A Study of Inert Gas Atmospheres on the Oxidation of Coal Mine Pyrites

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The production of iron salts and sulfuric acid by the oxidation of pyritic material in coal mines is a substantial source of water pollution. These compounds are generally believed to be the result of the chemical reaction

$$2\ Fe\ S_2 + 7\ O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

One means of controlling the rate of this reaction is to control the amount of oxygen in the atmosphere surrounding the pyrite. Investigators at Ohio State University[1] and Mellon Institute[2,3] have discussed the effect of limiting the oxygen concentration in such atmospheres. This paper describes the results of experiments in which pyrite is exposed to various gaseous atmospheres, in the presence of water.

The pyrite used was obtained from coal crusher reject material and was largely taken from strip mining sites in the Clearfield, Pennsylvania area. It was crushed from 6-8" lumps to less than 1" diameter, and loaded into six insulated cylindrical columns, 6' x 4" I.D. Approximately 40-45 lbs. of pyrite were used per column.

Demineralized water at a constant temperature of 56°F entered the top of each column, trickled over the pyrite bed, and was removed from the bottom. In a similar manner, the gases were injected into the top of each column and exited from the bottom. Each column was operated separately, with no interconnections.

TABLE 1

PYRITE ANALYSIS

Total Fe	40%
Total S	44%
Loss on Ignition	13%
Total Al	< 1
Total Ca	< 1
Total Mg	< 1

The results of the following gas systems are presented:

TABLE 2

COLUMN ATMOSPHERES

Air
Nitrogen
Nitrogen/Carbon Dioxide

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1 Shumate, K. S., and Smith, E. E., 2nd Symposium on Coal Mine Drainage Research, Mellon Institute, May, 1968.
2 Braley, S. A., Summary Report of Commonwealth of Pa. (Dept. of Health), Mellon Institute Fellowship No. 326B, February, 1964.
3 Personal Communication, R. A. Baker, September, 1968.

Column 1 - This column was loaded with 43 lbs. of pyrite having an average diameter of 3/8". After loading, the column was backwashed twice with demineralized water to flush soluble salts which had formed on the surface of the pyrite.

Air (40 cc/min) and demineralized water (12 cc/min) were percolated through the column continuously for seven days. Acid production was sporadic, as measured by frequent grab samples from the column effluent. It was surmised that the air, water and pyrite contact time was too short and therefore the procedure was changed to operate the column from 9 AM to 5 PM on Mondays through Fridays. The column was sealed at all other times with no water or air flow. This procedure produced a more or less steady production of acidic iron salts in the effluent, and was used as the method for operating the other columns.

After operating for twenty days under the modified alternate flow procedure, this column's gas atmosphere was abruptly switched from air to nitrogen, and was operated in a similar manner for thirty days. During each operating day, two grab samples and a daily composite sample were taken. This analytical data is plotted in Figures 1 and 2.

Column 2 - This column was loaded with the same size fresh pyrite as column 1, backwashed twice and then operated by trickling water from the top of the column to its bottom under a nitrogen atmosphere during eight-hour weekdays for a period of twenty days. Grab and composite samples were collected for analysis daily.

After twenty days, the nitrogen flow was discontinued and air substituted. The air/water system operated for thirty days until the termination of the experiment. The analytical data are plotted in Figures 3 and 4.

Column 3 - was loaded with fresh 3/4" O.D. pyrite, backwashed twice and exposed to a mixture of 90% ^{v}/v nitrogen and 10% ^{v}/v carbon dioxide, with the same water flow as before. This environment was maintained for fifty days until the experiment terminated. The analytical data are plotted in Figures 5 and 6.

Column 4A - was loaded with fresh 1/4" O.D. pyrite, backwashed twice and then exposed to a water/nitrogen atmosphere for thirty days the experiment terminated. The analytical data are plotted in Figures 7 and 8.

Column 5A - was operated exactly the same as column 4A, except air was used instead of pure nitrogen. The analytical data are plotted in Figures 9 and 10.

During the column experiments with the pyrite under study, two significant events common to all of the columns occurred.

a) An air leak was discovered sometime between the 10th and 11th of October, in all columns. The effects of this leak were immediately noted in plotting the grab sample analytical results, although the significance is masked in observing the data plotted for columns 2 and 5A, which were being operated in an air/water atmosphere.

b) Circumstances prevented taking the scheduled grab samples during the period of October 11th and October 21st, although the columns were in operation. Therefore, the point-to-point plot as

shown in the figures is possibly a distorted view of the overall reactions of the pyrite in each column.

DISCUSSION

The data obtained, as seen in the plotted figures (Figures 1-10), shows the definite trend for and rate of production of acidic salts to be markedly reduced when the atmosphere did not contain oxygen. Examination of the plots for columns 1-4 are particularly interesting, since the atmospheres in contact with the pyrite were switched to or from nitrogen and air. The pyrite response in each case was almost immediate when the atmosphere was reversed; the rate of acidic iron salt production decreasing when an oxygen-free atmosphere was used.

It is also of interest to note that the general shape of the curves plotted for total acidity, conductivity and iron content are the same.

None of the columns, when operated in an air free atmosphere completely ceased production of acidic iron salts. This could be due to small, undetected air leaks, or the more likely possibility that the reactions taking place had not reached a steady state.

Columns 4A and 5A represent nitrogen and air systems respectively, using smaller pieces of pyrite than used in columns 1 and 2. The increased surface area reduced the time for steady state conditions to be reached. Columns operated in nitrogen (4A and the latter 30 days of column 1) showed a steeper downward sloping curve for iron, acidity and conductivity when the smaller sized pyrite was used. The converse was true for the columns operated in air (column 5A and the latter 30 days of column 2).

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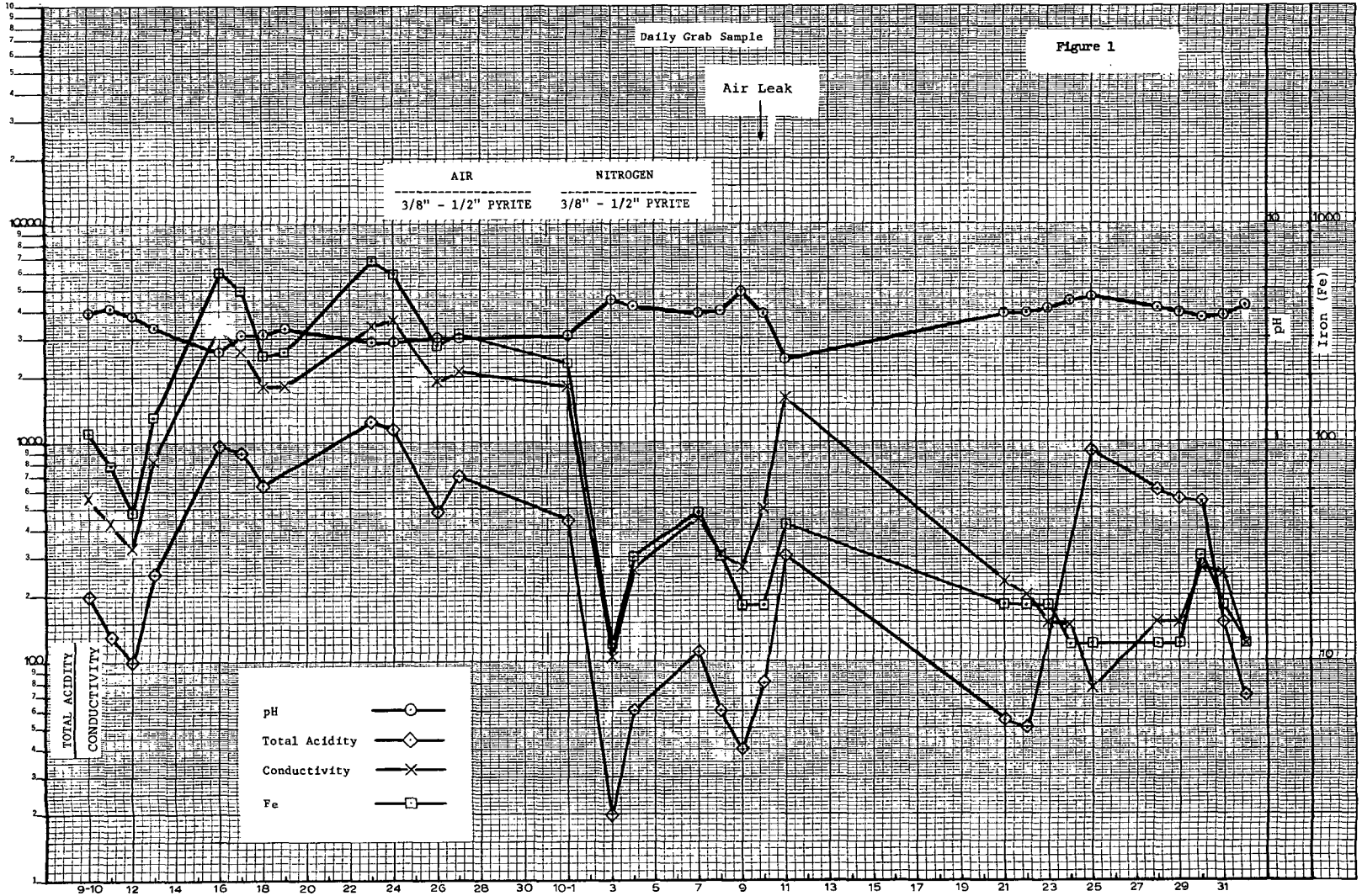
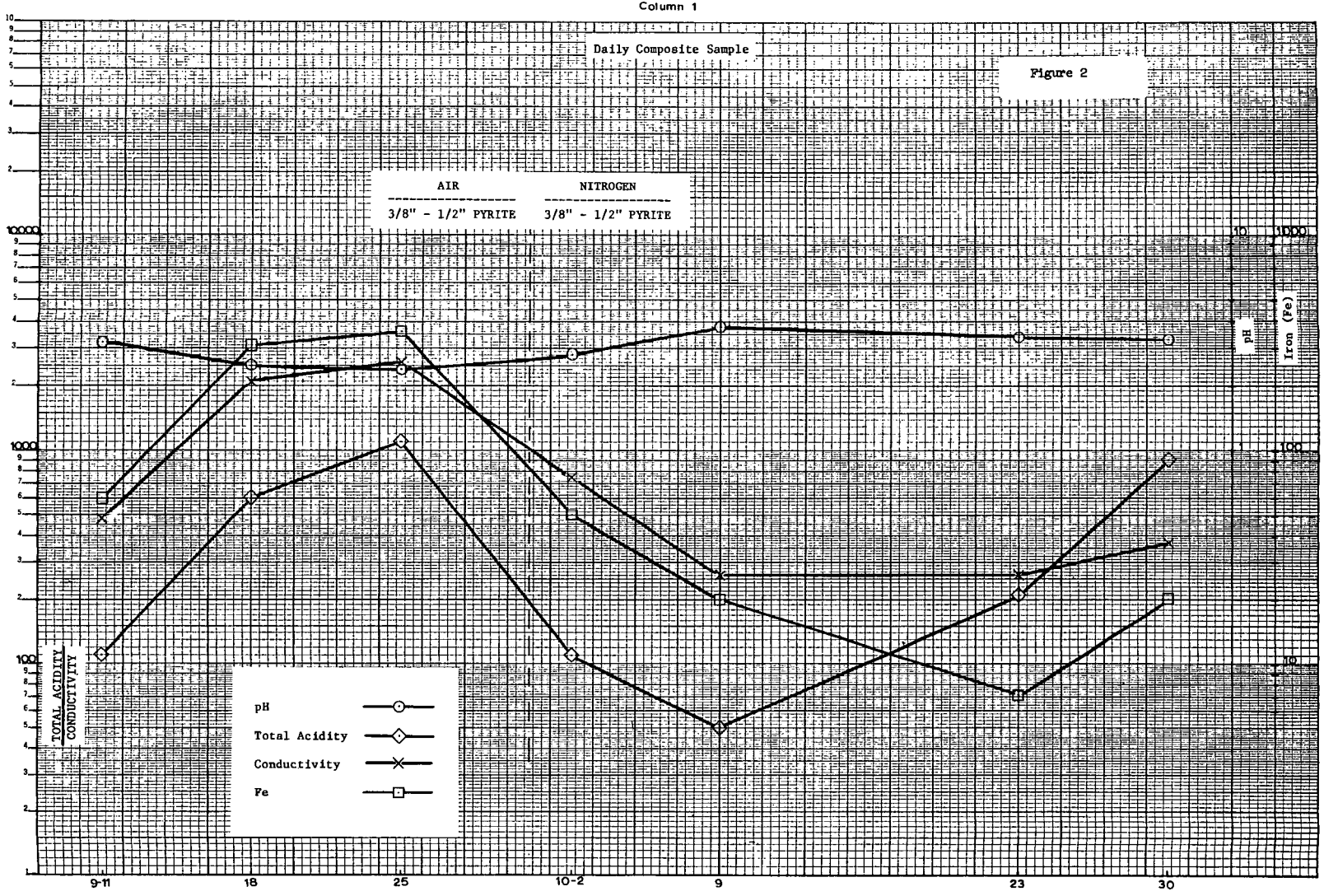
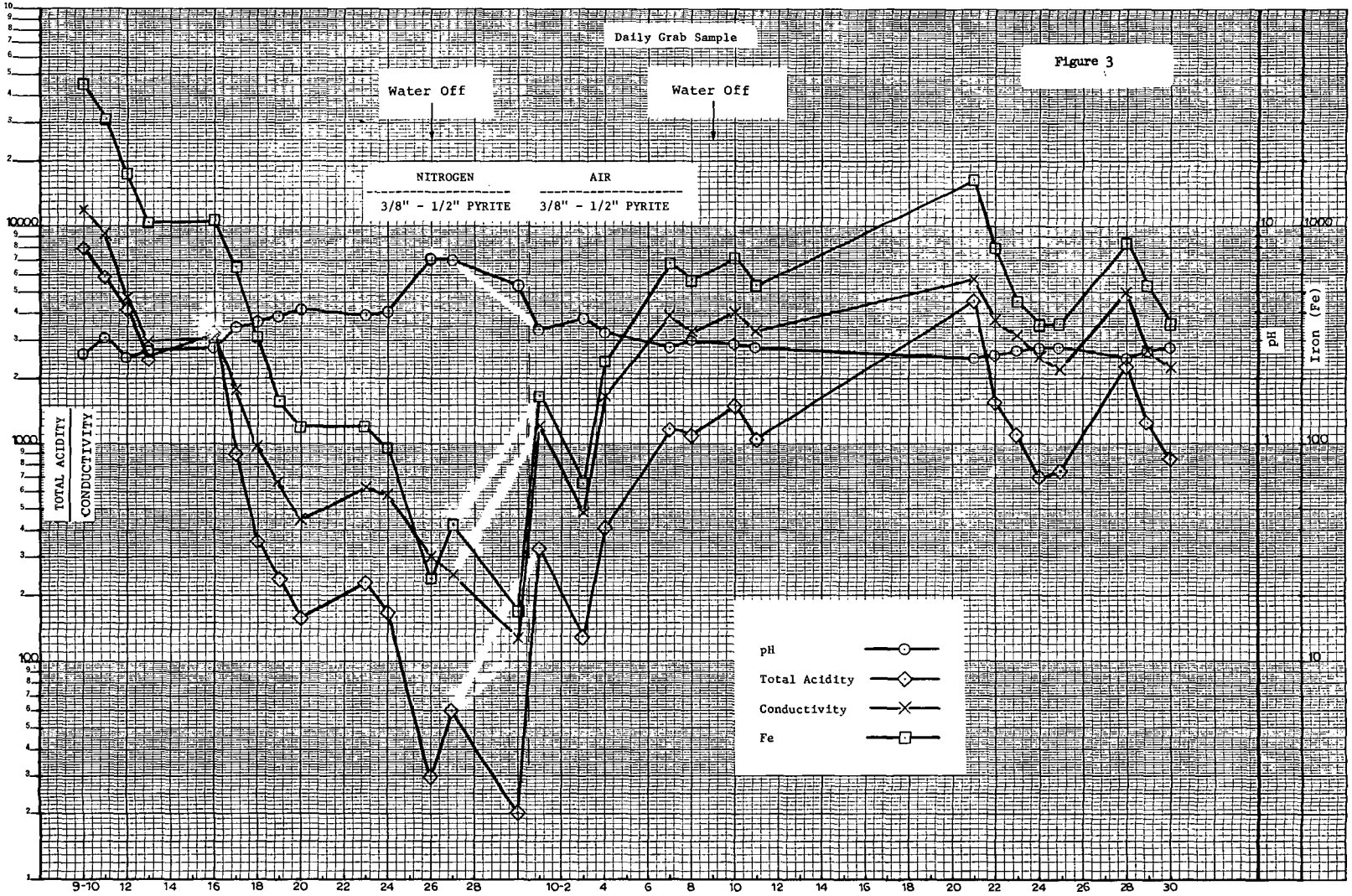
Column 1

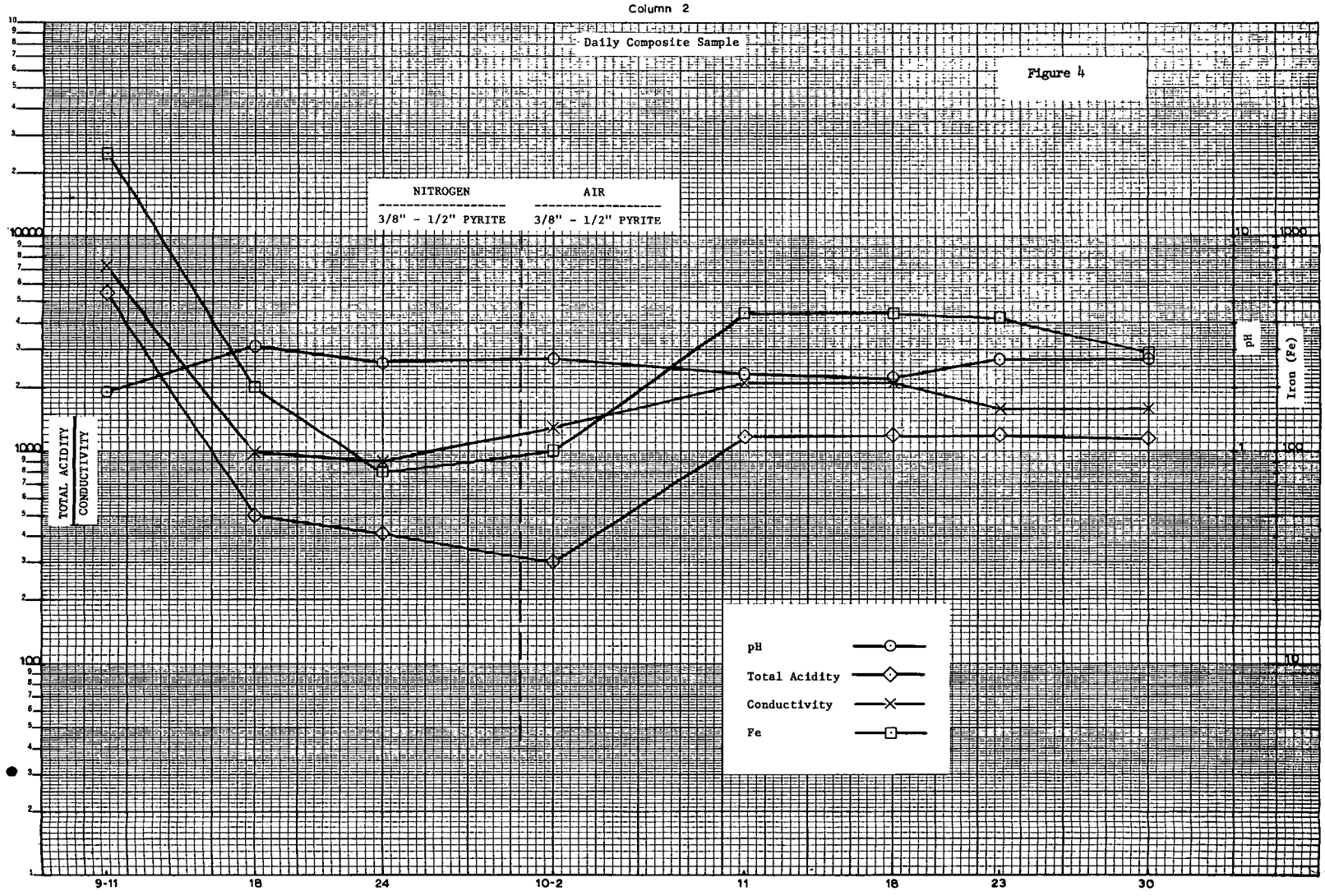

Daily Grab Sample
Figure 1
Air Leak
AIR
3/8" - 1/2" PYRITE
NITROGEN
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-10
12
14
16
18
20
22
24
26
28
30
10-1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31

Column 1

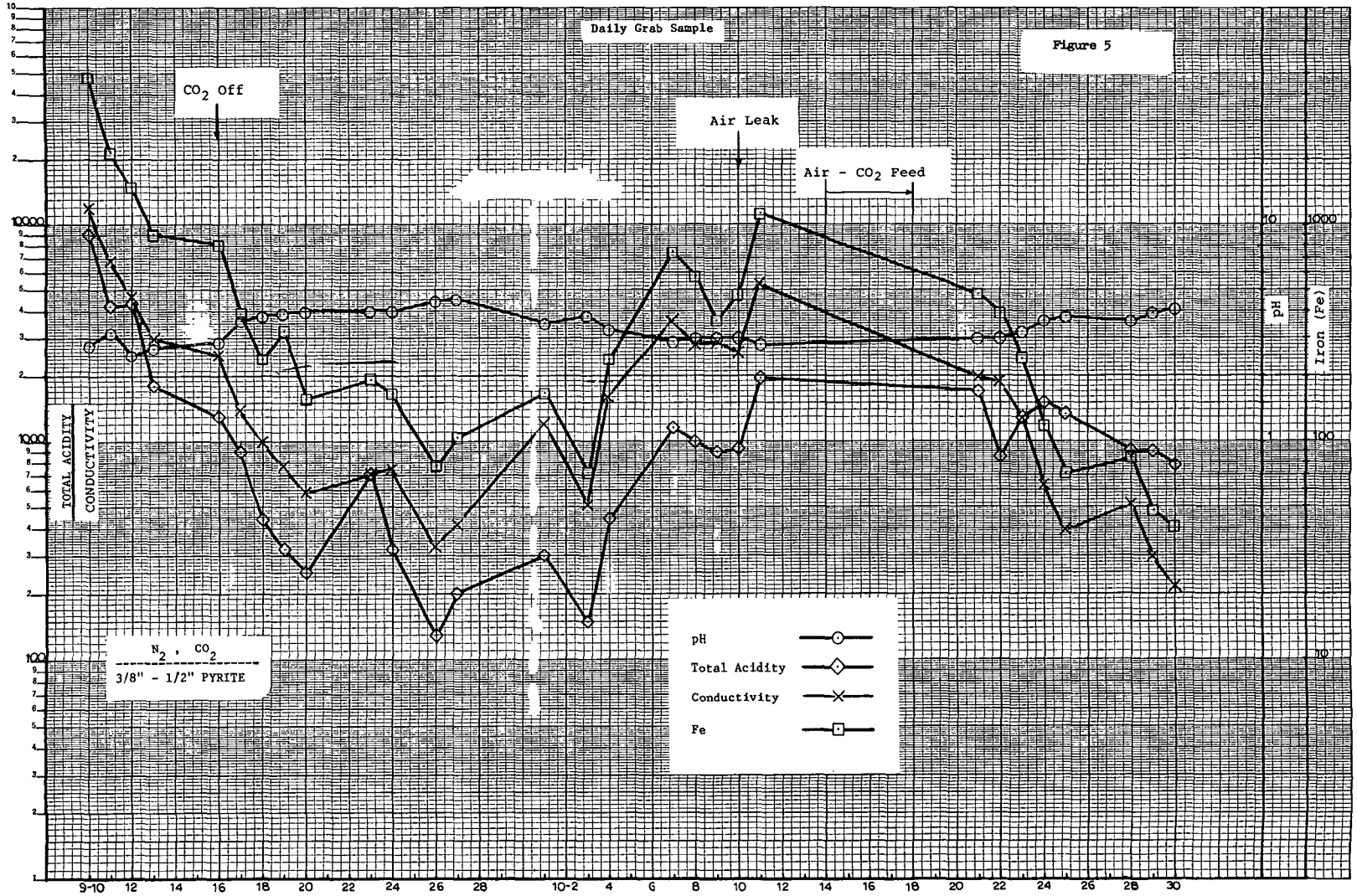

Daily Composite Sample
Figure 2
AIR
3/8" - 1/2" PYRITE
NITROGEN
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-11
18
25
10-2
9
23
30

Column 2

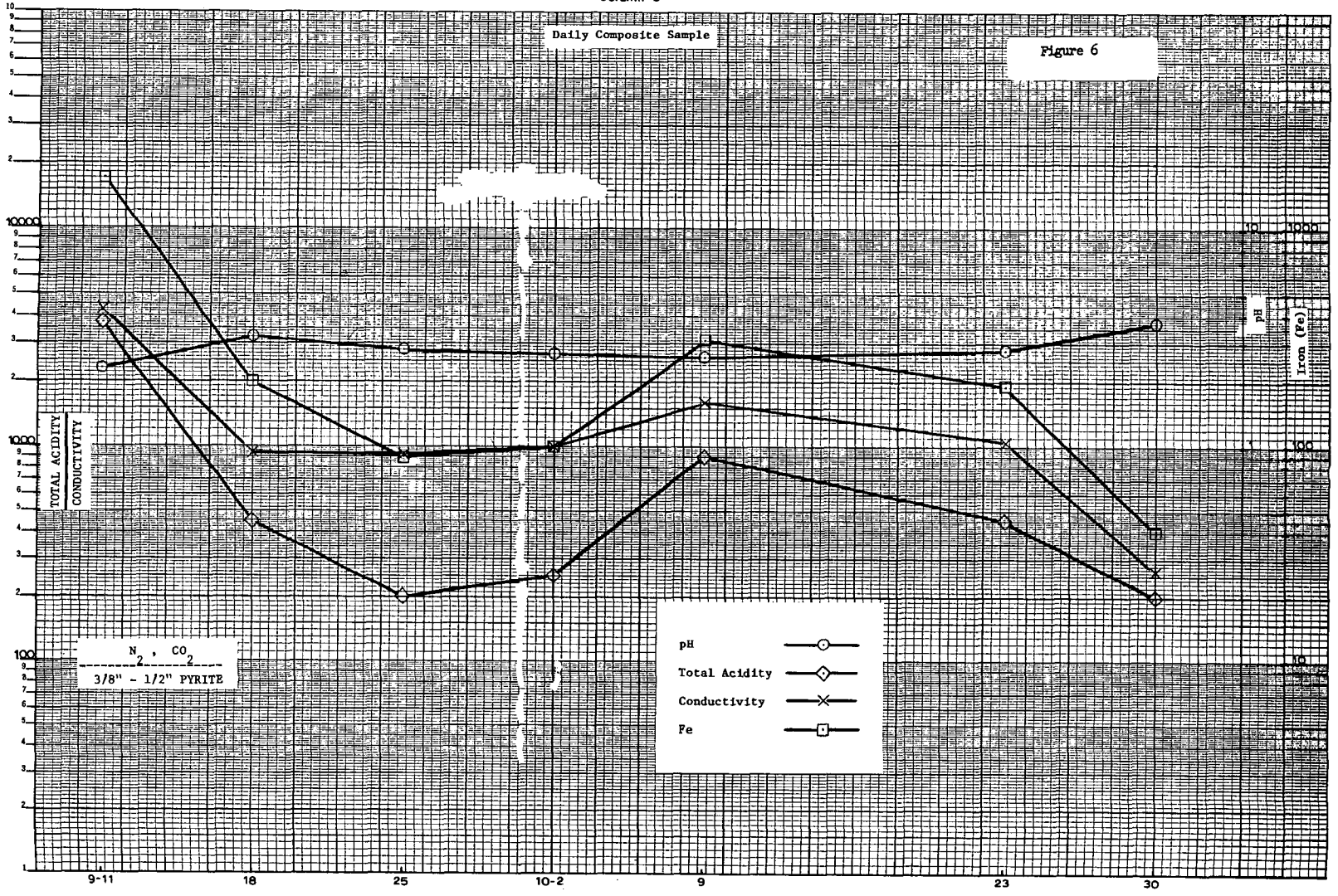

Daily Grab Sample
Figure 3
Water Off
Water Off
NITROGEN
AIR
3/8" - 1/2" PYRITE
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-10 12 14 16 18 20 22 24 26 28 10-2 4 6 8 10 12 14 16 18 20 22 24 26 28 30


Column 2
Daily Composite Sample
Figure 4
NITROGEN
3/8" - 1/2" PYRITE
AIR
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-11
18
24
10-2
11
18
23
30

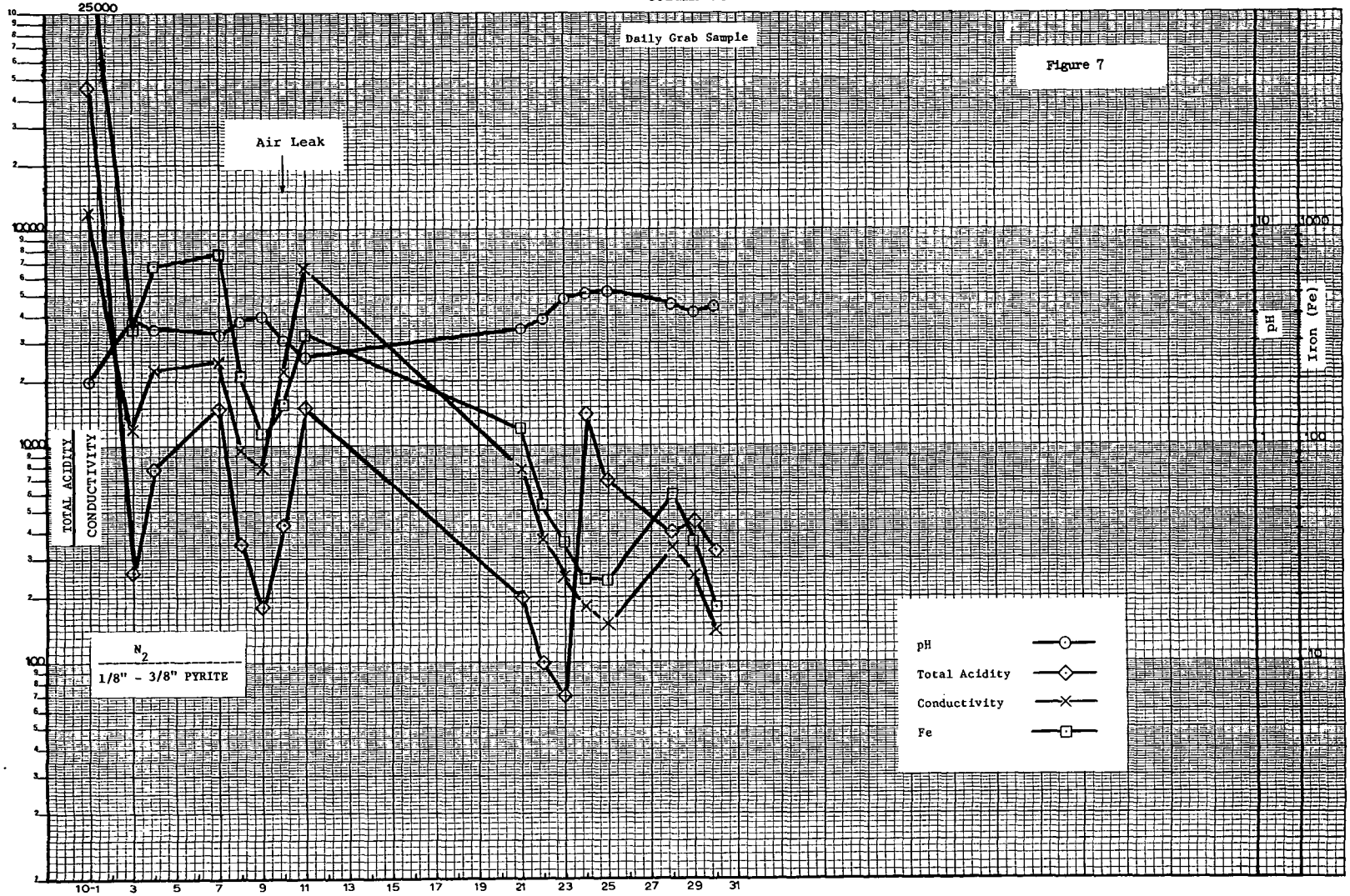
Column 3


Daily Grab Sample
Figure 5
CO_2 Off
Air Leak
Air - CO_2 Feed
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
N_2 , CO_2
3/8" - 1/2" PYRITE
pH
Total Acidity
Conductivity
Fe
9-10 12 14 16 18 20 22 24 26 28 10-2 4 6 8 10 12 14 16 18 20 22 24 26 28 30

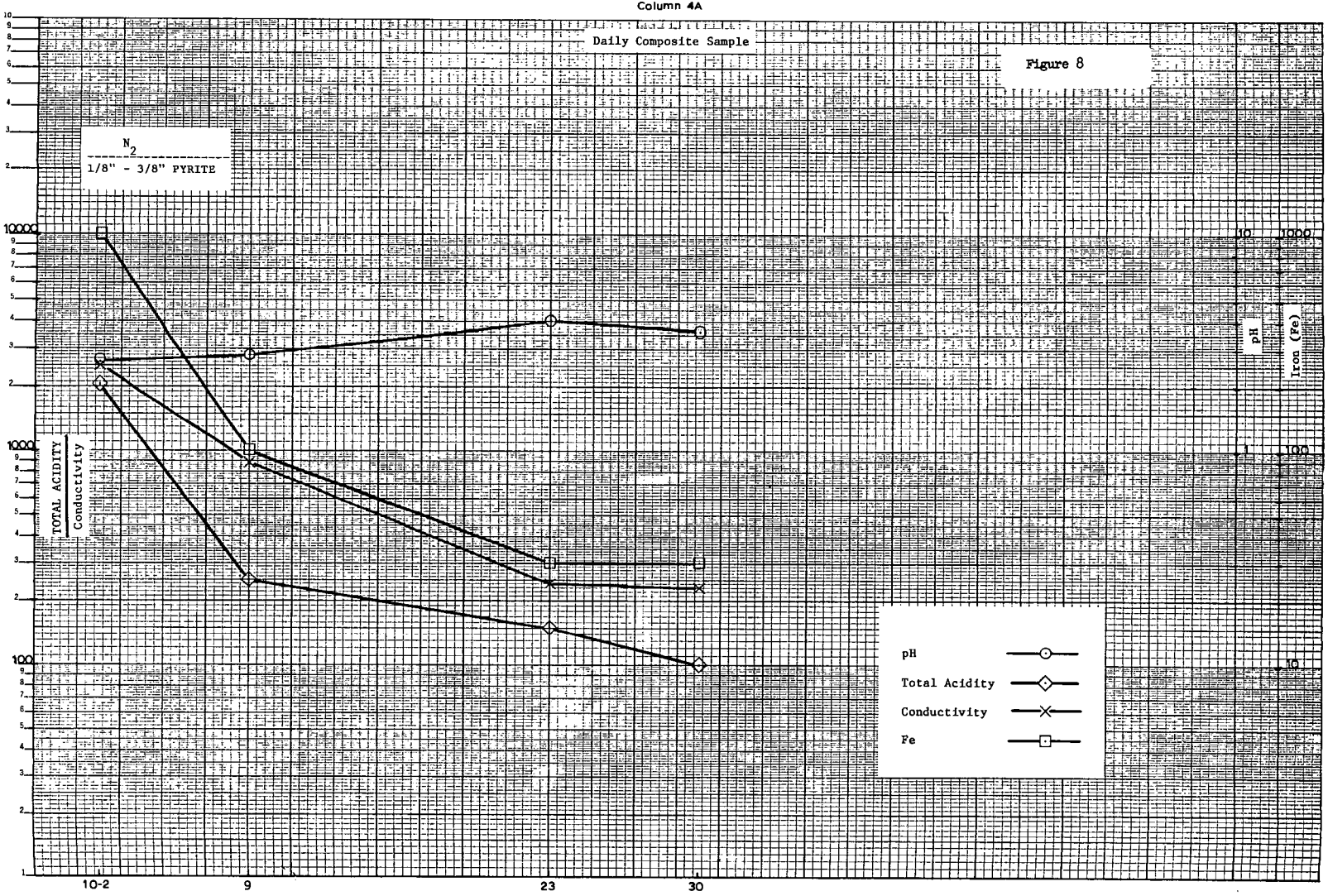
Column 3


Daily Composite Sample
Figure 6
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
N_2 , CO_2
3/8" - 1/2" PYRITE
pH
Total Acidity
Conductivity
Fe
9-11
18
25
10-2
9
23
30

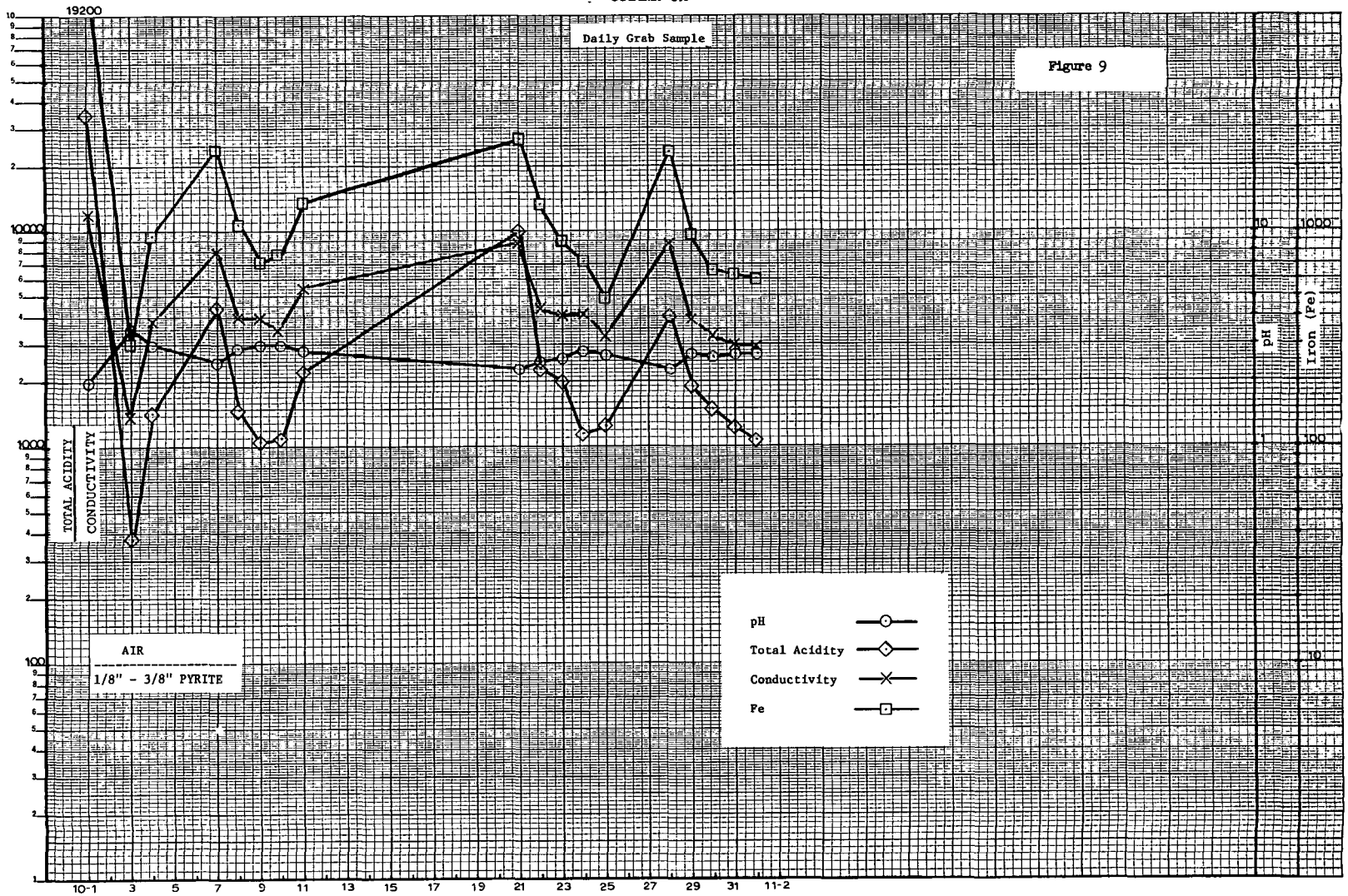
Column 4A


Daily Grab Sample
Figure 7
Air Leak
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
N_2
1/8" - 3/8" PYRITE
pH
Total Acidity
Conductivity
Fe
25000
10000
1000
100
10
1000
100
10
1
10-1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31

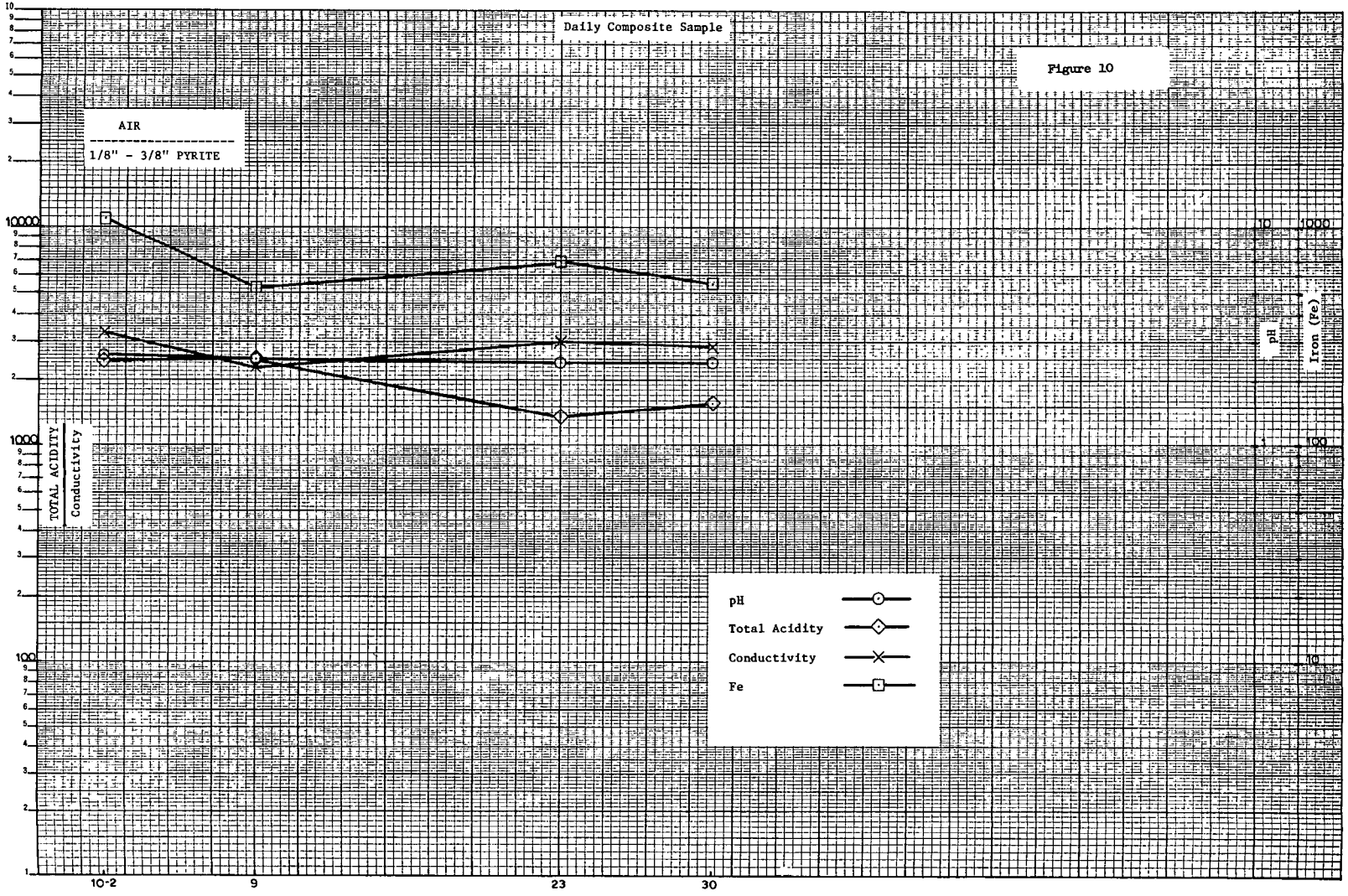
Column 4A


Daily Composite Sample
Figure 8
N_2
1/8" - 3/8" PYRITE
TOTAL ACIDITY
Conductivity
pH
Iron (Fe)
10-2
9
23
30
pH
Total Acidity
Conductivity
Fe

Column 5A


19200
Daily Grab Sample
Figure 9
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
AIR
1/8" - 3/8" PYRITE
pH
Total Acidity
Conductivity
Fe
10-1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
11-2

Column 5A


Daily Composite Sample
Figure 10
AIR
1/8" - 3/8" PYRITE
TOTAL ACIDITY
Conductivity
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
10000
1000
100
10
1
10-2
9
23
30