

**Tracing interaction of acid mine drainage and coal combustion byproducts in
a grouted coal mine: Application of strontium isotopes**

by

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Tracing interaction of acid mine drainage and coal combustion byproducts in a grouted coal mine: Application of strontium isotopes

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The inactive Omega Coal Mine in Morgantown, West Virginia was partially grouted in 1998 by injection of coal combustion by-products (CCB) in order to ameliorate acid discharge; but discharge continued with little measurable change. In this study, discharge chemistry and strontium (Sr) isotope ratios were determined to identify and quantify the extent of interaction between mine waters and the CCB material used to grout the abandoned mine.

Eight sampling sites were monitored around the downdip perimeter of the mine. The major and trace element chemistry of the discharges was not generally sufficient to differentiate between discharges that interacted with grout and those that did not. Elements that showed the most separation include potassium and arsenic, both of which were elevated in the waters that interacted with CCB grout. In contrast, the Sr isotope ratios were clearly able to distinguish between discharges from grouted and non-grouted areas. Discharges without exposure to the grout had $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.7151 to 0.7159, while two discharges that interacted with grout had ratios in the range of 0.7140 to 0.7146. The Treatment Inlet, which includes both grouted and ungrouted discharges, yielded intermediate isotopic ratios. Leaching experiments on CCB grout, coal, and surrounding rock formations are consistent with the isotopic trends observed in the discharges. Based on these results, waters that interacted with grout received 30-40% of their Sr (and Ca by assumption) from the CCB grout material. This novel application of Sr isotopes illustrates their ability to track fluid flow paths in grouted mine systems.

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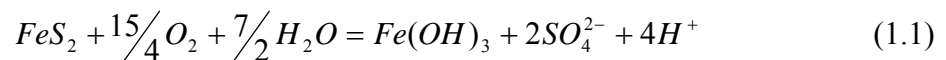
PREFACE

This study has been funded by the US Department of Energy (USDOE) under the University Partnership Program. I especially owe a debt of gratitude to Dr. Ann G. Kim of the USDOE for the mentorship she provided during this study. I thank Brian K. Games at the University of Pittsburgh and Robert Thompson from the Parsons Project at the USDOE for analytical assistance. In addition I thank: Dorsey Shreve and Mike Reese from WVDEP for their expertise and assistance at the site, Stephen Lamey and Carol Cardone at the DOE for their assistance during sample collection, Deborah Hreha and Kathy Rygle of the Parsons Project for their analytical work, and Richard Gray at GAI for providing invaluable samples of core material from the grouting project.

1. INTRODUCTION

Acid mine drainage (AMD) associated with coal mining negatively impacts surface and ground water throughout the world. It is commonly characterized by low pH and high metal content, especially iron, aluminum, manganese, calcium and sulfur in the form of SO_4^{2-} (Sullivan and Yelton, 1988; Rose and Cravotta, 1998). In 1970, eighty-eight per cent of the 19,308 km of streams degraded by acid mine drainage in the United States were located east of the Mississippi River in the Appalachian coal fields (Warner, 1970).

The interactions of water, atmospheric oxygen, *Thiobacillus ferroxidans*, and residual minerals (primarily pyrite, Stumm and Morgan, 1996) exposed by mining operations at the mine site occur through a series of reactions that can be summarized as follows:



(Williams, et al., 1982).

In addition to the acidity, mine outflows tend to be rich in iron which can form iron hydroxides downstream. These compounds flocculate and suffocate waterways (and the aquatic life in it) by reducing oxygen levels, coating surfaces, and clogging the breathing mechanisms of organisms (Hoehn and Sizemore, 1977).

Mining operations at The Omega Coal Mine, located 9.6 km south of Morgantown, West Virginia, were terminated in the late 1980's. At that time, AMD was already seeping into Owl Creek, downdip and to the west of the mine (EPRI, 2001). After the mine was closed AMD began to increase and new discharges developed toward the north and east. This AMD

contaminated the Cobun Creek watershed, significantly degrading the municipal water supply reservoir of Morgantown (Gray et al., 1997).

In a joint venture between the West Virginia Department of Environmental Protection (WVDEP) and the U.S. Department of Energy (USDOE), among others, the northern lobe of the mine was sealed with a grout composed of coal combustion byproducts (CCB) and cement. This grout mixture was injected into the segment of the mine from which the majority of the AMD was emanating. A slurry of the grouting material was injected into boreholes spaced close enough together to facilitate creation of a three dimensional barrier. The pre-existing AMD collection and treatment system was upgraded, with treatment slated to continue until abatement was achieved (Gray et al., 1997). The grouting project was completed 4 November 1998 and all former sampling locations continued to be monitored. As of 2001, unacceptable amounts of AMD were still discharging, requiring costly treatment.

In an effort to determine the source of the continuing outflows, I conducted a study using strontium (Sr) isotopic ratios of the AMD and its solid matrices. The goals of this study are (1) to determine the extent to which coal mine drainage waters are interacting with the CCB grout as opposed to circumventing the grouted portions of the mine, (2) to identify and quantify possible reactions with the CCB that could lead to improvement or deterioration of water quality, and (3) to evaluate the use of Sr isotopes as a tracer for other environmental applications of CCB.

2. BACKGROUND

2.1. Regional geology and history of the Omega Coal Mine

The Omega Coal Mine is located in Monongalia County, West Virginia, 9.6 km south of Morgantown in the Appalachian Plateau (Fig. 2.1). The region is characterized by nearly horizontal strata dissected by streams into mature dendritic drainage basins (Hennen, 1913; Ward

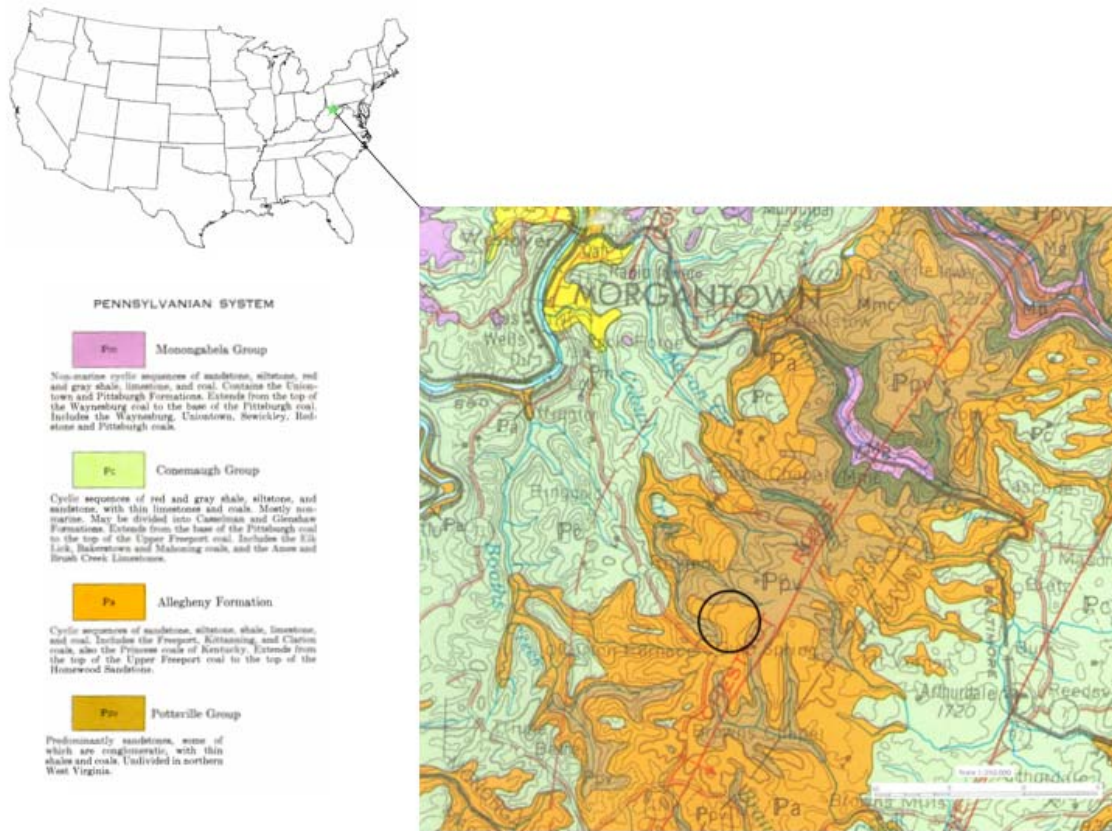


Figure 2.1 Location map showing geologic units within the Cobun Creek drainage basin surrounding the Omega Coal Mine Site (from C. W. Lotz, 1968). The study area is located within the circle.

and Wilmoth, 1968).

The Omega Mine targeted the Upper Freeport coal, which is the uppermost formation of the Allegheny Group. The Allegheny Group consists of interbedded clays, coals, limestones, shales, and sandstones. These are marine below the Upper Kittanning underclay and freshwater (with minor exceptions) above (Fig. 2.2; Hennen, 1913; Edmunds et al., 1999). The post-Kittanning formations consist of sediments deposited in a deltaic environment (Ward and Wilmoth, 1968) over a low lying planar landscape (Busch and Rollins, 1984).

In the vicinity of the Omega Mine, the Upper Freeport coal is a multi-bedded coal seam composed of four separate coal members and two parting slates or shales (Hennen, 1913). The coal seam ranges from 1.2 to 2.4 meters in thickness, contains no marine fossils (Hennen, 1913), and contains a small, but significant, amount of sulfur (roughly 0.41-5%) in the form of pyrite and marcasite (Ward and Wilmoth, 1968). Beneath the Upper Freeport coal is the Bolivar Fire Clay; a flinty, hard, freshwater clay ranging in thickness from 1.5 to 6.1 m (Hennen, 1913).

The Uffington Shale is located directly above the Upper Freeport coal and is the basal formation of the Conemaugh Group (Fig. 2.2). It is a dark, sandy, fossiliferous shale, ranging from 6.1 to 12.2 m, that contains both marine fossils and plant remains (Hennen, 1913).

The region is characterized by the interbedding of impermeable layers of shale and clay which create perched water tables. Lateral flow rates are far greater than vertical flow rates, so multiple low yield seeps and springs discharge from the hill slopes (Ward and Wilmoth, 1968).

The Omega Mine site is located on the western flank of the Chestnut Ridge Anticline (Fig. 2.3). The Upper Freeport coal seam at the site is approximately 1.4 m thick and varies in depth from 20-58 m. The dip of the coal seam follows the regional trend of the anticline's flank at ~11% to the northwest (EPRI, et al., 2001). In the northern lobe of the mine, the top

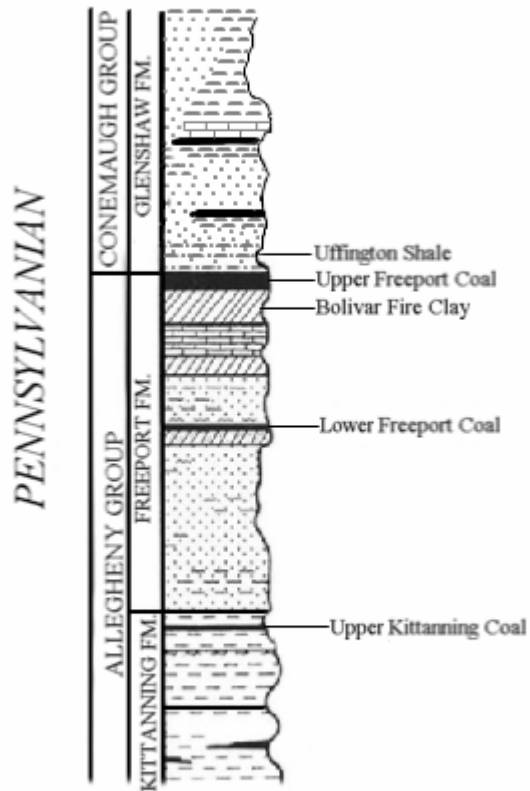


Figure 2.2 Stratigraphic section of local geologic units in Monongalia County, WV.

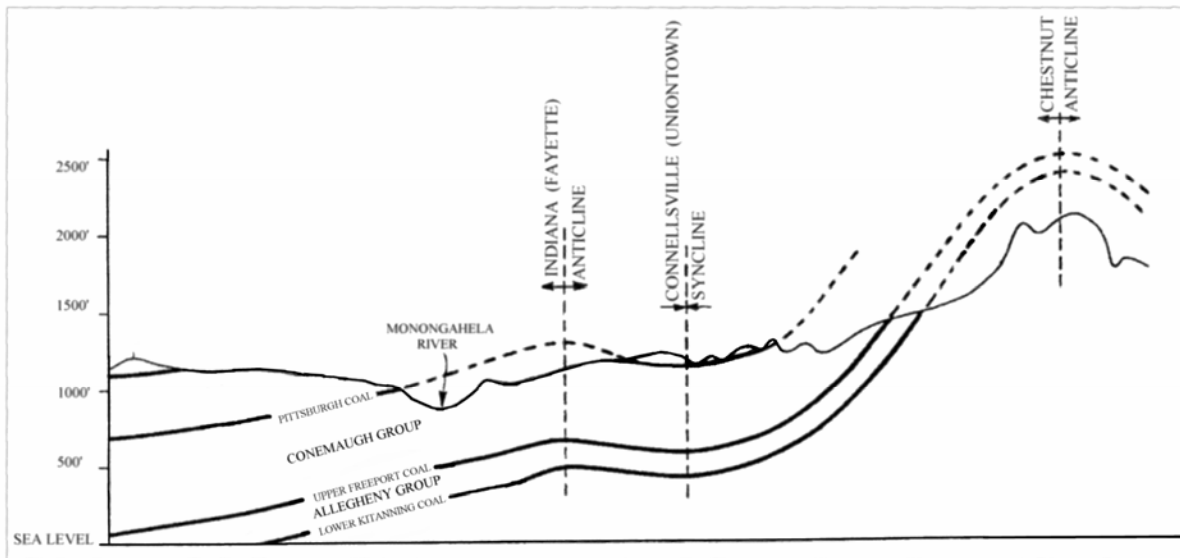


Figure 2.3 Geologic cross section from a location near the Omega Coal Mine (based on map by Repine, et al., 1983).

member of the coal seam is 0.5-0.8 m thick and contains enough pyrite to give a sulfur content of 5%. This bed was not removed during mining (Hennen, 1913; EPRI, 2001).

In the early 1980's, the Omega Mining Company, Inc. mined 68.8 hectares of Upper Freeport Coal in an operation called Omega Mine No. 100 (Gray, et al., 1997). The coal was extracted by the room and pillar method, with initial extraction of ~50% of the seam. During the mid-1980's second mining, or retreat mining, removed an additional 10-22% of the coal via pillar reduction and cross sectioning (EPRI, 2001). The roof of the mine was compromised allowing the residual top member of the coal seam to fall. Surface subsidence followed, with the formation of cracks as much as one foot wide. Meteoric water began to enter the mine coming into direct contact with the sulfur-bearing minerals in the remaining coal (EPRI, 2001).

2.2. Omega mine discharge and remediation

Acid mine drainage was discharging from the Omega mine during active mining, degrading Owl Creek and other watersheds that lie topographically downdip and west of the mine. In July of 1989, water that had accumulated within the central mine pool after closure, began to discharge into the Cobun Creek watershed (Cobun Creek contributes to the public water supply reservoir of Morgantown) to the north and east of the mine. This additional AMD was flowing at a rate of 0.95 L s^{-1} , had pH values as low as 2.8, and killed all aquatic life in a 2.4 km stretch of the creek (EPRI, 2001).

In 1989, horizontal drains were put in place to relieve the buildup of water pressure in the two mine pools and a collection system was established to route all discharges to a centralized AMD treatment facility (Gray et al., 1997). By January, 1995, the WVDEP had taken over the

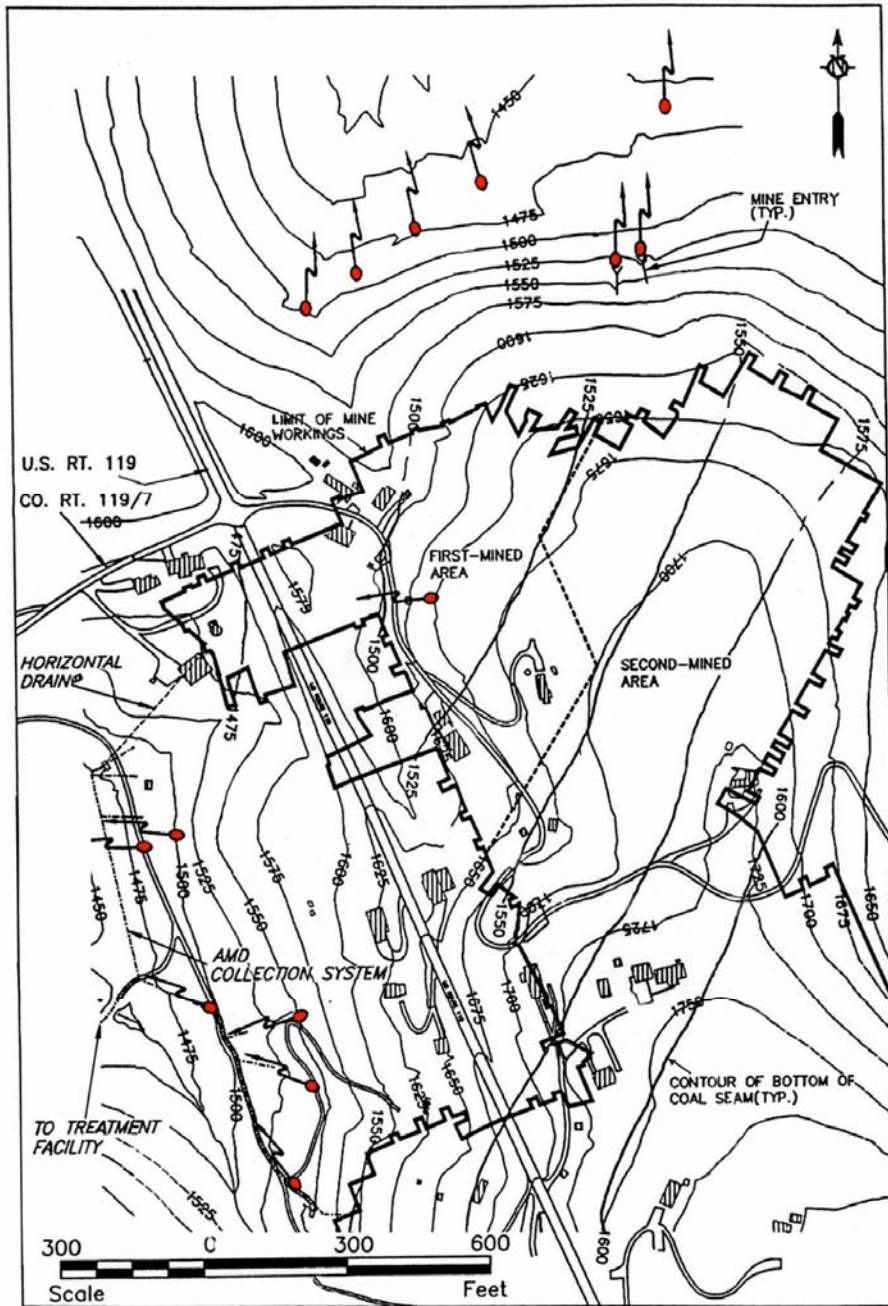
facility, because all other financial resources had been depleted. The annual operating cost at that time was approximately \$300,000 per year (EPRI, 2001).

During the early 1990's a feasibility study was done to appraise the value of a mine grouting operation to reduce AMD at the Omega Mine site. In March of 1996 an agreement was reached between WVDEP; Monongahela Power Company (a subsidiary of Allegheny Energy Supply); Anker Energy Corporation; Consol, Inc.; United States Office of Surface Mining Reclamation and Enforcement (OSMRE); and the Electric Power Research Institute (EPRI) for project funding (EPRI, 2001). Existing water quality data indicated that the northern lobe of the mine was the source of 70-90% of the total AMD load from the mine, so the agreement only supported grouting the 10.4 ha of the northern lobe with coal combustion byproducts (CCB) (Gray et al., 1997). The US Department of Energy (USDOE) joined the others as a project sponsor in the spring of 1998 (EPRI, 2001).

Extensive testing was done to determine the most effective mixture of CCB with which to grout the mine. The final recommended mixture consisted of 49% fluidized bed combustion (FBC) ash from Anker Energy Corporation, 49% pulverized coal fly ash from Allegheny Energy, and 2% portland cement. Approximately 290 liters of water were added per cubic meter of grout to give a flow value of 60 seconds. This mix demonstrated the ability to flow long distances without separation and to develop reasonable strength and dimensional stability (EPRI, 2001). The grout mixing was done on site at a temporary grout manufacturing plant.

Borehole spacing for the grouting operation varied across the site based on video reconnaissance that appraised the degree of slope, the amount of rubble on the mine floor, and the volume of grout needed to fill the void (Gray et. al., 1997).

Grouting was performed between May and November 1998 (Fig. 2.4). In addition to the



LEGEND

-  STRUCTURE
-  SEEP

Figure 2.4 Plan view map of study area showing topography, coal contours, and seeps associated with the northern lobe of the Omega Coal Mine (modified from EPRI, 2001).

primary boreholes, a series of nine barrier holes were injected along the southern edge of the lobe to prevent water from flowing downdip from the open mine above (EPRI, 2001). In October 1998, exploratory drilling was done in order to evaluate the thoroughness of the filling operation; voids were pressure-injected to ensure that they were completely sealed (EPRI, 2001).

Water sampling, initiated in 1993, continued during and after completion of the grouting activity. Flow rates exhibited a reduction immediately after grouting operations were completed in 1998, but 1999 was unusually dry and the actual reduction resulting from the grout barrier could not be ascertained. In 2000, precipitation was slightly above normal and flow rates at the Marshall House and Seeps DEF (both discharges emanating from the grouted area) were 25-70% of the pre-grouting flow rates. The flow rate from the Central Pool had been expected to increase since more water was pooling there as a result of the grout barrier placed between it and the northern lobe of the mine. It was unchanged, however, with a new rate of 0.83 L s^{-1} compared to the earlier one of 0.81 L s^{-1} (EPRI, 2001). Overall daily acid loads for the three largest AMD sources (Marshall House, Seeps DEF, and the Central Pool) were reduced by 58%, but this had a direct correlation with the reduction in flow rate and might not be the result of interaction between AMD and grouting materials (EPRI, 2001).

The chemistry of the discharge waters remained almost unchanged after completion of the grout injection project. Despite the high alkalinity of the grout, pH levels continued to be below 3.0 for the Central Pool and Seeps DEF. The Marshall House pH was at its highest in July 1999 at 3.34, and in December of 1999, the Treatment Inlet (final pre-treatment collection point for all AMD), still had a pH of 2.56. At the Marshall House, total Fe concentrations doubled along with those of Ca, Na, Mg, Mn and K. In addition, SO_4^{2-} and As were elevated far above their former levels (e.g., SO_4^{2-} rose to >6000 ppm and As rose above the detection limit to 0.32

ppm). No other sampling point had such extreme results, but the Central Pool did show a reduction in all elements.

After a large AMD discharge event in March of 1999, monitoring wells were installed into the strata above the mine roof. The pH in these wells was consistently circumneutral (EPRI, 2001) suggesting that the Uffington Shale contains very little pyrite and that the source of the AMD must be within the mine void.

2.3. Use of strontium isotopes to monitor water-rock interaction

Strontium (Sr) isotopes have been used effectively as a tracer for water-rock interaction in numerous drainage basin and groundwater system studies (e.g., Lyons et al., 1995; Négrel et al., 1997; Armstrong and Sturchio, 1998; Petelet et al., 1998; Böhlke and Horan, 2000; Pennisi et al., 2000; Probst et al., 2000; Aubert et al., 2002; Douglas et al., 2002; Banner, 2004; Gosselin et al., 2004). Because strontium is an alkaline earth element with an atomic radius near that of calcium (Ca) for which it commonly exchanges, it is frequently used as a proxy for Ca in geologic and hydrologic systems. Strontium will also substitute for potassium in some minerals when Si^{4+} is replaced by Al^{3+} simultaneously (e.g., vermiculite) (Faure, 1986). As Sr is present at relatively high concentrations in common Ca-rich minerals such as calcite, dolomite, and plagioclase feldspar, the weathering of these minerals will release concentrations of 5 to 1000 $\mu\text{g L}^{-1}$ in rivers. Through hydrological cycling it is typical to find $\sim 7,620 \mu\text{g L}^{-1}$ in seawater, 0.5 to 500 $\mu\text{g L}^{-1}$ in rain, and 0.01-1 $\mu\text{g L}^{-1}$ in snow (Capo et al, 1998, Banner, 2003).

Naturally-occurring Sr has four stable isotopes; ^{88}Sr , ^{87}Sr , ^{86}Sr and ^{84}Sr . In addition, ^{87}Sr is augmented by the decay of ^{87}Rb which has a half-life of 48.8 billion years. Very old rock

units with high Rb/Sr ratios tend to be enriched in ^{87}Sr , which is expressed as the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. As a result, rock units with different compositions and geologic histories will have different and distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Faure, 1986; Capo et al., 1998; Douglas et al., 2002). As groundwater interacts with its rock matrix, it can dissolve minerals and inherit their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios without measurable mass fractionation. In complex natural systems the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be used as tracers for groundwaters that interact with more than one geologic unit (Wadleigh et al., 1985; Faure, 1986; Goldstein et al., 1987).

Streamwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are a result of the combination of contributions from two distinct sources: the chemical weathering of drainage basin lithologic units via meteoric input, and the baseflow of the stream derived from the recharging and discharging of local and regional groundwaters (Wadleigh et al., 1985; Aubert et al., 2002; Douglas et al., 2002).

3. SAMPLING AND LEACHING PROCEDURES

3.1. Sampling sites

Each sampling location was part of the ongoing collection and treatment system at the Omega Mine site and had been historically tracked by USDOE and WVDEP sampling programs (Fig. 3.1). The general characteristics of each of the sampling sites are summarized in Table 3.1.

Central Pool. This location drains the central mine pool located updip of the grout barrier. Prior to the grouting operation this was the third largest source of AMD, despite the fact that it normally only flows from December through June. This discharge should have no contact with the CCB grout.

Punch Mines 21, 22, and 24B. These three sampling locations are seeps located on the westernmost hillside of the mine site. They are the locations of small, former mines dug by local

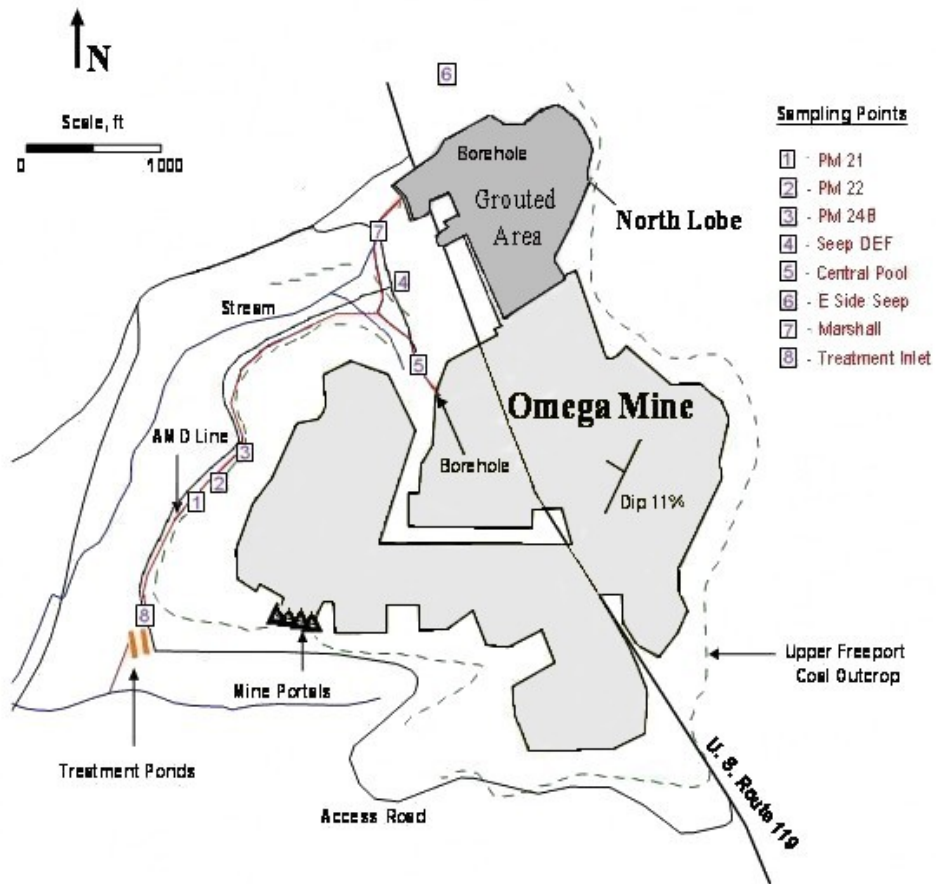


Figure 3.1 Plan view map of Omega Mine showing AMD collection and treatment systems, streams, and roads (modified from EPRI, et al., 2001).

Table 3.1 Sampling site names, location descriptions, flow rate, and pH at Omega Mine Site.

Name	Description	Flow L s ⁻¹							pH							Avg pH
		Collection Date							Collection Date							
		5/01	7/01	8/01	11/01	12/01	7/02	5/03	5/01	7/01	8/01	11/01	12/01	7/02	5/03	
PM 21	punch mine seep	1.06	1.03	0.596	0.309	0.245	0	0.315	2.93	2.98	2.82	2.84	3.71	ns ^a	na ^b	3.06
PM 22	punch mine seep	0.0398	0.0429	0.013	0.009	0	0	0.505	3.28	3.24	3.01	3.11	ns	ns	na	3.16
PM 24B	punch mine seep	0.195	0.252	0	0	0.084	0	0.505	3.73	3.68	ns	ns	2.89	ns	na	3.43
Seeps DEF	seep from W side of northern lobe	0.495	0.546	0.371	0.317	0.327	0.505	0.126	2.84	2.82	2.73	2.64	2.83	na	na	2.77
Central Pool	mine pool located up dip of grout	0.291	1.14	0.102	0	0	0.189	0.757	2.77	3.18	2.69	ns	ns	na	na	2.88
Seeps E Side	all seeps east of Route 19	n/a	0.284	0.115	0.068	0.095	0.126	0.883	ns	3.24	2.82	3.07	3.02	na	na	3.04
Marshall House	down dip of grouted lobe	0.847	1.76	0.695	0.434	0.352	1.01	1.45	2.88	3.50	2.70	3.64	3.01	na	na	3.15
Treatment Inlet	merging point for all AMD	3.78	4.61	ns	1.14	1.2	2.33	5.17	2.80	2.95	ns	2.95	2.88	na	na	2.90

^ans = not sampled

^bna = not analyzed

residents to collect personal coal supplies. These seeps are suspected of being deep enough to be hydrologically connected to the greater mine works, but they are located in a separate lobe of the mine. There is a second mine pool (i.e. the southwest pool) here that is not associated with the grouted area and so these seeps cannot be interacting with the grout (EPRI, 2001).

Seeps DEF. This is the location where several seeps on the west side of the hill encompassing the northern lobe of the mine, were tied together for the collection system. Prior to grouting, this was the second greatest source of AMD. At least one of these seeps was a former punch mine, and historically, the discharge rate was quite strongly tied to meteorological events. Dye testing conducted in the past showed no evidence that these seeps are hydrologically linked to the mine works.

Marshall House. At this site a borehole had been drilled horizontally into the northern mine pool for drainage purposes. Prior to grouting, 50% of the AMD load originated from this location making it the primary source of contamination. It is located at the lowest elevation of the collection system and downdip of the grouted northern lobe. Grout interaction was occurring at this site, as indicated by the grout material emerging from the drainage pipe. In addition to the drainage pipe at this location, there is a separate catch basin for waters being pumped over from the east side of US Route 119.

Seeps East Side. This is the only sampling location located on the east side of US Route 119. It is the collection point for all of the AMD emanating from the eastern hillside of the northern lobe, and consists of a retention basin containing a pump to transfer the AMD over to the Marshall House location. This site collects AMD waters that began to seep from the northern lobe after the mine closure; it is assumed that the discharging water has interacted with the grout.

Treatment Inlet. The final sampling location is at the point where all of the drainage water converges and flows into holding/treatment ponds. Samples were taken at a spillway where the drain pipe ends and the AMD falls to the treatment pond below.

The drainage collection system was updated before the study was completed and there was some slight modification to the punch mine sampling locations in an attempt to collect more of the escaping AMD. No changes were made in the sampling or analytical regimes and no significant variations were evident in the geochemistry for these sites.

3.2. Sample collection

Discharge samples were collected at various intervals over a two year time period, with an attempt to take samples during all seasons of the year (Table 3.1). Three samples were taken at each sampling location that was still in active use, and that had historical data records available. One sample was collected and kept cold so that electrometric pH, colorimetric ammonium, and ion chromatographic sulfate and chloride measurements could be taken in the lab. A second, acidified sample, was collected to be analyzed for metals by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The third sample was collected in acid-cleaned polyethylene bottles for strontium isotope analysis. These samples were filtered through 0.45 μm SFCA-membrane filters (Cole-Parmer) using 60 cc pre-rinsed syringes and then acidified to a pH of ~ 2.0 with ultrapure concentrated HCl.

In addition to the AMD collected from the perimeter of the mine, samples of dry grout, shale overburden, underclay, and coal were obtained for leaching studies. These were from two on-site core borings from the consulting firm that designed and oversaw the grouting project.

3.3. *Solid leaching procedure*

After a survey of established leaching methods and leaching studies (e.g., Morrison et al., 1990; EPA Method #1312, 1994; Bódog et al, 1996; Choi et al., 2002; Kim et al., 2004), a leaching method was developed that would simulate the interaction between AMD and the various matrix materials in the mine environment. The method was a batch leaching test (there was no evidence of species-dependent dissolution) in simulated acid mine drainage continuing until pH stabilization (Kim, et al., 2004).

Each solid sample of grout, shale overburden, coal, and the underlying clay was ground in a mixing mill with a pre-contaminated titanium carbide vessel for 10 minutes (to a fine powder). After grinding, 10.00 g of each sample was placed into an acid-rinsed polypropelene centrifuge bottle with 100.0 mL of 1.0 N hydrochloric acid (HCl). All samples were shaken and the pH was immediately measured. They were placed into a Boekel-Grant orbital/reciprocal shaking water bath which was set for linear agitation with 346 strokes min^{-1} and a constant temperature of 22.0° C. Agitation was continuous (to prevent settling of the solids), and the pH was measured periodically to verify that the final readings were stable. This would assure that all leachable Ca (and Sr by default) had been taken up in solution.

Two different tests were performed on the grout samples. The first was done in triplicate. Samples from three different locations of each of the two core borings were leached in order to account for the non-homogeneity of the grout mixture. This leaching period was approximately 24 hrs long and concluded with a final pH reading, centrifugation, and decanting of all clear leachate from the bottles.

The second test was done sequentially with 0.25 N HCl. One sample from each core boring was leached for a week, with small aliquots removed at the following time steps: three

minutes, fifteen minutes, one hour, one day, and one week. This test was designed to assess discrepancies that may be encountered over longer time spans encountered in a natural environmental system with weaker AMD acids. In this leach test, 10.00 g of ground grout sample were added to 200.0 mL of acid in order to minimize the impact of the removal of 20.0 mL aliquots. Each aliquot was immediately centrifuged and decanted to arrest further reactions between the acid and grout. Analytical testing was performed after all samples were collected.

All leachate samples were analyzed by ICP-AES for major and trace elements and then by TIMS for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

In addition to batch leaching of the solid samples, a ground fraction of each sample was completely digested by EPA method 3052. These were analyzed by ICP-AES in order to obtain data for calculating the per cent extraction.

4. ANALYTICAL METHODS

4.1. Metals analysis

The concentrations of 23 metals were determined for each of the samples with a Perkin Elmer Optima 3000 Radial View ICP-OES (purchased in 1996 by the National Energy Technology Laboratory (NETL)).

Analyses of the acidified AMD samples were usually performed the day after they were collected. The leachate samples were preserved by acidity and refrigeration until each batch sampling period was complete and then analyzed by ICP-AES within several days time. The method used was EPA 3052.

All solid matrix samples underwent complete digestion and immediate metals analysis at NETL. The method used for these samples was EPA 6010C.

4.2. *Strontium chemistry and isotope analysis*

All analytical preparatory work for Sr isotope ratio analysis was done under clean lab conditions to prevent contamination via ubiquitous local sources of Ca/Sr. With the Sr concentration of the AMD known from ICP-AES analysis, aliquots of filtered sample containing ~4.0 μg of Sr were poured into acid-washed Teflon beakers and evaporated on a hot plate at 195° C. The dried residue was dissolved in 0.5 mL 3.0 N ultrapure nitric acid (HNO_3). The resulting solution was centrifuged in order to remove any undissolvable solids and the supernatant was eluted through columns containing Sr-SPEC® resin in order to separate Sr from all other metal constituents in the sample.

An aliquot of the separated Sr solution containing 400-500 ng of Sr was fully evaporated at 195°C in an acid-washed Teflon vial. To prepare it for isotope ratio analysis, the strontium was dissolved in 1.0 μL of 1.0 N ultrapure HNO_3 . This 1.0 μL was placed onto a rhenium filament pre-loaded with a tantalum oxide carrier agent. The loaded sample was dried and cured and inserted into a carousel for loading into the Finnigan MAT 262 thermal ionization mass spectrometer (TIMS).

Strontium isotopes were measured by static multicollection, with ^{87}Rb monitored continuously on an additional Faraday collector. All four of the naturally occurring Sr isotopes were measured simultaneously, 100 times during the analyses, providing high precision measurements (2σ error $\leq 0.003\%$). In addition to the samples, a strontium standard (SRM 987) was analyzed at least once during each group of samples. Our average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for SRM 987 during the time of these analyses was 0.71026.

5. RESULTS

5.1. *Drainage chemistry*

Seven sets of mine drainage were collected at the mine site over a period of two years. Twenty-three metal concentrations were determined by ICP-AES for each acidified sample (Tables 5.1 and 5.2). The non-acidified samples were analyzed for ammonium, chloride, sulfate and pH (Table 5.1).

The cation chemistry of most Omega AMD discharges is dominated by Ca, Mg, and Fe, with subordinate Na and K (Fig. 5.1). Sulfur (predominantly as sulfate) is the major anion, although alkalinity was not determined for these samples. Iron and sulfur show a good correlation (Fig. 5.2), however, all waters have higher S than would be expected with stoichiometric dissolution of pyrite (FeS_2). This suggests that Fe is back-reacting, or precipitating, prior to discharging from the mine. There is no evidence that NaCl-type brines control the chemistry of Omega since there is a lack of correlation between dissolved Na^+ and Cl^- (Fig. 5.3).

Of all the discharges sampled, three sites (Marshall House, Seeps East Side, and the Treatment Inlet) were expected to show evidence of interaction with the CCB grout material. I compared the chemistry of these sites with the chemistry of discharges that could not have interacted with the grout in order to determine whether any combination of cations and anions were usable to identify water-grout interaction. There is little separation in major element concentrations between waters that interact with grout and those that do not. There are, however, some elements that can be used in part to differentiate between the two discharge types. For example, in a plot of aluminum vs. sulfur (Fig. 5.4) the waters that interact with the CCB grout usually show a higher S concentration at a given concentration of Al, but the separation is modest and there is no clear boundary function between the two data sets. In another example,

Table 5.1 Major element concentration in Omega Mine AMD discharges, mg L⁻¹.

Sample Location	Al	Ca	Fe	K	Mg	Mn	Na	S	Si	Cl	NH ₄	SO ₄
<i>Collected 5/30/01 Analyzed 6/4/01</i>												
Punch Mine 21	131	172	159	3.24	72.6	4.01	8.62	762	na ^a	12	40.60	na
Punch Mine 22	34.4	148	20.1	6.66	54.6	5.42	5.88	343	na	1.22	39.75	na
Punch Mine 24B	6.94	27.3	0.132	1.6	10.1	1.5	3.28	55.2	na	4.17	2.65	na
Seeps DEF	117	127	314	0.706	60.9	2.16	24.1	635	na	10.6	<0.10	na
Central Pool	111	103	423	4.29	58.3	1.75	27.2	635	na	12.2	<0.10	na
Marshall House	131	318	700	32.4	85.4	3.69	23.3	1010	na	7.67	1.200	na
Treatment Inlet	107	191	354	11.2	66.9	3.33	18.8	797	na	21.1	12.80	na
<i>Collected 7/18/01 Analyzed 7/25/01</i>												
Punch Mine 21	102	151	143	2.75	64.8	3.16	7.74	550	na	8.9	na	3268
Punch Mine 22	24.1	113	16.1	5.47	39.5	3.91	4.49	246	na	7	na	1134
Punch Mine 24B	3.63	19.9	0.107	1.33	7.26	1.17	3.2	35.7	na	5.8	na	247
Seeps DEF	73.9	98.2	215	0.803	47	1.6	29.6	481	na	68.6	na	2108
Central Pool	12.8	157	104	6.12	41.9	4.58	6.73	299	na	6.3	na	1298
Seeps East Side	137	137	547	5.03	74.1	2.49	11.6	815	na	19	na	4002
Marshall House	105	272	594	25.6	73.6	3.14	18.7	910	na	<0.1	na	4695
Treatment Inlet	95.7	173	342	9.5	62.8	2.85	14.9	657	na	13.8	na	2989
<i>Collected 8/20/01 Analyzed 8/28/01</i>												
Punch Mine 21	131	192	181	3.03	85	3.81	9.68	731	na	17.10	47.15	3623
Punch Mine 22	39.1	198	26.9	8.72	70.1	6.36	7.21	436	na	7.600	58.95	2449
Seeps DEF	108	131	301	0.741	64.2	2.24	23.4	653	na	58.90	0.4000	3472
Central Pool	102	101	395	4.46	57.9	1.69	26.2	610	na	4.500	0.19	3346
Seeps East Side	17.6	230	166	7.96	63.3	6.13	7.96	466	na	15.70	0.605	2674
Marshall House	107	279	577	25.2	76.7	3.24	18.9	935	na	17.00	1.1	4372
Treatment Inlet	No samples taken-system being flushed											
<i>Collected 11/2/01 Analyzed 11/7/01</i>												
Punch Mine 21	130	234	208	2.82	95.2	4.25	10	731	na	57.70	56.00	3251
Punch Mine 22	63.8	275	39.1	8.39	87	11.6	7.79	436	na	53.60	70.05	2121
Seeps DEF	113	159	376	0.756	70.6	2.72	21.9	726	na	61.00	0.64	1938
Seeps East Side	18.6	245	168	7.19	70.6	5.95	7.34	461	na	60.00	0.29	1387
Marshall House	95	221	426	24.5	72.1	2.8	19.8	766	na	43.00	1.1	3134
Treatment Inlet	101	206	301	8.69	76.3	3.42	16.5	693	na	38.00	11.8	3081
<i>Collected 12/7/01 Analyzed 12/13/01</i>												
Punch Mine 21	122	224	199	2.68	93.9	3.91	10.4	726	na	56	50.75	5911
Punch Mine 24B	3.79	25.2	0.117	1.52	9.09	1.73	3.94	42	na	16	1.000	1758
Seeps DEF	119	148	363	0.696	72.8	2.56	24.9	709	na	63	1.000	2512
Seeps East Side	14.5	209	109	5.64	56.2	5.33	6.1	352	na	20	1.000	1835
Marshall House	95.5	294	563	23.4	77.6	3.37	19	849	na	36	1.000	3480
Treatment Inlet	58.5	204	154	5.99	66.7	4.76	11.2	493	na	51	9.765	1850
<i>Collected 7/22/02 Analyzed 7/23/02</i>												
Seeps DEF	98.2	117	274	0.81	54	2.02	21.3	597	26.9	na	na	na
Central Pool	76.6	77.4	295	3.68	41.5	1.27	25.1	469	15.2	na	na	na
Seeps East Side	11.3	187	92	6.82	46.2	4.41	6.12	334	14.2	na	na	na
Marshall House	92.3	310	525	27.1	68.2	3.07	16.4	874	36.3	na	na	na
Treatment Inlet	94.4	195	276	9.66	62.6	2.96	14.9	657	29.1	na	na	na
<i>Collected 5/7/03 Analyzed 5/9/03</i>												
Punch Mine 21	103	124	164	2.86	50.8	2.65	5.48	501	25.8	7.9	16.6	2177
Punch Mine 22	86.3	108	143	3.35	49.2	3.96	5.54	462	26.1	8.5	16.4	2224
Punch Mine 24B	1.12	13.5	0.146	1.08	5.04	0.543	2.19	20.9	4.33	1.6	0.6	72
Seeps DEF	107	104	295	1.24	51.7	2.19	19.2	586	28.9	17.5	0.09	2660
Central Pool	99.8	80.5	319	3.79	47	1.44	25.2	517	20.6	37	0.09	2395
Seeps East Side	3.21	50.5	18	2.81	13.6	1.14	5.11	81.4	6.77	7.9	0.03	870
Marshall House	85.2	266	483	28.3	61.8	2.72	15.4	811	39.9	9.5	1.08	2988
Treatment Inlet	54.8	105	153	6.08	37.1	2.18	11	374	19.3	18	4.6	2065

^ana = not analyzed

Table 5.2 Trace element concentrations in Omega Mine AMD discharges, $\mu\text{g L}^{-1}$.

Sample Location	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	Zn	Sr	Nd
<i>Collected 5/30/01 Analyzed 6/4/01</i>														
Punch Mine 21	<8	6.2	177.1	23.9	1085	58	226	2290	<5	<6	<7.5	7230	592	na ^a
Punch Mine 22	<8	18.3	110.9	7.3	517	16.7	5.6	1030	<5	<6	<7.5	2880	529	na
Punch Mine 24B	<8	28.6	6.5	1.7	77	3.6	8.6	125	<5	<6	<7.5	456	95.6	na
Seeps DEF	<8	8.7	61.8	19.1	474	89.7	121	1150	7.5	<6	<7.5	3240	422	na
Central Pool	17.7	37.2	67.9	20.9	530	79.1	60.5	1250	7.7	<6	<7.5	3760	361	na
Marshall House	195	9.8	96.1	31.1	574	43	<1	1370	14.7	<6	<7.5	4430	1530	na
Treatment Inlet	37.4	16.8	95.58	21.1	608	52.8	56.4	1360	6.1	<6	<7.5	4190	793	na
<i>Collected 7/18/01 Analyzed 7/25/01</i>														
Punch Mine 21	<7.5	4.6	136	9.58	855	43.8	116	1810	<5	<6	<7	5580	500	73.5
Punch Mine 22	<7.5	20.7	80.7	3.78	390	10.2	6.2	752	6.3	<6	10.4	2110	386	29.1
Punch Mine 24B	<7.5	37.5	4.22	<1	49.7	2.3	5.5	74.2	<5	<6	<7	207	71	5.60
Seeps DEF	<7.5	7.6	41.4	2.07	320	55.4	68.8	740	<5	16	<7	2210	318	40.7
Central Pool	<7.5	17.3	31.2	<1	177	9.4	2.1	299	<5	<6	<7	967	406	15.9
Seeps East Side	18.3	<1	77	1.49	607	99.4	64.2	1420	<5	56.1	<7	4220	450	76.1
Marshall House	187	<1	77	<1	453	45	<1	1090	<5	59.5	<7	3440	1260	73.5
Treatment Inlet	28	3.6	82	3.02	538	51.8	42.7	1190	<5	29.3	8.1	3650	666	66.3
<i>Collected 8/20/01 Analyzed 8/28/01</i>														
Punch Mine 21	<7.5	1.2	173	11.1	1066	47.7	119	2260	<5	<6	<7	6810	645	83.9
Punch Mine 22	<7.5	18.5	134	5.51	660	19.6	4.1	1290	7.2	<6	<7	3370	662	51.0
Seeps DEF	<7.5	<1	58.4	1.75	444	80	68.6	1040	<5	13.4	<7	2950	426	58.2
Central Pool	<7.5	30.3	64.8	<0.75	480	70.3	38.7	1120	<5	23.2	<7	3280	347	55.6
Seeps East Side	<7.5	10.1	48.2	<0.75	255	15.7	<1	441	<5	8.6	<7	1270	577	26.2
Marshall House	157	<1	78.6	<0.75	456	47.2	<1	109	<5	34.6	<7	3300	1300	72.1
<i>Collected 11/2/01 Analyzed 11/7/01</i>														
Punch Mine 21	<7.5	<0.5	190	11.5	1182	19.4	57.6	2480	<5	<6	<7	7780	838	80.4
Punch Mine 22	<7.5	15.4	165	4.71	956	9	4.6	1750	<5	<6	<7	4990	855	79.2
Seeps DEF	<7.5	<0.5	70	8.28	568	23.8	44.6	1310	<5	<6	<7	4010	491	55.7
Seeps East Side	<7.5	17.8	41	3.78	261	5.3	<1	423	5.2	<6	<7	1420	733	29.6
Marshall House	147	4.7	69.9	11.3	384	30.8	<1	870	14.4	<6	<7	3060	1560	62.1
Treatment Inlet	13.3	3.2	94.1	8.16	618	44.1	31.4	1320	<5	<6	<7	4210	1010	67.6
<i>Collected 12/7/01 Analyzed 12/13/01</i>														
Punch Mine 21	<7.5	<0.5	175	10.1	1050	48.1	38.9	2210	<5	<6	<7	7060	798	82.5
Punch Mine 24B	<7.5	27.3	4	<0.5	57.6	1.8	5.8	76.6	6.7	<6	<7	205	85	5.9
Seeps DEF	<7.5	<0.5	68	8.26	537	70.1	39.9	1220	<5	<6	<7	3840	502	62.2
Seeps East Side	<7.5	13.8	29	2.65	210	4.3	<1	323	6.3	<6	<7	1510	491	25.9
Marshall House	146	2.9	77.2	12.7	454	32.5	<1	1020	15.4	<6	<7	3550	1340	70.8
Treatment Inlet	<7.5	11.3	69.7	4.89	464	24.5	13.5	908	<5	<6	<7	2920	640	48.5
<i>Collected 7/22/02 Analyzed 7/23/02</i>														
Seeps DEF	<7.5	10.3	53.1	17.9	408	66.2	76.6	901	13.0	<6	17.6	2720	358	52.4
Central Pool	11.8	51.9	47.2	17.4	366	48.9	30.8	807	18.4	<6	22.4	2580	244	44.7
Seeps East Side	<7.5	21.1	35.0	5.98	184	9.30	<1	302	7.10	<6	13.1	2810	427	17.3
Marshall House	185	9.60	75.1	31.8	444	22.7	<1	1000	33.7	<6	29.0	3420	1240	71.6
Treatment Inlet	24.7	12.8	93.7	19.9	567	42.5	48.7	1210	10.0	<6	22.0	3830	670	61.1
<i>Collected 5/7/03 Analyzed 5/9/03</i>														
Punch Mine 21	<7.5	11	128	14.6	702	40.4	164	1510	<5	<6	<7.5	4430	395	52
Punch Mine 22	<7.5	7.8	116	13	645	34.3	108	1370	<5	<6	<7.5	3980	388	52.7
Punch Mine 24B	<7.5	36.4	1.44	0.9	22.8	<1	2.5	27.5	<5	<6	<7.5	73.8	50.2	<5
Seeps DEF	<7.5	9.4	53.5	15.3	425	61.3	139	897	16.9	<6	<7.5	2660	354	50.3
Central Pool	7.8	43.9	54.4	15.3	435	57.3	110	958	16.3	<6	<7.5	2860	282	38.5
Seeps East Side	<7.5	22.1	7.26	1.7	42.9	<1	<1	68.3	<5	<6	<7.5	192	155	<5
Marshall House	173	5.1	70.1	21.2	409	9	<1	911	8.7	<6	<7.5	3030	1200	42.4
Treatment Inlet	14.9	16.5	51.1	8.9	312	22.3	51.9	662	<5	<6	<7.5	1940	400	28.2

^ana = not analyzed

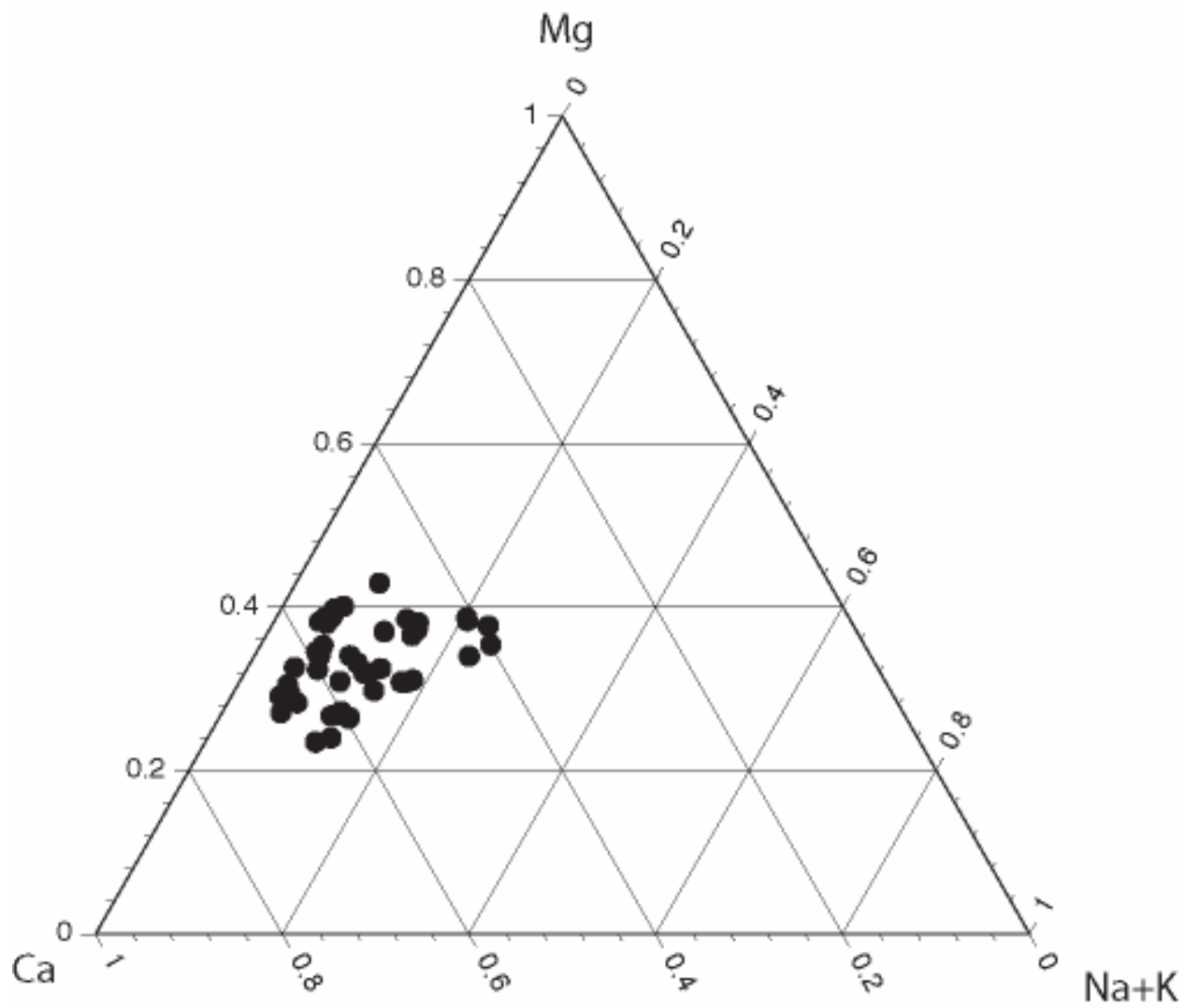


Figure 5.1 Trilinear cation plot of Omega Mine discharge waters.

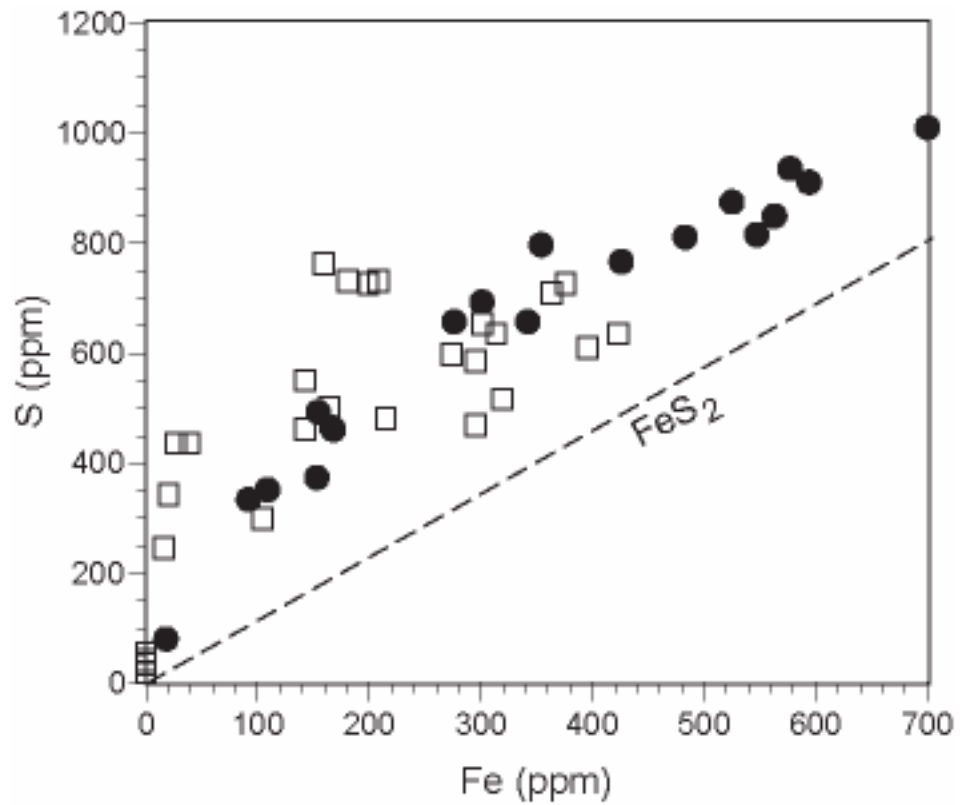


Figure 5.2 Plot of S vs Fe in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine. Dashed line indicates stoichiometric dissolution of pyrite.

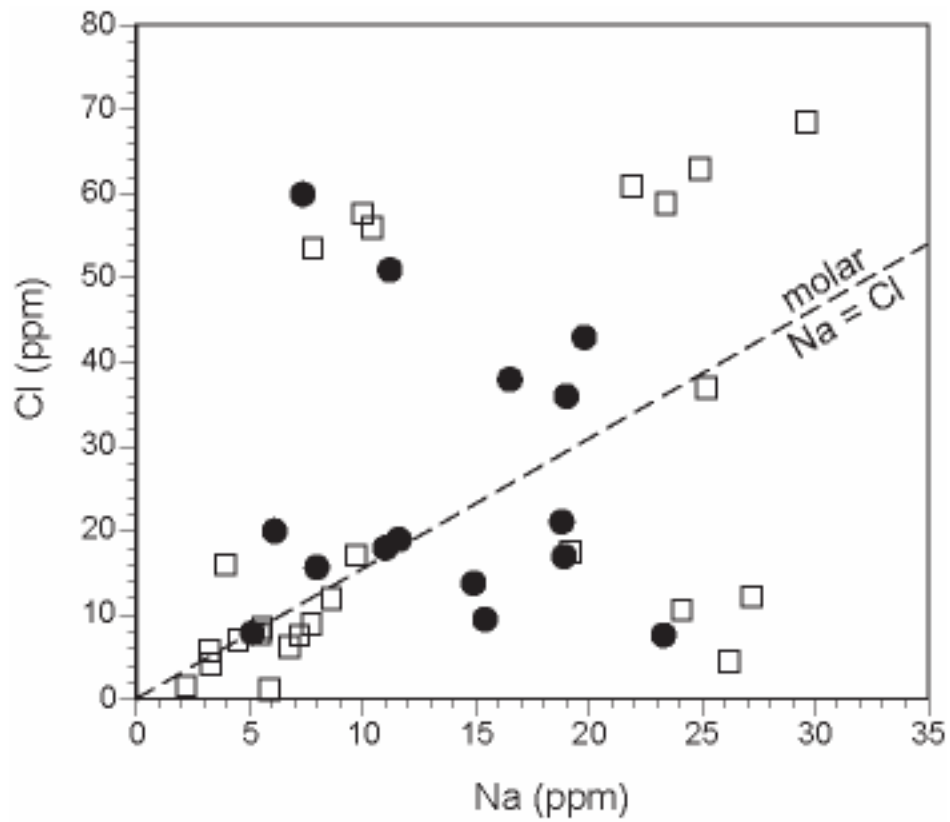


Figure 5.3 Plot of Cl vs Na in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine. Dashed line indicates NaCl brine.

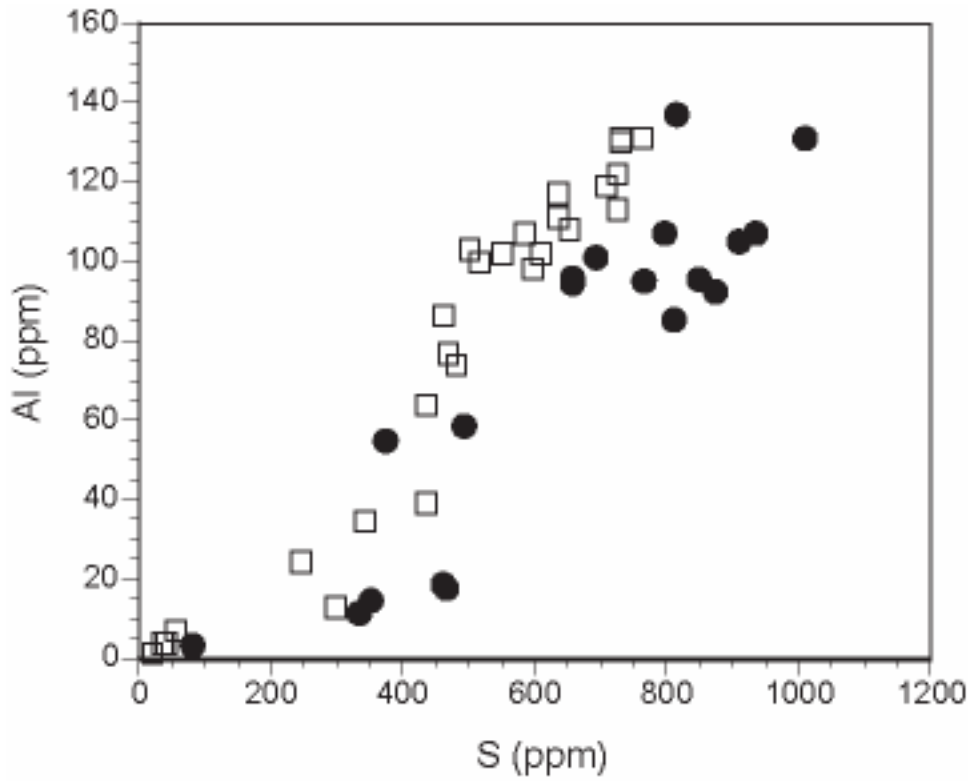


Figure 5.4 Plot of Al vs S in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine.

potassium tends to be higher in the grout-interacting samples, showing some differentiation between the discharge types (e.g., see plot of K vs. Fe, Fig. 5.5).

Similar results are found with the trace elements from the Omega Mine (Table 5.2). None of the trace elements clearly differentiate between waters that interact with CCB grout and those that do not, although a few show modest separation. The most notable example is arsenic, which tends to be enriched in waters that have interacted with the CCB grout (at concentrations above the ICP-AES detection limit of 8 ppb). This is illustrated by the correlation in the plot of As with K at K concentrations above ~10 ppm (Fig. 5.6).

5.2. *Strontium isotope ratios of discharges*

The strontium isotope ratios of Omega Mine discharges range from 0.71401 to 0.71594, with an external reproducibility of 0.00002 or better (Table 5.3). The variability in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for individual discharge sites sampled at different times over the two-year period is quite small (generally less than 0.0004; Fig. 5.7). The only exception is the sample collected from Punch Mine 22 on 7 May 2003. It yielded a significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ value than any other sample taken from that discharge site. The flow rate at Punch Mine 22 on 7 May 2003 was more than an order of magnitude higher than it was during any other sampling period. This suggests that the hydraulics could have been different during that high-flow period. Furthermore, the AMD collection system had been updated and re-routed prior to this sampling date, which may also account for some of the shift in isotopic ratio. Previously escaping AMD was now being captured for treatment. Overall, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios suggest that the discharges draining the Omega Mine have tapped waters with relatively consistent chemistries.

A linear correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $[\text{Sr}]^{-1}$ would be suggestive of mixing between

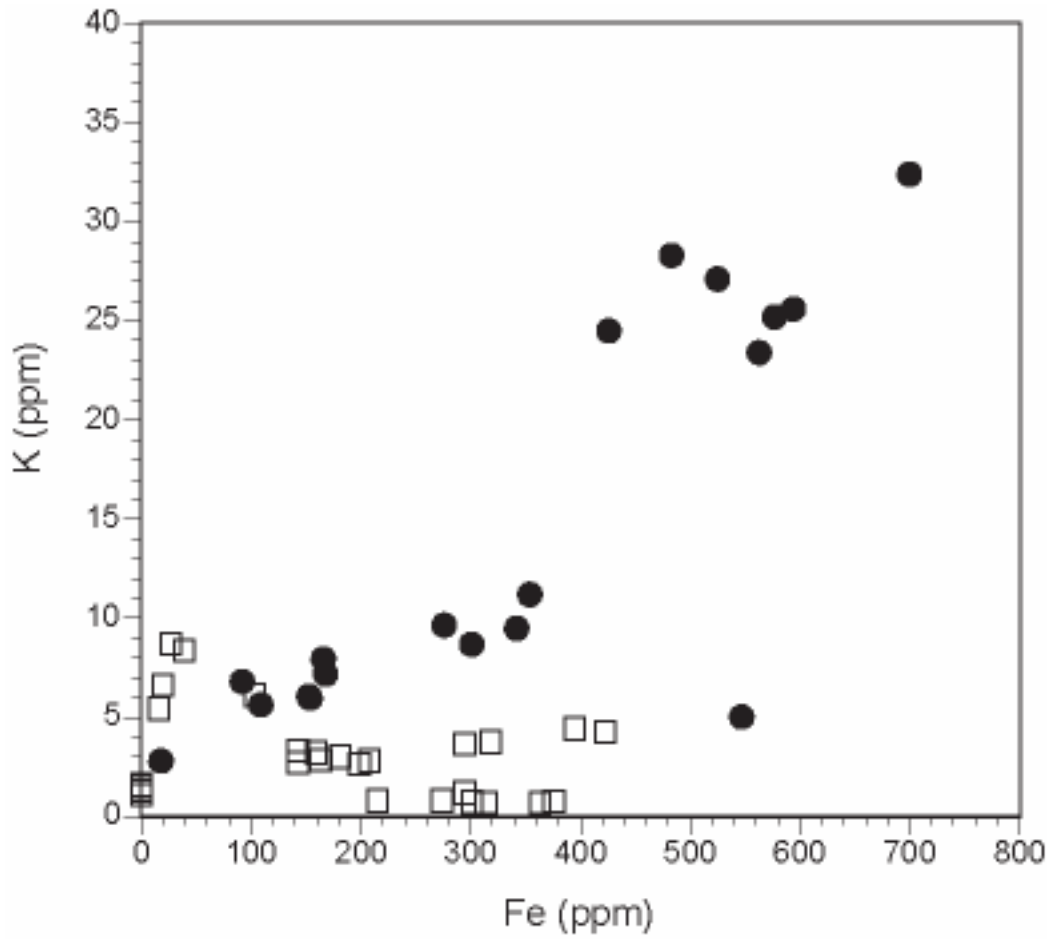


Figure 5.5 Plot of K vs Fe in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine.

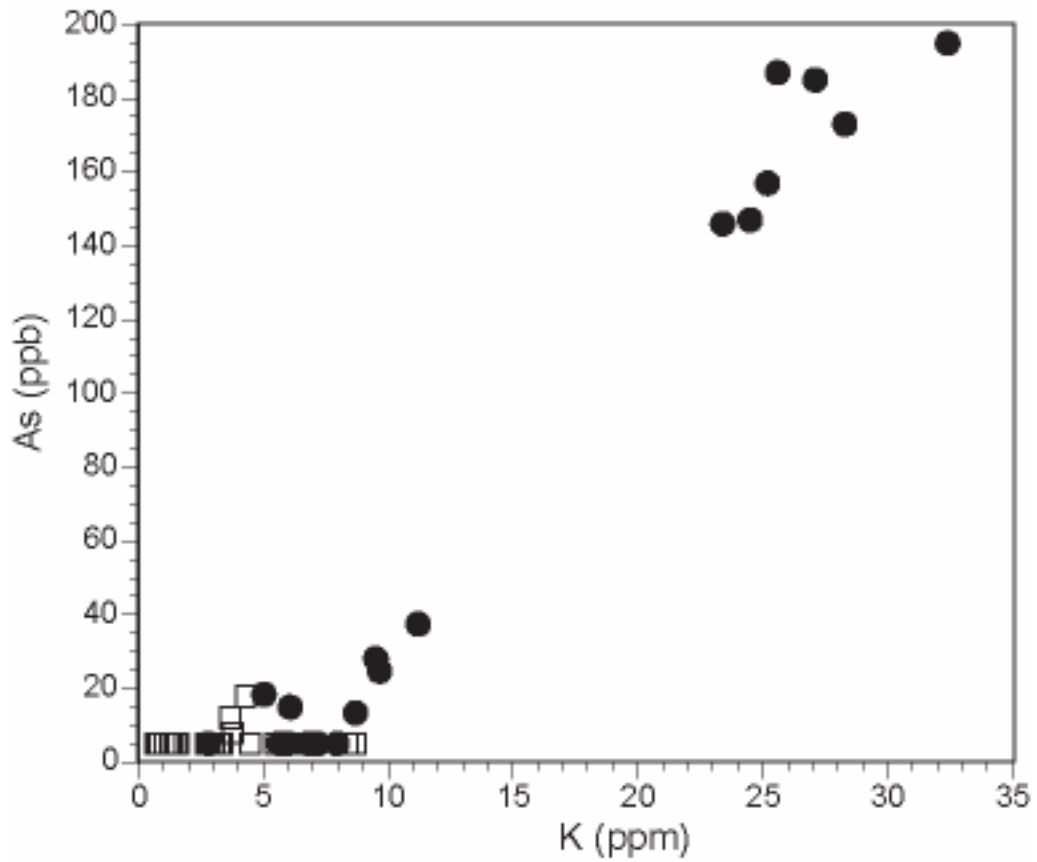


Figure 5.6 Plot of As vs K in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine. Samples that fall below the detection limit for arsenic (8ppb) are plotted at the As detection limit, however, actual values are probably lower.

Table 5.3 Strontium Concentration, flow, flux, and isotopic ratio in Omega Mine AMD.

Sample Location	Date Collected	[Sr] (mg L ⁻¹)	Flow (L s ⁻¹)	Sr Flux (mg s ⁻¹)	⁸⁷ Sr/ ⁸⁶ Sr
Punch Mine 21	5/30/2001	592	1.1	651	0.715883±09
Punch Mine 21	7/18/2001	500	1.0	500	0.715884±09
Punch Mine 21	8/20/2001	645	0.60	387	0.715902±11
Punch Mine 21	11/2/2001	838	0.31	260	0.715873±10
Punch Mine 21	12/7/2001	798	0.25	200	0.715852±12
Punch Mine 21	5/7/2003	395	0.32	126	0.715701±11
Punch Mine 22	5/30/2001	529	0.040	21	0.715241±11
Punch Mine 22	7/18/2001	386	0.043	17	0.715182±09
Punch Mine 22	8/20/2001	662	0.013	9	0.715101±11
Punch Mine 22	11/2/2001	855	0.0090	8	0.715187±09
Punch Mine 22	5/7/2003	388	0.51	198	0.715893±09
Punch Mine 24B	5/30/2001	95.6	0.20	19	0.715372±09
Punch Mine 24B	7/18/2001	71	0.25	18	0.715284±11
Punch Mine 24B	12/7/2001	85	0.084	7	0.715214±11
Punch Mine 24B	5/7/2003	50.2	0.51	26	0.715194±09
Seeps DEF	5/30/2001	422	0.50	211	0.715869±11
Seeps DEF	7/18/2001	318	0.55	175	0.715719±09
Seeps DEF	8/20/2001	426	0.37	158	0.715853±13
Seeps DEF	11/2/2001	491	0.32	157	0.715805±10
Seeps DEF	12/7/2001	502	0.33	166	0.715785±11
Seeps DEF	7/22/2002	358	0.51	183	0.715909±09
Seeps DEF	5/7/2003	354	0.13	46	0.715714±12
Central Pool	5/30/2001	361	0.29	105	0.715918±09
Central Pool	7/18/2001	406	1.1	447	0.715898±09
Central Pool	8/20/2001	347	0.10	35	0.715929±10
Central Pool	7/22/2002	244	0.19	46	0.715890±09
Central Pool	5/7/2003	282	0.76	214	0.715935±11
Seeps East Side	7/18/2001	450	0.28	126	0.714311±13
Seeps East Side	8/20/2001	577	0.12	69	0.714456±12
Seeps East Side	11/2/2001	733	0.068	50	0.714557±09
Seeps East Side	12/7/2001	491	0.095	47	0.714449±10
Seeps East Side	7/22/2002	427	0.13	56	0.714367±10
Seeps East Side	5/7/2003	155	0.88	136	0.714154±10
Marshall House	5/30/2001	1530	0.85	1301	0.714034±10
Marshall House	7/18/2001	1260	1.8	2268	0.714092±11
Marshall House	8/20/2001	1300	0.70	910	0.714125±07
Marshall House	11/2/2001	1560	0.43	671	0.714113±09
Marshall House	12/7/2001	1340	0.35	469	0.714146±09
Marshall House	7/22/2002	1240	1.0	1240	0.714095±09
Marshall House	5/7/2003	1200	1.5	1800	0.714008±10
Treatment Inlet	5/30/2001	793	3.78	2997.54	0.714700±10
Treatment Inlet	7/18/2001	666	4.61	3070.26	0.714793±10
Treatment Inlet	11/2/2001	1010	1.14	1151.4	0.714849±09
Treatment Inlet	12/7/2001	640	1.2	768	0.714744±09
Treatment Inlet	7/22/2002	670	2.33	1561.1	0.714822±11
Treatment Inlet	5/7/2003	400	5.17	2068	0.714729±12

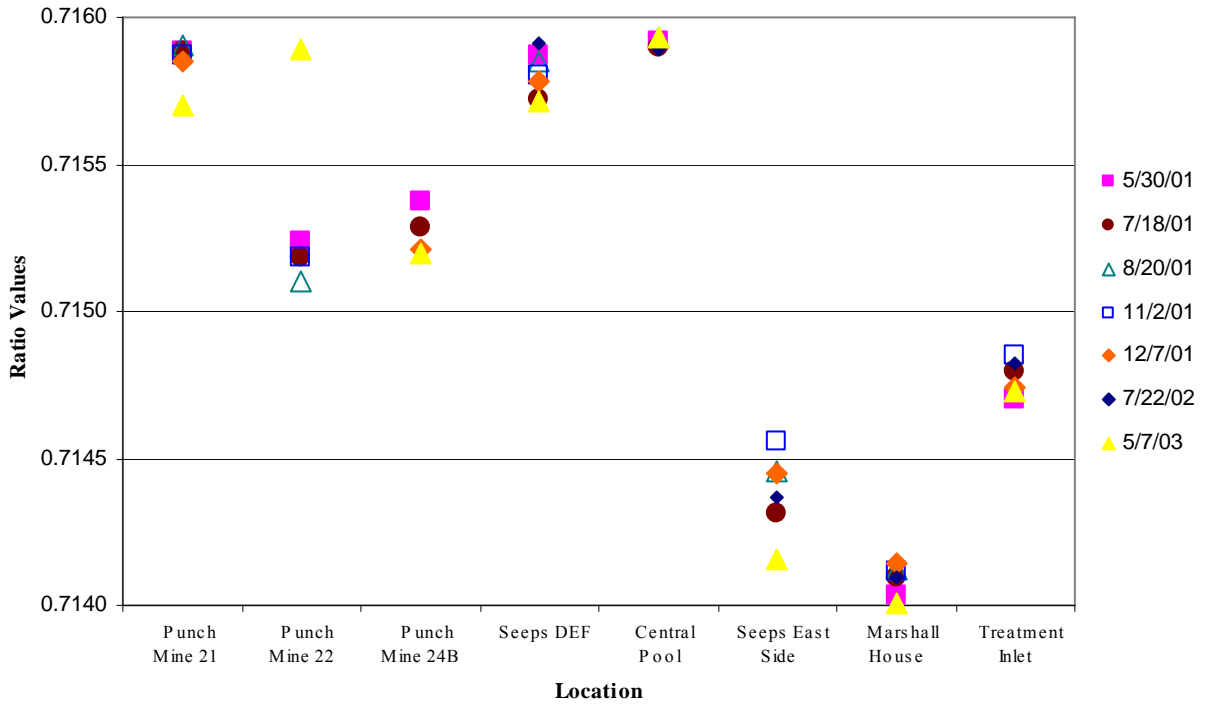


Figure 5.7 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of AMD samples shown in relation to collection location and date.

two sources with different $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr concentrations. The clear absence of such a correlation (Fig. 5.8) suggests that the variations in $^{87}\text{Sr}/^{86}\text{Sr}$ among the different discharges are not a result of simple mixing between two water reservoirs, but of complex water-rock interaction with multiple sources. In general, there is a strong correlation between Sr and Ca (Fig. 5.9) indicating that the trace element Sr is a good proxy for the major element Ca in this hydrologic system. However, the correlation for samples that interacted with the CCB grout (closed circles; $r^2 = 0.68$) is clearly not as strong as that for the samples that escaped grout interaction (open squares; $r^2 = 0.98$). This offers the possibility that the grout material might contain multiple components (e.g. CCB and cement from multiple sources) with different Sr/Ca ratios that are being leached by groundwaters flowing through the grouted section of the mine.

A striking aspect of the strontium isotope results is that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the three discharges with grout interaction (Marshall House, Seeps East Side, and Treatment Inlet) are clearly lower than those of waters that did not interact with CCB grout. Waters that did not interact with grout have values ranging from 0.7151 to 0.7159, while the two discharges from the grouted portion of the mine have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.7140 to 0.7146. The Treatment Inlet, which captures water from both the grouted and ungrouted portions of the mine, has intermediate ratios of 0.7147-0.7148. These Treatment Inlet ratio values are clearly skewed toward waters draining the grouted portion of the mine, which reflects both the high flow and the high Sr concentration (hence the high Sr flux) of the Marshall House discharge (Table 5.3).

Of all the chemical parameters analyzed in this study, the strontium isotope ratio is the only one that clearly and unequivocally differentiates between waters that interact with grout and those that bypass the grouted portion of the mine.

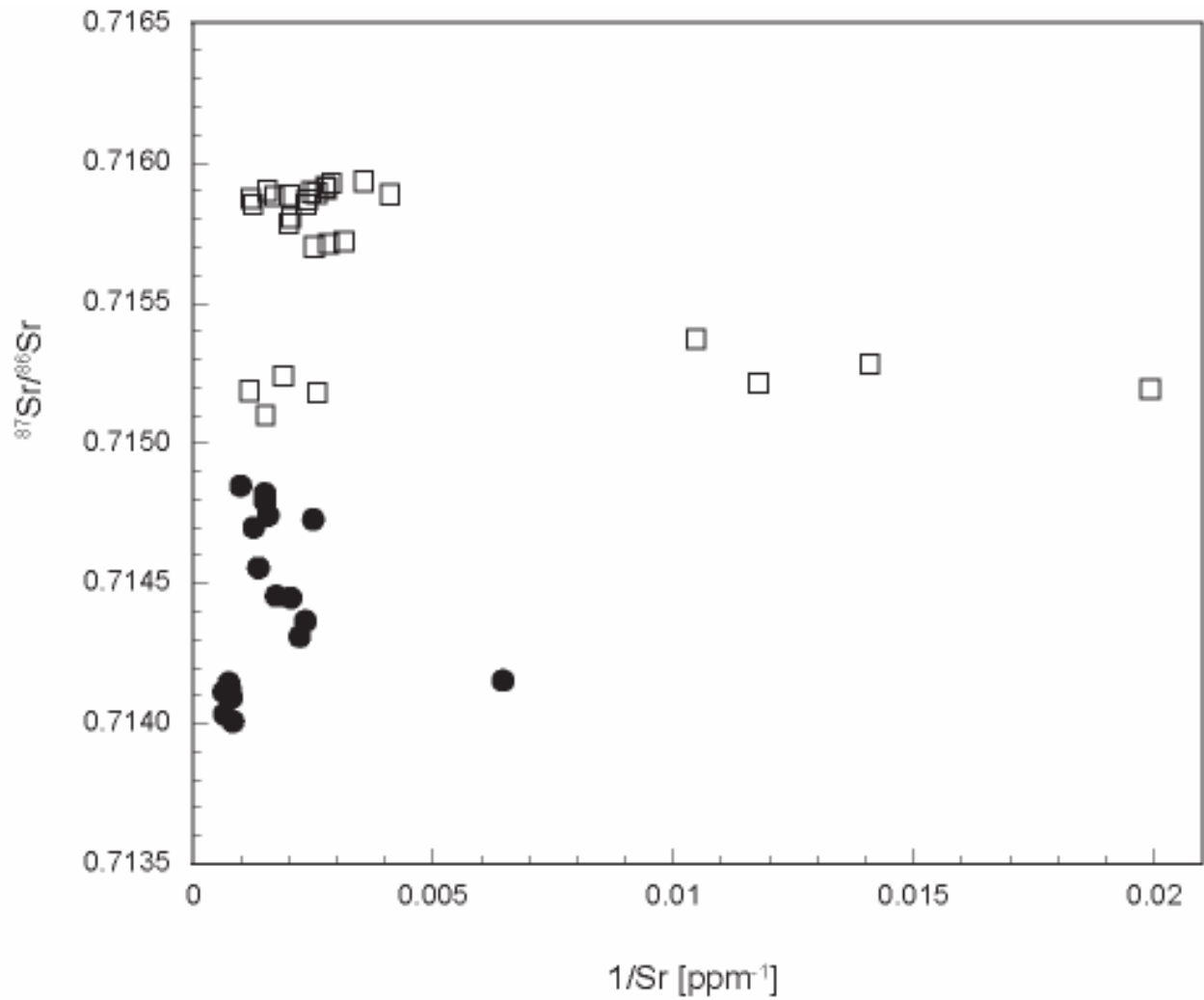


Figure 5.8 Plot of Sr isotope ratios vs inverse of Sr concentration in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine.

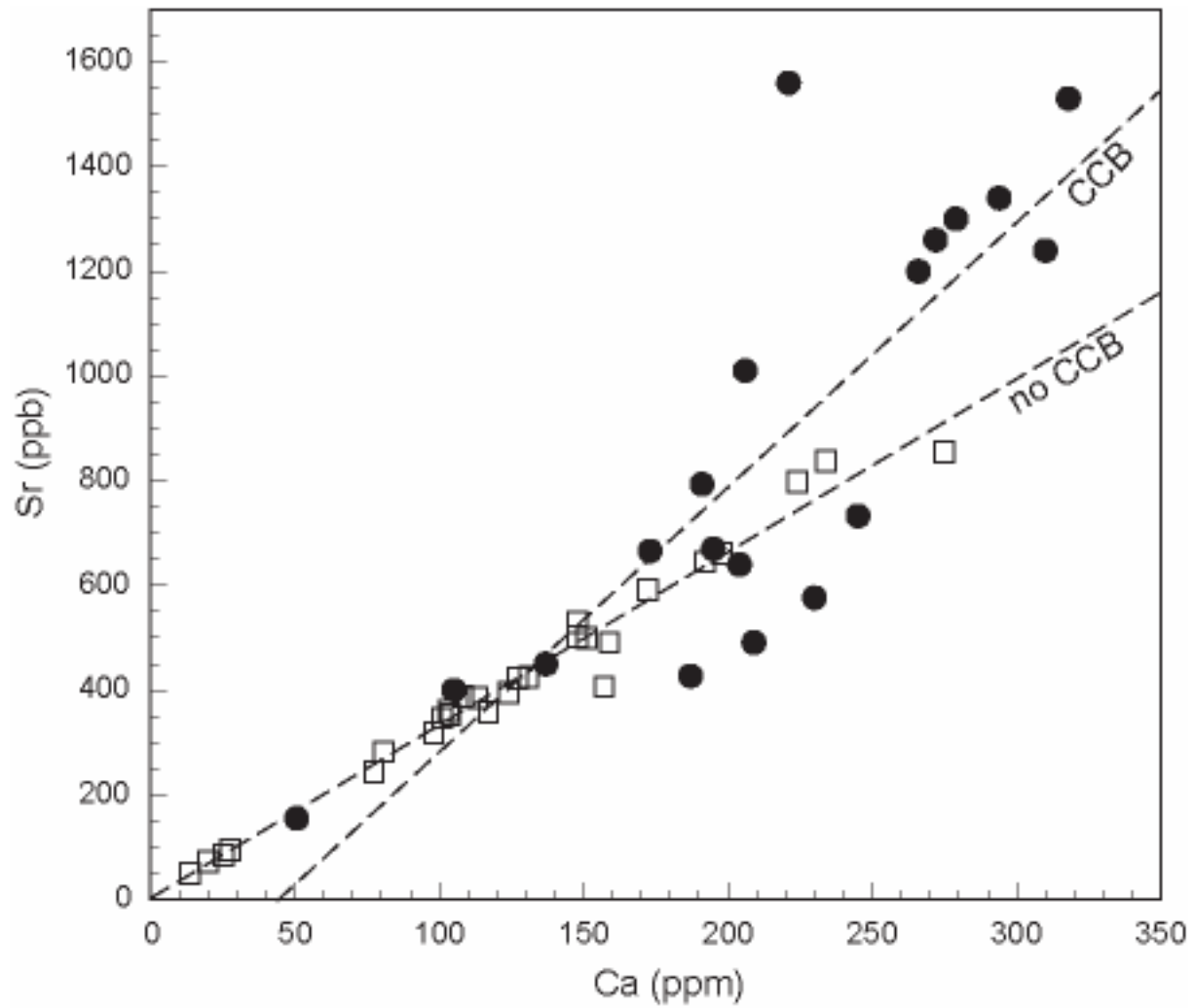


Figure 5.9 Plot of Sr vs Ca in Omega discharges. Filled circles represent waters that interacted with CCB grout, while open squares represent waters that bypassed the grouted portion of the mine. Dashed lines indicate best fit regressions for CCB vs non-CCB interacting waters.

5.3. *Chemistry of solid leachates*

All solid samples, including shale overburden, underclay, coal, and replicate samples of grout from on-site core borings OCB-3 and OCB-4, were batch leached in hydrochloric acid. The replicate leaches of grout in 1.0 N HCL yielded relatively constant leachate chemistry (Tables 5.4 and 5.5). Tables 5.6 and 5.7 give the major and trace element compositions of the digested solid materials for comparison. The total variation in major element concentrations for replicate leaches of each core grout sample was less than 15% of the average value for all elements except Na, which varied by nearly 50% in OCB-3 and was below detection in OCB-4. Total variation of major elements for leachates of both core grout samples combined, was less than 30% of the average value, again with the exception of Na. The dominant species were Ca and S, which were probably released by dissolution of Ca-sulfate and Ca-carbonate minerals in the CCB and cement materials. Silica and Al were also abundant in the leachates, reflecting partial dissolution of silicate CCB phases. Moderately high Fe levels were probably a result of dissolution of Fe-oxides, a by-product of burning FeS₂ (pyrite- and/or marcasite) bearing coal at high temperatures. Of the trace elements (Table 5.5), strontium, arsenic, chromium and zinc were the most abundant in the 1.0 N HCl leachates, yielding >2000 ppb in solution; Sr was present at the 15-25 ppm level which was comparable to Mn and Na. Most leachate trace element concentrations varied within the same ranges as the major elements.

Leachate concentrations from the shale, underclay and coal experiments yielded significantly different major and trace element concentrations than the grout. The concentrations were lower than those of the grout leachates and Fe was the dominant species.

In the 0.25 N HCl sequential leaching experiments, the total levels of elements leached were less than in the 1.0 N HCl experiments, but the relative proportions of most elements

Table 5.4 Major element concentrations in leachate from solid core samples OCB-3 and OCB-4, mg L⁻¹. GR represents grout material, S represents shale overburden, UC represents underclay, and C represents coal. Grout samples were leached in triplicate in 1.0 N HCl for 24 hours. In the 0.25 N HCl experiments, samples were extracted after 3 minutes, 15 minutes, 1 hour, 1 day, and 1 week.

1.0 N HCl Leaches	Al	Ca	Fe	K	Mg	Mn	Na	S	Si
OCB-3-GR1-L	1930	8200	680	264	287	11.6	26.1	2080	1940
OCB-3-GR2-L	1870	8810	693	268	277	12.4	29.0	2140	2070
OCB-3-GR3-L	1810	10100	789	219	262	13.8	11.5	2010	2100
OCB-4-GR1-L	1080	10800	1160	140	200	11.1	<0.03	2010	1200
OCB-4-GR2-L	1390	13000	954	161	230	15.2	<0.03	1940	1710
OCB-4-GR3-L	1270	13900	1050	146	239	14.2	<0.03	1700	1520
OCB-4-S-L	278	31.1	502	83.9	96.3	2.30	<0.03	33.6	119
OCB-4-UC-L	177	44.6	360	56.0	43.9	2.19	<0.03	202	73.2
OCB-4-C-L	72.3	32.3	1010	6.48	1.88	0.488	<0.03	914	5.57
0.25 N HCL Leaches									
OCB-3-GR2-3M	749	3680	194	135	117	4.68	21.8	891	1050
OCB-3-GR2-15M	753	3680	198	127	117	4.78	21.2	886	1050
OCB-3-GR2-1H	800	3760	203	134	125	5.01	23.1	926	1100
OCB-3-GR2-1D	959	3900	193	149	140	5.67	27.7	873	1220
OCB-3-GR2-1W	994	3710	171	152	142	5.75	29.6	736	1160

Table 5.5 Trace element concentrations in leachate from solid core samples OCB-3 and OCB-4, $\mu\text{g L}^{-1}$. GR represents grout material, S represents shale overburden, UC represents underclay, and C represents coal. Grout samples were leached in triplicate in 1.0 N HCl for 24 hours. In the 0.25 N HCl experiments, samples were extracted after 3 minutes, 15 minutes, 1 hour, 1 day, and 1 week.

1.0 N HCl Leaches	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	Zn	Sr	Nd
OCB-3-GR1-L	3910	631	145	48.3	636	2820	1880	1120	832	<75	<90	3930	25100	603
OCB-3-GR2-L	4610	719	156	47.8	690	2610	1940	1180	917	<75	<90	4630	25100	450
OCB-3-GR3-L	4960	801	160	50.8	793	3030	1670	1320	1100	<75	<90	4800	24500	453
OCB-4-GR1-L	3840	913	97.7	25.5	737	1990	1240	1350	700	<75	<90	3610	15900	379
OCB-4-GR2-L	5470	1050	138	56.7	823	2660	1280	1470	1040	<75	<90	4370	19300	415
OCB-4-GR3-L	5410	1160	127	58.4	832	2480	1190	1470	968	<75	<90	4210	18100	400
OCB-4-S-L	65	1370	80.9	10.5	444	425	61.7	445	567	<6	<7.5	5600	320	47.2
OCB-4-UC-L	1360	1840	38.8	13	989	346	2130	1710	1840	<6	<7.5	1790	362	270
OCB-4-C-L	3740	170	45.7	18.4	907	<1	143	975	417	<6	<7.5	5850	591	678
0.25 N HCl Leaches														
OCB-3-GR2-3M	1630	302	62.4	36.9	232	976	798	372	769	<42	<55	1910	10400	171
OCB-3-GR2-15M	1450	324	63.3	41.5	240	971	789	383	1030	<42	<55	2150	10400	180
OCB-3-GR2-1H	1290	309	67.8	41.5	240	1010	844	404	1030	<42	<55	2170	11000	195
OCB-3-GR2-1D	117	379	79.8	42.4	273	1090	975	467	909	<42	<55	2250	12900	254
OCB-3-GR2-1W	<55	364	81.1	43.7	281	1100	1030	487	931	<42	<55	2500	13700	243

Table 5.6 Major element concentrations in digested solid core samples from core samples OCB-3 and OCB-4, $\mu\text{g g}^{-1}$. GR represents grout material, S represents shale overburden, UC represents underclay, and C represents coal.

Core Sample	Al	Ca	Fe	K	Mg	Mn	Na	S	Si
OCB-3-GR1	54800	72000	50300	12100	2880	258	2580	33900	172000
OCB-3-GR2	60800	60300	49600	11800	2630	283	2580	31700	170000
OCB-3-GR3	49800	73400	51600	11500	2670	293	2600	32200	170000
OCB-4-GR1	79300	61200	37100	14200	3750	183	1880	33100	176000
OCB-4-GR2	59000	68700	39100	12800	3040	222	2250	32800	175000
OCB-4-GR3	68900	61500	39800	14100	4010	225	2000	41600	168000
OCB-4-S	45300	334	20200	20700	2210	103	644	15700	265000
OCB-4-UC	45700	338	20500	20900	2650	76.1	1010	21000	214000
OCB-4-C	24200	664	89200	573	182	17.9	7.2	209000	44100

Table 5.7 Trace element concentrations in digested solid core samples from core samples OCB-3 and OCB-4, $\mu\text{g g}^{-1}$. GR represents grout material, S represents shale overburden, UC represents underclay, and C represents coal.

Core Sample	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	Zn	Sr	Nd
OCB-3-GR1	41.6	482	3.11	5.9	28.3	112	58.3	50.6	16.6	<2	<2	102	515	7.7
OCB-3-GR2	49.5	413	3.27	5.8	28.8	107	59.7	50.2	17	<2	<2	110	487	25.8
OCB-3-GR3	51.6	466	3.37	6.1	29.7	111	60.1	51	16.9	<2	<2	112	537	5.4
OCB-4-GR1	35.1	368	1.83	5.4	22.9	100	53.5	40.4	13.8	<2	<2	83.3	340	12.5
OCB-4-GR2	49.1	383	2.55	5.2	24.6	101	53	43.8	14.1	<2	<2	91.6	419	12.1
OCB-4-GR3	48.3	348	2.2	5.3	23.7	93.8	49.6	42.1	12.6	<2	<2	86.3	383	24.7
OCB-4-S	<2	354	1.55	3.6	10.8	40.2	10.1	12	2.44	<2	<2	95.6	69.2	3.7
OCB-4-UC	27.1	464	1.53	3.6	23.8	97.5	44.9	37.7	19.9	<2	<2	71	121	5
OCB-4-C	242	14.7	5.64	6.2	26.0	30.6	18.9	29.9	3.3	<2	<2	99.8	21.4	14.3

remained consistent. In most cases, element concentrations increased with time, from the first sampling at three minutes to the final sampling after one week. The most significant exceptions were Fe and S, which may have been affected by modest precipitation of FeS₂. Overall, it appears that most of the dissolution took place within the first three minutes of the experiment, as subsequent increases in element concentrations were small. The trace elements behaved similarly to the major elements in this study with the striking exception of As. Arsenic decreased significantly and systematically, from the first sampling at >1600 ppb, to below detection limit (55 ppb) by the end of the week.

Leaching of the CCB grout in 1.0 N HCl yielded a very small range in ⁸⁷Sr/⁸⁶Sr ratios, from 0.71144 to 0.71154 (Table 5.8). The isotopic ratio was slightly lower, but still highly invariant (0.71137-0.71144) when the grout was leached with 0.25 N HCl. In contrast both the shale overburden and the underclay yielded leachates with very high ⁸⁷Sr/⁸⁶Sr ratios (0.7472 and 0.7337 respectively). Leaching of coal from the Omega Mine resulted in waters with ⁸⁷Sr/⁸⁶Sr ratios very near those of the CCB grout (0.71157). This is not surprising, as the grout contains ash from coal-burning energy plants in the area. These data are consistent with the findings from the Omega Mine AMD in which waters that interacted with CCB grout yielded lower ⁸⁷Sr/⁸⁶Sr ratios than those that bypassed the grouted portion of the mine.

Table 5.8 Strontium concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio values of leachate samples, strontium concentration in digested solid samples, and percentage of strontium extracted during leaching experiments. GR represents grout material, S represents shale overburden, UC represents underclay, and C represents coal.

1.0 N HCl Leaches	Leachate [Sr] ($\mu\text{g L}^{-1}$)	Leachate $^{87}\text{Sr}/^{86}\text{Sr}$	Solid [Sr] ($\mu\text{g g}^{-1}$)	% Sr Extracted
OCB3-GR1-L	25100	0.711454±11	515	48.7
OCB3-GR2-L	25100	0.711494±09	487	51.5
OCB3-GR3-L	24500	0.711470±09	537	45.6
OCB4-GR1-L	15900	0.711535±08	340	46.8
OCB4-GR2-L	19300	0.711513±09	419	46.1
OCB4-GR3-L	18100	0.711435±09	383	47.3
OCB-4-S-L	320	0.747178±10	69.2	4.6
OCB-4-UC-L	362	0.733662±10	121	3.0
OCB-4-C-L	591	0.711574±11	21.4	27.6
0.25 N HCl Leaches				
OCB-3-GR2-3M	10400	0.711397±11	487	21.4
OCB-3-GR2-15M	10400	0.711367±11	487	21.4
OCB-3-GR2-1H	11000	0.711393±09	487	22.6
OCB-3-GR2-1D	12900	0.711442±11	487	26.5
OCB-3-GR2-1W	13700	0.711388±11	487	28.2

6. DISCUSSION AND CONCLUSIONS

6.1. *Geochemical tracing of water-grout interaction using major and trace elements*

As discussed in the previous section, none of the major or trace elements was capable of clearly and unequivocally differentiating between waters that interacted with the CCB grout and those that bypassed the grouted portions of the Omega Mine. The best candidates were combinations of K, S, Al, and As, but all of these showed overlap between grouted and non-grouted discharges.

The AMD discharges draining grouted portions of the mine tended to have elevated concentrations of most elements, which suggests that significant leaching of CCB grout material could have been taking place. One reason for the overlap in chemistry could be that the CCB is derived from burning coal that is very similar to the coal remaining within the mine void (with the exception that it is more highly concentrated in mineral matter).

The geochemistry of leachates from the grout and surrounding rock units does not lead to accurate predictions about the expected major element composition of waters interacting with CCB grout and those that do not. For example, it might be expected that the normal mine discharge waters would pick up their chemical composition from interacting with a combination of the remaining coal, shale overburden, and underclay. However, for most elements, the mine waters do not fall within the field defined by the HCl leachates of these endmembers. In addition, the grout-interacting waters do not always reflect a composition that would be predicted by the HCl leachates of the CCB grout. There are consistencies between the grout leachates and the grout-interacting waters, such as high As levels (although As is also elevated in the coal leachate), but the geochemistry alone would not be sufficient to differentiate between grout-interacting and non-interacting waters.

A comparison of data from this study with historical data collected by DOE employees between 1991 and 1999 shows that the chemistry of the punch mine and seeps sampling locations remains almost unchanged. The new East Side location cannot be compared, because it has no early counterpart.

The grout in the northern lobe is affecting the discharge from the Marshall House location. Ca, Mg, Na, SO_4^{2-} , and Al are all elevated above their concentration levels prior to completion of the grouting project. In addition, the flow rate from the Marshall House location is higher, and has been increasing steadily, since the grouting operation was completed (D. Shreve, personal communication, 2003). Grout material is migrating out of the northern lobe causing frequent blockages in the collection pipeline which seems to indicate that the grout is breaking down, a fact that is also reflected in the water chemistry.

6.2. *Geochemical tracing of water-grout interaction using strontium isotope ratios*

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters that interact with CCB grout are clearly differentiated from those of waters that bypass the grout (as noted in Section 5.2). The degree to which the waters interact with different rock units can be estimated using a simple mixing model in which the fraction of Sr contributed to the groundwater from the two sources (source A and source B) can be calculated as:

$$F_A = \frac{(^{87}\text{Sr}/^{86}\text{Sr}_W - ^{87}\text{Sr}/^{86}\text{Sr}_B)}{(^{87}\text{Sr}/^{86}\text{Sr}_A - ^{87}\text{Sr}/^{86}\text{Sr}_B)} \quad (6.1)$$

where F_A is the fraction of Sr derived from source A and $^{87}\text{Sr}/^{86}\text{Sr}_W$ is the measured ratio of the groundwater. In the case of the Omega Mine discharges, the waters that do not interact with the CCB grout can be considered to be one endmember (~ 0.7157), and the grout leachates can be considered to be the other endmember (~ 0.7115). This allows the calculation of how much

strontium is derived from the CCB grout as these waters move through the mine void. For the Seeps East Side discharge (0.7144), I calculated that ~31% of the Sr is derived from leaching of the CCB grout and for the Marshall House discharge (0.7141), ~38% of the Sr would be from the grout.

Here it is noted that the waters that do not interact with the CCB grout are much closer in isotopic composition to the Omega Mine coal leachate than to the shale overburden or underclay. This suggests that coal remaining in the mine (either in pillars or as rubble on the floor of the mine void) exerts a strong influence on the chemistry of the mine discharge.

The above calculations can also be used to make rough estimates of the rate at which the grout is being chemically eroded by groundwater flowing through the mine. If I assume an average Sr concentration in the CCB grout solid of ~450 ppm (Table 5.7), and that the Marshall House and Seeps East Side discharges tap most of the water that interacts with the grout, I can use the Sr fluxes and calculated % Sr from grout for these discharges as follows:

$$E_{grout} = (J_{Sr})(F_{grout})/[Sr]_{grout} \quad (6.2)$$

where E_{grout} is the chemical erosion rate of the grout, J_{Sr} is the average Sr flux from the grout-interacting sites (Seeps East Side + Marshall House, Table 5.3; $\sim 1300 \mu\text{g s}^{-1}$), F_{grout} is the fraction of Sr derived from grout, as calculated from Equation 6.1 (assume ~ 0.35), and $[Sr]_{grout}$ is the Sr concentration in the grout solid (Table 5.7; $\sim 450 \text{ mg kg}^{-1}$). Using these parameters and the appropriate unit conversions, Equation 6.2 suggests that the CCB grout is being chemically removed at a rate of about $3 \times 10^4 \text{ kg yr}^{-1}$. This calculation is, of course, very approximate as it is dependent on assumed endmember isotope ratios and assumed congruent dissolution of the CCB grout (which is clearly not the case). However, it does provide a rough estimate of the rate of grout removal, which is difficult to achieve by any other measure.

To take these calculations one step further, the average density of the OCB-3 and OCB-4 grout core borings taken about one year after completion of the grouting operation was 1308 kg per cubic meter. Since ~60,500 cubic meters of grout were injected into the mine, it is loosely possible to project that all grout would be chemically and/or physically removed from the mine void in 3×10^3 years.

6.3. *Conclusions*

In this study, major and trace element geochemistry and strontium (Sr) isotope ratios were applied to evaluate the interaction of mine drainage waters with coal combustion byproducts (CCB) used to grout the inactive Omega Coal Mine in West Virginia. The goals of the study were to evaluate the effectiveness of Sr isotope ratios in identifying and quantifying water-CCB interaction and to determine the extent to which CCB grout can affect discharge water chemistry. The goals of this study were largely met. Based on the work presented here, my major findings are as follows:

- The major and trace element geochemistry of the discharge waters from the Omega Coal Mine suggests that interaction is occurring between the water and the CCB grout. This is indicated by elevated concentrations of certain elements in waters draining the grouted portion of the mine. Arsenic, in particular, was elevated significantly in waters discharging from the grouted section. This could become a concern in some situations. In addition, the geochemistry indicates that the coal remaining in the mine void is exerting a strong influence on the discharging waters that have no interaction with the grout.
- While certain elements such as As, K, and S appear to be elevated due to interaction with the CCB grout, no major or trace elements could be used to unequivocally differentiate between grout-interacting waters and those bypassing the grouted portions of the mine void.
- Strontium isotope ratios measured in any given Omega mine discharge were strikingly invariant, regardless of the time of year the sample was collected. This suggests that

overall flow patterns within the Omega Mine void do not change significantly throughout the year, despite variation in precipitation and discharge flow rate.

- Strontium isotope ratios clearly differentiated between waters that were in contact with the CCB grout ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7140\text{-}0.7146$) and those that were not ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7151\text{-}0.7159$). The direction of the shift in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters with CCB interaction is consistent with leaching experiments on CCB grout, shale overburden, and underclay solids. It is therefore proposed, that strontium isotope ratios can be a very effective tool in identifying water-CCB interaction when CCB is used in environmental remediation.
- The strontium isotope ratios and concentration data can be used to determine the approximate rate of chemical denudation of the CCB grout material in the Omega Mine. Based on the results of this study, approximately 3×10^4 kg of CCB grout are being dissolved and removed annually by throughflowing waters; this is in addition to the grout that has been observed to be physically discharging from certain sites. Quantification using Sr isotope ratios provides an estimated guidance for future use of coal combustion byproducts in environmental remediation projects.

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