LABORATORY STUDIES OF ACID GENERATION FROM COAL ASSOCIATED ROCKS

by

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INTRODUCTION:

The basic objective of this work is to understand and to be able to predict the chemical response to groundwater leaching of rock materials emplaced in reclaimed surface mining sites. The ideal way to conduct such an investigation would be to construct fills with various combinations of rock and treatment materials and observe the chemistry of the water emerging from the structures. Obviously, in terms of both time and money, such an approach would be impractical. The solution to the problem is to construct a MODEL of the fill using the same materials and evaluate the chemistry of the water produced from the model.

Modeling implies a reduction in size. Technically, modeling requires a reduction of ALL system parameters equal in proportion to that represented by the size reduction. Some parameters can be proportionately reduced. The size of the rock fragments used in the model can be proportionate to those in the real situation; layer thicknesses can be "modeled" as can the flow rate of water through the model. Other parameters cannot be changed; the grain size of the rock, the particle size of the iron disulphides contained within the rock, the chemical response rates of the various minerals involved. As a result, therefore, any model is a distortion of the original system. How applicable data generated from models are to the real situation may depend upon the degree of distortion and upon the importance of individual parameters. Interpretation of model data must always be done carefully with this in mind. In any case, the usefulness of model generated data lies in the success of its ability to predict the response of rock materials when applied to the real situation.

At the present time, studies are being conducted which represent three levels of modeling. At Island Creek, the models measure 50 feet by 50 feet by 4 feet and contain 375 tons of rock. An intermediate scale of modeling would be represented by Al Stiller's barrel experiments at West Virginia University which utilize 30 gallon plastic barrels containing 300 pounds of rock. The soxhlet experiments being conducted in the laboratories of the West Virginia Geological Survey represent the smallest model, utilizing a few hundred or a few thousand grams of samples. The advantages of the large scale models are obvious. Because of the minimum amount of model distortion, such models would provide the most potentially meaningful data. However, the utilization of such a model is impractical, if not impossible, for the average researcher. At the other extreme, the soxhlet studies are convenient and low cost but represent the maximum potential model distortion. The data must therefore be the most suspect. The data presented in this paper is an attempt to demonstrate both the utility of the soxhlet technique and that bench scale experiments can provide useful information pertaining to the understanding and prediction of the chemical response of rock materials in real life situations.

SOXHLET EXTRACTION

The standard soxhlet reactor is illustrated in figure 1. Two sizes of soxhlets are being used; the first utilizes a 44mm diameter by 123mm extraction thimble capable of extracting a few hundred grams of sample with particle diameters up to about 1/2 inch while the second uses a 125mm diameter by 310mm thimble accommodating a few thousand grams of sample with particle diameters up to 1 inch.

The soxhlets operate in one of two modes. In the basic operating mode, the solvent is boiled in the reservoir, the vapors pass into the condenser, the condensed liquid drips into the thimble and extracts the sample, then siphons back down into the reservoir. The leachate is, of course, the pure solvent. In the second mode of operation, the solvent is pumped from the reservoir by a peristaltic pump down into the extraction thimble via tygon tubing. (see figure 2). This mode of operation allows the use of various solutions as leachates. Both the temperature of the reactor and the pumping rate are controlled.

SAMPLE CHARACTERIZATION

Basic compositional characterization of all samples includes: (a) elemental analysis by XRF for all major (>10wt. %) and minor (1-10wt. %) elements, (2) mineralogical analysis by XRD and (3) EPA acid/base accounting. Additional analysis available for special samples include: (1) optical microscopy, (b) scanning electron microscopy and microprobe analysis and (c) trace element analysis by graphite furnace and A.A.

SOLUTION CHARACTERIZATION

Leachates are analyzed for pH, specific conductivity, acidity to pH 8.3, alkalinity to pH 4.5 and all common cations and anions.

SAMPLE REOXIDATION

For those studies which include the repetition of a leach-reoxidize cycle, reoxidation was performed by one of two ways: (a) exposure of the sample to 100% relative humidity at 45^0C for a specified interval of time or (b) exposure in a 105^0C drying oven for a specified interval of time.

RESULTS

One of the objectives of the first year was to begin the accumulation of a data base sufficiently large to allow meaningful statistical comparisons to be made. At this point, the data base is still small; complete data have been accumulated on fewer than 100 samples.

The samples analyzed to date include rocks of moderate to high toxicity with a few extremely toxic samples. Samples are now being analyzed which will extend the data base into the low toxic and alkaline range of materials. It is anticipated that by the end of the second year, the data base will include several hundred completely documented samples representing the range of chemical response from highly toxic to highly alkaline.

One of the objectives of building the data base was to devise an improved predictive model for the acid/base response of rock materials. The ideal predictive model would be one in which a single inexpensively determined parameter would allow the prediction of the acid/base response of the rock. No such technique exists. The EPA acid/base account procedure does, however, make such a prediction based upon only two compositional parameters. The EPA technique does in fact provide a good estimate of the chemical response of a rock to leaching. Figure 3 illustrates the relationship between the average acidity produced from 2 replicate 24 hour soxhlet extractions of 100 gram samples and the acid response predicted by the EPA procedure. The trend is obviously positive. The spread of points reflects in part the variability in the replicate leach data but perhaps more so, it reflects the result of the simplistic assumption that only two compositional parameters are needed to evaluate the acid/base response of a rock. Such an assumption implies that there are no other parameters of either the rock or the leach solution that significantly affect either the acid or base response of the rock. This is most certainly not the case. One of the objectives of the study will be to evaluate the combined data act utilizing non-parametric and parametric multi-variate statistics to determine whether or not the inclusion of any other parameter or combination of parameters into the present EPA acid/base calculations might not improve the correlation between the predicted and observed response and thereby reduce the "gray zone" of the present EPA predictive model.

An observation made by Al Stiller during the summer of 1982 initiated a study of the reoxidation of toxic materials. The basic formulae describing the oxidation of pyrite require water; they are hydrolysis reactions. The observations indicated that reoxidation might also be a thermal process not requiring water. To test the hypothesis, a series of samples were leached for 24 hours. Following the leach, the samples were split into two representative subsamples using a Jones splitter. One subsample was reoxidized by exposure to 100% relative humidity at 45% while the other subsample was reoxidized in a 105% drying oven. After equal periods of reoxidation, the samples were releached for 24 hours. The leach-reoxidization cycle was repeated four times between 21 October 82 and 7 January 83. The data are shown in figure 4. In every case, both the rate of reoxidation and the total acid generated were higher with the 105'C reoxidation by the end of the experiment. The data illustrate the importance of thermal effects upon disulphide oxidation and indicate that materials exposed at the surface and to depths of a few feet may produce acid at rates and loads disproportionately higher than that predicted by EPA acid/base accounting when they are subjected to cyclic wetting and drying during the summer months. This potential increased acid production should be taken into account when preparing the surface materials for reclamation and revegetation.

Perhaps the most potentially significant study of the past year was initiated by an observation reported to the author by Bill Grady of the West Virginia Geological Survey. In a study being conducted to investigate the relative reactivity of iron disulphide morphologies in polished coal surfaces, Grady observed that the massive varieties of iron disulphides showed consistently higher reactivity when exposed to the atmosphere than any of the euhedral forms. Most significantly, he had observed that the massive varieties were most reactive of all where intimately intercrystallized with calcite. This observation initiated a statistical study of the leach data from 50 moderate to low acid producing samples. The data were collected on the leachate from 2 replicate 24 hour soxhlet leaches of 100 gram samples.

The relationship between ppm Ca in the leachate versus acidity titrated to pH 8.3 is illustrated in figure 5. Assuming that the only major source of calcium in the rocks is calcium carbonate (verified by XRD), the data suggest that IN THESE SAMPLES the dissolution of calcium carbonate increased the rate of iron disulphide dissolution and oxidation with the subsequent production of acid in excess of the ability of the increased bicarbonate to neutralize. A plot of ppm Ca versus ppm $S0_4$= for the same samples (see figure 6) suggests the same interpretative, assuming that the major source of sulfate ion is the dissolution-oxidation of the iron disulphides. It is important to emphasize that these data apply <u>only to these samples</u> and, at this point in time, they CANNOT be extrapolated to any other samples or any other situation. As a followup to the observations, a series of experiments are now underway utilizing the pumping mode of soxhlet operation to leach a "standard" sample of constant temperature and pumping rate with solutions of various combinations and concentrations of cations and anions.

It is perhaps significant to note that in a recent EPA project summary (APEL, 1983) involving the column leaching of solid mine waste with various treatments, the following statement was made in the conclusions:

> "Placement of a lime layer between the mine waste and the cover soil did not appear to enhance leachate quality during the study period; in fact, leachate quality tended to be worse than that from the column control."

Studies are continuing in all the reported areas. The results reported here must be considered preliminary in nature and subject to possible reinterpretation with the acquisition of additional data.

REFERENCES CITED

Apel, M. Lynn, 1983, Leachability and Revegetation of Solid Waste from Mining, Project Summary, EPA-600/S2-82-093, March 1983, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

FIGURE 1 Soxhlet Reactor, Normal Mode

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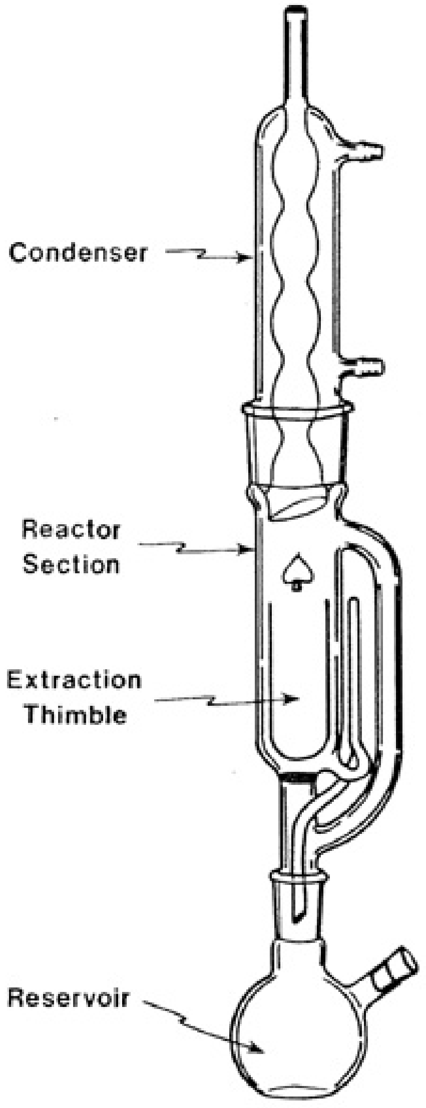

FIGURE 2 Soxhlet Reactor, Pumping Mode

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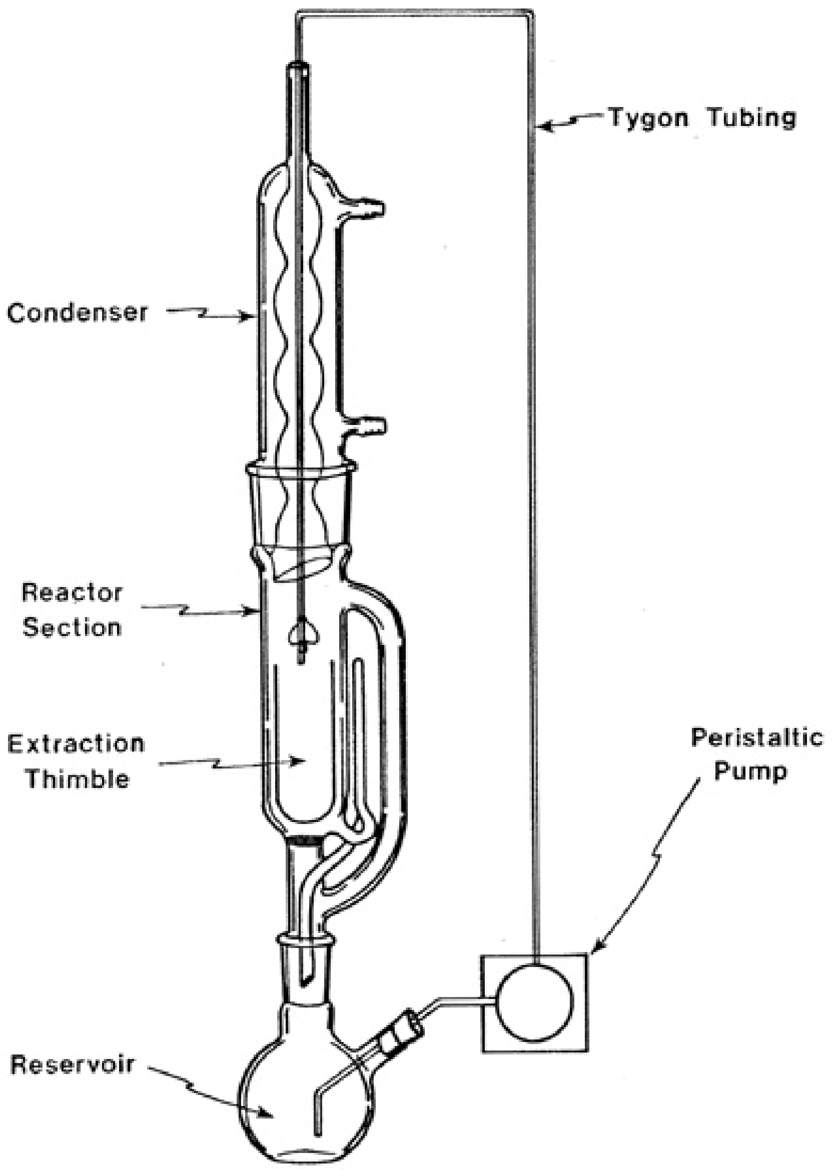

FIGURE 3 Correlation Between EPA Predicted and Actual Leachate Acidity

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[Data are averages of two 24 hr. leaches.]

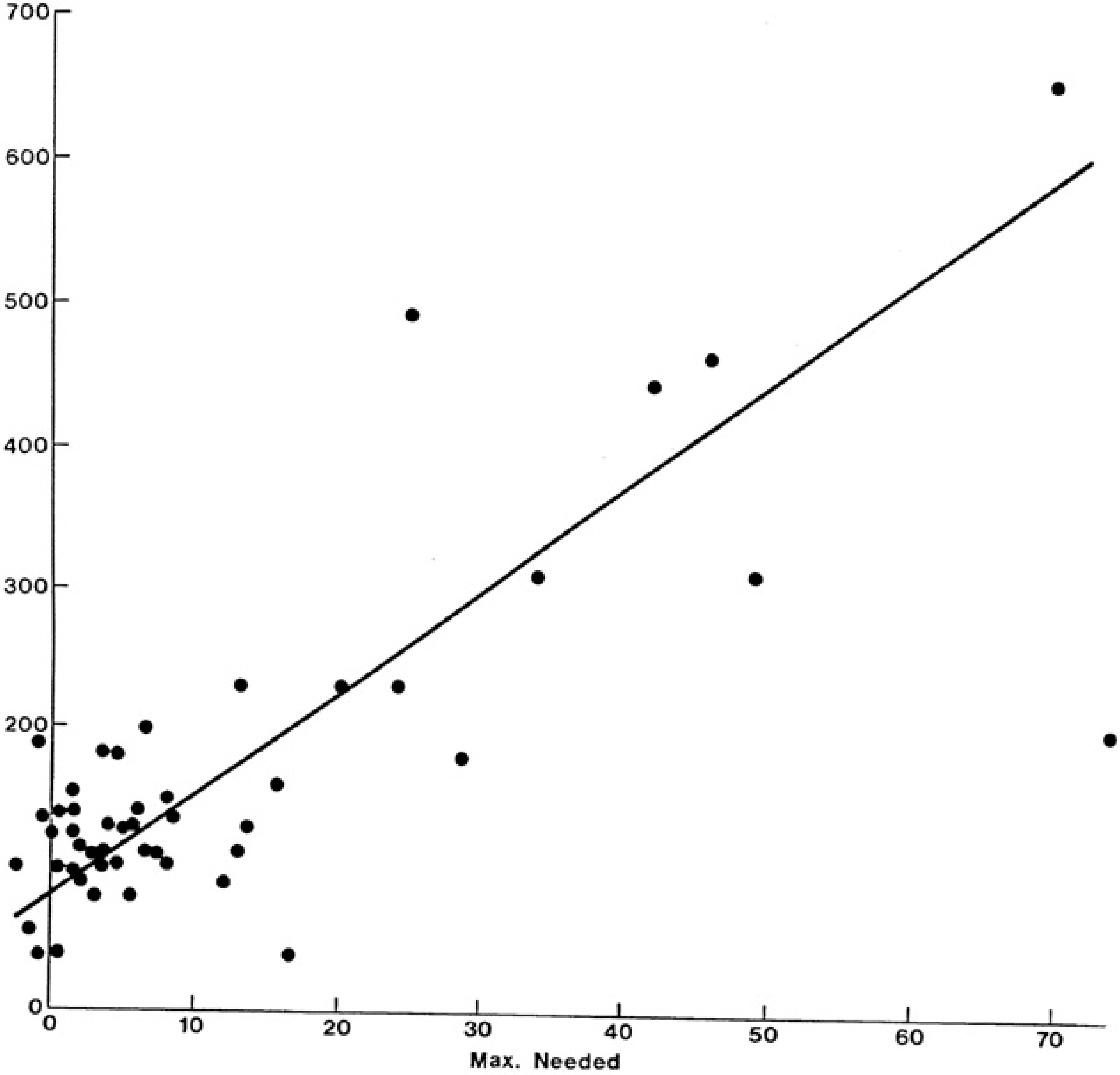

FIGURE 4 Comparison of Humidity Chamber Versus Oven Reoxidation
[Data are averages of two 24 hr. leaches.)

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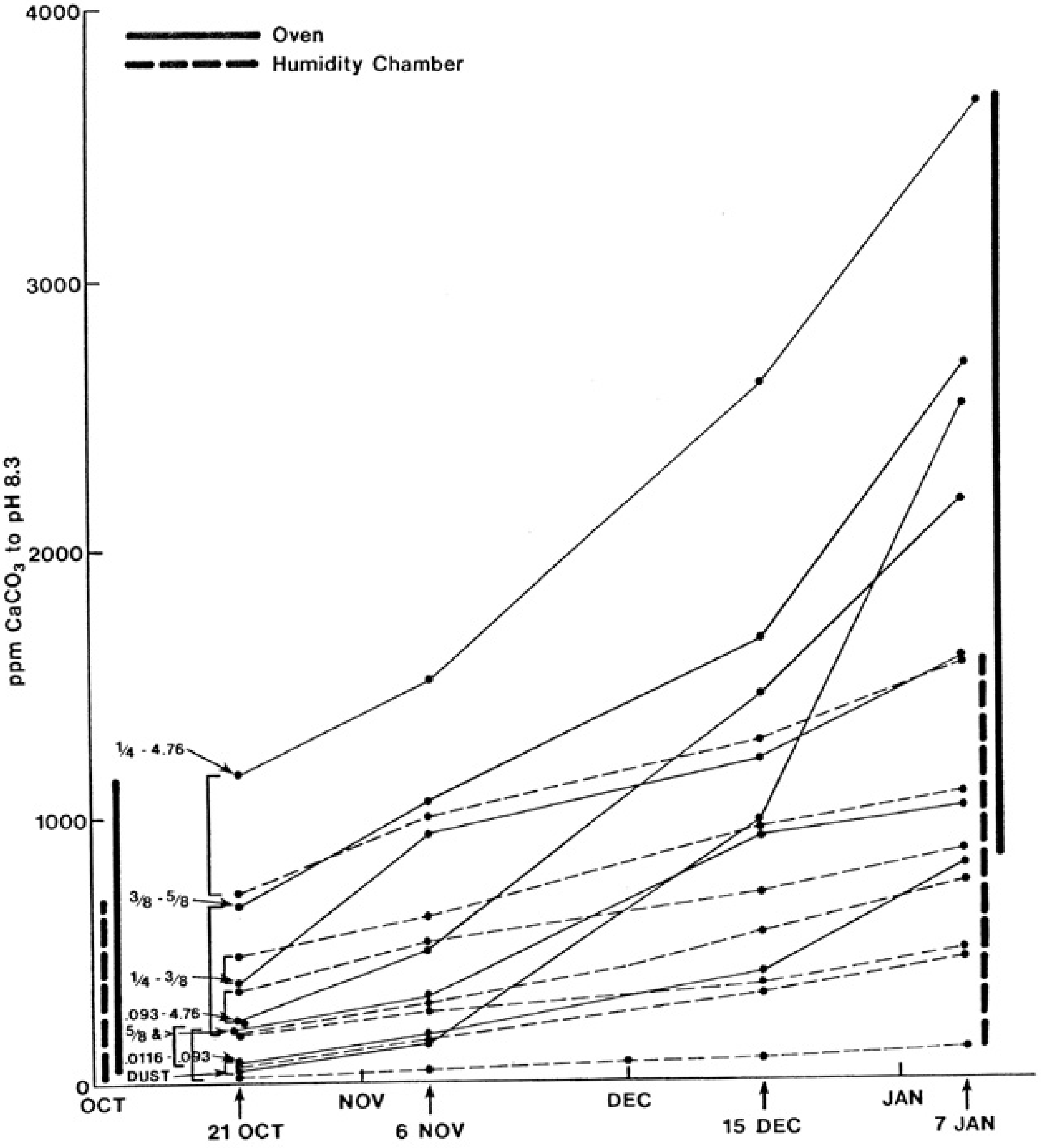

FIGURE 5 Comparison Between Calcium Content and Acidity to pH 8.3 of Leach Solutions [Data are averages of two 24 hr. leaches.]

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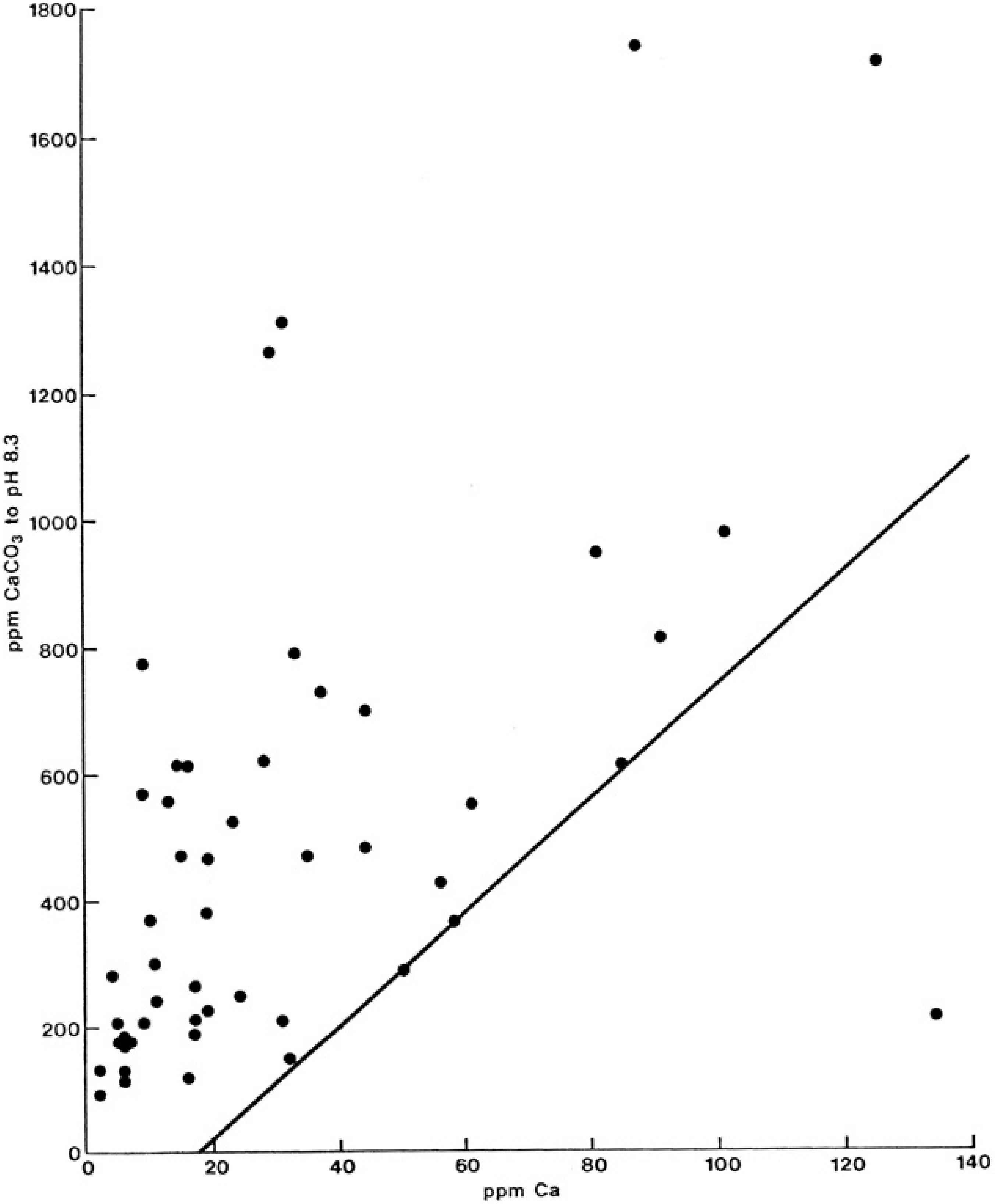

FIGURE 6 Comparison Between Calcium and Sulfate Concentration 10 in Leach Solutions [Data are averages of two 24 hr. leaches.]

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