THE IMPACT OF SCRUBBER SLUDGE ON GROUND WATER QUALITY AT AN ABANDONED MINE SITE

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Abstract. A sulfate-rich flue gas desulfurization scrubber sludge was used as a substitute backfill material in reclamation of an abandoned coal strip mine. The site was surrounded by monitor wells and the material was characterized for leaching behavior using open column experiments. A drain was placed directly beneath the 45 000 ton fill to enable sampling before dilution or attenuation. The column studies indicated that the scrubber sludge would adsorb manganese, iron, aluminium, cobalt, nickel, thallium and zinc contaminants from the water. Changes in pH appear inadequate to explain the removal by precipitation. The groundwater cleaning phenomenon has been confirmed on a field scale by the drain samples. Boron and molybdenum leach from the fly ash was used to fix the scrubber sludge and serve as marker elements enabling calibration of the dispersivity in computer models of the groundwater system at the site. The leachate front appears to be diluted by a factor of 8 : 1 within the first 15 meters. Since boron and molybdenum release are associated only with the first flush, environmental impacts will be minimal. Columns appear to create a time compression effect on the duration of leaching phenomenon. The effect for this site appears to be at least 5 : 1. The columns were effective in predicting which elements would leach or adsorb in the field and in predicting the actual source concentrations. Other shake tests such as the TCLP and the ASTM shake test were found to be less effective at predicting which elements would leach and were not helpful in predicting field concentrations.

Key words: Clean Air Act Amendments, coal combustion residues, ground water quality, mine reclamation, monitor wells, open column leaching, scrubber sludge

1. Introduction

Combustion of fossil fuels to generate electricity produces large volumes of solid wastes, known as coal combustion residues. While utilizing and/or disposing of coal combustion residues has always been a concern for electric utilities, this issue has additional significance in light of 1990 Federal Clean Air Act Amendments (CAAA), which will impact significantly the utilization of high sulfur coals. This is because clean coal technologies, e.g., flue gas desulfurization (FGD) and fluidized bed combustion (FBC), not only reduce atmospheric sulfur and nitrogen oxides emissions, but also generate residues in an amount equal to 20–30% of the coal combusted. The increased amount of residues may be utilized and/or disposed of in a manner that is economically and environmentally sound.

In 1993, about 88 million tons of CCRS (fly ash, bottom ash, boiler slag, FGD and FBC residues) were generated in the United States (American Coal Ash Association, 1994). Overall only 22% of these solid residues were used for beneficial

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purposes. The remainder accumulates in on site piles and ponds, or carried away to landfills for disposal and thus raising fears of groundwater contamination due to leaching of trace elements. A widespread concern about the groundwater preservation exists in the United States and there are regulatory guidelines for its preservation under various classes based on utility, source and vulnerability of groundwater to contamination (Alderdice and Petrie, 1994). Further disposal of these residues requires considerable land and extensive safety measures coupled with enormous costs. Therefore, development of low-cost high-volume utilization and disposal technologies, particularly for FGD residues, is highly emphasized, since their current utilization is only about 6% (American Coal Ash Association,1994). As an effort to develop low-technology high-volume utilization of CCRS, the Mining Engineering Department of Southern Illinois University at Carbondale, in cooperation with state and national agencies, is carrying out large-scale field demonstration of utilization and disposal of CCRs in mine reclamation.

Results obtained so far are quite encouraging and reflect that these residues can be utilized in an environmentally acceptable way without causing any significant impact on groundwater quality (Paul *et al.*, 1993, 1994, 1995). In a project sponsored by the U.S. Department of Energy, on the basis of environmental (chemical and leachate) properties, FGD residues have been blind injected into abandoned and sealed workings of the Peabody #10 underground mine near Pawnee, Illinois, in order to demonstrate control of surface subsidence (Paul *et al.*, 1995). This study highlights the high-volume utilization of the residues (FGD scrubber sludge) in an abandoned final cut pit from a strip mine in an environmentally acceptable manner.

2. Description of the Study Area

The Forsythe Energy #5 is a pre-law abandoned final cut pit from a strip mine located about one mile of the Williamson County Regional Airport near Herrin, Illinois. The pit is less than 40 feet from the Energy-Crenshaw road that runs parallel to it. There is a danger of damage to the road due to the collapse of the steep highwall at the edge of the pit. Any motorist loosing control near the pit may fall into it. The pit is near the airport runway, and a plane making an emergency landing may also fall into it. So it was important to reclaim the pit for a desirable topography. Thus the Mining Engineering Department at Southern Illinois University, Illinois Abandoned Mined Land Reclamation Council (IAMLRC) and National Mined Land Reclamation Council (NMLRC) are involved in this large-scale field demonstration to show that coal combustion residues can be disposed and utilized in an environmentally acceptable way in reclamation of abandoned mines. There was hardly any fill material available in close proximity to the pit at the mine site. More than 45 000 tons of scrubber sludge was used in two phases as substitute fill material, after more than a year of engineering and environmental characterization and site monitoring. Use of scrubber sludge as backfill material for reclamation of the pit provided benefits such as easy availability and cheaper transport because empty coal carriers returning from the power plant can 'back haul' it to the mine site. From the standpoint of the power plant, this is essentially a waste material which requires large costs of handling, a disposal to comply with environmental regulations. From the environmental point, this waste material will go back to the same place where it was mined and use of this material serves an extra benefit to power plants. Further, this may also be used as a neutralizing agent and liner by virtue of its alkalinity/buffering action and low permeability.

3. Description of Monitoring Wells

The monitoring wells at the mine site were installed by the Illinois State Environmental Protection Agency according to the guidelines and specifications of the U.S Environmental Protection Agency (USEPA, 1986). Wells were sampled by purging and bailing according to U.S. EPA protocols. Samples were analyzed in the field for pH and were then filtered, acidified and refrigerated pending analysis. Raw mine water as collected from the upgradient monitoring well was used as the leaching media for open columns and SLP experiments.

Preparatory to placement of the first 25 000 tons of fill, a 15 m long drain was dug in the bottom of the abandoned strip pit. The pit was filled with high quality sand and a slotted pipe was laid in the sand and connected to a vertical casing that was capped as a conventional monitoring well. Fill was then placed over the top of the drain. The scrubber sludge was brought to the site by dump truck, placed along the edge of highwall, and then dozed into place with a low ground bearing pressure dozer. Soil and GOB were not mixed with the fill material. This virtually created a column containing 25 000 tons of scrubber sludge covering just under a hectare in surface area and having a thickness of about 12 m. The drain allows collection of leachate from the fill before any significant dilution or attenuation of the leachate can occur in the field. The drain was sampled at regular intervals, using the same procedures as conventional well sampling.

4. Leaching Study

A Standard Open Column leaching test was conducted on the scrubber sludge sample to ascertain its leachate properties as briefly described below.

4.1. OPEN PERCOLATION COLUMN TEST

In this test, deionized water is percolated through a packed column in the presence of oxygen at a rate which depends on the natural permeability of the material. The open columns for leaching tests were made from PVC pipe 4 inches in diameter and 2 feet in length. The top end of the column was exposed to the atmosphere and the bottom end was connected to quarter-inch tygon tubing. The leachate was collected through this tubing into 250 ml polypropylene beakers. The columns, packed with scrubber sludge in 2 inches lifts to optimum moisture density as determined in the standard Proctor Test (ASTM D 698-78), were packed to within 4 inches of the tops, which were left empty to allow water to be ponded over the column. In addition, the columns were open to the air so that oxygen was present and flow was unsaturated. Every two days, up to 200 ml of mine water was added to the columns, leachates were collected below and a fresh beaker was placed to collect leachate for the following 2 days. Finally, the leachates obtained were vacuum filtered. This test was run for longest period of time, allowing the first flush of easily leached ions to be removed and permitting equilibrium with late, forming mineral phases to be reflected.

4.2. LEACHATE ANALYSIS

The leachates obtained from the field as well from the column experiments were potentiometrically analyzed for pH, conductivity (Fisher digital pH & conductivity meters), free chloride and fluoride ions (Orion Ion Analyzers) as per standard procedures (Greenberg *et al.*, 1992).

4.3. ELEMENTAL ANALYSIS OF LEACHATES

After the potentiometric determination leachate samples were filtered and acidified with 2 ml of nitric acid and then preserved in polypropylene sampling bottles. The samples were kept in a refrigerator until further analysis. Sodium and potassium were determined using flame photometry with a Perkin Elmer 603 AAS. Mercury was analyzed using cold vapor technique which utilizes a hydride system, with a Perkin Elmer AAS in conjunction with MH-10 Analyzer Assembly. The reaction unit has a container to hold the reductant (borohydride) solution and a flange to hook up the reaction flask. This method follows the standard AAS procedure. Lead was analyzed using graphite furnace AAS.

4.4. LEACHATE ANALYSIS BY ICP

Leachates from various leaching tests were analyzed for 21 elements using an inductively coupled plasma emission spectrometer (ICP) with a Perkin Elmer ICP 6500, supported with a Perkin Elmer 7300 professional computer. The ICP was subjected to the following operating procedures and QA/QC measures. The sample injection system was checked and adjusted for optimum operating conditions at the beginning of each operating period. Pump tubing was inspected and replaced when necessary. Instrument peaking routines were performed to optimize the torch placement and to align the optics. Standardization was performed using a three point calibration curve. Standards consisting of one blank and two solutions containing different concentrations of each element were analyzed. Standardization was done

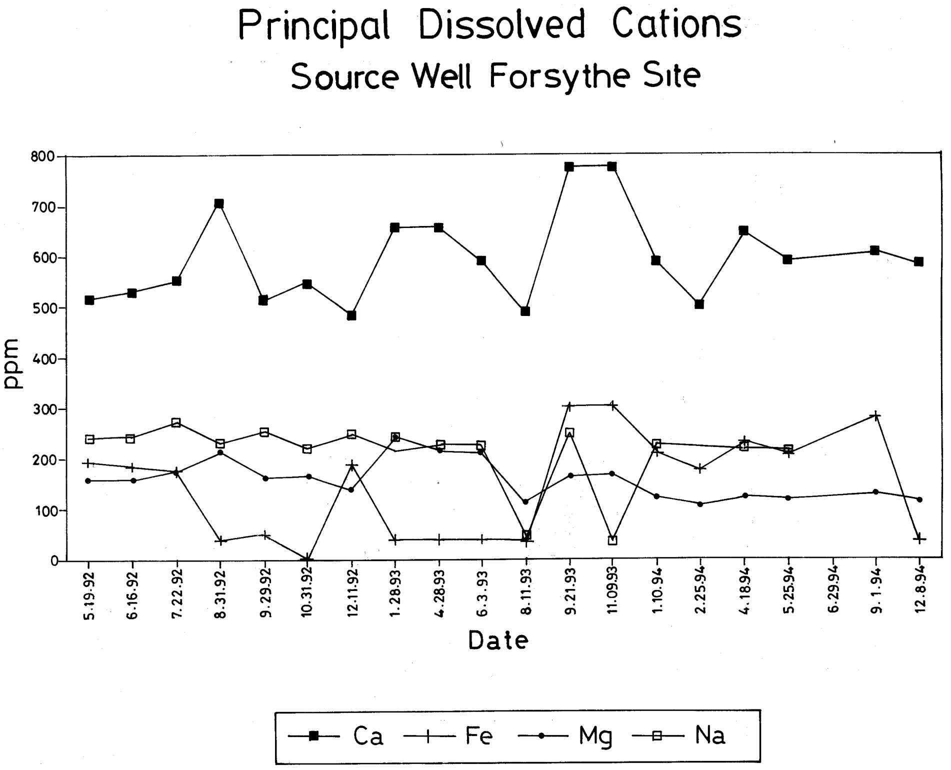

Figure 1. Water quality of upgradient source well with respect to principal dissolved cations.

with the aspiration of the highest concentration standard solution and completed with the lowest concentration standard followed by deionized distilled water. The low and high standard solutions served as check standards and were analyzed every ten samples and used to update the standardization. The recalibration of the ICP was also done every 25 samples.

Special precaution was taken to avoid the memory effect of boron from the previous samples. When a high boron reading is encountered, the system is purged for 3–5 minutes and then a blank is run to ensure that boron levels have returned to baseline. To further check the quality of analysis, a number of replicates generated from the leachate samples were analyzed and the analysis results were validated.

5. Results and Discussions

Water quality at the Forsythe Energy site is naturally poor. The hardness of the water, and the reddish brown color of the water from the high iron and manganese content, would limit the use of the water for drinking and domestic use. The quality of water in the upgradient source well is illustrated in Figures 1 to 3. In

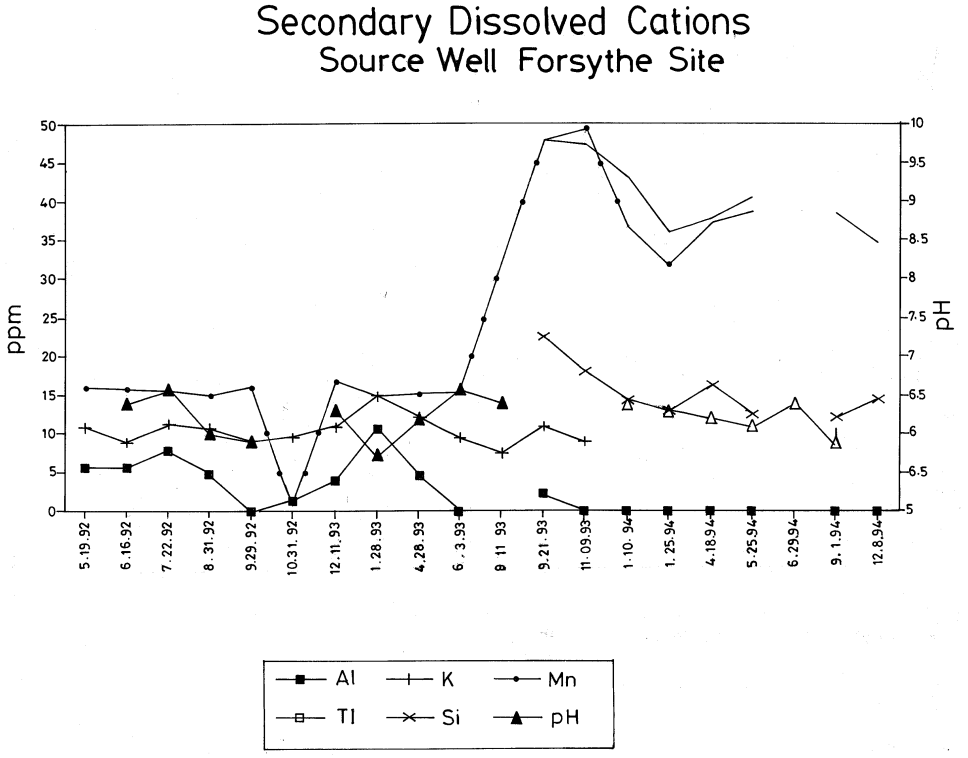

Figure 2. Water quality of upgradient source well with respect to secondary dissolved cations.

addition to the elements listed, the water was also tested for silver, arsenic, barium, beryllium, cadmium, chromium, copper, lead, antimony, selenium, and vanadium. These elements were found to be near the background levels for the instruments and laboratory procedures used, although arsenic, chromium, and lead were present in detectable concentrations.

The column studies were set up to determine if the scrubber sludge would contaminate and degrade the groundwater at the site. Instead, the column studies showed that the scrubber sludge would clean heavy and toxic metals from the groundwater. Figure 4 illustrates the effect for manganese. As can be seen, the manganese concentration in the source well varied seasonally and from year to year, but was generally around 15–35 ppm. The concentrations found in the column leachates were in the range of a few tens or hundreds of parts per billion and represented the almost complete removal of manganese from the system. The pH changes occurring as the water passed through the column were generally inadequate to have eliminated manganese by precipitation. The natural pH of the groundwater at the site was in the range of 6–6.5. Column leachate pH varied over time but averaged around 7.5. At times the column pH dipped to levels close to 5, with pH values lower than that of the source water. Despite this acidification,

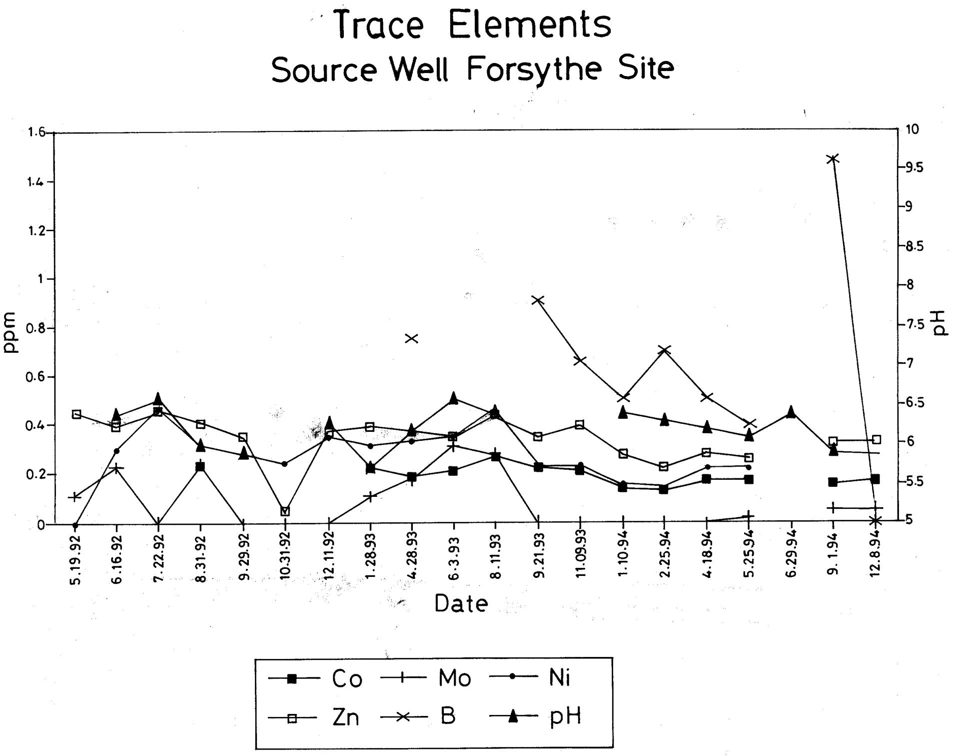

Figure 3. Water quality of upgradient source well with respect to trace elements.

manganese was still removed with the same effectiveness as was the case on the few occasions when the pH reached 9. It is widely regarded that manganese precipitation requires a pH above 9. These findings strongly suggest that an adsorption or ion exchange process was taking place. The drop in iron values from around 200 ppm in the source water to less than 5 ppm in the leachate is even more dramatic, and, as with manganese removal, this is independent of whether the leachate is more acidic or more alkaline than the initial leaching medium. Removal of aluminium and thallium and about 50% reduction in silicon were also observed.

The use of fly ash as a sorbant for lead at highly contaminated industrial sites is generally known. In this study, however, scrubber sludge was found to selectively remove even low concentrations of heavy and toxic metals. Figure 5 compares source and column leachate concentrations for cobalt, nickel, and zinc. Even though the concentrations of these metals were low enough initially to comply with potable groundwater standards in Illinois, contact with scrubber sludge reduced these concentrations by an order of magnitude. Mining activities are often considered to cause low level disturbances in groundwater quality. Little can generally be offered by way of mitigating measures, since disturbances are usually too small to warrant

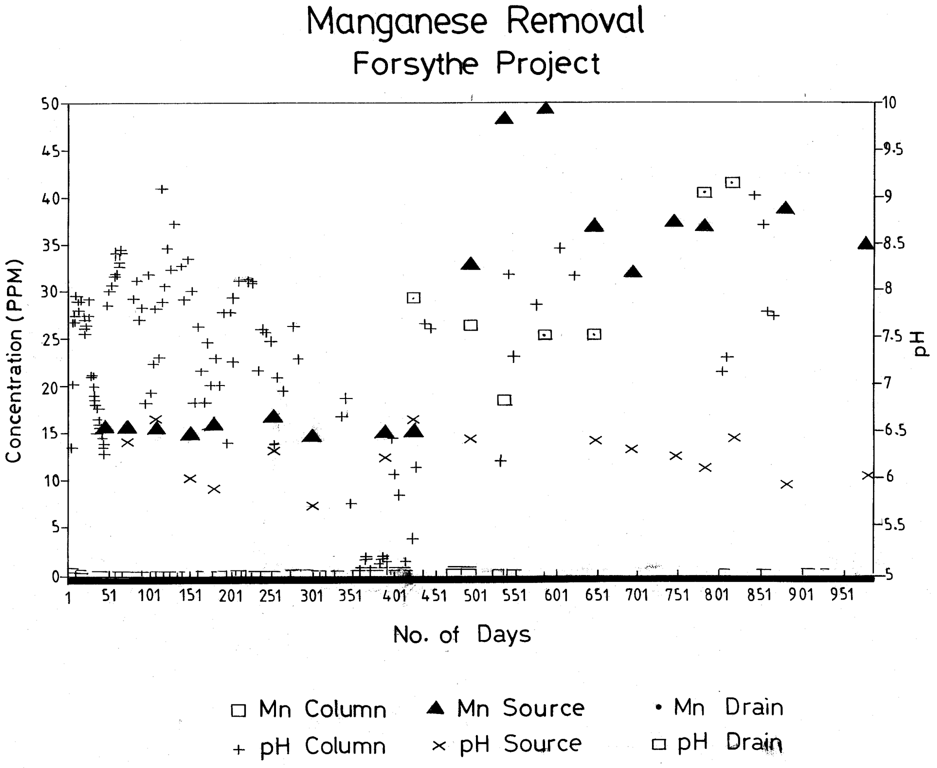

Figure 4. Manganese removal by scrubber sludge from ground water.

low level treatment. The use of scrubber sludge backfills may offer a groundwater remediation strategy not previously available.

A key question on the use of scrubber sludge as a ground water cleaning backfill might be whether the removal of heavy metals was due to some peculiarity in the column leaching procedure, such as the column being open to the atmosphere, or even a small scale effect that would be unrepeatable on the large scale. Figure 4 shows the manganese concentrations in the strip pit drain as well as the drain pH. The manganese concentrations in the drain are the same as those in the column leachates to within a few hundred parts per billion. As with the column study, the pH changes would be regarded as inadequate major precipitation of manganese. Iron, aluminium and thallium are also almost completely removed by contact with scrubber sludge in the field, and silicon concentrations fall by nearly 50%. Figure 5 does not show the cobalt, nickel, and zinc concentrations in the drain leachate in the field, since these values are below detection limits. Thus, the phenomenon of metals removal appears not to be a scale effect of the column experiment and is repeatable on a large field scale.

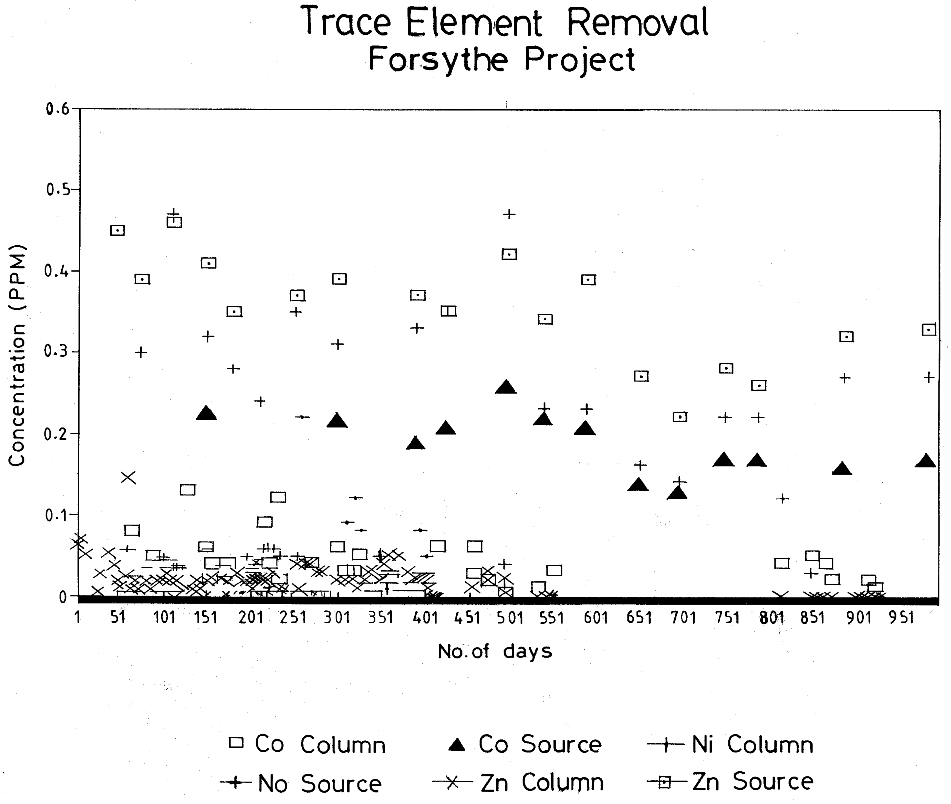

Figure 5. Trace elements removal by scrubber sludge from ground water.

Hafer *et al.* (1993) of the University of Kentucky have found nickel to be adsorbed onto the surface of fly ashes produced by the burning of Appalachian coals over the pH range used in this column study. Although the coal combustion residues tested as part of the Forsythe project resulted from the burning of Midwestern bituminous coal, this raises the question of whether removal of heavy metals by the scrubber sludge was due to the fly ash component, and not to the sludge itself. A total of 4 scrubber sludges were subjected to leaching in open column studies as part of the Forsythe project. The other 3 scrubber sludges were not fixed with fly ash and were pure except for trace amounts of fly ash that may have passed the electrostatic precipitators. All the scrubber sludges exhibited similar metals removal properties (Paul *et al.*, 1992, 1993) Thus it would appear that scrubber sludge is a heavy metals sorbant regardless of the presence of flyash.

The scrubber sludge delivered to the field site did contain significantly more fly ash than the grab sample used on initial laboratory testing. While the scrubber sludge grab sample was tan in color, flowed like a slimy clay, and was thixotrophic, the scrubber sludge delivered to the site was well fixed with fly ash (it would stick

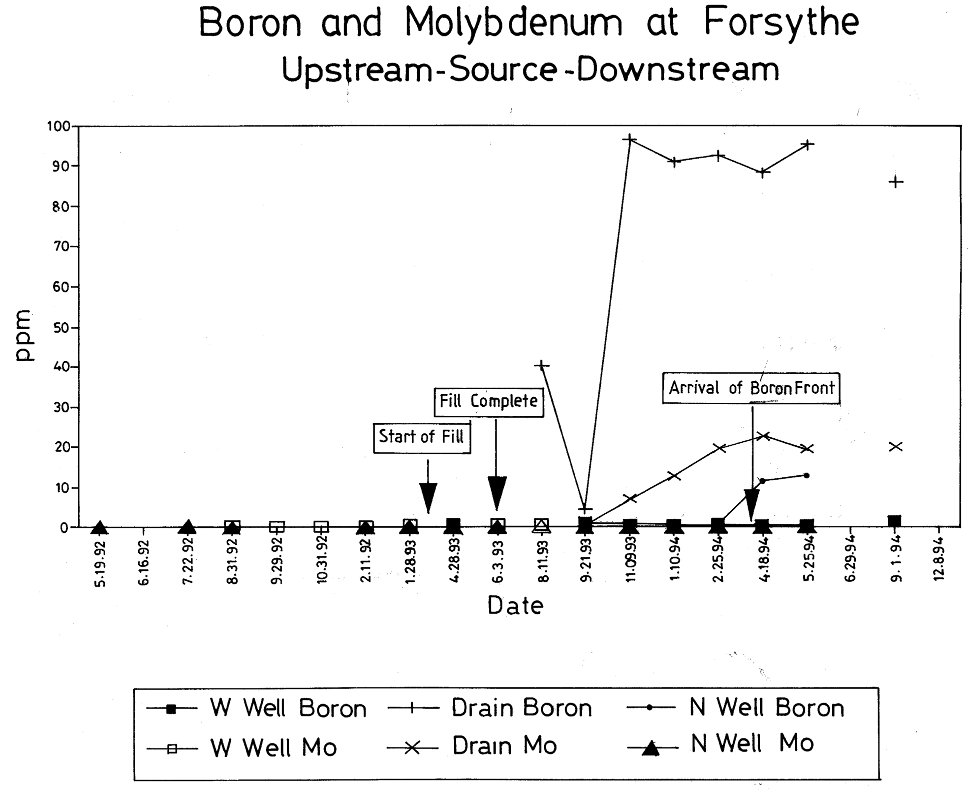

Figure 6. Boron and molybdenum concentrations at the upstream-source-downstream-monitoring wells.

to the truck beds otherwise), was dark brown in color, had a soil-like texture, and showed no tendency to flow or liquify. The extra fly ash in the sludge delivered to the site does appear to cause leaching of boron and molybdenum. The boron and molybdenum probably do come from the fly ash since of the six fly ashes tested in this program, including one from the same power plant as the sludges, all produced clear boron and molybdenum signatures in the first flush of leachates. Of the 3 scrubber sludges not fixed with fly ash, only one showed leaching of boron. The sorbant reagent (limestone) resulted from deposition in an ancient land-locked sea that would be expected to have had a high natural boron concentration in the water (Paul *et al.*, 1992, 1993).

The occurrence of boron and molybdenum in the leachate from the fill may prove useful. Since these elements are present only in low concentrations in the groundwater at the site, and since drain concentrations are three orders of magnitude higher than those occurring naturally, boron and molybdenum can be used as marker elements for calibration of the dispersivity in computer groundwater models that will allow prediction of any leachate plumes likely to develop at the site

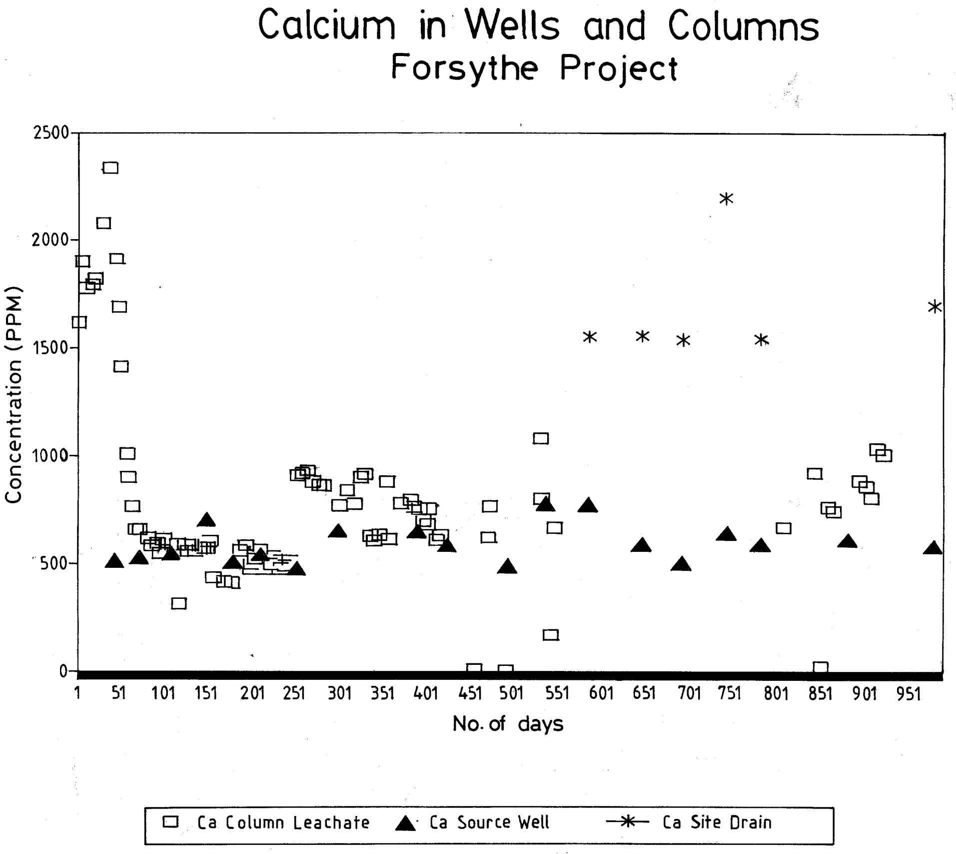

Figure 7. Calcium concentrations in monitoring wells and column experiments.

even hundreds of years into the future . Preliminary groundwater models of the site indicated that boron would be detected in the downgradient monitor wells approximately 12 months after placement and saturation of the fill (Paul and Esling, 1994). Figure 6 shows boron and molybdenum concentrations in the upgradient well, one of the down-gradient wells about 15 m from the edge of the fill, and in the drain under the fill. Placement of the fill began on April 6, 1993. Boron was detected in the down-gradient well on April 28, 1994. The average boron concentration in the drain is about 77 ppm, and the boron concentration in the leachate front is about 10 ppm, suggesting that dilution reduces concentrations by a factor of about 8 within the first 15 m.

While the boron and molybdenum leachate plumes may serve as a useful marker for research purposes, these elements are unlikely to be an environmental problem. Dilution is rapid and dramatic, and more importantly, column studies indicate that boron and molybdenum release is associated only with the first flush of leachate and then boron and molybdenum concentrations will fall to background levels within a relatively short length of time (Paul and Singh, 1995; Paul *et al.*, 1993). This, of course, means that groundwater models must not treat the fill as a steady state source of boron release into the environment. The limited duration of boron release will drastically limit its environmental impact compared to the effect of a steady state source.

The limited duration of the first flush raises the question of exactly how long the first flush will take in the field. Earlier work by Chowdhury (1993) considered columns ranging in size from 4.5 cm to almost half a meter in diameter. The data indicated that one apparent effect of laboratory columns was to create a time compression of events, with the first flush being shorter the smaller the column. Not surprisingly, calcium leaches from a fine-ground limestone based scrubber sludge rich in calcium sulfite. According to Figure 7, there is a burst of calcium that is easily released from the scrubber sludge over about the first 75 days. A burst of calcium is also seen to be released in the drain. The calcium burst has gone on for about 400 days so far. This suggests that the time compression in a 10.2 cm column is not less than 5 to 1. As monitoring continues, it is hoped that the time compression effect can be better quantified.

The last observation that can be made from the data at hand is the accuracy with which the column studies indicated not only which elements would leach or be absorbed, but the concentrations that would occur in the field. The concentration of calcium in the first flush shown in Figure 7 shows good quantitative agreement between the predictions of the column studies and the results seen in the field. The common effluent concentrations of the other elements discussed so far also show excellent quantitative agreement with those found on a field scale. This kind of agreement was not found either in determining which elements would leach, or their resulting concentrations when other shake tests such as the TCLP or ASTM procedures were performed (Paul *et al.*, 1994; Paul and Singh, 1995).

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References

Alderdice, L. and Petrie, L.: 1994, ‘Environmental Impacts of Coal Combustion Ash Utilisation: A Summary of Research Findings and Needs’, *Conference Proceedings Management of High Sulfur Coal Cumbustion Residues: Issues and Practices*, Springfield, Illinois.

American Coal Ash Association: 1994, '1993 Coal combustion Byproduct – Production and Use'.

Chowdhary, Ajit: 1992, A Study of the Characteristics of Column Leachates Generated from Coal Preparation Plan and FBC Boiler Residues, M.S. Thesis, Southern Illinois University at Carbondale (unpublished).

Greenberg, A. E., Clesceri, L. S. and Eaton, A. D.: 1992, 'Standard Methods For the Examination of Water and Wastewater', Baltimore, Maryland.

Hafer, A., Evangelou B. and Porting, E.: 1993, 'Influence of Carbon Oxide on the Release of Boron and Nickel from Fly Ash to Water and Remediation Technologies', IMMR Highlights, University of Kentucky, Vol. 12, No. 3, pp. 1–2.

Paul, B. C., Chaturvedula, S., Paudal H. and Chatterjee, S.: 1994, 'Use of Shake Tests as Predictors of Long Term Leaching of Coal Combustion Residues in Contact with Groundwater', *Proceedings Conference on Management of High Sulfur Coal Combustion Residues: Issues and Practices*, Springfield, Illinois, pp. 58–79.

Paul, B. C. and Esling, S.: 1994, 'Use of FGD By-products as a Substitute Fill Material in Reclamation: Preliminary Assessment of Groundwater Impacts', *Proceedings Conference on Management of High Sulfur Coal Combustion Residues: Issues and Practices*, Springfield, Illinois, pp. 167–181.

Paul, B. C., Esling, S., Pisani, S. and Krishnamurty, K.: 1992, 'Reclamation of Abandoned Strip Mines Using Coal Combustion Residues as Fill: Materials Characterisation for a Test at Energy #5, *Proceedings 14th Conference, National Association of Abandoned Mined Land Program*, Chicago.

Paul, B. C., Esling, S., Chaturvedula, S., Chatterjee, S., Paudal, H., Wireman, R. and Pisani, F.: 1993, 'Use of Coal Combustion By-products as Structural fill in Reclamation: Impacts on Ground Water', in: Y. P. Chugh and D. C. Davin (eds.), *Proceedings NMLRC Symposium*, Collinsville, IL, April, 20–22, 1993, pp. 201–217.

Paul, B. C. and Gurdeep Singh: 1995, 'Environmental Evaluation of Coal Combustion Residues for disposal and Utilization in Abandoned Mine sites', *Proceedings World Mining Environment Congress*, New Delhi, Dec 11–14, 1995, pp. 1015–1030.

Paul, B. C., Singh, G. and Chaturvedula, S.: 1995, 'Use of FGD By-products to Control Subsidence from Underground Mines: Ground Water Impacts', *Proceedings International Ash Utilization Symposium*, Lexington, Kentucky, October 23–25, 1995. (Accepted for publication in the FUEL.)

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response: 1986, 'Test Methods for Evaluating Solids Wastes', 3rd Edition.