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LEACHING OF METALS AND TRACE ELEMENTS FROM SULFIDE-BEARING COAL WASTE IN SOUTHWESTERN ILLINOIS

by

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Abstract. Metal sulfides, chiefly pyrite and minor sphalerite, associated with the Herrin (No. 6) coal member of the Pennsylvanian Carbondale Formation, have been concentrated in a coal refuse deposit in southern Illinois. Chemical, petrographic and X-ray diffraction data for 34 cores, show that the upper two meters of material have been leached of sulfides in the thirty years since washing operations ceased.

Oxidation of pyrite has produced highly acid waters with high concentrations of iron, zinc (up to 200 parts per million) and toxic trace elements that have leached downward to a water system perched on the underlying Illinoian glacial drift. Deep well samples in the refuse pile are more saturated with metals than are the runoff waters and shallow well samples. Metal recovery does not appear to be economically feasible at this site.

Introduction

An inherent problem in the disposal of solid waste on land is the possibility of ground-water contamination by leachates from the waste. In the few studies conducted on the effects of coal refuse disposal on ground-water quality, significant impacts have been observed. Based on past and present rates of coal refuse disposal and current knowledge of water chemistry of runoff and seeps from refuse sites, significant ground-water contamination may be occurring in the eastern and midwestern United States.

Coal after mining requires beneficiation to remove excess rock and mineral matter. After crushing, the low-density coal is separated from the more dense rock and mineral waste in a fluid medium. The rejected material is known as gob. Turbid waste water is sent to a holding pond for clarification by settling. The fine, laminated sediment is called slurry. In the past, coal wastes were deposited near the preparation plant, economic convenience being the only consideration.

Illinois Basin coals contain pyrite, much of which becomes concentrated in the coal waste. Broken and exposed to atmospheric moisture and oxygen, the pyrite is oxidized and dissolved thus releasing iron, sulfate and hydrogen ion to infiltrating waters. Catalyzed by an iron oxidizing

bacterium, *Thiobacillus Ferrooxidans*, the oxidation of pyrite proceeds rapidly. Highly acid, iron-sulfate waters develop in the wastes, leaching alkaline earths and heavy metals from associated minerals. Sulfide-bearing coal-waste deposits are characterized by a lack of vegetation, rapid erosion and serious degradation of surface drainages by silting.

There are currently over 14,000 acres of abandoned coal wastes in the Illinois Basin coal region. There are over 1,000 abandoned deposits in Illinois, and 711 of them are considered to pose serious environmental problems.

Each coal-waste deposit is chemically and physically unique because a given coal seam varies compositionally within a region and with one another, and efficiency of coal cleaning operations varied with time and place. As a result of these factors, chemical relationships to mineralogy are poorly understood. The questions of treatment, material recovery and reclamation may have to be evaluated for each deposit.

In order to better understand the physical and chemical properties of the waste material and associated ground water, one coal-waste deposit in southern Illinois was studied. The study was designed to determine oxidized zones in the coal waste, to study relationships of mineralogy to acid

leachate production and to provide information that could be used in environmentally sound planning of material recovery and reclamation.

Site Description

The Superior Coal Company washer is located in Macoupin County, Illinois (Fig. 1). It sets on an Illinoian ground moraine. The flat upland topography is primarily used as farmland, which is occasionally dissected by small streams. The washer site is drained to the northeast and southeast by two small streams that enter Spring Creek (Fig. 2), a tributary of Cahokia Creek, which flows to the southwest to join the Mississippi River. Cahokia, within an area of about 15 square miles on its upper reaches, receives acid drainage from at least 10 abandoned coal-waste deposits (Fig. 2).

The Superior Coal Company opened four deep mine shafts, labelled S#1, S#2, S#3 and S#4 (Fig. #2), between 1904 and 1918. The presence of gob materials at the four shafts and the absence

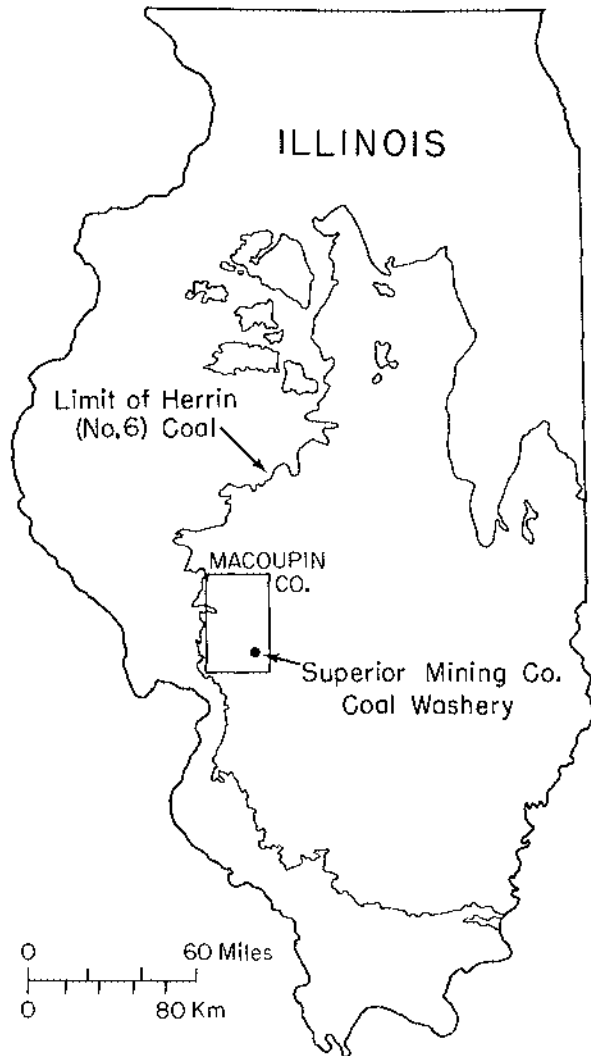


Figure 1. Map showing the location of the study area with the boundary of the Herrin (No. 6) Coal.

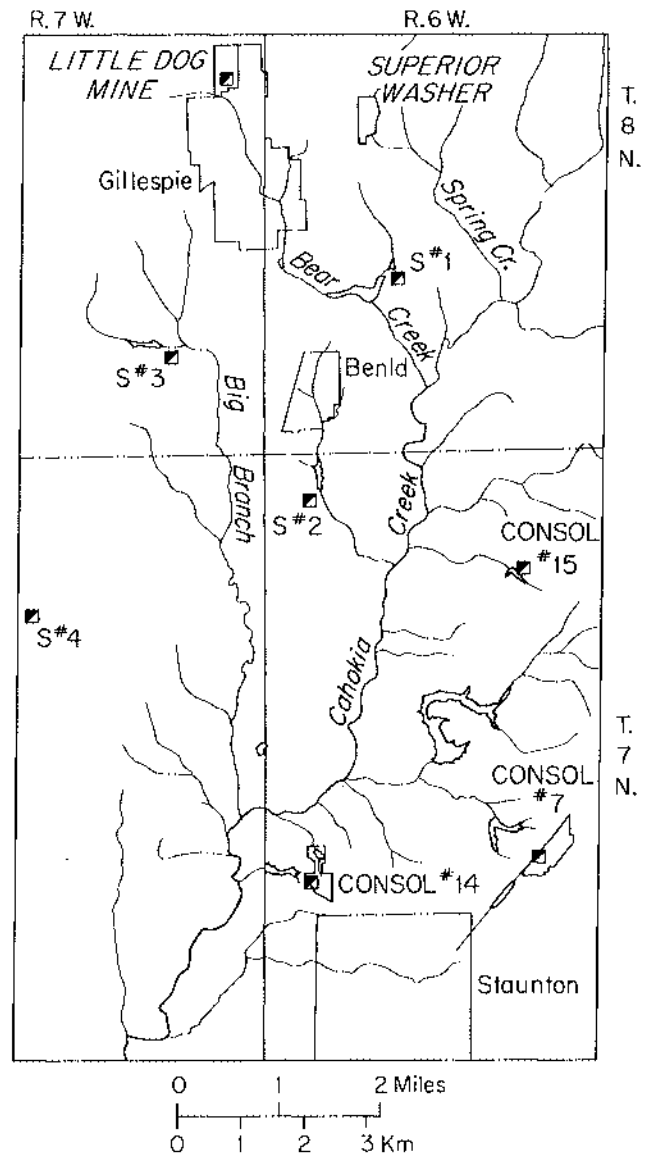


Figure 2. Map showing location of Superior Washer and important local streams.

of slurries indicates that there were no washing operations at the mine shafts or that wash-water slurries were discharged directly into streams.

The Superior Coal Company opened its washer station east of Gillespie (Fig. #2). Coals from all four mines were brought in by rail, mechanically processed and shipped on to consumers. The Superior washer resulted in the production of over 900,000 cubic yards (688,000 m³) of gob and slurry wastes covering roughly 58 acres. The mines were closed between 1951 and 1954, and washing operations ceased. Since that time, the gob and slurry wastes have been exposed to weathering and erosion.

Sulfur Analysis

In June of 1978, 34 cores were collected from the gob and slurry material on the Superior washer site. Stations were selected in a variety of morphologic settings to maximize the range of materials sampled and better characterize the site.

All samples were analyzed for total sulfide and sulfate and organic sulfur content using a LECO induction furnace equipped with an automatic sulfur titrator. Results of the various sulfur forms, reported as weight percent sulfur of whole sample, are shown in Table 1. A comparison of average sulfur forms and associated lithologies as reported by Gluskoter is shown in Table 2.

Gob samples have a larger average total sulfur content than slurries as shown in Table 2. Also, a greater portion of this total is because of sulfides in gob samples than in slurries. Organic sulfur is the dominant form in slurries and only a minor contributor in gob. The similarities of the slurry to the coal, and the gob to the lithologic units with regard to the total sulfide and total organic sulfur proportions, should be noted. The major difference between the waste and the coal seam occurs in the sulfate. The sulfate comprise a much larger proportion in the waste than coal seam. Note that sulfates, chiefly oxidation products of pyrite, occur mainly in samples from weathered mine walls and are minor in fresh samples.

The above relationships are what would be expected from beneficiation and deposition of wastes at the Superior washer. Density separation of pyrite and lithic fragments resulted in gob materials similar in total sulfur and sulfide content to the coal seam lithologies. Low-density coal

Table 2. Average Sulfur Forms as Weight Percent Sulfur in Whole Sample for 8 Slurry and 26 Gob Samples from the Superior Washer Compared to Similar Data for No. 6 Coal and Associated Lithologies after Gluskoter, and Others.

| | Slurry | Gob | No. 6 Coal | No. 6 Lithology |
|---------------------------------|--------|-------|------------|-----------------|
| weight percent sulfur total | 2.05 | 7.71 | 3.4 | 5.6 |
| weight percent sulfur (sulfide) | 0.69 | 5.13 | 1.7 | 4.9 |
| weight percent sulfur (sulfate) | 0.53 | 1.82 | 0.1 | 0.2 |
| weight percent sulfur (organic) | 0.83 | 0.76 | 1.6 | 0.5 |
| sulfide/total | 33.8% | 66.5% | 50.2% | 87.6% |
| sulfate/total | 25.8% | 23.6% | 2.8% | 4.1% |
| organic/total | 40.3% | 9.9% | 47.0% | 8.6% |

finer concentrated in the slurry waters reflect the higher organic sulfur content of the coal itself. Crushing, wetting and exposure to oxygen allow for the formation of more sulfates in the wastes than in the in-situ coal seam.

Table 1. Forms of Sulfur, as Weight Percent Sulfur in the Whole Sample, in 34 Cores (11 stations) from the Superior Coal Washer (SL=Slurry, GB=Gob).

| Sample (sta-#) | Type | Depth (m) | Total Sulfur | Sulfide Sulfur | Sulfate Sulfur | Organic Sulfur |
|----------------|------|-----------|--------------|----------------|----------------|----------------|
| 1-1 | GB | 0.13 | 2.28 | 0.50 | 1.15 | 0.63 |
| 1-2 | GB | 0.62 | 3.33 | 0.86 | 1.82 | 0.65 |
| 1-3 | SL | 1.10 | 2.46 | 0.58 | 1.01 | 0.87 |
| 1-4 | SL | 1.82 | 1.72 | 0.43 | 0.51 | 0.79 |
| 2-1 | SL | 0.16 | 1.31 | 0.14 | 0.45 | 0.73 |
| 3-1 | GB | 0.01 | 1.92 | 1.00 | 0.04 | 0.88 |
| 3-2 | GB | 1.46 | 15.89 | 13.41 | 1.29 | 1.19 |
| 3-3 | SL | 1.56 | 1.49 | 0.67 | 0.14 | 0.68 |
| 4-1 | GB | 0.10 | 1.74 | 0.60 | 0.38 | 0.76 |
| 4-2 | SL | 1.50 | 2.32 | 0.75 | 0.67 | 0.91 |
| 5-1 | GB | 0.10 | 2.75 | 0.57 | 1.70 | 0.48 |
| 5-2 | GB | 1.53 | 7.37 | 4.49 | 1.59 | 1.30 |
| 5-3 | SL | 3.05 | 2.60 | 1.15 | 0.35 | 1.10 |
| 6-1 | GB | 0.11 | 3.87 | 0.47 | 2.91 | 0.49 |
| 6-2 | GB | 1.50 | 3.66 | 2.91 | 0.49 | 0.26 |
| 6-3 | GB | 2.73 | 5.59 | 3.91 | 0.97 | 0.72 |
| 7-1 | GB | 0.13 | 2.95 | 0.53 | 1.81 | 0.61 |
| 7-2 | GB | 1.09 | 5.18 | 2.30 | 2.30 | 0.58 |
| 7-3 | SL | 1.48 | 2.39 | 0.96 | 0.58 | 0.84 |
| 7-4 | SL | 2.25 | 2.13 | 0.86 | 0.53 | 0.73 |
| 8-1 | GB | 0.10 | 6.50 | 2.16 | 3.70 | 0.65 |
| 8-2 | GB | 1.32 | 17.30 | 14.60 | 2.05 | 0.65 |
| 8-3 | GB | 3.11 | 22.48 | 19.89 | 1.80 | 0.78 |
| 8-4 | GB | 5.87 | 16.52 | 14.52 | 1.23 | 0.75 |
| 9-1 | GB | 0.13 | 4.61 | 1.85 | 2.20 | 0.56 |
| 9-2 | GB | 1.37 | 6.37 | 0.86 | 4.32 | 1.18 |
| 9-3 | GB | 2.97 | 9.46 | 6.31 | 2.67 | 0.48 |
| 10-1 | GB | 0.10 | 2.90 | 1.05 | 0.87 | 0.98 |
| 10-2 | GB | 1.54 | 3.20 | 0.67 | 1.73 | 0.80 |
| 10-3 | GB | 2.98 | 21.41 | 19.97 | 0.16 | 1.28 |
| 10-4 | GB | 6.55 | 12.09 | 8.66 | 2.48 | 0.95 |
| 11-1 | GB | 0.11 | 5.79 | 2.02 | 3.23 | 0.54 |
| 11-2 | GB | 1.57 | 3.75 | 1.56 | 1.31 | 0.88 |
| 11-3 | GB | 3.04 | 11.59 | 7.63 | 3.10 | 0.86 |

Weathering Interpretation

The Superior Coal Company deposited coal waste at the washer site for over 30 years. These materials have been exposed to the environment for about 26 years since operations ceased. It is assumed that acid conditions and mineral leaching developed and continued during the active period. This study was designed to determine the presence and extent of oxidation in the waste since the washer closed. Sulfur content (total, sulfide, sulfate and organic) was plotted against sample depth. There was little correlation of organic sulfur to sample depth, which is expected because organically bound sulfur is less susceptible to acid attack and leaching than sulfides and sulfates. A random distribution of coal and shale organics through the wastes is reflected in the organic sulfur distribution, which shows little response to oxidizing effects near the surface.

Initially it was thought that sulfates from pyritic oxidation might show larger values at depth, however, a wide range of sulfate exists in the shallowest samples indicating a lack of correlation with depth in general. One explanation for this lies in the high solubility of sulfate minerals in the study area. Laboratory studies show that the sulfate minerals dissolved rapidly in water and reprecipitated upon drying. In mid-summer, at the washer site sulfate minerals precipitated with afternoon heat on damp gully walls and in shallow drainages, only to dissolve again at night. This indicates that aqueous concentration is the prime control on sulfate occurrence. Rain water percolating downward through the wastes would leach sulfates and increase in total dissolved solids at depth where less dissolution, or possibly precipitation would be favored. This is indicated in the water analyses presented later.

If sulfides have been more oxidized at shallow depth and the resulting sulfates leached, then sulfide sulfur and total sulfur should both increase with depth. Evidence for this is the positive correlation of sulfide sulfur and depth (Fig. 3) and the strong dependence of total sulfur on sulfides (Fig. 4). A plot of total sulfur with depth shows the same trend as sulfide sulfur and depth (Fig. 3), and is not presented.

In order to reduce sample bias effects, and maximize the depth dependence of oxidized versus unoxidized sulfur, a ratio of sulfate to sulfide was plotted against sample depth (Fig. 5). When compared to the site-wide average, a marked increase in the sulfate/sulfide ratio is noted for depths less than two meters.

Water Quality

After collection of the solid sample cores, the hole at each station was augered to a depth below the water table and cased with PVC pipe for water collection. The wells are shown with surface-water collection points in Fig. 6.

Water samples were collected in September, 1978 and March, 1979. Field measurements included specific conductivity, temperature, Eh, pH and dissolved oxygen. Major cation, major anion and trace element analysis were performed using standard wet chemical, selective ion electrode and atomic absorption techniques.

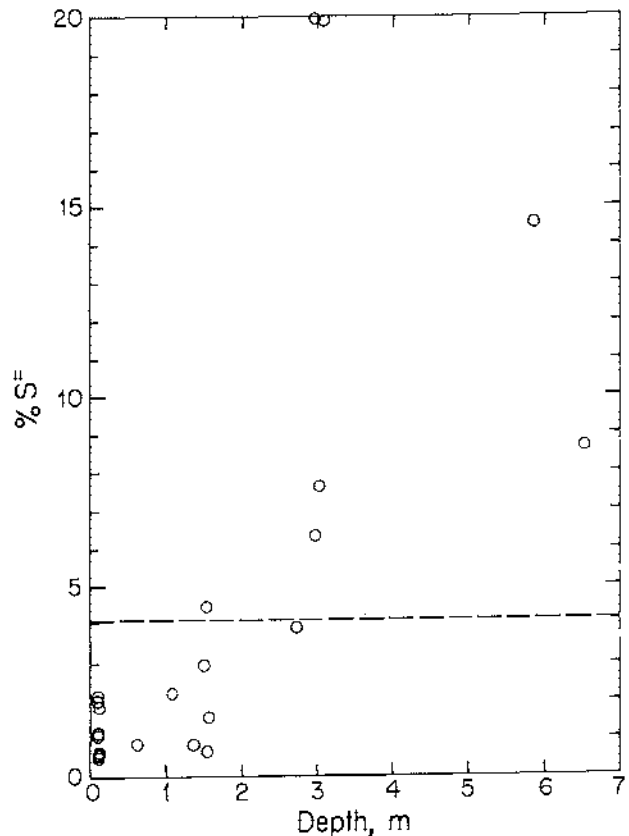


Figure 3. Plot of percent sulfide with depth showing increasing sulfide with depth.

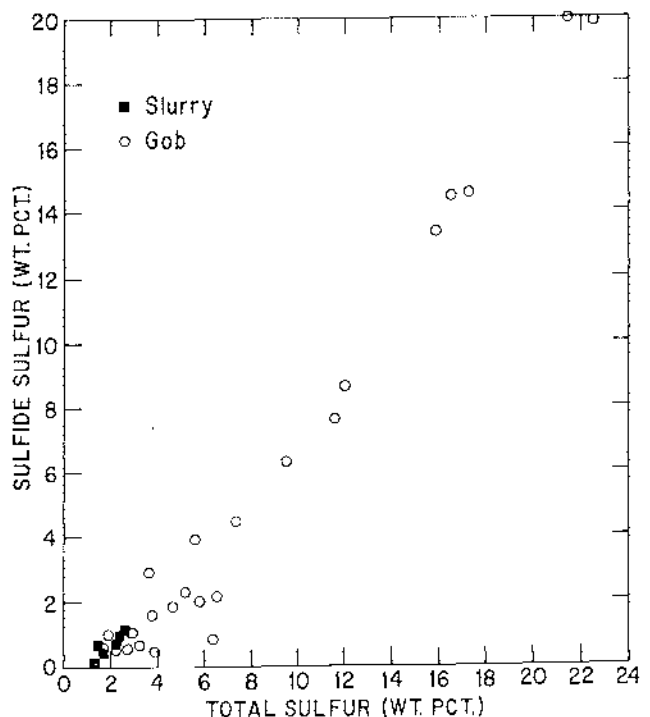


Figure 4. Plot of sulfide sulfur (weight percent) with total sulfur (weight percent) showing strong dependence of total sulfur with depth.

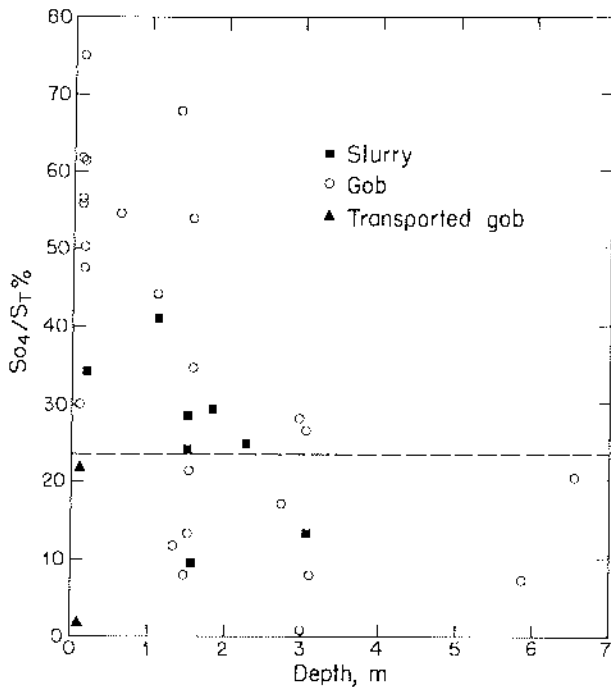


Figure 5. Plot of the ratio of sulfate to sulfide with depth.

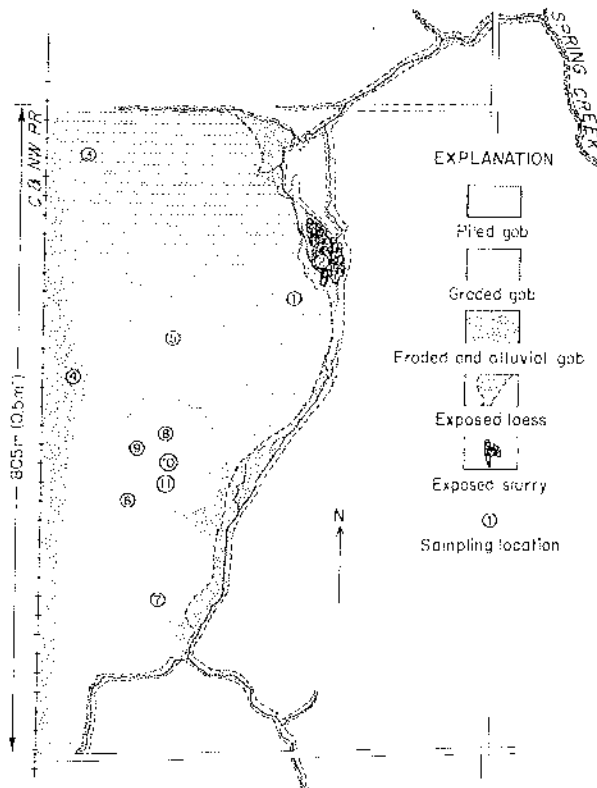


Figure 6. Map of study area showing types of waste material and location of sampling wells.

The well waters collected contained several hundred to several thousands parts per million of iron, aluminum, calcium and sulfate. Using thermodynamic constants and the Van't Hoff, extended Doby-Huckel and Nernst relations the relative oxidation states of iron were calculated by computer program. Ferrous iron was thermodynamically favored over ferric by five orders of magnitude for all samples. Final ionic strength and subsequent calculations were based on back-substitution of ferrous iron for total iron molality.

The dominant anion is sulfate, comprising 95 percent of the anion EPM (equivalent per million) total. Chloride accounts for most of the remaining anions. Carbonate species were not analyzed because the pH of all waters was below 4.0. With one exception the dominant cation in all well-water samples was ferrous iron. Other major contributors to the cation EPM were calcium, magnesium and aluminum. The EPM's of four cations are presented in Table 3.

The high iron and sulfate concentrations are due to the oxidation of pyrite and leaching of the resulting sulfate. The aqueous concentrations of Fe^{2+} and SO_4^{2-} are strongly correlated to the percent sulfide in the solids (Fig. 7). Gypsum also may contribute to the aqueous sulfate. Siderite, present in the No. 6 Coal and its wastes, was not found at the Superior washer. Siderite likely has been severely leached and now is insignificant as an iron source. Additional iron may result from the destruction of mixed-layer clays and illite.

Aqueous calcium results from the dissolution of gypsum and the stripping of adsorbed ions from mixed-layer clays. Calcite and dolomite, like siderite, may have been leached to a point where they no longer supply significant calcium or magnesium to the system.

Magnesium may have its prime source in the interlayer and octahedral coordination sites of the mixed-layer clays. Illite could also supply some magnesium. Chlorite may be present in the wastes, but was not found on X-ray traces, it has probably been destroyed by acid leaching.

The high aluminum concentrations are indicative of the extreme aggressiveness of the acid waters. Titratable acidity ranged from 800 to 82,000 ppm as $CaCO_3$ and pH varied between 1.3 and 3.4 for the monitoring well samples. In such environments, octahedrally bound aluminum (and magnesium) in clays would be released and the clay structure destroyed. Kaolinite, the most resistant clay, was the only clay mineral to exhibit good crystallinity on X-ray diffraction patterns. Acid springs flowing from solution conduits in the noncarbonate loess below the gob contact is further evidence of clay destruction. The importance of clays to leachate chemistries cannot be overemphasized, they are abundant in the wastes and responsible for the bulk of aluminum and magnesium, and probably a portion of calcium and iron.

Leaching Depth and Solid Sulfide Controls

The total of six sulfophilic trace elements (Zn, Cd, Cu, Ni and Pb) are summed and plotted against percent sulfide in Fig. 8. Zinc comprises approximately 95 percent and Ni about 3 percent

Table 3. Equivalents Per Million of Dominant Cations for September, 1978 and March, 1979 Samplings (nc = not collected).

| | MW-1 | MW-2 | MW-3 | MW-4 | MW-5 | MW-7 | MW-9 | MW-11 |
|-----------|------|-------|--------|--------|------|--------|--------|--------|
| Ca | nc | 37.62 | 61.93 | 98.85 | nc | 54.49 | 92.61 | 87.87 |
| Mg | nc | 41.72 | 14.81 | 14.89 | nc | 27.32 | 36.54 | 67.31 |
| Al | nc | 5.24 | 50.47 | 77.34 | nc | 46.99 | 185.93 | 315.77 |
| Fe | nc | 6.47 | 143.25 | 154.03 | nc | 299.00 | 625.21 | 972.98 |
| Temp (°C) | nc | 22.9 | 25.6 | 23.9 | nc | 26.7 | 30.7 | 27.5 |

EPM DOMINANT CATIONS 9/27/78

| | MW-1 | MW-2 | MW-3 | MW-4 | MW-5 | MW-7 | MW-9 | MW-11 |
|-----------|--------|-------|--------|--------|--------|-------|--------|---------|
| Ca | 26.10 | 18.23 | 17.71 | 15.40 | 2.33 | 17.31 | 28.34 | 26.05 |
| Mg | 1.08 | 31.24 | 1.88 | 3.88 | 1.19 | 2.63 | 2.85 | 4.42 |
| Al | 32.64 | 0.77 | 66.25 | 140.54 | 140.32 | 36.73 | 513.35 | 1231.96 |
| Fe | 137.66 | 1.19 | 180.49 | 175.84 | 189.45 | 84.16 | 920.37 | 1787.03 |
| Temp (°C) | 3.0 | 1.0 | 2.0 | 2.7 | 3.0 | 0.0 | 15.5 | 12.6 |

EPM DOMINANT CATIONS 3/10/79

of the total. Trace elements tend to increase with percent sulfide in the solid portion.

Two monitoring wells, MW-9 and MW-11, produced much higher acidities and total dissolved solids than the others. These wells are located in the gob piles where the depth to water is several meters greater. This suggests that the longer percolation path of waters to the water table may allow more

dissolution of minerals with increasing acidity. Plots of SO_4^{2-} , Fe^{2+} and sum of the trace elements (Figs. 9 and 10), versus depth to water indicate substantial increases with respect to these ions, with increasing depth to the water table.

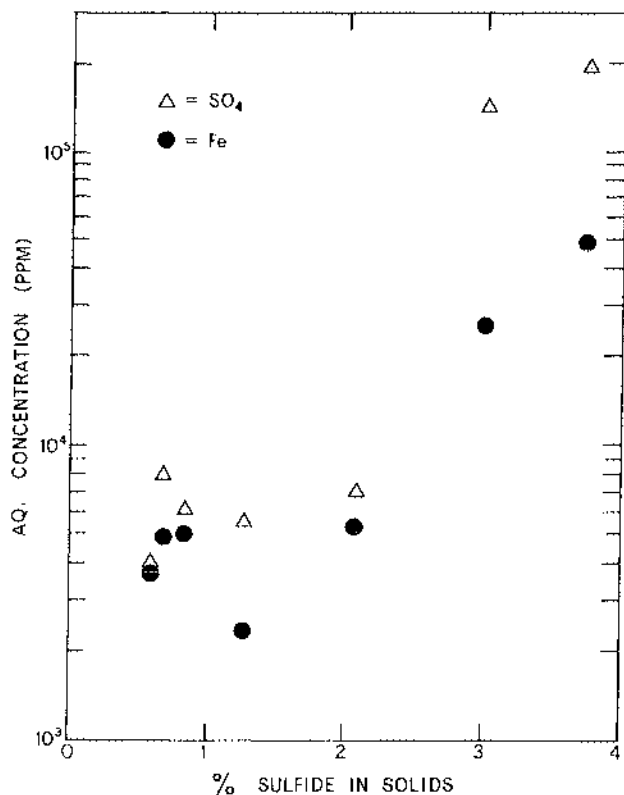


Figure 7. Plot of aqueous ferrous iron and sulfate versus percent sulfide in solids.

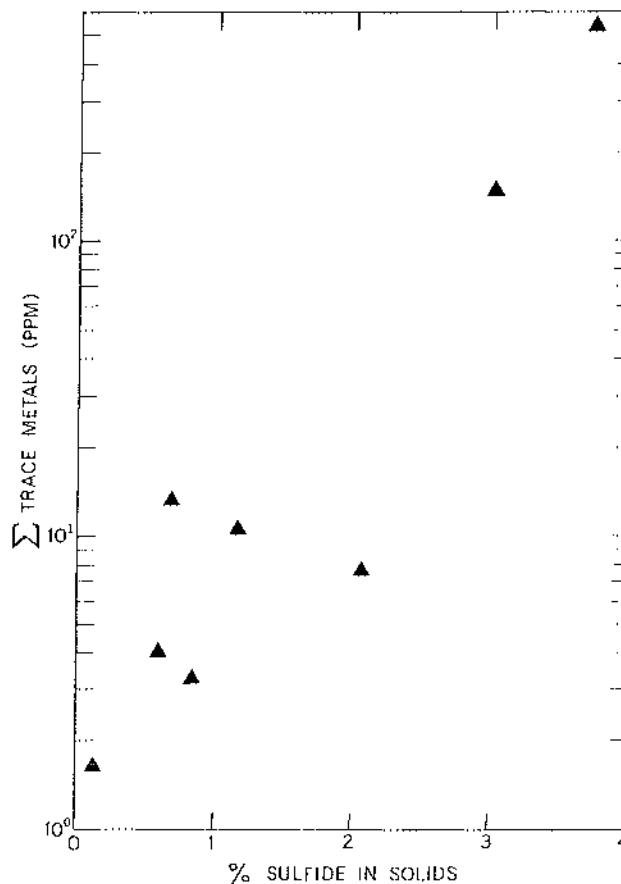


Figure 8. Sum of the trace elements plotted against percent sulfide in the solids.

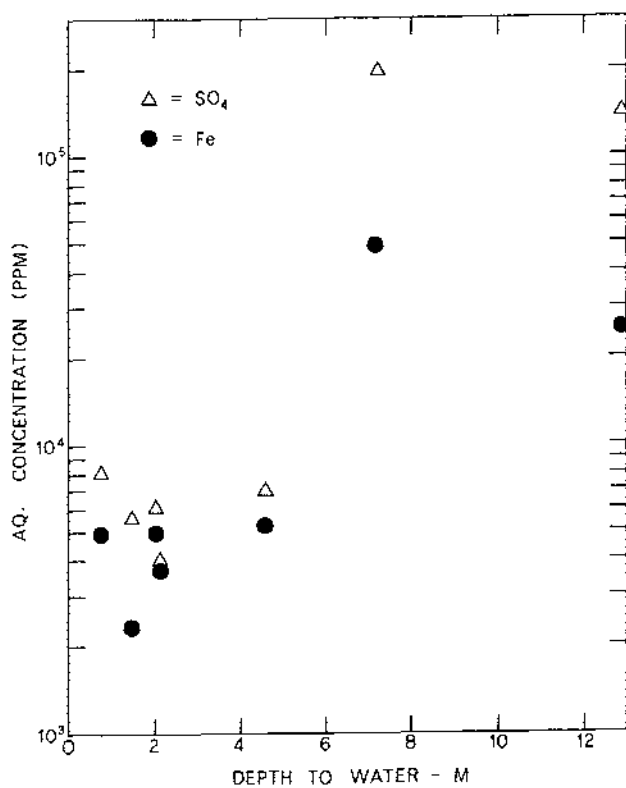


Figure 9. Aqueous concentrations of sulfate (SO₄) and iron (Fe) with depth to water.

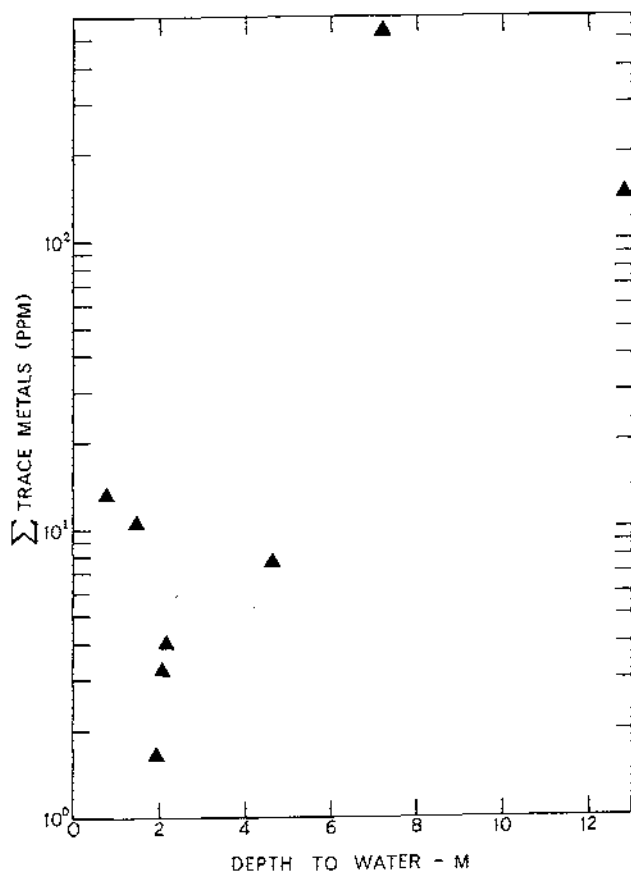


Figure 10. Sum of the trace metals in aqueous solution plotted with depth to water.

In drilling monitoring wells MW-1, MW-3, MW-4, MW-5, and MW-7, varying thicknesses of slurry were encountered beneath the gob. MW-2 was located in slurry alone. Only gob exists above the loess contact at the MW-9 and MW-11 stations. The difference in pyritic sulfide content between gob and slurry, may explain some of the variation in the well-water chemistries, however it is likely that other influences have not been taken into account yet.

The coal wastes are very inhomogenous with respect to material type and distribution. The more readily oxidized disseminated pyrites may dominate in one area, while massive pyrites dominate in another. Well-water chemistries may be influenced by lateral flow. There is no information available to indicate the relative vertical and lateral components or rates of flow at the gob/loess contact. However, the deep gob-pile materials did produce more highly concentrated waters than the surrounding graded gob. The graded-gob wastes are only 2 to 3 meters thick, and a 2-meter weathered zone, described earlier, may have removed a larger proportion of the sulfides here than in the piles. Water chemistry may reflect sulfide availability, yet sulfides themselves are a function of depth due to leaching.

Mineral-Water Interactions

The waters collected from the study area were high in total dissolved solids. For this reason, the chemical equilibrium model WATEQ 2 was selected to calculate aqueous speciation and saturation indexes. 9, 10 This program considers over 500 solid and aqueous reactions, including sulfate and sulfide complexing for heavy metals and trace elements. Water-chemistry data were formatted and sent to the U.S. Geological Survey office at Menlo Park, Calif. to be run on WATEQ 2.

Saturation indices for the clay minerals illite, kaolinite, montmorillonite and chlorite were calculated. Most waters are highly undersaturated with respect to clays. The gob-pile waters (MW-9 and MW-11) are more saturated than those from the graded-gob area. MW-11 reaches supersaturation for kaolinite (1.92) and montmorillonite (2.60) in the fall and saturation with respect to illite (0.18) kaolinite (3.17) and montmorillonite (3.74) in the spring. The gob solids at this station had the highest average sulfide content, and the well waters were highest in acidity and total dissolved solids of all the stations.

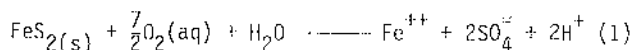
Saturation indices for sulfate minerals are given in Table 4. The waters are just above or below saturation for gypsum in all wells. The saturation indices follow the same pattern as the clays and decrease from fall to spring, probably due to dilution from rising water tables.

Table 4 shows the saturation indices for pyrite. Seasonal variation is not clear for pyrite. Between the fall and spring, pyrite saturations decreased for three wells and increased for two others. The notable feature of the pyrite indices is the persistence of high supersaturation values. At first it is surprising that the waters contain so much more iron and sulfur than is thermochemically predicted for pyrite dissolution. The only likely explanation is the

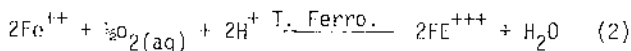
Table 4. Saturation Indices for Gypsum and Pyrite for the Fall (9/27/78) and Spring (3/10/79) Well Waters from the Superior Washer (nc = not Collected or not Available).

| | Saturation Index Gypsum | | Saturation Index Pyrite | |
|-------|----------------------------|--------|----------------------------|--------|
| | Fall | Spring | Fall | Spring |
| MW-1 | nc | 0.02 | nc | 5.29 |
| MW-2 | 0.49 | 0.15 | 11.25 | 9.12 |
| MW-3 | 0.56 | -0.13 | 9.03 | 5.11 |
| MW-4 | 0.82 | -0.07 | 4.54 | 7.28 |
| MW-5 | nc | -0.89 | nc | 5.21 |
| MW-7 | nc | -0.06 | nc | 8.20 |
| MW-9 | 0.62 | 0.23 | 8.02 | 6.38 |
| MW-11 | 0.61 | 0.17 | 2.94 | 10.53 |

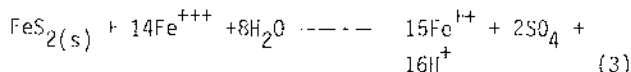
kinetic effect of Thiobacillus Ferrooxidans. The chemical mechanism is as follows: ^{1, 11} Pyrite is oxidized by dissolved oxygen, producing ferrous iron, sulfate and protons.



Catalized by Thiobacillus Ferrooxidans, ferrous iron is oxidized to ferric iron.



Ferric iron is then reduced in oxidizing pyrite, producing more ferrous iron, sulfate, and protons.



Ferric iron has been shown to be the primary oxidizing agent attacking the pyrite surface. Reaction 3 proceeds much more rapidly than reaction 1 and is rate-limited by the availability of ferric iron produced in reaction 2. Reaction 2 proceeds very slowly in abiotic systems, but is 10^5 to 10^6 times faster when catalized by the bacterium, ¹¹ this allows reaction 3 to proceed rapidly, with bacterial catalysis resupplying ferrous iron in a cyclic manner.

To verify the existence of Thiobacillus in the acid waters at the Superior washer, water samples were analyzed for the south surface drainage and three wells. The results are presented in Table 5.

The bacterium can exist as long as minimal oxygen is present.¹¹ All samples from the Superior washer contained dissolved oxygen (1.1 to 10.3 mg/l) and had positive Eh (+70 to +400 mv). Thermodynamic redox calculations for iron indicated ferrous iron to be highly favored over ferric in these waters. Whether ferric iron is greater than predicted, or is consumed in oxidizing pyrite as fast as it is produced, is not known.

Table 5. Thiobacillus Ferrooxidans Activity (in Most Probable Numbers per 100 Milliliters) in Four Water Samples from the Superior Coal Washer, Spring Collection.

| | S. Exit | MW-7 | MW-9 | MW-11 |
|------------------------------|---------|--------|--------|--------|
| T. Ferrooxidans (mpn/100 ml) | 1.7E+2 | 4.9E+5 | 1.4E+5 | 3.1E+4 |

Trace Metal Recovery

The highly acid waters at the Superior washer site leach quantities of trace metals (Table 6) most of which remain in objectionable or toxic concentrations in the stream draining the south end of the site.

The high zinc concentrations are from leaching of the mineral sphalerite. Sphalerite is also the source of cadmium in the waters. ⁹ Sphalerite concentrations in the No. 6 Coal and its wastes have lead some authors to suggest possible economic recovery of zinc from these materials. ^{12,13} The extraction of aluminum from coal refuse has also been considered. ¹⁴ Economic recovery of metals from coal refuse could offer a partial solution to trace-element pollution arising from these materials.

Five gob-pile cores (stations 8 and 9) and two graded-gob cores (station 7) were analyzed by ICAP spectroscopy for a number of metals and trace elements. All elements in the gob samples were under economic concentrations suggested by the Bureau of Mines, 1975. The whole-rock concentrations of zinc and aluminum are given in Table 7.

The average aluminum content is 2.85 percent, 9.5 percent is very marginal for economic recovery of aluminum from coal refuse. The Bureau of Mines considers the tenor for zinc ore to be about 3 percent Zn. This is 25 times the highest

Table 6. Trace Element Concentrations in Well Waters and the South Drainage for Fall and Spring Sample Collections (nc = not collected).

| | Zn | Cd | Cu | Ni | Pb | Mn | As |
|--------------------------|--------|-----|------|------|------|------|-----|
| MW-1 | nc | nc | nc | nc | nc | nc | nc |
| MW-2 | 1.25 | .02 | .01 | .66 | .13 | 55.5 | .02 |
| MW-3 | 8.12 | .16 | .56 | 1.38 | .44 | 35.6 | .19 |
| MW-4 | 12.40 | .14 | .56 | 2.55 | .44 | 5.6 | .17 |
| MW-5 | nc | nc | nc | nc | nc | nc | nc |
| MW-7 | 15.10 | .05 | .05 | 4.96 | .34 | 21.5 | .22 |
| MW-9 | 112.00 | .89 | .11 | 4.10 | .96 | 21.5 | .21 |
| MW-11 | 196.00 | .93 | .16 | 7.59 | 1.25 | 38.5 | .25 |
| South Drainage | 50.00 | .26 | .53 | 3.35 | .38 | 17.5 | .15 |
| Drinking water standards | 5.00 | .01 | 1.00 | 1.00 | .05 | .05 | .05 |

Table 7. Zinc and Aluminum Concentrations (As Weight Percent of Whole Sample) for Seven Gob Cores from the Superior Washer, Fall Sampling 1978.

| Sample (sta-#) | Depth (m) | Zn (wt %) | Al (wt %) |
|----------------|-----------|-----------|-----------|
| 7-1 | 0.13 | 0.0026 | 4.66 |
| 7-2 | 1.09 | 0.0166 | 3.77 |
| 8-1 | 0.10 | 0.0031 | 1.72 |
| 8-4 | 5.87 | 0.1205 | 4.11 |
| 9-1 | 0.13 | 0.0052 | 1.67 |
| 9-2 | 1.37 | 0.0056 | 1.11 |
| 9-3 | 2.97 | 0.0589 | 2.94 |

zinc value obtained (core 8-4) from the Superior site. Even though the wastes are easily accessible and handling costs would be low compared to mining operations, economic recovery of zinc and other trace metals from the Superior site is unlikely.

Conclusions

Conclusions drawn from the weathering study show an oxidized zone, as defined by oxidation of sulfides to sulfates, has developed in the wastes at the Superior coal washer in the 26 years since its abandonment. Weathering of sulfides has been most intense within the upper two meters. The highly soluble sulfate minerals formed from sulfide oxidation are leached and redistributed downward by percolating water. Organically bound sulfur has remained relatively inert to chemical attack.

Well waters from deep within the gob piles are more concentrated and more acidic than those in the lower, graded-gob area where the water table is shallow. Acidity and total dissolved solids appear to be poorly dependent on leaching depth, but show better dependence on available sulfide concentrations in the associated solids. The catalytic action of *Thiobacillus Ferrooxidans* on aqueous iron allows for greater solution of pyrite, and results in highly acid, iron sulfate waters that are supersaturated with respect to metal and trace-element sulfides. The acid waters are aggressive to clay minerals, which are abundant in the wastes and supply the bulk of aluminum and magnesium to the system.

Gypsum may supply calcium to the system in the vadose zone where percolating waters are less concentrated, but it is near saturation for most well waters. Temperature effects on the solubility products of Fe, Al, Ca and Mg sulfates, clays and gypsum may explain a relative concentration decrease of Ca and Mg and increase of Fe and Al in cooler waters. This also indicates the importance of sulfates to aluminum solubility. Lower saturation indices for clays and gypsum in the early spring may indicate a dilution effect.

Although high concentrations of zinc and aluminum occur in the water samples, the whole-rock concentrations of zinc and aluminum are not high enough to warrant economic considerations.

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References

1. P. C. Singer and W. Stuman, "Acidic Mine Drainage: The Rate-Determining Step," *Science*, Vol. 167, pp. 1121, 1123, 1970.
2. J. P. Schubert, R. D. Olsen, and S. D. Zellner, "Monitoring the Effects of Coal Refuse Disposal and Reclamation on Water Quality in Southwestern Illinois," *Proceedings, Fourth Joint Conference on Sensing of Environmental Pollutants*, American Chemical Society, pp. 725-731, 1978.
3. E. M. Wewerka, J. M. Williams, P. L. Wanek, and J. D. Olsen, "Environmental Contamination from Trace Elements in Coal Preparation Wastes," Environmental Protection Agency, EPA-600/7-76-007, 60 p., 1976.
4. A. A. Sobek, W. A. Schuller, J. R. Freeman, and R. M. Smith, "Field and Laboratory Methods Applicable to Overburdens and Mine Soils," U.S. Environmental Protection Technical Series, EPA-600/2-78-054, pp. 51-60, 1978.
5. J. H. Gluskoter, "Clay Minerals in Illinois Coals," *Journal of Sedimentary Petrology*, Vol. 37, No. 1, pp. 205-214, 1976.
6. C. P. Rao and H. J. Gluskoter, "Occurrence and Distribution of Minerals in Illinois Coals," Illinois State Geological Survey, Circular 476, 56 p., 1973.
7. J. E. Edkins, "Geochemical Assessment of a Sulfide-Bearing Coal Waste Deposit in Southwestern Illinois," Unpublished Masters Thesis, Indiana University, 100 p., 1980.
8. A. H. Truesdell and B. F. Jones, "WATEQ, a Computer Program for Calculating Chemical Equilibria of Natural Waters," U.S. Geological Survey, *Journal of Research*, Vol. 2, No. 2, pp. 233-248, 1974.
9. J. W. Ball, E. A. Jenne, and D. K. Nordstrom, "WATEQ2 a Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters," American Chemical Society Symposium Series 93, No. 36, pp. 815-835, 1978.
10. J. W. Ball, D. K. Nordstrom, and E. A. Jenne, "Additional and Revised Thermochemical Data and Computer Code for WATEQ2," U.S. Geological Survey, Water Resources Investigation, WRI 78-116, 109 p., 1980.
11. D. K. Nordstrom, E. A. Jenne, and J. W. Ball, "Redox Equilibria of Iron in Acid Mine Waters," American Chemical Society Symposium Series 93, No. 3, pp. 51-79, 1978.
12. J. C. Cobb, J. M. Masters, C. G. Treworgy, and R. J. Helfinstine, "Abundance and Recovery of Sphalerite and Fine Coal from Mine Waste in Illinois," Illinois State Geological Survey, IMN 71, 11 p., 1979.
13. J. C. Cobb, J. D. Steele, C. G. Treworgy, and J. F. Ashby, "The Abundance of Zinc and Cadmium in Sphalerite-Bearing Coals in Illinois," Illinois State Geological Survey, IMN 74, 28 p., 1980.
14. T. L. Robl, A. E. Bland, and J. G. Rose, "Kentucky Coal Refuse: A Geochemical Assessment of its Potential as a Metals Source, Second Symposium on Mine and Preparation Plant Refuse Disposal," *Proceedings, National Coal Association*, Louisville, Ky., pp. 152-159, 1976.

