# USING TRACERS TO UNDERSTAND THE HYDROLOGY OF AN ABANDONED UNDERGROUND COAL MINE[1]

by

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Abstract. Flooded underground mines pose a difficult problem for remediation efforts requiring hydrologic information. Mine environments are hydraulically complicated due to sinuous travel paths and variable hydraulic gradients. For an acidic mine remediation project, conducted by the University of Oklahoma in conjunction with the Oklahoma Conservation Commission, a tracer study was undertaken to identify basic hydrologic properties of a flooded coal mine. The study was conducted to investigate the possibility of *in-situ* remediation of acidic mine water with the use of alkaline coal combustion by-products. Information on the rate of flow and "connectiveness" of injection wells with the discharge point was needed to develop a treatment strategy. Fluorescent dyes are not typically used in mine tracer studies because of the low pH values associated with certain mines and a tendency to adsorb ferric iron precipitates. However, Rhodamine WT was used in one tracer test because it can be detected at low concentrations. Due to poor recovery, a second tracer test was undertaken using a more conservative tracer--chloride. Each tracer produced similar travel time results. Findings from this study suggest that Rhodamine WT can be used under slightly acidic conditions, with mixed results. The more conservative tracer provided somewhat better results, but recovery was still poor. Use of these tracers has provided some valuable information with regard to mine hydrology, but additional questions have been raised.

Additional Key Words: Fluorescent dyes, Rhodamine WT, chloride tracer

## Introduction

Remediation of abandoned coal mines requires a variety of information. Hydraulic characteristics of a flooded underground environment are particularly important if an effective *in-situ* remediation strategy is to be developed. Important characteristics include, *inter alia*, travel time, flow direction, diffusion gradient, and point-to-point flow paths. Unlike surface water bodies, difficulties arise because the mine "aquifer" cannot be accessed directly. Furthermore, the mine environment is heterogeneous, with tunnels, open and blocked, providing a large number of alternate flow paths. This dilemma was made evident in an abandoned mine remediation project conducted by the University of Oklahoma in conjunction with the Oklahoma Conservation Commission. Remediation efforts investigated the feasibility of introducing an alkaline coal combustion by-product (CCB) into an abandoned coal mine with the intent of neutralizing acidity, precipitating metals, and imparting alkalinity to the discharge water.

A tracer test was conducted to gain insight into the hydrologic nature of the mine. Three tracer tests were conducted, one using the fluorescent dye Rhodamine WT (RWT) and two using chloride. Rhodamine WT dye was selected because of its extremely low detection limit. Based on experience from other tracer investigations, recovery of the tracer material was expected to be problematic (Aljoe and Hawkins, 1992; Cox, 1994). Initial hydraulic characterization indicated that the mine environment may cause excessive tracer dilution. The large volume of flooded mine voids and the detention time suggested that a tracer with a low detection level would be desirable. However, dyes are not necessarily suited for use in mines because their fluorescent properties are inhibited at acidic pH levels and the dye can adsorb to ferric iron floc.

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From the available florescent dyes, RWT was chosen because it has a relatively low adsorption tendency, and because the equipment to measure it was available. However, after the initial tracer test was conducted, the anticipated concerns regarding the breakthrough of tracer did not appear. In fact, the breakthrough occurred in a relatively short time of period. This indicated that tracers with higher detection limits could be used. Two additional tracer tests were performed using sodium chloride to further characterize the hydrology.

The goal of this paper is to convey the results and findings generated from the tracer aspect of the study. Practical information is also provided, regarding the use of tracers in underground coal mines.

## Background

### Project Background

Numerous treatment methods have been devised to address the adverse environmental impacts associated with acid mine drainage (AMD). However, these developments have historically relied on control devices which fall short of addressing the problem. Control technologies are often expensive (estimated to exceed one million dollars a day nationwide, Kleinmann, 1991), elaborate, and require regular attention. Thus, many of the control techniques are impractical in the treatment of AMD from abandoned mine sites.

With respect to underground mines, a more practical approach may be the reclamation of AMD through treatment with CCBs. Water collects within the mine workings to form pools or reservoirs of AMD, creating a body of water similar to a karst aquifer. If this "aquifer" can be treated *in-situ*, then the adverse effects associated with the discharge can be avoided or prevented. This technology involves the introduction of fluidized bed ash (FBA) slurry at strategic locations within the mine void. Fluidized bed ash will address the problem by altering the chemical conditions in the injection area, thus precipitating the existing dissolved metal species, neutralizing the acid already produced, and imparting alkalinity to the drainage. As a result, the water discharged from the mine will have a reduced metal load, a higher pH, and improved buffering capacity.

The purpose of the tracer study was to generate basic hydrologic information regarding point-to-point connectiveness and also to estimate the travel time between the injection point and the seep outlet. As previously mentioned, a mine environment is similar to a karst aquifer. In a karst aquifer, the majority of the flow follows fractures or solutional conduits. In the mine aquifer, the corridors act as the pathways for flow rather than fractures. Assuming this to be true, a tracer study could be employed to supply information on connectivity, travel time, advection, and diffusion.

A general understanding of the potential pathways and theoretical flow directions was developed from the mine map. An injection strategy was devised, which consisted of six wells positioned around the discharge seep. Theoretically, if a buffered treatment zone can be created around the seep, then the water discharging from the mine will be of higher quality. In order for this to be effective, the major flow paths must intersect the buffer treatment zone. However, the actual pathways may be completely different from the expected flow directions (based on the available mine map) due to roof falls, gob storage, and walls constructed to direct airflow. Tracer studies were designed to supply insight on the actual conditions and to provide an explanation of what is occurring inside the mine.

### Mine Site

The project site is located in southeast Oklahoma, 160 miles east-south-east of Oklahoma City, near the town of Red Oak (S½, SE¼, Section 1, Range 21 east, Township 4 north, Latimer County). The area of interest is located in the Interior Province, Western Region Coal Field (Shannon, 1926), or more specifically, in the Howe-Wilburton Coal District. The district is located in the McAlester Marginal Geomorphic Province (Johnson, 1974) and is in the Arkoma Basin.

Bache and Denman Coal Company operated the mine from 1907 until at least 1925. Ownership and time of operation were based on several mine maps obtained from the Oklahoma Department of Mines, (Oklahoma City, Oklahoma); however, there is no readily available official record of ownership. All calculations and quantitative estimates are based on measurements from these engineering mine maps and best professional judgement.

The mine was a down-dip slope operation that undermined approximately 46.5 acres. From a map dated January 1925, the entire mine volume was estimated to be $8.1 \times 10^6$ ft$^3$. Mine map measurements indicated that approximately 30 to 50 percent of the coal was left in place to act as support. As a result, the actual mine void volume was calculated to be roughly $5.7 \times 10^6$ ft$^3$. An estimate of the flooded portion of the mine was based on the position of a portal on the mine map. The assumption was made that if the water volume was above the elevation of the portal, then the portal would be discharging acidic water. The portal has not discharged water; therefore, the elevation of the pool was estimated to be below the portal. Based on this assumption, approximately $3.9 \times 10^6$ ft$^3$ of void space is suspected to be flooded (29 million gallons).

The room and pillar extraction strategy utilized in this mine produced a tiered pattern that resembles a street grid. It consisted of one north-south corridor and at least five east-west corridors. Refer to Figure 1. The north-south corridor acts as the main street and bisects the five east-west corridors. Each east-west corridor or "side street" varies in length from a few hundred feet to a ¼ mile. For the purpose of description, the corridors have been named based on location. The north-south corridor will be referred to as the "main" corridor, and the east-west corridors have been numbered in a descending order. The first corridor is called "1" with the two halves named "1-east"(1E) and "1-west"(1W) depending on the location with respect to the main corridor. The names for the second tier are "2-east"(2E) and "2-west" (2W). The naming procedure continues in a similar manner for the remainder of the corridors.

As already mentioned, water has collected in the mine voids. The flow of water through the mine begins at the top of the ridge. Here, water infiltrates the coal outcrop and/or directly flows through cracks, fissures, and anthropogenic openings. It is believed that the water flows down-dip, through the mine voids, and collects in the side corridors. The side corridors gently slope such that the water drains toward the main corridor. However, there may be occasional openings that connect side corridors and would intercept flow. The flow of water just described is the theoretical path of least resistance, but cave-ins and other obstructions may cause the water to follow alternate routes. Direct down-dip flow and more sinuous paths are possible.

When the mine was operational, water drained to the base of the main corridor into a sump room. Here, water was collected and pumped to the surface. Since the mine closed, water has collected in the bottom and formed a pool. Over the past 70 years, the accumulation of water has increased and the pool elevation has risen to a point higher than the elevation of the valley floor. Thus, a gradient was created which allows water to discharge from the mine due to potentiometric pressure, forming an artesion well. The present day seep is believed to be the remnant of a sump discharge pipe, but there is no record of this feature on any of the available maps.

This flooded portion forms a reservoir or pool that maintains a relatively constant hydraulic head. Pool volume fluctuates with rainfall, but not drastically. As the pool rises above a certain point or elevation, a modest increase in seep flow is observed. Chemical and physical characteristics of the mine water were monitored over the past two years. A listing of the major chemical constituents and physical conditions are presented in Table 1.

## Tracer Background

Initial tracer selection was based on the hydraulic nature of the mine. Since the retention time of the mine pool was estimated to be 5.3 years (based on an average discharge of 15,000 gallons/day and an estimated flooded mine volume of 29 million gallons), a tracer breakthrough was anticipated to require a significant amount of time. During that period, the tracer material would have the opportunity to diffuse throughly throughout the flooded mine void, resulting in low equilibrium concentrations. Subsequently, a tracer with particularly low detection limits had to be selected. Otherwise, an extremely large mass of tracer would be required.

Table 1 Average values for chemical and physical characteristics of the mine water at the Red Oak, OK site

| Element | Conc. (mg/L) | Parameter | Value |
|---|---|---|---|
| Al | 6.2 | Temp (°C) | 17.2 |
| Ca | 62.6 | pH | 4.4 |
| Fe | 192.9 | Conductivity (mS) | 1.17 |
| Mg | 41.9 | Turbidity (NTU) | 0.1 |
| Mn | 6.6 | Acidity (mg/L $CaCO_3$) | 475 |

Detection limits for anionic tracers depend on the analyzing equipment and the background levels in the mine. Detection limit analysis conducted at the University of Oklahoma indicated that both chloride and bromide could be detected easily to 100 ppb using a Dionex 4300i Ion Chromatograph, following Method 300.0 (EPA, 1991). Lower detection limits are possible using other equipment and/or different analytical techniques. Given this detection limit, an excessively large amount of tracer salt would be required to produce a measurable concentration. Furthermore, for chloride, a 4000 ppb background level had to be overcome before the introduced chloride could be distinguished from background levels. Subsequently, the quantities of tracer required and the economic considerations, particularly for sodium bromide, were prohibitive for an anionic tracer study. Estimations on the amount of tracer were based on complete mixing in the mine and a concentration 10 times the detection limit. Approximately 200 tons of sodium chloride or 311 lbs of sodium bromide would have been required given these assumptions. As a result, a fluorescent dye tracer was proposed.

A significant advantage of fluorescent dyes is the particularly low detection limits that can be achieved. Information supplied by Tuner Design (1995) indicated that 1 part per trillion (0.001 ppb) is theoretically possible, under certain circumstances. In addition, the background level in the mine (for RWT) was particularly low.

Numerous florescent dyes are available, with various attributes that make them desirable for particular applications. Selection of a fluorescent tracer was dependent upon the response of the dye under conditions represented at the mine site. Smart and Laidlaw (1977) discuss the importance of temperature, pH, salinity, chlorine, and background fluorescence. Several of these factors may be a concern in a mine environment, particularly salinity and background fluorescence. If the mine of interest is subject to high fluorescent background levels or elevated salinity, then the results of the fluorescent tracer may be biased. In addition, mine water pH and the presence of ferric hydroxide influences dye recovery (Smart and Laidlaw, 1977; Aldous and Smart, 1988). Low (and high) pH values affect dye fluorescence, while ferric floc acts as an adsorption site.

Both pH and ferric hydroxide were of concern at the project site. The average pH at the mine was approximately 4.4, and the presence of ferric iron was anticipated to be a problem. A study conducted by Aldous and Smart (1988) was helpful is selecting the appropriate tracer. These authors investigated the use of tracers in a flooded mine environment in England. Further, they designed a laboratory study to examine the effects of adsorption on ferric hydroxide. Results from the Aldous and Smart study (1988) suggested that Sulpho Rhodamine G resisted adsorption to iron floc better than six other dyes investigated. According to their study, intracid Rhodamine WT (RWT) was second best and Fluorescein was third. In all situations, the dyes adsorbed to some degree, which indicates that fluorescent tracers are not conservative (Aldous and Smart, 1988) in mine environments where ferric hydroxide is present. A summary of pH values and ferric hydroxide effects is presented in Table 2.

Ideally, Sulpho Rhodamine G would have been chosen; however, RWT was selected because the available equipment was configured for RWT and, also, because the literature suggested that it would be an effective tracer given the mine conditions.

Anionic chemicals, such as chloride, are not subject to the adverse conditions described above. Both the chloride and bromide ions are considered to be conservative tracers, that is, they are not labile and tend to be inert under normal circumstances, and will not absorb to ferric iron floc. These ions were considered as alternative tracer chemicals. However, Aljoe (1992) hypothesized that the bromide ion may settle due to density differences. As a result, pockets of concentrated tracer may develop; subsequently, tracer study results may not accurately reflect hydrologic conditions.

Table 2 A summary of effective pH working ranges and effect of ferric hydroxide on fluorescence.

| **Tracer Dye** | **pH working range** | **% of initial fluorescence in presence of 40 g/L $Fe(OH)_3$ [2]** |
|---|---|---|
| Sulpho Rhodamine G | 3.5 - 10[2] | 90 |
| Rhodamine WT | 4 - 10[1] | 75 |
| Fluorescein | 5 - 10[2] | 70 |
| Pyranine | 9 - 11[2] | 70 |
| Sulpho Rhodamine B | 4 - 10[2] | 65 |
| Tinopal CBS-X | NA | 60 |
| Lissamine Yellow | 4 - 10[2] | 40 |

1=pH information provided by Tuner Design, 1995.
2=information taken from Smart and Laidlaw, 1977.

## Methods

A Turner Design Model 10 AU Fluorometer was used for reading the fluorescence. Unfortunately, the location of the tracer recovery point was prone to vandalism. As a result the unit could not be left in the field, which prevented the use of flow-through reading capabilities. Instead, grab samples were collected at discrete time intervals. Samples were gathered in a Sigma 24 bottle automatic sampler. The advantage of the sampling unit was the ability to collect several samples without being present. However, there were two significant disadvantages with respect to this application. First, the time interval for sampling may create a condition known as aliasing. That is, the sample collection frequency may not be sufficient to accurately depict the true shape of the recovery curve. Second, since the samples are not analyzed immediately, they have the opportunity to oxidize. When the mine drainage oxidizes, ferric hydroxide forms and the pH of the solution drops sharply. Iron concentration in the mine water was approximately 200 mg/L; thus, the oxidation of the water would lead to a significant amount of iron hydroxide. Furthermore, according to Shiau *et al.* (1993), precipitation of RWT is observed at pH values below <4.

Field Methods. Three independent tracer tests were conducted at the mine site. Two tests were performed at the portal location and a third test was conducted in well 3E (Figure 1). Adsorption and precipitation of the dye would lead to biased fluorescent readings.

As discussed previously, the purpose for this test was to determine if the injection wells were connected to the discharge point and to estimate travel time. The first test was designed to assess flow conditions in the main corridor. Review of the map suggested that the main corridor would act as a direct conduit from the portal well to the seep discharge. Assuming there is conduit flow in the mine, it was anticipated that this test would indicate the amount of flow through the main corridor.

The first test involved an injection of one gallon of 20 percent RWT on March 1, 1997. Injection was accomplished by diluting the concentrated dye in 18 liters of field mine water. A MasterFlex peristaltic pump was used to inject the dye solution directly into the mine void through a garden hose (as recommended by Turner, 1995). Since the mine well was cased using polyvinyl chloride (PVC) plastic, care had to be taken to avoid adsorption of the dye to the casing material. After the solution was injected, 150 L of water obtained from the seep was pumped through the system to flush the dye. An additional 50 L of seep water was poured into the top of the well to purge the casing. The volume of the casing was roughly 85 L, so the 200 L of flushing water was assumed to be adequate to purge the dye.

After the initial results of the first test were collected, a second tracer test was conducted using sodium chloride. On April 14, 1997, approximately 175 pounds of Morton food grade, canning sodium chloride, was injected into the mine. The salt was dissolved in 360 L of AMD. High density polyethylene (HDPE) plastic containers (100 L) were used to dissolve the salt. Based on the theoretical solubility of sodium chloride and accounting for the ionic strength of the AMD solution, approximately 30 to 50 pounds of salt could be easily solubilized in 90 liters of AMD. The salt was thoroughly dissolved with the aid of an impeller attached to an electric drill. Since the PVC casing was not a concern as a sorption site, the salt solution was poured into the well from the surface. Following the tracer addition, 180 L of AMD was used to flush the casing.

The third tracer test was conducted on July 2, 1997, when 300 pounds of Morton table salt were introduced into the mine. Approximately 50 pounds of salt was dissolved in 90 L of water and injected into the mine until a total of 540 L of salt solution had been added. Approximately 180 L of AMD was used to flush the casing of the well.

## Monitoring/Collection

Samples were collected from the seep discharge using a Sigma 24 bottle autosampler. The unit was calibrated to collect 500 mL of sample for each sampling period. Collection times were based on anticipated breakthrough and concern for aliasing. Depending on the test, the sampling frequency was balanced on the sampler capacity and the desired result; therefore, each test had different sampling frequencies. The mine wells (3E, 3W, 4E, 4W, 5W, and portal) were monitored prior to injection and also at certain intervals using a Kemmer sampling unit. At the time of the first tracer test, well 5W had not been completed so background conditions could not be determined.

Sampling frequency for the first tracer test was set for 480 minutes, or every 8 hours. It was assumed that the dye would take weeks or months to appear at the seep. Thus, the 8-hour sampling frequency was presumed to be more than adequate. However, breakthrough occurred within 11 hours of injection. Due to the unexpectedly fast breakthrough, the collection interval for the second tracer test was programed for every hour for the first 22 hours. The sampling interval was then increased to 850 minutes, or 1.7 samples per day. The sampling protocol was selected because the chloride tracer was expected to peak within the first 11 hours.

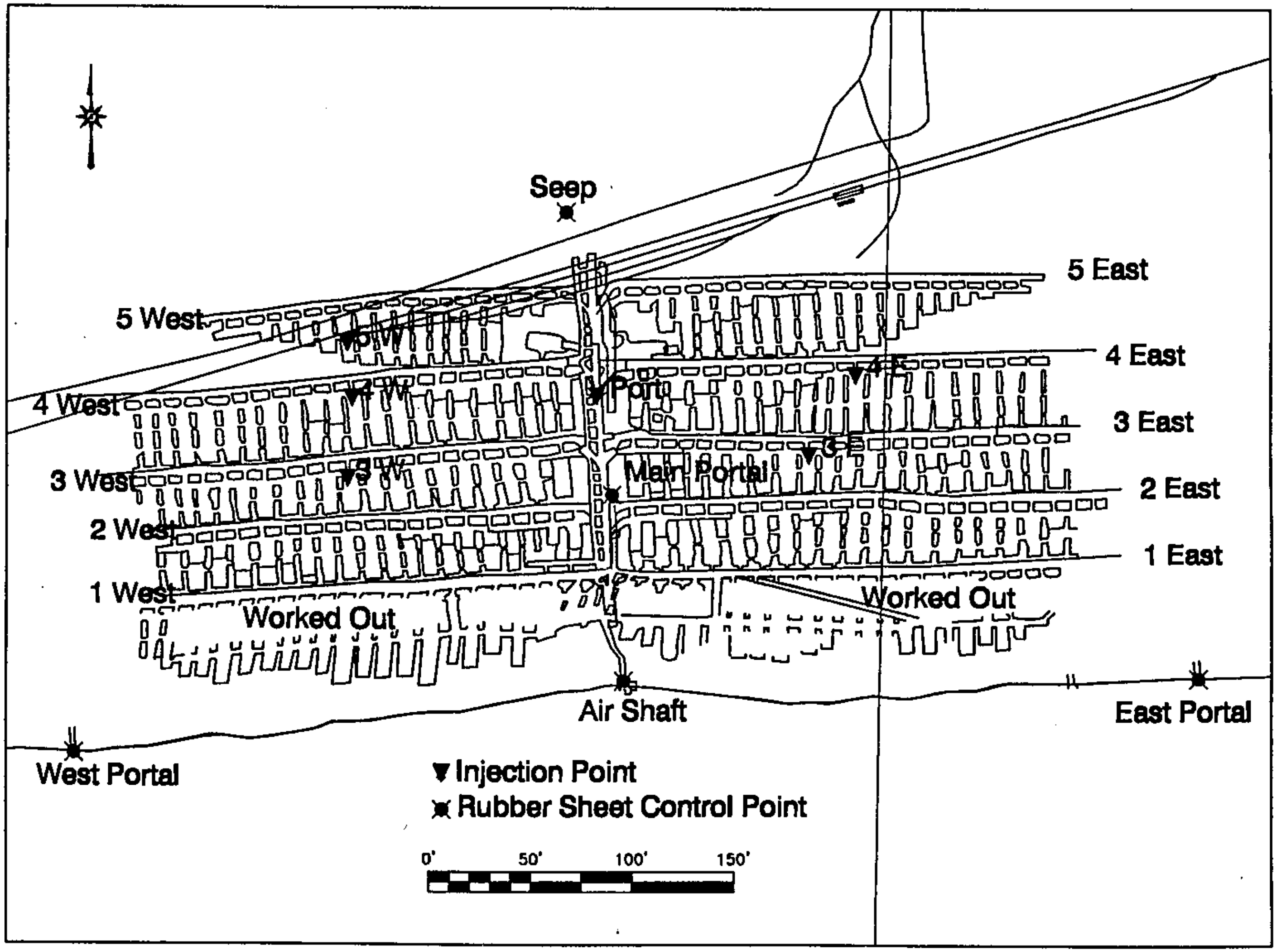

Figure 1 Digitized mine map with locations of corridors and injection wells.

Sample collection of the third tracer test was set at a 420 minute interval, or every 7 hours. Since the location of this well was several hundred feet away from the portal well and the main corridor, the amount of time required to reach the discharge point was anticipated to be longer than the previous two tests.

## Results and Discussion

### Field Results

Tracer Test 1. Results from the first tracer test are presented in Figure 2. All initial concerns about tracer breakthrough and adequate tracer concentration were dispelled by this test. Breakthrough from the point of injection to the seep discharge point occurred within 11 hours.

Travel time was calculated using the highest dye concentration divided by the distance traveled. A travel time of 23 feet per hour (ft/hr) was calculated, which was much faster than expected. Given the discharge rate of the seep (2,000 $ft^3$/day) and the estimated cross sectional area of the corridor between the injection point and the seep (36 $ft^2$), the calculated velocity would be 2.3 ft/hr--an order of magnitude lower. As described previously, the injection of the dye in the portal was designed purposely to maximize the possibility of breakthrough. The portal was assumed to be directly connected to the discharge point. However, the amount of dye recovered was less than 1 percent of the amount originally injected.

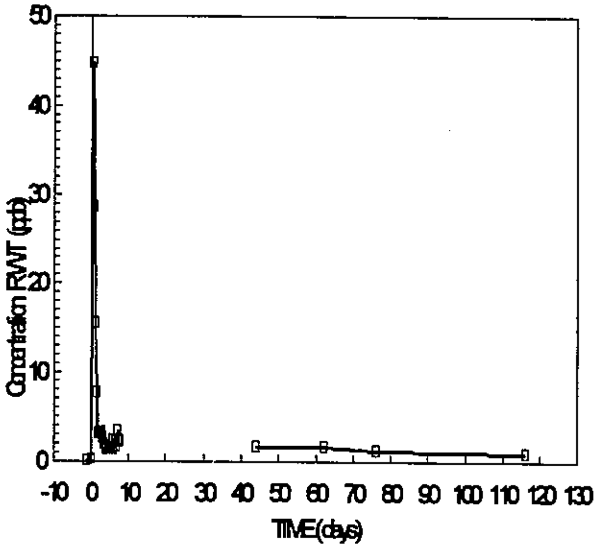

Figure 2. Breakthrough curve of tracer test 1--Rhodamine WT

Explanation for the poor recovery revolved around adsorption to iron floc and aliasing. If ferric hydroxide was present in the mine, precipitated on pillars, ceilings, and floors, then adsorption of the dye could be a cause of poor recovery. Another possibility was the collection frequency. When the largest peak was observed at 11 hours, it is possible that a larger peak of dye passed prior to the collection event. In order to determine if adsorption was occurring or if aliasing was a concern, a second tracer test was conducted using a more conservative tracer.

Oxidation of the samples did not limit fluorescent readings during the first part of March. Day time high temperatures were approximately 50° F, and night time lows still dropped below freezing. As a result, both abiotic and biotic oxidation were inhibited; therefore, fluorescence could be read without the loss due to adsorption to iron floc. However, fluorescent readings from the autosampler bottles were not possible during April and May. Once the temperature increased, samples were thoroughly oxidized before analysis, resulting in poor fluorescence values.

Tracer Test 2. The second tracer test was conducted 30 days after the first test. This test was conducted because of the lower recovery of tracer material. The sampling time interval was increased to every hour for the first 22 hours to minimize the effect of aliasing, and chloride was used because of its conservative nature as a tracer. Results from the second tracer test are presented in Figure 3.

Comparing the two breakthrough curves indicated that there were similar results occurring in both tests. For the second test, breakthrough occurred within 9 hours (28 ft/hr) after injection and the elevated concentration diminished within 3 days. However, due to the low discernable detection level, given the high background, the concentration of chloride was masked after approximately 5 days. Elevated concentrations at 7, 11, and 15 days may represent alternative flow paths, but the sampling frequency was not sufficient to provide confirmation. Quantitative recovery of the chloride again suggested that the majority of the tracer remained within the mine, because only 11 percent was recovered. However, this was an order of magnitude greater than the fluorescent tracer. These data results suggest that adsorption may have occurred during the fluorescent tracer test, or perhaps the more frequent collection interval was adequate to identify the highest concentration of chloride tracer on the breakthrough curve.

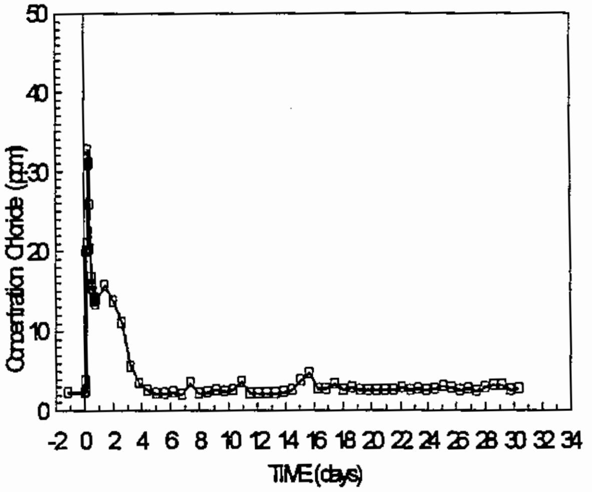

Figure 3 Breakthrough curve of tracer test 2--chloride

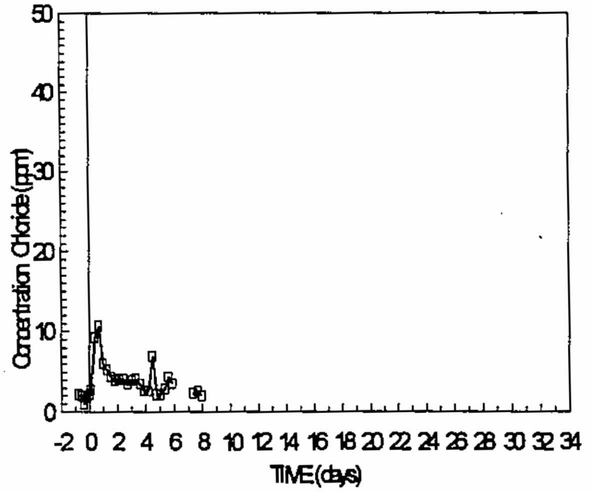

Figure 4 Breakthrough curve of tracer test 3--chloride

Analysis of these results suggested that adsorption probably was not the sole explanation for the poor recovery of dye tracer. In fact, the poor total recovery of the chloride suggested that something other than adsorption was preventing recovery. Unfortunately, the high background concentration of chloride and the limited amount of sodium chloride added to the mine made it impossible to monitor the other mine wells with any certainty.

Tracer Test 3. A third tracer test was conducted for the sole purpose of determining if an upper tier mine well was connected with the discharge point. The approximate distance from well 3W directly to the discharge site was 560 feet; the distance following the expected conduit flow path was 750 feet. Results from this test are presented in Figure 4.

Based on these results, the rate of travel from this site to the point of discharge was 34 ft/hr, or 46 ft/hr, depending on the flow path selected. This was much faster than expected, given the distance from the mine discharge. Review of Figure 4 suggested that there may have been breakthrough of an alternative pathway at approximately 4 days. However, the collection frequency was not sufficient to distinguish if this was an anomaly or an alternative flow path. Recovery of the material was less than 0.3 percent of the total amount injected, which again indicated that the majority of the tracer material remained in the mine.

Mine Well Results. Fluorescent tracer concentrations were evaluated in the wells to identify pathways and for predicting diffusion gradients in the mine. At the time of the first tracer test, 5 of the 6 wells (3E, 3W, 4E, 4W, and the portal) were complete. Background dye concentrations measured at these sites prior to injection of dye were less than 0.1 ppb. After the injection, the concentration of the dye was measured on a biweekly basis for approximately 45 days using a Kemmer sampler. A Kemmer sampler was selected to minimize the disruptive effect of bailing and prevent the generation of artificial gradients.

Results from this test indicated that the dye concentration in the mine wells were similar to the background levels, even at the point of tracer injection. In contrast, the seep discharge maintained a relatively constant 1.65 ±0.1 ppb concentration for the entire period. Subsequently, it was assumed that the dye did not move throughout the mine, and that most of the tracer was lost somewhere between the point of injection and the seep outlet. Another possibility was the loss of tracer material to other flows paths that did not end at the seep.

From these results, it was initially assumed that the test had failed to produce the desired information. However, during the April sampling event, when the wells were bailed for routine chemical analysis, a higher concentration of tracer (10.8 ppb) was observed at the point of injection and also at the other mine wells (range of 0.6 to 2.9 ppb). From this discovery, it was obvious that stratification was occurring in the mine. Less contaminated water, floating on top of a more concentrated mine water, was collected by the Kemmer sampler, resulting in low tracer concentration. Further analysis, with regard to pH and conductivity, produced similar findings. As a result, two conclusions were drawn. First, there was not turbulent flow in this region of the mine, and second, a Kemmer sampler was not the appropriate device to be used for this sampling protocol.

Fluorescent readings were then taken at monthly intervals along with regular chemical sampling. Results from these collection periods are presented in Figure 5. (The seep concentration reached a maximum at 40 ppb.) (This value was truncated to maintain the scale of the graph.) Review of Figure 5 indicated that there was a high concentration centered at the point of injection that diffused throughout the mine. Unfortunately, the rate could not be determined because the sampling frequency was not sufficient to identify the breakthrough at specific wells and also because of the inaccurate information collected using the Kemmer sampler. From the change in concentration monitored from 45 days to 118 days, there seemed to be some evidence to support movement of dye via diffusion rather than discrete conduit flow.

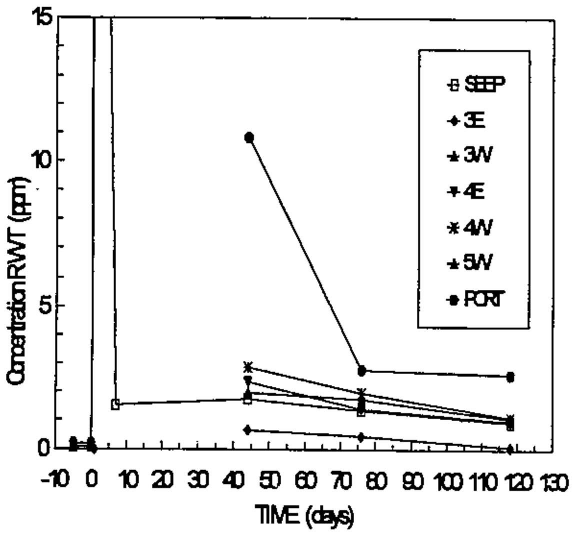

Figure 5 Mine well concentrations of Rhodamine WT with respect to time.

At 45 days after injection, the dye concentration was highest at the point of injection (10.8 ppb), followed by the wells nearest the injection—4W (2.9 ppb) and 4E (2.3 ppb). Well 3W and the seep were slightly lower than the 4th tier wells, but were similar to each other (1.95 and 1.76 ppb, respectively). Lower concentrations were expected because these sites were further from the injection point (Figure 1). Well 3E was the lowest (0.6 ppb), which was expected given the fact that it was located in a coal pillar. Diffusion through the coal and inadequate bailing made it difficult to obtain representative samples from this location. Samples taken at 76 days after injection indicated a decrease in concentration and a lessening of the variation in concentration between sites. After 118 days the concentrations at the seep and mine sites, including the newly drilled 5W, were very similar. The concentration varied from 0.98-1.1 ppb at sites 3W, 4E, 4W, 5W and the seep. The portal well was approximately 2.6 ppb; well 3E was still the lowest (0.1 ppb).

Although there were not enough data collected to make any firm conclusions, there were enough data available to generate a general hypothesis. The gradual decrease in concentration of the mine approached the concentration of the seep discharge. Even more interesting, the dye concentration seemed to approach a similar concentration at a consistent rate, suggesting that the dye diffused throughout the mine. This was observed at all sites except the injection location, PORT, and the well located in the coal pillar, 3E. Most likely, the concentration would continue to decrease similarly at all sites until it was below the detection limit of the analytical unit. Theoretically, the concentration of the dye should be greater than 6 ppb if the dye diffused equally throughout the mine. A decreasing trend to 1 ppb and less suggests that dye is stored in rooms and sumps and/or adsorbed to iron floc. Determining the actual cause for the loss of dye is beyond the capabilities of this study.

Hydraulic Characterization

The general shapes of the breakthrough curves were the same for all tests, and the time of travel and the percentage of tracer recovered were relatively consistent regardless of the distance from the seep. Findings such as these were perplexing. However, review of the mine well tracer concentration data provided insight into the actual hydrologic conditions.

If the breakthrough curves were the only data analyzed, then it would appear that the mine hydrology is a combination of conduit flow with storage and release. A sharp breakthrough peak is indicative of conduit flow, but the poor mass recovery and the trailing tail of dye are more representative of storage with slow release. In all three tests the flow velocities were much greater than anticipated. The amount of time that elapsed between the injection and breakthrough indicated that there was fast, conduit flow occurring. However, the occurrence of stratification and movement of tracer up-gradient indicated that laminar flow and diffusion were also important means of tracer movement.

In addition, the low mass recovery was also perplexing. Presumably, if rapid conduit flow was occurring in the mine, then the majority of the tracer should be carried by the flow to the exit point, but this was not the case. Perhaps there were other pathways that were not connected to the seep, or maybe there were other outlets. More likely, conduit flow is occurring within quiescent pools, but at a rate such that diffusion is also important. Results from the mine-well tests provided information that may support this hypothesis. Diffusion from the point of injection indicated that there was relatively consistent and equal diffusion of the dye to other points within mine. If there was direct flow via discrete channels, then there would not have been a uniform diffusion pattern observed at the other wells.

The flow velocity in the mine, indicated by the tracer test, was also far greater than expected for all tests. Furthermore, breakthrough times were relatively similar despite the differences in travel length. A fast, discrete breakthrough peak and uniform diffusion of dye are somewhat contradictory findings. Some gradient must be driving the initial movement of dye. Perhaps the amount of water used in the dilution and flushing of the tracer created a temporary additional hydraulic gradient. If this was occurring, then the major corridors would be obvious pathways of least resistance. Seep discharge was monitored on a daily basis, but a relatively crude method of measurement was employed. Flow was captured in a bucket and the amount of time to reach 10 L was recorded. Obviously, this method would not be sensitive enough to distinguish subtle changes in flow. However, the amount of flushing water is trivial when compared to the total amount of water in the corridor between the point of injection and the seep discharge. The injection volume accounted for approximately 0.1 percent of the water in the main corridor between the portal and the seep. Another possibility is that density differences between the liquids caused the fast breakthrough. The amount of dye added and the concentration may have been significant to induce a gradient. Further study is necessary to determine if the amount of flushing water and/or density effects decreased the breakthrough time.

## Summary

The study was conducted to investigate the possibility of *in-situ* remediation of acidic mine water with the use of FBA. Information on the rate of flow and "connectiveness" of injection wells with the discharge point was needed to develop a treatment strategy. Fluorescent dyes are not typically used in mine tracer studies, because of the low pH values associated with certain mines and a tendency to adsorb to ferric iron precipitates. Rhodamine WT was used in one tracer test because it can be detected at low concentrations. However, due to poor recovery, a second tracer test was undertaken using a more conservative tracer–chloride. Each tracer produced similar travel time results.

Use of these tracers has provided valuable information with regard to mine hydrology. In general, it appears that the hydrology of the mine is controlled by conduit pathways within pools, but that diffusion is a major transport mechanism. As identified during the tracer tests, the corridors act as direct conduits for flow. However, the background gradient or driving force does not appear to be significant enough to be the primary means of flow. In addition, stratification was observed in the mine which indicates that specific pathways have laminar flow rather than turbulent. Presumably, the mine is relatively quiescent and stratified. Without the creation of artificial gradients (e.g., tracer injection or density differences), movement of the dye in the mine could be compared with a tracer test conducted in a lentic environment. That is, the dye moves in a general direction, following a gentle gradient, but the flow rate is so slow that there is ample time for diffusion throughout the water body. Physical and chemical variability between mine wells was also low as measured prior to the tracer tests. These findings further support the diffusion hypothesis. If there was significant conduit flow, there would be flow paths with distinctly different chemical composition. When the dye was injected into the mine, an artificial gradient was created which caused the dye to follow a specific flow path. Corridors in the mine would act as direct routes which would contain the movement. Thus, the breakthrough curve would reflect a conduit flow path.

## Recommendations

The following recommendations are made based on the issues identified in this project.

- The use of RWT to identify basic mine hydrology conditions proved to be a relatively effective method. For the qualitative nature of this test, the use of non-conservative tracers worked sufficiently well. Point-to point tracing as well as flow velocity can be distinguished. However, an artificial gradient may be induced during the flushing process that would affect the rate of flow.

- The low detection limit of the fluorescent dye (1 ppb) made it a superior tracer material than the chloride for this particular study. In order to obtain the same results from chloride, approximately 200 tons of salt would have been required. Using RWT proved to be more economical.

- For future tests in mine environments where pH is acidic (3-5) Sulpho Rhodamine G is the recommended tracer. The Sulpho Rhodamine G is more active at lower pH values. In addition, the resistance to adsorption on iron floc is superior to other fluorescent dyes (Aldous and Smart, 1988).

- Collection of fluorescent tracer samples using an autosampler is not recommended unless the samples can be analyzed prior to oxidation.. A superior method of collection would involve direct fluorescent measurement using a fluorometer in the field. The Turner Model 10 AU is designed to read fluorescence using a flow-through cell. This feature allows for a more accurate recording of dye breakthrough. In addition, there is an internal data logger which can be programmed to record reading at any desired interval. Therefore, the problems associated with aliasing would not be an issue, and the adverse effects associated with sample oxidation could be avoided.

- The use of chloride as a tracer was instrumental in verifying the results of the fluorescent study. Without the confirmation of this test, an inaccurate conclusion may have been drawn with regard to adsorption of fluorescent dye. Where possible, tracers materials should be used in tandem to confirm results or indicate problems.

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