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REVIEW OF TRACER STUDY PROPOSED FOR THE SHERWIN-WILLIAMS COMPANY FACILITY, COFFEYVILLE, kANSAS

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prepared for the
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INTRODUCTION

The Kansas Department of Health and Environment requested that the Kansas Geological Survey review the procedure proposed for a ground-water tracer test at the Sherwin-Williams Company facility in Coffeyville, Kansas. The tracer test is designed to definitely determine whether a downward interconnection exists between the perched zone of ground water and the uppermost (limestone) aquifer at the site, and to allow direct measurement of the rates of vertical ground-water flow. The proposed tracer is bromide ion. The Kansas Geological Survey has special expertise in the geochemistry and analytical determination of bromide in natural water systems (Whittemore, 1988).

REVIEW

There are 4 areas of concern with the proposed tracer test: (1) the analytical method may not the best to use for the tracer test because it cannot be used to determine low background concentrations of bromide, (2) the amount of bromide tracer salt proposed is higher than needed at some locations, resulting in unnecessary contamination of portions of the ground water with high concentrations of tracer salt, (3) the concentration of the tracer solution to be used is so high that it could affect the permeability of the soil and portions of the aquifer, and could affect flow by introducing a density gradient, and (4) the volume of the tracer solution may not be sufficient to saturate a dry soil and soon enter the shallow, perched water zone.

The first 3 concerns primarily hinge on the background concentrations of bromide in the ground waters. Figure 1 is a mixing curve graph of the weight ratio of bromide/chloride versus chloride concentration for an estimate of what ground waters could contain in Pennsylvanian sediments with the range in dissolved solids such as at the Coffeyville site. The source of the chloride and a minor portion of the sulfate is assumed to be remnants of trapped, altered seawater, while the bulk of the sulfate could have come from oxidation of sulfide primarily in pyrite associated with the shales and coal beds. Another possible source of natural sulfate is gypsum. However, this mineral is much less common in Pennsylvanian rocks than in Permian rocks in Kansas.

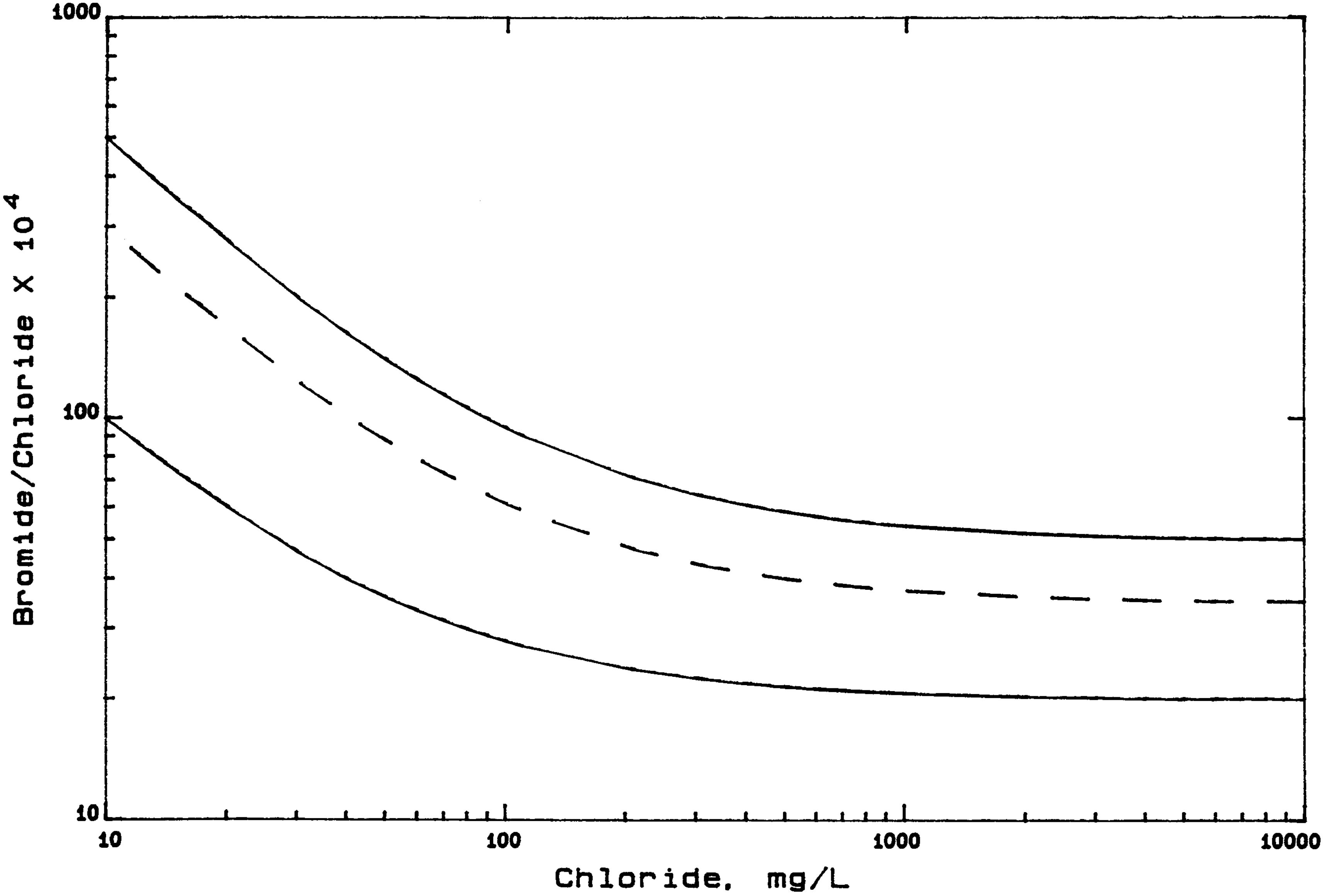

Figure 1. Bromide/Chloride Weight Ratio Versus Chloride Concentration and Mixing Curves Possible for Ground Waters in Pennsylvanian Rocks in Southeast Kansas.

Each curve in Figure 1 is generated by the conservative equation for mixing the two end points of the curve. The two solid curves are the estimated upper and lower limits of the bromide/chloride ratios for different chloride values. The dashed line is a "best guess" of a mixing curve for the hydrogeochemistry of the area. The end member ratio for the dashed curve is 0.00347, the ratio for seawater (Morris and Riley, 1966). If the geology were Permian sediments with similar chloride and sulfate concentrations in the ground waters, the bromide/chloride ratios would be about an order of magnitude lower across the graph at chloride contents above 30 mg/L, because evaporite minerals typically have low bromide/chloride ratios.

The range in average chloride concentrations for the shallow monitoring wells at the Sherwin-Williams site is 25-636 mg/L. The estimated bromide/chloride ratios for the range are 0.015 to 0.0039 based on the dashed curve in Figure 1, giving a range in background bromide concentrations of 0.4-2.5 mg/L. The range in average chloride for the deep monitoring wells is 119-2,535 mg/L, giving a range in bromide contents of 0.7-9 mg/L from the dashed mixing line.

The range for the bromide determination method proposed for sample analyses is EPA titrimetric method 320.1. The range for this method starts at 2 mg/L; the effective detection limit for natural waters such as at the Sherwin-Williams site is probably about 1 mg/L if great care were used in the analyses. Thus, the background concentration of bromide in the ground waters at the site with lower dissolved solids will probably be either below or at the detection limit.

The higher bromide contents probable in the natural mineralized waters of the site necessitate a higher concentration of bromide salt than usually used in tracer tests similar to that proposed. The plan includes the use of 29 different wells in the tracer test. The plan does not make clear whether tracer solution will be placed at each well or at sets of wells. The mass of bromide salt planned for the tracer solution is so high and the number of locations where tracer is to be used is so many, however, that the solution could lead to additional mineralization of the ground waters.

The high concentration of the tracer solution could also affect the tracer flow through the system. The density of the solution will be high enough to cause density-driven flow before substantial dilution of the tracer. The high concentration of the cation (potassium) accompanying the bromide in the tracer salt could affect the permeability of the soil and sediments containing clay through ion exchange and ion-fixation reactions, and thus alter the tracer flow in the subsurface.

The volume of 50 gal of tracer solution may not be enough to saturate a dry soil and move through the soil profile to the shallow ground water. Thus, if dry weather conditions prevail, the time before sufficient rainfall could saturate the soil and force the tracer solution downwards could be great enough that it could falsely affect the initial timing of tracer movement in the system.

SUGGESTED REVISIONS

Several shallow and deep monitoring wells representing the range in chloride concentrations should be sampled and the background bromide contents measured to better determine the tracer salt mass needed for each part of the test. An analytical method with a lower detection limit than the EPA titrimetric procedure 230.1 should be used to establish the background bromide levels. Methods such as the automated, colorimetric fluorescein procedure published by the U.S. Geological Survey (Fishman and Friedman, 1985) and used by the Kansas Geological Survey, or ion chromatography described in Standard Methods, (1989) would be more appropriate. The EPA titrimetric method could then be used to determine the presence of higher bromide concentrations indicative of tracer breakthrough in the ground water.

The concentration of the tracer solution should be reduced at many locations where less mineralized waters are located to that necessary for easy tracer detection. A shallow and a deep monitoring well are apparently located within 50 feet of one another at some locations. If the plan proposed included placing a tracer solution at each of the 29 wells in the test, then the number of locations where tracer solution is to be used should be decreased by locating the input upgradient of a well pair in which tracer flow could be detected at both the shallow and deep monitoring wells.

The well-site requiring the most tracer is that with the deepest screened interval below the surface and the highest background concentration of bromide. A calculation of the minimum tracer needed to produce a tracer concentration at least 3 times the highest bromide background can be made based on the maximum volume of ground water at the monitoring well that could dilute the added tracer. Assuming a depth to shallow water of 5 ft, a depth to the bottom of the deepest screen (44 ft), a tracer plume with an areal view approximated by a triangular area extending laterally twice the depth from the shallow water table to the screen bottom (78 ft), and an average maximum porosity of 20% of saturated sediments and/or rock, gives a total volume of ground water underlying the plume triangle of 177,500 gal (672,000 L). If the highest background bromide is about 9 mg/L, then the amount of bromide tracer needed to triple the background concentration by completely mixing with the ground water, assuming the volume of the tracer solution is negligible in comparison with the diluting ground water, is 12.1 kg.

The concentration of bromide in the proposed tracer solution is 74.53 g/L. Each tracer test involves 50 gal of KBr solution, resulting in a bromide mass of 14.1 kg. Thus, the amount of bromide planned for each of the tracer tests appears reasonable, although a little higher than necessary, for the deep monitoring well with the greatest depth to the bottom of the screened interval. However, the amount of tracer could be appreciably reduced for those wells with shallower depths to the bottom of the sample interval. A calculation should be made for each well or well pair similar to that in the above paragraph to determine the minimum tracer needed in order to reduce the contamination of the aquifer by tracer salt. Where one tracer input is to be used for a deep and shallow well pair, the calculation of the bromide needed should be made for the deep well.

The location of the tracer input should be at least the same distance upgradient in the ground-water flow direction as that of the depth from the shallow water table to the base of the sampling interval of the deep monitoring well in a well pair. The upgradient distance provides for both lateral and downward movement of the tracer in the ground water. Tracer solution placed too close to a deep well could possibly bypass the top of the screened interval by lateral movement before reaching the depth of the limestone. Tracer solution input too far away from the well could result in longer flow times and more dilute tracer concentrations.

The use of NaBr is probably more appropriate for the tracer tests than KBr. Sodium is generally much higher in mineralized waters than potassium. Thus, the effect on the clays in the soils and sediments by the difference in the cation composition of the tracer solution and the soil moisture and ground-water composition would be expected to be less for sodium than potassium.

A benefit of using NaBr is that it is cheaper than KBr; reagent grade NaBr is approximately 60% of the cost of KBr. The amount of KBr that is proposed in each tracer test is 50 gal of solution containing 111 g/L KBr. If the plan includes adding tracer to all 29 well sites to be monitored for bromide concentration, then the total KBr mass would be 609 kg. The cost of this amount of reagent grade KBr could be as high as $20,000, even including a cost reduction for the large volume. The same amount of reagent grade NaBr could cost about $12,000. Technical grade NaBr should be appreciably less expensive and should be suitable for the tracer test. If technical grade KBr is substantially cheaper than NaBr, then the cost factor should be considered against the preferability of sodium versus potassium for the tracer solution. In any case, the recommendation that appreciably less tracer should be needed for the many of the tests should substantially reduce the cost.

The volume of tracer solution should be appreciably increased at each location used in the test, especially if the test is conducted during dry soil conditions. A larger volume will allow more complete saturation of the soil immediately below the application location so that the tracer solution can enter the shallow ground water and meet the objectives of the tracer test, i.e., to determine the interconnection between the shallow, perched ground water and the deeper, limestone aquifer. The larger volume has the added advantage of a more dilute tracer solution that will affect the permeability of the soil less due to lower concentrations of the cation in the tracer salt. An alternative method of introducing the tracer solution is infiltration through a hole augered more deeply into the soil; this would allow more direct access of the tracer to the shallow ground water.

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