and thermophilic conditions was conducted at the Hyperion treatment plant during 2001. Data for October 2001 is described in this chapter. During this period, one digester was operated under thermophilic conditions (about 130^{o}F or 54^{o}C) and another digester was operated under sustained mesophilic conditions (about 96^{o}F or 36^{o}C) at similar feed rates, thereby allowing a direct comparison between these two operating temperatures.

Description of Facilities

Hyperion currently employs twenty new egg-shaped digesters and six conventional digesters to stabilize primary and waste-activated sludge. About 2 million gallons per day (MG/D) or 7.6 ML/day of Primary Sludge (PS) settling from the advanced primary treatment process is pumped and distributed equally into the 26 digesters through primary sludge lines. Another 0.8 MGD Thickened Waste Activated Sludge (TWAS) discharge from the Waste Activated Sludge Thickening Facility is also pumped and distributed into all the digesters.

The twenty egg-shaped digesters are grouped into three operational batteries called D1, D2, and E. Digester D1 was set at thermophilic conditions, and digester D2 was set at the mesophilic condition. A summary of their operational conditions and resulting process parameters is presented in Table 1.

Steam was used to maintain optimal process temperature. The mesophilic digester required about 80,000 lb (36,000 kg) of steam each day to maintain an average temperature of about 96^{o}F (36^{o}C) for an average retention time of about 18 days. The thermophilic digester required more than three times as much steam, about 269,000 lb (122,000 kg) each day, to maintain a temperature of about 130^{o}F (54^{o}C) for an average retention time of 19 days.

Both digesters produced a substantial amount of biogas, containing methane and carbon dioxide. The biogas is collected and conveyed to on-site gas storage and compressor facilities, where it is either piped to the Scattergood Power Generating Station, or is used in on-site boilers. The gas storage and compressor facility is also capable of routing excess digester gas through a gas flare facility.

Test Results

Figure 1 summarizes fecal coliform counts measured in digesters D1 and D2 during October 2001. Under thermophilic conditions, the fecal coliform count after discharge averaged about 88 MPN/g (most probable number per gram), thus meeting Class A pathogen requirements set by the U.S. EPA (less than 1000 MPN/g). Under mesophilic conditions, however, the fecal coliform count averaged about 290,000 MPN/g. The higher temperature conditions therefore provide enhanced biosolids treatment.

Figure 2 summarizes methane and carbon dioxide generated in digesters D1 and D2 during October 2001. Average biogas production rates are also summarized in Table 1. Under thermophilic conditions, approximately 1.31 MSCF/day (399 L/s @STP) of methane and 0.71 MSCF/day (216 L/s @STP) of carbon dioxide were generated from an average feed rate of about 0.85 MGD (37.2 L/s). Under mesophilic conditions, approximately 1.54 MSCF/day (469 L/s @STP) of methane and 0.83 MSCF/day (253 L/s @STP) of carbon dioxide were generated from an average feed rate of about 1.03 MGD (45.1 L/s). As illustrated in Figure 2, the pilot tests indicate that both thermophilic and mesophilic digestion will create biogas at roughly equal rates. In terms of volatile solids loading, about 6 to 8 scf (160–210 L @ STP) of methane were produced and about 3 to 4 scf (80–100 L @ STP) of carbon dioxide were produced per lb (0.5 kg) of volatile solids. The average quantity of volatile solids destroyed is about 58 wt. percent.

EXPERIMENTAL VERIFICATION OF BIODEGRADATION AND METHANE GENERATION UNDER SIMULATED DEEP SUBSURFACE CONDITIONS

In contrast to the operational conditions of the Hyperion plant, the biosolids in the subsurface would be exposed to higher salinity fluids, to pressure, and to minerals of the host formation. However, it would be expected that biodegradation would still occur, although initially at slower rates while bacteria adapt to the ambient environment. To test this hypothesis, laboratory experiments were conducted to demonstrate methane and carbon dioxide production from digested biosolids in the presence of high-salinity brine and core materials. Two sets of experiments were conducted. In the first set, Phase I, the effect of salinity, temperature, and the presence of core material on methanogenesis at ambient pressure were investigated. In the second set, Phase 2, the effect of biosolids degradation in the presence of brine was investigated at elevated pressure and temperature.

Phase I: Effect of Salinity, Temperature, and the Presence of Core Material on Methanogenesis at Ambient Pressure

A series of experiments were conducted to measure the impact of salinity, temperature, the effect of core material, and added organic nutrients on methanogenesis and carbon dioxide formation. The amount of biogas generation was measured at discrete time intervals of 9, 20, and 55 days, and in one case, 9, 27, and 59 days respectively. The materials preparation and conditions for the tests are described in the following paragraphs.

Materials Preparation

a. Biosolid Sample Preparation

Dewatered mesophilic Class B sludge samples (biosolids) from the Hyperion wastewater treatment plant were obtained on three separate days during November 2000. A composite biosolid sample was prepared by using an equal weight of sludge from each sampling date. The composite sludge was then manually mixed and homogenized with 50% by weight of an aqueous solution in a glass mortar and pestle.

b. Core Sample Preparation

The Southern California Gas Co. provided core samples from the Sesnon formation (Aliso Canyon, Porter 25R well; 164 slabs, approximately 300 g each; depth range: 7,820–7,958 ft.). Sesnon core samples are compacted sand and rocks. In order to transfer core material to the serum vials used for the test, it was necessary to manually crush the slabs to smaller pieces. Particles with a size diameter smaller than 12 mm and bigger than 4.7 mm were selected using sieve No. 4 (U.S. Standard). (Note: Twelve millimeters is the diameter of the mouth of the vial, and 4.7 mm is the biggest particle size that can be sieved with commercially available sieves.) A composite of core samples was prepared by manually mixing crushed material from cores 5 ft depth apart from each other. (The whole sampling depth range was covered, and enough core material was obtained for all the ambient pressure studies.)

c. Test Vial Preparation And Analysis Of Gas Produced

Thirty grams of crushed Sesnon core material were transferred to 120 mL serum vials and 30 g resuspended sludge (15 g of dewatered sludge) were then added. These amounts provided a 1:2 (w/w) biosolids to core material ratio, and approximately 60 mL headspace to collect the gas produced. Vials were sealed with butyl rubber stoppers and crimped with aluminum seals. Vials were manually shaken to blend the core material with the biosolids as much as possible. Air present in the headspace of the vials was flushed out with O_2-free nitrogen for five minutes. Vials were then equilibrated for one hour at the test temperature, and the pressure zeroed to atmospheric pressure using a 60 mL syringe. Sterile controls to determine the abiotic contribution to methanogenesis were also prepared. Killed controls were made by twice autoclaving vials containing core material/sludge, sludge only, or core material/fluid at 130^{o}C for 30 min.

The volume of gas produced was measured at ambient pressure with a 60 mL syringe and then wasted. The pressure in the vials was zeroed again to atmospheric pressure after the gas volume had been determined. A 0.5 mL gas sample was taken using a gas-tight syringe at atmospheric pressure, and gas composition (CH_4 and CO_2) was analyzed with a gas chromatograph equipped with a thermal conductivity detector. A stainless steel column packed with Carboxen 1000 (60/80 mesh, 8 ft length, 1/8 o.d.) was used. The oven, detector, and injector were maintained at 85^{o}C. Helium was used as carrier gas at a flow equal to 30 mL/min.

Methods of Evaluation

a. Effect of Temperature

The effect of temperature on methanogenesis was tested in a series of three experiments at 45, 55, and 65^{o}C (113, 131, and 149^{o}F), respectively.

b. Effect of Additional Carbon Sources on Methanogenesis

Although the use of additional carbon sources will not be practiced when injecting biosolids under actual field conditions, it was important to test whether the native bacteria present in the biosolids have the required metabolic activities to produce methane. Two substrates that can be easily used during the methanogenic process were added. In test series G, glucose, which is easily fermented to acetate and other volatile fatty acids, was added to the resuspended sludge with a final concentration of 5 g/L. In series A, acetate, which is the principal substrate for methane production, was added to the sludge with a final concentration of 50 mM.

c. Effect of Salinity on Methanogenesis

In order to test whether the salinity present in the brine would have any effect on methanogenesis, three levels of salinity were tested. Brine from the Porter well was provided by the Southern California Gas Co. Three series of experiments were prepared, one for each salinity level tested:

- Series B, full-strength brine (pH 7.2)
- Series BW, brine diluted with tap water to 50% (by volume) of full strength

- Series W, tap water

d. Effect of Core Material on Methanogenesis

The effect of the core material on methanogenesis was tested. Vials containing only sludge resuspended in brine and incubated at 55°C (131°F) were compared against vials containing the core material and sludge resuspended in brine.

e. Effect of Sample Size

A 1.1 liter bottle was filled with 300 g of reconstituted sludge, and 300 g of core material, and incubated at 55°C in order to address a potential effect of the size of the serum bottles (120 mL) used in this study on the CH_4 production.

RESULTS AND DISCUSSION

The experimental results are summarized in Tables 2 through 7, and illustrated in Figures 3, 4, and 5. Experiments are designated where appropriate according to the following notation: the fluid used (B for brine), the additional carbon source (G for glucose and A for acetate), and the temperature tested (in degrees Celsius).

Figures 3 and 4 show the overall results of the effect of temperature and additional carbon sources on CH_4 and CO_2 production from biosolids resuspended in full-strength brine. Labels at the bottom of each set of bars indicate the fluid used (B for brine), the additional carbon source (G for glucose and A for acetate) and the temperature tested (in degrees Celsius).

From Figures 3 and 4, it is clear that bacterial populations with the required metabolic activities (hydrolytic, fermentative, and methanogenic) were present in the biosolids. Also, it is clear that the enzyme systems of these microbes are nearly saturated, because vials with additional glucose only produced a slightly greater amount of CH_4 and CO_2 compared to those without glucose. Acetate addition did not produce any significant effect on CH_4 and CO_2 production. This result also indicates saturation of the enzyme systems related to the conversion of acetate to CH_4 and CO_2.

It is also apparent from Figures 3 and 4 that temperature exerts a greater inhibitory effect on CH_4 production than on CO_2 production. Figure 5 was obtained using the same data as for Figures 3 and 4 for those vials without an additional carbon source. Figure 5 shows that, at 45°C, methane was initially produced at a faster rate for the first 9 days than for the remainder of the incubation period. At 55 and 65°C, inhibition of CH_4 production was observed immediately after incubation with no indicated adaptation. Figure 5 also shows that CO_2 production was very similar for the three temperatures tested during the first 9 days of incubation, and inhibition was observed for the remainder of the incubation period. These observations can be explained by the hypothesis that the methanogenic bacterial populations are more sensitive to high temperatures than the fermentative bacterial populations. This difference in temperature sensitivity could produce an imbalance in the bacterial populations. Fermentative bacteria at any of the tested temperatures could initially produce a large amount of acetic acid and other volatile fatty acids (VFAs) and CO_2. Methanogenic bacteria grown at 45°C could further metabolize these VFAs to CH_4 and CO_2. However, at 55 and 65°C, methanogenic bacterial growth could be inhibited, and VFAs would not be further metabolized. As a consequence, acetate and other VFAs would accumulate, CH_4 and CO_2 production would decrease, and the pH would fall.

Levels of VFAs and pH were measured in the sludge resuspended in brine, and in contact with core material, after 55 days of incubation to obtain further support for the postulated hypothesis. Table 8 shows the concentration of VFAs and the pH values. The pH was similar for the three temperatures tested, but the higher the temperature, the higher the acetate level found. Levels of the other VFAs measured were very similar at the three temperatures tested. These results further indicate that high temperatures inhibit methanogenic bacteria that metabolize acetate to CH_4 and CO_2. The observation that the accumulation of acetate did not produce a decrease of the pH at high temperatures may be explained by the alkalinity present in the brine.

Table 9 summarizes the effect of the temperature on the total amount of CH_4 produced after 55 days of incubation. Methane produced is referred to the total organic carbon (TOC) present in the reconstituted sludge. Also, it is referred to kg of dewatered sludge.

The cumulative amounts of CH_4 and CO_2 in a 1-L bottle are shown in Figure 6. Methane produced per unit of TOC and kg of dewatered sludge is also reported in Table 9. The data indicate that the size of the container used for the test has no significant effect.

The effect of salinity on CH_4 and CO_2 production is shown in Figure 7. Methane production is initially inhibited by full-strength brine (Figure 7a). However, after 55 days of incubation, the levels of CH_4 produced in the presence of water and full-strength brine become similar, indicating a gradual adaptation of methanogens to the high salinity. This observation is in agreement with reports of methanogenesis in other hypersaline environments (i.e. marine sediments). Inhibition of carbon dioxide production was not observed at any level of salinity.

The core material initially inhibited CH_4 production (Figure 8a). However, after 55 days of incubation, partial recovery of the methanogenesis was observed. The reason for this inhibitory effect is unknown. A possible explanation is that residues of oil present in the core material may inhibit methanogenic bacteria. However, this needs further verification. No inhibitory effect by the core material was observed on CO_2 production (Figure 8b).

After 55 days of incubation, methane production declined to very low values with core material in the presence of either water, 50% brine, or brine. Production of a few milliliters of carbon dioxide was observed in vials containing core material and brine, or 50% brine amended with glucose. This observation may indicate that fermentative bacteria present in the brine have a very slow growth rate under these conditions.

No CH_4 or CO_2 production was observed from sterile controls, indicating that the gases produced in the described experiments are of biological origin.

Phase 2: The Effect of Pressure on the Anaerobic Digestion of Biosolids in the Presence of Saline Fluid

In contrast to the Phase 1 experiments in which mesophilic Class B biosolids were used, the Phase 2 experiments employed Class A thermophilic biosolids.

Equipment Used

The experiment was conducted using a 250 cc stainless steel Tempco pressure vessel able to compress a mixture of biosolids to high pressure, as might be expected to occur within a fracture in the subsurface injection zone. The experimental arrangement is illustrated in Figure 9. The pressure vessel was wrapped with Thermodyne/BriskHeat heating tape, and surrounded by a 1.5

in. thick cylinder of insulation. Fisherbrand digital temperature controller and indicator were used to maintain a constant temperature as recorded with an RTD-type contact sensor placed on the outer vessel wall. The controller set output power to the heating tape, maintaining a constant set temperature. The sensor had been previously calibrated to take into account small differences in temperature between the interior and exterior of the vessel wall.

An external Enerpac hydraulic pump, connected to the downstream piston chamber, was used to maintain a constant pressure during the testing period.

Experimental Procedures

The basic laboratory test procedure may be described as follows:

1. 135.5 gm of Class A biosolids (wet cake) from the thermophilic digester of the Hyperion treatment plant was combined with 25 mL of brine and placed into a 250 cc stainless steel Tempco pressure vessel. The initial biosolids wet cake contained 30.2% total solids and 69.8% water by weight. The salinity of the brine mixture was 10,000 mg/L. The vessel was placed vertically, with the biosolids mixture placed above the piston.
2. Air was displaced from the vessel by slowly moving the piston upwards until only liquid could be seen exiting the upper vessel isolation valve. This valve was then closed.
3. Vessel temperature was increased to 50ºC.
4. Piston pressure on the sample was increased to 2200 psia (15.17 MPa).
5. The sample was then left to biodegrade for a total of about 85 days. The vessel assembly was checked daily to verify that temperature and pressure remained at the set points.
6. Gas samples were collected and analyzed after 34, 56, and 85 days, in accordance with the procedures described in the following section, and transferred to the California Institute of Technology Petroleum Energy and Environmental Research (PEER) laboratory for gas component analysis.
7. At the conclusion of the test period, the remaining gas was purged, and the remaining biosolids mixture was removed and analyzed for volatile solids content.

Sample Analysis

Identification and quantification of individual hydrocarbons and non-hydrocarbon gas components was carried out using a two-channel Hewlett-Packard 6890 Series Gas Chromatograph (GC), which was custom-configured by Wasson ECE Instrumentation. This gas chromatograph (HP 6890) is designed to analyze small volumes of gas samples (a few mL of gas at atmospheric pressure) for light hydrocarbons (up to hexane), carbon dioxide, carbon monoxide, hydrogen sulfide, hydrogen, helium, nitrogen, and oxygen/argon. The GC was fitted with a capillary column, five packed columns, a flame ionization detector (FID), and two thermal conductivity detectors (TCD). For hydrocarbon analysis, the GC oven was programmed from 85°C (5 min hold time) to 180°C at 15°C/min (10 min hold time) with FID detection on Channel 1. The non-hydrocarbon analysis was run on Channel 2 with the packed column array and dual TCDs for detection. Detector responses were calibrated using certified gas standards from Scott

Specialty Gases (precision to within 1 mol.% for each compound). The chromatogram was integrated using PE Nelson Turbochrom 4 software.

The sample arrived in an assembly that had a valve at either end of a piece of tubing. After connecting the sample assembly into the system, one valve was opened into a custom-made glass vacuum line with a residual pressure of 0.001 mbar. After isolation from the vacuum pump, the product gases were volatilized into the glass vacuum line.

The heavier gaseous components were cold-trapped with liquid nitrogen (–196ºC), while the lighter gases were concentrated into a precalibrated volume using a mercury Toepler pump. Replacing the liquid nitrogen with a mixture of dry ice and acetone (–80ºC) released the other volatile species, excluding water and organic compounds heavier than C_5. These gases were drawn into the same calibrated volume in order to determine the moles of gas. The number of moles of gas was calculated via the ideal-gas relationship.

Experimental Results

The gas component analyses reported by the Caltech PEER Center verified that biodegradation did in fact occur within the high pressure and high temperature reaction vessel within thirty days, and continued during the entire test period. Table 10 presents a summary of the current laboratory test results. Figure 10 presents a plot of methane and carbon dioxide content versus time. At the conclusion of the test, methane content is about 70 vol.% and carbon dioxide content is about 27 vol.% of the generated biogas.

These percentages of methane and carbon dioxide reported are generally consistent with large-scale, high temperature, anaerobic digestion tests previously conducted by the City of Los Angeles, as discussed above.

SUMMARY AND CONCLUSIONS

The pilot plant tests, using the Hyperion treatment plant digesters under both mesophilic and thermophilic conditions, i.e., at 36°C and 54°C respectively, show that both methane and carbon dioxide were generated in significant quantities in a ratio of approximately 2:1. The average quantity of volatile solids destroyed was about 60 wt.% after 18–19 days. Although the thermophilic conditions resulted in incrementally less methane and carbon dioxide production, the coliform bacterial count was drastically reduced to 88 MPN/g, thereby meeting Class A pathogen requirements set by the U.S. EPA.

When dewatered Hyperion mesophilic sludge samples were subjected under laboratory conditions to elevated temperatures between 45 and 65^{o}C in the presence of brine and core material, it was found that methane production is strongly inhibited at 55 and 65^{o}C, i.e., elevated temperature is the most inhibitory parameter for methane production during anaerobic digestion in the presence of brine and core material. Carbon dioxide production was also curtailed, but to a lesser extent. The methanogenic bacteria that metabolize acetate to CH_4 and CO_2 (aceticlastic methanogens) seem to be the most sensitive to inhibition at elevated temperature.

The high salinity present in the brine also inhibited the methane production. However, after 55 days of incubation, a gradual acclimation of methanogens was observed. This may indicate that longer incubation times will relieve the inhibitory effect caused by the brine. Also, the use of water to pump the dewatered biosolids may improve the CH_4 production rate. Core material also

inhibited methane production, although the reason for this effect is unknown. However, methanogenesis was observed to recover partially after 55 days of incubation.

The Phase 1 studies suggest that the presence of brine, core material, and high temperature adversely affect the anaerobic digestion of wastewater biosolids. However, the process still is capable of transforming organic matter into CH_4 and CO_2 at a lower rate. After 55 days of incubation, 63 $ft^3$of CH_4 per metric ton of dewatered biosolids were produced under the most unfavorable conditions (65^oC, full strength of brine and in presence of core material). Over time the microbial populations present in the injected biosolids would be expected to adapt to the conditions found in the deep well.

The use of biosolids digested under thermophilic conditions (55^oC) could solve the inhibitory effect observed on sludge that was treated under mesophilic conditions (35^oC), as was demonstrated in the Phase 2 laboratory tests. In these tests, conducted at 2,200 psia (15.17 MPa) at 50°C using biosolids from the thermophilic digester in the presence of brine, gas production was similar to that observed during the thermophilic digestion at the Hyperion plant. In the Phase 2 tests, biogas was clearly generated with relatively high methane content (about 70 vol.%).

Although the conditions encountered in the subsurface can never be precisely duplicated, a similar biodegradation process to that observed in the Hyperion and laboratory-scale tests should occur when biosolids are injected into a deep subsurface reservoir. The underground in situ temperatures would autoclave and digest the biosolids, thereby sterilizing and converting the sludge into benign materials. The biosolids would be exposed indefinitely in situ to natural thermophilic conditions, which would be similarly anaerobic (lacking oxygen). Therefore, it is reasonable to assume that the biosolids will biodegrade into methane and carbon dioxide in a similar manner.

The observations from all of the tests conducted to date provide some insight on expected methane generation volumes in the field. In the Phase 2 tests, almost 20 percent of the available volatile solids were destroyed within 90 days. We can therefore expect that in the deep subsurface within the four year demonstration period, most of the volatile solids content injected during the first year would be destroyed, and converted to approximately 70% methane and 30% carbon dioxide. Furthermore, the tests have demonstrated that methane can be generated even from highly digested Class A biosolids. The Phase 2 tests have demonstrated that biodegradation of municipal biosolids can occur at the high pressure and high-temperature conditions expected in the subsurface, at about 1,500 m depth at Terminal Island, providing an incentive to proceed with field experimentation and demonstration. In the field experiment, it is planned to inject Class B material with a higher organic volatile solids content, which should lead to additional gas generation.

ACKNOWLEDGMENTS

Some of the laboratory experiments described in this paper were conducted by Felipe Alatriste-Mondragon and Birgitte Ahring at the University of California, Los Angeles. Gas sampling was completed by Mark Haught and Yongchun Tang at the Caltech PEER Center.

Figure Captions

Figure 1. Comparison of fecal coliform count under thermophilic and mesophilic conditions. [color]

Figure 2. Methane and carbon dioxide production from D1 and D2 digesters. [color]

Figure 3. Production of methane from 15 g biosolid samples resuspended in 15 g of brine in the presence of 30 g core material. See text for sample designations. [color]

Figure 4. Production of carbon dioxide from 15 g biosolid samples resuspended in 15 g of brine in the presence of 30 g core material. See text for sample designations. [color]

Figure 5. Biogas production from resuspended biosolids in brine mixed with core material as a function of temperature. (a) Methane (b) Carbon dioxide. [color]

Figure 6. Biogas production from 300 g of resuspended biosolids with 300 g brine mixed with 300 g core material at 55°C. [color]

Figure 7. Biogas production from resuspended biosolids as a function of brine concentration at 55°C. (a) Methane (b) Carbon dioxide. [color]

Figure 8. Biogas production from resuspended biosolids in brine with or without core material at 55°C. (a) Methane (b) Carbon dioxide. [color]

Figure 9. Generalized schematic for high-pressure biodegradation test apparatus. [color]

Figure 10. Methane and carbon dioxide content of sampled gas at 2,200 psi pressure. [color]

Table 1. Hyperion plant mesophilic and thermophilic test summary.

	Mesophilic Digester-D2	**Thermophilic Digester-D1**
Average Temperature	96°F (36°C)	130°F (54°C)
Retention Time	18 days	19 days
Average steam consumption	80 k lb/day (0.42 kg/s)	269 k lb/day (1.41 kg/s)
Average sludge feed rate	1.03 MG/D (45.1 L/s)	0.85 MG/D (37.2 L/s)
Average digested gas production	2.37 MSCF/day	2.02 MSCF/day
	(721 L/s @STP)	(615 L/s @STP)
Average CH_4 produced	1.54 MSCF/day	1.31 MSCF/day
	(469 L/s @STP)	(399 L/s @STP)
Average CO_2 produced	0.83 MSCF/day	0.71 MSCF/day
	(253 L/s @STP)	(216 L/s @STP)
Average fecal coliform count	290,000 MPN/g	88 MPN/g
EPA Pathogen Requirement Met	Class B	Class A

Table 2. Methane production (in mL) from biosolids resuspended in brine with core material present.

Experiment	**9 days**	**20 days**	**55 days**
B45	48.2	77.2	147.3
BG45	58.9	84.8	177.5
BA45	53.3	86.0	144.3
B55	19.3	25.5	46.6
BG55	32.5	40.6	51.0
BA55	16.9	33.0	44.9
B65	13.6	17.3	26.8
BG65	12.7	18.9	26.7
BA65	3.5	10.6	17.7

Table 3. CO_2 production (in mL) from biosolids resuspended in brine with core material present.

Experiment	9 days	20 days	55 days
B45	38.4	68.1	103.4
BG45	47.1	75.9	119.4
BA45	43.2	73.7	104.1
B55	37.3	53.7	74.8
BG55	52.2	71.3	81.8
BA55	36.1	59.0	71.0
B65	33.9	44.1	60.5
BG65	36.7	53.6	67.6
BA65	20.6	39.8	53.0

Table 4. Effect of temperature on CH_4 and CO_2 production from biosolids resuspended in brine and mixed with core material.

	CH_4			CO_2		
Days	**45°C**	**55°C**	**65°C**	**45°C**	**55°C**	**65°C**
Volume in mL						
0	0.0	0.0	0.0	0.0	0.0	0.0
9	48.2	19.3	13.6	38.4	37.3	33.9
20	77.2	25.5	17.3	68.1	53.7	44.1
55	147.3	46.6	26.8	103.4	74.8	60.5
Volume in cf/ton biosolids						
0	0.0	0.0	0.0	0.0	0.0	0.0
9	102.9	41.2	29.1	82.0	79.7	72.3
20	164.8	54.5	37.0	145.3	114.6	94.2
55	314.5	99.5	57.2	220.6	159.6	129.1

Table 5. Methane and carbon dioxide production from biosolids resuspended in brine and mixed with core material (55°C, 1-L Bottle).

Days	CH_4 (mL)	CO_2 (mL)
0	0	0
9	208.7	412.1
27	281.5	587.7
59	365.0	705.3

Table 6. Effect of salinity on CH_4 and CO_2 production from biosolids mixed with core material (55°C).

	CH_4 (mL)			CO_2 (mL)		
Days	brine	50% brine	water	brine	50% brine	water
0	0.0	0.0	0.0	0.0	0.0	0.0
9	19.3	16.9	50.9	37.3	35.6	41.8
20	25.5	33.0	58.8	53.7	54.7	59.3
55	46.6	44.9	69.9	74.8	71.2	75.5

Table 7. Effect of core material on CH_4 and CO_2 production from biosolids resuspended in brine (55°C).

	CH_4 (mL)		CO_2 (mL)	
Days	with	without	with	without
0	0	0	0	0
9	19.3	41.7	37.3	41.7
20	25.5	56.3	53.7	56.3
55	46.6	70.3	74.8	70.3

Table 8. Effect of temperature on levels of volatile fatty acids (VFAs) and on pH.

	Concentration (mM)		
VFA	**45ºC**	**55ºC**	**65ºC**
acetic	8.99	115.10	118.49
propionic	41.22	35.76	36.90
i-butyric	14.22	14.89	16.93
butyric	3.07	5.88	3.78
i-valeric	12.86	12.65	14.35
valeric	0.94	0.93	0.75
Total	**81.32**	**185.24**	**231.21**

Table 9. Amount of methane produced at tested temperatures from biosolids resuspended in brine in presence of core material.

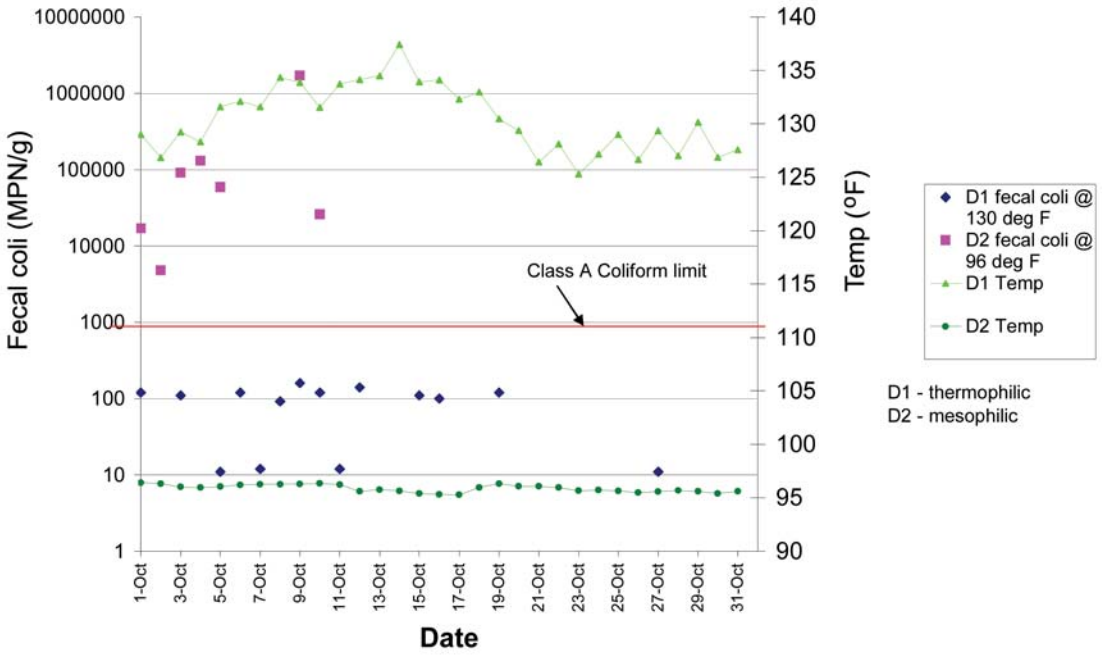
	CH_4 (L/kg TOC)		CH_4 (ft^3/ton biosolids)*	
Temperature (ºC)	**120 mL bottle**	**1 L bottle**	**120 mL bottle**	**1 L bottle**
45	273		347	
55	86	68	110	86
65	49		63	

* Metric tons of dewatered biosolids.

Table 10. Summary of laboratory results for high-pressure and high-temperature biodegradation tests. Test Conditions: Temperature (°C): 50; Pressure (psig.): 2,200.

	Materials load in the vessel			
	Weight (g)/ vol (mL)	**%Total solid (%) Salinity (mg/L)**	**% Volatile Solids**	**Fecal coliform (MPN/dry g)**
HTP Class A biosolids **(12/18/02)**	135.5 g	30.20	61.30	< 6.9 (under detection limit)
Brine solution (NaCl w/ digester effluent)	25 mL	10,000		
At end of test **(03/13/03)**			56	< 6.9 (under detection limit)
	Test results reported by Caltech			
Gas Sampling Date	1/21/2003	2/12/2003	3/13/2003	
Sampling time after initial test (days)	34	56	85	
Volume (%)				
Methane CH_4	53.815	71	69.622	
Carbon Dioxide CO_2	15.353	26.1	26.809	
Nitrogen N_2	29.19	2.98	3.5	
Oxygen/Argon	0.425	0.07	0.248	
Hydrogen Sulfide H_2S	N.D.*	N.D.	N.D.	
Total %	98.783	100.15	100.179	
Volume (mL @ STD)				
Collected for analysis	5.302	37.29	17.76	
Vent out and waste	5.302	37.29	>80	
Gas collected	10.604	74.58	>97.76	
Total Gas Collected (mL @ STD)		**>183**		

*Nondetectable.



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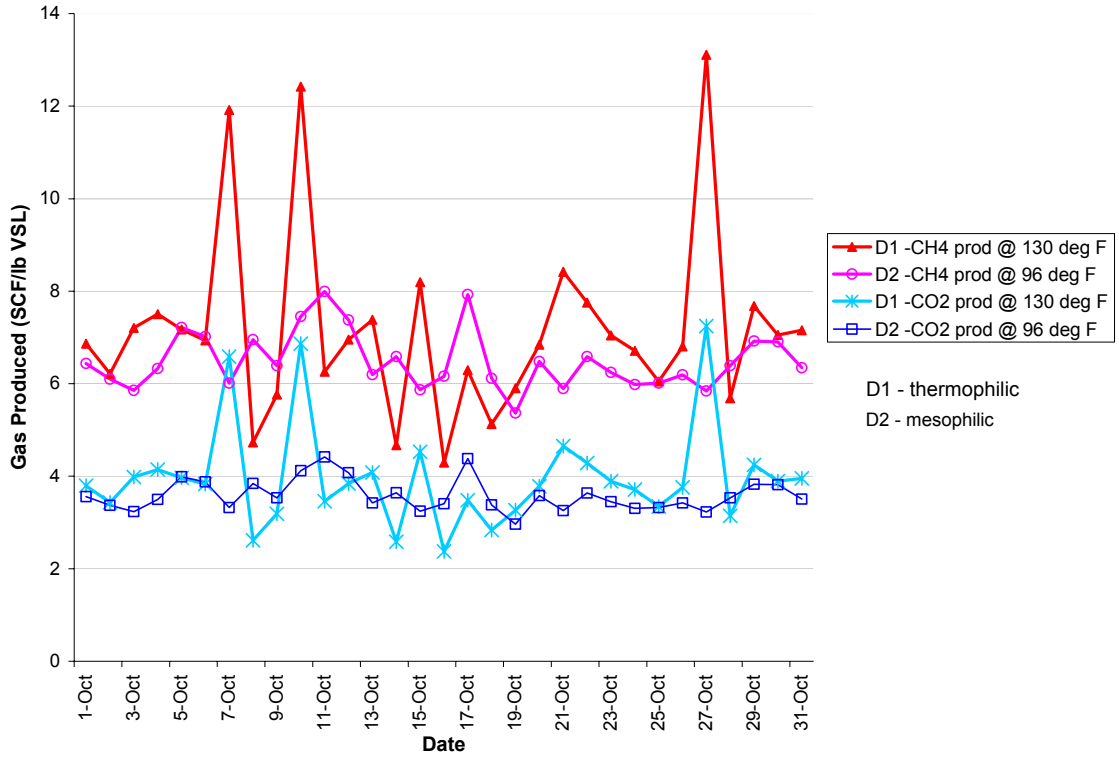

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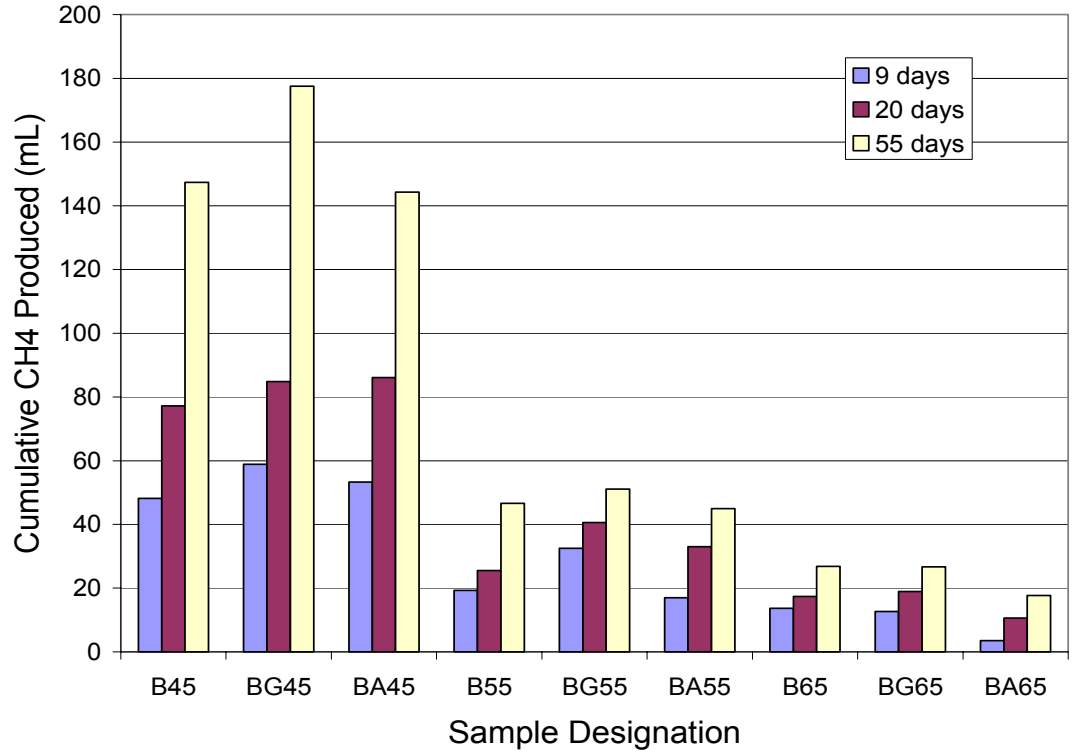

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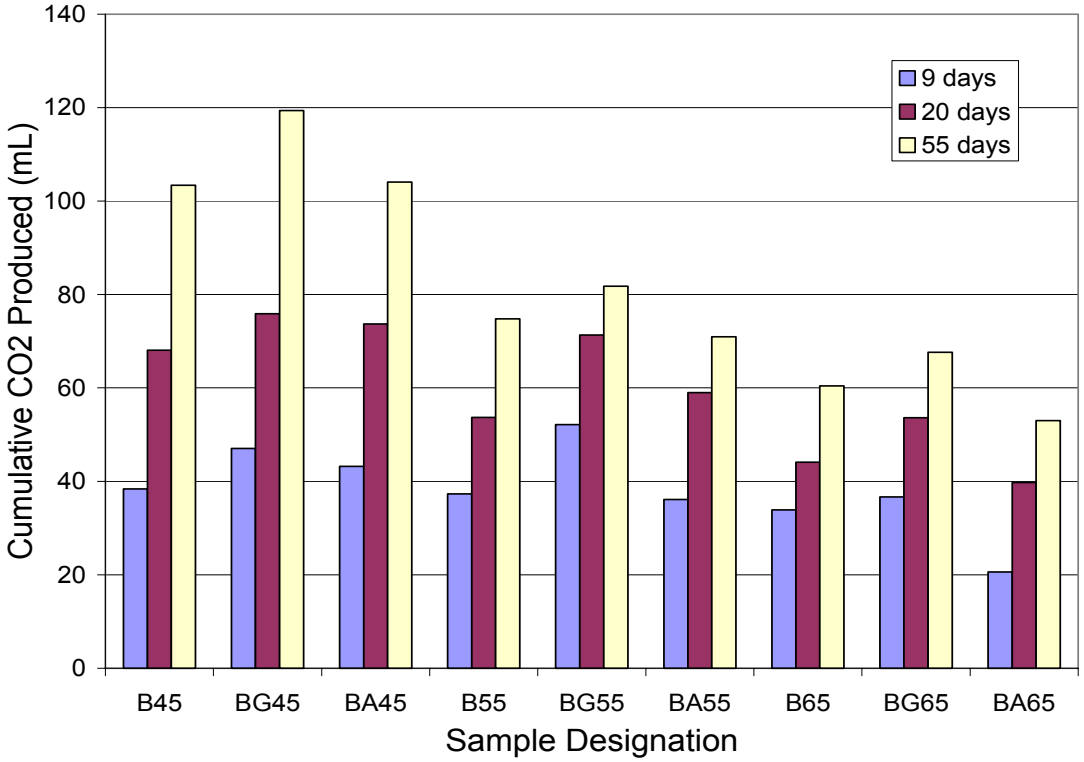
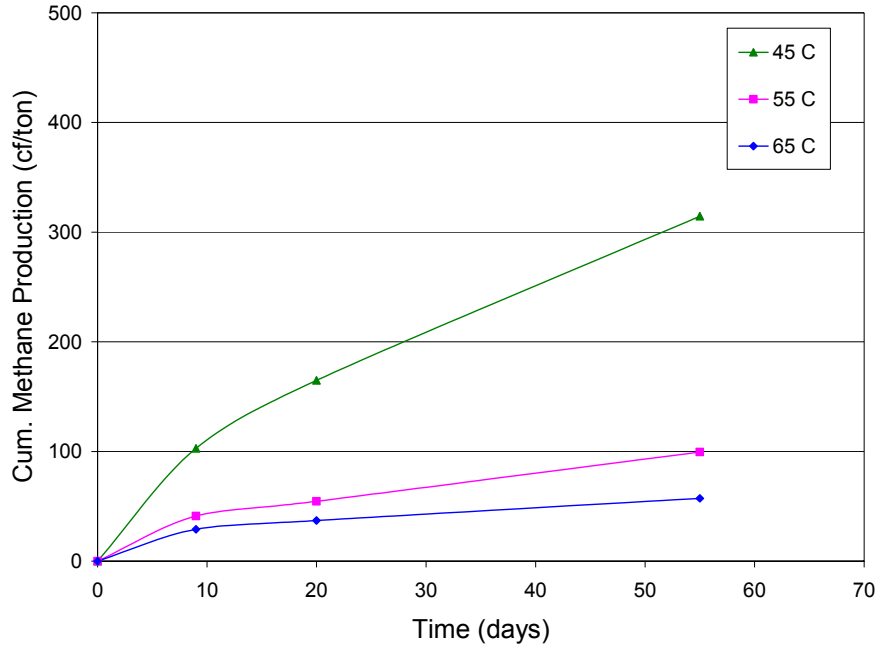


Figure 4.

(a)


Cum. Methane Production (cf/ton)
Time (days)
45 C
55 C
65 C
0
100
200
300
400
500
0
10
20
30
40
50
60
70

(b)

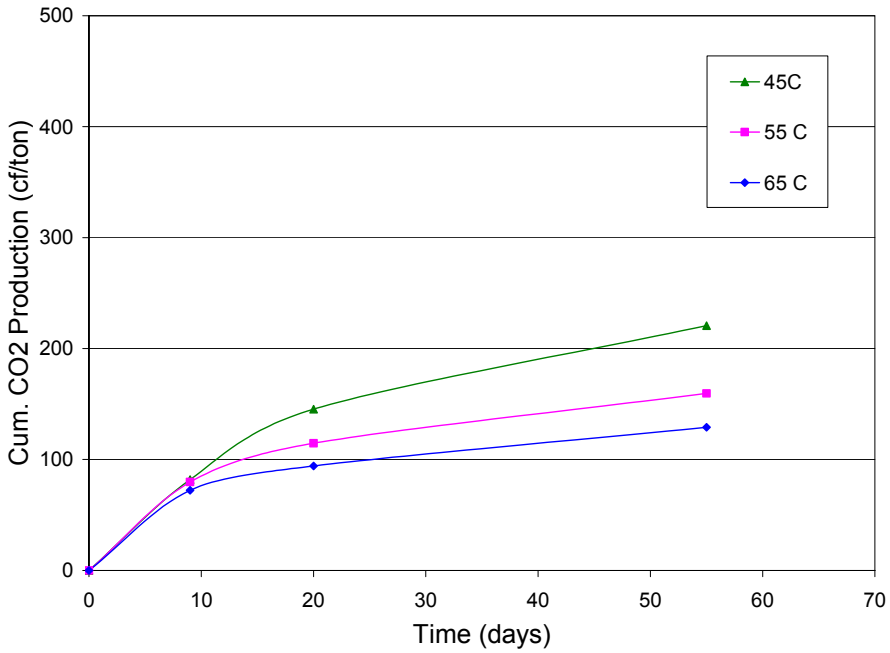

Cum. CO2 Production (cf/ton)
Time (days)
45C
55 C
65 C
0
100
200
300
400
500
0
10
20
30
40
50
60
70

Figure 5

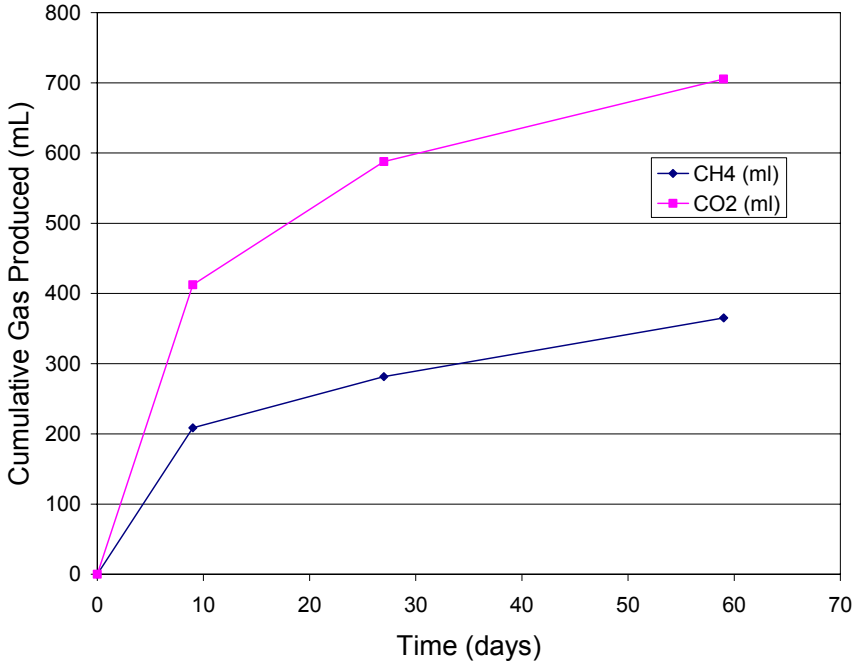
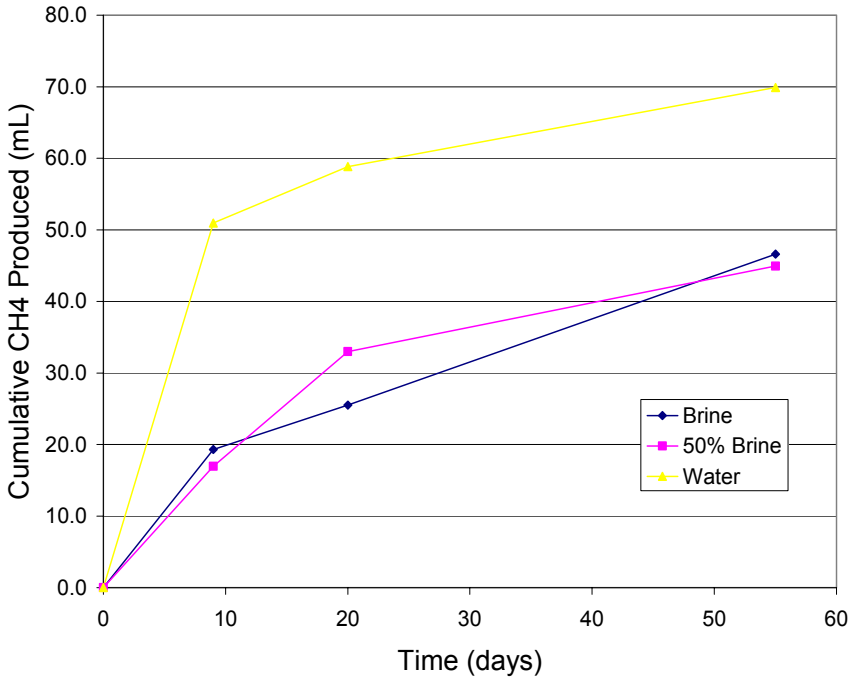

800
700
600
500
400
300
200
100
0
Cumulative Gas Produced (mL)
0
10
20
30
40
50
60
70
Time (days)
CH4 (ml)
CO2 (ml)

Figure 6

(a)


Cumulative CH4 Produced (mL)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0
10
20
30
40
50
60
Time (days)
Brine
50% Brine
Water

(b)

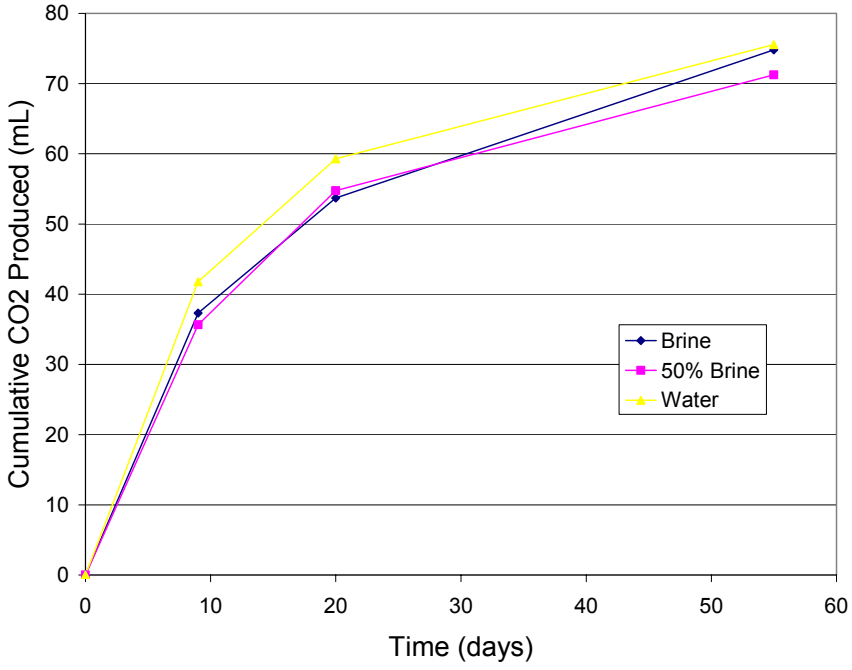
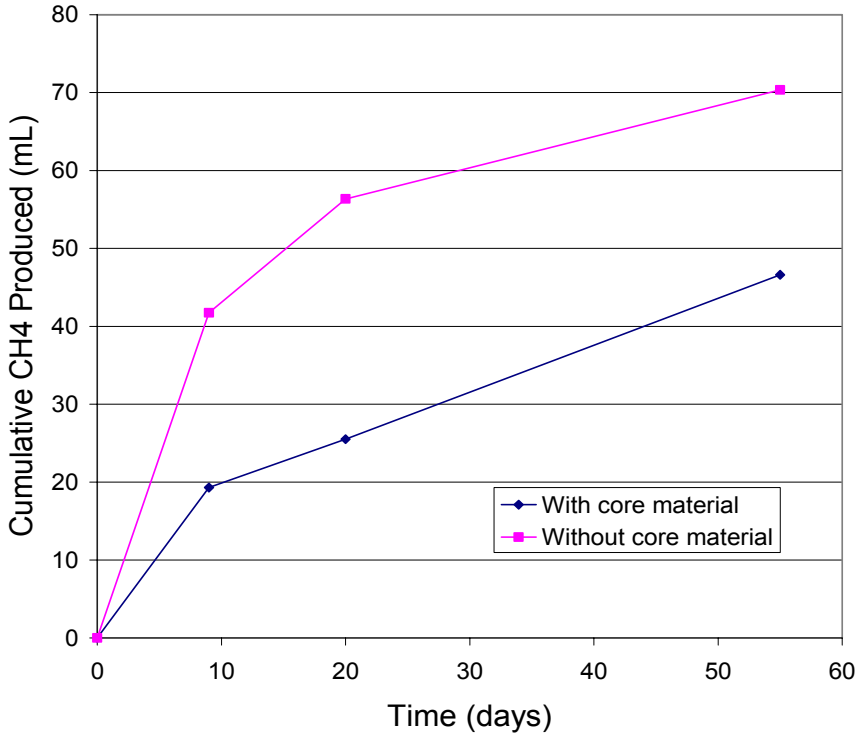

Cumulative CO2 Produced (mL)
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (days)
Brine
50% Brine
Water

Figure 7

(a)


Cumulative CH4 Produced (mL)
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (days)
With core material
Without core material

(b)

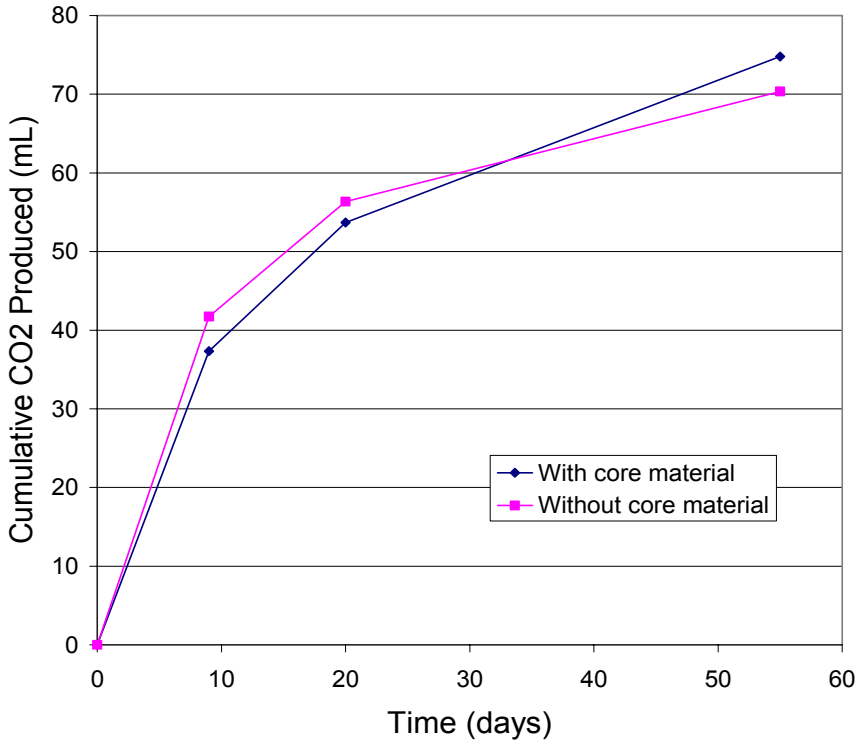

Cumulative CO2 Produced (mL)
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (days)
With core material
Without core material

Figure 8.

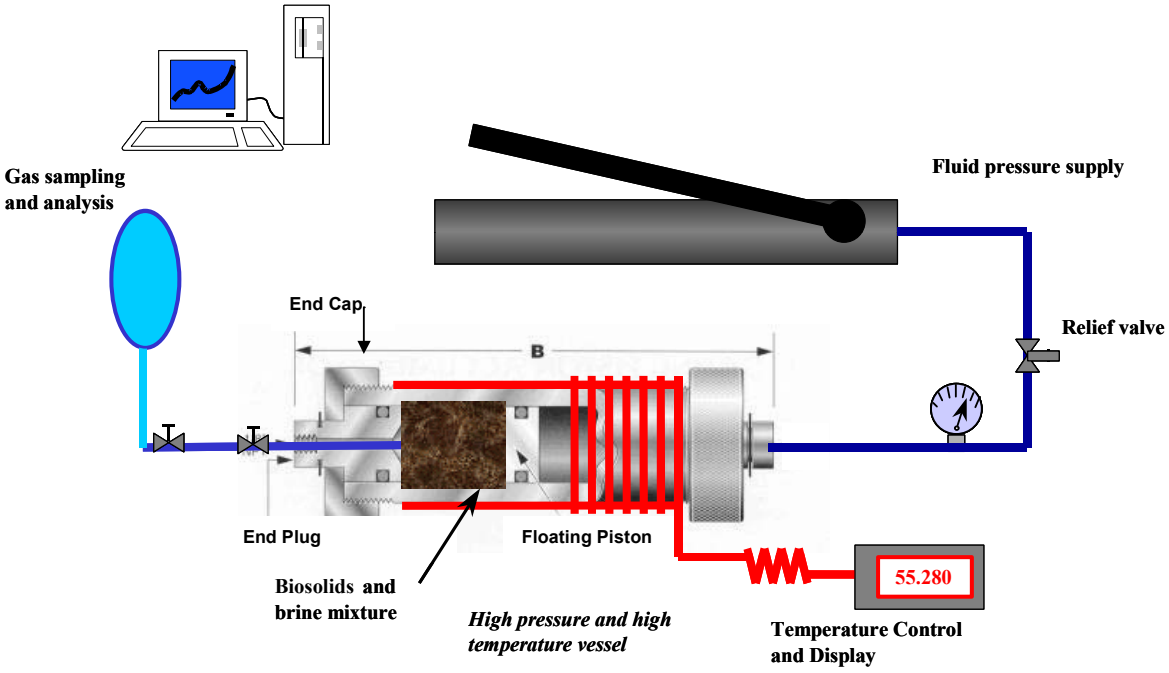


Figure 9

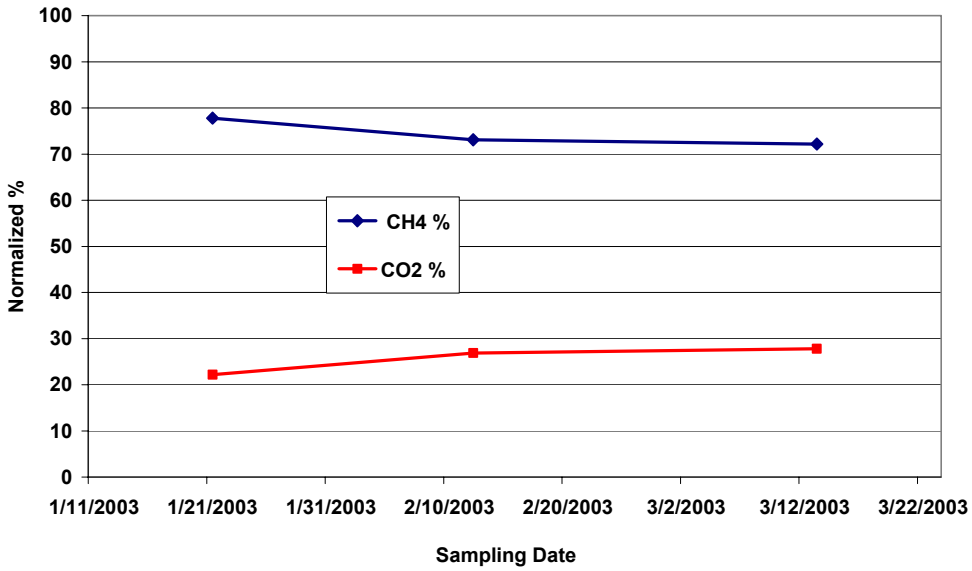


Figure 10