HYDROLOGIC EVALUATION OF INDUSTRIAL-WASTE INJECTION AT MULBERRY, FLORIDA[1]

W. E. Wilson,[2] J. S. Rosenshein,[2] and J. D. Hunn[2]
Tampa, Florida

ABSTRACT Florida's deepest waste-injection well, completed in 1972 at a chemical plant at Mulberry, will inject acid industrial waste into carbonate rock. The plant produces sodium fluosilicate from the reaction of sodium chloride with fluosilicic acid, a byproduce of nearby phosphate-processing plants. The resulting liquid waste, which is to be injected into the subsurface, has a high chloride content and a pH that is generally less than 2, and at times less than 1.

The cased injection well is finished as a 6 1/4-in. open hole in dolomite and limestone, from 4,040 to 4,984 ft below land surface. The injection-well annulus has two monitor wells, one open near the base of the Floridan aquifer from 1,254 to 1,264 ft, and the other open to the saline-water aquifer below the Floridan aquifer, from 2,755 to 2,788 ft. Before injection tests were made, geophysical logs and a tracer test were run on the well. The radioactive-tracer test indicated that several permeable zones are exposed in the open hole.

The native fluids, sampled prior to injection, and the waste fluid are markedly different in density, chloride content, and temperature.

Two injection tests were run in the fall of 1972 using the waste fluid. The injection rates during the first test were inadequately controlled. During the second test, waste fluid was injected for 118 hours at 270 gpm and pressure readjustment after shutdown was observed for 5 days. Injection pressure measured at the surface increased for the first 31 hours, and then decreased for the remainder for the injection period. The decrease in pressure after 31 hours is attributed to the net effect of reactions that occurred in the injection zone during the tests. Dissolution of limestone by the low-pH waste substantially increased the permeability of the rock adjacent to the well bore and increased the density and temperature of the injection fluid as it moved into the injection zone. These changes, coupled with the unavailability of direct bottom-hole pressure measurements in the injection well and the lack of water-level measurements in an observation well finished in the injection zone, complicated the evaluation of test results. As a result, only a general estimate of injection-zone transmissivity (less than 800 sq ft/day) could be made.

Where acid wastes are to be injected into carbonate rocks, evaluation of aquifer coefficients would be facilitated by the use of a fluid other than a reactive waste as the injection fluid during initial tests, and by measuring bottom-hole pressures in the injection well and water levels in observation wells open to the injection zone.

INTRODUCTION

Florida's deepest waste-injection well was completed in 1972 at the Kaiser Aluminum and Chemical Corporation plant at Mulberry, about 30 mi east of Tampa (Fig. 1). As of 1972, the well was one of seven deep-well disposal systems in the State and was the first to be completed in the west-central part of the peninsula. When operational, the well will inject acidic, high-chloride industrial wastes into a carbonate zone about 4,000-5,000 ft below the land surface.

The U.S. Geological Survey participated in the collection and evaluation of data during the initial injection tests at the request of the Florida Department of Pollution Control. Evaluation of the results indicates some of the difficulties associated with the assessment of hydrologic conditions when acid wastes are injected into a carbonate environment, especially where monitoring facilities are limited. The study is part of the Geological Survey's research program to evaluate the effects of underground waste-injection on the nation's subsurface environment.

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[2] Hydrologists, U.S. Geological Survey.

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HYDROGEOLOGIC FRAMEWORK

The injection well at Mulberry penetrates nearly 5,000 ft of sedimentary rocks, chiefly limestone and dolomite, ranging in age from Late Cretaceous to Holocene (Fig. 2). The log shown in Figure 2 is based on a preliminary examination of well cuttings from the injection well by the Florida Bureau of Geology; lithologic descriptions and the positions of formation contacts may be subject to revision.

Freshwater supplies in the area are obtained principally from the Floridan aquifer. This aquifer is present throughout Florida and parts of other southeastern states and yields abundant supplies for industrial, agricultural, and municipal uses. In Polk County, groundwater withdrawals for these purposes averaged about 420 million gal/day in 1970 (Pride, 1973). As a result of long-term withdrawals of similar magnitudes, the potentiometric surface of the aquifer declined more than 40 ft in Polk County from 1949 to 1969 (Stewart et al., 1971).

At Mulberry, the Floridan aquifer consists of about 1,300 ft of limestone and dolomite (Fig. 2). As in most of Polk County, the uppermost unit of the aquifer is the Suwannee Limestone, and the aquifer base coincides with the base of the Avon Park Limestone (Stewart, 1966). At the well site, this base is about 1,545 ft below land surface. The underlying Lake City Limestone is chiefly dolomite containing 1-5 percent of intergranular anhydrite and gypsum. The Oldsmar Limestone and the upper part of the Cedar Keys Limestone, designated the saline-water aquifer, consist of limestone and dolomite with as much as 20 percent porosity.

The middle part of the Cedar Keys Limestone, 780 ft thick, consists of alternating beds of anhydrite and dolomite. Impermeable anhydrite makes up about 45 percent of the unit; the beds are mostly 10-50 ft thick, but the upper anhydrite bed is 135 ft thick. The interbedded dolomite has low permeability and a porosity of about 5-10 percent. This anhydrite-dolomite section has been recognized in oil test wells in central Florida and apparently is regionally extensive.

The lower part of the Cedar Keys Limestone of Paleocene age and the underlying Lawson Limestone of Late Cretaceous age and beds of Tayloran age, more than 880 ft thick, consist of poorly to moderately indurated, vuggy dolomite and chalky limestone containing brine. Examination of well cuttings and analyses of sidewall cores indicate that this section generally has low permeability. Permeabilities of 8 sidewall cores of the Cretaceous rocks, taken from 4,500 to 4,950 ft below land surface, ranged from 5.0 to 28 md; the hydraulic conductivities ranged from 0.021 to 0.120

ft/day. Average values were 13 md, or 0.055 ft/day. However, radioactive-tracer tests indicate the presence of several zones with relatively high permeability; the most permeable of these is near the base of the lower part of the Cedar Keys Limestone, from about 4,340 to about 4,480 ft below land surface. The porosity of this section ranges from 5 to 10 percent.

The permeable zones of the lower part of the Cedar Keys and underlying units constitute potentially usable deep injection zones. Under undisturbed conditions, or before pumping or injection, fluid in this section was effectively confined by overlying low-permeability dolomite and anhydrite in the lower and middle parts of the Cedar Keys Limestone.

Head Relationships

Substantial differences exist among the hydraulic heads in the Floridan aquifer, saline-water aquifer, and injection zone. Measured heads in the lower part of the Floridan aquifer and in the saline-water aquifer before injection testing were about 76.5 and 60 ft below land surface, respectively. These water levels are equivalent to freshwater heads of 72 and 46 ft below land surface. In the 1950's, the head in the Floridan aquifer was about 32 ft below land surface, and the local vertical gradient in the upper 3,000 ft of rock was downward. Since that time, large-scale withdrawals of water from the Floridan aquifer for industrial and agricultural uses have resulted in a lowered head and a reversal in gradient between the Floridan aquifer and the saline-water aquifer. Before injection was started, the static level of the brine in the injection zone was about 125 ft below land surface, or equivalent to a freshwater head of about 150 ft above land surface. The injection zone is possibly hydraulically isolated from the overlying flow system, and little regional circulation of water occurs under natural gradients at this depth.

INJECTION FACILITIES

The Kaiser plant at Mulberry produces sodium fluosilicate from the reaction of sodium chloride with fluosilicic acid, a byproduct of nearby phosphate-processing plants. Prior to drilling of the injection well, this acidic, high-chloride waste was discharged into a 30-acre lake, where it overflowed and seeped into nearby streams.

When the injection well goes into operation, the plant effluent will flow by gravity to a lined storage pond from which it will be transferred to a 40,000-gal rubber-lined surge tank. From there the waste will be pumped into the well. Average injection rate is expected to be about 250 gpm (gallons per minute), with an anticipated range of 150 to 300 gpm.

The injection well is cased and grouted to 4,040 ft below land surface, and is a 6 1/4-in. open hole from 4,040 to 4,984 ft (Fig. 2). The 7 5/8-in. casing does not extend through the full thickness of the anhydrite-dolomite confining beds. One of the anhydrite beds is exposed in the upper part of the open hole, from 4,084 to 4,104 ft below land surface. A 4 1/2-in. fiberglass injection tubing extends 411 ft into the open hole; the bottom 30 ft of the tubing is slotted. The 140-ft zone of relatively high permeability in the lower part of the Cedar Keys Limestone is in the upper third of the open-hole section. About 80 ft of this zone is above the top of the slotted section of injection tubing.

The annulus between the fiberglass injection tubing and the steel casing is sealed off from the open hole by a noncorrodible packer assembly. The annulus contains sensors to monitor changes in pressure and conductivity that might reflect leaks in the casing, packer, or injection tubing.

Two monitor wells were installed in the grouted part of the injection-well annulus between the 10 3/4-in. casing and the rock wall. The wells consist of 2 3/8-in. tubing and are open to the surrounding rock formations by perforations that extend through the tubings and grout (Fig. 2). The shallower one is open to the lower part of the Floridan aquifer, from 1,254 to 1,264 ft, and the deeper one is open to the saline-water aquifer from 2,775 to 2,788 ft. The wells are equipped for collecting water samples and measuring water levels.

WATER QUALITY

Chemical analyses of samples from the two monitor wells, the injection zone, and the waste effluent are summarized in Table 1. The analyses show that groundwater increases in mineralization in the three successively deeper zones sampled. On the basis of dissolved-solids content (Hem, 1970, p. 219), the waters are classified as moderately saline in the basal part of the Avon Park Limestone and in the Oldsmar Limestone, and as brine in the injection zone. The waters also increase in temperature and density with depth, and water in the injection zone contains substantially higher concentrations of trace metals than those in the two shallower zones.

The waste effluent contains hydrochloric acid and sodium chloride and has a very low pH. In the sample analyzed, the pH was 1.5 (Table 1), and values less than 1.0 have been measured. Chloride content was 66,000 mg/l, similar to that of the native fluid in the injection zone (Table 1). Compared to the native fluid, the waste sample contained higher concentrations of fluoride, arsenic, chromium, copper, mercury, nickel, and zinc. The waste effluent is cooler and less dense than the native fluid. These differences in temperature and density were considered in analyzing the response of the injection zone during injection tests.

The highly acid waste will be neutralized by reacting with the calcium carbonate in the injection zone. Under temperatures and pressures of the system, the carbon dioxide produced by the reaction is expected to remain in solution. Solution of calcium sulfate will also occur wherever the acid waste comes in contact with anhydrite; the 20-ft bed exposed in the open hole is directly subject to this solution activity.

INJECTION TESTS

Two tests were conducted on the injection well during the period from August 29 to October 14, 1972. In both tests, the injection fluid was waste effluent containing 4 percent by weight of hydrochloric acid. Pressure at the well head and water levels in the two monitor wells were observed during injection, and the decline in fluid level in the injection well was measured after injection ceased. The change in fluid level (partially adjusted for temperature and density differences) with time was used with the nonequilibrium-type curve of Theis, and Hantush's nonsteady-state-type curve for leaky artesian aquifers, to estimate the transmissivity of the injection zone (Ferris et al., 1962; Walton, 1970).

The first test, a preliminary one, began on August 29 and ended on September 1, 1972. The injection rate averaged 180 gpm for the 53-hour test and ranged from 100 to 300 gpm, with two periods of no injection lasting 2.8 and 0.8 hours. During the last 1.8 hours, injection was maintained at about 320 gpm. Pressure in the injection well at the surface rose to a maximum of 155 psi after 9 minutes (0.2 hours) and then declined. At the maximum pressure, the head of the brine in the injection zone (corrected for friction loss) was 46.9 ft above land surface. During the rest of the test, pressure and head varied markedly with variations in the injection rate. The head in the injection zone at the end of injection was 96.9 ft below land surface. The fluid level declined to 128.4 ft below land surface 12 hours after injection stopped. Measurement of fluid-level decline during the early part of recovery was hampered by foam in the injection well. A fit to the data for the first 200 minutes (3.3 hours) of recovery was obtained with the Theis curve. After 210 minutes (3.5 hours) of recovery, the data began to deviate from the Theis curve, and a fit of the data was obtained with the Hantush curve for r/B = 0.01. The apparent transmissivity of the injection zone using the type-curve match point and the average injection rate was computed to be 800 sq ft/day. The rate of pressure increase during the first few hours of injection indicates that the transmissivity of the injection zone is probably less than 800 sq ft/day and may be as small as 400 sq ft/day.

The second injection test consisted of a 118-hour injection phase and a 76-hour recovery phase ending October 14, 1972. Waste effluent with a pH of 1.5 was injected at a nearly constant rate for 118 hours. During the first 9 minutes of injection, the pressure in the well at the surface increased to 69 psi as the injection rate increased to 280 gpm. At this pressure, the head of the brine in the injection zone (corrected for friction loss) was 67 ft below land surface. The injection rate was adjusted to 270 gpm and remained constant for the rest of the test. The injection pressure declined to 62.5 psi at the surface and the adjusted head dropped to 77 ft below the surface. At the end of 31 hours, the pressure had gradually risen to 65.5 psi and the head to 70.1 ft. From 31 to 112.5 hours the pressure gradually declined to 40.5 psi and the head to 127.7 ft, where they remained until the end of the injection phase of the test.

After 76 hours of shutdown, the fluid level in the injection well had declined (recovered) from 127.7 to 151.7 ft below land surface. A match to the Theis curve was obtained using data from the first 330 minutes (5.5 hours) of recovery (Fig. 3). After about 330 minutes, the data deviate from the Theis curve, and a fit to a Hantush curve was obtained from 330 to 4,560 minutes (5.5 to 76 hours). These data fit the curve r/B = 0.01. The apparent transmissivity computed from this test is 2,000 sq ft/day.

Water-level fluctuations in the monitor wells during both tests showed no direct response to injection. For the second test this lack of response is shown by hydrographs in Figure 4. Semidiurnal fluctuations and broad trends during the tests are chiefly related to changes in barometric pressure; the water level in the shallow monitor well may also be affected by pumping of nearby wells.

HYDROLOGIC IMPLICATIONS OF TEST RESULTS

The different values of transmissivity obtained from the recovery phases of the two tests are attributable principally to the reaction of acid waste on the rock in the injection zone. With each injection test the permeability and porosity of the injection zone in the immediate

vicinity of the well apparently increased significantly. Although the test data were adjusted for temperature and density differences where possible, some of the difference in apparent transmissivity may be caused by undefined changes in conditions between the two tests.

The increase in permeability and porosity probably was concentrated along certain zones and occurred at a nonuniform rate. Although the interval from 4,040 to 4,984 ft in the injection well is completed as open hole, only part of the exposed rock is permeable. Radioactive-tracer tests conducted prior to waste injection indicated that the most permeable zone extends from about 4,340 to about 4,480 ft below land surface. Because most of the waste undoubtedly moved from the well into the rock along this permeable zone, the increase in porosity and permeability was probably also concentrated along this zone. However, it is possible that additional permeable zones were opened to the well by the acid waste. During the second test, the rate of increase of permeability and porosity, as a percent of the original values, was probably greatest from 6 to 80 hours and smallest during the later part of the test.

The injection zone apparently responded as though it were a leaky-layer system, as indicated by the deviation of test data from the Theis curve. Although this response may be attributed partly to the effects of rock dissolution in the injection zone, it also indicates possible leakage of fluid into the overlying and underlying confining layers.

The limited test facilities and complex test conditions at this site complicate the analysis of the data. Because of density differences between the waste and the native fluid in the injection zone, monitoring of pressure at the injection-well head provided only partial information on the changes occurring in the injection zone, and no reliable information on leakage through the confining layers. Using a fluid that reacted with the rock and with the confining layers for the initial testing posed major difficulties in data collection and analysis. Sufficient acid waste was injected during the second test to dissolve more than 5,000 cu ft of carbonate rock and raise the temperature of the injected fluid several degrees Celsius. This temperature increase further complicated the problem of data analysis, particularly because significant temperature and density differences already existed between the native fluid and the waste.

Despite these complications, the injection tests indicated that the permeability and porosity of the carbonate rock in the injection zone were altered by reaction with the acid waste and that there may be some leakage through the confining layers. However, the tests were inadequate to provide reliable estimates of the hydraulic characteristics of the injection zone or a leakage coefficient of the confining beds. The amount of leakage, if any, through confining beds has not been assessed.

The inconclusive results obtained from the analysis of the injection test emphasize the need to include at least one observation well in the injection zone and to obtain bottom-hole pressure measurements in systems designed to place a reactive waste fluid at depth. The results further indicate that leakage through confining beds may occur even at depths as great as 5,000 ft below land surface if a deep hydrologic system is stressed. Initially this leakage probably would represent chiefly movement of displaced native fluid. However, as the cone of influence of the injected fluid spreads, enough waste may leak and react with confining beds to reduce their effectiveness as confining units.

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Table 1. Chemical Analyses of Native and Injection Fluids[1]

		Floridan Aquifer (Shallow monitor)	Saline-Water Aquifer (Deep monitor)	Injection Zone	Waste Effluent
Date of collection		10-4-72	10-4-72	8-29-72	10-10-72
Calcium (Ca)		670	850	4,800	400
Magnesium (Mg)		200	200	1,600	400
Sodium (Na)		26	1,200	39,000	16,000
Potassium (K)		6.0	50	1,200	45
Bicarbonate (HCO_3)		230	144	340	0
Sulfate (SO_4)		1,800	2,400	3,200	55
Chloride (Cl)		220	1,800	72,000	66,000
Fluoride (F)		2.7	3.0	13	1,500
Dissolved solids[2]		3,100	6,600	120,000	84,000
Hardness as $CaCO_3$ (Ca, Mg)		2,500	3,000	19,000	2,700
Alkalinity as $CaCO_3$ total		189	118	279	0
Acidity (H^{+1})		--	--	--	1,530
pH		7.7	7.4	6.6	1.5
Specific conductance (micromhos @ 25°C)		3,440	8,750	131,000	364,000
Temperature (°C)		28.0	28.5	41.0	30.0
Density @ 20°C (grams/milliliter)		1.001	1.003	1.078	1.042
Aluminum (Al), total	micrograms/liter	0	0	300	0
Arsenic (As)		10	10	10	7,800
Cadmium (Cd)		0	0	210	10
Chromium (Cr), total		0	20	150	230
Cobalt (Co)		1	1	750	7
Copper (Cu)		10	10	110	600
Iron (Fe), total		1,500	3,500	53,000	19,000
Lithium (Li)		20	80	1,700	10
Mercury (Hg), total		0	0	0.3	6.0
Nickel (Ni)		0	0	780	950
Strontium (Sr)		14,000	15,000	120,000	10,000
Zinc (Zn)		10	260	300	680

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[1] Analyses made by U.S. Geological Survey. Chemical constituents in milligrams per liter except as noted.

[2] Calculated from determined constituents.

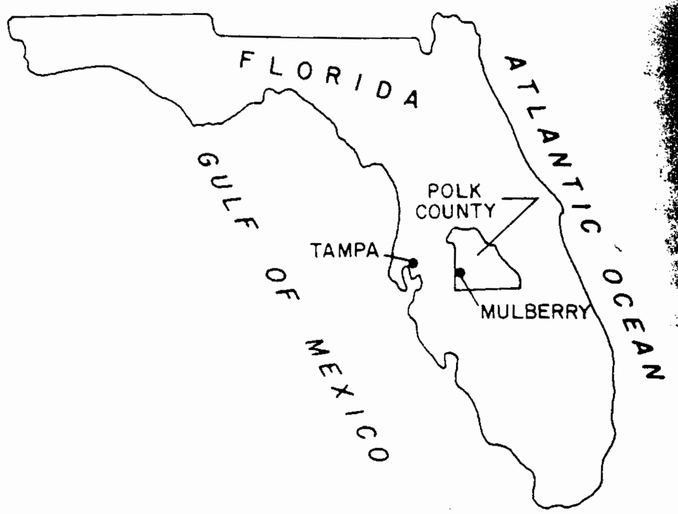

FIG. 1--Location of Mulberry, Florida.

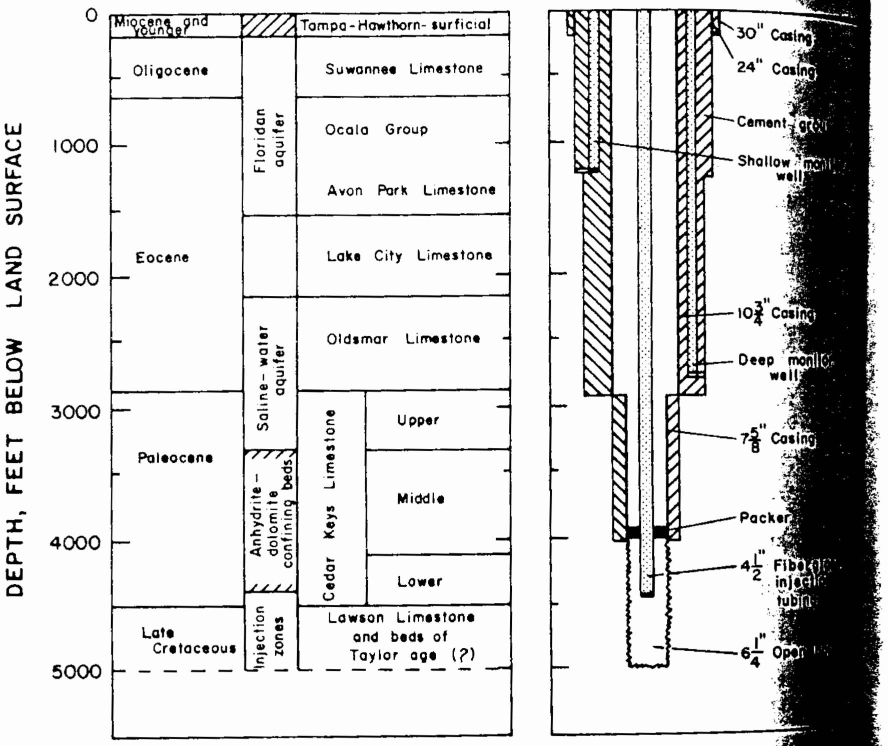

FIG. 2--Geologic column and injection-well construction.

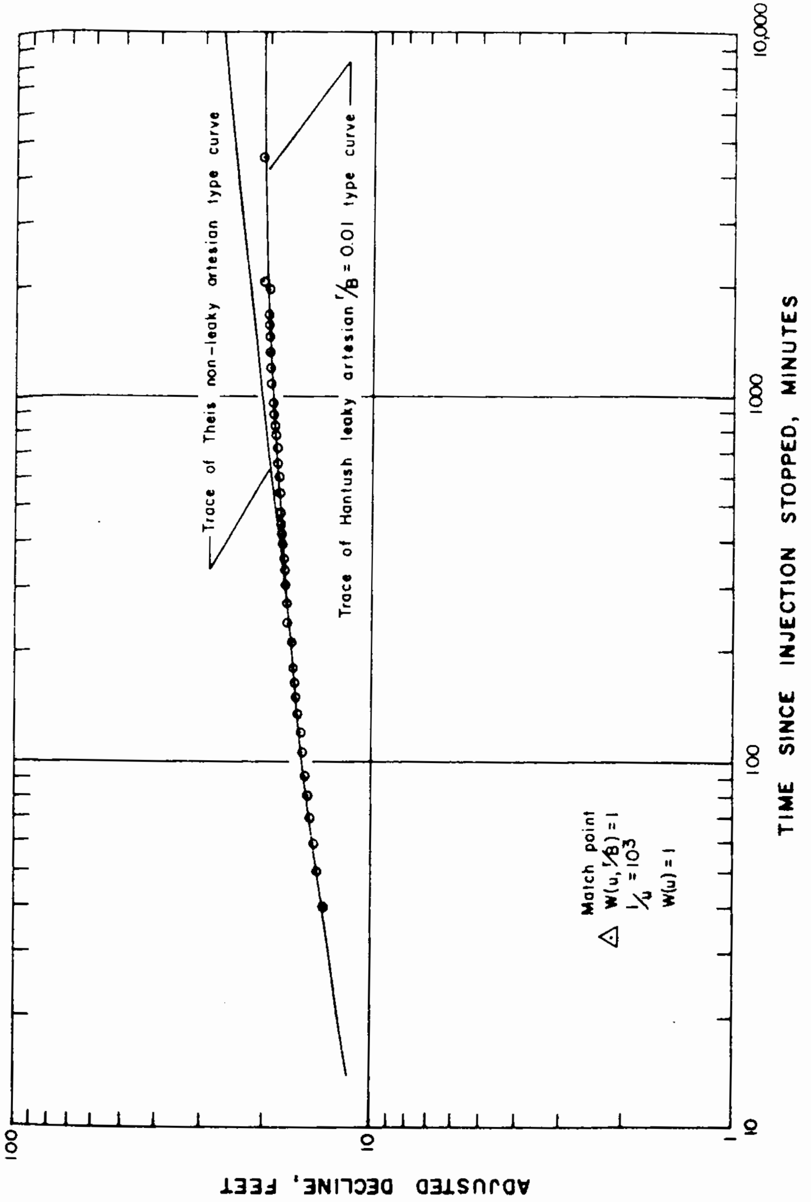

FIG. 3--Plot of recovery data and matching-type curves for second injection test.

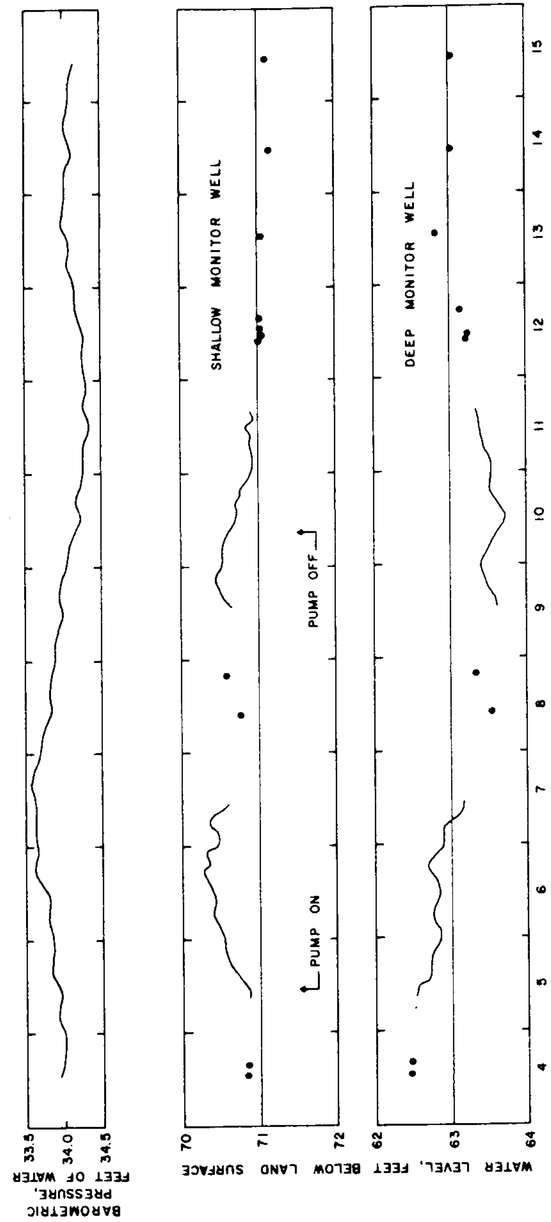

FIG. 4--Fluctuations of barometric pressure and water levels in monitor wells during second injection test.

CASE HISTORY OF SUBSURFACE WASTE INJECTION OF AN INDUSTRIAL ORGANIC WASTE[1]

J. A. Leenheer[2] and R. L. Malcolm[2]
Denver, Colorado

ABSTRACT From May 1968 to December 1972, an industrial organic waste was injected at rates of 100-200 gal/minute into an Upper Cretaceous sandstone, gravel, and limestone aquifer near Wilmington, North Carolina. The waste, an aqueous solution of formic, acetic, and phthalic acids, interacted with the aquifer to dissolve carbonate, aluminosilicate, and iron-containing minerals, and to produce carbon dioxide, methane, and hydrogen sulfide gases.

Water samples obtained from four observation wells that penetrate the aquifer near the injection well show a 3-fold increase in silica, a 5-fold increase in iron, and a 28-fold increase in aluminum over background data, indicating dissolution of aquifer aluminosilicate and iron-containing minerals. Gas that effervesced from these water samples contained up to 85 percent carbon dioxide by volume resulting from the reaction between carbonate minerals and the acidic waste.

Water samples obtained from an observation well 1,500 ft (457 m) north of the original injection wells gave evidence for biochemical waste transformations during passage of the waste front. Gas that effervesced from these water samples contained up to 54 percent methane by volume. Ferrous iron concentrations as high as 35 mg/l, hydrogen sulfide gas, and sulfide precipitates were additional indicators of biochemical reductive processes in the subsurface environment.

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[2] Research Hydrologist, U.S. Geological Survey.