

Effectiveness of Surfactant Retreatment of Acid Producing Coal

by

Dewey L. Smith

Vista Chemical Company
Ponca City, OK 74601

Introduction

The success of anionic surfactants in inhibiting acid mine drainage under carefully controlled conditions is well documented (1-4). It is also well documented that the surfactant and dosage that works on one site may not work on another. The success of surfactant control of acid mine drainage depends on many factors. Among these are site hydrology (1), coal characteristics (5) and the type of site, i.e., whether the site is active or being reclaimed. If a site is a good candidate, it is very desirable to predict before treatment the appropriate surfactant and dosage level. Such predictions are often based on accelerated weathering tests. Given the many variables affecting results, a weathering test should be carried out under conditions representative of those in the field. This paper reports on an accelerated weathering test using sodium lauryl sulfate (SLS), VMCTM 100 and sodium benzoate for acid mine drainage control under conditions approximating an active site. Three conditions were chosen as important for simulating an active site:

1. The coal will already be producing acid before treatment.
2. The treatment will be applied by draining *through* most of the coal such as might occur by a spray application of a coal pile.
3. On failure of the first application the effect of retreatment will be investigated.

A weathering test was run so that these conditions were met as closely as possible. It should be kept in mind that the specific results of the test apply only to the coal that was used and to the chosen conditions. Prediction of results for another site would require repeating the test with the coal from that site.

Experimental

The weathering columns used in this test were made from 4 inch diameter PVC pipe. A perforated plastic cap formed the bottom of each column. To prevent smaller coal particles from falling through the cap, a plug of glass wool was placed in the bottom of each column prior to adding the coal. A polyethylene funnel directed drainage from the column to a 1 quart glass bottle.

The coal used in this test was from the Pittsburgh seam and was 1.5 percent by weight pyrite. To accelerate weathering, the coal was crushed to a size that would pass through a 1/4" x 1/4" screen opening. To insure an acid producing coal (condition 1 of the test), the crushed coal was inoculated with the bacterium Thiobacillus ferrooxidans. This bacteria has been identified as responsible for much of the acid production from pyritic coal at low pH (6). To inoculate the coal, equal volumes of crushed coal and the acidic bacteria culture containing 10^6 - 10^7 bacteria / ml were mixed for one hour. The resulting inoculated slurry was drained overnight and one kilogram of the drained coal was added to each column.

The weathering of the coal was initiated by trickling 200 ml of distilled water through each column on Monday and Friday. This represented a rainfall of 3.4 inches / week. After each "rain" the drainage pH was checked to see if the coal was producing acid (condition 1 of the test). It took about four weeks for all the columns to show a descending trend in pH.

Three treatment levels of SLS ' VMCTM 100 and sodium benzoate were tested: 0.1 lbs. of active / ton of coal, 0.3 lbs. active / ton of coal and 0.5 lbs. of active / ton of coal. The distinction of "active" rather than weight is important for surfactant based treatments since the SLS that was used was 30% active by weight whereas the VMCTM 100 was 60% active by weight. Prior to treatment, the pH range of the columns varied from 2.4 - 3.4 with a mean pH of 2.8 (see Table 1). For treatment, the columns with the lowest pH received the 0.5 lbs. active / ton dosage of SLS, VMCTM 100 and sodium benzoate. The columns with a pH near the mean received the 0.3 lbs. active / ton dosage. The columns with a pH near the high end of the range received the 0.1 lbs. active / ton dosage level. Three sets of columns were run in duplicate, a set of untreated control columns, and a set treated with 0.3 lbs. active / ton of SLS and a set treated with 0.3 lbs. active / ton of VMCTM 100.

After the coal was acid producing it was treated with the various surfactants. To simulate a spray-on application, 200 ml of the treatment solution trickled through the coal. The coal in the lower part of the column was only treated by what percolated down through the column (condition 2 of the test). After treatment, a plug of glass wool was put on the top of the coal to diffuse subsequent "rainfalls" and conserve moisture.

The columns were assayed for acidity, pH, Fe^{+2} , $\text{Fe}^{+3} \text{SO}_4^{-2}$ and bacterial activity for the duration of the test. When the bacterial level in the drainage reached 10^4 bacteria / ml, the treatment was considered exhausted. Retreatment was then done using the "trickle" method (condition 2 of the test). The benchmark of 10^4 bacteria / ml was chosen as representing failure since in all cases when the bacteria population had reached this level, the coal was on the verge of a rapid increase in acidity. The contribution of an active bacteria population to acid mine drainage has been noted elsewhere (6,7) and is discussed below.

Results

Sodium Benzoate

The food preservative, sodium benzoate, was ineffective at all levels tested at controlling Thiobacillus ferrooxidans bacteria in this test. The acidity measurements for the 0.1 lbs. active / ton and 0.5 lbs. active / ton treatment levels are shown in Figure 1. The numbers

above the points in Figure 1 correspond to the order of magnitude of bacteria / ml in the drainage. Immediately after treatment (day 32) the drainage had a bacterial population of 10^6 bacteria / ml. Since sodium benzoate never reduced the bacteria level below the benchmark of 10^4 bacteria / ml, the treatment was considered ineffective at all the concentrations tested. On day 61, the column with the 0.1 lb active / ton treatment level was retreated. Though the acidity temporarily dropped, the bacteria level did not. In all of the sodium benzoate treated columns, the $\text{Fe}^{+3} / \text{Fe}^{+2}$ ratio remained high as did the SO_4^{-2} concentration. This indicates an active bacterial population at low pH.

0.1 lbs. active/ton of coal SLS and VMC™ 100

For the lowest concentration of SLS and VMC™ 100 tested, the results were similar to that found for sodium benzoate. The acidity results are shown in Figure 2. The bacterial counts for VMC™ 100 are shown above those points. The counts for SLS were within 1 and often identical with those for VMC™ 100. The counts for SLS are excluded from Figure 2 for clarity. As with the benzoate, the bacterial count never dropped below the "effective treatment" level of 10^4 bacteria / ml. On day 61 the columns were retreated and the acidity level dropped. The bacterial count however remained above 10^4 bacteria / ml. The $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio and sulfate levels (not shown) support the conclusion that the treatment level of 0.1 lbs. active / ton of coal was not effective for either SLS or VMC™ 100 in this test.

0.3 lbs. active / ton of coal SLS and VMC™ 100

For the next highest treatment level, 0.3 lbs. active / ton, bacterial control is found. The acidity results for SLS and VMC™ 100 are shown in Figure 3 and 4 respectively. The corresponding metal ion concentrations and sulfate ion concentrations are given in Figure 5 and Figure 6 for SLS and Figure 7 and Figure 8 for VMC™ 100. On day 89 of the test, the columns were retreated with 0.3 lbs. active / ton of agent. The results are seen in Figures 3 and 4. As with retreatment at 0.1 lbs. active / ton, the acidity immediately dropped. Unlike the retreatment at 0.1 lbs. active / ton however, the bacterial count dropped below 10^4 bacteria / ml indicating that retreatment was successful. Since these columns were run in duplicate, some idea of the reproducibility of the results can be obtained by comparing the duplicates. The acidity for the duplicate columns is shown in Figure 9 for SLS and Figure 10 for VMC™ 100.

0.5 lbs. active / ton of coal-SLS and VMC™ 100

The acidity data for the 0.5 lbs. active / ton treatment level is shown in Figure 11 for SLS and Figure 12 for VMC™ 100. The ferric and sulfate ion data as well as the bacterial activity increase with weathering as expected and are not shown. The columns treated with 0.5 lbs. active / ton were not retreated. The SLS treated column failed by day 120 of the test and was not followed after that time. The VMC™ 100 treated column did not fail until day 138 of the test. This column was followed until the end of the test on day 193.

Controls

The acidity results from the duplicate control columns are shown in Figures 13 and 14. Initially acidity, sulfate ion and ferric ion concentration increased as expected. The bacterial count also increased as expected. After 100 days, the acidity, sulfate ion concentration and ferric ion concentration decreased but the bacterial count remained high.

Discussion

Sodium Benzoate Treatment

The successful use of food preservatives such as sodium benzoate has been reported in the literature (6). In the test described in reference 6, a sample of refuse that was treated with 60 mg of sodium benzoate / kg of refuse (0.12 lbs./ton) delayed the production of acidity by two weeks compared to an untreated sample. At a concentration of 600 mg / kg of refuse (1.2 lbs. / ton) the protection time increased to 8 weeks. As reported in the results section above, sodium benzoate was ineffective at inhibiting acid formation in this test. The explanation for this discrepancy is not known however, there were several differences in the way the current test was carried out from the one reported in reference 6.

The refuse that was treated in the successful test was apparently not acidic at the time of treatment since the time for the refuse to become acidic was measured. As noted above, the coal treated in this test was acidic when it was treated. The distinction is important because of the proposed mechanism by which sodium benzoate retains its permanence after it is applied. In neutral pH solutions, sodium benzoate forms insoluble salts with ferric and ferrous ions. These salts collect on the material being treated and slowly dissolve as the pH drops providing a sort of "time release" of the benzoate. In a low pH solution, the precipitate does not form since the benzoate anion is already strongly protonated and so the benzoate washes through without being strongly absorbed on the treated material. This means that in the present test, much of the sodium benzoate may have washed through the column without absorbing on the coal.

Another explanation for the difference in results may be due to how the treatment was applied in the two test. In reference 6, refuse was saturated with the sodium benzoate solution for 24 hours and then drained off. Saturating the coal should give thorough absorption. In the current test sodium benzoate was trickled through the column (condition 2). This trickle method puts a premium on rapid absorption on the coal. Since I was trying to simulate a spray on application, I feel that the "trickle" method is more appropriate. A comparison of the amount of sodium benzoate remaining in the effluent after saturation and after trickling through the material should establish the importance of rapid absorption in a successful treatment. In any event, the discrepancy in results between the earlier test and this one emphasizes the unreliability of generalizations about "correct" treatments for acid mine drainage.

Treatment Level 0.1 lbs. active / ton of coal SLS and VMCTM 100

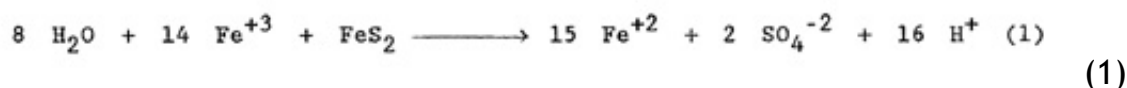
By the guideline that a treatment must reduce the bacterial count below 10^4 bacteria / ml to be effective, the 0.1 lb active / ton treatment by VMCTM 100 and SLS failed. As seen in Figure 2 there is a slight reduction in acidity immediately following treatment but this is not accompanied by a dramatic decrease in the bacterial count in the effluent. In about ten days,

the bacterial count was back to pre-treatment levels and the acidity increased rapidly. An interesting result of the test was the observation that a decrease in acidity always occurred immediately after initial treatment or retreatment. The decrease in acidity occurred even when the bacterial count did not dramatically drop. In fact, because the acidity always dropped following treatment, I adopted the "decrease of the bacterial count below 10 bacteria / ml" as the measure of success rather than a decrease in acidity. A possible explanation for the acidity drop is proposed in the next section where the results from the 0.3 lb s. active / ton treatment are discussed.

Treatment Level 0.3 lbs. active / ton of coal SLS and VMC™ 100

The treatment level of 0.3 lbs. active / ton of coal was the lowest level at which bacterial control was observed in this test. As seen if Figure 3 for SLS and Figure 4 for VMC™ 100, the bacterial count was reduced to below 10 bacteria / ml immediately after treatment on day 32 of the test and again on day 89 of the test after retreatment. After treatment, ferrous ion concentration increased and ferric ion decreased reflecting the decrease in bacterial activity. The trend in metal ion concentration, bacterial activity and acidity is expected based on the chemistry of acid mine drainage formation.

A large amount of the acid produced at pH less than 3 is the result of ferric ions reacting with pyrite to produce ferrous ion and sulfuric acid:

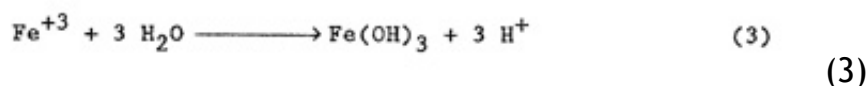


The available ferric ion to run the reaction would eventually be exhausted if it were not for the bacteria Thiobacillus ferrooxidans. These bacteria have the capability to convert ferrous ion to ferric ion and replenish the ferric ion:



As a result, when bacteria are active the drainage is characterized by high concentrations of Fe^{+3} , SO_4 and high acidity. When bacterial activity is reduced, less ferrous ion is converted to ferric ion by reaction (2) and so reaction (1) slows down as the ferric ion is exhausted.

As noted in the results section, a decrease in acidity may occur immediately after treatment even if bacterial activity does not decrease. Besides reaction (1), ferric ion can produce acidity by hydrolysis. For example



The surfactants used in this test precipitate ferric and ferrous ion from solution and so limit acid production by the hydrolysis of ferric ion. This may explain the decrease in acidity immediately after retreatment, even when the bacterial count remained high. The sulfate ion concentration for the columns treated with SLS and VMC™ 100 are shown in Figures 6 and 8

respectively, In general, sulfate was not as dramatic an indicator as the metal ion concentration, but high sulfate ion concentration corresponded to high acidity as expected.

One of the major goals of this study was to see what the effect of retreatment was on controlling production of acid. By comparing Figure 3 for SLS and Figure 4 for VMC™ 100, it is seen that the bacteria level and acid production increased sooner for SLS after retreatment than for VMC™ 100. This may be due to some of the SLS decomposing in the acidic environment. The acid hydrolysis of SLS is well established and is a factor to be considered *when treating* an acidic material. In contrast VMC™ 100 is chemically stable in acid and so is not susceptible to decomposition. There seemed to be a carry over effect with VMC™ 100 since even taking into account its better acid stability, it lasted longer after retreatment than after the initial treatment. This was seen in the duplicates shown in Figure 10.

The duplicate columns are shown in Figure 9 for SLS and Figure 10 for VMC™ 100. Agreement between duplicates is good especially for the VMC™ 100 columns. For the SLS columns, one of the columns was slightly more acidic than the other (the "+" symbols) and on retreatment it did not delay acid production as well. This may be more evidence of the decomposition of SLS under acidic conditions of the test.

Treatment level 0.5 lbs. active / ton of coal SLS and VMC™ 100

The acidity measurements for the coal treated with SLS and VMC™ 100 are shown in Figures 11 and 12 respectively. For brevity, the metal ion and sulfate ion concentrations are not shown though they change as expected with increasing bacterial count and acidity. The SLS treated coal failed by day 100 of the test. The VMC™ 100 treated coal did not fail until day 125 of the test.

As suggested by the time to failure, the control of bacteria was better for VMC™ 100 than for SLS at the 0.5 lbs. active / ton level. In fact, no advantage was found by increasing the concentration of SLS from the 0.3 lbs. active / ton level to 0.5 lbs. active / ton. This may be due to hydrolysis of SLS under the acidic conditions of application. Even though more SLS was applied in the 0.5 lbs. active / ton treatment, the columns treated with this dosage were the most acidic of the entire test. Hydrolysis of SLS should have been greatest for these columns and therefore less SLS would have been available to control acid and bacteria. In contrast, increasing the concentration of VMC™ 100 did increase the protection time.

There was still some increase in acidity even when the bacteria population was controlled. This can be seen between days 80 and 125 in Figure 12. Acid production without bacterial activity is possible if ferrous ion is oxidized by the air to ferric ion. Ferric ion subsequently hydrolyzes as shown in equation (3) to form acid. A similar region can be seen following retreatment with VMC™ 100 between days 130 and 165 of Figure 4. The abiotic production of acid by air oxidation brings out an important consideration. Surfactants may only supplement neutralization treatment in some situations and not eliminate it. Surfactants are still beneficial, however since their use can reduce neutralization costs, sludge removal costs, corrosion to equipment and decrease the hazard to workers.

Control

The acidity from the two control columns is shown in Figures 13 and 14. Both were treated only with water and both developed very active bacterial populations as expected. It was not expected however that the acidity would decrease after day 90 in one case and day 110 in the other. The ferric ion and sulfate ion also decreased. The ferrous ion remained low throughout the test in keeping with an active bacterial population. I do not know why these columns "ran out of gas" but since they were stimulated to produce acid at the greatest rate possible through out the test, they may simply have expended most of the available pyrite. Additionally, a coating of ferric hydroxide may have slowed the reaction of pyrite with the air by providing an oxygen barrier. However, on later examination of the coal from the columns, no evidence of this was found.

Conclusions

Under the conditions of this test, SLS and VMCTM 100 were effective at dosage levels of 0.3 lbs. active / ton and higher. Sodium benzoate was ineffective up to 0.5 lbs. / ton. It is important to recognize that with a different coal or different test conditions, different results might be obtained.

Retreatment was successful and gave approximately the same protection time as the initial treatment for the 0.3 lbs. active / ton of coal treatment level for SLS. For VMCTM 100, a greater protection time was seen on retreatment than on initial treatment.

Hydrolysis may explain why SLS did not give proportionally longer protection at higher concentrations when more acidic coal was treated. The possibility of hydrolysis should be recognized if the coal to be treated in the field is already strongly acidic.

Not every situation is a candidate for using surfactants for acid mine drainage control. Appropriateness of use depends on cost compared to alternatives, site hydrology and the nature of the material to be treated. To help decide if surfactants are a viable approach to controlling acid mine drainage, an accelerated weathering test, under "field" conditions should prove useful.

Acknowledgements

I would like to thank the Consolidation Coal Company for providing samples of coal used in this study. I would also like to thank Geoff Russell for much of the lab work and Lee Matheson for many useful discussions. Finally, I would like to thank Vista Chemical Company for permission to publish this work.

Table 1.
Initial pH Values of Columns

Table 1.
Initial pH Values of Columns

Column	pH	Treatment
1	2.71	0.3 lbs. active / ton of coal sodium benzoate
2	2.73	Control
3	2.89	0.1 lbs. active / ton of coal sodium benzoate
4	2.73	0.3 lbs. active / ton of coal SLS
5	2.32	0.3 lbs. active / ton of coal SLS
6	3.42	Control
7	2.87	0.1 lbs. active / ton of coal SLS
8	2.66	0.5 lbs. active / ton of coal sodium benzoate
9	2.63	0.3 lbs. active / ton of coal VMC™ 100
10	2.48	0.3 lbs. active / ton of coal VMC™ 100
11	2.67	0.5 lbs. active / ton of coal SLS
12	2.86	0.1 lbs. active / ton of coal VMC™ 100
13	2.62	0.5 lbs. active / ton of coal VMC™ 100

References

1. Kleinmann, R. L. P. and Erickson, P. M. , "Control of Acid Mine Drainage from Coal Using Anionic Surfactants" BuMines RI 8847, 1983, 16 pp.
2. Kim, G., Heisey, B.S., Kleinmann, R. L. P., and Deul, M., "Acid Mine Drainage: Control and Abatement Research" BuMines I. C. 8905, 1982, 22pp.
3. Dugan, R. P. and Apel, W. A., Appl. and Envir. Microbiology, 46(l), 1983, p 279.
4. Olem, H., Bell, T. L. and Longaker, J. J. , J. Energy Eng. v. 109, 1983, p 103.
5. Shellhorn, M. A., Sobek, A. A. and Rastogi, V. , Proceedings of the National Meeting of the Am. Soc. of Surface Mining and Reclamation, Denver, Co. Oct 8 - 10, 1985.
6. Onysko, S. J. , Erickson, P. M. and Kleinmann, R. L. P. , Proceedings of 1984 Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Dec. 2 - 7, 1984 p 35.

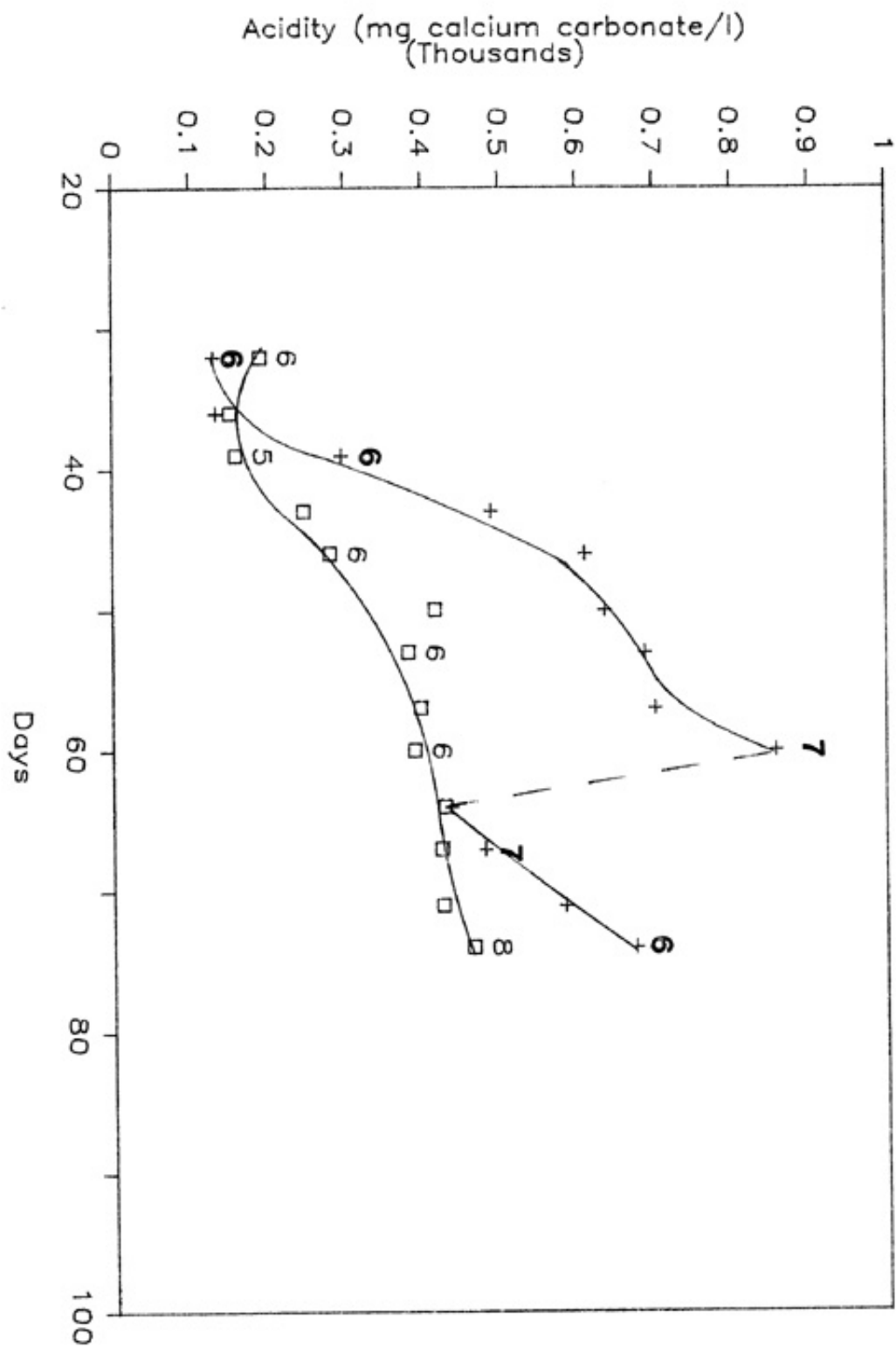


Figure 1: Acidity of effluent from sodium benzoate treated coal. Crosses are 0.1 lbs. active / ton of coal dosage. Rectangles are 0.5 lbs. active / ton dosage. Numbers above points are the order of magnitude of bacteria / ml of effluent.

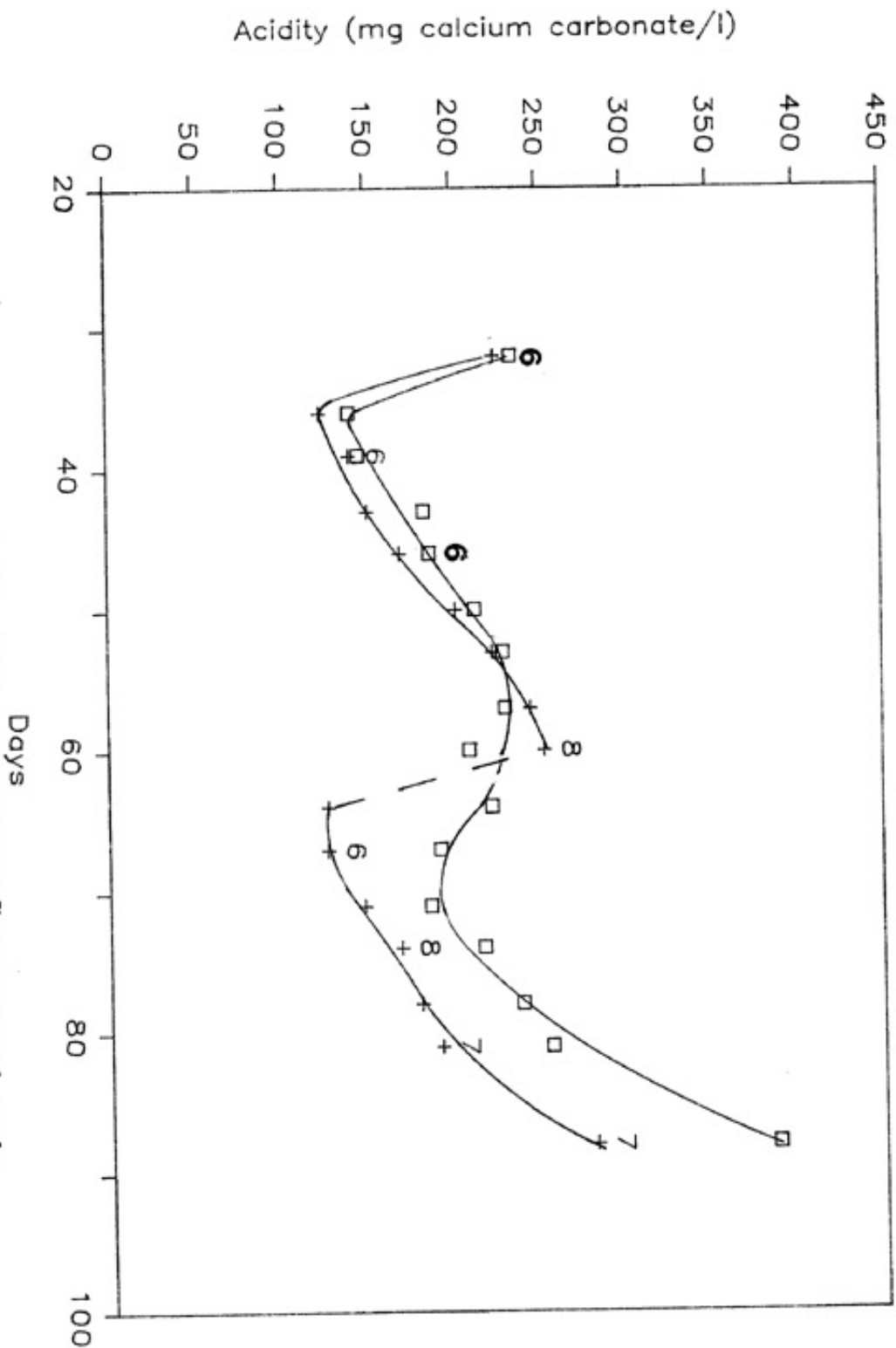


Figure 2: Acidity of effluent from SLS and VMC™ 100 treated coal. dosage is 0.1 lbs. active / ton of coal. Crosses are for VMC™ 100 treated coal. Rectangles are for SLS. Numbers above the crosses are the order of magnitude of bacteria / ml of effluent.

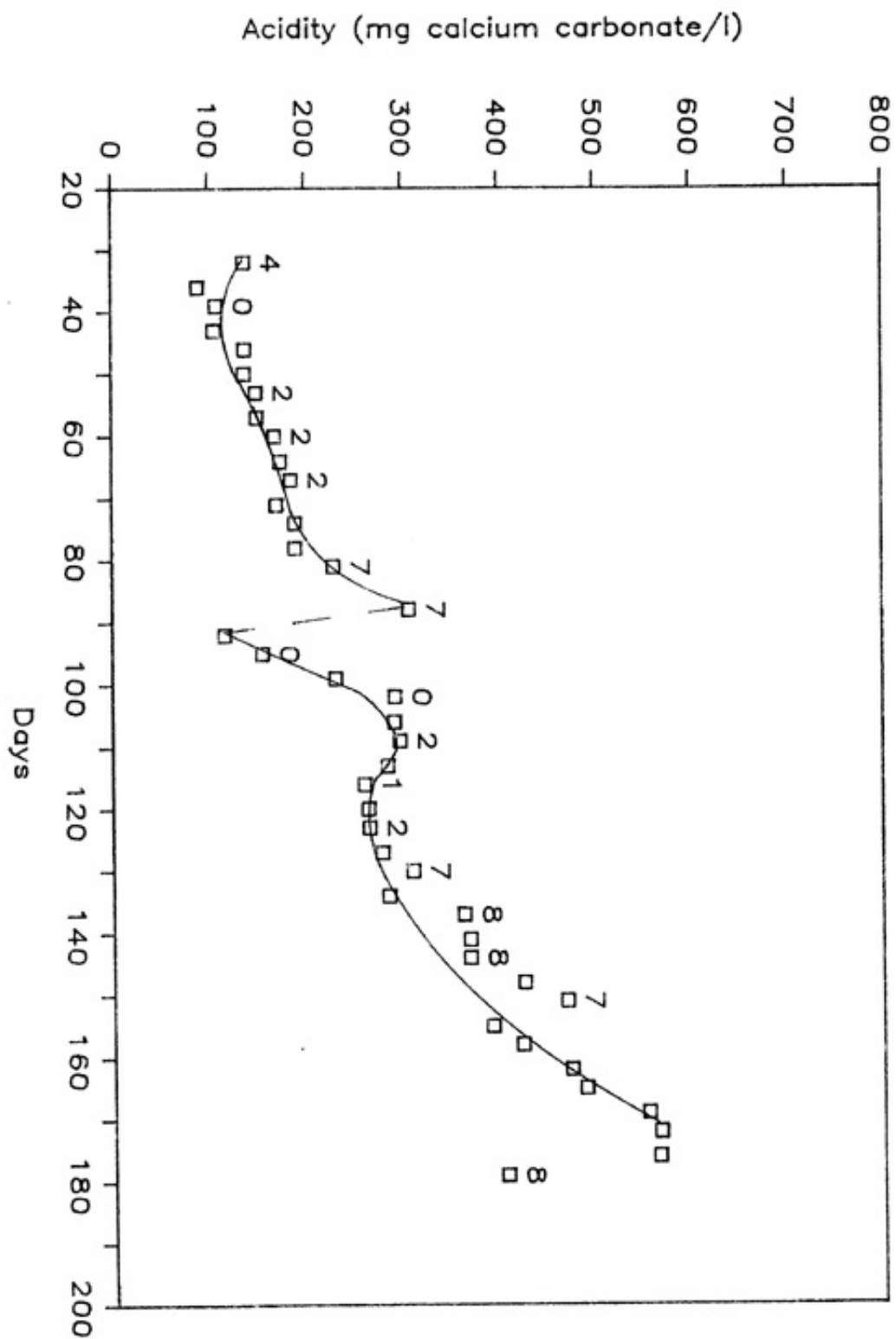


Figure 3: Acidity of effluent from SLS treated coal at dosage level of 0.3 lbs. active / ton of coal. Numbers above the points are the order of magnitude of bacteria / ml of effluent.

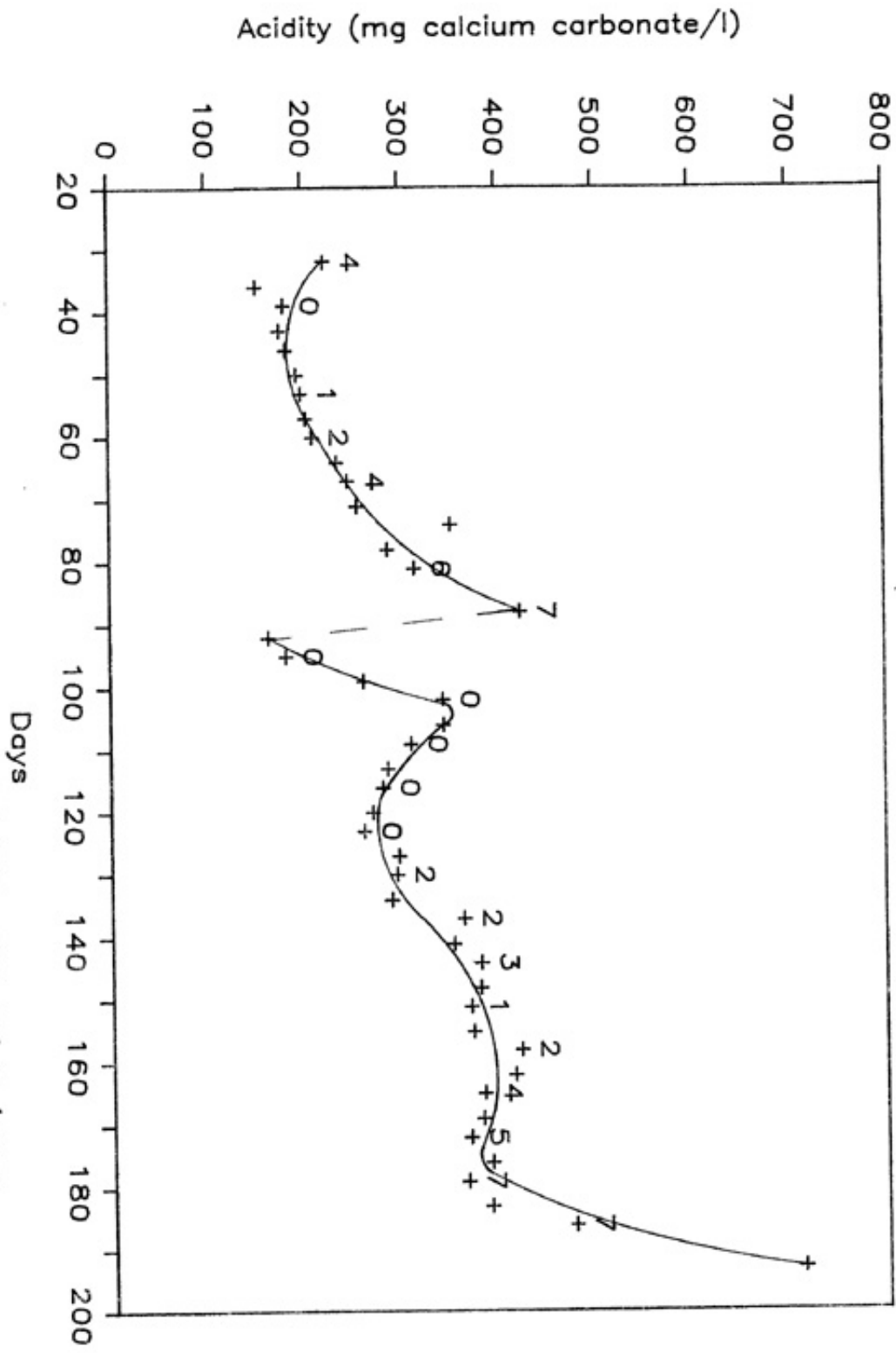


Figure 4: Acidity of effluent from VMC™ 100 treated coal at dosage level of 0.3 lbs. active / ton of coal. Numbers above the points are the order of magnitude of bacteria / ml of effluent.

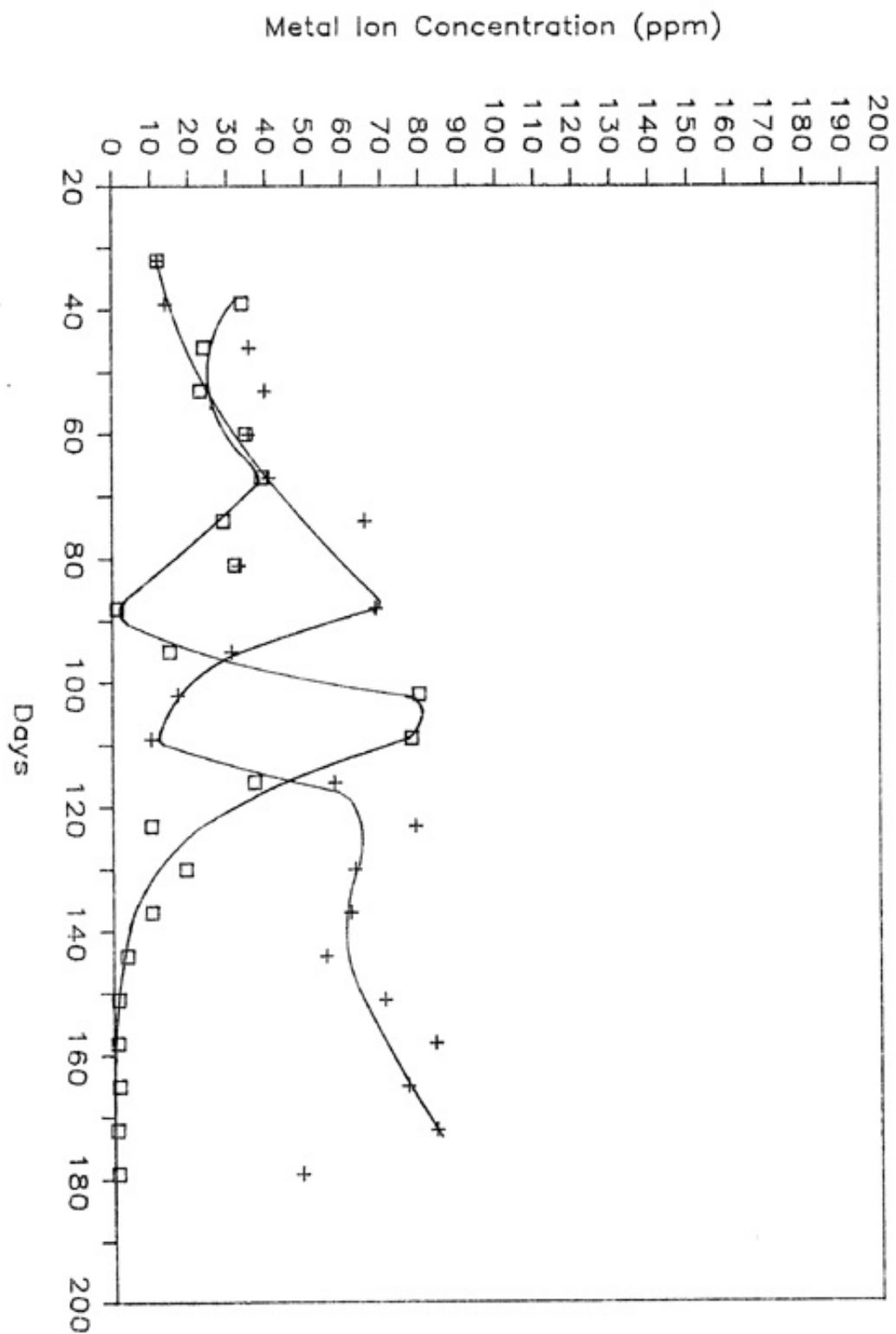


Figure 5: Metal ion concentration of effluent from coal treated with 0.3 lbs. active SLS / ton of coal. Crosses are ferric ion concentration and rectangles are ferrous ion concentration.

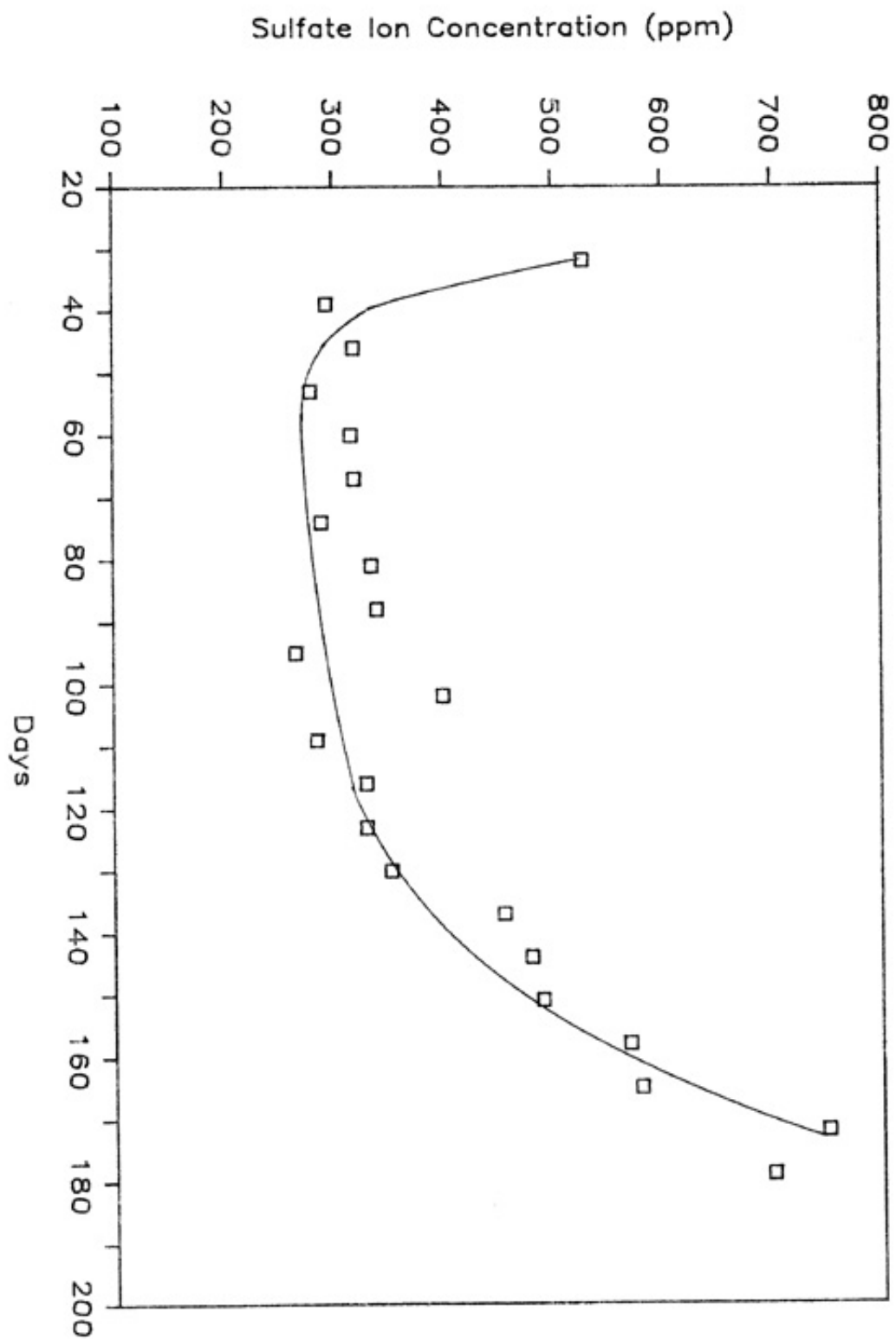


Figure 6: Sulfate ion concentration of effluent from coal treated with 0.3 lbs. active SIS / ton of coal.

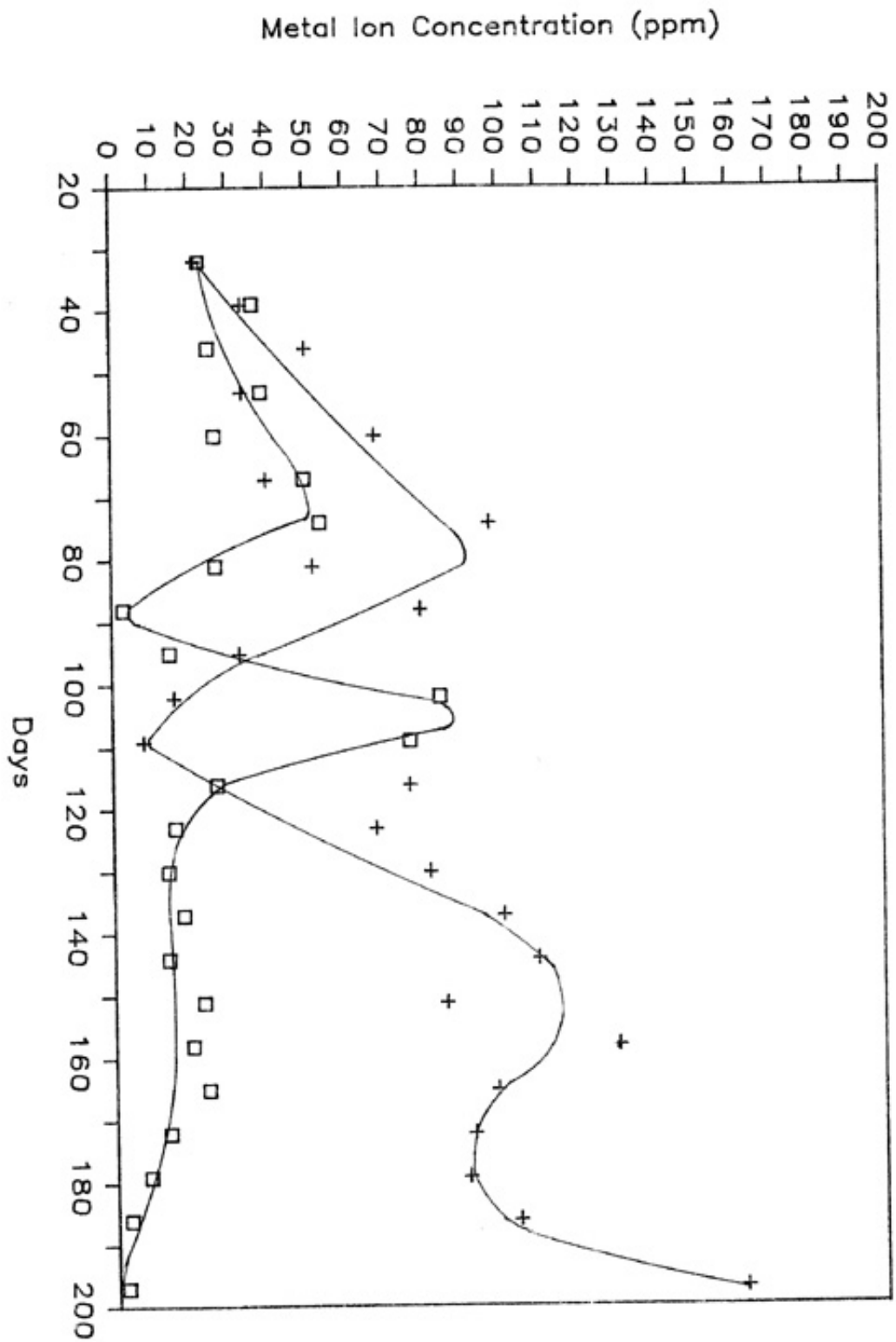


Figure 7: Metal ion concentration of effluent from coal treated with 0.3 lbs. active / con of coal VMG[™] 100. Crosses are ferric ion concentration and rectangles are ferrous ion concentration.

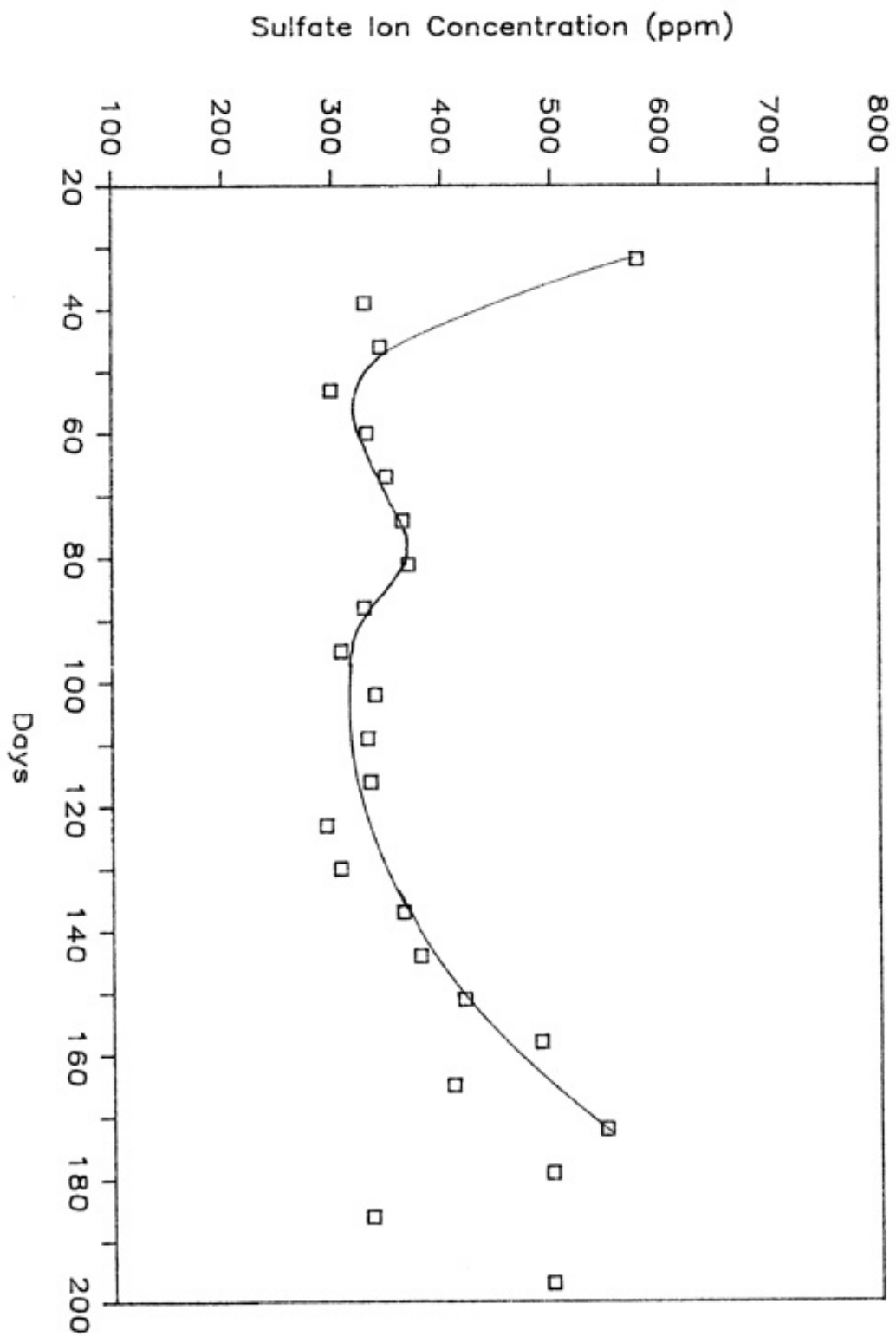


Figure 8: Sulfate ion concentration of effluent from coal treated with 0.3 lbs. active / ton of coal VMG™ 100.

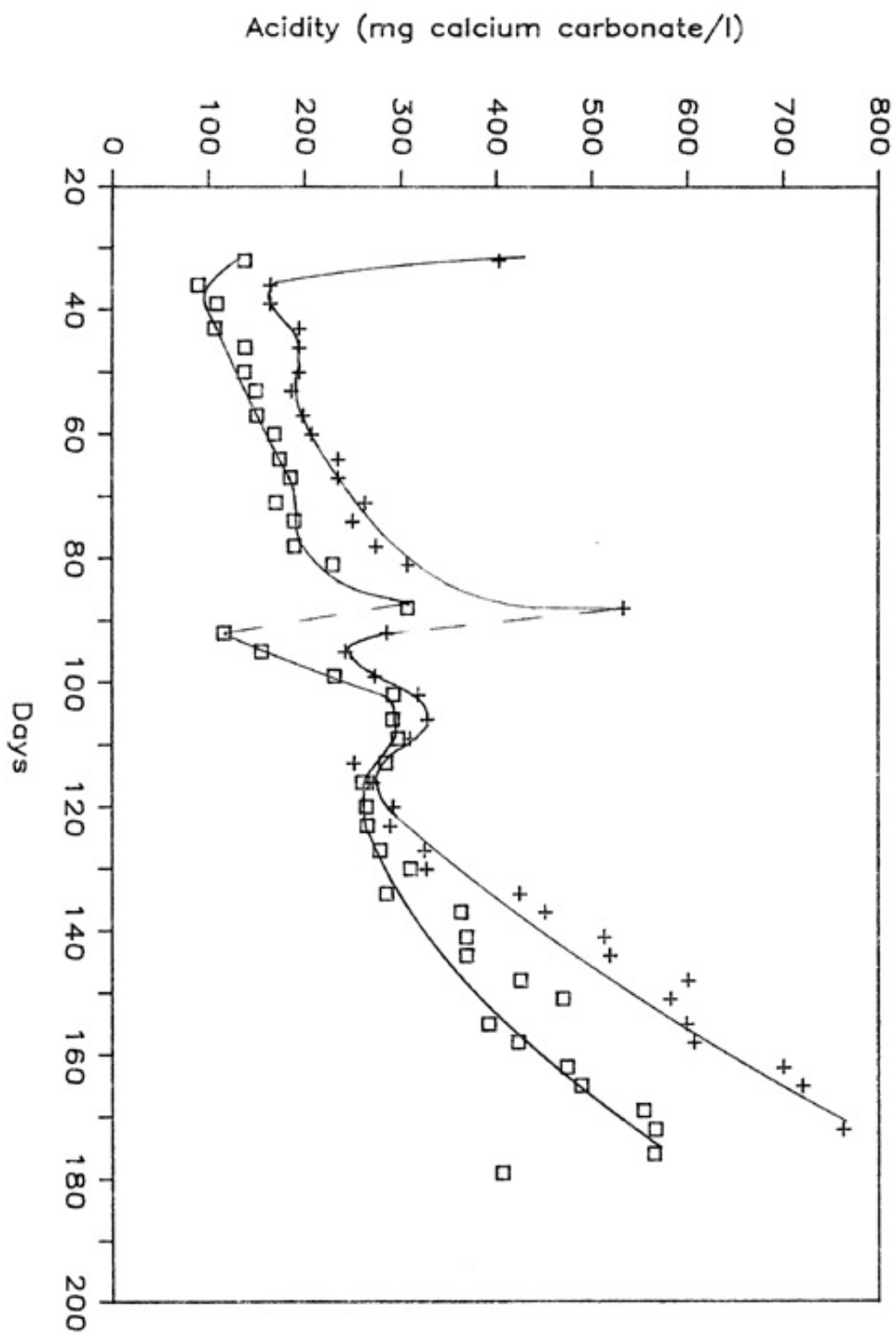


Figure 9: Acidity of effluent from duplicate columns treated with 0.3 lbs. active SLS / ton of coal.

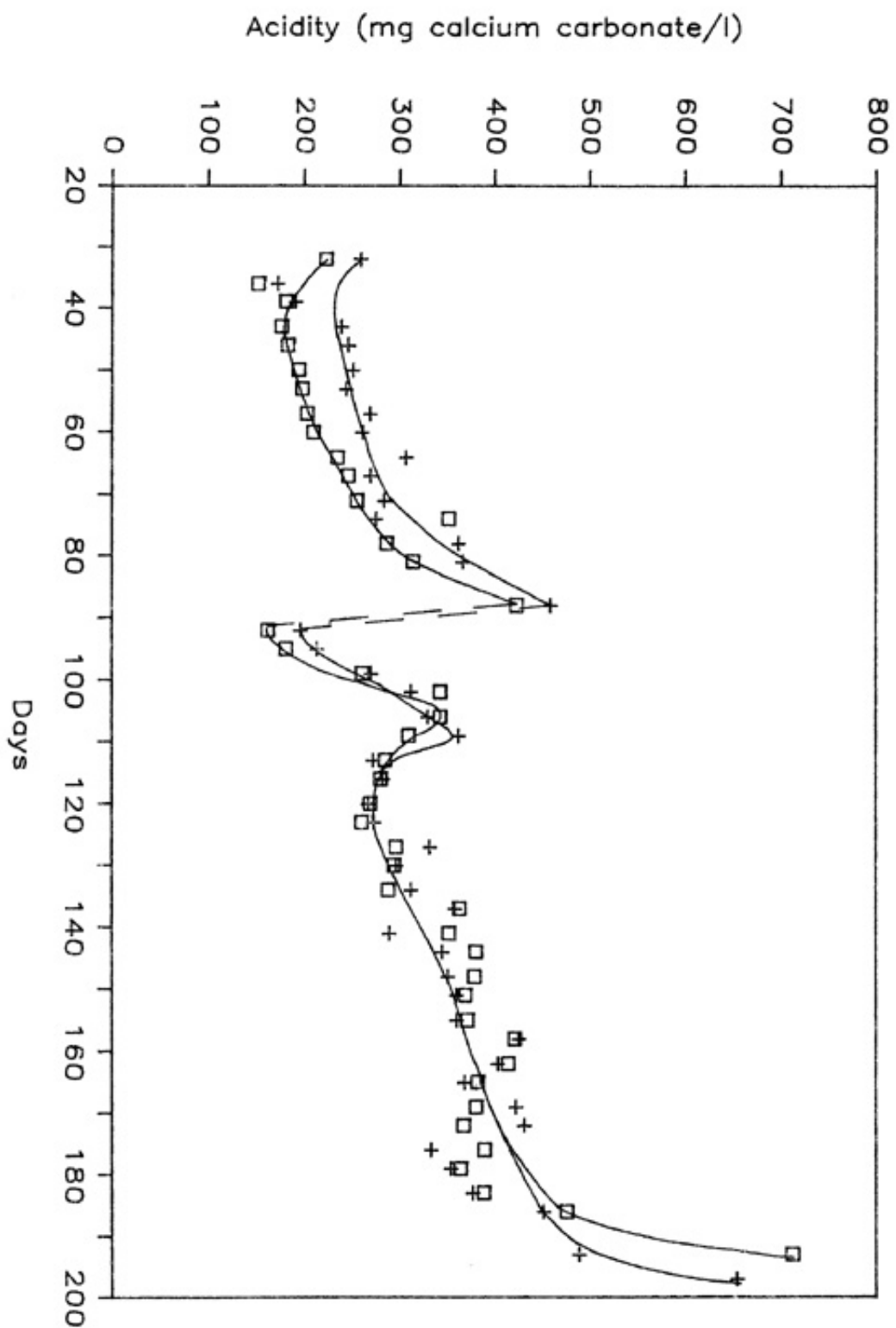


Figure 10: Acidity of effluent from duplicate columns treated with 0.3 lbs. active / ton of coal VMG™ 100.

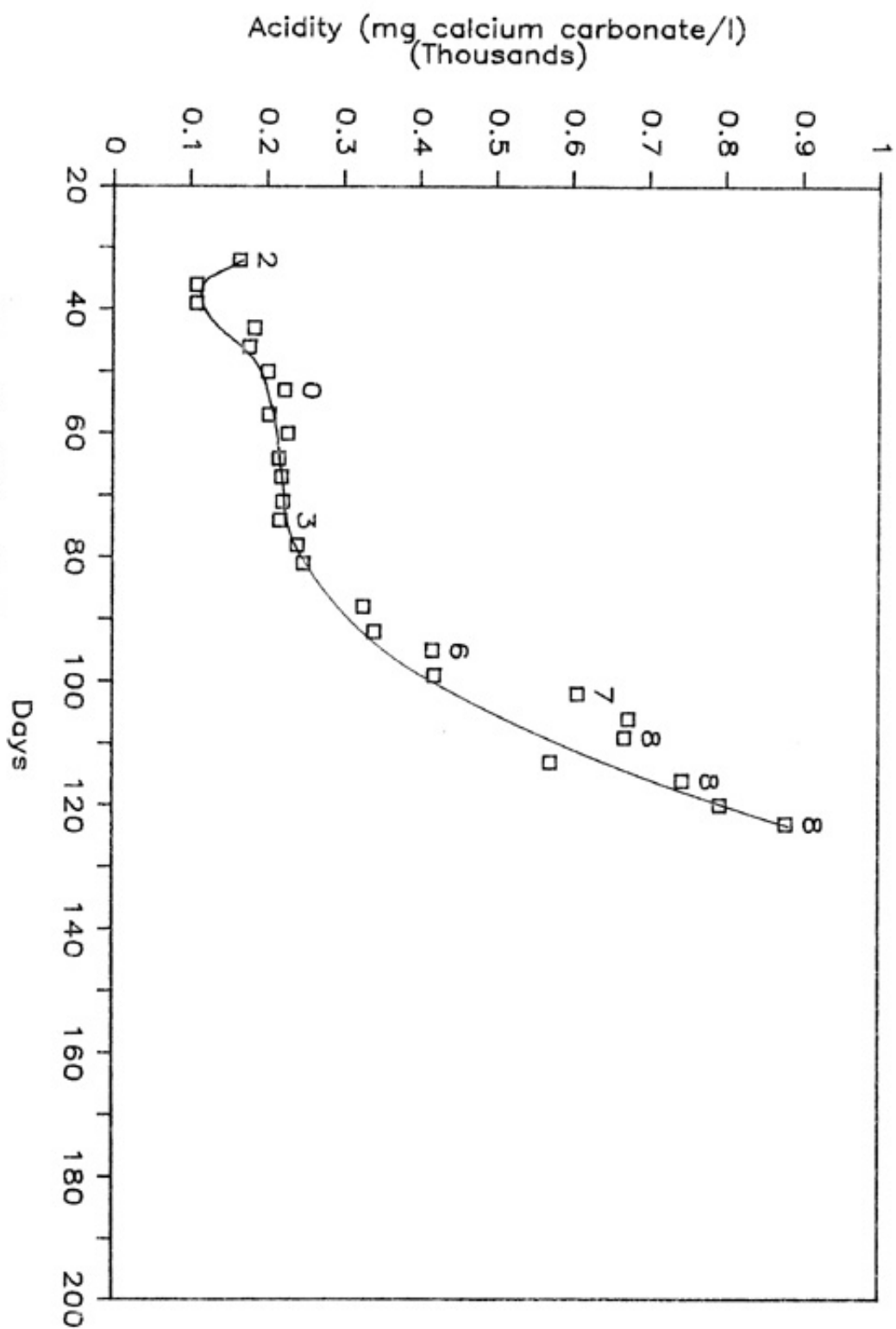


Figure 11: Acidity of effluent from coal treated with 0.5 lbs. active SIS / ton of coal. Numbers above points are the order of magnitude of bacteria / ml in the effluent.

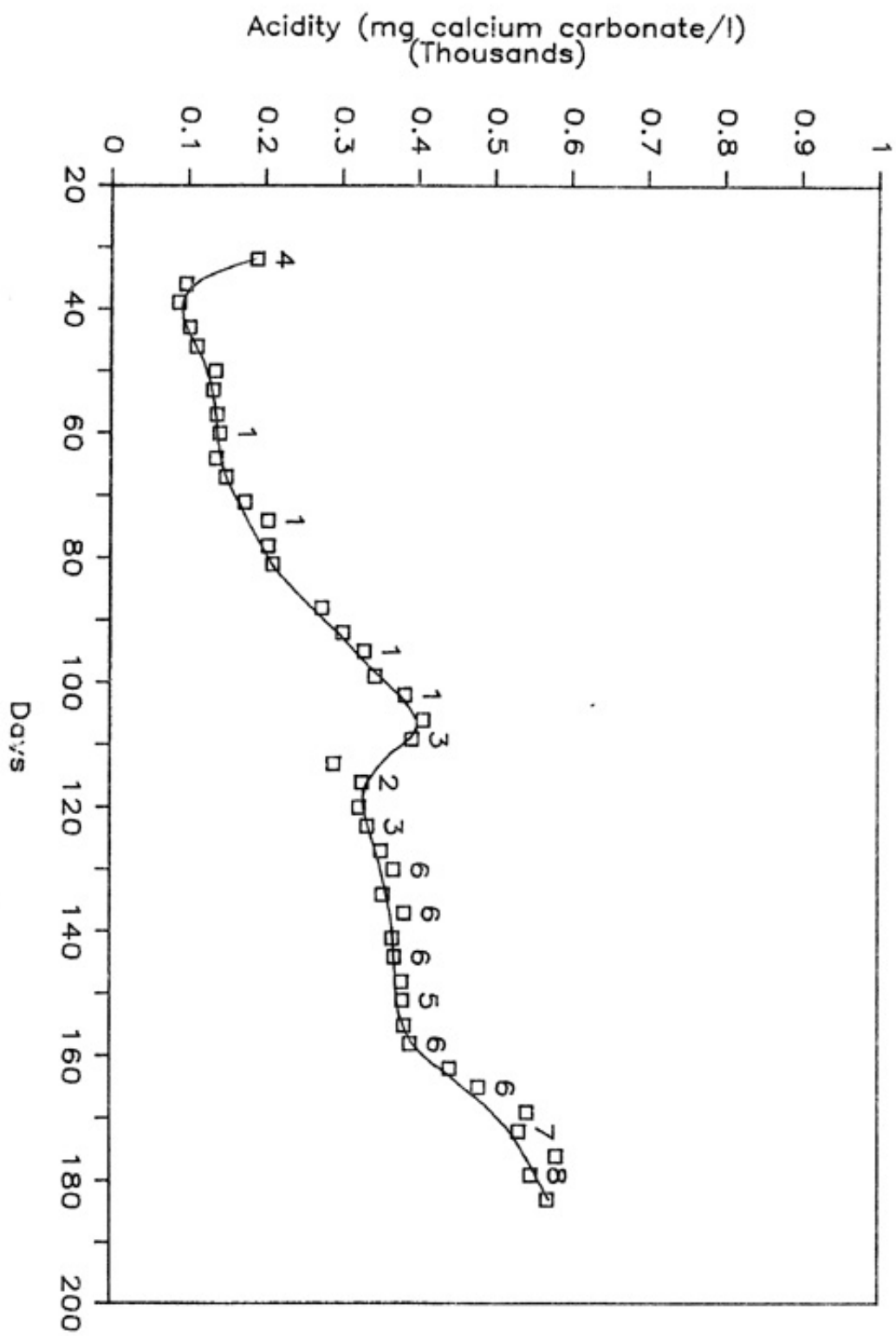


Figure 12: Acidity of effluent from coal treated with 0.5 lbs. active / ton of coal VMG™ 100. Numbers above the points are the order of magnitude of bacteria / ml in the effluent.

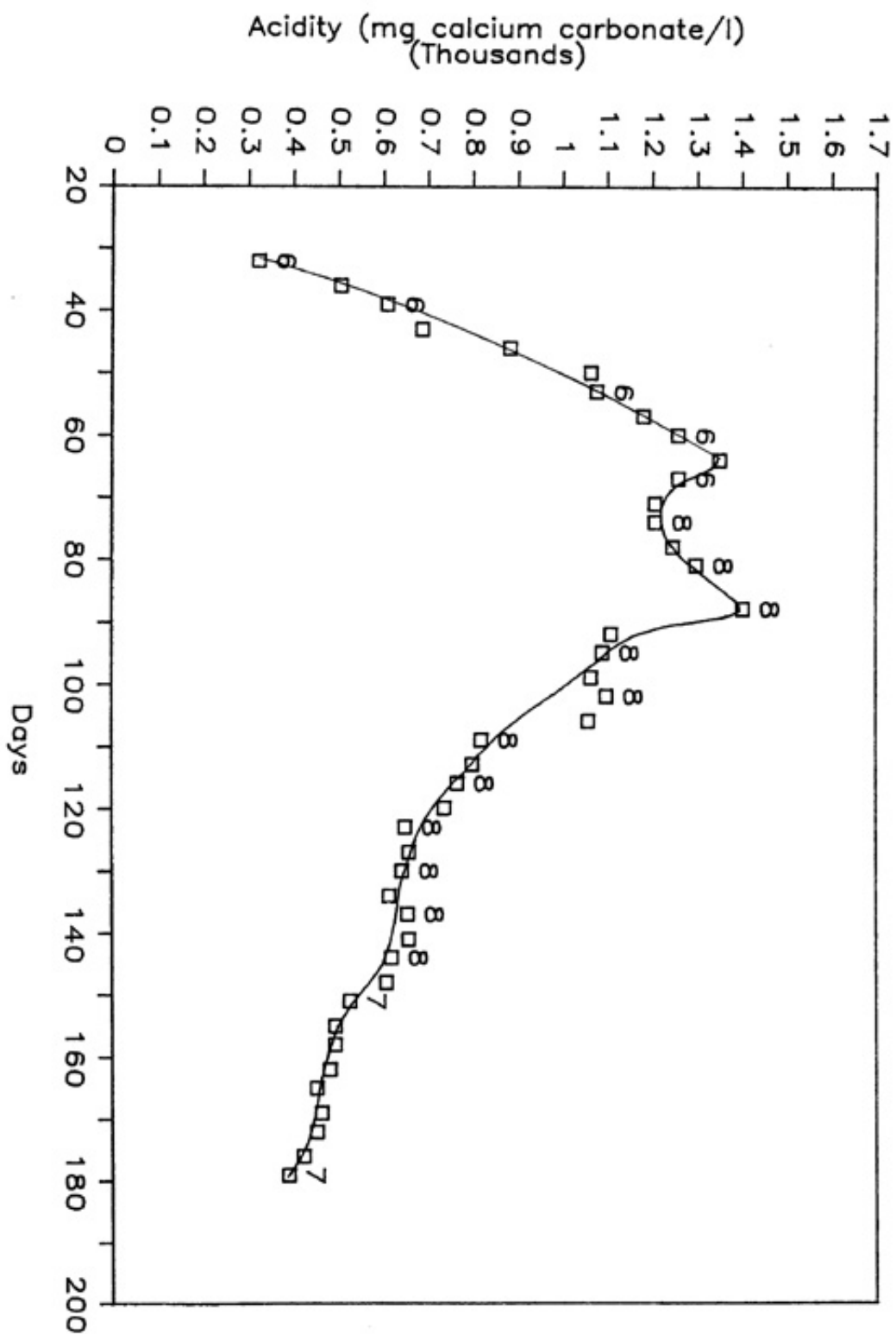


Figure 13: Acidity of effluent from coal control column. Numbers above the points are the order of magnitude of bacteria / ml in the effluent.

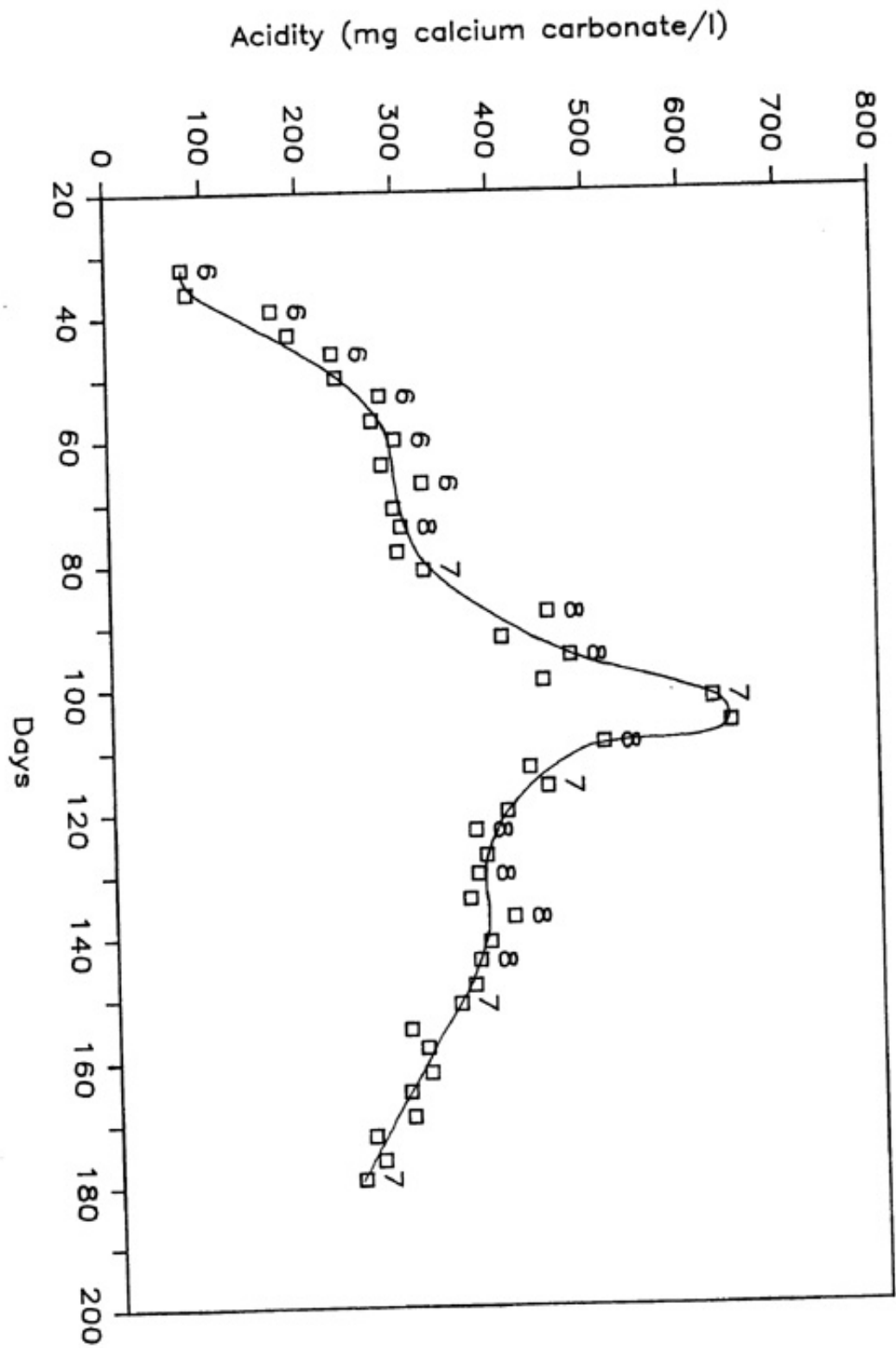


Figure 14: Acidity of effluent from coal control column. Numbers above the points are the order of magnitude of bacteria / ml in the effluent.