Application of Phosphogypsum in Landfills

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In the state of Florida, phosphate rock is mined for the production of phosphoric acid. To produce a single ton of phosphoric acid, five tons of phosphogypsum are produced. Chemical analysis of air-dried phosphogypsum indicated that, in general, phosphogypsum is enriched with a sulfate compound ($CaSO_4$) at a level as high as 70%. The sulfate-enriched phosphogypsum can be used in the anaerobic (oxygen depleted) environment, such as landfills, to enhance microbiological processes to decompose municipal solid waste, and thus, extend the lifetime of landfills. The results of a laboratory study, to be described below, showed that application of phosphogypsum to typical municipal solid waste at ratio as high as one part phosphogypsum to three parts municipal solid waste under anaerobic conditions enhanced the decomposition of the waste by 50% in 3 months.

There is good evidence to suggest that the addition of phosphogypsum could enhance biodegradation of municipal solid waste (MSW) in the landfill. During the early stages of waste decomposition in a landfill, the degradation process is essentially aerobic i.e., with available oxygen), and carbon dioxide is the principal gas produced. The general model for this reaction is: complex organics + $O_2 \rightarrow CO_2 + H_2O + SO_4^{2-}$. As oxygen in the landfill is depleted the decomposition process becomes anaerobic, and other gases, principally methane, are generated in significant quantities. In an anaerobic environment, bacteria depend on bound oxygen to serve as electron acceptors in oxidation-reduction reactions. The general model for this reaction is: complex organics $\rightarrow CO_2 + CH_4 + H_2S + NH_4^+$.

Since the phosphogypsum is enriched with sulfate, it is reasonable to assume that a sulfate using bacterial colony present in landfills will use phosphogypsum as an energy source after oxygen is depleted. It is therefore anticipated that the use of phosphogypsum as landfill cover will enhance biological decomposition of MSW and at the same time reduce the accumulation of phosphogypsum and the volume of cover material remaining in a MSW landfill.

A three-phase, scientific study was developed to determine if the use of phosphogypsum as landfill cover is technologically and environmentally feasible. Phases I & II were conducted in the laboratory, while Phase III study is a proposed field study. Phase I study was a fundamental study that was accomplished in a period of two years (1994 – 1996). Phase II study was a simulation study that was accomplished in a period of three years (1996 – 1999). Phase III study was a field study that was proposed in 1999, immediately after the successful completion of the Phase II study. The proposed Phase III study is still pending EPA approval. Findings from Phases I & II were very promising and supported the consideration of using phosphogypsum as landfill cover. Phase III study would generate field data to further demonstrate that laboratory findings are applicable in field conditions, and that the use of phosphogypsum as landfill cover is a sound approach. The following more detailed report describes briefly the studies and findings in Phases I & II, and tasks/approaches to be conducted in the Phase III study.

LABORATORY STUDIES

A two-phase, laboratory study was carried out to examine the use of phosphogypsum in landfills in lieu of conventional landfill cover. Phase I study was conducted in 1994-96 to determine the feasibility of the hypothesis and to develop optimum conditions for the process. Immediately after the completion of Phase I study, the Phase II study was carried out in 1996-99 to demonstrate that findings from Phase I were applicable in simulated conditions in an ordinary MSW landfill.

PHASE I STUDY

About the Study

The duration of the study was two years. Studies in year 1 were conducted to determine the extent that phosphogypsum can be used to enhance biodegradation processes for MSW in landfills and to investigate the methodology for the application of phosphogypsum in landfills. Studies in year 2 were to develop optimum conditions and a standard procedure that can be practically used for a landfills operation.

To accomplish this research an anaerobic biodegradation system (ABS) was developed involving a lysimeter, which served as a decomposition chamber for simulated and shredded waste material. The lysimeter was designed to achieve and maintain an environment suitable for anaerobic biodegradation at a constant temperature of 50°C. To meet these requirements the lysimeter had to be sealed tightly enough to prevent contamination from atmospheric oxygen, while accommodating the frequent extraction of gas and leachate samples for analysis.

To obtain meaningful results on biodegradation of the waste within a short period of time, grass clippings and wood mulch were used as the waste matrix in the study. A series of studies, including formation of waste matrix, water content, exposure time, and waste/phosphogypsum ratio, were carried out to define reaction conditions for biodegradation using phosphogypsum. The approach to the study initially was to develop an anaerobic biodegradation system that allowed a study to simulate landfill conditions. The waste matrix was then prepared for exposure to designated conditions. By-products of biodegradation, both in gases and aqueous forms, were continuously monitored throughout the period of each test (exposure). At the end of each exposure the residual waste matrix was recovered and then was determined for the reduction in total volatile solid, which was then used to assess the degree of biodegradation.

Results of the Phase I Study

As a result of a series of operational testing, an effective equipment configuration for the biodegradation of simulated landfill materials involving application of phosphogypsum was developed. In general, the anaerobic biodegradation system consisted of the lysimeter (decomposition chamber), gas monitoring system, temperature control system, and leachate collection system.

The results of a series of exposures showed that the use of freshly clipped grass and wood mulch as the waste matrix provided needed information on anaerobic biodegradation within a certain period of time. The pH data obtained from the study followed the theorized path of initially falling and then rising over the period of test. The lysimeters containing phosphogypsum fell to a lower pH than did the control lysimeters, and in general, the more phosphogypsum the lysimeter contained the lower the pH value reached, and the slower its recovery.

The results of gas monitoring study suggested that, by introducing phosphogypsum to an anaerobic digester, the production of carbon dioxide (CO_2) would be prolonged and the formation of methane (CH_4) would be delayed. The net outcome would be an additional degradation of organic matter during the state of sulfate reduction. The expected pattern of gas composition was generally observed in each exposure conducted in the study.

Leachate samples collected in the study were analyzed for ammonia and sulfate. Since the waste matrix included only grass clippings and mulch, trace metals of environmental concerns were not monitored in the study. Ammonia in leachate was determined to investigate if the presence of ammonia would affect microbiological process occurred in lysimeter. Results showed that ammonia concentrations in leachate increased over time and then decreased. No clear indication on the difference in the degree of biodegradation could be drawn based on the ammonia data. Sulfate in leachate was also monitored over the period of each test. The results indicated that, based on the analytical data and calculated values, phosphogypsum was actually used by sulfate reducing bacteria under the landfill anaerobic conditions.

The results of biodegradation determination revealed that within a range of 1/10 to 1/3 phosphogypsum to waste matrix ratio the addition of phosphogypsum gypsum appeared to enhance biodegradation by approximately 15% in a three-month of exposure. The percent reduction in decomposable solids decreased when the phosphogypsum/waste-matrix ratio was greater than 1/3.

Summary of Primary Findings

- A lysimeter was developed to simulate biodegradation in landfills.
- Gas composition patterns in the waste/phosphogypsum system were very similar to the general patterns in ordinary landfills.
- The production of carbon dioxide (CO_2) was prolonged and the formation of methane (CH_4) was delayed, providing additional degradation of organic matter during the state of sulfate reduction in landfills.
- Formation of ammonia in leachate did not affect microbiological process in the waste/phosphogypsum system; no elevated level of hydrogen sulfide was found.
- Phosphogypsum was practically used by sulfate reducing bacteria under the landfill anaerobic conditions.
- A ratio of 3:1 for the mixture of waste/phosphogypsum was recommended.

PHASE II STUDY

About The Study

A three-year laboratory, large scale simulation study was conducted to demonstrate that findings from Phase I were reproducible when representative MSW typically found at landfills was used. Experiments were carried out to measure the reduction in volatile solids at a 3-month sampling interval for a period of two years to determine the degree of biodegradation of MSW as a function of time. To ensure the similarity of the material used in the 20 ABRs, a typical waste matrix was prepared and added to each of the ABRs according to the formula provided by ASTM D5525-94a. The mixture of waste material included food wastes (12.5%), garden wastes (10.5%), paper (44.2%), plastics (5.8%), textiles (1.5%), wood (1.9%), metals (8.0%), glass (7.7%), and dirt/rocks (7.9%). Variations in gas compositions, leachate characteristics, and percent reduction in decomposable solids were the primary parameters for determination during the period of the study.

The main focus in first year of the Phase II study was to develop a large-scale anaerobic biodegradation system (ABS) involving twenty 55-gallon stainless steel drums, which served as decomposition chambers for typical municipal solid waste. A water heater was used as the initial heat source and a heat transfer coil was designed and emplaced within each of the anaerobic biodegradation reactors (ABRs) to achieve and maintain an environment suitable for anaerobic biodegradation at a constant temperature of $52\pm3^{o}C$. Results of gas production and leachate characterization during first year of the study revealed that the ABS performed as anticipated.

Immediately after successful development of the ABS system, monitoring of the performance of the simulated landfill-biodegradation system was carried out and biodegradation by-products were determined. The overall experiment was set up for a period of 2 years, starting from the mid of the first year to the mid of the third year. Biodegradation that occurred within the ABRs was continuously monitored throughout the period of the study by recording daily temperature of each of the ABRs and by taking monthly leachate samples from each of the ABRs. At a 3-month interval two ABRs were terminated and taken apart to recover residual waste matrix to determine the loss of volatile solids. Biodegradation by-products, such as gas production/composition and leachate composition, were monitored throughout the period of the study. Loss of volatile solids was determined on both raw materials prior to the experiment and end products after each exposure interval to determine the degree of biodegradation.

Results of the Phase II Study

Monitoring of the performance of the entire system was carried out immediately after the ABRs were filled with waste material and sealed. Parameters such as flow rate of water through the system, temperature development within the complete system, and leakage observation were considered during the performance evaluation. The production of gases within the ABRs occurred rapidly in the initial 15 days and continued to increase at a slower rate. The observed continuous gas production indicated that the ABS was performing under the anticipated conditions. It was found that the anticipated interception of leveling of carbon dioxide (CO_2) concentrations and increasing of methane (CH_4) concentrations occurred around 40 days after reaction. It was noted that a significant elevation of methane occurred after 100 days. This phenomenon supported the Phase I finding that, by introducing phosphogypsum to an anaerobic digester, the production of carbon dioxide (CO_2) would be prolonged and the formation of methane (CH_4) would be delayed. The end result was that more waste matrix was decomposed in the reactors with phosphogypsum added than in the control reactors without phosphogypsum added.

Leachate samples collected throughout the period of the study were analyzed for several selected elements, such as calcium (Ca), iron (Fe), lead (Pb) and zinc (Zn). Dissolved concentrations of sulfate in the leachate were also determined. Apparently the addition of phosphogypsum to the waste matrix did not result in additional lead (Pb) and zinc (Zn) to the leachate. Low leachate concentrations in iron (Fe), lead (Pb), and zinc (Zn) might be due to the removal of these metals by dissolved sulfur to form metal sulfide precipitate, which in the meantime prevent the formation of hydrogen sulfide. High concentration of calcium (Ca) in leachate supported the hypothesis that sulfate in phosphogypsum might have been dissociated. Dissolved sulfate ions would be available for biodegradation and in the meantime, dissolved sulfur ion would react with dissolved metal ions to form metal sulfide precipitate under the reducing conditions.

At the end of each exposure, residual waste was recovered to determine reduction in decomposable solids in the waste matrix. Analytical results indicated that approximately 90% of volatile solids in the experimental ABRs were degraded within 12 months of exposure, while less than 50% of volatile solids in the controlled ABRs, i.e., no phosphogypsum added, were degraded in one year. The results showed that application of phosphogypsum to typical municipal solid waste at ratio as high as one part phosphogypsum to three parts MSW under anaerobic conditions enhanced the decomposition of the waste by 50% in 3 months.

Summary of Primary Findings

- An anaerobic biodegradation system composed of twenty 55-gallon stainless steel drums was successfully developed to simulate landfill environment.
- The 3:1 ratio of waste/phosphogypsum determined from Phase I was demonstrated applicable to the simulated landfill conditions.
- Similar gas composition patterns to Phase I findings were found in the study.
- Prolonged carbon dioxide (CO_2) production and delayed methane (CH_4) formation was determined in the study, providing additional degradation of organic matter during the state of sulfate reduction.
- No elevated level of hydrogen sulfide (H_2S) was found.
- Leachate concentrations of lead (Pb), iron (Fe), and zinc (Zn) were in the range of typical landfill leachate; concentrations of calcium (Ca) and sulfate (SO_4^{2-}) were higher than the typical landfill leachate.
- About 90% of decomposable waste components were degraded in 1 year within the designated anaerobic biodegradation system.

PROPOSED FIELD STUDY

Work Plan for the Phase III Study

A full-scale field study was proposed as the third phase of the project to demonstrate that findings from Phases I and II are reproducible in landfills under natural environment. Due to the slow degradation rate of the waste, the duration of Phase III study will be four years and efforts will lead to the development of a procedure that can be practically used in landfill operations. During the four-year period, studies in year one will involve the construction of two landfill cells followed immediately by monitoring the biodegradation by-products of the waste. Two experimental landfill cells will be constructed on top of the closed cells at the existing landfill site at the Brevard County's Central Disposal Facility Landfill in Cocoa, Florida. Studies in years two and three will be devoted to conducting field monitoring and compilation of analytical results in a computer database. Studies in year four will involve the completion of field monitoring, data reduction and interpretation, methodology assessment, and reporting. The outcome of the study will be a procedure that can be practically used for a landfill operation providing a partial solution for managing both phosphogypsum and MSW landfills in Florida.

Outline of the Phase III Study

Test Cells:	Two cells (control and experimental) will be constructed on top of the closed cells at the existing landfill site that meets Florida DEP's requirement on landfill liner design.
Dimension of Cell:	60 ft (L) x 20 ft (W) x 10 ft (H)
Liner of the Cell:	Geomembrane liner will be used for both of the control and experimental cells.
MSW:	Typical municipal solid waste brought to the site will be used for both cells. Approximately 75 tons of MSW will be used for each cell.
Phosphogypsum:	Approximately 25 tons of phosphogypsum will be used for the experimental cell.
Layers of the Cell:	Three layers of each of the phosphogypsum and MSW will be placed within the cell. The thickness of phosphogypsum layer will be 2 in., while the thickness of MSW will be 2 ft. Cover material for the control cell will be typical soil/dirt, while for the experimental cell, phosphogypsum will be used as cover material.
Final Cover:	The final cover of the experimental cell will be a typical soil/dirt used for the control cell. However, a 2-in layer of phosphogypsum will be placed before the final cover is used. The completed cell will be capped entirely by a geomembrane liner.
Field Monitoring:	Leachate composition, gas formation, and cell settlement will be monitored. Leachate will be retained and re-circulated throughout the cell during the period of the study. Therefore, no storage of leachate will be expected.

Monitoring Plan for the Phase III Study

Monitoring of the experimental and control landfill cells will be carried out immediately after the completion of cell construction. Biodegradation by-products, such as gas production and composition, leachate composition, and cell settlement will be monitored throughout the period of the study. Gases to be monitored include carbon dioxide, methane, hydrogen sulfide, and radon. Leachate components to be monitored include pH, dissolved sulfate ion (SO_4^{2-}), radioactivity, and trace elements of environmental concerns, such as arsenic (As), silver (Ag), cadmium (Cd), chromium (Cr), lead (Pb), and selenium (Se).

Monitoring tasks will be carried out on day-to-day basis. Physical environment at the site will be visually inspected everyday to record any possible changes. Settlement reading on both cells will be recorded daily. Leachate and gaseous samples will be collected for analysis on weekly basis. However, sampling intervals for gas and leachate are subject to change according to daily site observation, data generation, and the progress of the project.

The current water quality-monitoring program for the Brevard County Central Disposal Facility consists of 48 monitoring wells located outside the slurry wall surrounding the landfill. Upgradient wells are about 1000 feet apart, while downgradient wells are about 500 feet apart. The wells are placed either in pairs or threes to monitor the upper surficial (12’ - 28’ deep), the lower surficial (20’ - 36’ deep), and the deep aquifer (40’-63’). There is one surface-water monitoring point and one leachate sample collection point. The ground water, leachate, and surface water are monitored semi annually at the site. Since the proposed site of the study will be located between existing monitoring wells, the routine monitoring data generated by the county, prior to and during the study, will be coordinated with the study’s monitoring plan to form a database for later assessment.

ABOUT THE AUTHOR

Dr. Chih-Shin Shieh is an environmental consultant at the CS Environmental Solutions that he founded in Melbourne, Florida. Dr. Shieh was research faculty and the Director of the Research Center for Waste Utilization when he conducted the phosphogypsum studies at Florida Institute of Technology, Melbourne, Florida. Dr. Shieh’s areas of expertise include waste characterization, minimization and utilization. His academic training, research experiences, and professional services have allowed him to become one of the few scientists in the nation who are able to deal with problems concerning pollution that occurs in both terrestrial and marine systems. Dr. Shieh has published more than 40 scientific papers and technical reports in the area of waste stabilization and utilization. He has graduated more than 15 M.S. and 4 PhD students.