ORGANIC WASTE AS A TREATMENT FOR ACID MINE DRAINAGE

OCC Task 71a
FY 1995 319(h) Task #900
EPA Grant C9-996100-03

Submitted to:

Oklahoma Conservation Commission
Water Quality Division
Oklahoma City, Oklahoma

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FINAL REPORT
August 2001

ACKNOWLEDGEMENTS

University of Oklahoma Health Sciences Center, College of Public Health, Department of Occupational and Environmental Health prepared this report in fulfillment of a §319 Clean Water Act demonstration project overseen by the Oklahoma Conservation Commission, Water Quality Program. Dr. Mark Cox served as principal investigator, co-author, and editor. Steven Johnson served as the project engineer, co-author and editor. The Water Quality Program staff contributed as follows:

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Sincere appreciation and thanks to: the EPA -Region 6 for funding of the project, The Oklahoma Conservation Commission, Oklahoma Department of Transportation, Oklahoma Environmental Information Systems, Dale Dalton, Subsurface Investigations, Association of General Contractors.

A special thanks is extended to the Latimer Country Conservation District and Latimer County Commissions for their ancillary assistance.

A heartfelt thanks is extended to the William Reynolds family. Bill and Benny Reynolds (posthumously) were instrumental in providing a direct and indirect support during the preliminary assessment and project implementation.

Field construction: Bill and Benny Reynolds, and Wayne Hendrick.

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ABSTRACT

The University of Oklahoma Health Sciences Center (OUHSC) conducted an EPA § 319(h) of the Clean Water Act (CWA) demonstration project to evaluate the use of organic substrate as a passive means to treat acid mine drainage (AMD) from abandoned, underground coal mines in southeastern Oklahoma. The premise for the study is based on the metal precipitation and acid neutralization via alkalinity generation from biological sulfate reduction processes. A bench scale study was initially conducted using a series of 25 L bioreactors containing AMD and various organic waste materials, including: hay, cow manure, horse manure, chicken litter, pig manure, saw dust, alfalfa and sewage sludge. From the results of the precursory lab study, a hay-cow manure mixture was selected for field demonstration. A pilot sized treatment system was built near the 1900's coal town of Gowen in Latimer County, Oklahoma. The system was designed to treat a small portion of the total mine flow (approximately 5 gpm out of 70-130 gpm discharge). The treatment system consisted of three cells and a constructed wetland. The first cell was design to control the hydraulics. The second cell was the primary treatment pond. It contained a mixture of hay and cow manure and was designed to promote sulfate reducing bacteria. After a 2-3 day detention period the treated mine drainage flowed to the third cell. It functioned as an oxidation and sedimentation basin. Treated water then flowed through an under-drain to a small constructed wetland for polishing. The final design system was in operation for approximately 10 months. Results of the demonstration showed that organic substrate treatment is effective at adjusting pH and removing iron and reducing acidity. During the fall of 1997, once the system was optimized, pH values increased from 4.1to 6.3, iron and acidity removals were approximately 95% and 84%, respectively. As expected, the removal of manganese was not as effective. Modification to the flow design is needed in order to prevent clogging due to filamentous bacteria and to maximize the treatment efficiency of the system.

Key Words: acid mine drainage (AMD), organic substrate treatment, sulfate reducing bacteria (SRB), 319 demonstration project.

EXECUTIVE SUMMARY

The University of Oklahoma Health Sciences Center (OUHSC) conducted a benchscale and field demonstration project to evaluate the use of organic substrates as a passive means to treat acid mine drainage (AMD). This project was funded through EPA's Clean Water Act and was designed to serve as a technology transfer tool for local coal operators provided the results of the treatment were favorable. Currently most coal operators are treating AMD actively through the use of chemicals and aeration (active treatment) which is very expensive and many times more prohibitive in the case of abandoned coalmines.

The premise for this study is based on the metal precipitation and acid neutralization via alkalinity generation from the biological sulfate reduction processes (Sulfate Reducing Bacteria or SRB). After a review of the literature, benchscale study was conducted using AMD water from the Pit Creek watershed in SE Oklahoma (site of the demo project). Each specific media tested was placed in a 25 L column bioreactors containing AMD water. Changes in the chemistry were followed for a period of two weeks for most of the reactors. The tests were conducted in duplicate under a lab safety hood at room temperature. A control bioreactor containing only AMD was maintained and tested under the same conditions as the media containing reactors. Organic media tested included: hay, cow manure, horse manure, chicken litter, pig manure, sawdust, alfalfa and sewage sludge. From the benchscale study and literature reviews the hay-cow manure mixture was selected for the demonstration project.

Demonstration project- A small-scale passive treatment system using SRB was built near the town of Gowen in Southeast Oklahoma. This area was undermined for coal in the late 1800's and early 1900's. The treatment system was sized to treat approximately 5-10 gal/min and required a 2-3 day detention time in the primary treatment (SRB) cell. The design was as follows: Cell 1-control cell constructed as a circular earthen pit 40ft diameter designed to regulate the flow of the AMD through the test system. Plastic ball valves and overflow piping controlled water levels in this structure. Cell 2-Primary treatment cell containing the hay-cow manure mixture to facilitate the SRB activity. This cell was 30 ft by 24 ft by 6ft deep and had a retention time of approximately 2-3 days. Cell 3-Secondary cell was a smaller and shallower pond that served as a settling pond with a retention time of one-day (approximate size 21 ft by 27 ft by 4 ft deep). Wetland-From the secondary cell the water flowed into a 30 ft by 30 ft wetland which was planted with cattails and grasses. The wetland served as the final polishing step before discharge to the nearby drainage channel. This demonstration project operated for a period of 10 months. Results of the demonstration indicate that hay-cow manure substrates are effective at adjusting pH and removing iron and reducing acidity. During the fall of 1997, when the system's flow was optimized, the median pH values increased from 4.1 to 6.3, iron and acidity removals were approximately 85% and 90%, respectively. Median iron values before treatment were 244 mg/L and after treatment were 37 mg/L (85% reduction). Median acidity values before treatment were 748 mg/L and after treatment were 77 mg/L (90% reduction). Manganese removal was not effective. Modification to improve the treatment should include changes in the flow design since the system was prone to clogging due to filamentous bacteria and sedimentation.

I. INTRODUCTION

Coal mining was an important part of the Oklahoma's early history and was the center of economic prosperity for several decades, but the boom was short lived. When coal became less profitable, the mines closed leaving behind undermined areas ranging in size from a few to several thousand acres. Overtime, many of these mined areas filled with water with the unfortunate result of acidic discharges. These discharges vary from a trickle to tens of thousands of gallons per day. Consequently, several watersheds in the coal region of Oklahoma are degraded.

The quality of water that is discharged varies between mines, but typically, it is characterized by low pH values with elevated concentrations of aluminum (Al), manganese (Mn), iron (Fe), and occasionally other trace metals such as nickel (Ni) and zinc (Zn). Given the low pH of the discharge, the term acid mine drainage (AMD) has been widely adopted. Coal mine drainage has been identified in Oklahoma's Section 319 Assessment as being a significant source of NPS pollution in several watersheds.

Numerous methods have been devised to address the adverse environmental impacts associated with AMD. However, these developments have historically relied on control devices or "active treatments". These techniques are very effective, but tend to be expensive, elaborate, and require regular attention. Thus, many of the control techniques are impractical in the treatment of AMD particularly from derelict or abandoned mines.

More recent treatment strategies have involved passive systems, which are less intensive from an operation and maintenance standpoint and subsequently less expensive. Alkaline generating "wetlands" and anoxic limestone drains (ALDs) are two passive treatments that have received considerable attention. In the past 20 years significant advancements have been made in designing and developing these systems.

Following along similar lines, the University of Oklahoma, Health Sciences Center (OUHSC), conducted an EPA § 319(h) of the Clean Water Act (CWA) demonstration project to evaluate the use of organic substrate as a passive means to treat AMD. The premise for the treatment is based on the metal precipitation and acid neutralization via alkalinity generation from biological sulfate reduction processes. These processes are the fundamental bio-chemical reactions that are exploited in the alkaline generating wetlands and sequential alkaline producing systems (SAPS).

The goal of project was to demonstrate the effectiveness of using organic waste material as a treatment media for AMD. Since this was a demonstration project slated for technology transfer, two important objectives were also evaluated: identification of the most effective organic waste material, and determination of the most appropriate method of treatment application.

In order to demonstrate the effectiveness, a mine site was selected in eastern Oklahoma. The site was located in an infamous watershed notorious for AMD pollution—Pit Creek. Given the magnitude of the problem, the demonstration project could only target a fraction of the total AMD load to the stream. However, this treatment could potentially be expanded to include the entire discharge and/or applied to other AMD seeps in the watershed.

A. BACKGROUND

Acid Mine Drainage

Coal contaminants, particularly metal-sulfide compounds, are the principle sources of pollution associate with mining. A series of chemical weathering reactions occur when subsurface pyretic materials are exposed to the atmosphere. These reactions are analogous to "geologic weathering" which takes place over extended periods of time, (i.e. hundreds to thousands of years) but the rate of reaction is orders of magnitude greater than "normal" weathering. In most mine systems bacteria mediate oxidation is 10^6 times the rate of chemical oxidation. The accelerated reaction rates can release significant quantities of acidity, metals, and other soluble components to the environment.

Acid mine drainage results when metal sulfide minerals, particularly pyrite (FeS_2), come in contact with oxygen and water. When oxidation occurs, either by chemical and/or biological processes, sulfide is converted to sulfate and the acidic-metal components are oxidized to higher valence states. Consequently, there is a release of protons that is manifested as sulfuric acid (H_2SO_4). Under acidic conditions, iron and sulfur-oxidizing bacteria drive the oxidation of pyrite to ferric sulfate and sulfuric acid. *Thiobacillus ferroxidans* obtains its energy from the oxidation of the either iron or sulfur. The following equations represent the various oxidation steps.

$$4FeS_{2(s)} + 14O_2 + 4H_2O \leftrightarrow 4Fe^{+2} + 8H^+ + 8SO_4^{-2}$$

Ferrous iron (Fe^{2+}) can be further oxidized to ferric iron (Fe^{3+}).

$$4Fe^{+2} + 4H^+ + O_2 \leftrightarrow 4Fe^{+3} + 2H_2O$$

This is an important reaction, because pyrite can also be oxidized by ferric iron in the absence of oxygen.

$$FeS_{2(s)} + 14Fe^{+3} + 8H_2O \leftrightarrow 15Fe^{+2} + 16H^+ + 2SO_4^{-2}$$

With the formation of acidic conditions, trace metals become more soluble and can be dissolved in toxic concentrations. These constituents are typically introduced to the environment via mine water discharge. Ground water and infiltrating surface runoff tend to create a hydraulic system that transports the pollutants to the environment. When the water reaches the surface the following effects are commonly observed: an over-powering of the receiving stream's buffering capacity, a toxic load of heavy metals, and an adverse physical impact on the biota. The degree to which AMD affects the receiving environment depends on the ambient biological, chemical, and geologic conditions. To put the impact in perspective, the acidity concentrations typically associated with AMD is approximately 20 - 300 times greater than the acidity commonly found in acid rain (10 - 15 mg/L as $CaCO_3$) (Kleinmann, 1990).

In general, drainage from most coal mines tends to have elevated concentrations of Al, Ca, Fe, Mg and Mn, with Fe being typically most prevalent. Trace elements such as Ag, Be, Cd, Co, Cr, Pb, and Hg are not typically found in concentrations greater than 1 mg/L (Paine, 1987). Other trace heavy metals, such as Ba, Ni, Sr, Ti, V, and Zn are not commonly found at concentrations greater than 2 – 10 mg/L (Paine, 1987).

Like most environmental pollutants, AMD was largely ignored until it was addressed by legislation in the early 1970s. Specific provisions of the Clean Water Act of 1972 granted the United States Environmental Protection Agency (EPA) the freedom to establish standards for AMD discharge. In addition, with the passage of the Surface Mining Control and Reclamation Act of 1977 (SMCRA), specific regulations and geotechnical standards were established for existing mines. As of May 4, 1984, all active mines were required to meet effluent discharge regulations as developed by the EPA (see Table 1).

Table 1 Effluent limitations for AMD sites as developed by the EPA (Hedin *et al*., 1994).

PARAMETER	DAILY MAXIMUM	MONTHLY AVERAGE
pH	6 – 9	-
Total Fe	6.0	3.0
Total Mn	4.0	2.0

Even with the passage of environmental protection measures, AMD is still a pressing problem. Kleinmann (1991) estimated that AMD adversely affects 12,000 miles (19,300 km) of rivers and streams and over 180,000 acres (730 km^2) of lakes and reservoirs. Most of the problem is due to older, derelict mines rather than active coal operations. In fact, mines that were closed before the regulations went into effect cause the majority of environmental problems. Without a liable party to assume responsibility, privately funded remediation efforts are unlikely. If these socalled “abandoned mines” are to be addressed, it will be at public expense. The lack of funding accentuates the need for cost effective alternative treatment methods such as the one demonstrated in this study.

B. HISTORICAL OVERVIEW AND DESCRIPTION OF THE PROJECT AREA

The project site is located in southeast Oklahoma near the coal mining community of Gowen (SW ¼ of Section 23, T 5N, R 17E, Latimer County). Refer to Figures 1 and 2 (Exhibits A and B). The mine was owned by Rock Island Railroad and operated under the name #40. This was a slope operation that mined the Lower Hartshorne Coal beginning in the late 1800's. Mining began near the outcrop of the Hartshorne seam and continued down dip towards the base of the syncline. Over a period of roughly 30-40 years several hundred acres were worked-out. Adjacent to the Rock Island Mine #40 was the Kali-Inla Coal Company and the Rock Island Mine #3—refer to Figure 2. Consequently, a significant portion of the upper Pit Creek watershed was undermined, which resulted in a massive underground mine pool that is hydrologically connected to the surface.

Sometime since the mine closed, an acidic discharged formed. The magnitude of the discharge along with the severity of the water quality led to a pollution load that overwhelmed the stream’s buffering capacity. Consequently, Pit Creek has been significantly degraded due to AMD. Fish and macroinvertebrate populations are impaired or not supporting along several miles of the main stem, and the watershed has been placed on the 303 d list.

Project Proposal

Given the magnitude of the problem from a size and water quality impairment perspective, standard engineering control techniques are impractical in the treatment of AMD. Passive treatment options are more sensible alternatives when abandoned mines are involved. Promoting the technology and disseminating information will benefit the coal region of Oklahoma. The OUHSC, conducted an EPA § 319(h) of the CWA demonstration project to evaluate the use of organic substrate as a passive means to treat AMD. The premise for the treatment is based on the metal precipitation and acid neutralization via alkalinity generation from biological sulfate reduction processes.

Sulfate reducing bacteria (SRB) are obligate anaerobes that decompose liable organic matter using sulfate as the terminal electron acceptor (Hedin et al, 1989). The result is the production of sulfide that may be given off as hydrogen sulfide gas or react with metals to form metal sulfides. Equations below illustrate the breakdown of organic matter forming hydrogen sulfide and bicarbonate followed by the precipitation of the heavy metals as metal sulfides.

$$SO_4^{+2} + 2\ \text{"CHO"} \rightarrow H_2S + 2HCO_3^-$$

$$H_2S + Me^{+2} \rightarrow MeS + 2H^+$$

Several agencies including the former US Bureau of Mines, the Tennessee Valley Authority and the Colorado School of Mines have performed bench scale, beta testing, and field trials of SRB

Figure 1 (Exhibit A)	Map of the state of Oklahoma; the star denotes the project location
Figure 2 (Exhibit B)	Map of the Pit Creek Watershed and the associated underground mining activities. The star denotes the project location.

systems. It has been documented that SRB occurs in the substrate of wetlands and is a part of natural occurring bogs, which were first discovered as a natural treatment approach to the treatment of AMD. Bacteria of the genus *Desulfovibrio* are the principal sulfate reducing bacteria. Others include: *Desulfotomaculum, Desulfomonas, Desulfobacter, Desulfobulbus, Desulfosarcina* and *Desulfonema* (Widdel, 1988).

Several authors described the mechanisms by which this water quality improvement takes place (Cohen, 1992; Hedin, et al, 1994). In general, the low oxygen conditions and highly negative redox values promote the activity of the SRB, which generate alkalinity through various chemical reactions, including the reduction of sulfate to sulfides, precipitation of metals as metal sulfides and the formation of bicarbonates. The idea is to promote the generation of alkalinity so the acidity generated by the metal oxidation will be buffered. A treatment methodology was designed to compartmentalize the various bio-chemical reactions so that the quality of the water improves as it flows through the series of cells. All of this occurs in a relatively passive manner.

II. METHODOLOGY

A. BENCHSCALE STUDY

A laboratory bench scale study was conducted using 25 L bioreactors, of AMD from the project mine seep along with various sources of organic waste material. The tests were conducted at ambient temperature (~25°C), under a laboratory safety hood, and in duplicate. A control bioreactor of AMD alone was maintained under the same conditions.

Table 2 A description of the treatment media tested

TEST DATE (1996)	DESCRIPTION
1. Jan 28 to Feb 10	Bioreactor 1 and 2 -composted hay Bioreactor 3 and 4 -mix of cow manure with hay
2. Feb 10 to Feb 18	Bioreactor 1 and 2 -composted hay Bioreactor 3 and 4 -mix of horse manure with hay
3. Feb 21 to Mar 04	Bioreactor 1 and 2 -composted sewage sludge Bioreactor 3 and 4 -mix of hog manure and saw dust
4. Mar 08 to Mar 21	Bioreactor 1 and 2 -chicken manure Bioreactor 3 and 4 -mix of chicken manure and hay
5. Apr 04 to Apr 29	Bioreactor 1 and 2 -peanut hulls Bioreactor 3 -saw dust Bioreactor 4 -hay Bioreactor 5 -mix of cow manure and alfalfa

Laboratory analyses were conducted on each bioreactor, on a daily schedule. For QAQC, samples were collected from each bioreactor and sent to an outside laboratory for confirmation. The daily lab tests included temperature, dissolved oxygen, oxidation-reduction potential, conductivity, pH, and visual notations. The outside laboratory also performed analysis for metals, sulfate, and acidity.

B. FIELD DEMONSTRATION

A passive system was designed based on the information generated from the laboratory bench scale tests. The hydrologic design included the following (Refer to Figure 3):

> Control Cell -This earthen cell was built at the AMD seep point. A circular structure approximately 40 feet in diameter and six feet deep was constructed to regulate the flow to the demonstration. By raising the elevation of mine water at this location, a relatively constant head could be maintained and the flow could be regulated to the treatment system. Four-inch PVC conduits with ball valves were installed, along with three (4-inch) PVC overflow pipes. Water from these structures allowed for the variation in flow of the seep and directed the water down gradient away from the demonstration site.
>
> Raw AMD flow is supplied to the system via a 2-inch PVC pipe, controlled with a 2-inch ball valve. An access dock was constructed over the 2-inch pipe to provide better access for operation of the flow control valve.
>
> Primary Treatment Cell -This earthen structure measures approximately 30 ft x 24 ft x 6 ft deep. It was located approximately 30 feet to the south and east of the origin of the seep. The bottom of the cell was lined with 2 feet of compacted clay. The sides of the cell were sloped (3:1) to prevent bank erosion. At least 2 feet of freeboard was maintained.
>
> The water entered the cell at the bottom via a 2 inch line, which was connected to a 4 inch perforated, PVC piping system. These distribution lines were bedded in 1 ½ inch diameter limestone. The underdrain distributed the untreated water along bottom of the cell. Flow was from the north to the south where the treated water exited through a 2-inch PVC pipe approximately 3 feet from the bottom of the cell.
>
> Organic matter in the form of three 1,000 lb, round hay bales and 4 cubic yards of hay-cow manure mixture from the McAlester Union Livestock barn were evenly distributed in the cell. A backhoe bucket was used to keep the organic matter evenly distributed. This cell had a retention time of approximately 2-3 days. Retention time in the treatment cell was a function of volume and rate of discharge at the effluent point.
>
> Secondary Treatment Cell - This earthen structure measures approximately 21ft x 27 ft x 4 ft deep. It was designed to serve as a settling pond with a retention time of one day. The bottom of the cell was lined with clay and bentonite. Flow into this cell was controlled by a 2" ball valve. The cell dikes were sloped 2:1 horizontal to vertical.

Wetland Construction -The wetland covered a 30 ft x 30 ft area and served as a polishing step before the treated water entered the main flow channel. Construction of the wetland began by lining the bottom and the planting of cattail roots. An underdrain system was constructed by excavating a 2 x 2 ft trench along the north border and then down both sides of the wetland. A 4-inch PVC perforated pipe carried the treated water to the wetland. Water left the wetland through a 4 inch conduit on the south end. Water samples and flow measurements were taken at this location.

Flow measurements -A wooden "V" notch weir was constructed and placed in the flowline of the main seep drainage channel, approximately 200' south of the origin of the surface seep. A nomograph was used to convert the flow in inches at the weir to gallons per day.

Water Sampling

Water samples were taken each month at the field demonstration from August 1996 - November 1997. Field measurement using portable equipment were made for the following parameters:

1. pH
2. Dissolved oxygen
3. Redox potential
4. Temperature
5. Specific conductivity

Parameters analyzed by an approved laboratory included:

1. Total Kjeldahl Nitrogen (TKN)
2. Nitrate
3. Total phosphate
4. Sulfate
5. Iron
6. Manganese
7. Alkalinity
8. Ammonia
9. Aluminum
10. Chromium
11. Zinc

Sample bottles were labeled with water proof marker and included the following information:

1. Date and time of collection
2. Project name and location of the sampling point
3. Parameter(s) to run
4. Preservative used
5. Name of collector

Samples were transported to the lab on ice within 24 hours. At the lab a chain of custody form was submitted with each sample with specific lab numbers assigned to facilitate sample tracking.

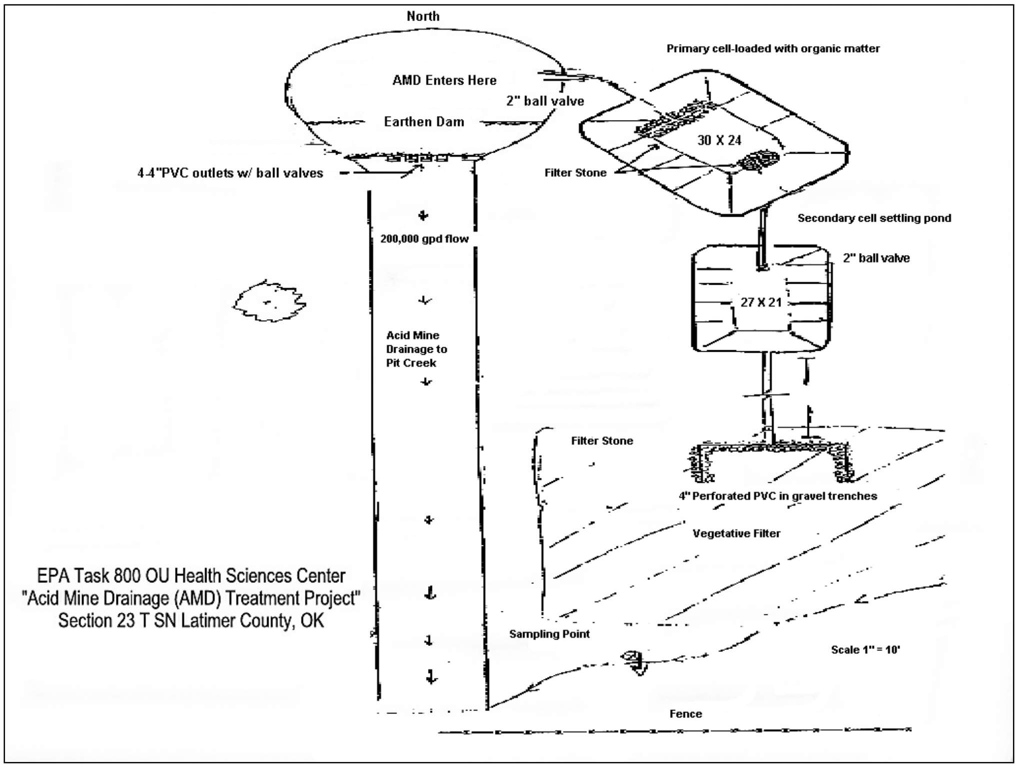

Figure 3 Schematic of treatment design.

Quality Control

The Oklahoma City-County Health Department (OCCHD) was the analytical lab used for this project. The OCCHD uses a frequency of 10% of all samples analyzed for analysis of blanks, duplicates and sample spikes. Acceptance criteria for the data resulting from these samples follow the guidelines outlined in the 1992 edition of Standard Methods for Analysis of Water and Wastewater.

All field meters and testing kits were inspected and calibrated before they were used in the field. All buffers and calibrating solutions were dated and discarded at manufactures recommended expiration dates.

The project officer and the principal investigator reviewed the data collection activities throughout the project to ensure completeness and appropriateness of values. Data collected from the contract lab (OCCHD) was reviewed with respect to the project's Data Quality Objectives to evaluate the effectiveness of the treatment.

III. RESULTS & DISCUSSION

A. BENCHSCALE STUDY

Organic Media Selection

Of the six different types of organic waste material tested, the hay-cow manure mixture had the best overall performance. Refer to Figures A1–A17 in the Appendix. Performance was defined as the ability to quickly neutralize the acidity of the AMD and provide for the removal of iron and sulfate. Manganese removal proved more difficult, with very little removal achieved. The hay-cow manure mixture was selected for use at the project site. Hay and manure serve well as an inexpensive nutrient source for the bacteria. Under anaerobic conditions, metal and acidity levels are lowered and pH rises from 3.8 to circum-neutral (close to 7.0).

The following parameters were considered in selecting the organic media for the treatment of this AMD:

1. Nutrient content for the microorganisms;
2. Hydraulic conductivity of the media to insure good flow characteristics;
3. Buffering capacity of the media to prevent upset of the treatment processes;
4. Alkalinity generation/pH adjustment (higher alkalinity; pH 8-9);
5. Stability of the organic matter to insure a proper life span of the media;
6. Cost, important since treatment duration is indefinite; and
7. Availability, the proximity of the waste material to the site and its abundance.

Media selection (organic matter) was based on the results of the lab test with regard to the factors listed above, along with a review of the literature. A cow manure and hay mixture was selected because of its performance at the Colorado School of Mines project, it was available in quantity, and it was free of charge (with the exception of the trucking cost).

B. FIELD DEMONSTRATION

The baseline design of the treatment system was centered on the concepts developed by the Colorado School of Mines (Cohen et al., 1992). Applying this information to the field was somewhat involved and required 3 iterations to develop an effective methodology. Results from the 3 approaches are presented below.

Approach 1

Initially, hay in burlap bags were placed directly in the AMD channel and evaluated over a 6-week period. The intent was to evaluate the effectiveness of the "treatment" bags in physically trapping/filtering the precipitates while providing an organic substrate for SRB. This approached was a “beta test” designed to supply valuable information on how to best design the treatment system. It was also hoped that the bags could be used to estimate the effectiveness of the treatment through mass balance calculations. Based on preliminary results, the approach failed as an effective method. There was minimal improvement in pH adjustment and iron concentrations were reduced by only 25%. Subsequently, an alternative treatment approach had to be applied.

Approach 2

The second approach involved the construction of a treatment cell that would promote anaerobic processes. Due to the magnitude of the problem, only a fraction of the seep flow was addressed. Roughly 5-10 gpm were diverted for treatment. The actual flow rate fluctuated proportionately to the seep discharge. The treatment cell design was roughly circular (30 ft diameter, 6 ft depth) with a retention time of roughly 2 days.

After 6 months, this approach failed to produce the desired SRB activity. Consequently, the improvement in water quality was marginal. There was an increase in pH to 6.6, but the design did not reflect the true potential of this treatment. Results are presented in Figures 4 - 9. However, since the effectiveness of the treatment was minimal, the results are not discussed in any detail.

Approach 3

Approach 3 proved to be the most effective treatment design. (The plans and specifications are presented in the Methods Section.) This design improved over the last two attempts by developing a sequential approach that segregated specific physical-chemical and biological activities while simultaneously integrating several treatment options. The results of Approach 3 are presented in Figures 4 – 9.

Over the 9-month treatment period, the design performed well, that is, the effect on water quality was noteworthy (refer to Table 4). All of the parameters of interest (pH, Al, Fe, Mn and alkalinity), with the exception of Mn, were treated to within the scope of the project goals. A Mann-Whitney test was performed to evaluate the statistical significance of the treatment (refer to Table 4). Using the data collected during Approach 3, there was a statistically significant change between the pre-treatment and post-treatment water quality for all parameters except Mn.

The primary objective of this demonstration was to show that SRB can be used to effectively treat AMD to meet water quality criteria listed in the CWA. The CWA targets pH, Fe and Mn (refer to Table 1 and Figures 4 - 6). This treatment process was effective at increasing the pH from 4.08 to 6.31— greater than a 100x increase. Iron concentrations were also reduced significantly from 243 to 11 mg/L—roughly 95 percent removal based on the median values. During ideal operating conditions, Fe was virtually completely removed. In contrast, Mn was unchanged between pre and post treatment condition. This was anticipated because of the chemical interaction between Fe and Mn. Manganese will not oxidize before Fe; subsequently, all of the Fe would have to be removed before there would be observable Mn removal. Pre-treatment Mn concentrations were 10.4 mg/L while post treatment values were 9.5 mg/L—not a statistically significant change. The lack of treatment for Mn is not necessarily an important concern necessarily. The Mn standard was created based on conventional waste water treatment plant processes involving chemical oxidation and precipitation. Since Mn will not chemically precipitate as a hydroxide until a pH of ~11, it served as a segregate for other metals. In other words, if Mn concentrations were low, then other metals of concern would also be low. Otherwise, Mn is not a concern from a toxicity perspective.

The effectiveness of this treatment was also observed in the decrease in acidity and increase in alkalinity. The pre-treatment acidity levels were significantly reduced via this treatment (619 to 100 mg/L as $CaCO_3$). Furthermore, alkalinity increased from 0 to 60 mg/L as $CaCO_3$. Unfortunately, the reduction in acidity was not significant enough to create net alkaline conditions all of the time. Although the reduction in total acidity is a benefit to the receiving stream, if this was released to Pit Creek, the natural buffering capacity would be overwhelmed, and the pH would drop below State standards and EPA criteria for Warmwater Aquatic Community (pH = 6).

This treatment was also effective at reducing the Al and Zn concentrations. Aluminum contributes to acidity and is toxic to aquatic fauna. Zinc is also of concern particular to mollusk species. Through this treatment process, both Al and Zn concentrations were reduced significantly 29 to 0.5 mg/L and 2 to 0.1 mg/L, respectively. However, given the elevated pH (6.31), Al should theoretically precipitate as a hydroxide and should be below the detection level. Zinc should also be theoretically lower than the observed value of 0.1 mg/L. Only one sample was taken during post treatment process for Al and Zn, so no any conclusions are tentative. More samples would have to be taken to confirm the actual treatment results for Al and Zn, but in general, SRB treatment should greatly reduce the loading of these metals to the environment.

As one would expect, sulfate concentrations decreased as well. In this process, alkalinity is generated in the form of bicarbonate as bacteria oxidize labile organic matter. Although no effort was made during the field experiment to calculate the mass balance of sulfur, the reduction from 1207 mg/L to 523 mg/L suggests that sulfate reduction was occurring.

Table 3 Water quality comparison of pre and post treatment results.

	PRE-TREATMENT				POST-TREATMENT			
Parameter	Median	High	Low	STD	Median	High	Low	STD
Acidity (mg/L)	619	809	475	105	100	195	7	70
Alkalinity (mg/L)	0	0	0	0	60	112	41.2	28.2
Conductivity (uS/cm)	2160	2470	1300	293	1170	2006	889	373
PH	4.08	4.27	3.86	0.12	6.31	6.72	5.82	0.31
Sulfate (mg/L)	1207	2018	1072	238	516	1600	321	428
Al (mg/L)	29.2	37.7	20.7	-	0.5	-	-	-
Fe (mg/L)	243	346	173	53.5	107	1.45	0.6	49
Mn (mg/L)	10.4	14.4	9.5	1.7	9.5	14.9	5	3.4
Zn (mg/L)	1.95	2.6	1.3	-	0.1	-	-	-

Table 4 Results of a the Mann-Whitney statistical evaluation (post-treatment data)

PARAMETER	SIGNIFICANT	P VALUE
Acidity	Yes	0.0009
Alkalinity	Yes	0.0022
Conductivity	Yes	0.0049
pH	Yes	0.0009
Sulfate	Yes	0.0101
Fe	Yes	0.0009
Mn	No	0.2030

Note: Al and Zn were not evaluated because there were not enough data points

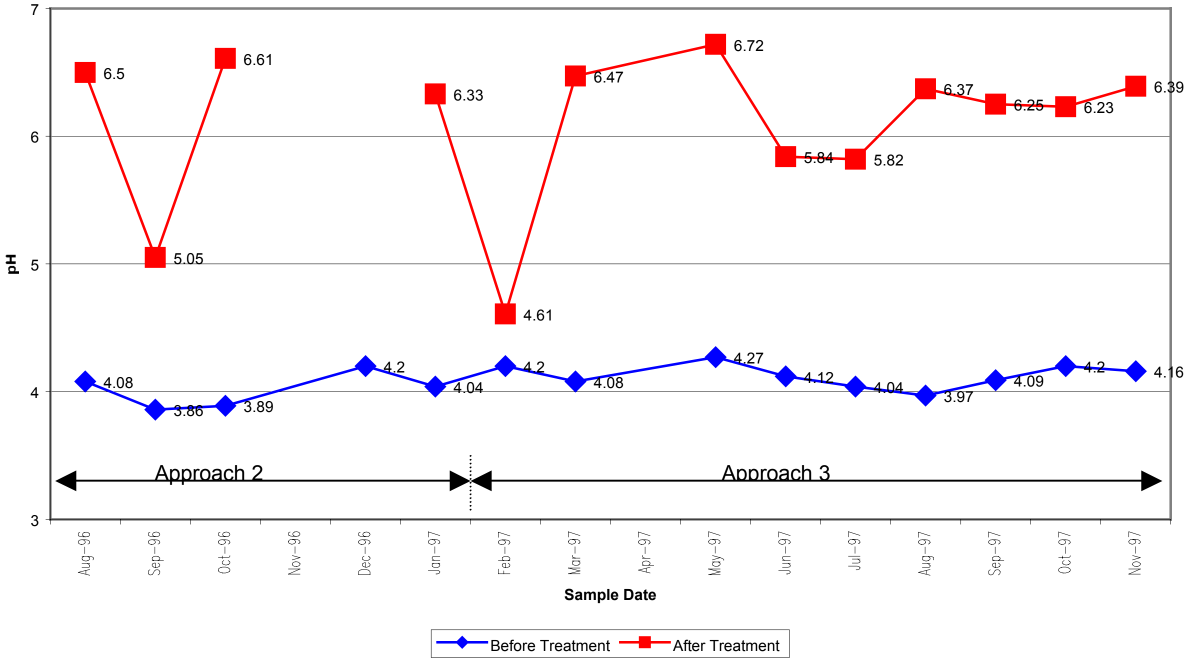

Figure 4 Changes in pH with treatment

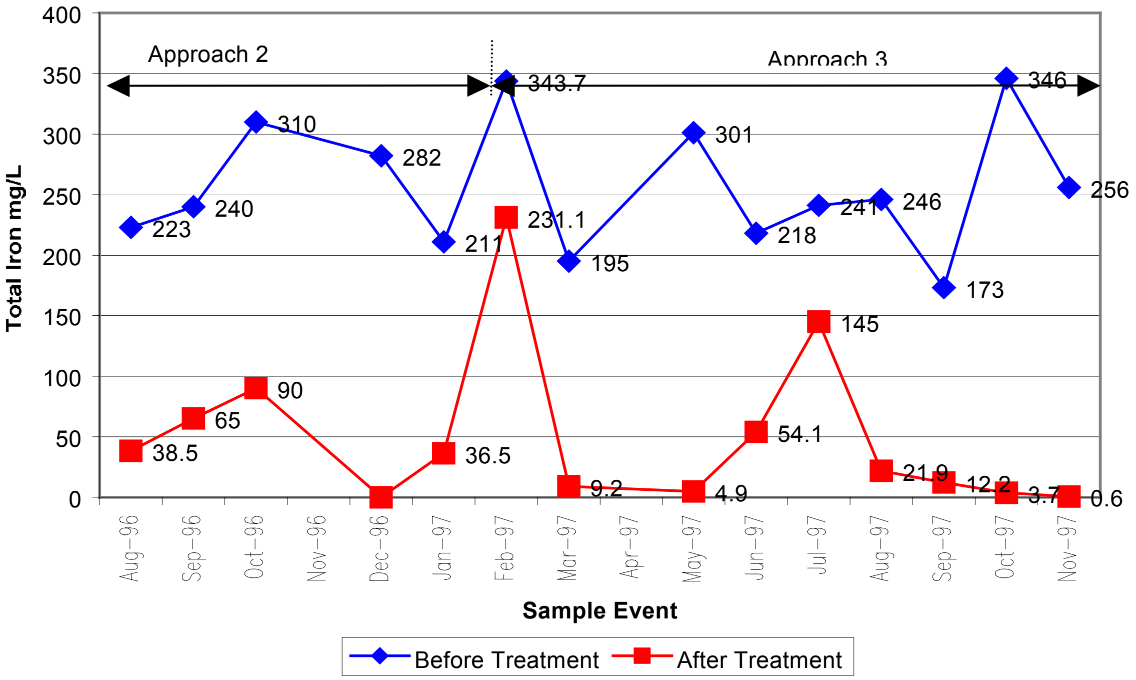

Figure 5 Changes in total Fe with treatment

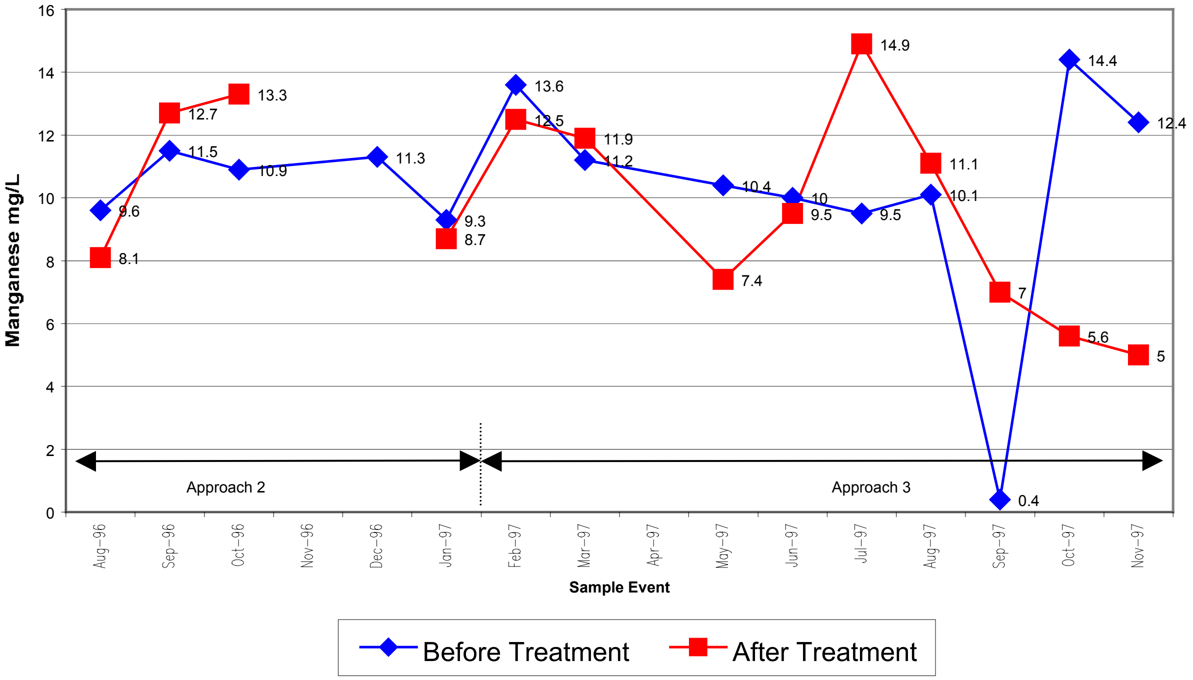

Figure 6 Changes in Mn with treatment

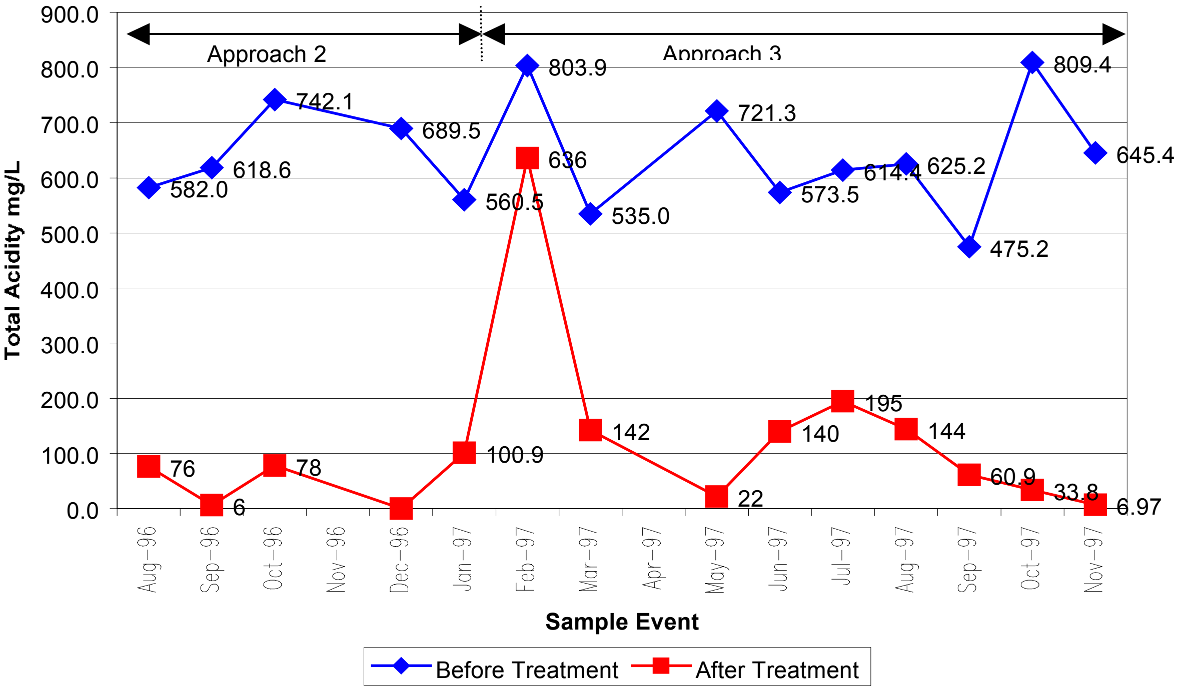

Figure 7 Changes in Acidity with treatment

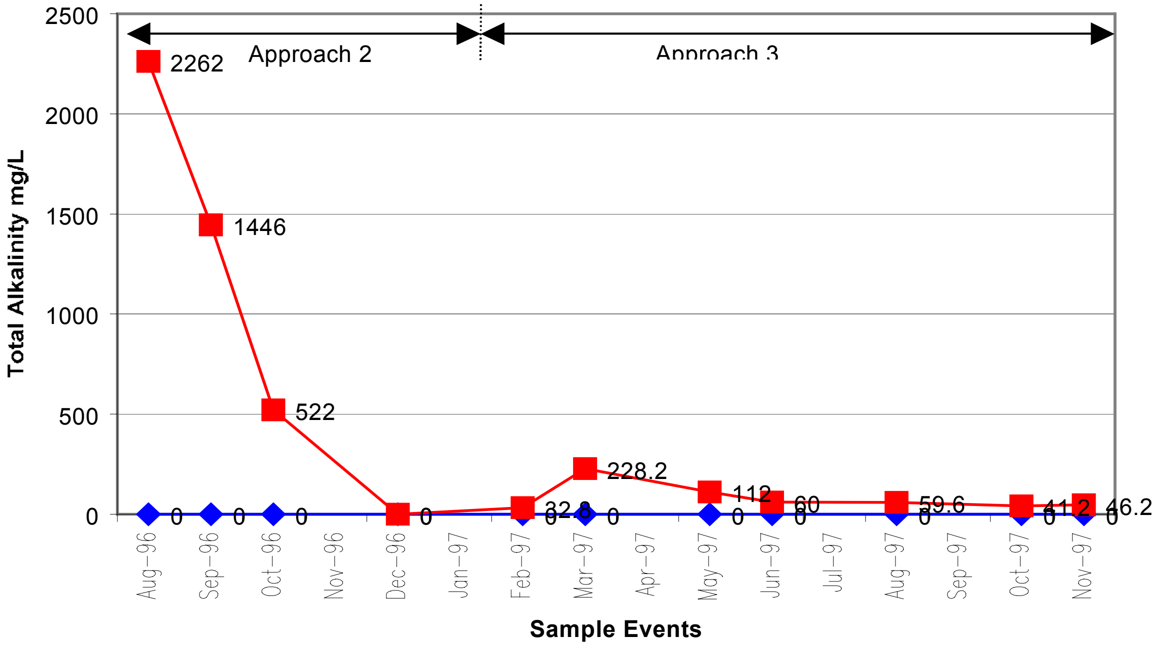

Figure 8 Changes in Alkalinity with treatment

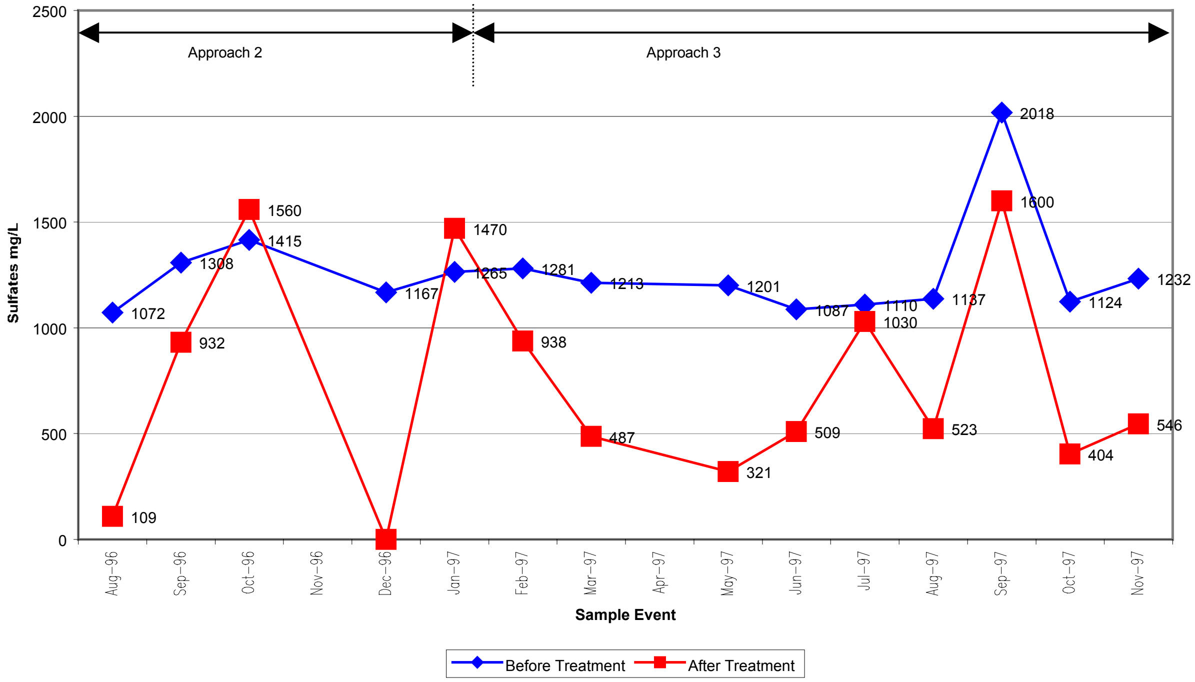

Figure 9 Changes in Sulfate with treatment

Treatment Application

This demonstration project only addressed a fraction of the total seep flow (7200 gpd). A larger scale system would have to be designed to treat the 100,800 gpd – 650,000 gpd flow rate observed at this site. The hay-manure treatment process was effective at reducing metals loads and increasing the pH; however, this treatment was not completely successful at addressing the impact AMD. Acidity levels were effectively reduced by 84%, so the magnitude of the impact would be lessoned, but the severity of the problem would still exist. Recall that net acidic conditions still existed in the effluent (100 mg/L as $CaCO_3$, median value). Consequently, the receiving stream would still experience a decrease in pH as the dissolved metals oxidize. This would be a particular problem in eastern Oklahoma where stream alkalinity levels are typically well below 100 mg/L. The acidity load would overwhelm the stream's buffering capacity.

With further refinement, this treatment process could be designed to effectively treat AMD so that the receiving stream could support healthy fish and macroinvertebrate populations. Most likely the system efficiency could be improved either by increasing the retention time of Cell 2 or by adding a second SRB cell in series. The second cell would be placed after the first settling pond and would treat any acidity or metal loading that passed through the first SRB cell. Unfortunately, further research is needed to calculate acidity removal rates for complete AMD treatment.

Comparison of (SRB) Treatment to Conventional AMD Treatment

The most common active treatment techniques for AMD include the following:

1. Calcium carbonate (Limestone);
2. Calcium hydroxide (Hydrated lime);
3. Sodium carbonate (soda ash);
4. Sodium hydroxide (Caustic soda);
5. Magnesium oxide (Mag);
6. Ammonia (NH_3);
7. Biocides which inhibit acid forming bacteria (i.e., Promac biocide brand); and
8. Biological treatment (Wetland and or sulfate reduction bacteria).

In the selection of the appropriate treatment technique several factors should be considered. These include at a minimum the flow rate and chemistry of the AMD, the local climate and terrain, the hydrology and geology of the area, the receiving stream characteristics such as flow and water quality, the accessibility of the area and the proximity to populated areas.

The following cost comparison was modified from an Office of Surface Mining publication derived from research conducted for the US Bureau of Mines at the National Mine Land Reclamation Center at West Virginia University. This article provided costs for four different treatment scenarios (Skousen, 1995). The one selected to compare with this project was scenario 3, which had the next to the worst water quality. The AMD at the Rock Island #40 site is somewhat higher in both acidity and iron than the published scenario selected, but it should provide a comparison of the technologies which is accurate.

Based on the economic comparison, the SRB treatment was roughly ½ or less of the cost of conventional treatments (refer to Table 5). Although, this demonstration failed to completely treat the AMD to net neutral conditions, the treatment significantly improved the water quality and proved to be cost effective. This is an import consideration given the magnitude of abandoned mine land problem. As previously stated, if AMD associated with AML sites are to be treated the resposibility will fall primarily on the public sector. A cost effective partial treatment the reduces the magnitude of the problem may be an acceptable alternative to no treatment.

Table 5 Comparison of various AMD treatment costs[1]

METHOD	HYDRATED LIME	CAUSTIC SODA	AMMONIA	MAG OXIDE	SRB
Installation	$10,000	$1,500	$3,000	$8,000[2]	$7,600
Annual Repair	$3,500	$-0-	$1,000	$4,000	$3,000
Annual Reagent	$13,158	$107,237	$27,904	$13,000	$2,000
Annual total	$26,638	$108,737	$31,904	$25,000	$12,600[3]

1: The following table is based on the following parameters:
- Flow 250 gpm (our flow is closer to 200 gpm)
- Acidity 500 mg/liter (our acidity is 700 mg/liter*)*
- Iron 100 mg/liter (our iron is 200 mg/liter)
- Treatment duration-5 years

2: Installation costs were based on estimated equipment and labor to install and amortized over a 5 year period. Cost of Mag Oxide system came from actual costs of treatment of an AMD effluent problem in SE Oklahoma by P&K coal company (now GCI Operating Co.). This location is in the same watershed and in close proximity to the demonstration project.

3: Cost estimate for the SRB system were based on a 4 day detention time for the treatment process in anerobic lagoons, constructed of earthen pits with liners and underdrain systems. The items making up the total annual cost for a five year period are listed below. Please note that the cost includes land purchase, which may not be necessary if leasing of the land is an option.

SRB Cost Estimate for a flow of 250 *gpm and the chemistry referenced above:*
- Land 12 acres total, 6 acres for lagoons and wetland, 1 acre for roads and infrastructure, 5 acre for sludge handling. Land cost estimated at $1,000 per acre, $12,000 total for land.
- Pipes, valves, liners and construction -$12,000
- Gravel for road and underdrain system -$8,000
- Wetland area for secondary and polishing the effluent from the lagoons -$4,000

IV. CONCLUSIONS AND RECOMMENDATIONS

- The hay-cow manure mixture proved to be quite effective as a media to support SRB, and consequently reduce metal and acidity levels in AMD while increasing the pH.

- The design needs to be refined to increase the effectiveness of the treatment. Perhaps increasing the detention time or placing a second SBR treatment cell in series with the existing system may improve acidity removal.

- General factors of importance –refer to Table 6

Table 6 Factors, which were important to the success of this project

Volume	Depth of the primary cell is important since anaerobic conditions must be maintained. Water depth was maintained close to 6’.
Configuration of Cells	Cells or containment area were in series for ease of construction. One large cell is adequate if final stage treatment is not necessary, i.e. polishing cell.
Substrates	Composted hay and cow manure had the best characteristics in the lab and is easily obtained in SE Oklahoma.
Retention Time	Minimum of 2.5 days preferably longer for maximum SRB activity. Retention time is based on the amount of sulfide that can be removed per unit volume of area in the reaction cell.
Acclimation Period	This is the time period necessary to initiate SRB Activity and ranged from a few days to a week.
Temperature	The higher the temperature, the greater the sulfate reduction activity.

- Bio-fouling was a recurrent problem that plagued the distribution system. Also, during particularly elevated flow episodes, the retention time in the SRB cell was decreased and the system became aerobic.

- Other miscellaneous factors include: Adsorption of metals to the substrate by physical filtration and chemical complexities with the organic matter in the cell. Metal uptake by plants in the wetland contributed to a small portion of the overall metal removal from the AMD, since during upset of the treatment cells the quality of the discharge leaving the wetland had high levels of iron, manganese and sulfate. Wetland growth was consistently lush throughout the year due in part to the consistent nutrient supply from the effluent.

- A logical extension of this research would be to utilize the spent media as a nutrient supply in the plant industry. The sludge, which is a by-product of treatment, has many desirable properties and could be very beneficial for citrus, roses and golf course grasses after appropriate processing (special note: The Gowen AMD does not have toxic metal properties).

- An important notation to this work was that this project was certainly region specific, i.e., the characteristics of the Gowen AMD, use of a local organic product, rainfall, etc. The successes of this project to other projects could vary widely, based on the AMD chemistry of that location and the local conditions.

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APPENDIX A

A. LABORATORY RESULTS

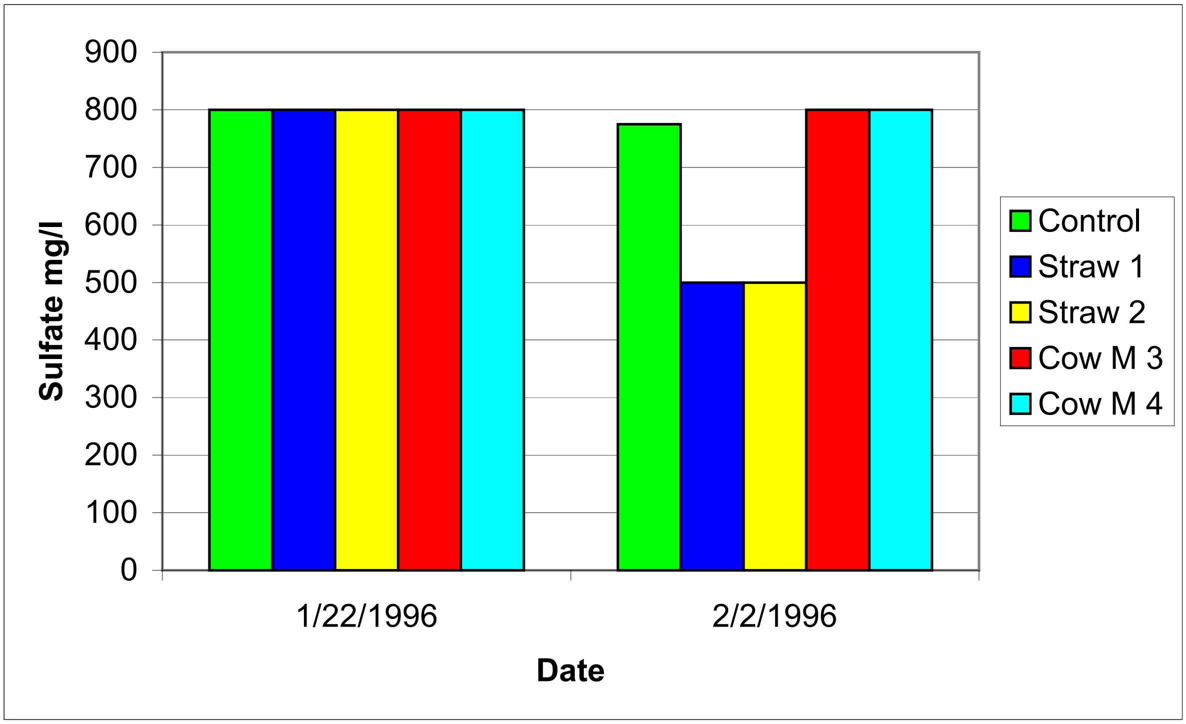


Figure A1 Compost Bioreactor Test #1: Sulfate

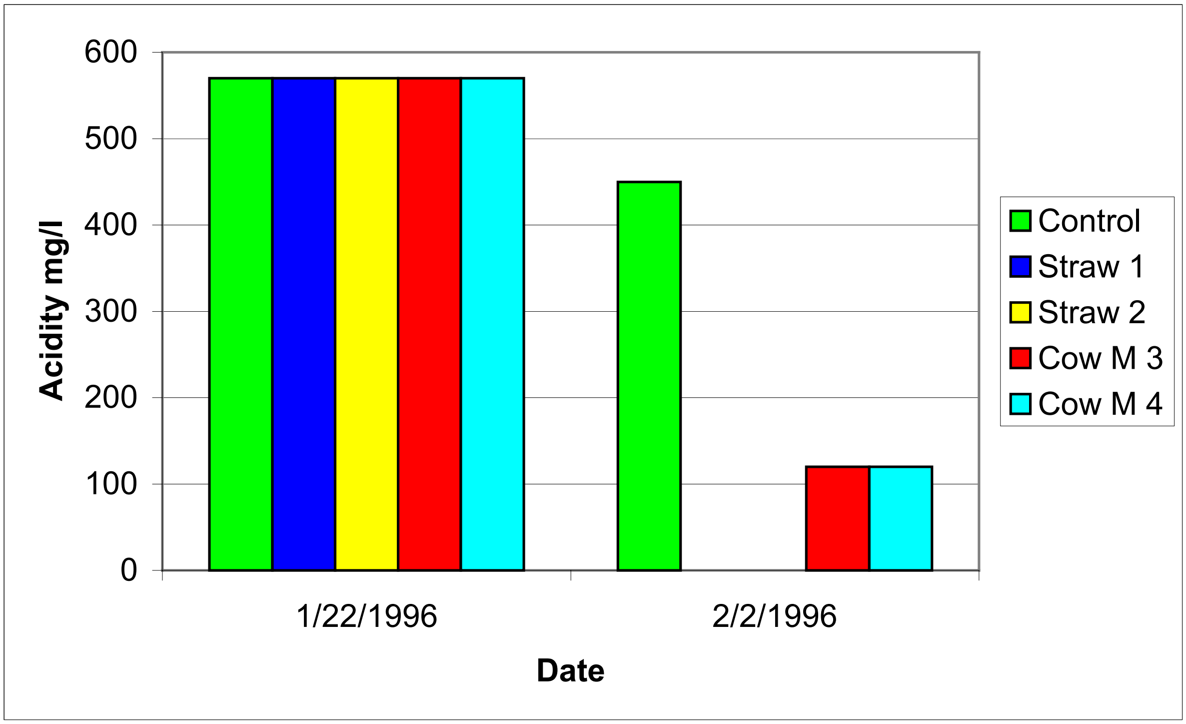


Figure A2 Compost Bioreactor Test #1: Acidity

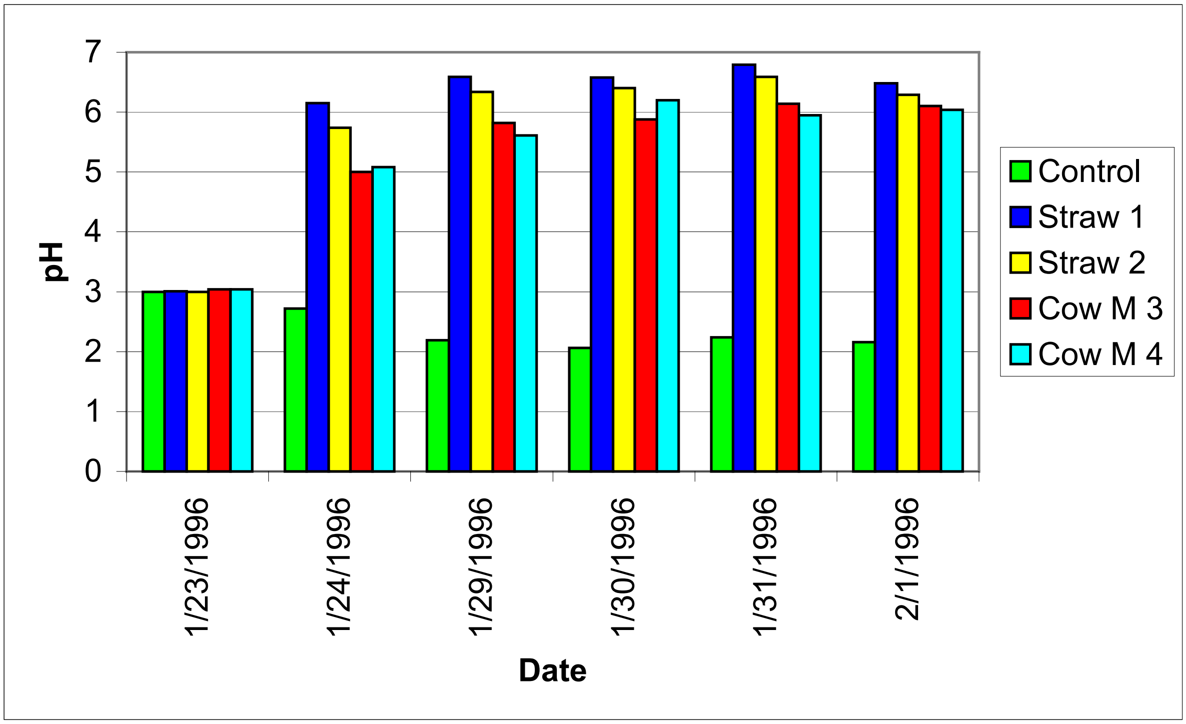


Figure A3 Compost Bioreactor Test #1: pH

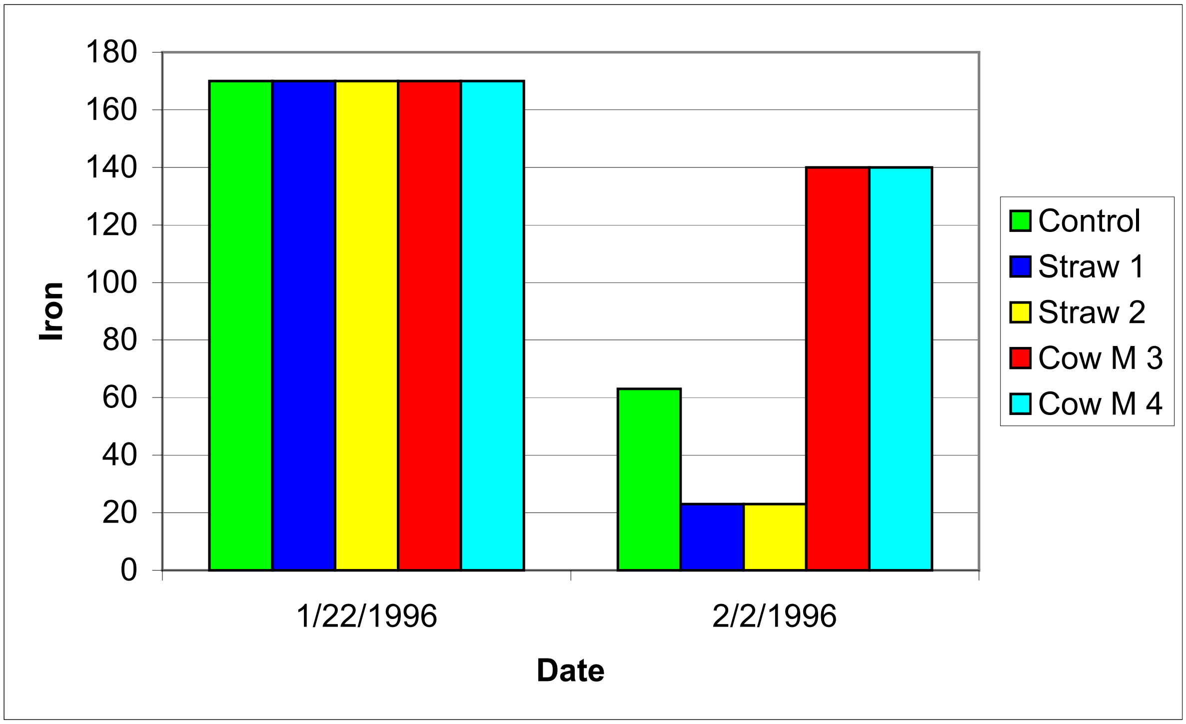


Figure A4 Compost Bioreactor Test #1: Iron

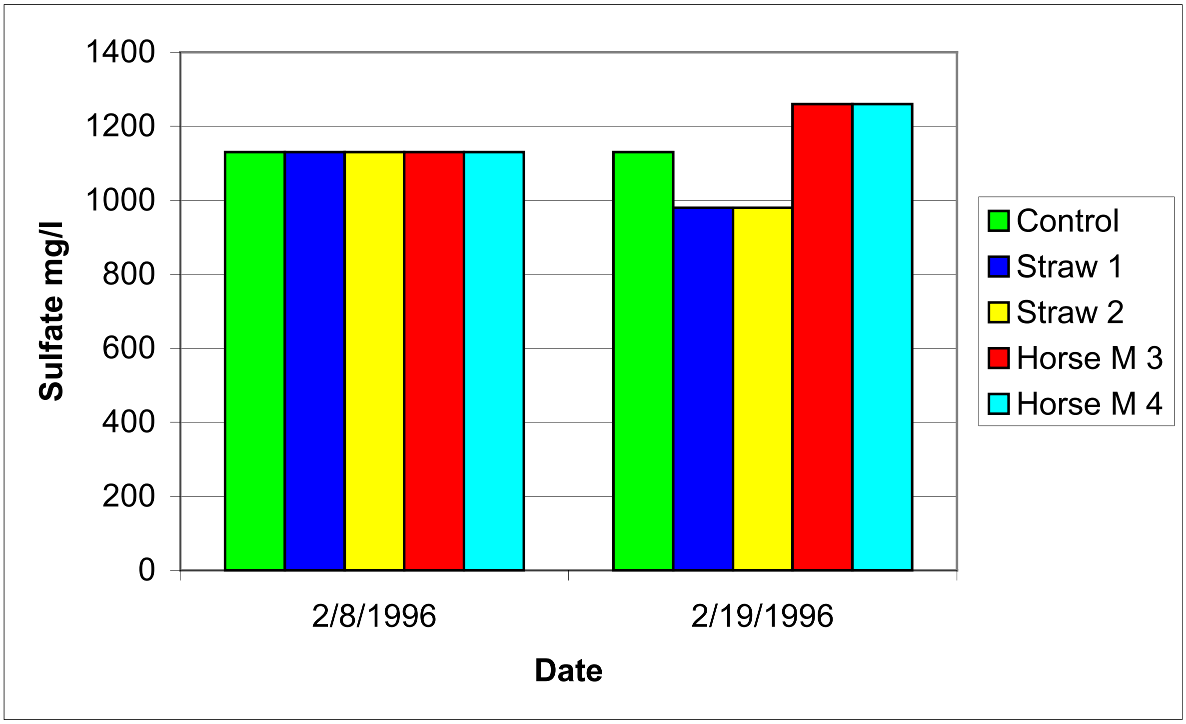


Figure A5 Compost Bioreactor Test #2: Sulfate

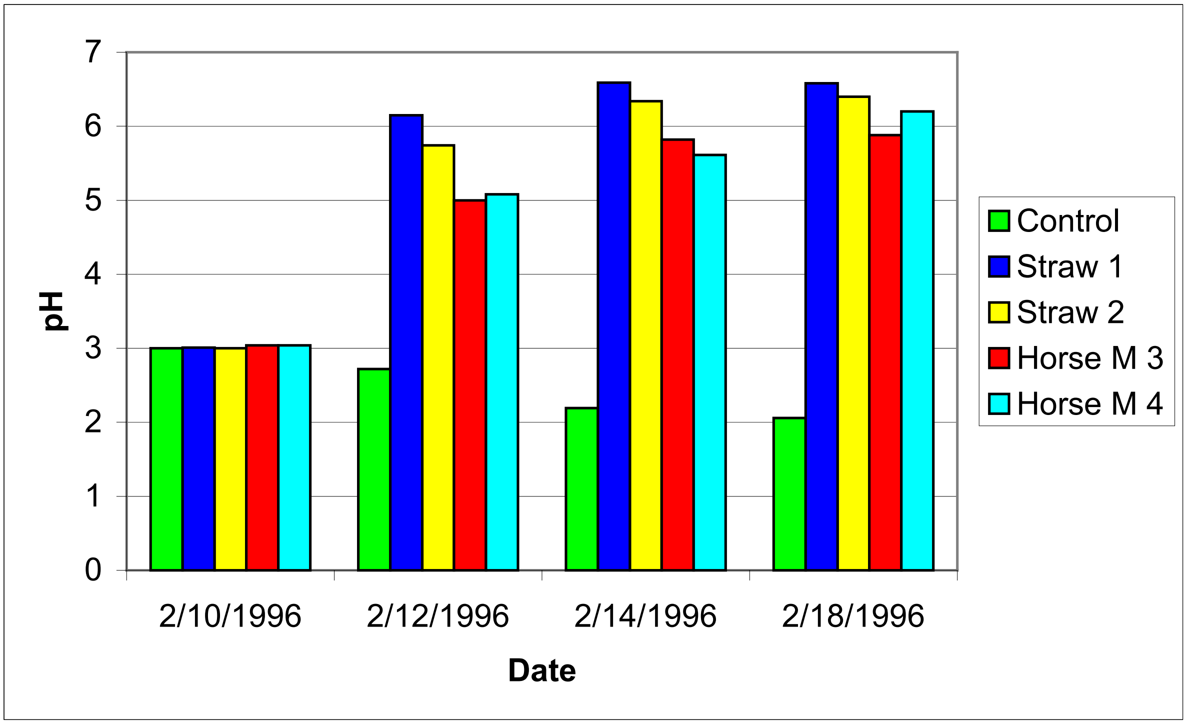
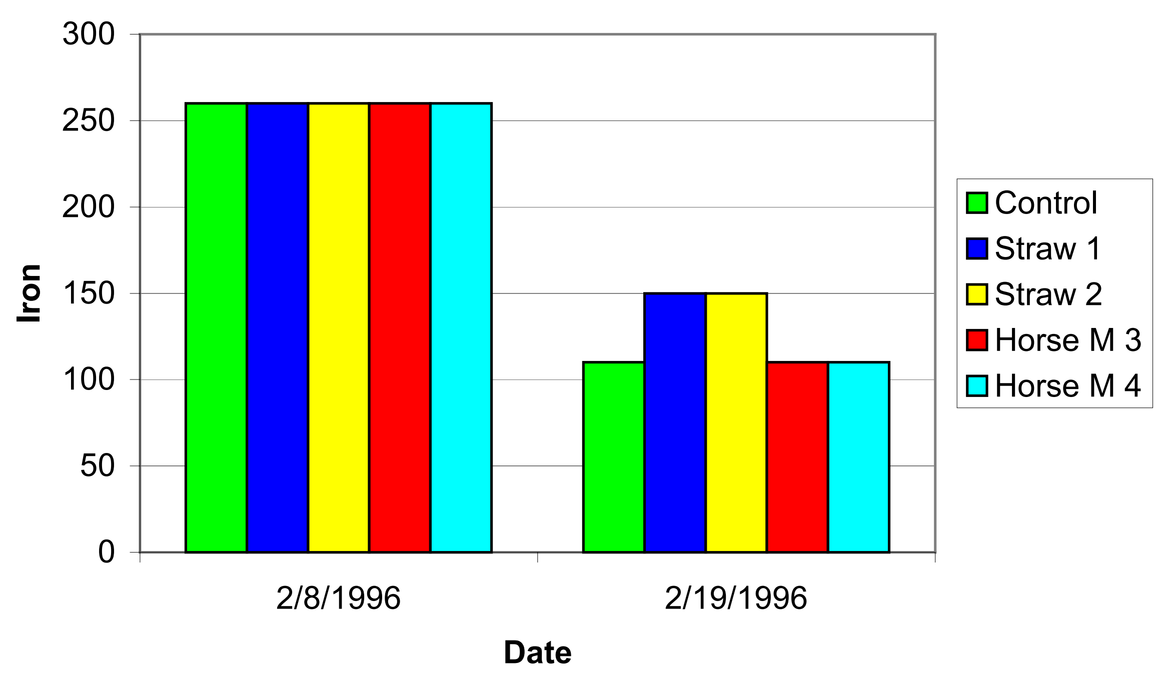


Figure A6 Compost Bioreactor Test #2: pH



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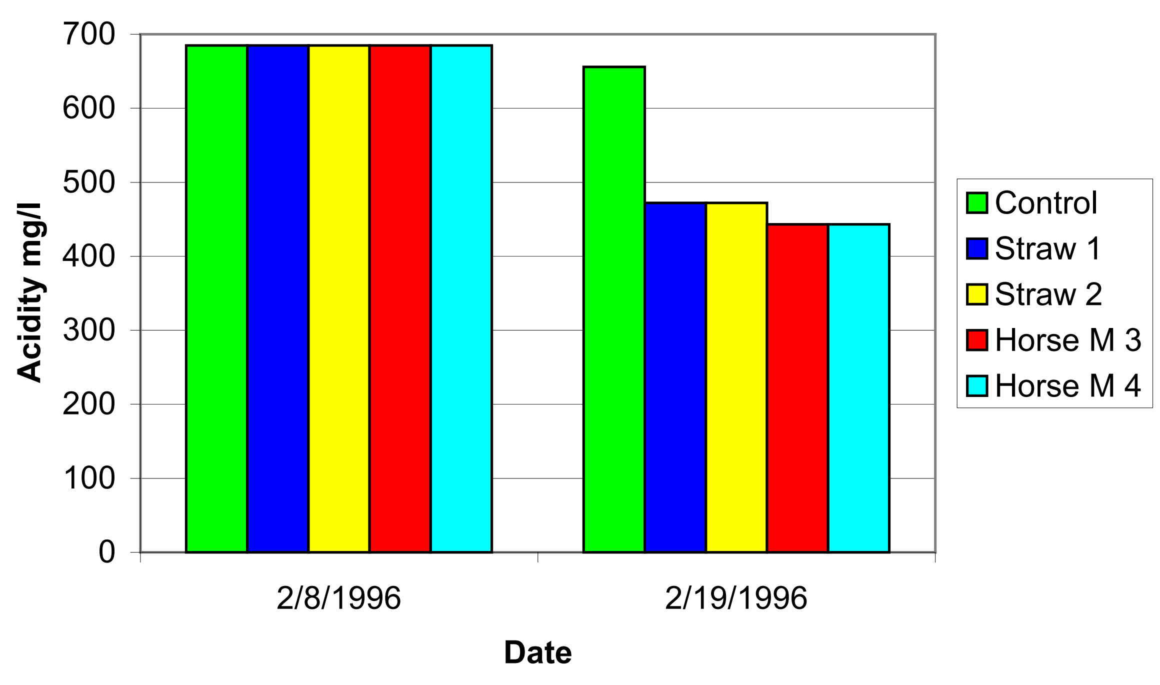

Figure A8 Compost Bioreactor Test #2: Acidity

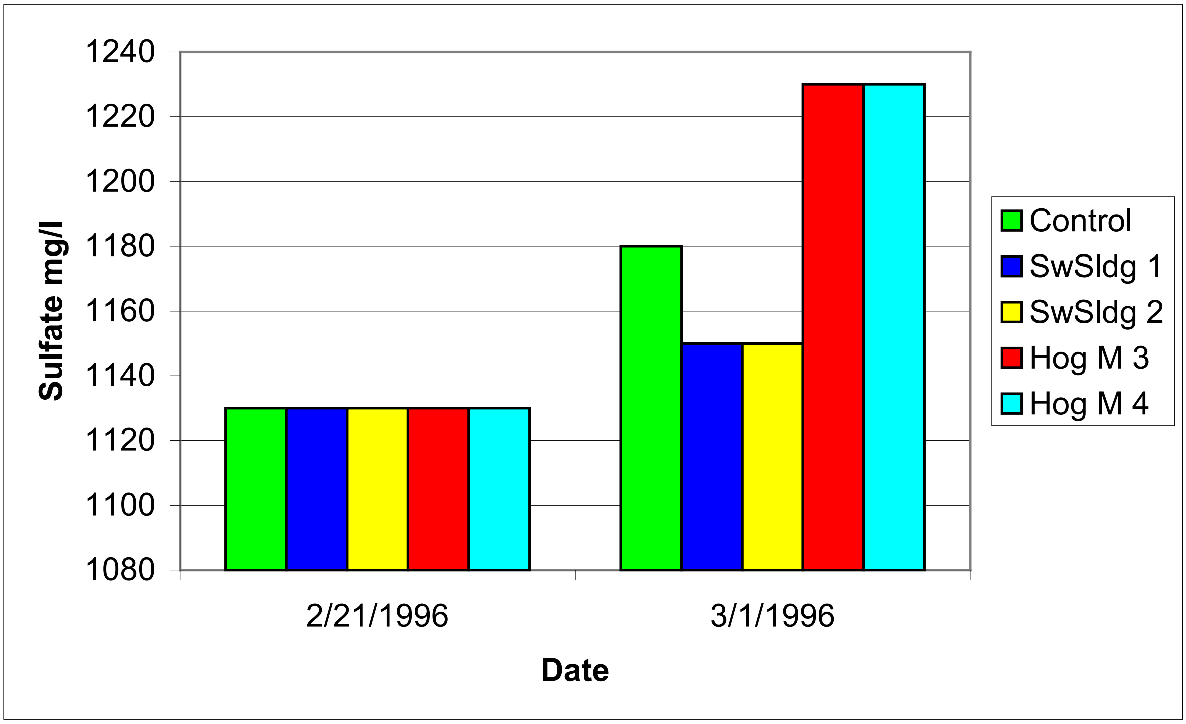

Figure A9 Compost Bioreactor Test #3: Sulfate

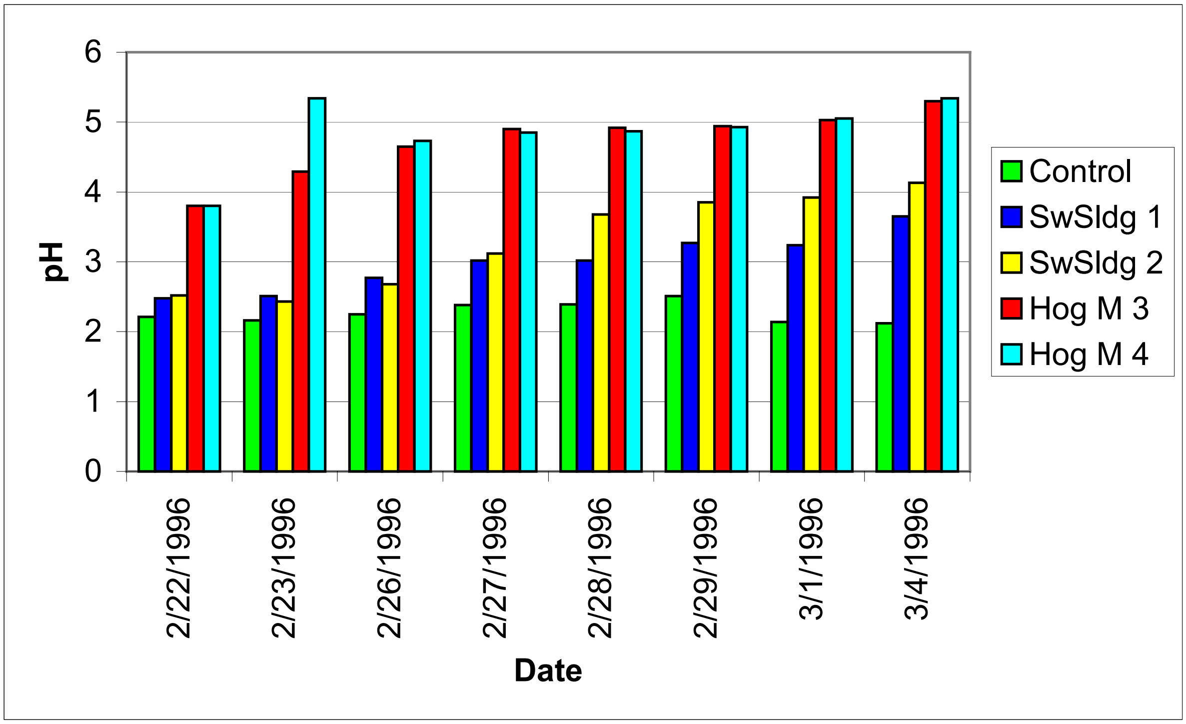

Figure A10 Compost Bioreactor Test #3: pH

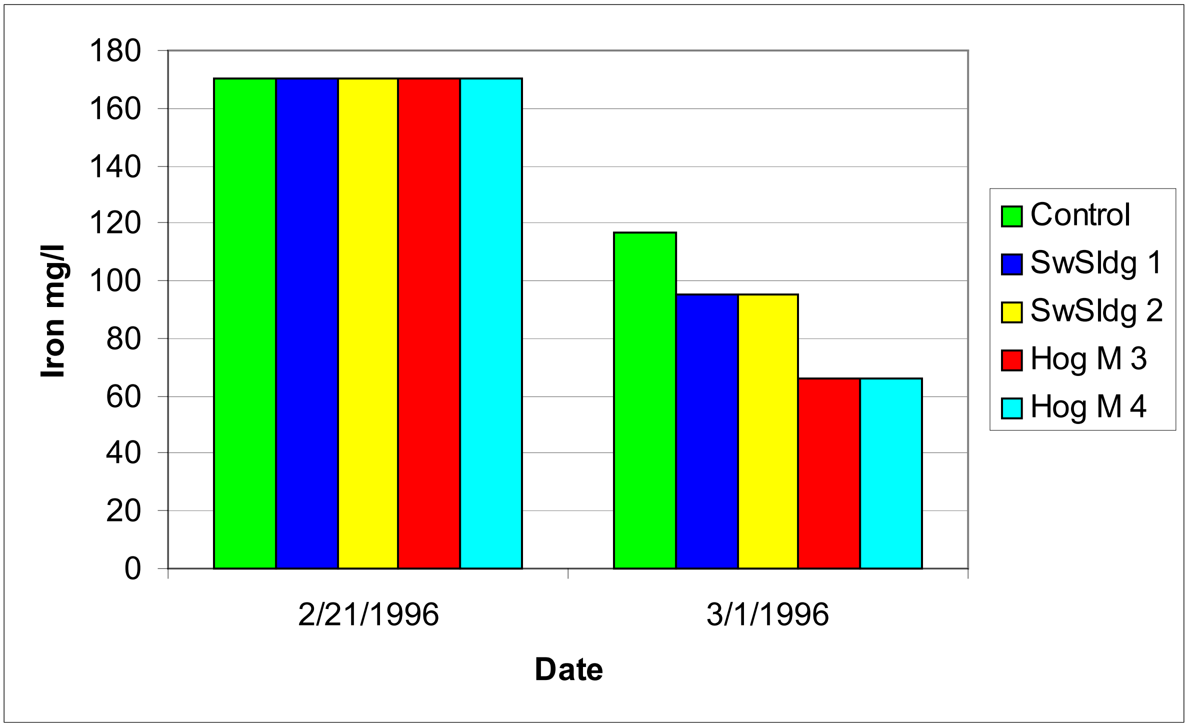

Figure A11 Compost Bioreactor Test #3: Iron

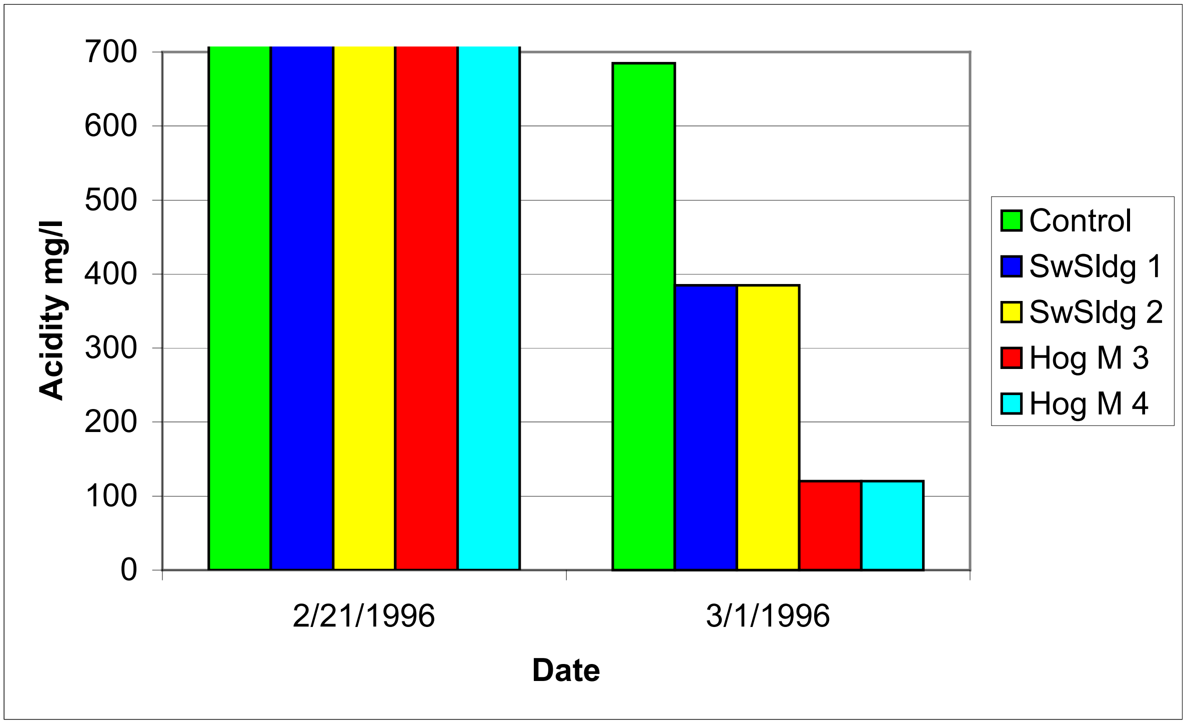

Figure A12 Compost Bioreactor Test #3: Acidity

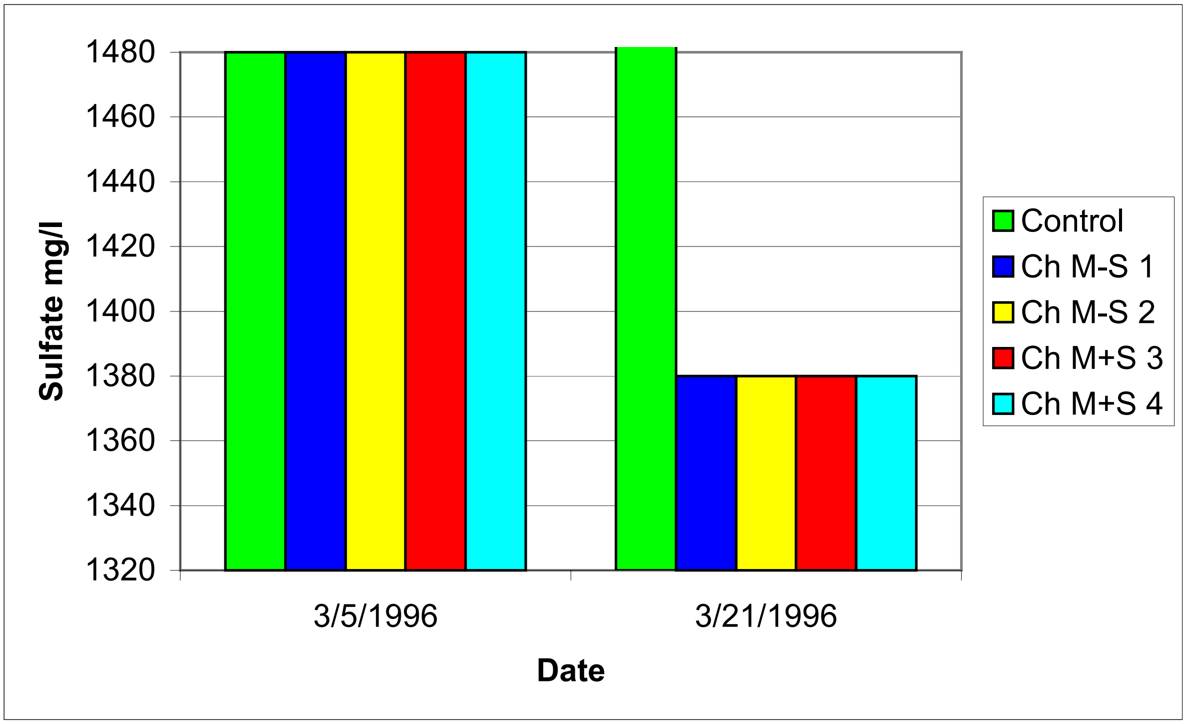

Figure A13 Compost Bioreactor Test #4: Sulfate

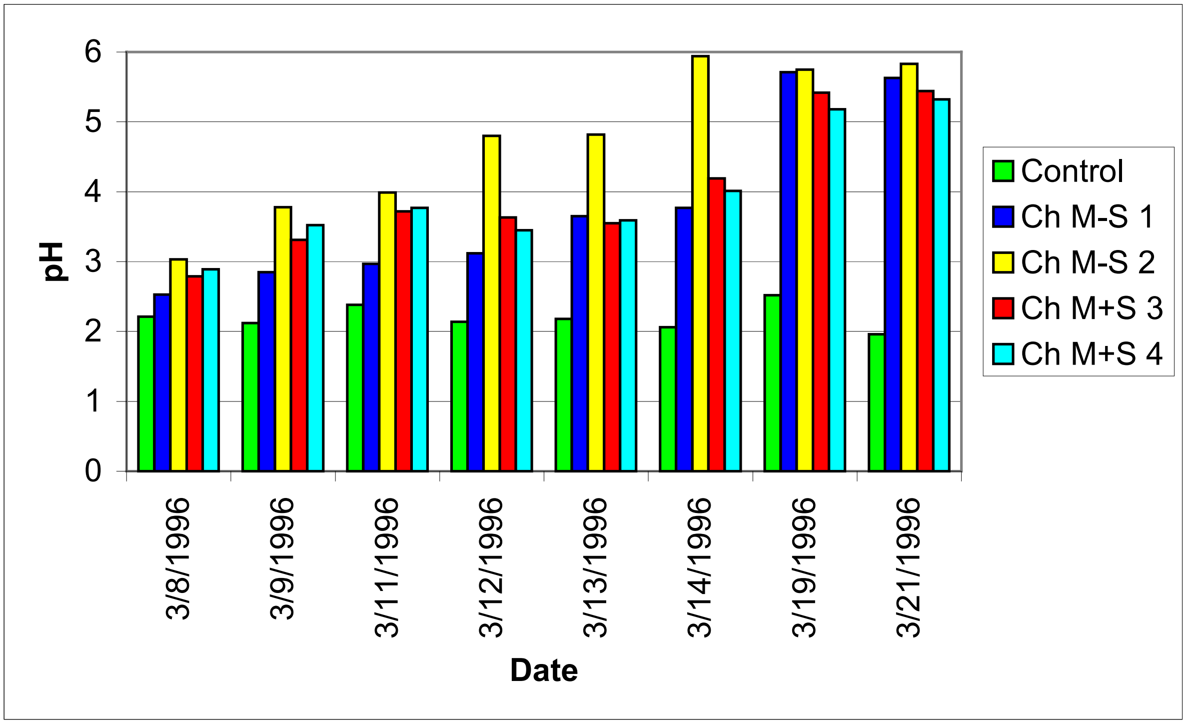

Figure A14 Compost Bioreactor Test #4: pH

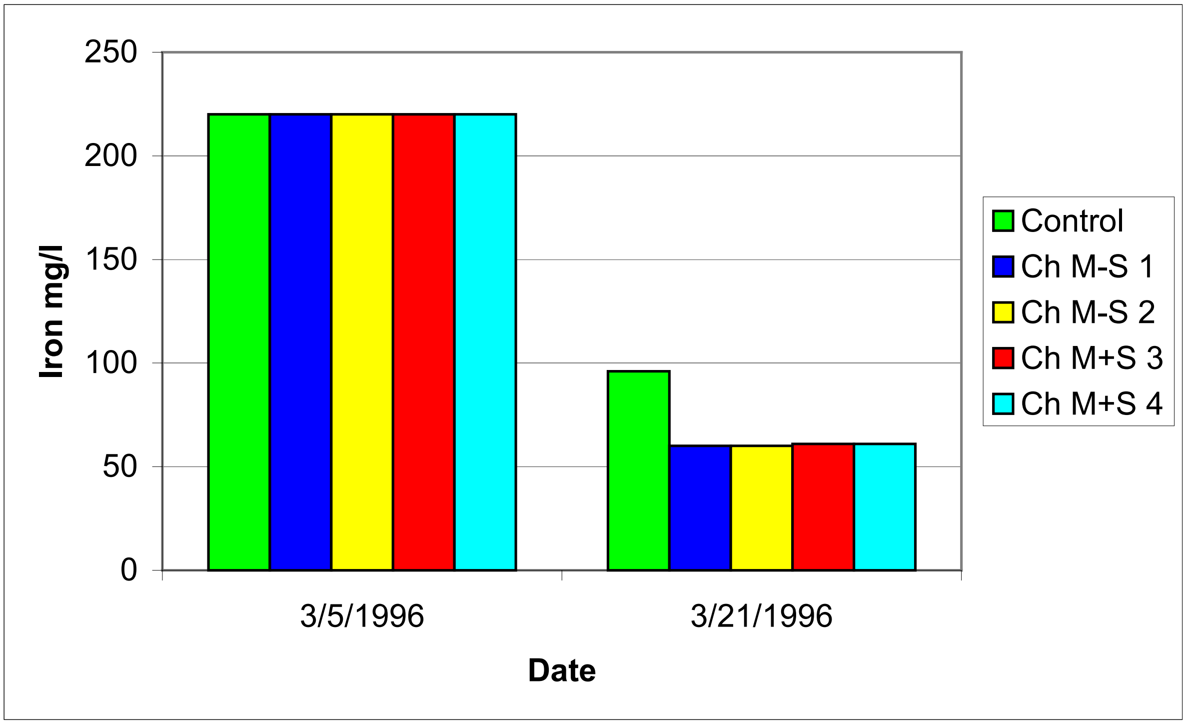

Figure A15 Compost Bioreactor Test #4: Iron

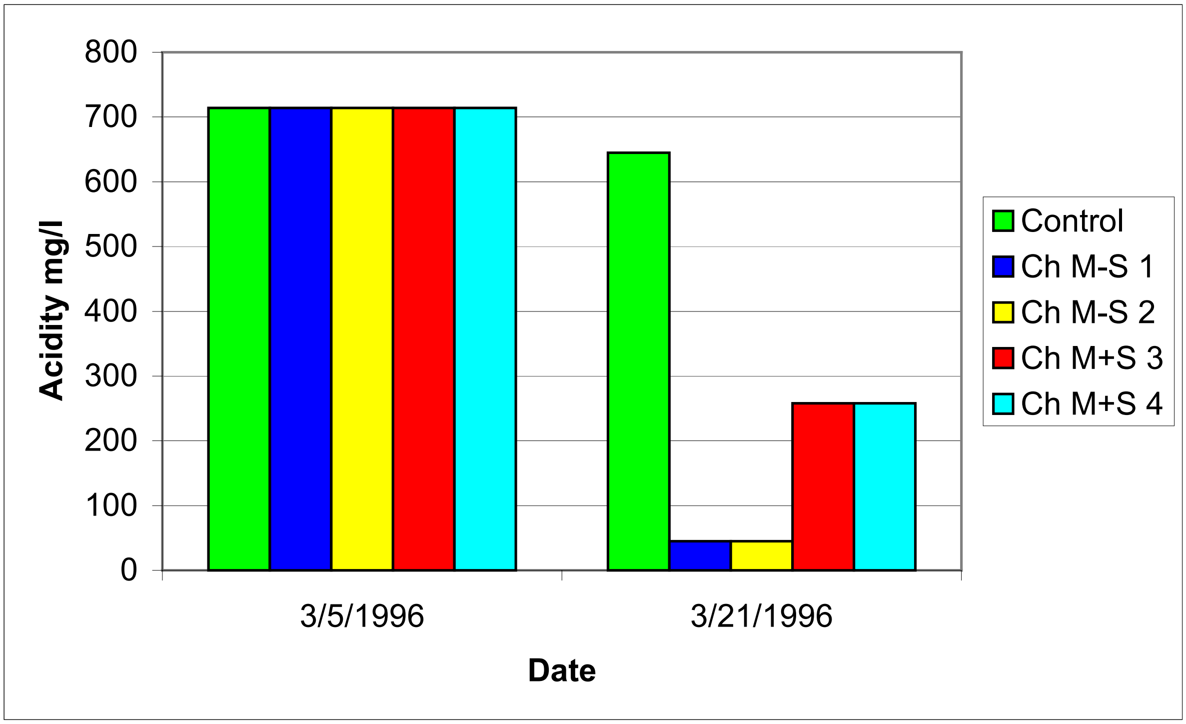

Figure A16 Compost Bioreactor Test #4: Acidity

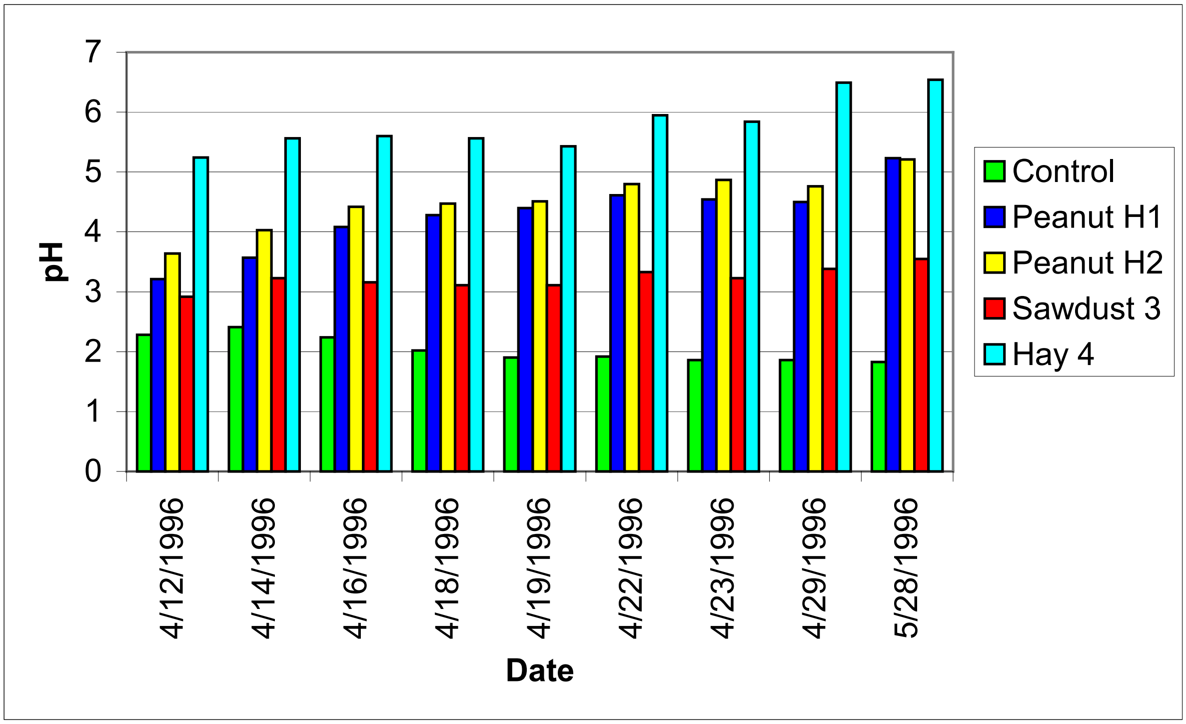

Figure A17 Compost Bioreactor Test #5: pH