

GEOCHEMISTRY OF ABANDONED LIGNITE
MINE SPOIL IN TEXAS

Jan K. Horbaczewski and Frank Van Ryn

Morrison-Knudsen Company, Inc.

Abstract--Geochemical investigations of lignite mine spoils ranging in age from 10 years to over 35 years were performed at an abandoned mined land reclamation project near Rockdale, Milam County, TX. A primary objective was to determine the degree to which oxidation of pyritic material had progressed for the design of an appropriate reclamation plan. For this purpose, eight continuous cores were recovered from the project area. The results indicated that within 10 years, consistent trends had already developed in the spoil among the principal sulfur forms (organic sulfur, pyritic sulfur, and sulfate sulfur). Three principal trends were identified: a gradual decrease in the proportion of sulfate sulfur to pyritic sulfur from the spoil surface downwards; a change, marked by a transition zone which varied in location and definition according to the age of the spoil, from low pH values (less than pH 4.0) in near-surface spoil to higher pH values (greater than pH 5.0) at greater depths; a trend with age of spoil to the correlation between the pH transition zone and the proportion of sulfate sulfur. These trends, associated with the processes of oxidation and leaching, are depicted on triangular graphs which are also used to show the reconstructed evolution of the spoil sulfur forms at ten-year intervals. The results of the geochemical investigations have been incorporated in the reclamation plan which is designed to minimize the exposure, through regrading, of spoil still containing pyritic sulfur forms.

Additional Key Words: pyritic sulfur, acid-forming material, sulfur forms, vadose zone.

Proceedings America Society of Mining and Reclamation, 1987 pp 157-163

DOI: 10.21000/JASMR88010157

<http://doi.org/10.21000/JASMR88010157>

INTRODUCTION

The work described in this paper was part of a reclamation program prepared for the Railroad Commission of Texas for the mitigation of an abandoned mined land reclamation project, near Rockdale, TX. Significant mining of lignite with draglines began in this area in the early 1950's and terminated in the project area with the passing of the Surface Mining and Reclamation Act of 1977. The spoils in the area, therefore, range in age from over 35 years old to 10 years old.

One of the principal objectives of the project was to determine the degree to which oxidation of pyritic sulfur had progressed and thus to assess the extent of acid and acid-forming materials for the reclamation plan (Railroad Commission of Texas, 1987). This paper deals specifically with the relationships discovered among the sulfur forms and pH values in the spoil.

MATERIALS AND METHODS

The data presented in this paper are based on eight continuous cores collected in the project area spoil. The project area covers approximately 1,200 acres and is located near Rockdale in Milam County, TX. The spoils are derived from the lignite-bearing formations of the Eocene Wilcox Group.

Core sites were selected on the basis of geographic and geologic settings to be representative of the project area. Since there was no detailed information available on the premining overburden geology and geochemistry, the principal criteria in site selection were to represent the 4 project subareas with an appropriate spatial distribution, to select sites showing a regular dragline spoiling pattern, and to distribute the sites in both geologically up-dip and geologically down-dip locations.

At each site, a small bulldozer was first used to prepare a drilling platform on the spoil ridge. This resulted in a small loss of sample corresponding, on average, to the top 5 ft. of the spoil.

¹Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement, April 17-22, 1988, Pittsburgh, P.A.)

²Jan K. Horbaczewski is Senior Environmental Specialist and Frank Van Ryn is Staff Environmental Specialist, Morrison-Knudsen Company, Inc., San Antonio, TX.

All sample depths have been adjusted accordingly and are reported in relation to the original spoil surface. A truck-mounted, hollow-stem auger (3-inch internal diameter) with a wire-line attachment for a Shelby tube was then used to collect the spoil samples. The hollow-stem system eliminated the potential contamination from drilling fluids or material falling in from the sides of the borehole. Cores were recovered to a depth approximately 4 ft. below the expected final topography after regrading. The core lengths varied in depth from 19.0 to 49.7 ft. A total of 264.4 ft. of spoil core was collected.

Each core was inspected and described in the field by an experienced geologist, sealed in plastic bags, labelled and boxed. Selection of sampling intervals was performed by an experienced soil scientist on the basis of the lithologic description and further examination of the core. A total of 51 sampling intervals were selected with a range of sample interval length from 0.6 ft. to 13.8 ft. and an average of 5.2 ft.

The laboratory methods used for the analysis of the spoil samples were those recommended by the Railroad Commission of Texas (1985). Sulfur forms (organic sulfur, pyritic sulfur, and sulfate sulfur) were determined according to EPA method 3.2.6 (EPA 1978), which separates the sulfur forms by extractant: HCl-extractable sulfur (mostly sulfates), HNO₃-extractable sulfur (mostly pyritic sulfur), and non-extractable sulfur (mostly organic sulfur). The extracted fractions were then submitted for sulfur analysis using an induction furnace and automatic sulfur titrator. The spoil reaction (pH) was determined on a 1:1 soil:water extract according to Black's method 60-3.4 (Black 1965).

A quality check was performed on the laboratory results testing for internal consistency with other geochemical parameters (not described in this paper).

RESULTS AND DISCUSSION

An examination of the proportions of sulfur forms (organic sulfur, pyritic sulfur, and sulfate sulfur) in the spoil showed that there were some general trends in the geochemistry with depth (Table 1). The principal trend is illustrated in spoil core GC-1 (fig. 1). Near the surface of the spoil [sample 1 (7.0-11.0 ft)] the pyritic sulfur content is zero and the only sulfur forms present are organic sulfur and sulfate sulfur. At successively greater depths [sample 2 (11.0-12.6 ft); sample 3 (12.6-16.4 ft); and sample 4 (16.4-24.0 ft)] the proportion of sulfate sulfur decreases while the proportion of pyritic sulfur increases. At still greater depths [sample 5 (24.0-31.2 ft)] the pyritic sulfur proportions are high and the sulfate sulfur proportions are low (generally below 15% of the

TABLE 1 - Contents of Sulfur Forms in Spoil Cores From Abandoned Lignite in Mine Spoil.

Spoil Core	Sample Number	Depths (feet)	Laboratory Analyses of Sulfur Content				Relative Content Among Sulfur Forms				pH
			Total Sulfur	Sulfate Sulfur	Pyritic Sulfur %	Organic Sulfur	Total Sulfur	Sulfate Sulfur %	Pyritic Sulfur	Organic Sulfur	
GC-1	1	7.0-11.0	0.23	0.14	<0.01	0.09	100	61	---	39	3.8
	2	11.0-12.6	0.83	0.37	0.04	0.42	100	45	5	50	3.7
	3	12.6-16.4	0.32	0.13	0.07	0.12	100	41	22	37	3.6
	4	16.4-24.0	0.84	0.10	0.49	0.25	100	12	58	30	5.8
	5	24.0-31.2	0.10	<0.01	0.04	0.06	100	---	40	60	6.2
	6	31.2-34.3	0.18	0.01	0.10	0.07	100	6	56	38	6.5
	7	34.3-39.3	0.24	<0.01	0.14	0.10	100	---	58	42	5.9
	8	39.3-45.0	0.12	0.01	0.04	0.07	100	8	33	59	6.6
	9	45.0-52.0	0.33	0.09	0.14	0.10	100	27	43	30	4.6
	10	52.0-56.9	0.53	0.02	0.38	0.13	100	4	72	24	5.7
GC-2	1	12.0-16.0	0.26	0.20	<0.01	0.06	100	77	---	23	3.8
	2	16.0-26.4	0.09	0.03	0.01	0.05	100	33	11	56	4.4
	3	26.4-31.9	0.07	0.03	<0.01	0.04	100	43	---	57	4.8
GC-3	1	5.0-9.0	0.19	0.14	0.01	0.04	100	74	5	21	3.7
	2	9.0-10.6	0.29	0.23	0.01	0.05	100	79	3	17	4.1
	3	10.6-14.0	0.51	0.36	0.06	0.09	100	71	12	17	3.3
	4	14.0-18.1	0.55	0.28	0.21	0.06	100	51	38	11	3.8
	5	18.1-21.2	0.39	0.14	0.17	0.08	100	36	44	20	5.6
	6	21.2-29.0	0.58	0.05	0.41	0.12	100	9	71	20	5.3
	7	29.0-32.0	0.77	0.10	0.53	0.14	100	13	69	18	5.5
	8	32.0-35.0	0.77	0.01	0.61	0.14	100	2	80	18	5.3
GC-4	1	10.0-14.0	0.07	0.02	<0.01	0.05	100	29	---	71	4.8
	2	14.0-21.7	0.04	<0.01	<0.01	0.04	100	---	---	100	4.9
	3	21.7-23.0	0.29	0.21	0.01	0.07	100	72	3	25	3.6
	4	23.0-29.3	0.04	0.01	0.02	0.01	100	25	50	25	4.4
	5	29.3-31.3	0.22	0.12	0.07	0.03	100	55	32	13	4.7
	6	31.3-35.0	0.12	0.07	0.01	0.04	100	58	8	33	4.5
	7	35.0-36.0	0.28	0.12	0.08	0.08	100	42	29	29	5.3
	8	36.0-42.3	0.12	0.05	0.03	0.04	100	42	25	33	4.7
	9	42.3-48.3	0.41	0.07	0.22	0.12	100	17	54	29	6.1
	10	48.3-50.4	0.09	0.04	0.01	0.04	100	44	12	44	5.2
GC-5	1	8.0-12.0	0.05	<0.01	<0.01	0.05	100	---	---	100	7.6
	2	12.0-22.0	0.05	<0.01	0.01	0.04	100	---	20	80	7.5
	3	22.0-32.2	0.06	<0.01	0.02	0.04	100	---	33	67	7.5
	4	32.2-46.0	0.06	0.02	<0.01	0.04	100	33	---	67	7.3
	5	46.0-57.7	0.05	<0.01	0.01	0.04	100	---	20	80	7.4
GC-6	1	4.0-8.0	0.37	0.28	0.01	0.08	100	76	3	21	3.7
	2	8.0-9.4	0.78	0.68	<0.01	0.10	100	87	---	13	3.5
	3	9.4-10.2	0.27	0.22	<0.01	0.05	100	81	---	19	3.8
	4	10.2-19.6	0.35	0.25	0.03	0.07	100	71	9	20	4.1
	5	19.6-27.3	0.27	0.11	0.09	0.07	100	41	33	26	5.9
	6	27.3-30.1	0.14	0.04	0.04	0.06	100	29	29	42	6.5
	7	30.1-35.9	0.27	<0.01	0.19	0.08	100	---	70	30	7.3
GC-7	1	3.0-7.0	0.04	<0.01	0.03	0.01	100	---	75	25	7.0
	2	7.0-16.0	0.05	<0.01	0.02	0.03	100	---	40	60	5.2
	3	16.0-24.0	0.04	0.03	<0.01	0.01	100	75	---	25	6.5
GC-8	1	4.0-8.0	0.51	0.38	0.04	0.09	100	75	8	17	3.5
	2	8.0-12.8	0.33	0.26	0.01	0.06	100	79	3	18	3.7
	3	12.8-13.9	0.06	0.02	<0.01	0.04	100	33	---	67	5.0
	4	13.9-19.0	0.23	0.15	0.01	0.07	100	65	4	31	7.0
	5	19.0-24.0	0.25	0.09	0.09	0.07	100	36	36	28	7.1

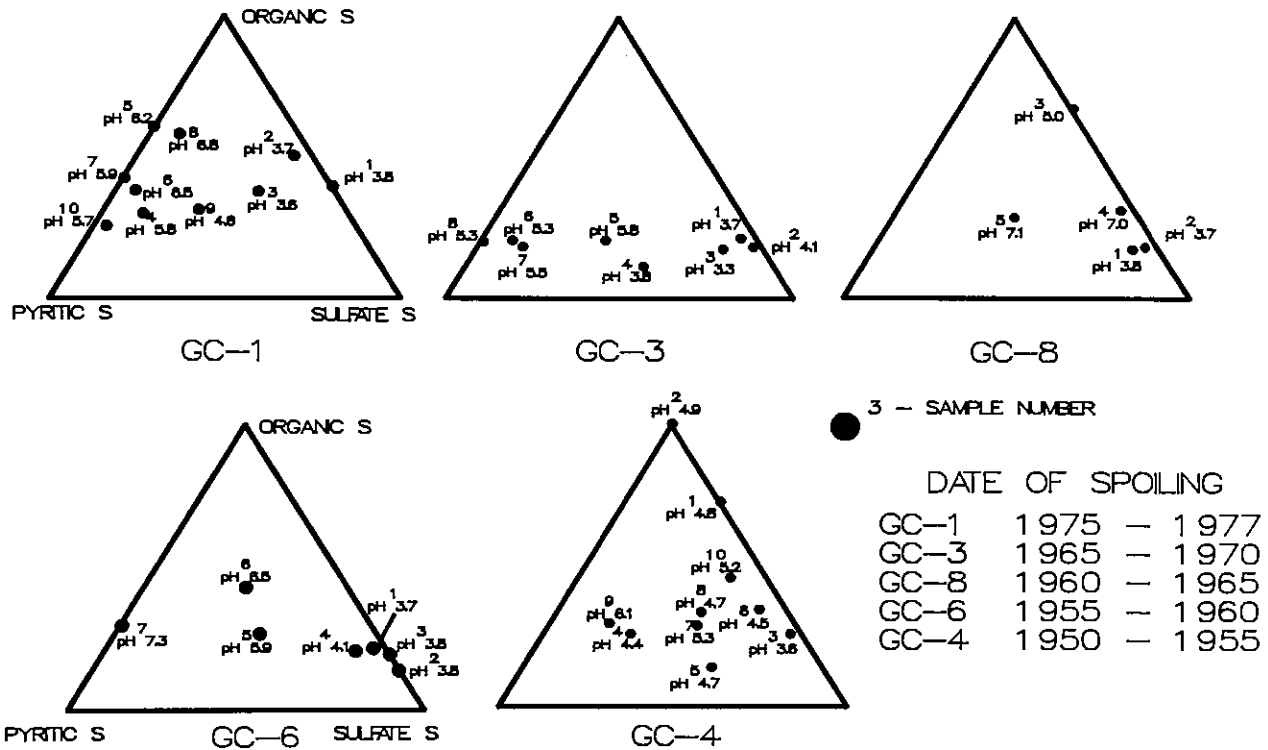


FIGURE 1. SULFUR FORMS IN SPOIL CORES FROM ABANDONED LIGNITE MINE SPOIL.

total sulfur forms). The trend is general, but there are exceptions, such as sample 9 (45.0-52.0 ft.) which has an anomalously higher sulfate sulfur content.

Associated with this trend is a secondary trend from low pH values (pH 3.6 for sample 1) in the near-surface samples to higher pH values (pH 5.8 in sample 4) in the deeper samples (fig. 1). Spoil core GC-1 shows a trend in acidity from pH 3.8 [sample 1 (7.0-11.0 ft)] decreasing to pH 3.6 [sample 3 (12.6-16.4 ft)] and increasing to pH 5.8 [sample 4 (16.4-24.0 ft)].

A similar trend can be observed in spoil core GC-3 (fig.1) which has a pH value of 3.7 in near-surface spoil [sample 1 (5.0-9.0 ft)] which decreases with depth to pH 3.3 [sample 3 (10.6-14.0 ft)] and finally increases to pH 5.6 [sample 5 (18.1-21.2 ft)] at still greater depth. Similar trends can also be seen in cores GC-4, GC-6, and GC-8, although not so clearly.

A third trend becomes apparent when the pH change is compared to the relative percentage of sulfate sulfur. In spoil core GC-1, pH values as low as 3.6 occur in a sample with sulfate sulfur proportions of 41%; in spoil core GC-3 a pH value of 3.8 occurs at a sulfate sulfur proportion of 51%; and in spoil cores GC-4, GC-6, and GC-8, pH values less than 4.0 are associated with proportions of sulfate sulfur greater than 70%.

The first trend indicates that, even in spoil material which has been mixed by regular dragline side-casting, a vertical sequence in the proportion of sulfate sulfur to pyritic sulfur becomes established within approximately 10 years (e.g. spoil core GC-1). The results indicate that the highest proportions of sulfate sulfur to pyritic sulfur occur within the near-surface spoil and the ratio decreases with depth to the point where there is little or no sulfate sulfur. In the 10-year-old spoil at GC-1, the absence of sulfate sulfur occurs at a depth of approximately 24 ft.; in spoil core GC-3 (20 years old), this point is reached at a depth of approximately 29 ft.; in spoil core GC-6 (30 years old) at over 30 ft.; and in spoil core GC-4 (35 years old) at over 48 ft.

These depths are based solely on the proportions of sulfur forms and may be misleading because they do not take into account the effects of leaching. An appreciable sulfate sulfur content at a depth in the spoil may represent the in-place sulfate generated from pyritic sulfur oxidation, or it may represent the sulfate leached from the overlying spoil column above into a zone in which no significant pyrite oxidation has occurred, or it may represent a combination of both processes.

To determine the significance of leaching in the distribution of sulfate sulfur, the pH of the spoil may be used as an indicator of pyritic sulfur oxidation. For example, in spoil core GC-1, the low pH values (less than pH 4.0) in sample 1 (7.0-11.0 ft), sample 2 (11.0-12.6 ft), and sample 3 (12.6-16.4 ft) are indicative of active pyritic sulfur oxidation. The sample below sample 3 [sample 4 (16.4-24.0 ft)] shows a value of pH 5.8, suggesting that oxidation has scarcely commenced. Similarly, based on pH values in spoil core GC-3, active oxidation of pyrite appears to be occurring to a depth of 18.1 feet (sample 4 - pH 3.8). The next lower sample (sample 5) has a pH value of 5.6. In spoil core GC-8, the transition to higher pH values occurs below 13.9 ft; in spoil core GC-6 below 19.6 ft; and in GC-4 below 23.0 ft (although the distinction is not clear in this case).

If pH transitions are compared to the sulfate sulfur proportions, there appears to be a relationship that varies consistently with the age of the spoil. For example, the 10-year-old spoil in core GC-1 has a pH transition zone associated with a sulfate sulfur proportion of approximately 40%; the 20-year-old spoil in core GC-3 has a pH transition zone associated with a sulfate sulfur proportion of approximately 50%; and the spoil which is over 25 years old in cores GC-8, GC-6, and GC-4 has a pH transition zone associated with a sulfate sulfur proportion of over 70%.

If leaching of sulfate had occurred to any significant degree, then the greatest depletion of sulfate would be expected in the near-surface spoil samples where rainfall leaching would be most intense. Such a depletion of sulfate would be marked on the triangular graphs by an upswing of the near-surface spoil samples towards the organic sulfur apex, since these samples are also depleted in pyritic sulfur as shown earlier. Such trends are indeed exhibited by the older spoils. Spoil core GC-4, representing material that is over 30 years old, shows the first two samples [sample 1 (10.0-14.0 ft.) and sample 2 (14.0-21.7 ft.)] with no pyritic sulfur contents and very low sulfate sulfur contents. Similarly, spoil core GC-8 shows a near-surface sample [sample 3 (12.8-13.9 ft.)] with no pyritic sulfur content and a moderately low (33%) sulfate sulfur content.

The spoil samples depleted of both pyritic sulfur and sulfate sulfur exhibit pH values that are higher than those associated with active oxidation of pyritic sulfur. In spoil core GC-4, sample 1 (10.0-14.0 ft) shows a value of pH 4.8 and sample 2 a value of pH 4.9; in spoil core GC-8 sample 3 (10.6-14.0 ft) shows a value of 5.0. These pH levels indicate that either pyritic sulfur oxidation never occurred (because no pyritic sulfur was present in that depth interval) or that it has gone to completion and the original low

pH has been raised by subsequent base resaturation.

The distribution of sulfur forms in three other spoil cores provides further information on different geochemical conditions to those already described (fig. 2). Spoil cores GC-2 and GC-7 have very low overall total sulfur contents and the sulfur forms were determined near the level of detection. Very small variations in content in any of the sulfur forms are therefore reflected in a very wide scatter on the triangular graphs. With the exception of sample 1 in spoil core GC-2, these cores do not show significant reductions in pH due to pyritic sulfur oxidation. Spoil core GC-5 is atypical in that it displays a combination of very low total sulfur contents and high pH values (above pH 7.0) due to the probable presence of carbonates. The absence of pyritic sulfur and sulfate sulfur results in a cluster of data points on the triangular graph near the organic sulfur apex.

SUMMARY AND CONCLUSIONS

A number of general trends in the area associated with the age of the spoil can be observed that can be attributed to processes of sulfide oxidation and leaching. These may be examined using the proportions of the three sulfur forms (organic sulfur, pyritic sulfur and sulfate sulfur) and pH. From the available data, the hypothetical evolution of the spoil geochemistry in the vadose zone is reconstructed as follows:

- In 10-year-old spoil (fig. 3) there would be a relatively clear sequence of samples with decreasing sulfate sulfur contents and increasing pyritic sulfur contents from the surface down. A transition zone would be observed in which there is a marked pH increase downwards from values less than 4.0 (indicating active and full oxidation of pyritic sulfur) to values greater than 5.0 (indicating that oxidation of pyritic sulfur is, at best, commencing).
- After 20 years, the same samples would show a number of changes on the triangular graph. Since a large proportion of pyritic sulfur would have been oxidized, the entire string of data would be drawn closer to the sulfate sulfur apex. The pH transition zone would spread and would be less well-defined. Penetration of oxygen in the vadose zone would have allowed some oxidation of pyritic sulfur even in the deepest sample (No. 10) producing some sulfate sulfur. Some of the sulfate values in the lowermost samples might also represent accumulations of material leached from above.

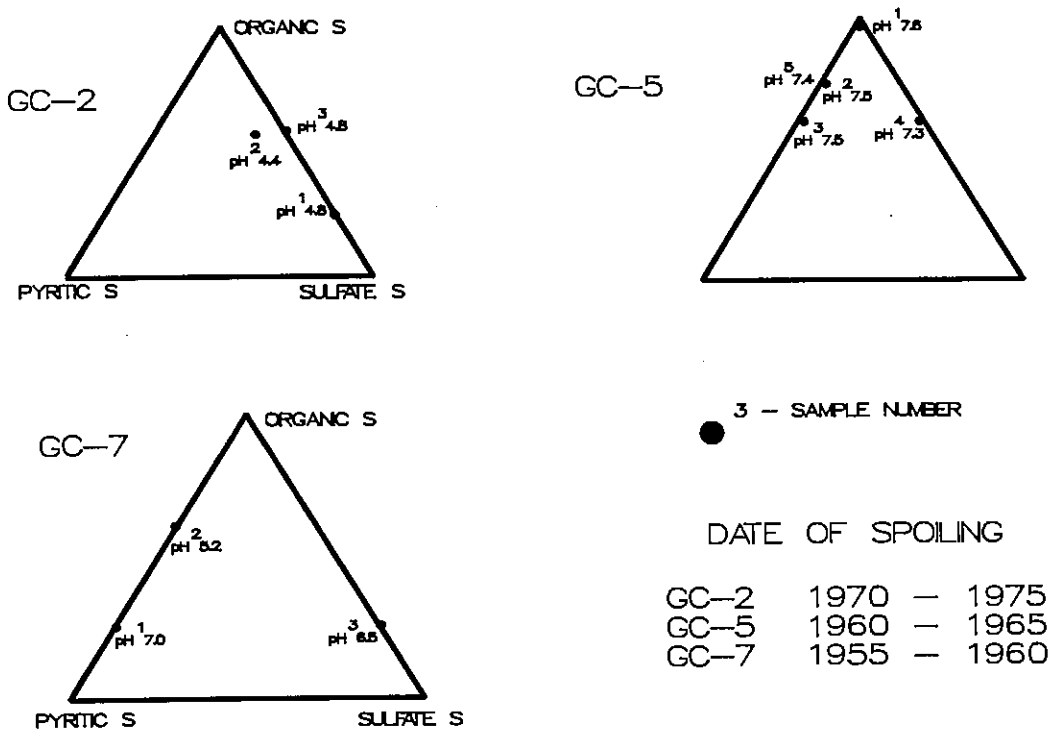


FIGURE 2. SULFUR FORMS IN SPOIL CORES FROM ABANDONED LIGNITE MINE SPOIL

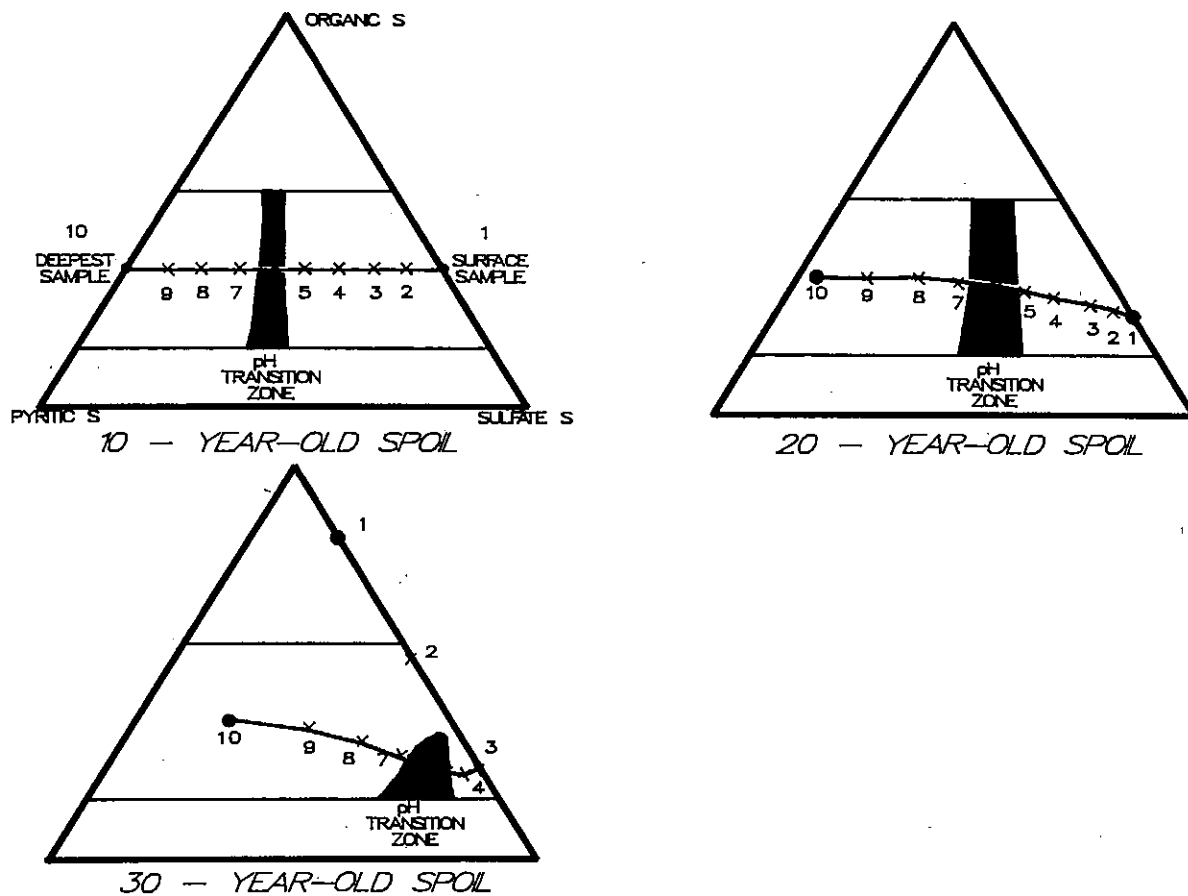


FIGURE 3. RECONSTRUCTED EVOLUTION OF SULFUR FORMS IN SPOIL CORES

° After 30 years, even more oxidation would have occurred and the top 5 samples would show the pyritic sulfur proportion to be less than 10% of the total sulfur forms. The pH transition zone would be very diffuse and difficult to define although it would be closer to the sulfate sulfur apex. Leaching of sulfate from the surface samples would have been significant.

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