

PENETRABILITY AND HYDRAULIC CONDUCTIVITY OF DILUTE
SULFURIC ACID SOLUTIONS IN SELECTED ARIZONA SOILS¹

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INTRODUCTION

Sulfuric acid (H_2SO_4) is the common oxidation product of the sulfur liberated in large amounts from smelting, oil and coal burning, and mining processes. In the Southwest, the H_2SO_4 comes mostly from the oxidation of SO_2 produced from copper smelters in the amount of 5 million tons H_2SO_4 /year (McKee, 1965). Waters draining from coal and metal mining sites contain H_2SO_4 from the natural oxidation of sulfides and sulfhydryl groups are known as acid mine wash and cause contamination of streams and some-times soils (Elevins, et al., 1970; Terkeltoub, 1971).

The application of H_2SO_4 to soils and water can be harmful or beneficial for plant growth depending primarily upon application rates, methods and the buffering capacities of the soil and water against acidification. In southern Arizona, soils are generally calcareous and the water contains substantial amounts of bicarbonate. Both are basic buffering constituents against acidification. The proper application of H_2SO_4 to such soils and water is not only safe but also beneficial for plant growth mainly through increasing micronutrient availability (e.g., Ryan, et al., 1973) and decreasing sodium hazard (e.g., Tisdale, 1970).

For deciding better H_2SO_4 application practices, the flow properties of H_2SO_4 solutions in soils must be know. This paper presents the effect of H_2SO_4 concentrations on the solution penetrability, (the rate of solution entry into dry soil, Mustafa, et al., 1970) and the hydraulic conductivity of the solutions in selected Arizona soils.

EXPERIMENTAL

Surface soils collected in southern Arizona were air dried and sieved through a 1 mm screen. Some of their properties are listed in Table 1. The soils, except Mohave, have high carbonate contents as indicated by the acid-titratable basicity (Miyamoto, et al., 1973). The acid-titratable basicity is the measure of readily-reactive basic constituents and is slightly greater than the carbonate content.

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Table 1. Some properties of the selected Arizona soils (<1 mm fraction).

Soil	Acid-titratable	Silt and	Saturation Extract		Clay Minerals
Series	Basicity	Clay	Na	Ca + Mg	
	eq/kg	%	-----ppm-----		
Neutral					
Mohave	0.08	29	4	65	Mica, Kaol.
Calcareous					
Elfrida	.54	76	230	1190	Mont.,Mica,Kaol.
Anthony	.72	36	13	313	Mica, Mont.
Perriville	1.04	59	95	1870	Mon.,Mica
Cogswell	1.36	79	42	341	Mica, Mont.
Cave	1.92	53	13	61	Mica, Kaol.
Karro	2.48	57	55	410	Mont. Mica
Sodic					
Stewart	0.99	79	1500	4	Mica, Analcine

The synthetic irrigation water contained 3.1 meq/l total salts (NaCl, CaCl₂ and MgCl₂) with a sodium adsorption ratio of 30. No bicarbonate was present. Streptomycin (50 ppm) was added to suppress microbial growth. The water was not deaerated. The H₂SO₄ concentrations were 0, 500, 1,000, 5,000, 10,000 and 20,000 ppm by weight, having pH values 6.8, 2.2, 2.0, 1.6, 1.4, 1.0 and 0.7, respectively.

The soil samples were packed with a vibrator into a plastic column (7.5 cm ID) to depths of 10 cm and 30 cm. The depth of the solution penetration front was measured with time in 10 cm and 30 cm columns at a constant 2 cm water-head to determine penetrability. The hydraulic conductivity was measured periodically for a week or more in the 10 cm soil column at a constant 10 cm water-head. The differences in duplicate penetrability and conductivity values were approximately within 5 and 15% of the average values, respectively.

Some soil columns were divided into 1 cm sections and analyzed for the changes in acid-titratable basicity after penetration of the 1000 ppm H₂SO₄ solution.

RESULTS

Penetrability. The depth of the solution penetration front is plotted vs. the square root of penetration time for three soils in Fig. 1. This plot gave a good linear relation for all the soils, including the 30 cm column, but did not pass through the origin when extrapolated back to zero time. This positive intercept is probably due to the positive water-head applied. The penetrability values, more strictly the vertical penetrability, is the slope of the lines in Fig. 1. Corrections for the density, viscosity and surface tension of the solutions were neglected because their changes were insignificant under the experimental conditions used here. Since the positive intercepts are less than 0.5 cm, the penetrability value alone should approximate the infiltration under shallow pondings.

The penetrability values are plotted vs. the log of the H_2SO_4 concentration in Fig. 2 for the three types of soils. In the neutral Mohave soil, the penetrability decreased gradually with the concentration, and in the sodic Stewart soil it increased with H_2SO_4 concentration up to 10,000 ppm, then decreased. In the calcareous Anthony soil, little change occurred up to 10,000 ppm. The identical trend was observed for all calcareous soils tested.

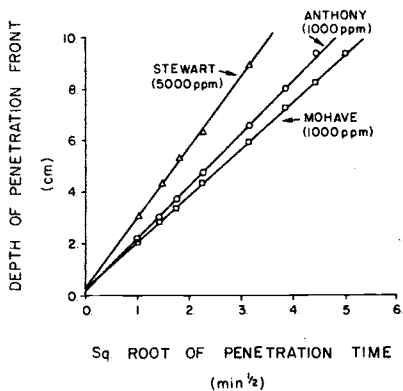


Figure 1. Depth of penetration front vs. square root of penetration time in three selected soils. H_2SO_4 concentrations are shown in parenthesis.

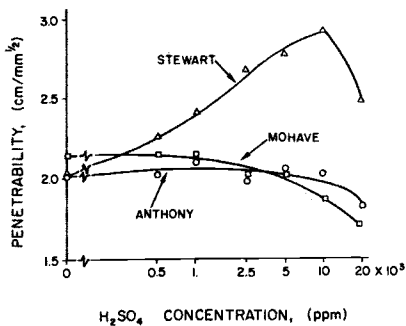


Figure 2. Effect of H_2SO_4 concentration on the penetrability of three types of soils; Mohave (neutral), Anthony (calcareous) and Stewart (sodic).

Hydraulic Conductivity

The conductivity changed with time or the volume of solutions passed. At 0 and 500 ppm solutions, it approached a stable value after 2 to 8 days. Those stable conductivities are listed in Table 2.

Table 2. Penetrability and hydraulic conductivity of selected Arizona soils.

Soil Series	Penetrability Water	Hydraulic Conductivity			Average Conductivity 500 ppm H_2SO_4
		Water	500 H_2SO_4	Increase	
	cm/min ^{1/2}	-----cm/hr-----			cm/hr
Mohave	2.13	0.75	2.40	220	--
Elfrida	1.08	0.05	0.24	380	0.25
Anthony	2.00	1.63	1.82	11	1.80
Perryville	1.50	0.22	0.48	118	0.42
Cogswell	1.46	0.60	0.51	-15	0.55
Cave	2.79	2.10	2.14	19	2.11
Karro	1.91	1.00	1.70	70	1.64
Stewart	2.02	0.42	0.42	0	0.75

In the calcareous soils, the conductivities of 500 ppm solution were significantly larger than those of water only in montmorillonitic ones; Elfrida, Perryville and Karro soils. In the neutral Mohave soil, the significant increase was also observed. In the sodic Stewart soil, the conductivity increased significantly at 1000 ppm. Also presented in Table 2 is the average hydraulic conductivity until the applied H_2SO_4 solution (500 ppm) neutralizes the basicity to a 10 cm soil layer. Those values are approximately the same as the stable conductivities at 500 ppm.

At higher concentrations, the conductivity in all calcareous soils decreased at first, then increased with time. The time of the onset of flow reduction increased with higher acid-titratable basicity of the soil and lower flow rates. The initial reduction was severe at the higher H_2SO_4 concentrations; flow ceased temporarily at 10,000 and 20,000 ppm H_2SO_4 , then increased erratically. When flow ceased, the CO_2 was observed as a distinct layer in the soil column. This mechanism is different from air entrapment (Christiansen, 1944). The smoothed data obtained from the Anthony soil are shown in Fig. 3 as an example of all the calcareous soils. The erratic recovery of flow, indicated by the dashed arrows, usually occurred when the amount of added H_2SO_4 equalled the basicity of the soil in the column. At this time, of course, CO_2 production ceased. This equivalence of H_2SO_4 and acid titratable basicity is shown by the saturation point in Fig. 3.

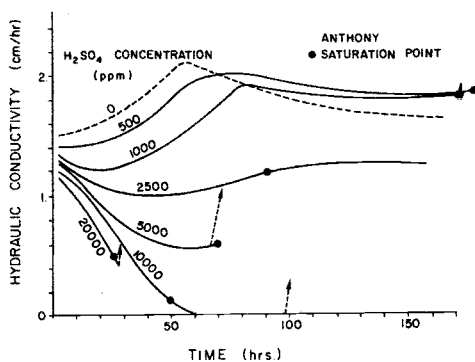


Figure 3. Changes in hydraulic conductivity of H_2SO_4 solutions with the percolation time in a calcareous soil. Saturation point referred to the neutralization of soil's basicity by applied H_2SO_4 .

In the sodic Stewart soil, the hydraulic conductivity changed with time similar to the calcareous soils, but the initial reduction was less. The conductivity increased after a small reduction to large values such as over 5 cm/hr when the concentrations were between 1,000 and 10,000 ppm. At 20,000 ppm, the conductivity decreased continuously and approached a smaller value. In the neutral Mohave soil, the conductivity of all solutions did not decrease initially, but increased to stable values which are presented in Figure 4.

For calcareous and sodic soils, the average conductivity of each solution to neutralize the basicity to a depth of 10 cm layer was determined. The results are shown in Fig. 4 for the Anthony and the Stewart soils. The average conductivities of other calcareous soils are presented in Fig. 5 as a

relative value to those at 500 ppm. (The average conductivities at 500 ppm are listed in Table 2). The symbols in Fig. 5 are not identified because the relative values are about the same for all calcareous soils tested.

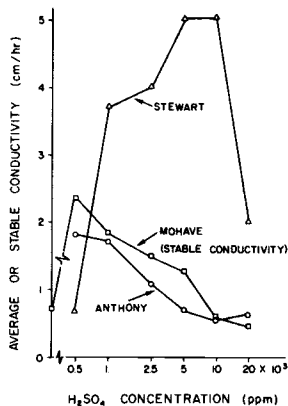


Figure 4. Effect of H₂SO₄ concentration on the average hydraulic conductivity in Stewart and Anthony soils, and on the stable conductivity in Mohave soil.

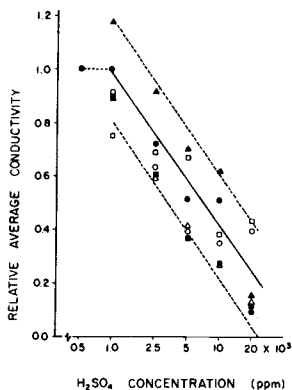


Figure 5. Effect of H₂SO₄ concentration on the average conductivity relative to 500 ppm solution in calcareous soils. Dashed lines are \pm 20% variance.

Changes in Acid-titratable Basicity

The changes in the acid-titratable basicity with depth after penetration of the H₂SO₄ solutions (1000 ppm) to the designated soil depth are shown in Fig. 6 for the Anthony and the Cave soils. The H₂SO₄ reacted at the soil surface and lagged behind the solution penetration front, indicating the faster reaction rate than the rate of water entry. As the volume of the solution applied increased, the reacting front moved down. During the penetration of the H₂SO₄ solutions, CO₂ evolved extensively upon the reaction with carbonates in the calcareous and the sodic soils.

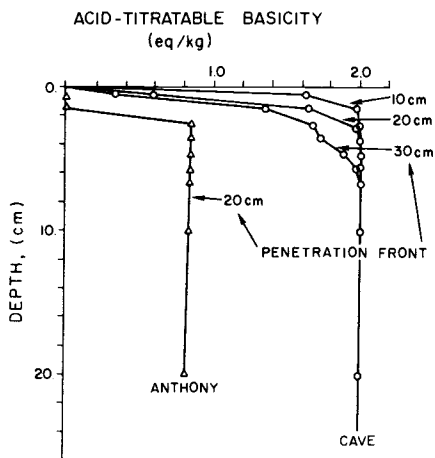


Figure 6. Distribution of acid-titratable basicity after penetration of 10,000 ppm H₂SO₄ solution to the designated depth.

DISCUSSION

The most important findings of these preliminary experiments are probably the severe decrease in hydraulic conductivity in calcareous soils with increasing concentrations over 1000 ppm, and that little change occurred in penetrability. The applied H_2SO_4 reacts with the basicity, mostly carbonates, and generates CO_2 . Based on the acid-titratable basicity of the soils, the volume of CO_2 evolved should be about 10 to 50 times the reacted soil volume. The reacted layer during the penetration is limited in a few centimeters in the soil surface (Fig. 6). The CO_2 generated probably escaped through this thin layer without interfering with the penetration. As the volume of H_2SO_4 solution passing through the soil increases, the reacting front moves to depths from which CO_2 may not readily escape. The conductivity, then should decrease with time as shown in Fig. 3. At the peak of CO_2 "build-up", it forms a distinct layered space in the soil even though both sides of the 10 cm soil column are open to the atmosphere. Upon completion of the neutralization reaction, the CO_2 evolution ceases. Then the conductivity increases to some large values due to leaking through channels formed by the escaping CO_2 .

This finding suggests that the disposal of H_2SO_4 solutions into calcareous soils will result in plugging by the CO_2 at concentrations of 1 or 2%. Even at lower concentrations, the solution movement will decrease with time if discharged continuously. For the purpose of maintaining good solution movement, the H_2SO_4 concentrations less than 1000 ppm would be safe for disposal (Fig. 5). Approximately 3,500 tons H_2SO_4 /hectare/meter (or 3.5×10^6 tons of 1,000 ppm H_2SO_4 solution) can be disposed without lowering the conductivity and the pH of leached water for the soils with a basicity of 5 eq/kg. The increase in salt concentration of the leached water, however, requires the special attention when solutions with higher concentrations of H_2SO_4 are applied to the soil surface for improving micro-nutrient availability in calcareous soils, the effect on solution penetrability is of little significance.

In the sodic Stewart Soil, both penetrability and conductivity increased with increasing H_2SO_4 concentrations up to 10,000 ppm, but decreased at 20,000 ppm. At least two opposing factors are involved; increase in salts, especially divalent cations which increase the conductivity (McNeal, et al., 1966), and increase in the CO_2 evolution which decreases the conductivity. The significant increase in conductivity of the H_2SO_4 solutions over the water indicates the possibility of using dilute H_2SO_4 for reclaiming salt and sodium affected soils. It would be especially effective in decreasing the time required for completing leaching and presumably in replacing sodium. Further studies are needed to determine the amounts, methods of application and subsequent changes in water movement.

The stable hydraulic conductivity of 500 ppm H_2SO_4 solutions was significantly higher than that of water alone in montmorillonitic calcareous soils. Similar results were also reported in some California soils (Mohammed, 1972). The disposal of H_2SO_4 , SO_2 , and acid mine wash into the irrigation water (Bohn and Westerman, 1971; Terkeltoub, 1971) will promote water movement in such soils. In the Elfrida and Perryville soils which tend to accumulate salts, the improvement of water movement will be especially effective for maintaining the salt balance in the plant root zone. The addition of H_2SO_4 will be more effective in increasing water movement when the irrigation water contains relatively high sodium and bicarbonate yet low

total salts (McNeal, et al., 1966). The acidity of water will remain above pH 5 if the application rates of H_2SO_4 do not exceed the bicarbonate of the water content (Bohn and Westerman, 1971). In sodic soils, such a practice will not improve water movement within a short time. Heavy pre-treatments with higher concentrations of H_2SO_4 should accomplish a faster response in improving water movement.

SUMMARY

The penetrability and hydraulic conductivity of dilute H_2SO_4 solutions in selected Arizona soils were measured in preliminary laboratory experiments. In six calcareous soils, the penetrability decreased slightly with increasing H_2SO_4 concentration. The conductivity decreased at concentrations greater than 1000 ppm and flow ceased temporarily at 10,000 and 20,000 ppm. CO_2 evolution appeared to be responsible for the flow reduction and cessation at higher H_2SO_4 concentrations. The stable values of hydraulic conductivity for 500 ppm H_2SO_4 were significantly higher than that for water in montmorillonitic calcareous soils. In a sodic soil, the penetrability and conductivity increased markedly with H_2SO_4 concentration between 1000 to 10,000 ppm. In a neutral soil the penetrability decreased with increasing H_2SO_4 concentration but the stable conductivity for 500 to 5,000 ppm was higher than for water alone.

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