ENVIRONMENTAL MANAGEMENT OF ACID WATER PROBLEMS IN MINING AREAS

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ABSTRACT

Acid Mine Drainage (AMD) originates from the oxidation and leaching of sulphide minerals present in coal and metalliferrous ore bodies and gives rise to several environmental degradation problems. An investigation has been carried out to combat the acidic water problems.

Results of this investigation indicate that application of anionic surfactant (sodium lauryl sulphate) and food preservatives (sodium benzoate and potassium sorbate) effectively abate the acid formation at low concentration levels (15-40 ppm) as tested in laboratory as well as at pilot-scale levels. Acidity, sulphate and iron concentrations are found to reduce by over 70 percent and remained low for more than three months after treatment. Thus this investigation demonstrates the management of these problems in an environmentally safe manner by controlling acid formation at its source.

INTRODUCTION

Acidity in mine drainages represents a major environmental problem in regions associated with the mining of high-sulphur coal and sulphide minerals. The adverse effects of acidity are many and potentially serious. The well known adverse biological effects when added to the loss of recreational values, potable water supplies, corrosion and other adverse impacts, add to the other mining imposed pollution problems in the mining areas.

This paper presents the results of the investigation carried out in abating acidity at source from high-sulphur coal and refuse material by the employment of anionic surfactant (sodium lauryl sulphate) and food preservatives (sodium benzoate and potassium sorbate).

CHEMISTRY OF AMD FORMATION AND CONTROL

Prevention and/or control of AMD depends upon an understanding of the chemical, biological and geological factors as described by Rawat and Gurdeep (1983). A series of chemical reactions (given below) describe AMD that results from exposure and weathering of pyritic material (FeS_2) normally present in coal and the associated strata to the combined effects of atmospheric oxygen, water and iron-and sulphur-oxidising bacteria such as Thiobacillus ferrooxidans (T. ferrooxidans):

$$2FeS_2(s) + 7O_2 + 2H_2O = Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad \text{----} \ (1)$$

$$Fe^{2+} + 1/2\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \quad \text{----} \ (2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3\ (s) + 3H^+ \quad \text{----} \ (3)$$

The stoichiometry of equation (1) shows that one mole of FeS_2 produces two moles of acid (H^+). In turn Fe^{2+} generated by reaction (1) can readily oxidize into Fe^{3+} and produces additional three moles of acid (equation 3). The net result is that for every mole of pyrite oxidized, four equivalents of acid (H^+) are produced.

As the pH in the immediate vicinity of the pyrite falls to less than 3, the increased solubility of iron and the decreased rate of $Fe(OH)_3$ (yellowboy) precipitation affects the overall rate of acid production (kleinmann 1979). At this point, ferrous iron is oxidized by T. ferrooxidans and the ferric iron in turn oxidizes the pyrite :

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + SO_4^{2-} + 16H^+ \quad \text{----} \ (4)$$

The rate of acid production is high and is limited by the concentration of ferric ions. Fe^{3+} activity becomes significant at a pH of approximately 2.5; a vicious cycle of pyrite oxidation and bacterial oxidation of Fe^{2+} results from the combined effects of reactions 2 and 4. The rate of reaction 2 exerts primary control on the cycle by limiting the availability of Fe^{3+} which is the major oxidant of pyrite. Inhibition of the activity of T.ferrooxidans would prevent ferric oxidation of pyrite and should therefore reduce acid formation by at least 70 percent (Gurdeep & Bhatnagar, 1986) AMD control by the application of SLS, benzoic acid and sorbic acid had been successfully demonstrated by Onysko et.al.(1984). The mechanism of the action of these organic compounds in inhibiting the activity of T. ferrooxidans has been studied by Gurdeep and Mridula (1991).

EXPERIMENTAL INHIBITION STUDIES IN SIMULATED MINE ENVIRONMENTS

Coal samples were collected from northeastern coal mines (NEC) of India where AMD problems are quite prevalent. Coal sample used for this study had the following sulphur distribution:

Pyritic sulphur	2.40%
Sulphate sulphur	0.63%
Organic sulphur	3.07%
Total sulphur	6.10%

Sample was crushed and sieved to range in size from 0.2 to 2.0 cm, and rinsed repeatedly with deionised, distilled water. Variation within the size range from one experiment to next did occur, but pains were taken to ensure that for any one experiment particle size distribution was random.

Simulated natural mine infiltration consisted of synthetic groundwater formulations which consisted of : 50 ppm $CaCO_3$; 25 ppm $MgSO_4$; 2 ppm $(NH_4)_2SO_4$ and 0.25 ppm KH_2PO_4. Three compounds - SLS, SBZ and PSB were used as inhibitors. Tubulated dessicators were used to simulate the humid environment of natural mine infiltration. 10 g of crushed, rinsed coal was placed in perforated polypropylene beakers which were in turn positioned so as to drain into slightly large beakers. The entire double beaker assemblage was autoclaved and then placed inside the dessicator. Two 0.5 cm diameter tubes inserted through the dessicator lid allowed a controlled and limited contact with the atmosphere. To simulate the presence of <u>T. ferrooxidans</u> (having 10^7 cells/ml) was trickled onto the samples every five days. Immediately following this, 2.0 ml of synthetic groundwater, with varying concentrations of inhibitors was applied. Sterile controls received no inoculum.

At the end of each run (20 days), the contents of the beakers were filtered and rinsed. Approximately 0.5 g of the test material was removed and placed in 9-k liquid culture media to test for <u>T.ferrooxidans</u> . The collected filtrates were analysed for total disolved iron and acidity.

PILOT-SCALE EXPERIMENTS

The experiments were carried out in seven plastic barrels. Two holes were drilled in the bottom of each barrel and were plugged with removable rubber stoppers. Below each barrel, a plastic bucket was positioned for collection of leachate during the experiment. Fresh coal refuse for the experiment was obtained from NEC mines. 10 kg of coal refuse (having pyrite content 40%) was placed in each barrel. Three treatment chemicals used were - SLS, SBZ and PSB. Of the seven barrels, one was designated as control (that would not receive any chemical treatment). The remaining six barrels were designated for treatment with 200 ml of a 0.5 g/l (low dose) or 5 g/l (high dose) solution of SLS, SBZ or PSB. Each barrel was sprinkled with 200 ml of distilled water thrice a week. Of 600 ml of water added per barrel per week, only 490 ml was recovered, indicating an average evaporation of 110 ml per week. To establish an equilibrium after transfer of coal refuse from field to laboratory, each of the seven barrels was treated identically for first four weeks. After four weeks, each of the six barrels designated for chemical treatment was sprinkled with 200 ml of appropriate solution. The control barrel was sprinkled only with distilled water.

This treatment was repeated every week for a total of four treatments. This was equal to a chemical dose of 40 or 400 mg/kg refuse. Beginning on week 9, each barrel was again treated with only distilled water.

Leachate from each barrel was collected every seventh day and analysed for acidity, sulphate and iron. Bacterial population estimates and in case of SLS treated samples, SLS determinations were also performed in leachates.

CHEMICAL DETERMINATIONS

Acidity, iron and sulphate were determined by standard methods (Am. Publ. Heath Assoc. 1985; Tamura et. al 1974). Weekly estimations of iron oxidising bacterial population in leachates were performed by most probable number (MPN) technique, in which a large number of culture tubes were inoculated with progressive dilution (usually ten-fold) of the samples and the cultures were observed for bacterial growth. SLS was determined in leachate samples by benzene extraction and spectrophotometric quantification of methly green-SLS complex formed (Moore and Kolbeson, R.A., 1956).

INHIBITORY EFFECTS OF SLS, SBZ AND PSB IN SIMULATED MINE ENVIRONMENTS:

These in-vitro experiments, although important, do not necessarily reflect inhibitory effectiveness in actual mine environment. Therefore, laboratory simulations of coal mine environments were used to test the effects of SLS, SBZ and PSB on the formation of acid drainage.

RESULTS AND DISCUSSION

Results of a 20 day experiment to reflect the inhibitory effects of SLS, SBZ and PSB in simulated mine environments, are discussed below :

INHIBITION BY SLS

The effect of SLS on acidity and dissolved iron is shown in figure 1 and 2 respectively. SLS was found to be quite effective in limiting bacterial population. Samples containing SLS at concentrations increasing from 5 to 25 ppm showed proportionately delayed growth when transferred to 9-K culture medium; however it stopped bacterial growth at 30 ppm. Hence, SLS can be regarded as bactericidal at 30 ppm and higher concentrations. As indicated by figure 1 and 2 at concentrations of 30 ppm and above, acidity and iron concentrations were reduced to about that of sterile controls.

At low concentrations, SLS acts by altering the semipermeable properties of bacterial cytoplasmic membrane; disorganising some component of bacterial cell membrane, thereby allowing the seepage of H^+ ions into the cell (Schafa and Salton, 1960). SLS induced seepage of H^+ ions into the cell, can be expected to have an initial effect of reducing metabolism and consequently slowing Fe^{2+} oxidation. Higher concentrations of SLS would cause actual damage to membrane and thereby kill the bacteria SLS levels below bactericidal concentrations (5-25 ppm) delayed bacterial growth while at and above bactericidal levels (> 30ppm) reduced acidity and iron concentrations to approximately that of sterile control.

INHIBITION BY SBZ AND PSB

Effects of SBZ and PSB on acidity and dissolved iron are shown in figure 3 and 4 respectively. When the samples containing inhibitor concentrations upto 30 ppm were placed in 9-k media to test for T. ferrooxidans, oxidation of the medium in 6-10 days showed low population density due to partial inhibition of bacteira. At 40 ppm and above, SBZ and PSB reduced acidity and iron concentrations to about that of sterile control.

SBZ and PSB can readily react with Fe^{3+} in synthetic mine waters to yield sparingly soluble organic precipitates. These precipitates are expected to liberate benzonic acid or sorbic acid during redissolution in acidified waters. Both benzoic and sorbic acids have been found to effectively inhibit T. ferrooxidans as demonostrated by Gurdeep and Bhatnagar (1985), and Onysko et.al (1984).

The concentrations of SLS, SBZ and PSB to inhibit T.ferrooxidans in simulated mine environments were greater than that required in 9-K liquid culture media. It is posible that substrate material may have reduced the vulnerability of the bacteria or that the chemical inhibitors may not have saturated all of the crushed material before draining. Alternatively, the effectiveness of these compounds in synthetic groundwater may differ from that in 9-K medium.

Studies were further continued to evaluate the mine drainage control effectiveness of SLS SBZ amd PSB in pilot-scale experiments using coal refuse. The use of coal refuse in AMD control experiments offers the opportunity for study of worst-case conditions. Since refuse contains greater proportion of pyritic material than the exposed coal and rock in draining mines, refuse pile AMD is often representative of most severely contaminated AMD.

PILOT SCALE STUDIES ON CHEMICAL INHIBITION OF AMD

Data for 20 weeks of leachate samples for six treated and single untreated (control) refuse barrels are shown in figures 5-8 SLS concentrations in leachates treated with low (40mg/kg) and high (400 mg/kg) SLS doses are shown in figure 6 and 8, respectively; comparable data for leachate concentrations of benezoate and sorbate were not obtained.

During the initial four week equilibrium period, there was some decrease in titratable acidity, total iron and sulphate (figure 5 and 7) and bacterial MPN (figure 6 and 8) which may be because of the reason that the rate of washout from refuse exceeded oxidation within the refuse, i.e. equilibrium had not been reached. The variability of data is to be expected in such a system because refuse size and composition were heterogeneous with aggregate size ranging from 20 cm to 1 micron; some sedimentation occuring within the barrels and water channelisation as well as pockets of acid formation are likely (Dugan, 1983). During the period after treatment began, the control barrel leached increasing amount of acidity (figure 5 and 7) and bacterial counts remained high (figures 6 and 8) showing a marked comparable reduction of pyrite oxidation and acid formation between control and treated barrels. There was also a marked difference in acidity after week 6. A longer response time for the differences in acidity to become apparent is anticipated because any pyritic iron which has been oxidised to ferric iron before bacterial inhibition, is already committed to acid formation, ($Fe^{3} + 3H_2O = Fe(OH)_3 + 3H^{+}$).

By the time of third application of SLS (week 7), iron oxidising bacteria had disappeared from the drainage (figure 6 and 8). However, a considerable amount of SLS was leached during that period and these bacteria would not survive in the leachate in the presence of SLS (Dugan, 1975). An important observation of this study was the rapid rate at which populations of iron oxidising bacteria that were reduced to very low levels by SLS returned to the normal levels present in control. There is a possibility that pockets of iron oxidisers were active in the barrels due to incomplete contact between bacteria and SLS, i.e. number increased after SLS was flushed out. The result of this study clearly indicated that iron oxidising bacteria did not undergo wholescale cell destruction because significant number were subsequently counted within a few weeks of SLS application. Similar results were obtained with SBZ and PSB which indicated that iron oxidising bacterial populations returned to normal levels present in untreated samples. However, the absence of data on residual benzoate and sorbate in the relevant leachate samples prevented corroboration of the inference.

In samples treated with low and high doses of chemicals distinict time delays were observed in build-up of acidity, iron and sulphate to normal levels present in control. The observed delay in leachate acidification for control and treated samples is summaried in Table 1. During the periods of effective AMD suppression, acidity concentrations in leachates from treated samples were at least 70% less than in leachates for the untreated sample. Similar results in iron and sulphate build-up can be seen from data presented in figures 5 and 7. Results summarises in Table 1 indicated that for each treatment chemical, a high treatment dose (400 mg/kg) resulted in longer sustained suppression of AMD formation than a low treatment dose (40mg/kg). However, the increase in duration of AMD suppression asociated with dramatic increase in chemical dose (x10) was disproportionately small for the three treatment chemicals SLS (x3), SBZ (x2) and PSB (x1.7). In case of SLS (retained via sorption), a higher dose is likely to be exceeded the sorptive capacity of the refuse. Whereas, in case of SBZ and PSB (retained via precipitation), the higher dose is likely to be exceeded the availability of Fe^{3+} in the refuse. Thus much of the higher doses of all three chemicals may have been washed from the refuse samples during the leaching cycle.

Although the data presented here are quite variable, any actual field trails are likely to show even greater variability due to uncontrolled environmental influences. However, this experiment represents a scale up from the highly controlled laboratory experiments and demonstrates that pyrite oxidising bacteria can be inhibited by SLS, SBZ and PSB with a concomitant reduction in the formation of over 70 percent acidity.

Although commonly used, neutralization has several inherent problems. Base can produce water with an unacceptable high pH (greater than 9) and also give rise to sludge disposal/handling problems apart from high cost. Treatment is not the best solution to AMD problems as it has the disadvantage of being necessary for as long as the discharge continues and thus requires manpower, surface facilities, and a sludge disposal area indifinitely. Since AMD results from the oxidation of pyrite associated with coal and overburden strata, limiting the rate of pyrite oxidation would reduce the amount of acid formed.

SLS is water soluble and effective at low pH. It has got additional advantages of being low in mammalian toxicity and is readily available in biodegradable forms. SBZ and PSB are safe chemicals and effective food preservatives. They are expected to persist in acidic environments via a mechanism more tenacious than sorption since they result in the formation of precipitates with acidic waters.

Table -1

Time Delay In Build-Up of Acidity

Refuse sample	Lag period before build-up of acidity
Control	6 weeks
Low Dose Treatment	
SLS	6 + 4 weeks
SBZ	6 + 6 weeks
PSB	6 + 6 weeks
High Dose Treatment	
SLS	6 + 12 weeks
SBZ	6 + 12 weeks
PSB	6 + 10 weeks

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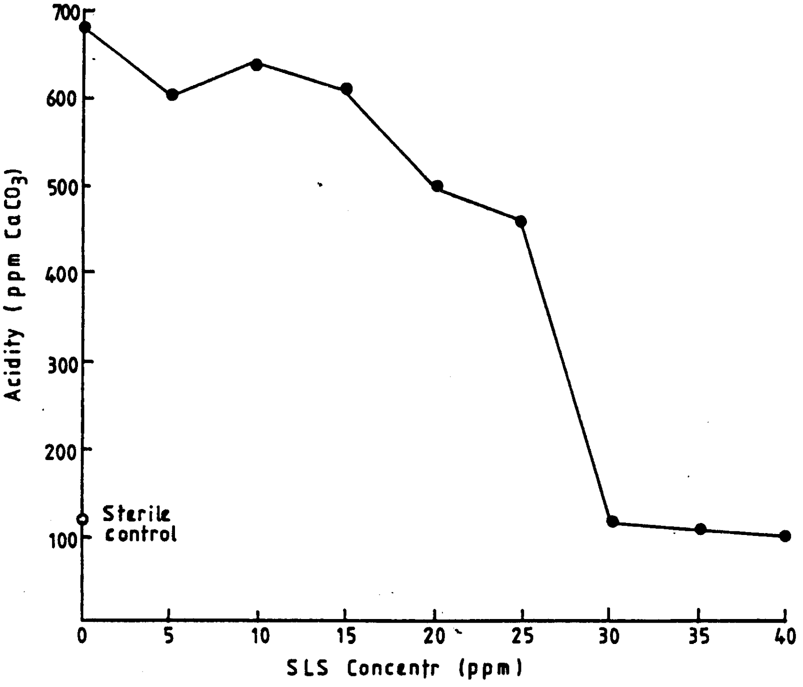

FIG. 1 EFFECT OF SLS ON ACIDITY

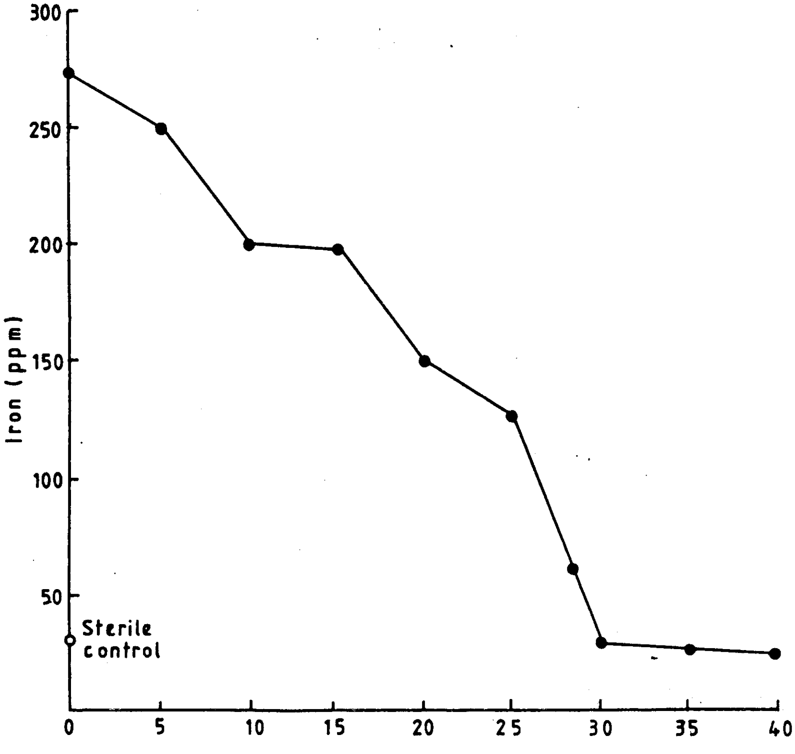

FIG. 2 EFFECT OF SLS ON DISSOLVED IRON

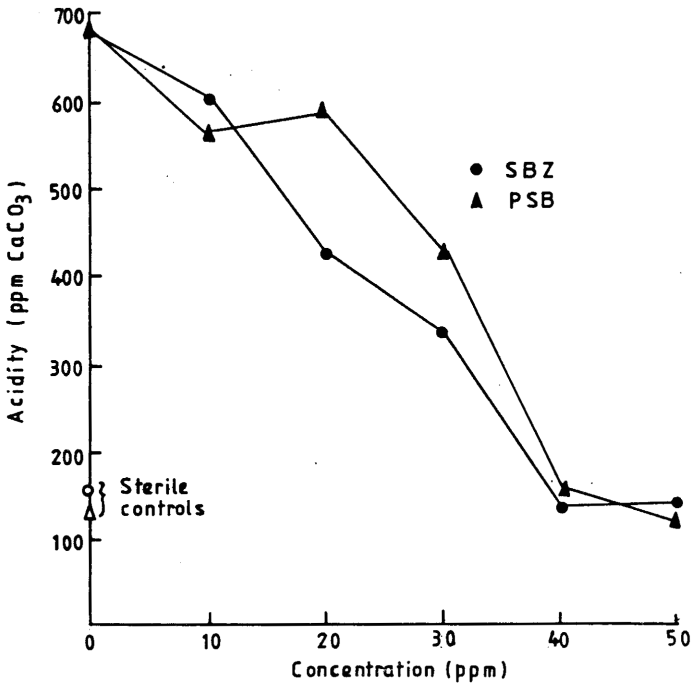

FIG. 3 EFFECT OF SBZ AND PSB ON ACIDITY

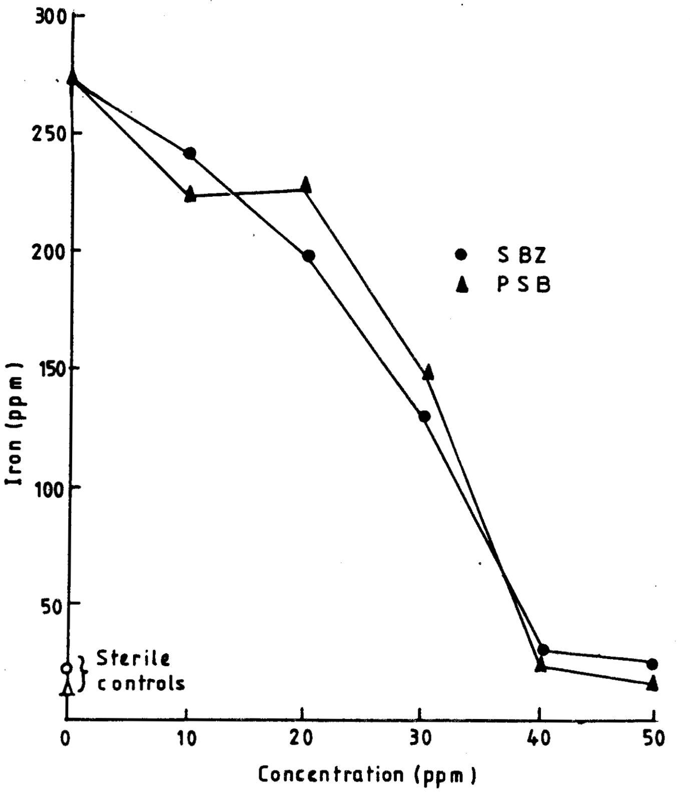

FIG. 4 EFFECT OF SBZ AND PSB ON DISSOLVED IRON

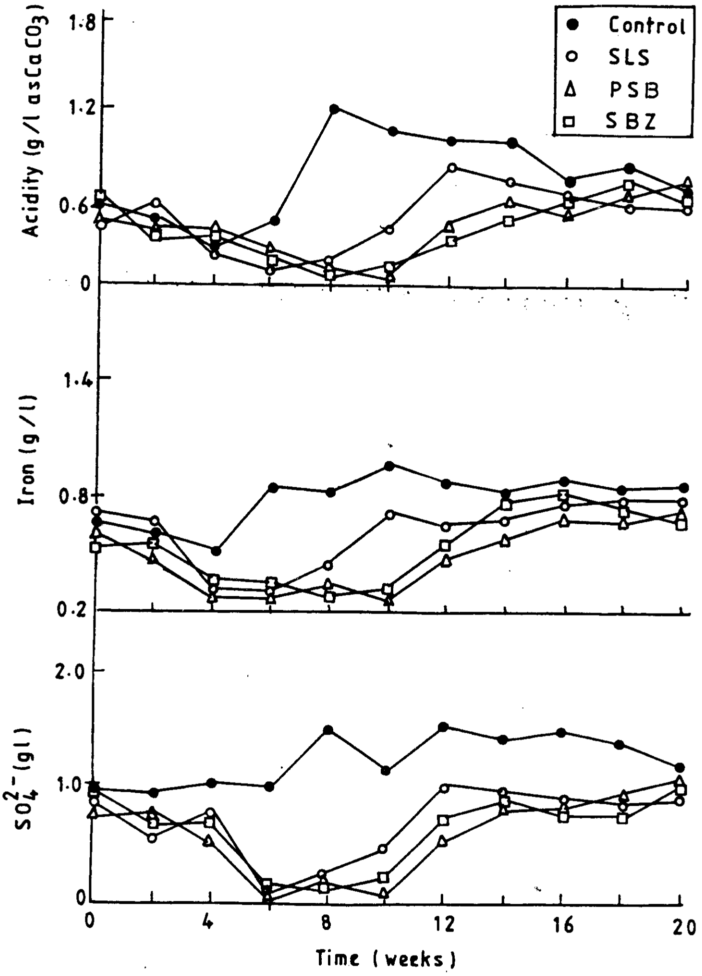

FIG. 5 SULPHATE, IRON AND ACIDITY DATA FOR LEACHATE FROM REFUSE SAMPLES (LOW DOSE TREATMENT)

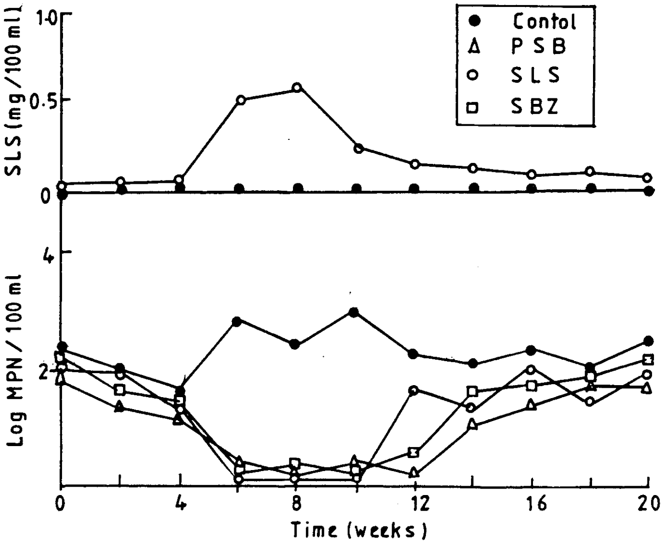

FIG. 6 SLS CONCENTRATION AND BACTERIAL MPN IN LEACHATE FROM REFUSE SAMPLES (LOW DOSE TREATMENT)

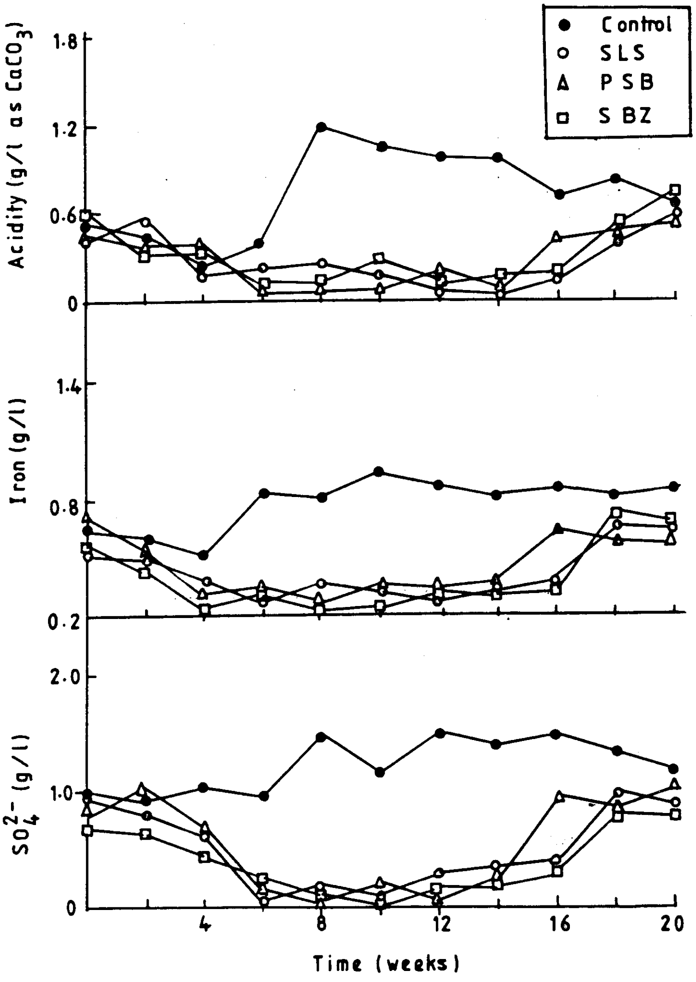

FIG. 7 SULPHATE, IRON AND ACIDITY DATA FOR LEACHATE FROM REFUSE SAMPLES (HIGH DOSE TREATMENT)

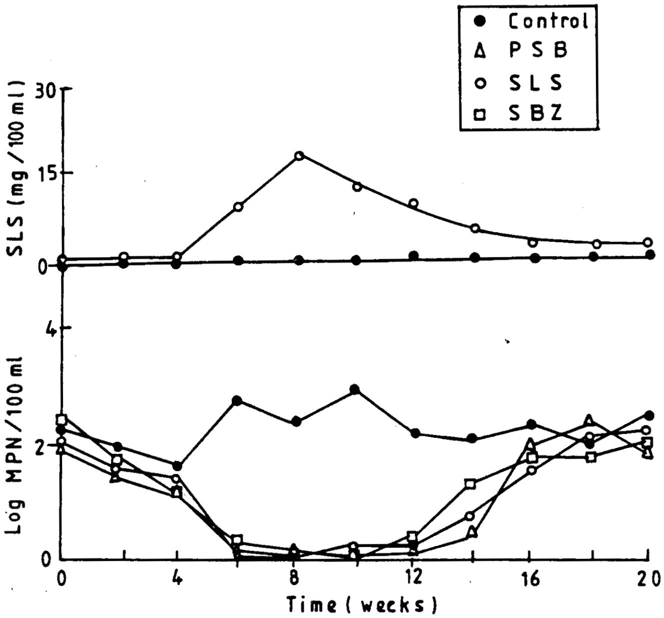

FIG. 8 SLS CONCENTRATION AND BACTERIAL MPN IN LEACHATE FROM REFUSE SAMPLES (HIGH DOSE TREATMENT)