Water Quality at an Abandoned Ohio Coal Mine Reclaimed with Dry Flue-Gas Desulfurization Byproducts

This Fact Sheet summarizes part of a multidisciplinary investigation of an industrial waste material known as flue-gas desulfurization byproduct. This material was applied to the land surface during reclamation of an abandoned coal mine to help counter the effects of acid-forming mine wastes.

In 1994, the U.S. Geological Survey (USGS) began a study of ground water beneath an abandoned coal mine where flue-gas desulfurization (FGD) byproducts were used as a neutralizing agent during reclamation. FGD byproducts are produced by scrubbers that use a sorbent such as limestone or dolostone to reduce sulfur emissions from coal-fired boilers. The byproducts are highly alkaline—pH ranges from 9 to 12. Because FGD byproducts may neutralize acid mine drainage (AMD) that can damage hydrologic systems near a mine site, these materials are of great interest with regard to reclamation of abandoned coal mines.

The abandoned coal mine selected for this research is in Tuscarawas County, Ohio (fig. 1), and was treated with 125 tons per acre of FGD byproduct and 50 tons per acre of yard-waste compost during reclamation. Rainwater, unsaturated-zone pore water (interstitial water), ground water, and surface water were sampled 9 to 16 months after reclamation. Water from all sampling sites was analyzed for chemical constituents related to AMD and the FGD byproduct.

Site Description

At the study site, the Lower Kittanning (No. 5) coal and clay were mined in the early 1960's and 70's. Before reclamation, the surface of the 45-acre site consisted of exposed underclay and mine spoil (rubble and overburden removed during coal mining); pH of surface water ranged from 2 to 3, and concentrations of dissolved iron, sulfate, and aluminum in surface water were high compared to adjacent unmined areas. Erosion from the site caused sedimentation problems on local roads. The site was reclaimed by regrading the mine spoil and planting grasses and legumes in late 1994.

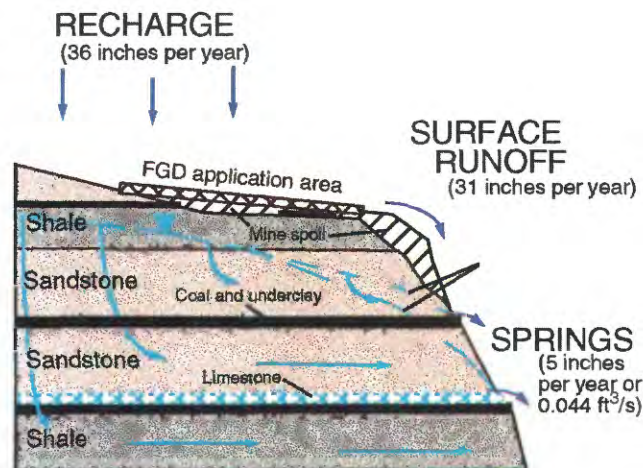**Figure 1.** Location of study area in Tuscarawas County, Ohio.

Figure 2. Conceptual model of ground-water flow. Arrows indicate direction of flow.

The site is underlain by sandstones and shales of Pennsylvanian age, interbedded with coal, clay, and limestone (fig. 2). Four core holes (fig. 3) were drilled to approximately 150 ft each to define subsurface rock characteristics and determine thickness of aquifers (ground-water-bearing zones).

Site Hydrology

The study site lies atop a hill (figs. 2 and 3) and is bounded by ridges that function as surface- and ground-water divides. The sole source of water is infiltrating precipitation; thus, surface- and ground-water inflows are negligible. The surface of the study site is covered with mine spoil, but immediately underlying the spoil are a discontinuous clay layer (partially removed by mining) and shale. Recharge to the aquifers is limited by the low vertical hydraulic conductivity of the impermeable units, so most precipitation leaves the site by surface runoff. Precipitation that does infiltrate and recharge the aquifers may travel preferentially within sandstones and coals or along fractures. Thus, ground-water flow beneath the site is predominantly horizontal, the only exit from the system being through downgradient springs or seeps (fig. 2).

Ground-water flow beneath the site is from north to south with a gradient of approximately 0.004 foot per foot. South of the study site, where springs flow into small streams, three sampling sites were established. Spring discharge was measured during base flow; combined spring discharge from the site was 0.044 cubic feet per second.

A numerical ground-water flow model was constructed and calibrated to water levels and springflows measured at the study site during the summer of 1995. The movement of particles of water as they flowed from the water table to springs was analyzed by using particle-tracking simulations. Particles, which can conceptually represent inert solutes, were simulated as originating in areas that received FGD byproduct as a
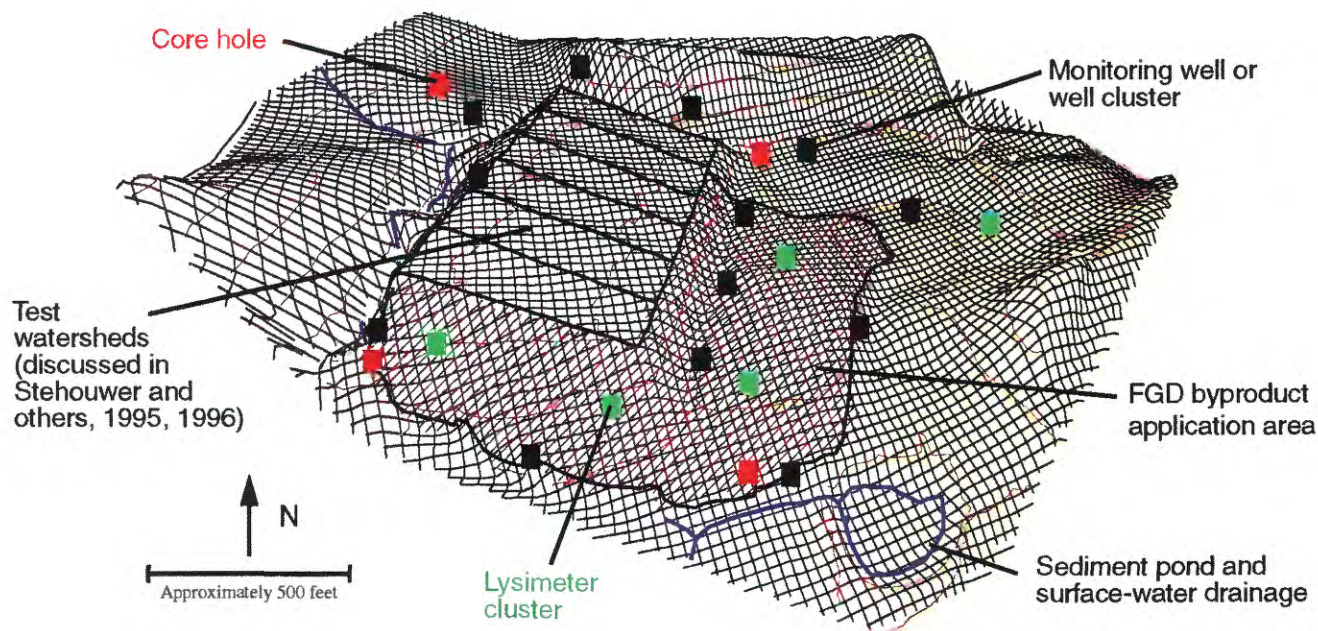
Figure 3. Location of core holes, lysimeter clusters, and monitoring wells. Contour interval (red lines) is 10 feet.

surface amendment. The minimum time for particles released on the water table to travel to the spring at the base of the hill was approximately 228 days. The maximum time for a particle to travel from the upgradient edge of the FGD byproduct application area to the spring was 26.9 years. The average traveltime (for 251 particles) from the water table to the springs was 9.5 years.

FGD Byproduct Chemistry

The chemistry of FGD byproducts has been studied extensively by other researchers (Stehouwer and others, 1995, 1996). The composition of FGD byproducts can change dramatically in response to the type of FGD process being used, operating conditions of the coal-fired boiler, coal quality, and chemistry of the sorbent used in the FGD process.

The FGD byproduct used for this study was created by the pressurized fluidized bed combustion (PFBC) process at the

Figure 4. Median concentrations of selected trace elements in lithologic units at the mine site, FGD byproducts (PFBC and AFBC), and yard-waste compost (C). All concentrations are in parts per million, except iron (Fe), which are in weight percent.

Tidd Plant, an experimental powerplant in Brilliant, Ohio. Major-element chemistry of FGD byproducts is dominated by calcium, aluminum, magnesium, sulfur (as sulfate), and carbon (as carbonate). Solid phases identified in previous studies include calcium oxide (lime), calcium hydroxide (portlandite), calcium-magnesium carbonate (calcite, dolomite, magnesite), magnesium oxide (periclase), calcium sulfate (gypsum or anhydrite), and hydrated calcium-aluminum-sulfate-hydroxide (ettringite) (Stehouwer and others, 1996). Tests indicated that 125 tons per acre of FGD byproduct was necessary to raise soil pH to a neutral value of 7.0. Additionally, 50 tons per acre of yard-waste compost was added to increase the organic content of the soil. The soil amendments were applied to the seven-acre area shown in figure 3.

Median concentrations of selected trace elements are shown in figure 4 for two types of FGD byproducts, compost, FGD byproduct/compost mixtures, and various rock types that underlie the reclaimed mine spoil. These data indicate that concentrations of many trace elements found in the FGD byproduct/compost mixtures are greater than those found in coal, clay, or shale. Exceptions to this generalization include barium and chromium, which are found in greatest concentrations in clay and shale. The highest concentrations of selenium are found in coal samples. The data also indicate that a significant percentage of trace elements such as barium, chromium, and lead are from the compost component of the FGD byproduct/compost mixture.

Water Chemistry

Water samples were collected from rainwater, the unsaturated zone, offsite domestic wells, onsite monitoring wells, and surface water. Rainwater was sampled monthly for a period of 1 year. Interstitial water from 35 soil-suction lysimeters installed at the site (fig. 3) was sampled three times. Nine offsite domestic wells were sampled once, and 19 onsite monitoring wells distributed among 13 locations (fig. 3) were sampled twice. Three surface-water sites were sampled once,
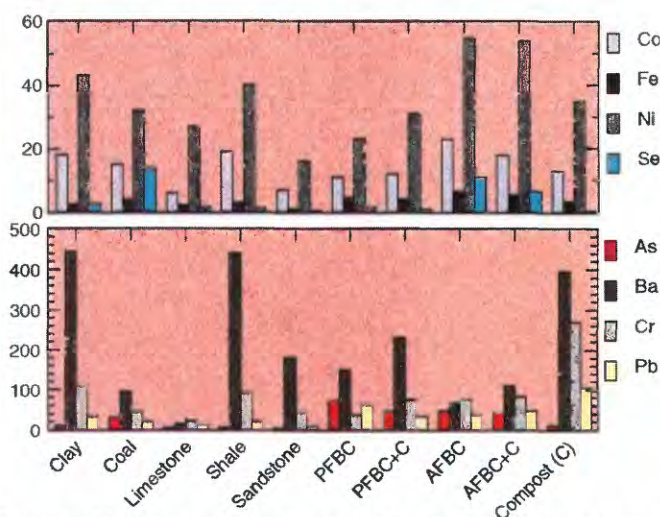
The median pH for rainwater was 4.2, and median specific conductance was 38 µS/cm (microsiemens per centimeter at 25 degrees Celsius) (fig. 5 and table 1). The dominant cation was calcium and the dominant anion was sulfate. With the exception of manganese and zinc, concentrations of trace elements were at or below analytical detection limits. These values are similar to those reported for rainwater in other areas of the northeastern United States (National Atmospheric Deposition Program/National Trends Network, 1996).

Four lysimeter clusters were installed in the FGD byproduct application area; one cluster was placed outside the application area (as control) where traditional reclamation methods were used. Interstitial water in the application area had higher pH and higher specific conductance than water in the control area (fig. 5). Other constituents found at higher concentration in interstitial water from beneath the FGD byproduct application area included sulfate, chloride, fluoride, calcium, magnesium, and boron. Trace elements such as nickel and cobalt were found at high levels in interstitial water from both the application area and the control area; thus, the source of these elements probably is mine spoil and (or) clay.
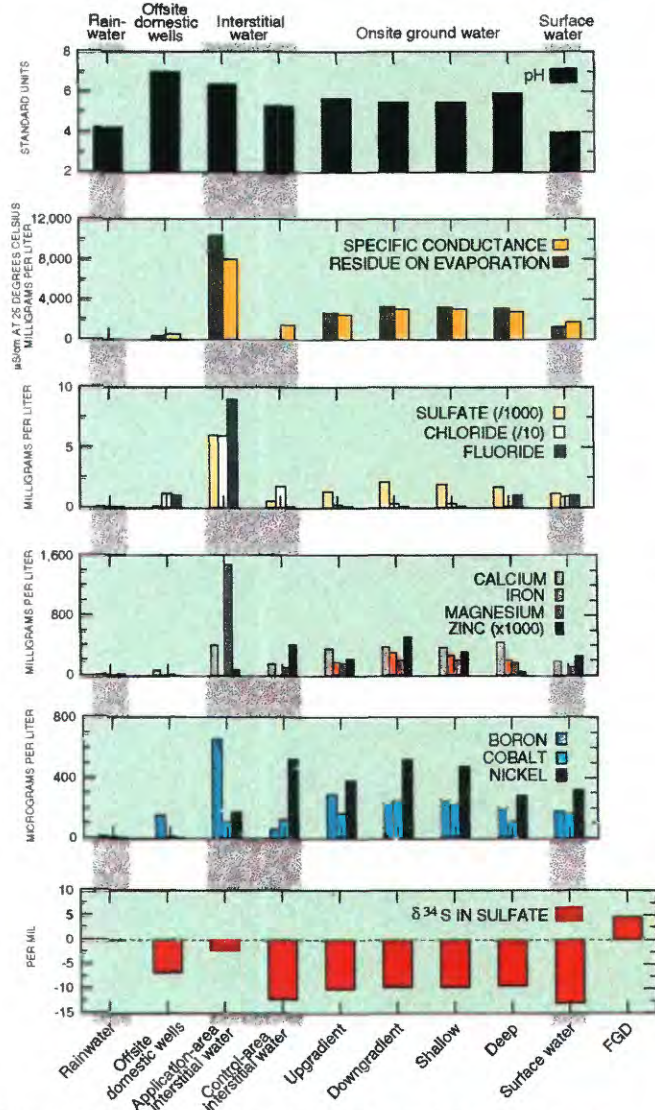

Figure 6. Magnesium:calcium mole ratio and dissolved sulfate for all water samples.

Figure 5. Concentration of selected constituents in waters collected at or near an abandoned mine reclaimed with FGD byproducts.
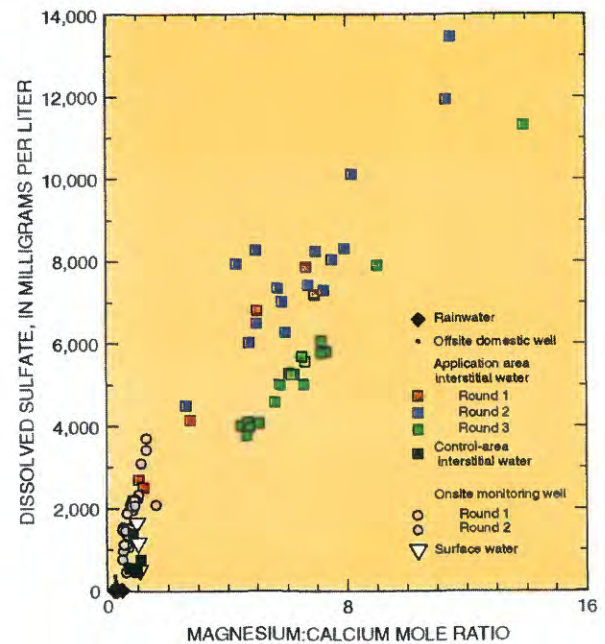
Constituent concentrations in interstitial water may be strongly affected by surface recharge or evaporation, so simple concentrations may not be a reliable indicator of source material. Mole ratios of certain constituents may be more reliable; for example, magnesium:calcium mole ratios were used to differentiate application-area interstitial water from all other water, including control-area interstitial water (fig. 6).

Water from offsite domestic wells had much lower concentrations of dissolved constituents than did water from onsite monitoring wells. The median pH of domestic-well water was 7.0. Specific conductance and residue on evaporation for domestic-wells were an order of magnitude lower than those for onsite monitoring-well samples.

Onsite ground water was evaluated by categorizing samples by sampling round (1 or 2), depth (shallow or deep), and position relative to the FGD byproduct application area (upgradient or downgradient). No significant changes in quality of ground water were found between rounds 1 and 2. Water from the shallow aquifer was more acidic and more mineralized than water from the deep aquifer for both sampling rounds. The greatest differences in water quality were between upgradient and downgradient wells, as seen by downgradient increases in specific conductance, residue on evaporation, and concentrations of sulfate, iron, cobalt, and nickel (fig. 5).

Surface water had relatively low pH (median for three samples was 4.0) and specific conductance (median of 1,680 µS/cm). Surface water had lower concentrations of most constituents than did interstitial water or ground water.

To distinguish sulfate derived from FGD byproduct and sulfate from AMD, sulfur-isotope ratios were determined and are reported as $\delta^{34}S$, in per mil (parts per thousand deviation from the standard). Values of $\delta^{34}S$ in sulfate in the PFBC FGD byproduct range from +4.6 to +4.8 per mil. Values for application-area interstitial waters are isotopically lighter than

Table 1. Median concentrations of selected dissolved constituents from water samples collected at an abandoned mine site reclaimed with FGD byproducts. Shading of fields corresponds to shading in figure 5.

[µS/cm, microsiemens per centimeter; ROE, residue on evaporation at 180 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than]

Source	pH (standard units)	Specific conductance (µS/cm)	ROE (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Calcium (mg/L)	Iron (mg/L)	Magnesium (mg/L)	Boron (µg/L)	Cobalt (µg/L)	Nickel (µg/L)	Zinc (µg/L)	$\delta^{34}S$ (per mil)
Rainwater	4.2	38	no data	3	0.04	0.05	0.34	0.011	0.45	<6	<6	<4	14.5	no data
Offsite domestic wells	7.0	581	319	95	1.2	1.0	68.4	0.44	10.1	152	<6	<4	<4	-6.7
Interstitial water														
Application area	6.4	8,050	10,430	6,050	6.0	9.0	411	0.50	1,490	656	110	175	81	-2.1
Control area	5.3	1,445	no data	554	1.8	<0.1	158	0.23	104	56	124	528	422	-12.2
Onsite ground water														
Round 1														
Shallow	5.5	2,920	3,340	1,840	3.0	<1.0	355	298	206	234	235	462	363	-9.6
Deep	5.8	2,640	3,140	1,530	<1.0	<1.0	449	176	167	202	106	261	87	-9.6
Round 2														
Shallow	5.5	3,090	3,200	2,030	3.0	<0.1	395	240	203	276	222	488	465	-9.9
Deep	6.1	2,880	3,100	1,880	3.0	<0.1	440	227	177	209	112	309	5	-9.4
Upgradient	5.7	2,455	2,680	1,325	0.2	<0.1	360	176	162	294	164	384	219	-10.1
Downgradient	5.5	3,005	3,330	2,125	0.3	<0.1	386	305	204	233	251	524	518	-9.7
Surface water	4.0	1,680	1,221	1,178	0.9	1.0	184	0.7	114	177	163	319	259	-13.0

the FGD byproduct (median of -2.1) but heavier than control-area interstitial water, ground water, or surface water (fig. 5, table 1). The $\delta^{34}S$ data for the application-area lysimeters indicates the mixing of isotopically light sulfate derived from onsite AMD with isotopically heavier sulfate from FGD byproducts.

Concentrations of several constituents in interstitial and onsite ground and surface waters, including beryllium, cadmium, and nickel, exceeded U.S. Environmental Protection Agency's Maximum Contaminant Levels (MCL's) for drinking water. Downgradient shallow wells were most commonly associated with these exceedances. Fluoride concentrations above the MCL were detected in water from application-area lysimeters but were below the MCL in all but one ground-water sample. Concentrations in surface water that exceeded MCL's were only noted for nickel. No constituent concentrations exceeding MCL's were found in offsite domestic-well water. Review of all the data indicate that, of the elements exceeding the MCL, only fluoride is derived from the FGD byproduct.

Trace elements of concern that are typically associated with FGD byproduct include arsenic, mercury, lead, and selenium. Concentrations of these elements in interstitial waters sampled during this study were well below the MCL's (arsenic, 50 µg/L (micrograms per liter); mercury, 2 µg/L; lead, 15 µg/L; and selenium, 50 µg/L). Furthermore, concentrations in interstitial waters rarely exceeded the detection limit. Although no MCL has been established for boron, the median concentration in application-area interstitial waters (656 µg/L) may be a cause for concern because an important aspect of mine reclamation is re-establishment of vegetation, and elevated boron concentrations can be toxic to plants.

Conclusion

FGD byproducts are desirable for use as an amendment in surface-mine reclamation because of their acid-neutralizing capacity. The ground-water part of the multidisciplinary study revealed that pH in interstitial waters from the FGD byproduct application area is higher than the pH in interstitial water from traditionally reclaimed areas. Data collected 16 months after reclamation show no evidence that FGD byproduct leachate has adversely affected the chemistry of ground water beneath the reclamation area. Water-quality data from interstitial water could potentially be used to predict the effects of FGD byproduct on future ground-water quality; however, the chemical environments from which the two sample types were collected are quite different, so the results of such predictions would be somewhat speculative. Water-quality indicators that hold the most promise in tracing the movement of FGD byproduct leachate in shallow ground water include pH, boron, fluoride, calcium:magnesium ratios, and sulfur isotopes.

References

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Stehouwer, R., Dick, W., Bigham, J., Forster, L., Hitzhusen, F., McCoy, E., Traina, S., Wolfe, W., and Haefner, R., 1995, Land application uses for dry flue gas desulfurization by-products: Electric Power Research Institute Research Project 2796-02, Report TR-105264, 284 p.

Stehouwer, R., Dick, W., Bigham, J., Forster, L., Hitzhusen, F., McCoy, E., Traina, S., Wolfe, W., Haefner, R., and Rowe, G., 1996, Land application uses for dry FGD by-products: Columbus, Ohio, The Ohio State University, 302 p.

For more information:

Information on technical reports and hydrologic data related to this study can be obtained from:

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Information on other U.S. Geological Survey programs can be found by accessing the World Wide Web home page at http://www.usgs.gov/.