

Experimental Investigation to Limit Trihalomethane Production

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The Southern Nevada Water System (SNWS) operates two facilities that treat water from Lake Mead on the Colorado River and provide over 90 percent of the municipal supply to purveyors within the Las Vegas Valley. One purveyor, the Las Vegas Valley Water District (LVVWD), conducts the nation's largest deep-well aquifer storage and recovery (ASR) program, which since its inception in 1987 has placed over 330,000 acre-feet of water into the Valley's primary producing aquifers. Both SNWS and LVVWD routinely monitor water quality parameters including trihalomethanes (THMs).

THMs form through the reaction of dissolved organic matter (DOM) and/or bromide with hypochlorite ("chlorine" or "free chlorine"). For Lake Mead water, the reactions are 90 percent complete within about five days. The principal controls on total THM (THM4) levels include DOM and chlorine concentrations, contact time, pH, and temperature. Ozonation during treatment eliminates some DOM but enough remains that the THM4 concentration triples during the two- to three-day transit time between the treatment facility and the ASR wellhead.

Three Treatments Tested

In November 2005, we performed a bench-scale experiment to test selected chemical treatments that degrade free chlorine in the presence of aquifer lithic material. The experiment was part of a proactive effort to develop field-scale treatment methodologies to limit THM formation in aquifers following ASR injection. Three treatments—sodium thiosulfate, ammonium hydroxide, and hydrogen peroxide—were chosen based on reaction rate, safety, ease of handling, availability, and cost. Hypothesized chemical reactions between hypochlorite

and each treatment compound were used to define stoichiometry and estimate the required amount of reagents. In SNWS injectate, these compounds

Hydrogen peroxide and sodium thiosulfate treatments appear to neutralize free chlorine in delivery system water at rates sufficient to allow their use at ASR injection wells.

would likely be innocuous. At low concentrations, hydrogen peroxide and sodium thiosulfate both exhibit no toxicity. Some utilities use ammonia to produce chloramines as disinfectants for drinking water. Moreover, reaction with chlorine would eliminate the treatment compounds at time scales comparable to transit time down an injection well. Little or none would enter the aquifers.

The experiment consisted of two components. The first measured the chlorine destruction rate for four stoichiometric proportions of each treatment. The second measured THM4 concentrations in treated and untreated samples after different incubation periods under conditions similar to those encountered by ASR water in the valley's aquifers.

Sample Collection and Treatment

Initially, a 20-liter bladder was filled, and free chlorine measurements were taken at a sampling tap that had a delivery system hydraulic residence time similar to that of many ASR wells. To prevent hypochlorite photolysis and to maintain temperature, the bladder was placed in an opaque cooler

and transported to the SNWS analytical laboratory. A control sample was taken, and 13 1,000-ml bottles were filled from the bladder and placed in a separate cooler. Stoichiometric proportions of 50, 75, 100, and 150 percent of each treatment were then added to individual bottles.

After one minute of agitation, we measured the free chlorine concentration in each bottle, placed some of the water in 60-ml bottles containing lithic fragments, and returned the bottles to the container. The lithic material consisted of drill cuttings (primarily limestone and dolomite) archived from the screened intervals of four ASR wells. Previously, the cuttings had been sieved at 100 mesh, both to emulate the coarser aquifer material that is present around a developed well and to minimize entry of fine particulates to the analytical apparatus. Control samples for each treatment without lithic material were prepared at approximately 100 percent of the concentration required to degrade all free chlorine. At intervals, colorimetric measurements were made of free chlorine in the bottles and in the bladder. The filled bottles were incubated under lightless conditions for periods of 1, 2, 7, 14, 21, and 49 days at 16 degrees Celsius, which approximates the average ASR injection temperature.

Results: Hypochlorite Decay

The upper chart at right illustrates the hypochlorite decay for different stoichiometric proportions of hydrogen peroxide. Irrespective of concentration, the reaction progressed substantially within about four minutes, and was essentially complete after eight to 20 minutes. Comparable reaction rates were obtained with sodium thiosulfate, but ammonia treatments required more than twice as long to achieve

similar reduction of hypochlorite. At short times, greater stoichiometric proportions of all treatments resulted in greater free chlorine neutralization. At longer times, the distinction among stoichiometric proportions could not be determined because the limit of free chlorine detection had been reached.

For each incubation period, the THM4 concentration in an untreated control blank matched the formation potential for system water, and was thus assumed to represent the maximum THM4 produced in typical ASR water. The center chart plots the ratio of THM4 concentration to THM4 in the control blanks against incubation time for three treated samples with no lithic material and one untreated sample with lithic material. The minimum ratio shown is about 50 percent because THMs were present in the original tap sample.

At approximately one stoichiometric equivalent, both hydrogen peroxide and ammonium hydroxide essentially eliminated THM production in samples containing no lithic material. Similarly, sodium thiosulfate at a calculated 33 percent equivalent inhibited roughly half of the potential THM. This apparent disproportion is because more than one reaction between thiosulfate and hypochlorite is possible. The results indicated that neutralization of free chlorine will prevent THM genesis, which is consistent with published studies and previous SNWS investigations.

Lithic Fragments Cause Unexpected Results

Additionally, the lower chart shows that the presence of

drill cuttings in an untreated sample prevented THM formation, probably due to lithic chlorine demand. This result was unexpected because no such effect had been observed in ASR wells. The cause of the lithic chlorine demand is unclear, but investigations tentatively indicate an association with the finer-grained fraction of the cuttings. Either bacterial

growth during archival storage or residual drilling agents may be responsible.

Another unanticipated result is illustrated in the lower chart. For the hydrogen peroxide treatment, the ratio of THM4 produced relative to its formation potential rapidly stabilized at approximately 50 percent for the control sample without lithic material, but declined even further when lithic fragments were present. This indicates that over time the THM4 concentration continued to decrease below that of the initial sample – more so at higher treatment proportions. Similar though less pronounced effects occurred using ammonium hydroxide and sodium thiosulfate. Presently, the cause of the decline is conjectural and not clearly attributable to THM biodegradation. ASR sample data will be reviewed to determine whether this behavior can be identified at field scale.

Results Show Promise for ASR

The bench-scale experiment suggests that hydrogen peroxide and sodium thiosulfate treatments neutralize free chlorine in delivery system water at rates sufficiently rapid to allow their use at ASR injection wells. The degree of neutralization roughly equates to the stoichiometric proportion of treatment used, and similarly limits production of THM. The presence of drill cuttings inhibited THM formation and produced anomalous THM declines in a manner not yet observed in wells. We hope that these results may aid others' efforts to reduce THM genesis and encourage further experimentation at ASR sites.

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