Guide to using tracers in coal mining situations

U.S. Office of Surface Mining Reclamation and Enforcement
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Tracer testing of ground water situations related to coal mining, while not a common practice, is occasionally needed. There are several types of materials that can be used as tracers. However, this document will concentrate on primarily on optical (fluorescent) dyes and common chemical (ionic) tracers. Bear-in-mind, this is a brief discussion of tracers and tracer testing. There numerous books and lengthy articles entirely devoted to this subject as well as graduate level courses that cover ground-water tracing thoroughly.

The decision whether or not to use a tracer during investigations related to coal mining should be made with much caution. As stated in Davis and others (1980), "Tracer tests using artificially introduced tracers commonly fail." Use of tracers to determine hydrologic connection, direction of ground-water movement, and/or the speed of movement is not always a recommended practice for mining situations. There are numerous problems with errors in or misinterpretation of the tracer results that can occur under any circumstances, plus there are a few additional complications that can become pronounced when coal mining situations are involved. Potential problems with conducting tracer tests include but are not limited to:

- Use of the wrong tracer for the conditions and type of test to be performed.
- When insufficient tracer is introduced at the input point, the concentration may become so dilute by the time it reaches the measurement point it will not be noticeable or even measurable. This is especially true if a tracer is placed in an underground mine pool that may have tens of millions to more than a billion gallons of water in storage and/or flushing of the pool is usually relatively slow.
- Receiving a non-detect at a sample point does not necessarily mean that there is no connection. Some reasons for this include:
    - If the sampling interval is too broad, the appearance and passing of the tracer was missed.
    - The flow rate may be so slow that the tracer may not appear for many months if not years after it is introduced; well after sampling has ended.
    - The tracer was diluted below detection limits by the time it reaches the sampling point(s).
    - The tracer was adsorbed, absorbed, or chemically altered along the flow path to the point where it is undetectable or is no longer the same chemically.
- A positive reading at one monitoring point does not mean that the tracer is not also showing up at other areas related to the hydrologic system.
- Use of fluorescent dye tracers in mining situations has its own specific set of problems. The geochemical environment common to underground and surface coal mines has a tendency to adversely affect many optical dyes. Most fluorescent dyes will adsorb to iron hydroxides, clays, and organic materials. All of these materials are extremely common in coal mines and can be contacted by the ground (mine) water. Additionally, these dyes are negatively impacted by changes in temperature, pH and Eh, which are also very common to coal mine hydrologic regimes. Fluorescent dyes also tend to decompose under strong (sun) light exposure (Davis and others, 1980). The adsorption or chemical alteration of fluorescent dyes by mine environments or water chemistry can cause false negative determinations. Aley (1999) suggests that for acid mine drainage fluorescein may be the best choice of the fluorescent dyes. However, experience indicates that rhodamine WT may be less susceptible to adsorption in mining environments.
- Fluorescent dyes are frequently used in every-day products such as detergents and paper as optical brighteners, tooth paste, antifreeze (fluorescein), and numerous other products. These common uses often cause these dyes to be released into the environment and interfere with dye tracing possibly causing false positives. This one reason why rigorous background sampling is vitally important.

Types of tracers:

- Fluorescent (organic or optical) dyes. They have the advantage of being detectable up to parts per trillion – Commonly used dyes include:
    - Eosine – color index name "Acid Red 87"
    - Fluorescein – color index name "Acid Yellow 73"
    - Rhodamine WT – color index name "Acid Red 388"
    - Sulforhodamine B – color index name "Acid Red 52"
    - Pyranine – color index name "D&C Green 8"
- Chemical tracers –commonly-used ones used include:
    - Sodium Chloride – common salt, both the sodium and the chloride are relatively chemically conservative so both can act as tracer ions, if background concentrations are low.
    - Calcium chloride
    - Bromide
    - Iodide
    - Fluoride
- There are also radioactive and other types of tracers that are not recommended due to the cost of using them and the potential negative reaction by those with a vested interest in the situation.
- Some gases can be employed as tracers. These include dissolvable noble gases such as helium, neon, argon, xenon, and krypton as well as ethlmercaptan. While these gases tend to be chemically inert, they at times pose diffusion and outgassing problems.

Conducting a Tracer Test: The following steps are somewhat generic, but basically standard procedures for performing a tracer test.

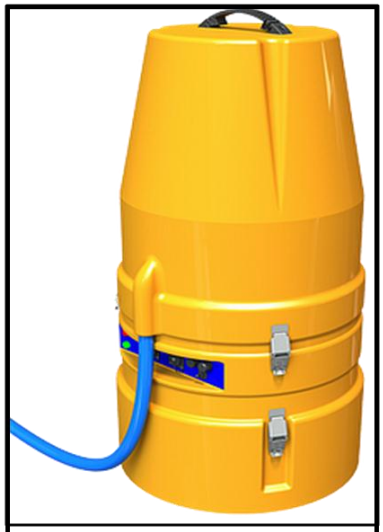
1. Create a conceptual model of the flow system using existing physical and geochemical data. Based on the model, define what you are trying to prove or disprove by conducting a tracer test. What direction do you anticipate the tracer moving, how much dilution may occur along the flow path, and where do you expect it to show up and how quickly? Get a good conceptual idea of the likely ground water flow regime prior to the test.
2. Ascertain what type of tracer you intend to use based on the environment and ambient water quality. Aley (1999) recommends that when selecting optical dyes that bench tests be conducted emulating expected conditions.
3. Prior to the test, sample the outfall points were you expect the tracer will appear. Analyze for background concentration of the tracer you have selected. It is recommended that you sample the outfall points more than once in order to create a sound baseline data set to which to compare the test data against.
4. The background concentration data along with estimations as to the amount of ground water that will be encountered, which act to dilute the tracer, will provide input as to how much tracer and at what concentration will be required. The goal is to put enough tracer into the system that it will be clearly discernible when it comes out. Davis and others (1980) stated that dilution of a tracer slug injection by ten to ten thousand fold are common. There needs to be a substantial enough spike in concentration that there is little doubt that you are seeing the tracer. It is a good rule to set up the test so that when the tracer is observed, a concentration increase of several times the background concentration is recorded. Design the test to expect a tracer concentration above the upper bound of a 95% confidence interval about the background data (if enough background data exist).
5. Introduce the tracer. If you are putting the tracer into a monitoring well located in undisturbed ground, it is recommended to follow (chase) it with additional water to help force it into the formation. If you are introducing tracer into an underground or surface mine, the additional chase water will act to push the tracer out of the well bore and into the mine pool or spoil, respectively.
6. Begin sampling at expected outfalls shortly after tracer introduction. Be sure to sample at intervals that the initial arrival of the tracer will be recorded as well as the peak concentration. Remember

ground water generally flows very slowly. In undisturbed strata, ground water seldom moves faster than 1 to 10 feet per day (fpd) (Davis and others, 1980). In underground mines the movement may be faster or slower depending on the flow regime and degree of flooding as well as from section to section within the workings. In surface mine spoil ground water velocities of 3 to 1,200 fpd have been recorded (Hawkins, 1998).

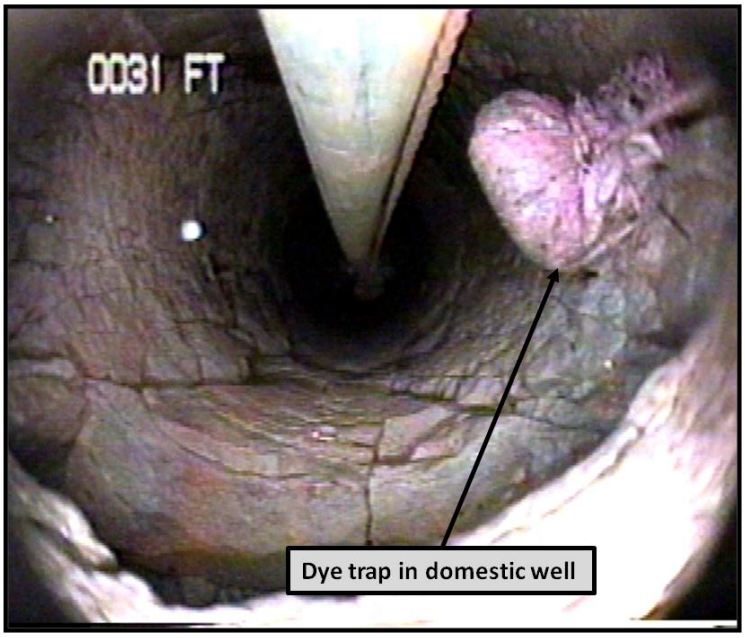
7. Once the tracer arrives at your sampling point, continue to sample until well after the peak concentration has passed. Ideally, continue sampling until the concentration returns to background levels. This will permit calculation of the total amount of tracer that has passed through the system. Ascertaining how much tracer is lost between the introduction point and the outflow will yield information as to the flow system and possible adsorption and/or geochemical reactions.

There are a variety of techniques to test for the presence of tracer including: grab or composite sampling, dye traps, or continuous monitoring (e.g., ion probes). Which one you use is predicated on the type of tracer and the nature of your test. A series of discrete grab samples collected on a predefined systematic interval is frequently employed. Composite samples taken over a period time are less often used. Small aliquots are collected at predetermined intervals and these samples are combined to form a composite sample. There is commercially-available remote sampling equipment that can collect grab or composite samples at preprogrammed time intervals (Figure 1a).

For optical dyes, the most common method to sample for the tracer is to use dye traps or receptors. More than one dye can be used during the same test to improve the likelihood of a successful operation. The traps are flow-through packets of activated charcoal which will adsorb all of the fluorescent dyes available (Figure 1b). These traps are generally about the size of a conventional teabag. The dye traps are elutriated with an alcohol solution to remove the dye. A spectrofluorophotometer is used to determine the presence and concentration of the dye in the elutriate. The recent development of relatively smaller field-deployable spectrofluorophotometers and fiber-optic probes allow direct recording of readings to data loggers on a systematic or nearly continuous basis.



Example Automatic Sampler



Figures 1a and 1b.

Ion probes can be installed at points where chemical tracers are anticipated to show up. These probes can be read manually on predetermined intervals or interfaced with automatic data loggers set to record at the desired intervals. The data loggers are periodically downloaded to computers for subsequent analysis.

In situations where litigation is a distinct probability, caution needs to be exercised to prevent tampering with the samples and/or sampling devices. For example, there have been cases where automatic samplers were purposely vandalized by persons unknown and damaged by wildlife (e.g., nesting mice). There also have been cases that dye traps, which were adequately anchored down, have disappeared during testing. Additionally, chlorine bleach (sodium hypochlorite) can be used to neutralize the effect of optical dyes. So, caution should be used to protect against these types of sampling irregularities.

Data analysis discussion: The peak concentration of a tracer breakthrough graph represents the average ground water velocity (Figure 2). The portion of the concentration that increases above background observed prior to and after the peak (spreading out of the tracer concentration) is caused by hydrodynamic dispersion. Hydrodynamic dispersion is a combination of mechanical dispersion (mixing) and molecular diffusion of the tracer. Molecular diffusion is the spreading of the tracer driven mainly by its thermal kinetic energy in the direction of the concentration gradient.

Sampling beyond the peak will allow for estimations as to how much of the tracer that was put into the system actually came out, which yields information such as flushing rates in the case of underground mines and provides insight into the ground-water regime of surface mine backfills. The area under the graph along with the discharge rate will allow for mass loading calculations.

Bear-in-mind that multiple concentration peaks can occur in certain situations. Multiple peaks are indicative of more than one flow path from the point of tracer introduction to the point or points of emanation (e.g., bimodal or polymodal flow systems).

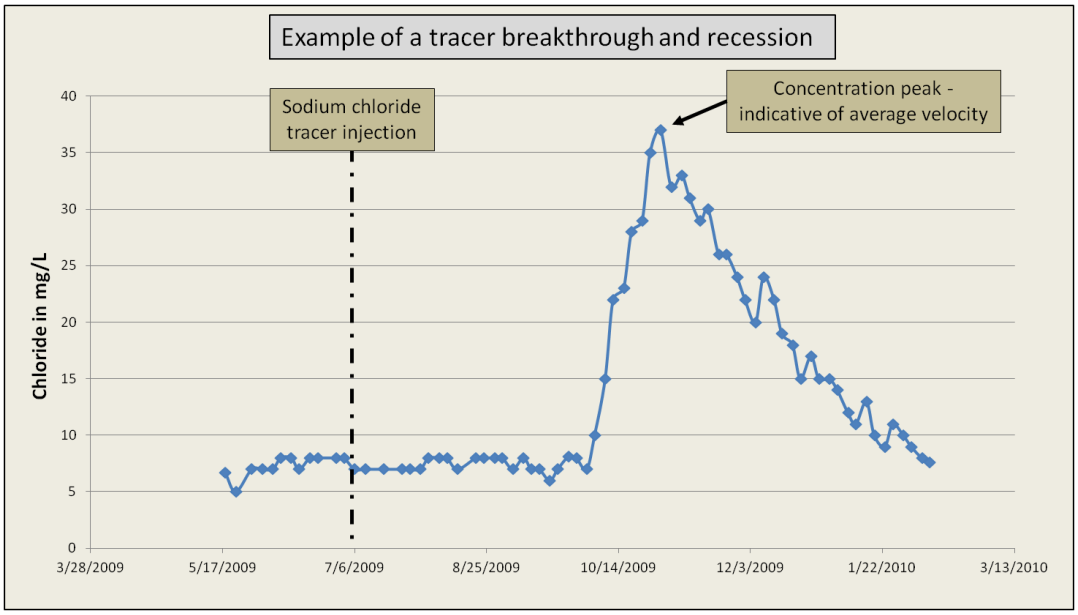


Figure 2.

Tracer test results: On a rudimentary level, tracer tests will yield information as to the presence point or absence of a physical connection between Point A (e.g., a mine) and Point B (e.g., a discharge or contaminated well). However, the velocity of the ground water may also be of importance. In the graph above, the tracer was introduced on July 6, 2009 and the concentration peak at a discharge point down

gradient was on October 30, 2009 so, the calculated travel time was 116 days. The distance between the two points is 168 feet; so, the average linear velocity of the ground water was 1.45 feet per day (fpd) (168 feet/116 days = 1.45 fpd). Using the velocity of the ground water along with other aquifer properties (e.g., hydraulic conductivity and/or transmissivity), if known, the effective porosity of the unit can be estimated as well. Conversely, if the flow velocity and porosity are known, hydraulic conductivity and transmissivity can be estimated.

Loading calculation example: On November 14, 2009, the concentration of chloride was 29 mg/L (see the above graph) and the discharge rate was 42 gpm. The equation to convert the mixed units of concentration in milligrams per liter (mg/L) and discharge rate in gallons (gpm) per minute is:

Load in pounds per day (lbs/day) = concentration in mg/L x discharge in gpm x 0.012073851 (units conversion factor) (1)

Therefore, on November 14, 2009, the loading rate calculation is 29 mg/L of chloride x 42 gpm x 0.012073851 = 14.7 lbs/day. This is just the loading for one day during the passage of the tracer. The same loading calculation would have to be estimated for each day starting when the tracer first shows up until the concentration returns to background levels. Days when no sample or flow rate was taken will have to be extrapolated from the immediately preceding and following days where those data are available. The sum of these calculations can then be compared to the total tracer injected into the system.

For example:

> In a hypothetical situation, 200 pounds salt (sodium chloride) is injected into an underground mine pool. In sodium chloride 60.7% by mass is chloride, based on the molecular weight. So, of the 200 pounds of salt, 121.3 pounds of chloride was injected. If the sum of loading rates indicate that approximately 103 pounds of chloride came through, then 18.3 pounds (15.1%) was likely taken up along the way (adsorbed, absorbed, chemically bound, etc.), has not come through yet, or was missed by the sampling. Be sure to subtract out the background loading levels from the tracer loads in your calculations. Otherwise, you could end up with more of the tracer element than was introduced.

In addition to the types of tracer tests discussed above there are a few methods by which conduct a tracer test to determine ground-water velocity using a single well. For one type of test, the tracer is introduced into the well and allowed to drift away via natural ground-water movement during the “rest period.” After an extended period of time, the well is pumped at a low rate and the water is sampled repeatedly for the tracer. Based on the pumping rate, length of the rest period, the rate of tracer return, and associated peak concentration, the velocity of the ground water can be estimated. A second type of single-well tracer test is to inject the tracer into the well and allow it to naturally drift down gradient. The well is sampled repeatedly during the test at prescribed intervals. Very small samples of water are removed to minimize the loss of tracer in the well bore and reduce the amount of water drawn into the well. Based on the rate of dilution of the tracer, the velocity of ground-water movement can be estimated.

If additional information is required, contact any of the hydrologists at the Appalachian Regional Office or you can consult any of the following references:

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