

# A Sulfur-Isotope Mixing Model to Trace Leachate From Pressurized Fluidized Bed Combustion Byproducts in an Abandoned Coal Mine Setting

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## ABSTRACT

Approximately 125 tons per acre of dry pressurized fluidized bed combustion (PFBC) byproducts were applied to a seven-acre abandoned coal mine in eastern Ohio during reclamation. The purpose of the application was to raise pH and allow for reestablishment of vegetation. To trace leachate derived from the PFBC byproduct, sulfur-isotope ratios ( $\delta^{34}\text{S}$ ) were measured from solid-phase materials and water samples. The  $\delta^{34}\text{S}$  value for the PFBC byproduct ranged from +4.6 to +4.8 per mil. Spoil samples had  $\delta^{34}\text{S}$  values less than +3.2 per mil. Unsaturated-zone waters within the PFBC byproduct application area had isotope signatures representative of the byproduct whereas similar waters from outside the application area had signatures representative of the spoil. A sulfur-isotope-mixing model indicated that up to 75 percent of the sulfate in application area unsaturated-zone waters was derived from PFBC byproduct leachate. Sulfate concentrations in ground water increased after reclamation; however, the sulfur-isotope data indicated that only small amounts of sulfate in ground water were derived from leaching of the PFBC byproduct. Therefore, increase of dissolved sulfate in ground water was caused by reclamation activities, not addition of the PFBC byproduct.

## INTRODUCTION

Large-volume, beneficial uses of coal-combustion byproducts (CCB's) are important for the continued and economic use of coal for the nation's energy needs. However, regulatory agencies require supporting data that ensures leachate derived from the CCBs is not environmentally hazardous. Trace elements such as arsenic and selenium are present in many CCB's, but their mobility in environmental settings has not been documented. Because many CCBs are alkaline, one of the proposed uses is in the reclamation of abandoned mine sites, where low pH and high dissolved solids concentrations cause significant water-quality problems. In 1994, 125 tons per acre of dry pressurized fluidized bed combustion (PFBC) byproduct produced at the American Electric Power Tidd Plant in Brilliant, Ohio were applied to an abandoned mine site in eastern Ohio. The Tidd Plant burned Pittsburgh (No. 8) coal and used dolostone from northwest Ohio as a sorbent. The resulting dry PFBC byproduct was incorporated into the spoil along with 50 tons per acre of yard-waste compost to enhance establishment of vegetation. Water-quality

monitoring of unsaturated-zone water, ground water, and downgradient spring water began soon after reclamation and continued through 1998.

## METHODS

The mine site, hereafter referred to as the Fleming site, is located in Tuscarawas County, Ohio. After surface grading and application of PFBC byproduct and yard-waste compost, four, 150-foot deep rock cores were taken to define site stratigraphy and to obtain rock samples. Additional rock samples were obtained from spoil and rock outcrops adjacent to the site.

The Fleming site was instrumented with 36 soil-suction lysimeters and 20 ground-water-monitoring wells. Five clusters of lysimeters were installed in the unsaturated zone at depths ranging from 1.5 to 4.5 feet below land surface. Four clusters were installed within the PFBC byproduct application area and one cluster was installed in a control area where traditional reclamation methods were used. Monitoring wells were installed around the perimeter and within the application area, with completion depths ranging from 16 to 100 feet. Wells were screened in a shallow aquifer (the Clarion sandstone and the Brookville coal) and a deep aquifer (the Tionesta coal). Discharge measurements and water-quality samples were obtained from three downgradient springs during baseflow conditions, when the source of the spring water was ground water and not surface runoff.

Water-quality samples were obtained five times between 1995 and 1998. Chemical analyses included major constituents and trace elements associated with acid-mine drainage (AMD) and the known composition of the PFBC byproduct (Stehouwer and others, 1995, 1996). Sampling and analytical methods are discussed in detail in Haefner (1998b). In an attempt to differentiate the effects of leachate derived from the PFBC byproduct from the effects of traditional reclamation, sulfur-isotope ratios ( $\delta^{34}\text{S}$ ) were measured in the PFBC byproduct, rock samples, and water samples. Specific sampling methods for all solid-phase and water samples are given in Haefner (1998b). Sulfur-isotope ratios from sulfate ( $\text{SO}_4$ ) and sulfide ( $\text{FeS}_2$ ) fractions were analyzed on a mass spectrometer, and results are reported relative to the Canyon Diablo troilite (FeS) reference standard by use of the following notation and calculation:

$$\delta^{34}\text{S} = \left[ \frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}} - {}^{34}\text{S}/{}^{32}\text{S}_{\text{standard}}}{{}^{34}\text{S}/{}^{32}\text{S}_{\text{standard}}} \right] \times 1000 \quad (1)$$

$\delta^{34}\text{S}$  is reported in units of per mil (parts per thousand relative to a standard). Sulfur-isotope values have a standard error of  $\pm 0.2$  per mil.  $\delta^{34}\text{S}$  was measured in sulfide for solid-phase materials, whereas  $\delta^{34}\text{S}$  was measured in sulfate for water samples (only trace amounts of sulfide (as hydrogen sulfide) were measured in the field at or near the detection level of 1.0 ug/L). All water analyses were conducted by the National Water Quality Laboratory of the U.S. Geological Survey in Arvada, CO, the water quality laboratory at the Ohio Agricultural Research and Development Center (OARDC) in Wooster, OH, or the stable isotope laboratory of the U.S. Geological Survey in Reston, VA. Only the results of the analyses for dissolved sulfate and sulfur isotopes will be reported here. For the remaining water-quality data, the reader is referred to Stehouwer and others (1995, 1996) and Haefner (1998a, 1998b).

## RESULTS

$\delta^{34}\text{S}$  in the surface-mined coal (Lower Kittanning, No. 5) ranged from -13.7 to +3.0 per mil whereas Lower Kittanning underclay samples ranged from +3.2 to +13.6 per mil (fig. 1). The total sulfur content of the Lower Kittanning coal ranged from 1.48 to 2.20 weight percent whereas the sulfur content in the Lower Kittanning underclay was 0.22 weight percent. Sulfur-isotope compositions of the underlying (unnamed) shale and the Clarion Sandstone ranged from -5.0 to +7.1 per mil. The Brookville coal (No. 4a), which is part of the shallow aquifer at the site, had  $\delta^{34}\text{S}$  values in the range of -5.8 to -26.3 per mil. The Tionesta coal (No. 3b) had  $\delta^{34}\text{S}$  values ranging from -5.9 to -17.8 per mil.

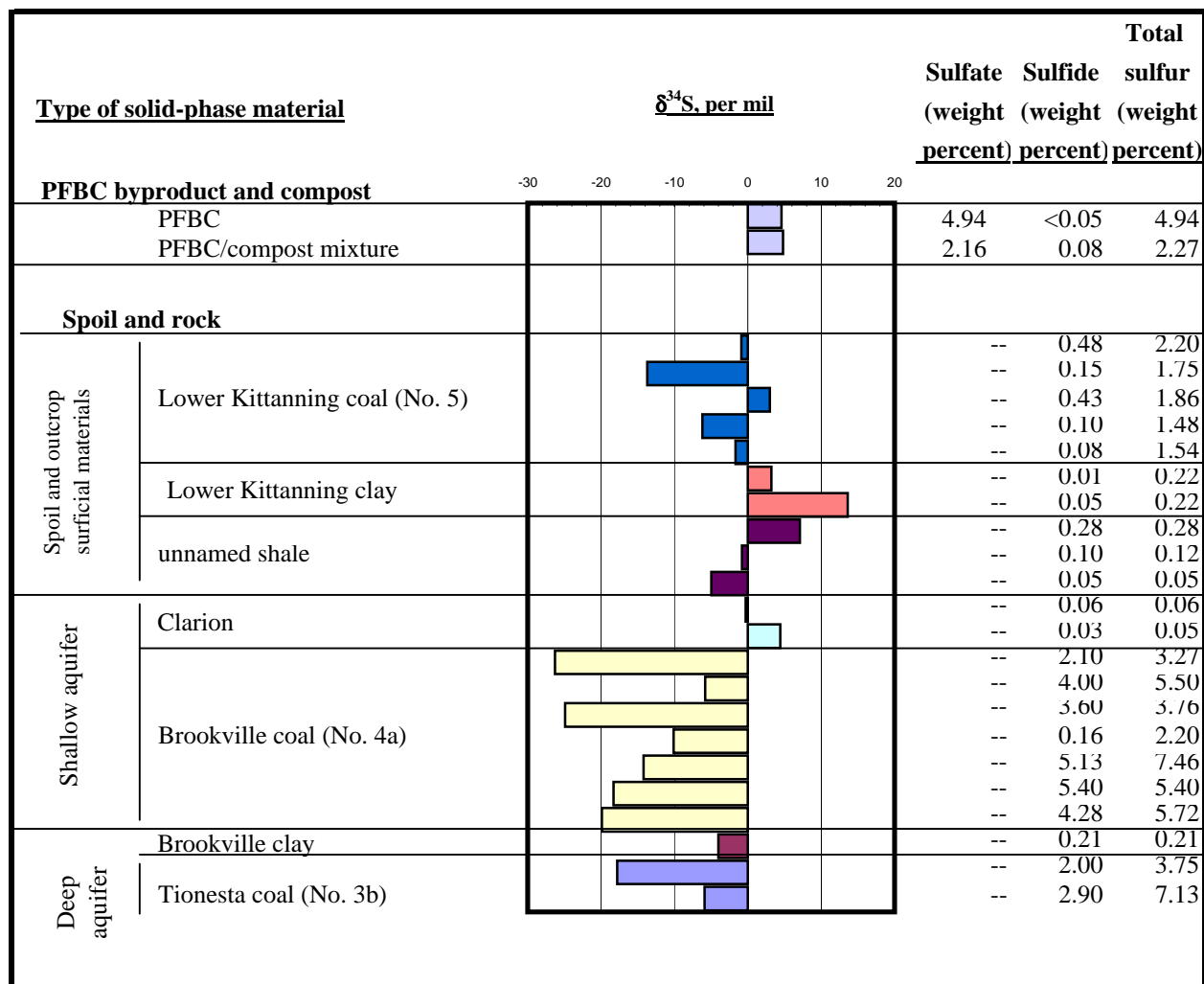
$\delta^{34}\text{S}$  in sulfate fractions of the PFBC byproduct was +4.6 per mil (figure 1). Analysis of sulfate in the PFBC byproduct/compost mixture resulted in  $\delta^{34}\text{S}$  values of +4.8 per mil. Sulfide constituted less than 0.05 percent by weight of the pure PFBC sample, whereas slightly greater sulfide concentrations (0.08 percent by weight) were present in the PFBC byproduct/compost mixture. Thus, the sulfur in the PFBC byproduct was primarily in the form of sulfate.

Median concentrations of sulfate in water from the application-area unsaturated zone (interstitial) waters were highest during the first sampling round, and then decreased significantly during sampling round 2 (no samples were obtained during round 3, table 1). Samples for round 2 were collected immediately after a major snowmelt event and dilution may have reduced the sulfate concentrations. Interstitial water samples collected during rounds 1, 4, and 5 were done during relatively dry conditions. Sulfate concentrations in the control area increased throughout the monitoring period (table 1). Increases of sulfate concentrations in the control area are likely due to the slow oxidation process induced by disturbance of the spoil by reclamation activities.  $\delta^{34}\text{S}$  in application-area interstitial waters had median concentrations ranging from -7.5 to -1.1 per mil, whereas median concentrations in control-area interstitial waters ranged from -15.4 to -12.2 per mil. Comparison of  $\delta^{34}\text{S}$  values from all sampling rounds reveals that the application-area interstitial waters were isotopically enriched (-2.8 per mil) as compared to those in the control area (-15.2 per mil).

Median concentrations of sulfate in upgradient and downgradient ground water have increased slightly or remained stable between sampling rounds (table 1). Sulfur-isotope values have remained relatively constant.  $\delta^{34}\text{S}$  in sulfate from ground-water samples from upgradient of the application area were very similar to those from downgradient of the application area, indicating little, if any, influence of PFBC product leachate on ground-water quality. This is confirmed by examination of other constituents in ground water such as pH, boron, and magnesium to calcium mole ratios, the latter of which are unaffected by dilution effects (Haefner, 1998a, 1998b). Additionally, concentrations of potentially toxic trace elements such as arsenic and selenium have only been measured at or near the detection limit of 1 microgram per liter ( $\mu\text{g/L}$ ) in interstitial and ground-water samples (Haefner, 1998b).

## DISCUSSION

Sulfur-isotope ratios from rock samples and water were measured to differentiate between sulfur derived from the PFBC product and sulfur derived from spoil and aquifer materials. The primary



**Figure 1.** Sulfur isotope composition of solid-phase materials from the Fleming abandoned mine site, Tuscarawas County, Ohio.(--, no data)

**Table 1.** Median dissolved sulfate and sulfur isotope ( $\delta^{34}\text{S}$ ) compositions for water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio.

[mg/L, milligrams per liter; per mil, parts per thousand relative to standard; --, no data]

	<b>Round 1</b>		<b>Round 2</b>		<b>Round 3</b>		<b>Round 4</b>		<b>Round 5</b>	
	<b>Jun/Oct-95</b>		<b>Jan-96</b>		<b>Jun-96</b>		<b>Jun-97</b>		<b>Jun-98</b>	
	<b>Dissolved sulfate</b> (mg/L)	<b><math>\delta^{34}\text{S}</math></b> (per mil)	<b>Dissolved sulfate</b> (mg/L)	<b><math>\delta^{34}\text{S}</math></b> (per mil)	<b>Dissolved sulfate</b> (mg/L)	<b><math>\delta^{34}\text{S}</math></b> (per mil)	<b>Dissolved sulfate</b> (mg/L)	<b><math>\delta^{34}\text{S}</math></b> (per mil)	<b>Dissolved sulfate</b> (mg/L)	<b><math>\delta^{34}\text{S}</math></b> (per mil)
<b>Interstitial water</b>										
Application area	7680	-3.2	5260	-1.1	--	--	3390	-4.1	3470	-7.5
Control area	--	--	740	-12.2	--	--	1090	-14.7	1240	-15.4
<b>Ground water</b>										
Upgradient	1110	-10.2	1740	-10.6	1920	-10.6	2120	-10.6	2100	-10.3
Downgradient	1770	-9.7	1750	-9.5	1840	-9.6	1880	-10.7	1810	-9.5
<b>Spring water</b>										
	1180	-9.4	--	--	810	-9.6	750	-9.5	840	-10.3

source of sulfur from spoil and aquifer materials is reduced sulfur (sulfide); whereas sulfur in PFBC byproduct and water is in the form of oxidized sulfur (sulfate).

Comparisons of sulfur-isotope ratios between those in sulfide and sulfate are possible because fractionation does not significantly occur during the oxidation of inorganic sulfide minerals (Ohmoto and Rye, 1979). Other forms of sulfur, including organic sulfur from the compost, were assumed to be insignificant from a mass-balance perspective. Rainwater also contributes sulfate to the interstitial and ground waters at the site; however the median concentration of sulfate measured at the site over a period of a year was only 3.1 milligrams per liter (mg/L; Haefner, 1998b). Additionally, Haefner (1998b) determined through a mass balance of sulfate for the site, that during any given year, only about 1 percent of the total sulfate in interstitial water was derived from rainwater. Thus, rainwater was not considered to contribute significantly to sulfate concentrations in water samples.

Because high dissolved sulfate concentrations are characteristic of acid mine drainage and disturbance due to reclamation, it is important to know whether a reclamation material such as PFBC byproduct contributes additional sulfate to ground water. The relative contributions of the two sources of sulfate at this site can be examined by application of a mixing model to sulfur-isotope ratios. An advantage of using isotope ratios in mixing evaluations is that dilution or concentration does not affect isotope ratios whereas concentrations of individual elements are subject to these processes. The mixing model assumes that the constituent under consideration is conservative, that there are only two components that contribute sulfur to the system, and that the chemical and isotopic compositions of the end members are constant (Faure, 1991). The isotopic composition of any mixture can be described as a straight line with the form:

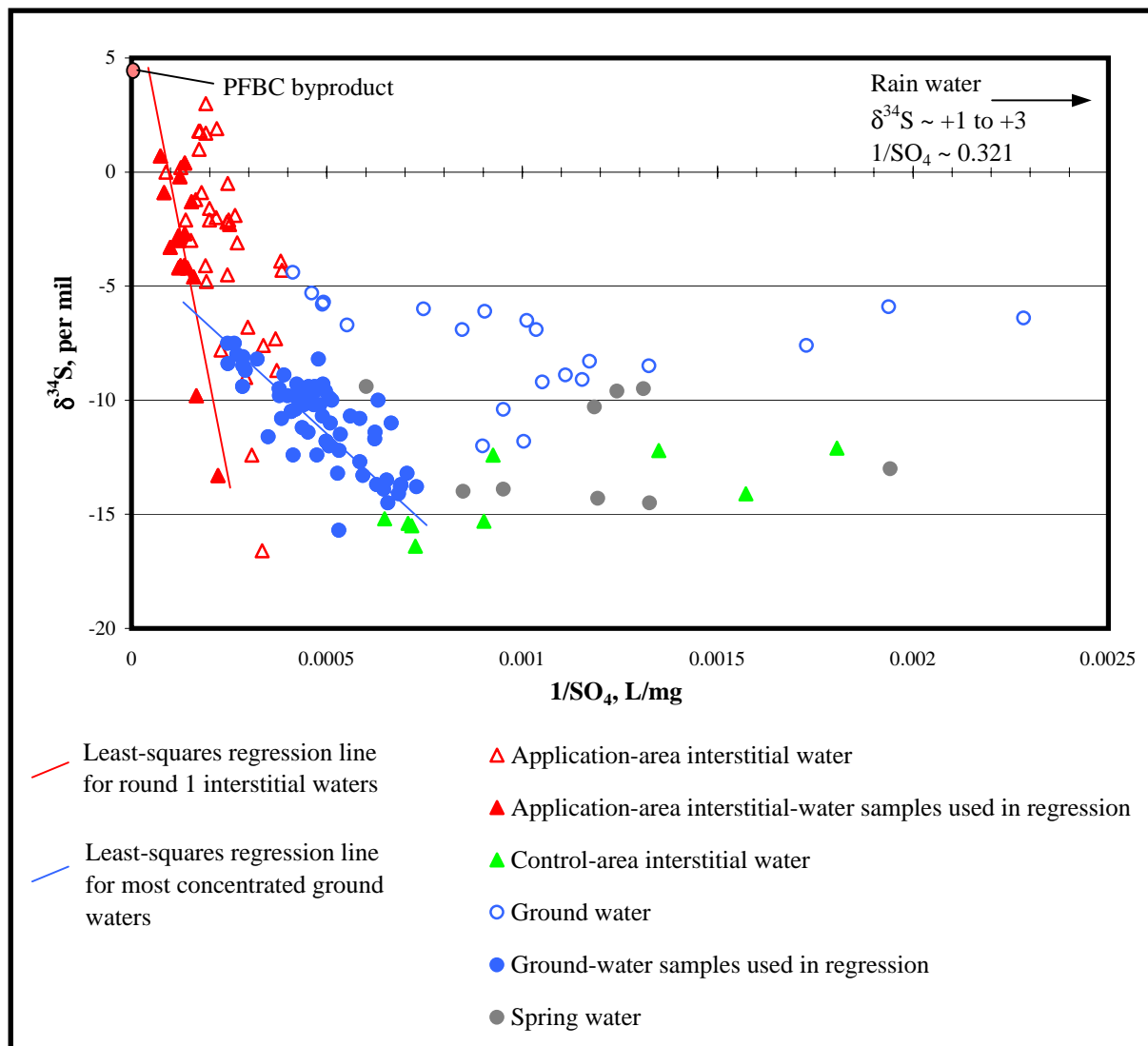
$$\delta^{34}\text{S} = \frac{a}{S_M} + b, \quad (2)$$

Where  $\delta^{34}\text{S}$  is the isotope ratio in sulfate,  $S_M$  is the concentration of sulfate in the mixture, and  $a$  and  $b$  are constants specified by the concentrations and  $\delta^{34}\text{S}$  values of sulfate in the two end-member components (Faure, 1991). Because the sulfate concentration in equation 2 is in the denominator, the inverse of sulfate is used for all subsequent mixing relations.

To estimate the abundance of sulfate derived from PFBC byproduct in interstitial waters, an equation for the relation between the inverse of sulfate and  $\delta^{34}\text{S}$  was calculated for the most concentrated samples using least-squares regression (figure 2). The regression line was generated for a selected set of water samples only and does not include data from the end members. The regression analysis provided the following mixing equation:

$$\delta^{34}\text{S} = \frac{-82194.5}{\text{SO}_4} + 7.302 \quad (3)$$

Because the concentration of sulfate in water is subject to the effects of dilution, all sulfate values were adjusted to fit the regression line displayed by the most concentrated waters (figure 2). Selection of end members is critical to the interpretation of the mixing model. The  $\delta^{34}\text{S}$  value from the PFBC byproduct was selected as one end member (+4.6 per mil) and  $\delta^{34}\text{S}$  from the most depleted interstitial water sample from the control area (-16.4 per mil) was selected as the other



**Figure 2.** Sulfur-isotope composition in relation to the inverse of dissolved sulfate for water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio.

end member. These end members represent the two extreme isotope values that bound all observed isotope values in interstitial water at the study site. The sulfate in all application-area interstitial-water samples was assumed to be derived from varying percentages of each end member. The percentage of each end member was computed based on the sulfur-isotope ratio and the relative position of the water sample along the mixing line expressed as equation 3.

The average amount of sulfate derived from PFBC byproduct in interstitial waters varied from 61 percent during round 1, 75 percent in round 2, 51 percent in round 4, to 46 percent in round 5 (figure 3). The data for each sampling round show differing degrees of variance about their means, thus statistical tests of differences in population means were not done. However, the general decrease in the percent of sulfate derived from PFBC byproduct between the last three sampling rounds can be used to make some inferences regarding the persistence of sulfate from the PFBC byproducts in water. If the observed trend continues, it will take approximately 30 years for all the sulfate to be leached from the PFBC byproduct. The leaching of the PFBC byproduct is directly related to the amount and magnitude of recharge that enters the application area, as was shown by the relative increase in percentage of sulfate derived from PFBC byproduct during the snowmelt event.

Ground water at the mine site has very different  $\delta^{34}\text{S}$  values compared to application or control-area interstitial waters. Ground water at the site is a mixture of sulfate derived from dissolution and oxidation of sulfide from spoil and rock sources. All previous chemical data indicate that mixing of leachate derived from the PFBC byproduct and ground water has not occurred (Haefner, 1998b).

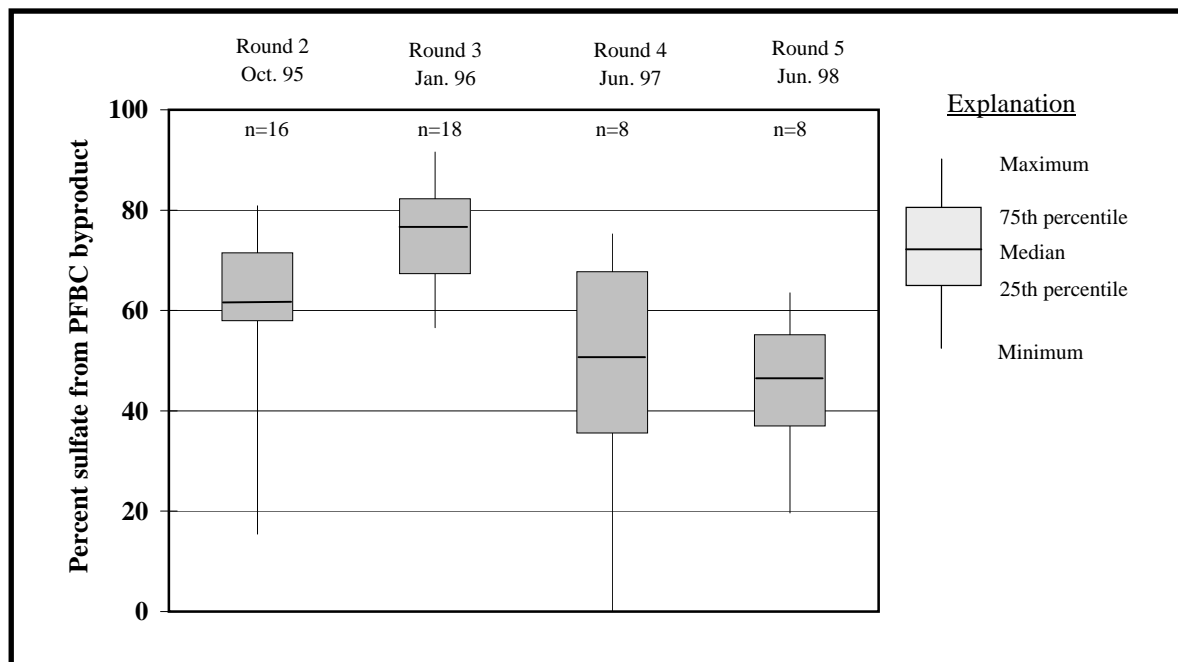
To assess mixing relations between sulfate derived from surface-mined coal and aquifer materials in ground water, a process similar to that applied to the interstitial waters was used. A subset of the most concentrated ground-water samples was selected from all samples ( $\delta^{34}\text{S}$  less than -7.5 per mil and inverse sulfate concentrations of less than 0.00075 L/mg). The linear regression equation for ground-water samples had the following form:

$$\delta^{34}\text{S} = \frac{-12444.2}{\text{SO}_4} - 4.326 \quad (4)$$

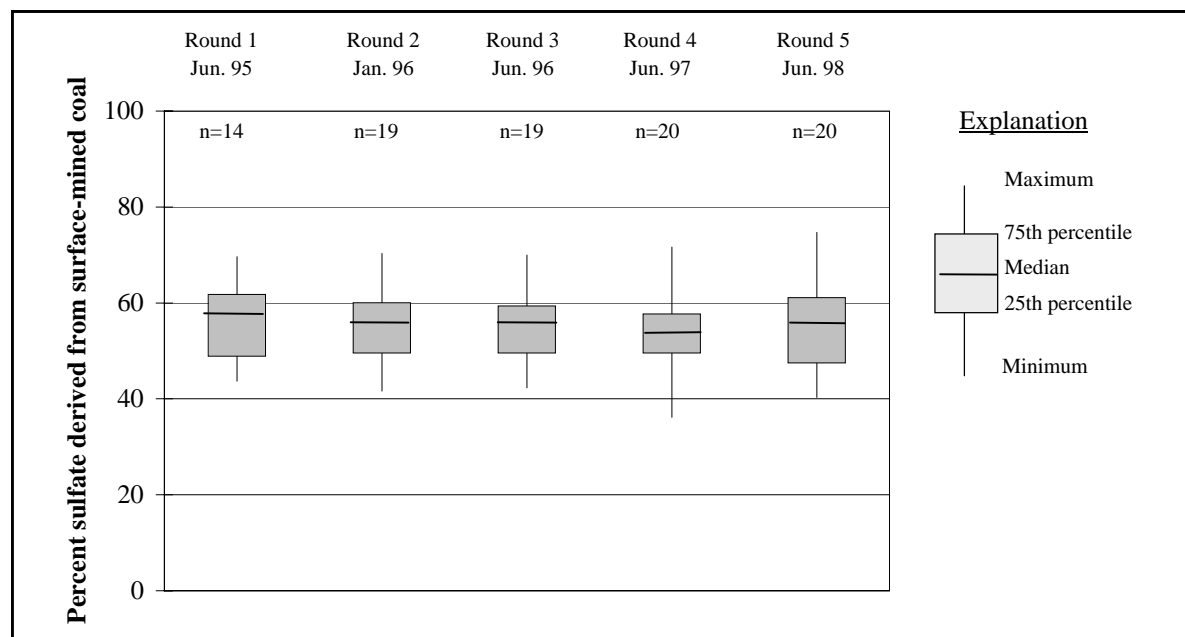
The value of the Y intercept for this equation is very close to the mean  $\delta^{34}\text{S}$  value of the Lower Kittanning (No. 5) coal of -3.9 per mil indicating that weathering and oxidation of sulfide from the surface-mined coal (which is now spoil) is a likely source of sulfate in ground water. End members of mixing were selected from the surface-mined coal and aquifer materials: the most enriched sample was a sample of Lower Kittanning (No. 5) coal with a  $\delta^{34}\text{S}$  value of +3.0 per mil, whereas the most depleted sample (-26.3 per mil) came from the Brookville (No. 4a) coal (part of the shallow aquifer).

Application of mixing theory to ground-water samples reveals that most of the water contains sulfate that is from 50 to 60 percent derived from the surface-mined coal (figure 4). The remaining sulfate was derived from the aquifer materials and represents the concentration of sulfate in ground water had mining and reclamation not occurred. Concentrations of sulfate in





**Figure 3.** Boxplots of percent of sulfate derived from PFBC byproducts during each sampling round at the Fleming abandoned mine site, Tuscarawas County, Ohio.



**Figure 4.** Boxplots of percent sulfate derived from surface-mined coal in ground water at the Fleming abandoned mine site, Tuscarawas County, Ohio.

ground water from unmined areas in eastern Ohio are generally less than 500 mg/L (Sedam and Francy, 1993). Thus, it is possible that the amount of sulfate derived from oxidation of surface-mined coal is underestimated due to selection of an end member that is too isotopically light. Therefore, the estimates of the amount of sulfate derived from oxidation of surface-mined coal provided in this study are likely minimum values.

Differences in the percentage of sulfate derived from surface-mined coal between sampling rounds are slight (less than 2 percent); however, these calculations indicate that the amount of sulfate derived from surface-mined coal decreases with time from 57 percent in 1995 to 53 percent in 1997. If this trend were to continue, about 1.5 percent of the sulfur would be lost from the spoil each year and, therefore, it would take 30 to 50 years for the sulfate to be flushed through the aquifers at the mine site. This assumes, however, that the loss of sulfur continues at a constant rate. Cunningham and Jones (1990) and Eberle and Razem (1985) show that this loss is not linear with respect to time and occurs quickly at first, but much slower in later years (similar to an asymptotic curve).

The sulfur-isotope composition of spring water should be similar to the sulfur-isotope composition of downgradient ground waters. The median value of  $\delta^{34}\text{S}$  at the springs ranged from -10.3 to -9.4 per mil for the four sampling rounds. These values are approximately the same as those determined in ground water at a downgradient well cluster. Application of the mixing equation used for ground water reveals that approximately 60 percent of the sulfate in spring water was derived from oxidation of sulfide in the surface-mined coal. As was the case for ground water, spring water shows little, if any, influence of leachate from the PFBC byproduct.

## CONCLUSIONS

The use of sulfur-isotope ratios to identify sources of sulfate in water from an abandoned mine site reclaimed with PFBC byproducts revealed that up to 75 percent of the sulfate in interstitial waters was derived from leaching of the PFBC byproduct. Additional water-quality analyses have shown that trace elements such as arsenic and selenium are only at or near the detection limits of 1.0  $\mu\text{g/L}$  (Haefner, 1998b). Thus, even though interstitial waters contain abundant amounts of sulfate derived from the PFBC byproduct, elevated concentrations of potentially toxic trace elements were not measured during this sampling period. Additionally, sulfate concentrations in upgradient ground water have increased after reclamation, but sulfur-isotope data and other chemical data show that the source of the sulfate is from reclamation activities, not the PFBC byproduct. The added sulfate derived from the PFBC byproduct in the unsaturated zone may be precipitated as gypsum or other sulfate salts and may take many more years to appear in ground water at the site. Saturation indices calculated with WATEQ4F (Ball and Nordstrom, 1991) indicate that interstitial waters are saturated with respect to the minerals gypsum and jarosite (Haefner, 1998b).

This method of tracing leachate derived from PFBC byproducts was effective in this setting because the source coal for the PFBC process that was burned at the Tidd Plant was different from that which was mined at the site. The difference in sulfur-isotope composition between the two coals was great enough to allow differentiation using mixing theory. The mixing relations documented for sulfur isotopes could be strengthened by examining similar relations between other elements or ratios of elements, such as boron and magnesium to calcium mole ratios

(Haefner, 1998a). Although each CCB is unique in its composition and the environmental setting may change for different uses of the material, studies such as this are important to determine the fate and transport of leachate in the environment.

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