Quantitative Determination of the Acid Producing Potential of Toxic Overburden

by

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INTRODUCTION:

At the present time, the most widely used technique to evaluate the chemical response of rock materials encountered in the mining of coal is the acid-base accounting technique reported by Sobek et al. The procedure is based upon two analytical parameters, (1) the total sulfur content of the rock and (2) the total HC1 soluble carbonate minerals contained within the rock. All of the sulfur is assumed to be contained within iron disulphide minerals, pyrite and/or marcasite. It is also assumed that all of the contained disulphide minerals react to produce acid. The combined carbonate minerals, on the other hand, are assumed to totally dissolve to produce alkaline solutions. The procedure then stoichiometrically compares the acid and base producing potentials of the samples and evaluates the rock in terms of Tons Of CaC03 per 1000 Tons of material needed to (1) dissolve and neutralize the net acid potential or (2) represent the net alkaline potential. The procedure actually works quite well to predict the response of those rocks that will definitely produce either acidic or alkaline solutions. It's shortcomings are two-fold: (1) where the predicted net acid or base producing potentials are low, the actual rock response may be opposite to that predicted and (2) the technique provides no mechanism by which time dependent parameters such as rate of production can be evaluated.

The purpose of this research was to devise and test an analytical procedure that would more precisely estimate the chemical response of a rock to water leaching and to incorporate a mechanism to evaluate time dependent parameters of production.

WEATHERING MODELS:

Laboratory procedures devised to predict the chemical response of a rock to natural conditions of water leaching are weathering models. Weathering models can be of two basic types: (1) the procedure can assume some basic chemical reactions and resultant stoichiometric relationships and then calculate the concentration of reaction products based upon the analytically determined concentrations of major reactants. (The acid-base accounting technique of Sobek et al would be of this type) or (2) the sample can be subjected to experimentally controlled conditions of leaching with a chemical analysis of the leachate being used to evaluate the chemical response of the rock. A number of different procedures have been proposed representing this type of approach including the use of humidity chambers, packed columns and soxhlet reactors.

The problem that rises with the utilization of a leaching model is that, by virtue of being a model, certain basic physical parameters such as particle size and volume of material are significantly reduced in magnitude from those that exist in the "real life" situation. On the other hand, certain other basic parameters such as the rates of chemical reactions, material solubilities and grain size of the rock cannot be changed or modeled, resulting in a non-uniform modeling of the natural system. That these distortions of the natural system may preclude the usefulness of data generated from models must be considered as a possibility and the usefulness of the data must be proven by combining bench scale and field scale experiments; remembering that even field scale experiments will be models. The purpose of the research reported in this paper was to determine whether or not a weathering model utilizing the soxhlet leaching of a toxic material would reproduce the chemistry and kinetics of weathering of the same material when exposed to under atmospheric conditions.

EXPERIMENTAL MATERIALS:

Several tons of cleaning plant waste was acquired from the Dobbin Mine of Enoxv Coal Co. The material was initially screened to exclude particles in excess of 5/8" diameter. The upper size limit of 5/8" was imposed by the size of the barrels used in the field experiments in order to conform to the requirements of a plug flow fixed bed reactor. The material was then subdivided into six size ranges and the weight percent of each size range was quantified (see Table 1). Also indicated in the table is the total sulfur content of each size.

Representative samples of each size were collected, sealed in plastic bags and frozen until used for the soxhlet experiments. The remainder of the material was divided for use in the field experiments.

TABLE 1: SIZE CONSIST OF DOBBIN REFUSE SAMPLE

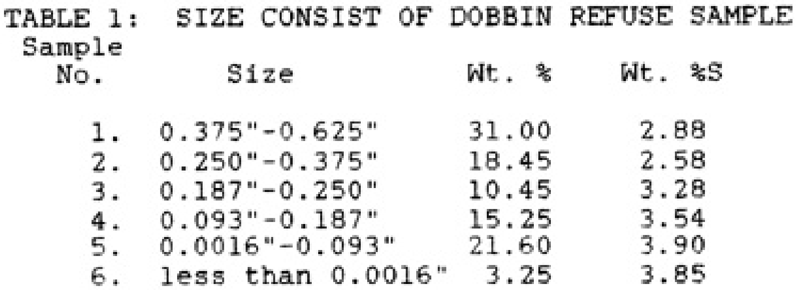


TABLE 1: SIZE CONSIST OF DOBBIN REFUSE SAMPLE

Sample No.	Size	Wt. %	Wt. %S
1.	0.375"-0.625"	31.00	2.88
2.	0.250"-0.375"	18.45	2.58
3.	0.187"-0.250"	10.45	3.28
4.	0.093"-0.187"	15.25	3.54
5.	0.0016"-0.093"	21.60	3.90
6.	less than 0.0016"	3.25	3.85

EXPERIMENTAL DESIGN:

The experimental design consisted of conducting two simultaneous but totally independent weathering experiments utilizing the same rock materials. In one experiment, the materials were oxidized by exposure to 105^0 C conditions for 2 weeks in a standard coal drying oven followed by a 24 hour period of leaching in a soxhlet reactor. The above procedure was considered one cycle; the materials were subjected to four cycles after an initial 24 hour leach. The composition of the leachate was determined after each leach and was used to describe the chemical response of the rock material. The materials used in the soxhlet experiment were the individual sizes Of the composite sample.

The second experiment consisted of packing three 35 gallon plastic barrels with the composite sample which were in turn exposed to atmospheric conditions for a period of approximately one year. Leachating was effected by percolating rain water and snow melt. Leachates were collected after each Precipitation event. The leachates were analyzed and the compositions used as in the soxhlet experiments to describe the chemical response of the rock materials to natural conditions of weathering.

Mathematical models were then generated to describe each of the two experiments. The usefulness of the bench scale model was tested by comparing the two models. If the two models were basically the same, then the bench scale model could be used to predict actual field response; if they did not compare favorably, the bench scale model was too distorted from actual conditions of weathering to be of any predictive value.

FIELD SCALE EXPERIMENTS:

The field scale experiments were conducted by placing 300 pounds of sample into each of the three 35 gallon plastic barrels. Each barrel was fitted at the bottom with a distribution plate and a single air-lock exit port (see figure 1). All fluids that passed through the barrel were required to enter through the top and exit through the air-lock exit port to be collected in a plastic container; no air could enter the barrel from the bottom. Rainwater and snow melt water that passed through the barrel was collected. A rain gauge monitored the amount of precipitation. The field experiments were conducted for nearly a year.

SOXHLET EXPERIMENTS:

A standard soxhlet was used for all experiments (see figure 2). The soxhlet employed a 47mm x 123mm porous cellulose thimble. A 100 gram sample was weighed and transferred to a 250ml beaker where it Was thoroughly wetted with a measured volume of distilled water. The sample was then quantitatively transferred to the cellulose thimble. A wad of cotton was placed on top of the sample to minimize streaming and channeling through the sample. The thimble was then placed into the reactor assembly. Distilled water was added to the reservoir such that including the water used to wet the sample, a total of 250ml was in the system. The sample was then leached for 24 hours. Previous experiments showed that more than 90% of all soluble materials was leached within extraction periods of 12-20 hours. The 24 hour leaching period was chosen for convenience.

At the end of the leaching period, the thimble with sample was removed and transferred to a drying oven maintained at 105^0 C for reoxidation. At the end of a 2 week reoxidation period, the thimble was removed, returned to the soxhlet and releached.

LEACHATE ANALYSES:

All soxhlet leachates and barrel effluents were subjected to the following analyses:

1. pH before and after the addition of 5 ml of 30% H_2O_2 followed by 30 minutes of boiling followed by cooling to room temperature.

2. specific conductivity
3. automatic titration to pH 4.5, 7.0 and 8.3
4. A.A. analyses for Ca, Mg, Na, K, Al, Si, Fe and Mn
5. SO_4 =

From the time of collection, all solutions were stored refrigerated until the analyses were performed.

The SO_4 = concentration was chosen as the analytical parameter to monitor the amount of acid produced. The actual acidity of a leachate could be less than original acid produced because of internal auto neutralization while the concentrations of iron is pH dependent. solution in acid load. The SO_4 = on the other hand, once produced, stays in solution concentrations proportional to the original produced

CONTROL BARREL DATA:

The analytical data for the three control barrels are summarized in table 2. The data are cumulative milligrams sulfate for each barrel over the duration of the experiment with the "aggregate" sample being the summation of milligrams for all three barrels (a total of 900 pounds of samples) over the duration of the experiment. The cumulative data for the aggregate sample are plotted in figure 3.

Included in table 2 is the calculated concentration of sulfur remaining in the sample after leachate collection. The percent unreacted sulfur, %Su, was calculated based upon (1) the amount of sulfur released into solution as sulfate ion, (2) the total weight of the sample (900 pounds) and (3) the total sulfur content of the original sample (3.15%). A plot of %Su versus time in days for the aggregate sample is illustrated in figure 4. The plot is a pseudo first order decay curve. Note that at the point where the plot becomes asymptotic to the time axis, about 30 to 35 weight percent sulfur yet remains in the sample. A plot of ln%Su versus time is shown in figure 5. The time=0%Su intercept, Alpha, is 4.5896. The value e taken to this power should be 100%; the actual value is 98.45%. The correlation coefficient R=0.966: the slope of the plot is 0.0050 $days^{-1}$; the slope of course bring the measure of the rate of release of sulfate into solution, i.e. the reaction rate constant.

TABLE 2. CUMULATIVE mg SO_4 = - BARREL EXPERIMENTS

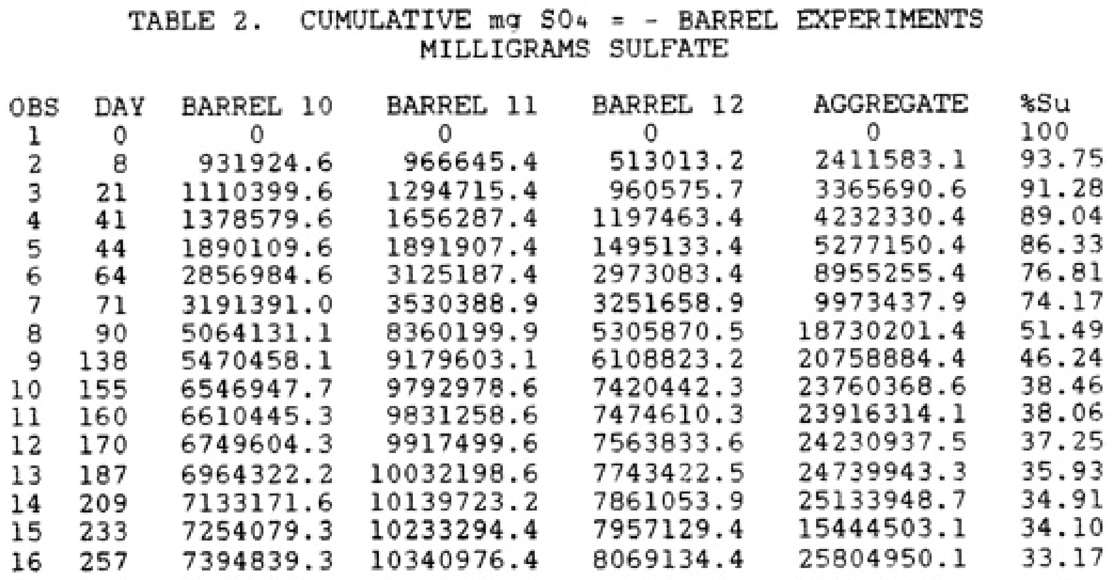


TABLE 2. CUMULATIVE mg SO_4 = - BARREL EXPERIMENTS
MILLIGRAMS SULFATE

OBS	DAY	BARREL 10	BARREL 11	BARREL 12	AGGREGATE	%Su
1	0	0	0	0	0	100
2	8	931924.6	966645.4	513013.2	2411583.1	93.75
3	21	1110399.6	1294715.4	960575.7	3365690.6	91.28
4	41	1378579.6	1656287.4	1197463.4	4232330.4	89.04
5	44	1890109.6	1891907.4	1495133.4	5277150.4	86.33
6	64	2856984.6	3125187.4	2973083.4	8955255.4	76.81
7	71	3191391.0	3530388.9	3251658.9	9973437.9	74.17
8	90	5064131.1	8360199.9	5305870.5	18730201.4	51.49
9	138	5470458.1	9179603.1	6108823.2	20758884.4	46.24
10	155	6546947.7	9792978.6	7420442.3	23760368.6	38.46
11	160	6610445.3	9831258.6	7474610.3	23916314.1	38.06
12	170	6749604.3	9917499.6	7563833.6	24230937.5	37.25
13	187	6964322.2	10032198.6	7743422.5	24739943.3	35.93
14	209	7133171.6	10139723.2	7861053.9	25133948.7	34.91
15	233	7254079.3	10233294.4	7957129.4	15444503.1	34.10
16	257	7394839.3	10340976.4	8069134.4	25804950.1	33.17

SOXHLET DATA:

The sulfate data for the individual sample sizes for each of the experimental cycles is summarized in table 3. The data are in milligrams SO_4 =. The data were recalculated in terms of a composite sample based upon the weight percent of the original sample represented by each of the size fractions. The data for the composite sample were calculated for a 1000 gram sample. The composite data and the calculated %Su are summarized in table 3A.

TABLE 3. CUMULATIVE <u>mg </u>SO_4 = - SOXHLET EXPERIMENTS

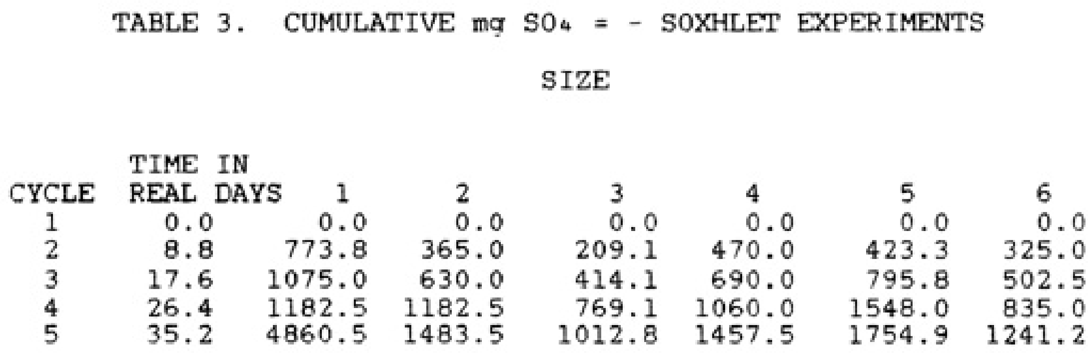


TABLE 3. CUMULATIVE mg SO_4 = - SOXHLET EXPERIMENTS

SIZE

CYCLE	TIME IN REAL DAYS	1	2	3	4	5	6
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	8.8	773.8	365.0	209.1	470.0	423.3	325.0
3	17.6	1075.0	630.0	414.1	690.0	795.8	502.5
4	26.4	1182.5	1182.5	769.1	1060.0	1548.0	835.0
5	35.2	4860.5	1483.5	1012.8	1457.5	1754.9	1241.2

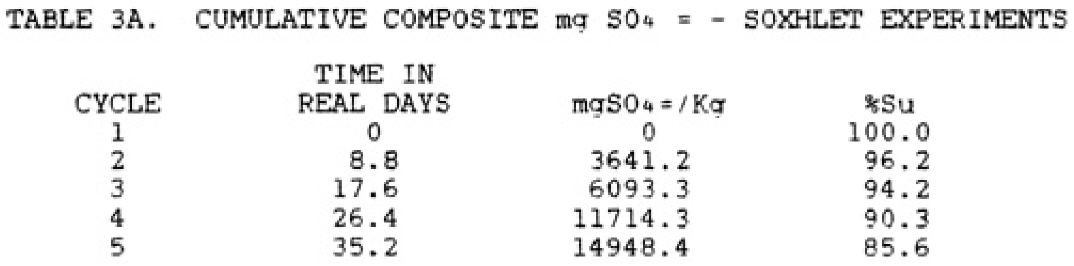


TABLE 3A. CUMULATIVE COMPOSITE mg SO_4 = - SOXHLET EXPERIMENTS

CYCLE	TIME IN REAL DAYS	mgSO_4=/Kg	%Su
1	0	0	100.0
2	8.8	3641.2	96.2
3	17.6	6093.3	94.2
4	26.4	11714.3	90.3
5	35.2	14948.4	85.6

In an attempt to relate the time involved in the soxhlet experiments to the time (real time) involved in the barrel experiments, the %Su data of the two data sets were compared as to the time required to reduce the original sulfur content to equal levels of %Su. Using the %Su for each of the consecutive soxhlet leach cycles, the number of soxhlet "days" required to achieve the corresponding %Su were plotted against the number of real days required to produce the same %Su during the barrel experiments (see figure 6). The plot indicates that there is a direct linear relationship (R=0.989) and that 14 soxhlet "days" are equal to 8.8 real days. For all subsequent discussions of the soxhlet data, the soxhlet "time" will be converted to and discussed in terms of real time.

The cumulative milligrams SO_4= for the soxhlet leaches are plotted versus real time for the composite sample in figure 7. A plot of %Su versus real time for the composite sample is shown in figure 8.

Figure 9 illustrates the ln%Su versus real time relationships for the individual sizes. Note the marked divergence of the dust size sample. The %Su data and corresponding statistics are summarized in table 4.

TABLE 4. PERCENT UNREACTED SULFUR-SOXHLET EXPERIMENTS

WITH APPROPRIATE STATISTICS

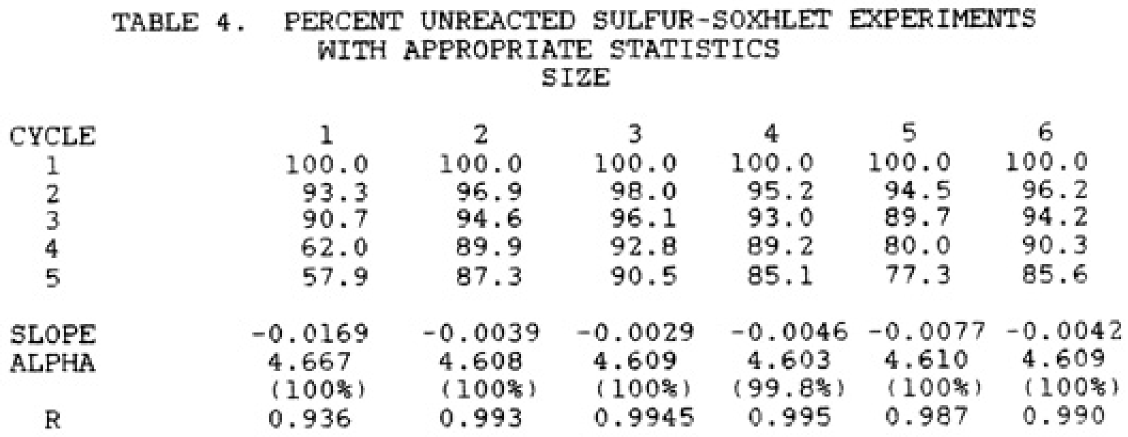
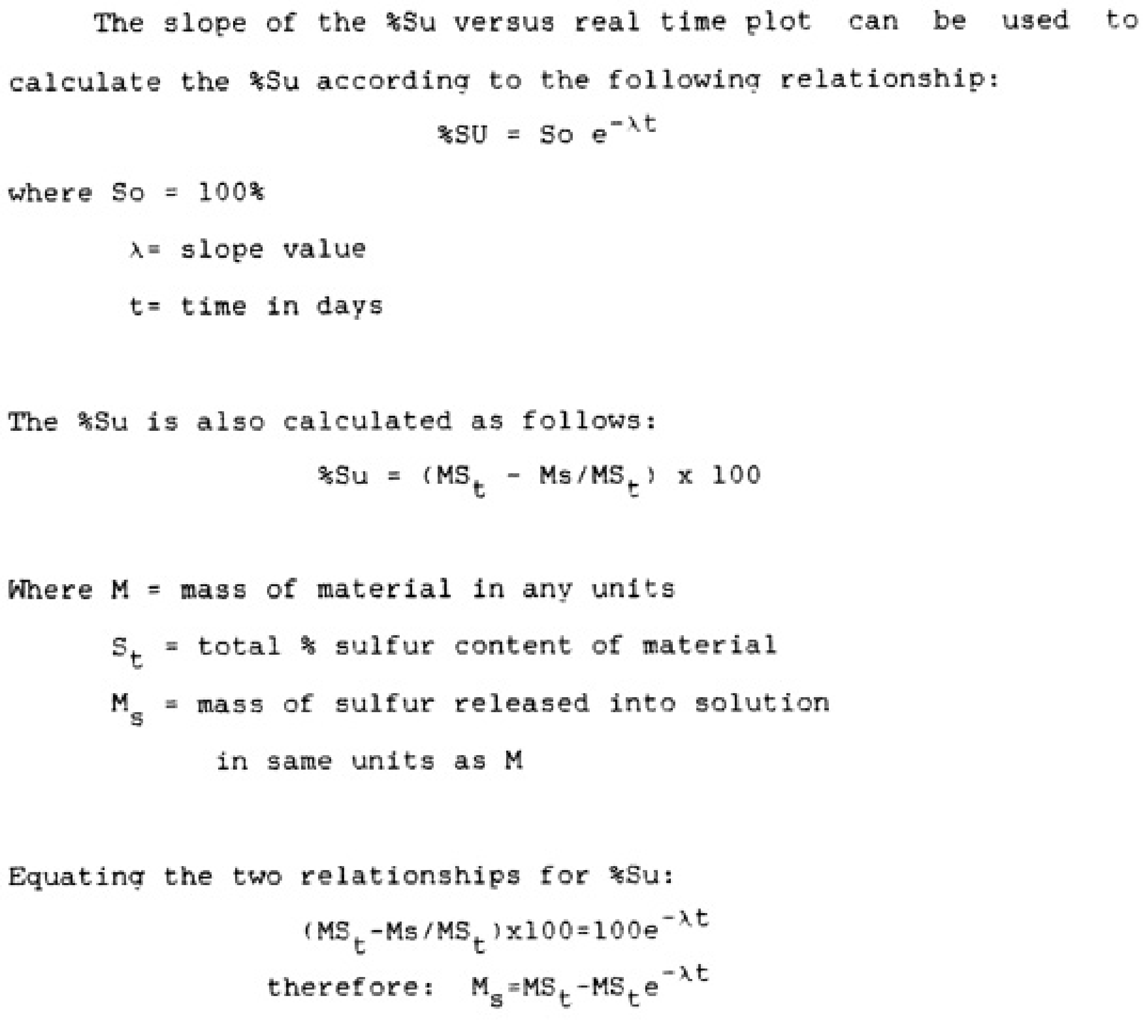


TABLE 4. PERCENT UNREACTED SULFUR-SOXHLET EXPERIMENTS
WITH APPROPRIATE STATISTICS
SIZE

CYCLE	1	2	3	4	5	6
1	100.0	100.0	100.0	100.0	100.0	100.0
2	93.3	96.9	98.0	95.2	94.5	96.2
3	90.7	94.6	96.1	93.0	89.7	94.2
4	62.0	89.9	92.8	89.2	80.0	90.3
5	57.9	87.3	90.5	85.1	77.3	85.6
SLOPE	-0.0169	-0.0039	-0.0029	-0.0046	-0.0077	-0.0042
ALPHA	4.667	4.608	4.609	4.603	4.610	4.609
	(100%)	(100%)	(100%)	(99.8%)	(100%)	(100%)
R	0.936	0.993	0.9945	0.995	0.987	0.990

The ln%Su versus real time for the calculated composite sample is shown in figure 10. The time=0 intercept is 4.61; $e^{4.61}$=100.48. The slope of the plot, the reaction rate constant, is 0.0050 days-1. Note that the reaction rate constants for the aggregate barrel data and the corresponding composite soxhlet data are equal.

The slope of the %Su versus real time plot can be used to calculate the %Su according to the following relationship:



The slope of the %Su versus real time plot can be used to calculate the %Su according to the following relationship:

$$\%SU = So\ e^{-\lambda t}$$

where So = 100%

λ= slope value

t= time in days

The %Su is also calculated as follows:

$$\%Su = (MS_t - Ms/MS_t) \times 100$$

Where M = mass of material in any units

S_t = total % sulfur content of material

M_s = mass of sulfur released into solution in same units as M

Equating the two relationships for %Su:

$$(MS_t - Ms/MS_t) \times 100 = 100e^{-\lambda t}$$

$$\text{therefore:}\quad M_s = MS_t - MS_t e^{-\lambda t}$$

Using the above relationship, a sulfate production value was calculated at various times for both the barrel and soxhlet samples. The calculated and observed values are compared in table 5.

TABLE 5: COMPARISON OF CALCULATED AND OBSERVED DATA

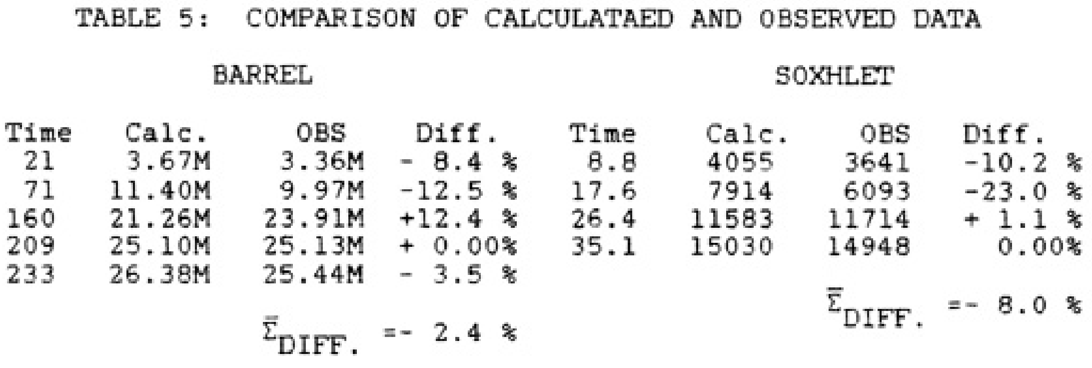


TABLE 5: COMPARISON OF CALCULATAED AND OBSERVED DATA

BARREL				SOXHLET			
Time	Calc.	OBS	Diff.	Time	Calc.	OBS	Diff.
21	3.67M	3.36M	- 8.4 %	8.8	4055	3641	-10.2 %
71	11.40M	9.97M	-12.5 %	17.6	7914	6093	-23.0 %
160	21.26M	23.91M	+12.4 %	26.4	11583	11714	+ 1.1 %
209	25.10M	25.13M	+ 0.00%	35.1	15030	14948	0.00%
233	26.38M	25.44M	- 3.5 %				
		$\bar{\Sigma}_{DIFF.}$	=- 2.4 %			$\bar{\Sigma}_{DIFF.}$	=- 8.0 %

DISCUSSION

Based upon the equality of the slopes of the %Su versus time plots for the barrel and soxhlet data, the bench scale experiments produced acid at exactly the same rate as the field experiments. A rate measurement can therefore be determined from bench scale experiments which will accurately predict field response. The lithocries of all the samples are similar. The Al/A+Si value for the samples are listed in table 6.

TABLE 6

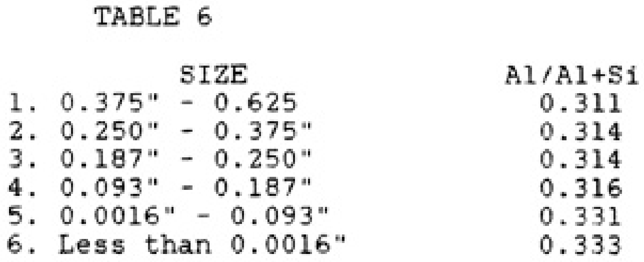


TABLE 6

	SIZE	Al/Al+Si
1.	0.375" - 0.625	0.311
2.	0.250" - 0.375"	0.314
3.	0.187" - 0.250"	0.314
4.	0.093" - 0.187"	0.316
5.	0.0016" - 0.093"	0.331
6.	Less than 0.0016"	0.333

The ratio is approximately equivalent to a clay/quartz ratio which for these kinds of rocks would be the major parameters determining the lithology. The divergent response of the dust sample was obviously reflecting the small size.

It is anticipated that, exclusive of dust size, different rock lithologies would have slope values reflecting the particular lithology with variations depending upon specific composition. A comprehensive study of a wide range of rock lithologies would probably establish an average reaction rate for a particular lithology. Such an average value could be used as preliminary evaluations of the acid producing potential for a mine site. On the other hand, such values could be disregarded and the actual rate constant for a sample can be determined by the soxhlet-leaching-reoxidation technique. Combined with the total sulfur value, the acid load per mass can be calculated.

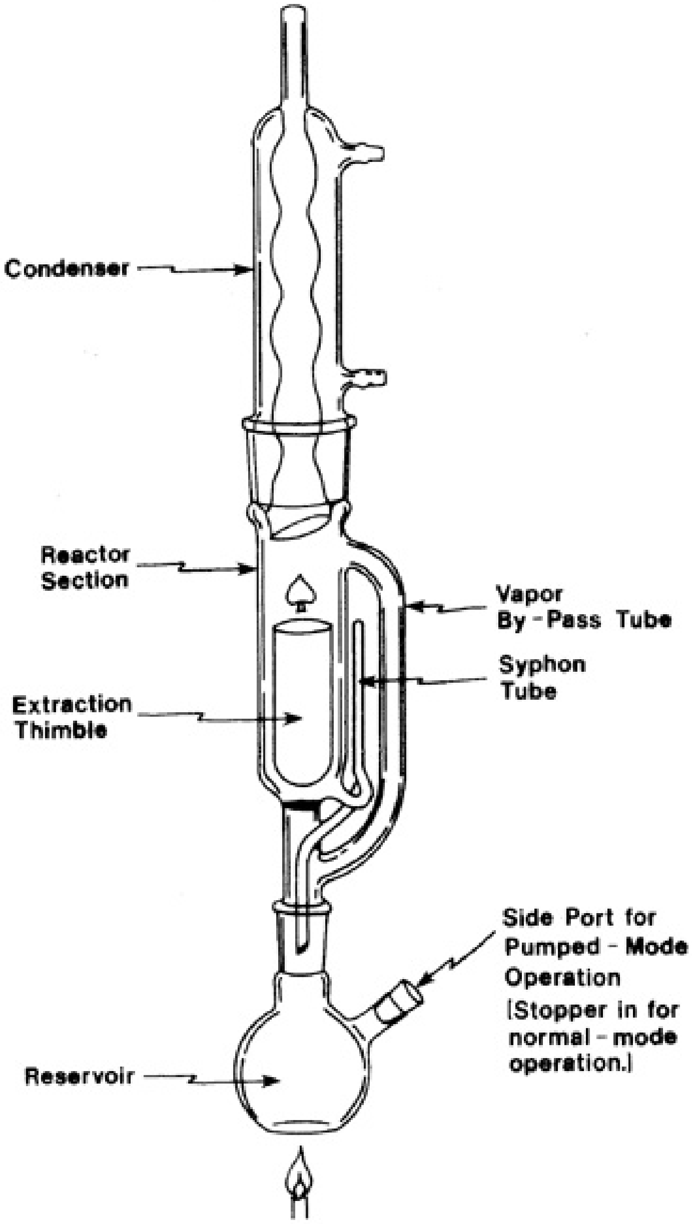


Figure 1 **SOXHLET EXTRACTOR**

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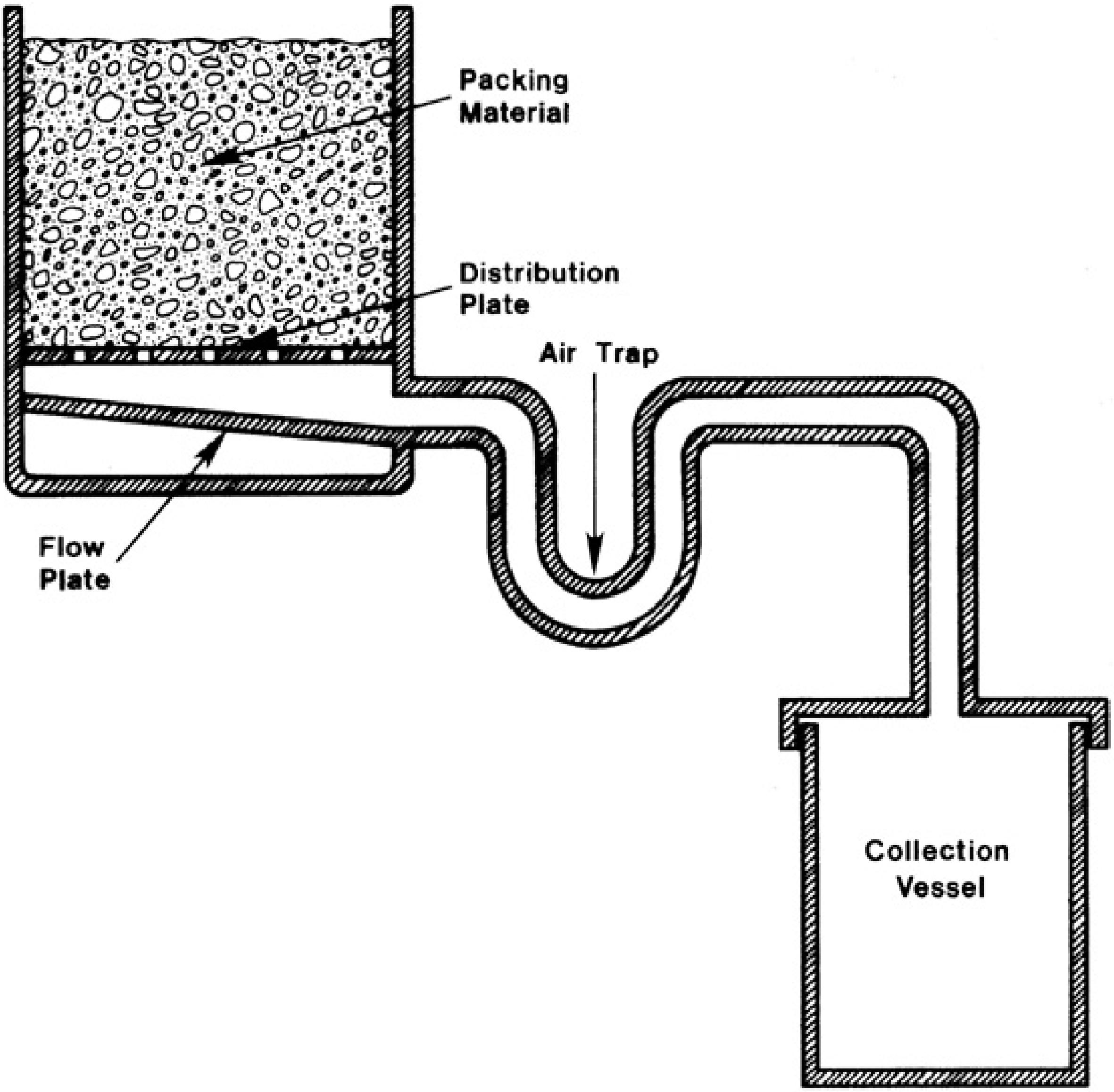

Figure 2. Small Scale Field Experiment

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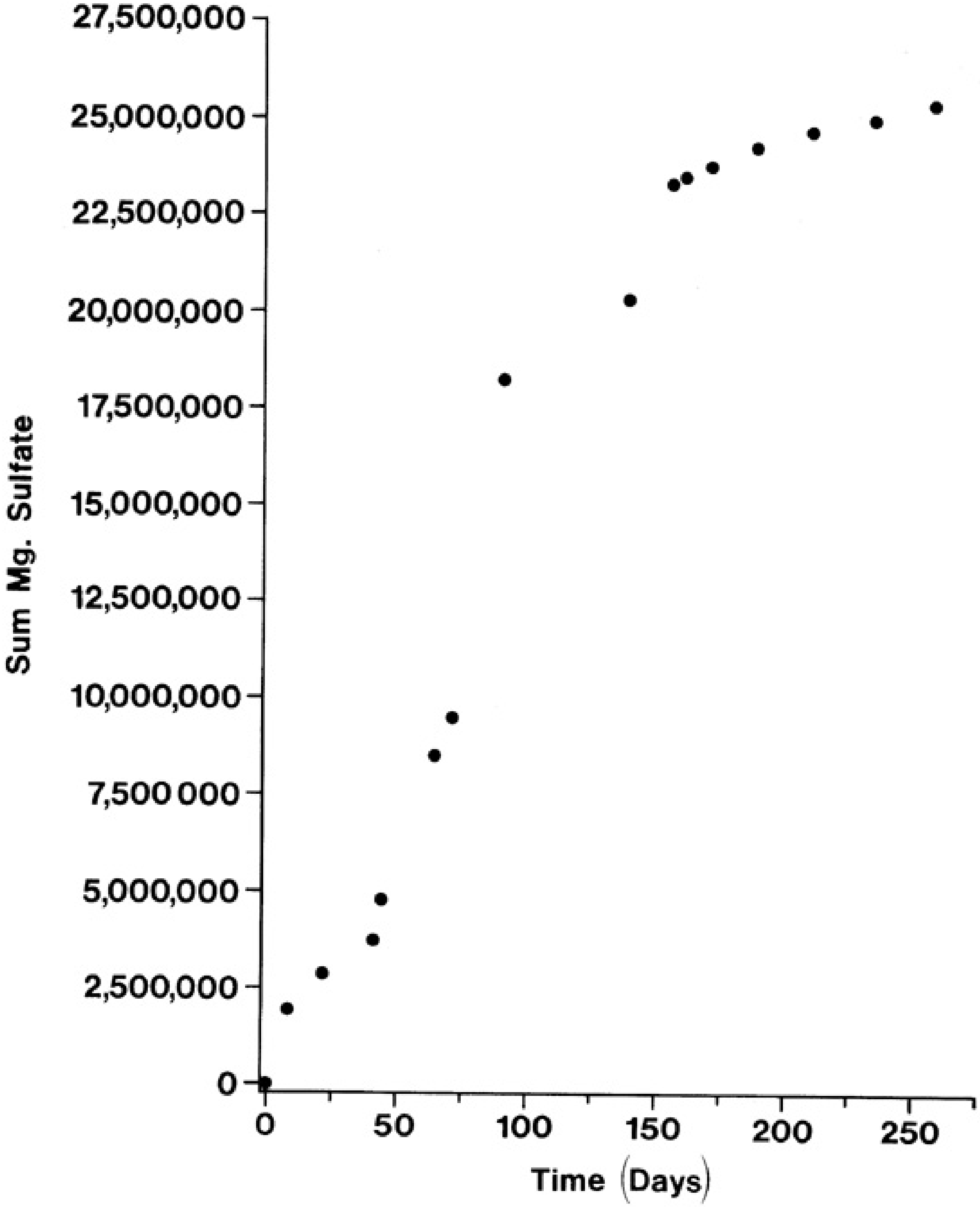

Figure 3 Cumulative milligrams $SO_4^{=}$ vs Time for Aggregate Barrel Data

Figure 3 Cumulative milligrams SO_4 = vs Time for Aggregate Barrel Data

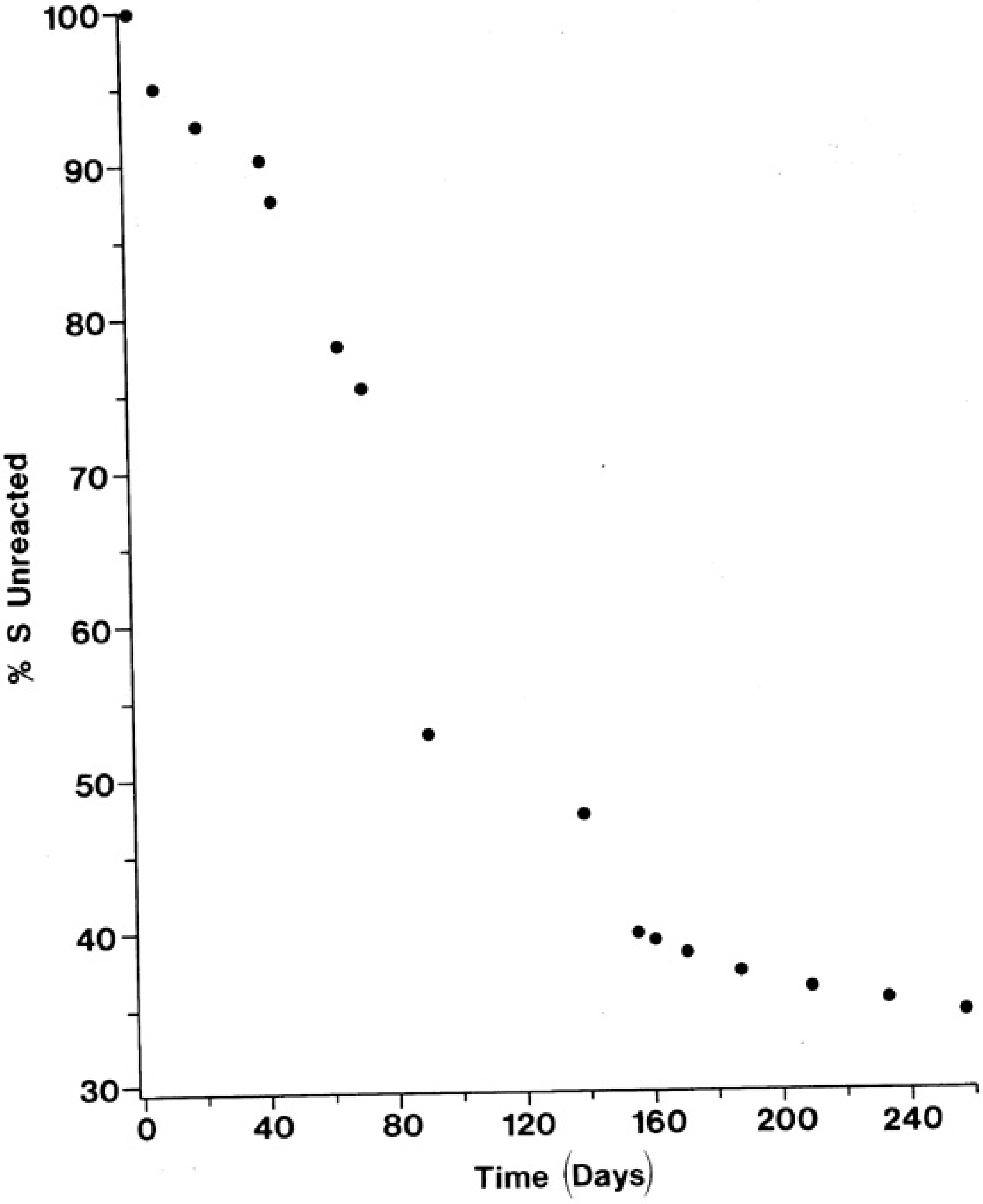

Figure 4 %Su vs Time for Aggregate Barrel Data

Figure 4 %Su vs Time for Aggregate Barrel Data

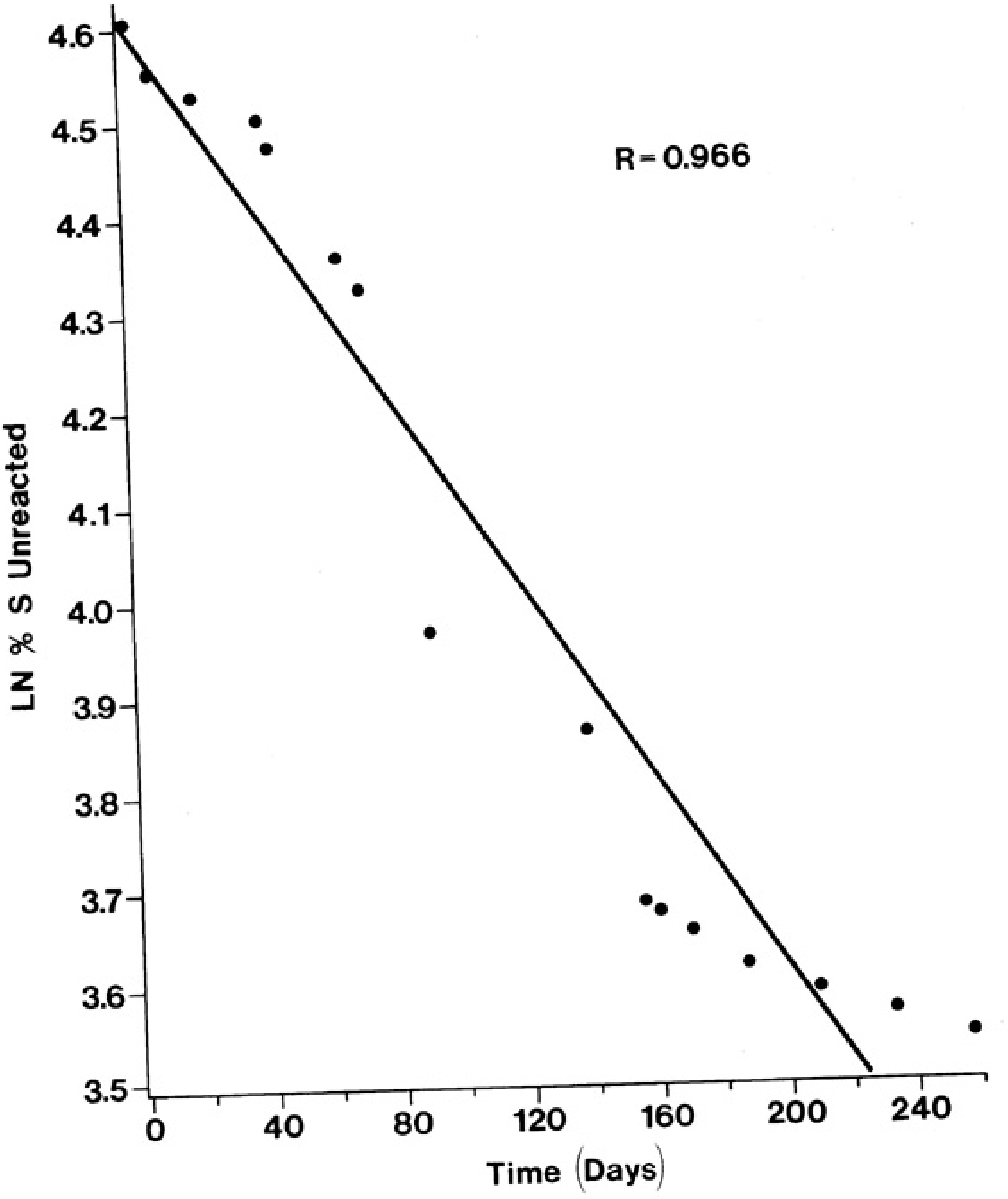

Figure 5 Log %Su vs Time for Aggregate Barrel Data

Figure 5 Log %Su vs Time for Aggregate Barrel Data

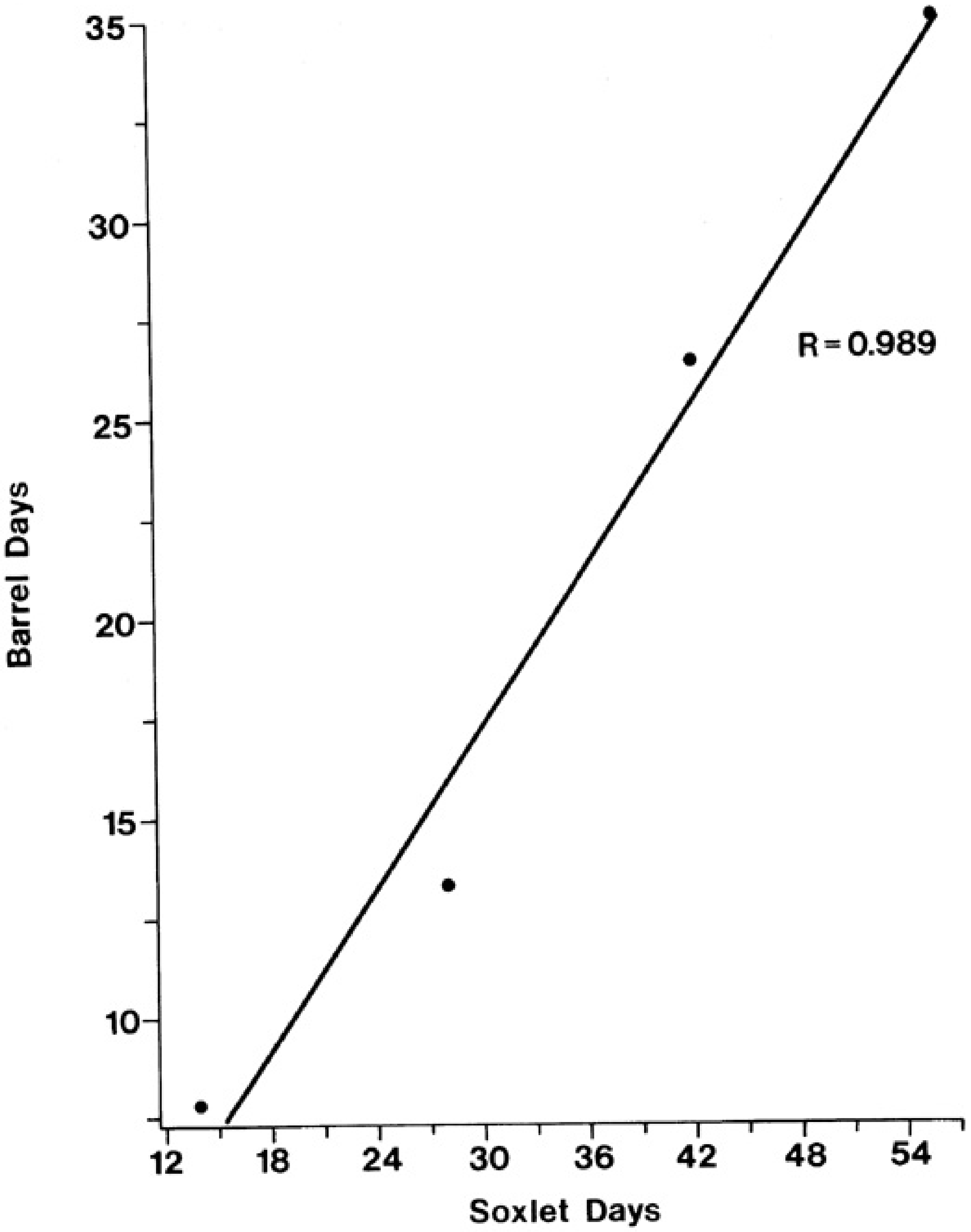

Figure 6 Real (Barrier) Days vs Soxhlet "Days" for equal values of %Su

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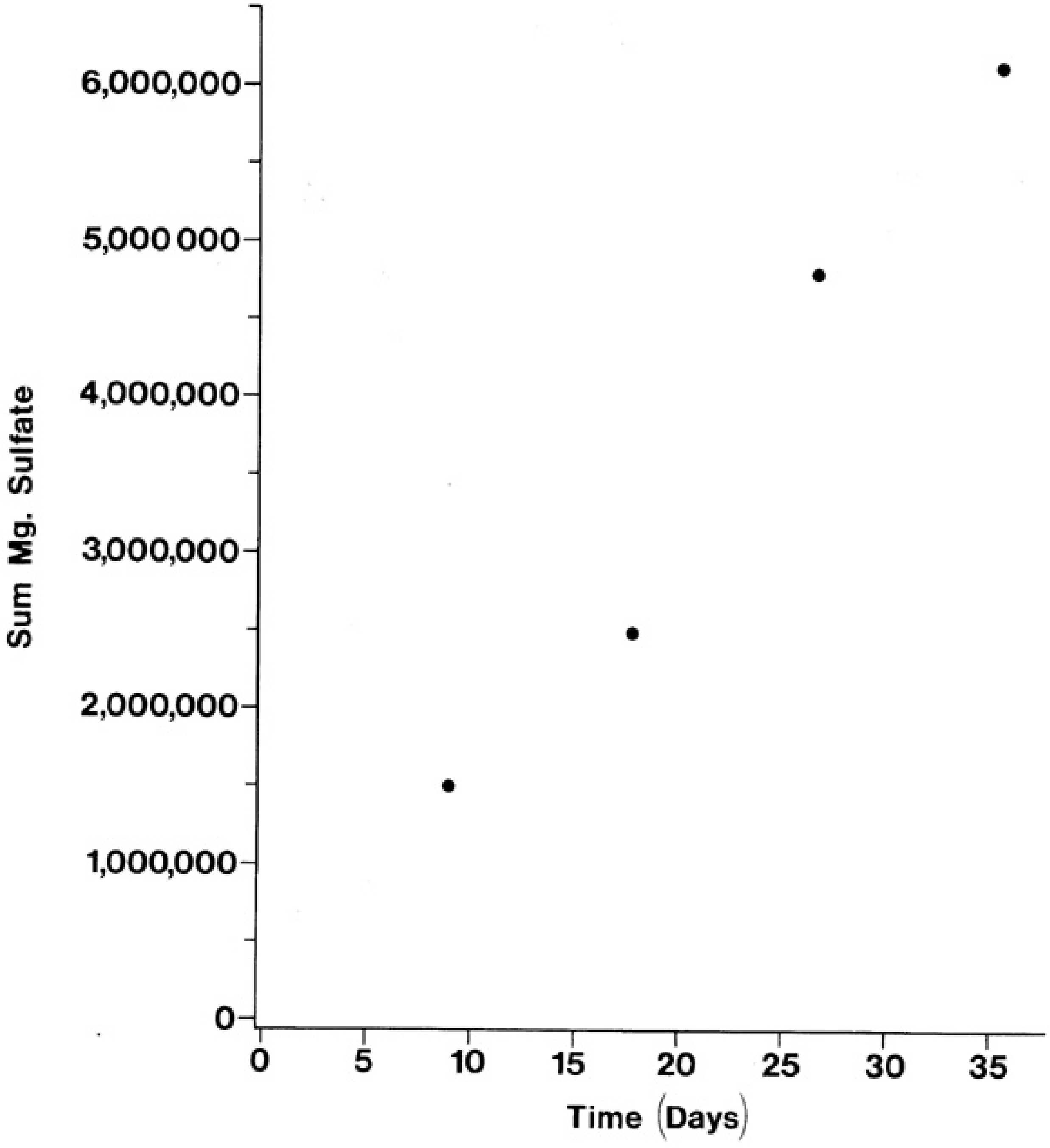

Figure 7 Cumulative Milligrams $SO_4^=$ vs Real Time for Soxhlet Data

Figure 7 Cumulative milligrams SO_4 = vs Real Time for Soxhlet Data

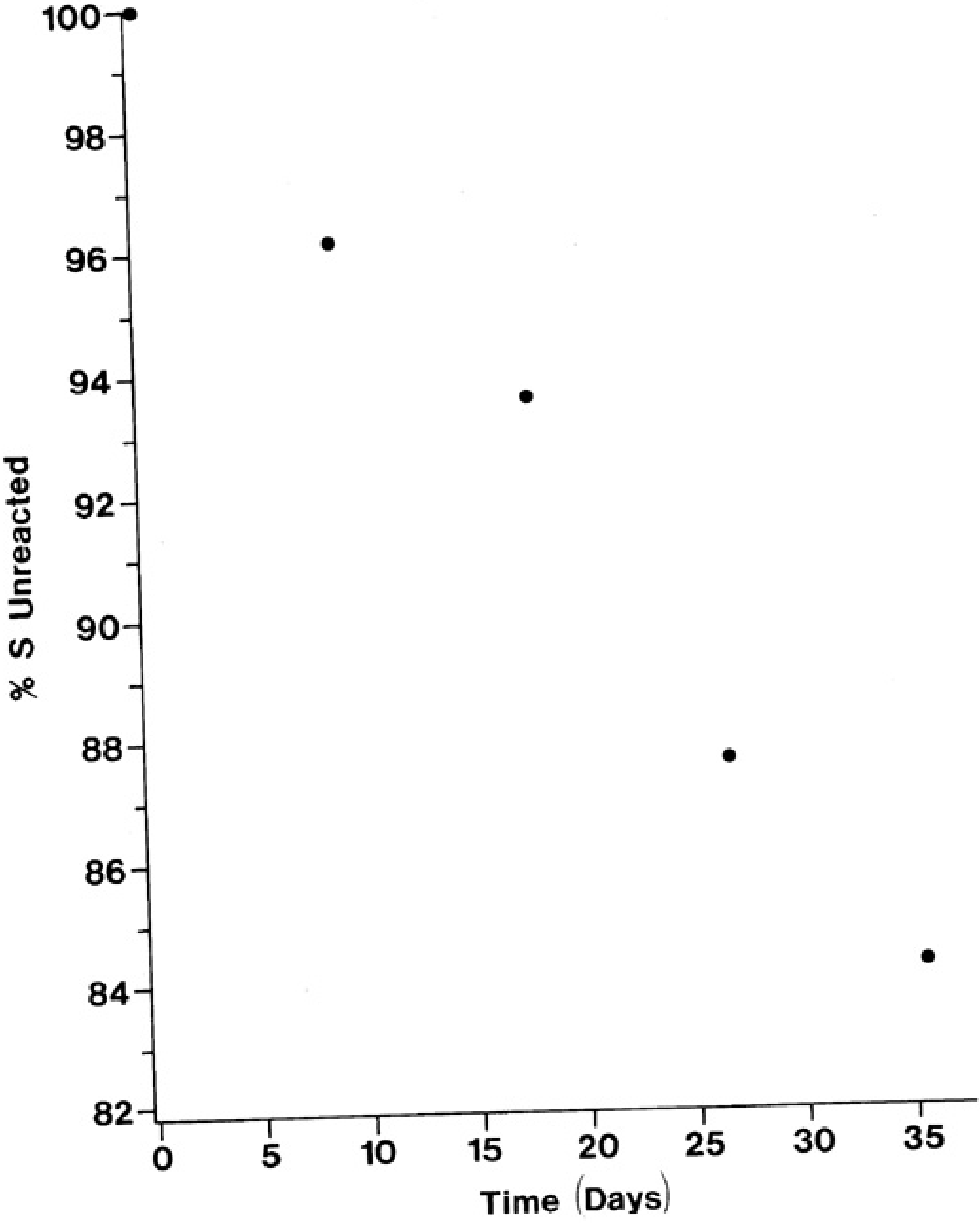

Fig. 8 %Su vs Time for Soxhlet Data

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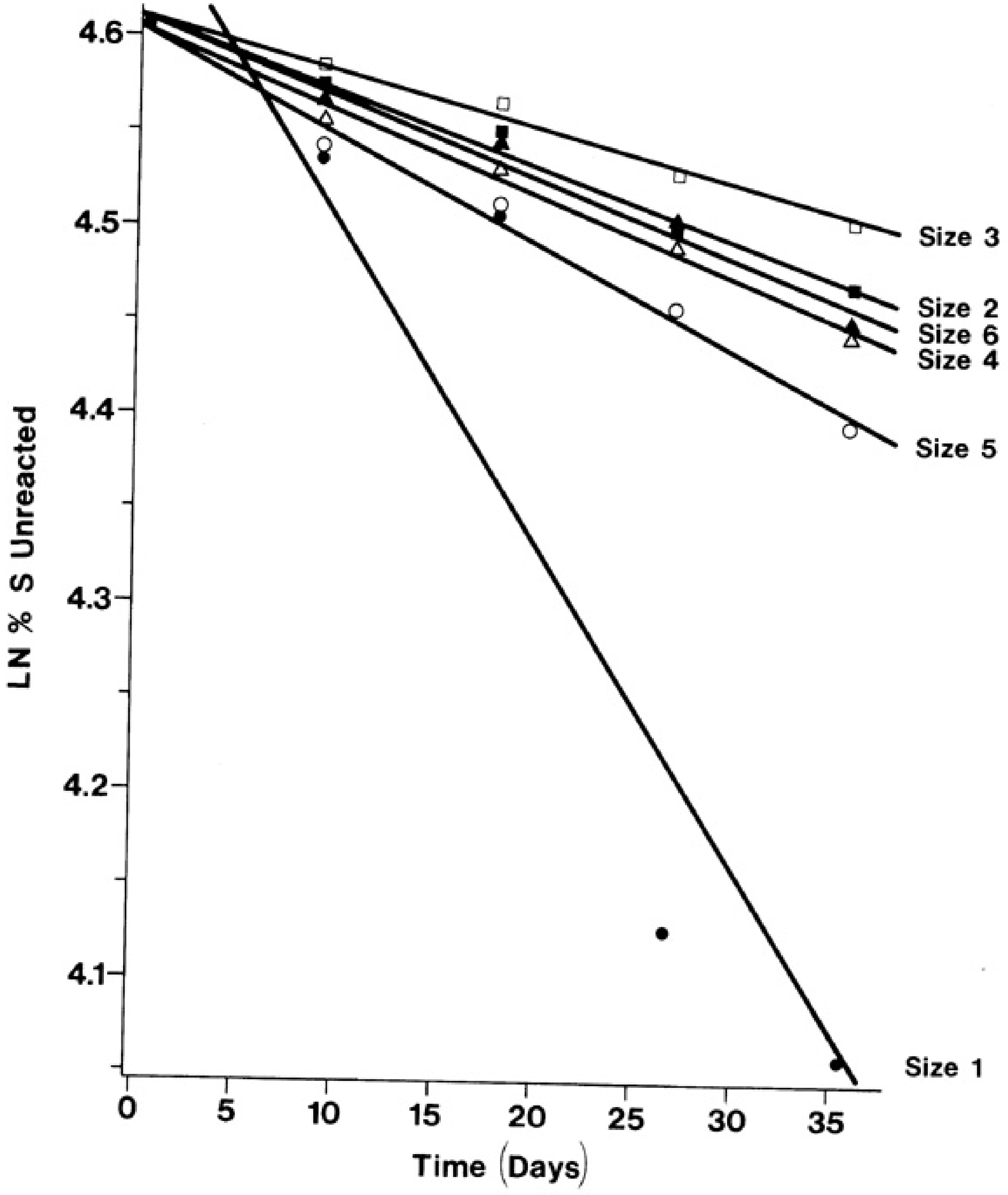

Figure 9 LOG %Su vs Time for Individual Sized of Sochlet Data

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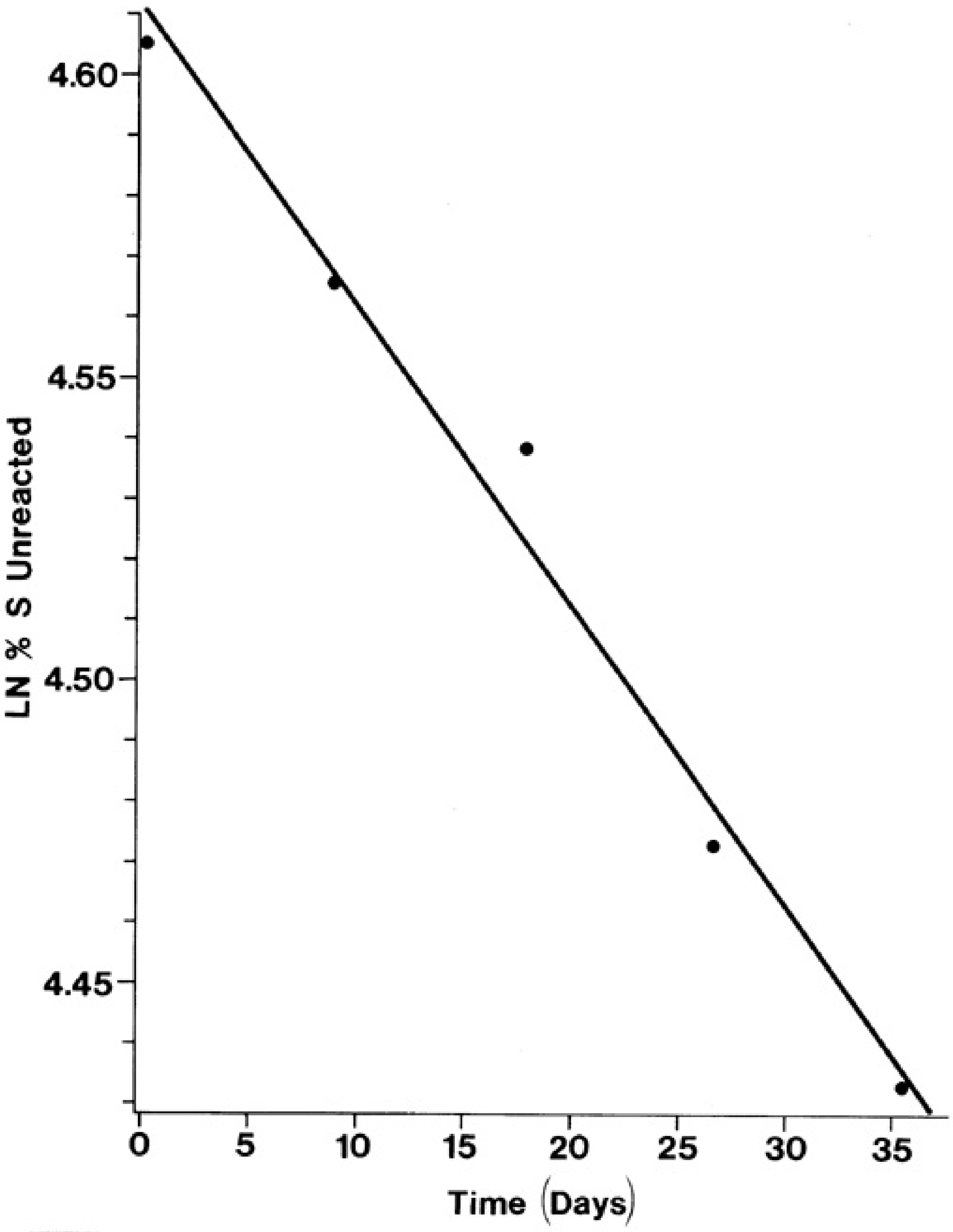

Figure 10 LOG %Su vs Time for Composite Sample from Soxhlet Data

Figure 10 LOG %Su vs Time for Composite Sample from Soxhlet Data