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Abstract. -- Acid mine drainage is produced by the oxidation of iron sulfide minerals in the presence of air and water. Once this drainage enters a saturated ground-water system, oxidation is inhibited by the absence of air. The aquifer minerals will not be in equilibrium with the acid water and one or more reactions may proceed which results in acid drainage amelioration. In order to predict the rate and direction of migration of acid drainage contaminants within ground water, it is essential to be able to quantify the natural abatement capacity of the mine drainage affected rock. A laboratory procedure has been developed which may quantify the "acidity distribution coefficient" of acid mine drainage contaminated aguifers in which flow is dominated by fracture porosity. This technique is a modification of the batch adsorption tests commonly used to describe ion-exchange and adsorption reactions in porous media. All mathematical models which describe the transport of a reactive contaminant must employ the distribution coefficient. For aquifers in which ground-water flow occurs primarily through fractures rather than intergranular pores, the distribution coefficient is a measure of the amount of contaminant adsorbed by the aquifer per surface area of rock exposed to the solution. Lower and Middle Kittanning cores, drill cuttings, and strip mine highwall samples have been analyzed for their capacity to ameliorate acidic solutions. All laboratory batch tests resulted in an increase in pH, regardless of the rock sample's acid-base account. All samples without carbonate material and with a low sulfur content were found to have a significant acid consuming capacity. All samples with an acid-base account greater than -40 (tons CaCO3 equivalent per thousand tons of material) consumed acidity in the batch experiments. Some samples with an acid-base account greater than -140 but less than -40 consumed acidity in the batch tests. Field tracer

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tests are another way of obtaining values for reactive contaminant transport parameters. Small scale acid-injection tests have been performed in wells from which the drill cuttings have been collected. The results of these tests illustrate that the developed laboratory technique has potential for predicting field occurrences.

INTRODUCTION

Acid mine drainage is produced by the oxidation of iron sulfide minerals in the presence of air and water. Once this drainage enters a saturated ground-water system, oxidation is inhibited by the absence of air. The aquifer minerals will not be in equilibrium with the acid water, and one or more reactions may proceed which results in acid drainage amelioration. All mathematical models which describe the rate and direction of migration of a contaminant that chemically interacts with the medium through which it flows must employ a parameter termed the "retardation factor". A reactive contaminant, such as acid mine drainage, will migrate at a rate slower than that of the surrounding ground water. The retardation factor is a measure of the difference between these two flow velocities. Such delays in the transport of acid mine drainage have been noted in western Pennsylvania aquifers. Prior to the research presented in this paper, there had been no serious attempt to quantify acid drainage transport parameters. Hence, the ability to predict the migration of acid mine drainage within soils, aquifers, and confining beds had been very poor.

Reactive Contaminant Transport Parameters

Much work has been conducted in quantifying the retardation of reactive contaminants other than those relating to acid mine drainage. These analyses most often involve the determination of the distribution coefficient (Kd). As discussed by Freeze and Cherry (1979), in systems dominated by intergranular flow, the definition of the distribution coefficient and its relation to the retardation factor (R) are described by the equations:

K_d = (mass of solute on the solid phase per unit mass of solid phase) / concentration of solute in solution

 $R = 1 + (bulk density/porosity) * K_d$

The method most often employed for Kd measurement is the laboratory batch experiment. These tests are performed by placing crushed rock in contact with a contaminated solution. The mixture is agitated on a shaker until equilibrium is reached. The effluent is then withdrawn and analyzed for the amount of contaminant retained by the rock. Knowing the initial

and final solute concentrations, the volume of the solution, and the mass of the dry rock, the K_d can then be calculated (Pickens et al. 1981). Another approach for K_d measurement is the field tracer test. This test is conducted by injecting the contaminated solution into a formation via a drillhole. After a certain amount of contact time with the rock, water samples are then collected and analyzed for the amount of contaminant retained by the formation.

For systems dominated by fracture flow, Burkholder (1976) defines the distribution coefficient (K_a) and the retardation factor:

R = 1 + (ratio of surface area to void space * K_a)

Previous Work

The majority of previous work relating to chemical changes of acid mine drainage has been concerned with the effectiveness and practicality of various acid drainage treatment procedures. However, more closely related to the research presented in this paper, Crouse and Rose (1976) analyzed the natural ameliorative processes occurring in an acid mine drainage affected stream. concluded that the stream sediments effected beneficiation by consuming hydrogen ions as a result of cationexchange reactions and reactions with primary and secondary silicates. Ciolkosz et al. (1973) conducted soil percolation experiments and laboratory batch tests to analyze the ability of soils to renovate acid mine water. They discovered that maximum effect on pH, total acidity, conductivity, and iron content of the solution occurred within five minutes and in a 1:1 solid to solution ratio. They batch tested 21 Pennsylvania soils and learned that most of the variation of pH. total acidity, and iron were accounted for by cation-exchange capacity and CaCO3 equivalent.

A time-distance acid-front migration finite element analysis is incorporated into the GEOFLOW model of D'Appolonia Waste Management Services, Inc. (Haji-Djafari 1983). The determination of the acidity retardation factor in this model is based only on the neutralization

capacity of the porous media. Through a conversation with one of the GEOFLOW modelers it was learned that much difficulty exists in obtaining reliable results with this acid-transport routine (Snyder 1986). A discussion exists within the GEOFLOW user's manual suggesting the use of laboratory test data "to simulate acid-front migration and variations in solute retardation factors".

Research Objectives

One goal of this research is to determine whether a lithology completely lacking carbonate material, or otherwise possessing a negative acid-base account as determined by Environmental Protection Agency procedures (Sobek et al. 1978), can nevertheless consume acidity through ion-exchange and surface adsorption reactions.

This question was addressed with the development of a laboratory procedure derived from the batch adsorption tests commonly used to describe ion-exchange and adsorption reactions in porous media (Relyea et al. 1980). Upon establishment of a reproducible batch test experimental method, the nature of contaminant transport in coal measure strata was consid-It has been observed that much ered. ground-water flow in the coal measures of western Pennsylvania occurs in rock with very little if any intergranular porosity. The main avenues for ground-water movement in these fracture-dominated flow systems are joints and bedding plane partings in which acid abatement reactions are limited by the available surface area of the fractures and the mineralogy exposed on these surfaces. For these reasons, both weathered and unweathered rock have been analyzed, and available surface area is a controlled parameter in the developed laboratory batch technique. Through additional research it is hoped that this laboratory procedure will be modified into a valid procedure for quantification of the natural acid abatement processes occurring in a fracture-dominated flow system.

DESCRIPTION OF RESEARCH

Rock Sample Collection and Preparation

Figure 1 describes each rock sample used in the laboratory batch experiments. Weathered surfaces were broken off of the highwall samples and treated as separate samples. All samples except the drill cuttings were crushed by a jaw crusher. Representative splits were taken from each sample; part of the split was used for cation-exchange capacity tests. The rest of the split was pulverized for analyses including neutralization potential, maximum potential acidity, x-ray diffraction, and carbonate carbon content. In preparation for the batch experiments, the material not part of these splits was separated into size fractions by mechanical sieving with a nested sieve series and

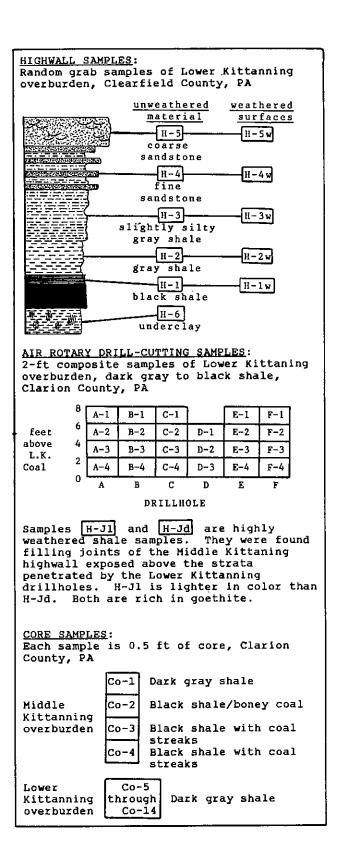


Figure 1.--Description of rock samples used in laboratory batch experiments.

shaker. X-ray diffraction analyses were performed on different size fractions of highwall samples H-2; the material retained on sieve #4 was pulverized and its x-ray pattern was compared to that of the particles passing sieve #100 and the pattern of the initial representative split. All three patterns indicate identical mineralogy.

Batch Test Procedure

Each sample was analyzed for its natural acid abatement capacity through the Following laboratory batch experiment procedure. Rock particles passing the #3 mesh sieve (6.680 mm) and retained on the #4 mesh sieve (4.699 mm) are rinsed in distilled water to remove all silt and clay-sized material. The gravel is then thoroughly dried by compressed air. One hundred grams of the dry particles are placed in a 500 mL Erlenmeyer flask with 100 mL of hydrochloric acid solution (pH = 2.1). The mixture is gently agitated on a wrist-action shaker for 5 hours. The solution is then carefully poured from the rock and its pH, Eh, and temperature are measured. The sample is then filtered, and 50 mL are set aside for total acidity titration. The remaining solution is again measured for pH, Eh, and temperature as well as specific conductance. After these measurements are made the sample is acidified and stored for later analyses of cations and sulfate. At this time the total acidity titration is performed. The rock particles are again rinsed in distilled water, dried, and stored. All water analysis procedures conform to the methods of the U.S. Environmental Protection Agency (1979) and/or the American Public Health Association (1980). The research which led to the development of this laboratory batch test procedure is discussed in the next section.

At this point it should be stressed that at the present stage of research and development, the established laboratory technique can not predict field occurrences. A calibration procedure would need to be developed in order to allow laboratory batch test results to be used in field transport models under variable conditions. The batch experiment procedure described above was derived to yield reproducible results that will address questions such as that stated earlier; i.e., whether lithologies with a negative acid-base account can consume acidity through ion-exchange and adsorption reactions. It is recognized by the authors that a hydrochloric acid solution at a pH of 2.1 does not realistically mimic an acid mine drainage plume. We do feel, however, that this is a logical starting point for continuing research.

Derivation Of The Batch Test Procedure

Highwall samples H-2 and H-3 were used for the trial and error experimentation

which resulted in the procedure described above. These samples were chosen after preliminary rock analyses and batch tests produced favorable results. H-2, a gray shale, has no noticeable intergranular porosity. H-3, a slightly silty gray shale, has very little if any intergranular porosity. They were found to have no carbonate carbon and very little sulfur. The batch tests resulted in significant increases in pH and decreases in total acidity and specific conductance.

Many of the preliminary batch experiments were devoted to the careful control of available rock surface area. One major problem was prevention of particle abrasion and rounding during the contact time. As expected, there was a direct relationship between the decrease in acidity and the amount of mud generated by abrasion. A very specific agitation level was found to be ideal for preventing abrasion; the shaking intensity on the wrist-action shaker was adjusted so that the solution remained slightly turbulent while the rock particles remained stationary. Also contributing to the available surface area are silt and clay-sized particles adhering to the larger particles. It was feared that briefly rinsing the particles in distilled water might cause desorption of ions thereby artificially creating adsorption sites. However, batch tests conducted without rinsing resulted in a greater decrease in acidity than tests conducted with rinsing; the exposed surface area of the fine particles consumed more acidity than did artificially created adsorption sites. Therefore, in evaluating the amount of acidity consumed per unit surface area of rock, not rinsing the particles introduces more error than does rinsing. It was learned that drying the rinsed particles with heat caused them to become brittle and very easily abraded. Drying with compressed air caused no such problem.

Once the above problems were resolved numerous batch tests were conducted on H-2 and H-3 in order to determine a contact time, particle size, and initial solution concentration that would be reasonable and would yield a reproducible batch test procedure. The established values have been mentioned above.

As discussed earlier, numerous rock and water analyses have been performed. However, considering the scope of this paper and space limitations, much of these data are excluded and will be published in the near future. This includes, in particular, cation-exchange capacities of rock samples, and batch-test solution sulfate and cation concentrations. The only data discussed in this paper are of those parameters found in table 1. Furthermore, the geochemical reactions and their kinetics deserve a much more elaborate discussion than can be presented here.

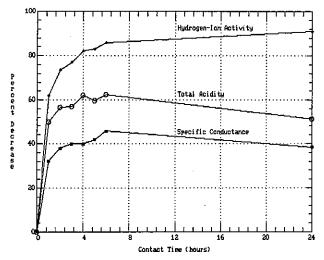


Figure 2.--Change in chemistry versus contact time, sample H-2.

Figures 2 and 3 illustrate the change in chemistry versus contact time for H-2 and H-3 respectively. Particles retained on the #4 mesh sieve were equilibrated with a hydrochloric acid solution of pH = Batch tests were conducted for 1, 2, 3, 4, 5, 6, and 24 hours. Five hours was chosen as the contact time for the remaining tests. Figure 2 shows the decrease in hydrogen-ion activity continuing after 5 hours (the pH continued to rise). In this case it appears 5 hours is a conservative choice. In contaminant transport considerations it is always better to underestimate the adsorption capabilities of an aquifer rather than overestimate it. A peak in the consumption of total acidity and conductance is indicated at about 6 hours. It may be that oxidation of the small pyrite content of H-2 may eventually become an influencing factor. In natural ground-water systems there is much less available oxygen compared to the oxygen available in these batch adsorption experiments. Therefore, in aquifers, pyrite oxidation

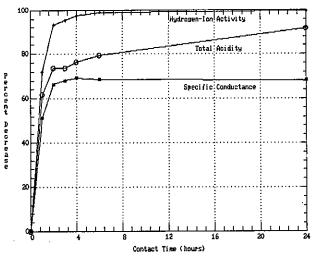


Figure 3.--Change in chemistry versus contact time, sample H-3.

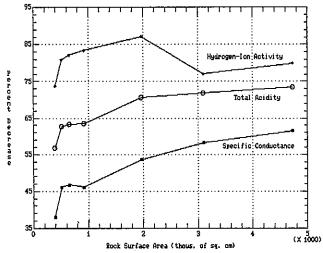


Figure 4.--Change in chemistry versus rock surface area, sample H-2.

is usually limited or prevented. Data supporting this statement are presented later. As will also be discussed later, the occurrence of pyrite oxidation in the batch test versus in the aquifer is an aspect of this research that needs further investigation. Figure 3 shows a relatively constant pH and specific conductance The continued consumption after 5 hours. of acidity may be related to the slight intergranular porosity that H-3 may possess. Once again, it is more conservative and safe to assume only fracture flow when in actuality, some intergranular flow does occur.

Figures 4 and 5 illustrate the change in chemistry versus rock surface area exposed for H-2 and H-3 respectively. The rock was equilibrated with a hydrochloric acid solution of pH = 2.1. Batch tests were conducted for particles retained on mesh numbers 4, 5, 7, 10, 20, 30, and 45. The x-axis scale of these figures is thousands of cm². This surface area was calculated assuming the particles to be

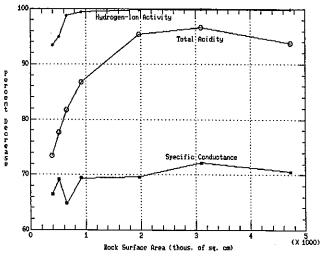


Figure 5.--Change in chemistry versus rock surface area, sample H-3.

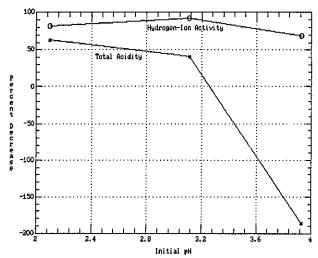


Figure 6.--Change in chemistry versus initial solution pH, sample H-2.

spheres of diameter equal to the average of the mesh sizes of the sieve on which the particle was retained and the sieve the particle last passed. Also assumed was an average density of 2.7 g/cm³. In almost all cases consumption of acidity, hydrogen ions, and conductance increases with increasing surface area. The choice of the largest particles, those retained on #4 mesh sieve, is the most conservative. It is not clear why H-2 did not continue to increase its consumption of hydrogen ions with increasing surface area.

Figures 6 and 7 illustrate the change in chemistry versus initial concentration of the hydrochloric acid solution for H-2 and H-3 respectively. Rock particles retained on the #7 mesh sieve were equilibrated with the solutions. Batch tests were conducted with initial pH values of 2.1, 3.1, 3.9, and 5.4. Once again, the y-axis scale is labeled "percent decrease". Negative values indicate levels of total acidity or hydrogen-ion

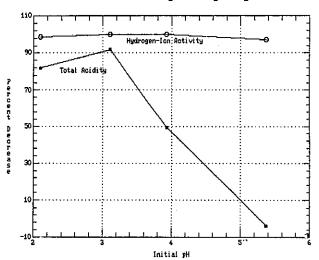


Figure 7.--Change in chemistry versus initial solution pH, sample H-3.

activity greater than the initial solution values. Both H-2 and H-3 consumed a large percentage of hydrogen ions from each of the test solutions. H-3 consumed larger percentages of acidity from the two solutions of higher initial concentration (low pH) than from the solutions of lower initial concentration. The same trend is seen for H-2 (fig. 6). The difference is, however, that H-2 produced acidity when equilibrated with the two solutions of lower concentration. For graphical clarity, the H-2 batch test data with the lowest initial concentration are not presented on figure 6. The test results are an increase of total acidity of 6.5 times and a slight decrease in pH. These data suggest that batch tests conducted with solutions of low initial concentration may not accurately describe field occurrences. As discussed above and below, acid production is suppressed in saturated ground-water systems. Therefore, the solution of highest initial concentration was chosen for the remaining batch experiments.

The above discussion indicates the complications involved with using batch test analyses for predicting the total acidity of ground water in an acid drainage-contaminated aquifer. With further research this problem should be better understood. However, the data do not suggest the same problem with hydrogen-ion activity. Although this parameter will continue to be referred to as the "percent decrease in hydrogen-ion activity", it may also be valid to present the results as the "hydrogen-ion distribution coefficient" as discussed in the introductory sections of this paper. Helfferich (1962) discusses the equation, known as the Freundlich isotherm, which describes ion-exchange equilibria. When considering surface area rather than rock mass, the equation can be written:

$$log S = b log C - log K_a$$

C = Final Concentration

K_a = Distribution Coefficient
b = Slope of the log - log

Adsorption Relation

In order to calculate the distribution coefficient (Ka) from laboratory batch experiment results, it must be shown that the Freundlich isotherm is such that b=1. Figure 8 shows the linear regression of log S versus log C for hydrogen-ion activity measurements of H-3 batch experiments. The slope of the regression line is 0.93 with a correlation coefficient of 0.89. This suggests that the developed batch test procedure may be valid for quantitative measurement of the hydrogen-ion distribution coefficient. Once again, until more field and laboratory research is conducted, this parameter will continue to be referred to as the "decrease in hydrogen-ion activity".

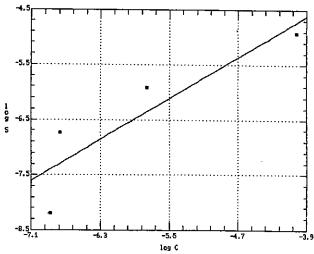


Figure 8.--Log-log adsorption relation with regression line of sample H-3 batch test data.

RESULTS AND CONCLUSIONS

Batch Test And Field Tracer Test Results

Table 1 contains rock analysis and batch test results for all samples shown on figure 1. All batch tests were performed with the technique described above.

All highwall samples are found to be free of, or have very low levels of carbonate material. This includes the highly weathered joint-fill material collected from the Middle Kittanning highwall. H-1 and H-1w are the only highwall samples which have a high potential acidity as calculated from their sulfur content. With the exception of the sulfur-rich samples, the batch test results indicate each of the highwall samples to possess a significant capacity for consuming acidity.

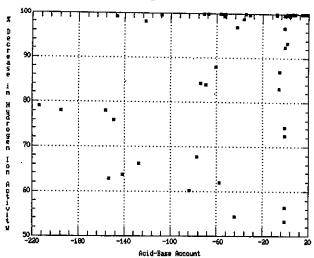


Figure 9.—Decrease in H⁺ activity versus acid-base account (all samples, account in tons of CaCO₃ equivalent per thousand tons of material).

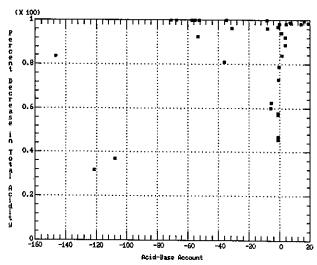


Figure 10.--Percent decrease in total acidity versus acid-base account of samples which consumed acidity (y-axis in hundreds of percentage points).

Figure 9 is a scatter plot of the percent decrease in hydrogen-ion activity versus rock sample acid-base account. All batch tests performed resulted in a decrease of hydrogen-ion activity, including batch tests where total acidity increased and the acid-base account was strongly negative. This adds more support for considering this a measurement of the hydrogen-ion distribution coefficient.

Figure 10 is a scatter plot of percent decrease in total acidity versus acid-base account. The only data presented on this figure are the results of batch tests where total acidity decreased. Acidity was consumed by all samples having an acid-base account greater than -40 tons CaCO3 equivalent per thousand tons of material.

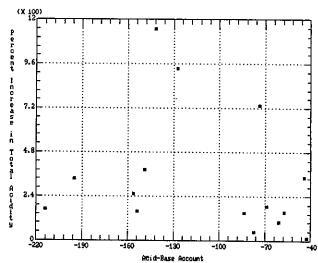


Figure 11.--Percent increase in acidity versus acid-base account of samples which produced acidity (y-axis in hundreds of percentage points).

Table 1.-- Rock Sample characteristics and batch test results.

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0.113 0.444 0.277 0.264	0.0 10 5.2 0.0 0.0 6.0	74 18 4.0 43 200	-74 -8.0 1.2 -43 -200	84 99 100 97	-730 96 94	~89 60 61
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0.277 0.264	5.2 0.0 0.0 6.0	4.0 43 200	1.2 -43 -200	100 97	94	61
1.264	0.0 0.0 6.0	43 200	-43 -200	97		
	0.0 6.0	200	-200		-13	U-71
	6.0				-340	-26
3.551			_36	78 99	-340 81	47
). 293	6.9	3.3	3.7	99	92	62
0.653	11	10	1.0	99	94	51
J. 249	0.0	160	-160	7 8	-260	-18
3.513	5.7	59	-53	99	92	57
3.460	10	3.4	6.6	100	99	63
3.514	16	25	-9.0	100	100	69
0.058	0.0	130	-130	66	-940	-98
598	18	3.3	15	100	98	64
3.442	6.9	130	-123	98	32	35
3.469	7.9	150	-142	99	84	54
3.774	20	12	8.0	100	98	64
o. 920	24	4.5	20	100	99	61
0.715	21	82	-61	88	-99	-29
3.517	5.2	74	-69	84	-190	-42
J. 524	5.4	_37	-32	99	96	48
3.724	8.8	5,2	3.6	99	89	70
0.000	0.0	44	-44	54	-340	~22
0.000	0.0	58	-58	62	-150	-0.1
0.000	0.0	77	-77	68	-48	20 46
1.274	91	75	16	100	100	46 39
						28
0.609						33
0.338						41
0.338 0.309						_
0.338 0.309 0.473						45 30
0.338 0.309 0.473 0.287						-1.6
0.338 0.309 0.473 0.287 0.333	1.1					-1.6 -38
0.338 0.309 0.473 0.287						-6.3
	609 338 309 473 287 333	.609 42 338 31 .309 31 .473 42 287 27 333 32 127 11 001 0.0	609 42 77 938 91 83 939 91 88 479 42 97 287 27 98 933 92 99 127 11 120	609 42 77 -35 338 31 83 -52 309 31 88 -57 473 42 97 -55 287 27 98 -71 393 32 99 -67 127 11 120 -109 001 0.0 150 -150	609 42 77 -35 100 338 31 83 -52 100 309 31 88 -57 100 473 42 97 -55 100 287 27 98 -71 100 333 32 99 -67 100 127 11 120 -109 99 001 0.0 150 -150 76	609 42 77 -35 100 100 338 31 83 -52 100 100 309 31 88 -57 100 100 473 42 97 -55 100 100 287 27 98 -71 100 100 333 32 99 -67 100 100 127 11 120 -109 99 37 001 0.0 150 -150 76 -390

Figure 11 is a scatter plot of percent increase in total acidity versus acid-base account. The only data presented on this figure are the results of batch tests where total acidity increased. A comparison of this figure to figure 10 shows that some batch tests of samples with acid-base accounts greater than -140 and less than -40 resulted in a decrease in total acidity while others resulted in am increase in total acidity. Analysis of rock parameters not listed in table 1 did not clearly show which characteristics indicate whether a sample will increase or decrease acidity in the laboratory batch experiments. Further research is needed in this area.

Figure 12 shows the acid-base accounting for all of the drill-cutting samples. Fifteen of the 23 samples are found to have a negative account. The average acid-base account of the 23 samples is -53 tons CaCO3 equivalent per thousand tons of material. Figure 13 shows the percent change in total acidity for each drill-cutting sample. Positive numbers indicate percent decrease of the initial total acidity. Negative numbers indicate percent increase of the initial total acidity. Fifteen of the 23 samples consumed acidity. As mentioned earlier, each test resulted in a decreased hydrogen-ion activity. Field acidinjection tracer tests were conducted

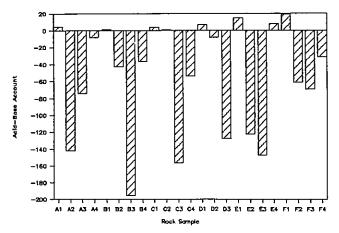


Figure 12.--Acid-base account of drill cutting samples (in tons of CaCO₃ per thousand tons of material).

in the drillholes from which these samples were collected. The tests resulted in an approximate 50% decrease in both the hydrogen-ion activity and total acidity. These calculations consider the natural dispersion of the aquifer. Although the aquifer rock was found to have a negative acid-base account, and some drill-cutting batch tests resulted in significant acid production, these field tests suggest that the natural abatement processes dominate in an acid-contaminated aquifer. If pyrite oxidation does occur, it is of secondary importance in acid migration predictions. A detailed description of the field methods and the results is not presented here, but will be published in the future.

Summary Statements

(1) A laboratory technique has been established which may enable the quantification of the hydrogen-ion distribution coefficient. With additional research, it

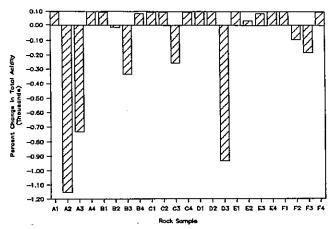


Figure 13.--Percent change in total acidity for drill-cutting samples (y-axis in thousand of percentage points. Positive no. indicates acidity consumed, negative no. indicates acidity produced).

may eventually provide the necessary information for modeling acid contaminant transport.

- (2) All laboratory batch tests resulted in an increase in pH, regardless of whether acidity was consumed or produced and regardless of the acid-base account.
- (3) All samples lacking carbonate material and having low sulfur content were found to have a significant acidconsuming capacity.
- (4) All samples having an acid-base account greater than -40 (tons CaCO₃ equivalent per thousand tons of material) consumed acidity in the batch experiments.
- (5) Some samples having an acid-base account greater than -140 but less than -40 consumed acidity in the batch experiments.
- (6) Field tracer tests show that an aquifer can have a significant natural capacity to abate acid mine drainage even if it has an overall negative acid-base account and contains some rock which will produce acidity in laboratory batch experiments.

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