ON THE COVER—This photograph shows a vein of massive barite in Archean syenite on the shore of Browning Lake, near Matachewan, Ontario. The barite was mined for use in drilling mud and as an extender in paints and other applications. Barite veins are common in the Matachewan area, and are general perpendicular to fault-controlled lakes. Glacial erosion (right to left) has eroded a depression in the soft barite on top of the hill. Barite ore (white) is stockpiled in the foreground in front of the adit. Photograph by Bob Stewart, CPG-8332, summer 1984
ASR Using Sodium Bisulfide Treatment for Deoxygenation to Prevent Arsenic Mobilization

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Abstract

This paper summarizes a portion of the information presented at the joint September 2010 AIPG/AGWT conference held in Orlando, Florida. The discussions in this paper address three topics: 1) the observed variations in arsenic mobilization that have occurred within Florida; 2) methods that have been introduced to minimize arsenic mobilization; and 3) the use of sulfides (as HS\(^{-1}\) or S\(^{-2}\)) to prevent the mobilization of arsenic at a site in DeLand, Florida.

Keywords:
ASR, aquifer recharge, arsenic, trace metals, mobilization, sulfides, NaHS

Introduction

Aquifer Storage and Recovery (ASR) is the term used to describe the injection of water into a subsurface aquifer for storage during periods when water is available and recovery at a later date when water is less available. An example of an ASR cycle in Florida would be the injection of 100 million gallons (MG) of water at 1 million gallons per day (mgd), followed by a storage period of one to four months. At the end of this period, when surface water resources are reduced due to lack of rain, the water is recovered as needed or to a water quality limit such as 250 mg/l chloride, the current drinking water standard.

The ability to store and recover water below the surface resulted in the implementation of numerous ASR projects in Florida over the last three decades as more and more utilities grew concerned about growing needs and dwindling supplies. ASR technology offers the ability to store potable water, partially treated surface water, and reuse water from waste water treatment plants without the need to develop above-ground storage facilities.

By regulation, all water stored in the subsurface must meet primary drinking water standards when it is injected into an aquifer defined to be an underground source of drinking water (USDW) by the US Environmental Protection Agency (EPA). A USDW is defined as an aquifer containing less than 10,000 mg/l total dissolved solids (TDS). The Federal regulations also require that the injected water not cause changes in the native formations which would result in concentrations of regulated chemicals to exceed primary drinking water standards or exceed native formation water quality if the concentrations in the native formation water exceed primary drinking water standards for a given parameter.

As the number of ASR projects increased in Florida and around the country, additional water analyses were required by the regulating bodies to further establish water quality in the injected and recovered water. Additional monitoring of arsenic levels was required between 2000 and 2004 since the EPA planned to lower the primary drinking water standard for arsenic from 50 ug/l to 10 ug/l. The new rule went into effect on January 1, 2005 in Florida and January 1, 2006 nationally. Early reviews of thirteen ASR sites indicated that arsenic levels in recovered water commonly exceeded the regulatory standard of 10 ug/l during the first cycle, but that arsenic levels often dropped below the 10 ug/l limit during additional cycles (Pyne et al; 2004). This information was based on the review of twelve ASR sites in Florida. As arsenic monitoring continued after 2006, it became clear that arsenic was a continuing problem at some sites in Florida (Llewellyn, 2008). In order to fundamentally address the arsenic issue, entities tied to the water resource industry in Florida began reviewing the literature for a broader understanding of the source of arsenic mobilization and the development of treatment alternatives where they were needed. The work by Stuyfzand (1998) showed that arsenic mobilization within subsurface aquifers is closely associated with the injection of oxygenated water into anoxic aquifers containing pyrite. Unfortunately, this observation is not sufficient to explain the different behaviors manifested by arsenic mobilization at different sites. The observed behavior of mobilized arsenic varies between sites as enumerated below: 1) The maximum measured concentration of arsenic observed during recovery at different ASR wells varies. Initial arsenic concentrations range from below the detection limit of 3 ug/l to more than 90 ug/l; 2) The point during recovery when the maximum arsenic concentration is observed at ASR wells during cycle recovery varies. At some sites, the maximum arsenic level occurs in the first few samples at the start of recovery. At other sites, the maximum value is reached at the end of recovery. A third observed type of behavior is represented by sites where the maximum arsenic level occurs at an intermediate point during recovery. 3) A third difference between sites is how arsenic concentrations vary during recovery. At some sites, arsenic concentrations decline rapidly during recovery and do not exceed regulatory levels during additional cycles. At other sites, little arsenic is recovered during the initial recovery cycle. However, arsenic levels start low at the start of additional cycles, but increase with recovered cycle volume. Finally, at one site, the arsenic level during the first cycle increased at the very start of each recovery from an initial low of approximately 90 ug/l on the first cycle to a record high of almost 900 ug/l on the third cycle. At this site, arsenic concentrations declined to a steady level between 60 to 100 ug/l during the remaining stages of each recovery. Also, over 2.5 times the volume of water
stored in the aquifer was required to be recovered before arsenic levels fell below 3 ug/l at this site. The varied behavior observed for arsenic mobilization suggests that there are multiple reaction pathways operating even though the dissolved oxygen content in the injected water and the arsenic content and location of the arsenic within the formations are similar. If it is assumed that the reaction rate associated with the basic reactions are likely similar, then the variation in arsenic concentrations and behavior is most likely associated with different formation flow properties such as flow paths (heterogeneous versus homogenous) and dispersivity, injected water quality (presence or absence of organic materials), and other parameters that are more easily conceptualized than demonstrated.

Based on site-specific circumstances and the insights provided by Stuyfzand (1998), the water resource industry began to address arsenic mobilization following four different approaches that were partially dependent on the site. For sites where arsenic did not rise above regulatory standards, additional monitoring was required. For sites where arsenic was continuing to experience arsenic at elevated levels, additional cycles were undertaken and additional monitoring wells were sometimes required. These sites appear to be operating under the assumption that arsenic could be completely leached from the formation after an unspecified number of cycles (CH2MHill, 2007). The third approach was designed to remove the dissolved oxygen from the water using a membrane technology (Kohn, 2009) or catalytic removal using hydrogen and a palladium catalyst (ENTRIX, 2009). Finally, a fourth approach was undertaken in response to the difficulties encountered by the membrane and catalytic treatments. The fourth treatment method was based on the addition of sulfides (HS\(^{-}\) and S\(^{-}\)) in the form of sodium bisulfide (NaHS), since the NaHS could both react with dissolved oxygen and could chemically oppose the dissolution of pyrite (Pearce and Waldron, 2010).

**Prevention Of Arsenic Mobilization**

**Natural Attenuation**

Natural attenuation is likely associated with the formation of iron oxyhydroxides that adsorb and bind arsenic, and is likely represented by those sites where arsenic levels fall below regulatory limits within a few cycles. In the absence of sulfide ions or other ions capable of reducing the iron, it is likely that the arsenic will remain trapped within these oxides (Pearce, 2005).

**Leaching Process**

It has been suggested that the arsenic in a formation may be removed completely by leaching arsenic from a formation using multiple ASR cycles and high oxidant concentrations (CH2MHill, 2007). This expectation appears unlikely. As an example, the Florida Department of Environmental Protection (FDEP) has estimated that an average concentration of arsenic in Florida’s aquifer matrices utilized for storing water is on the order of 3 mg/kg of formation (Haberfeld, 2009). Further, the bulk, if not all, appears to be bound in the pyrite located within the matrix pore spaces (Price and Prichler 2005). A simple mass balance analysis shows that 12 billion gallons of water would need to be cyclicly through an aquifer to remove all of the arsenic from a pore volume of 100 million gallons assuming that the concentration of arsenic in the recovered water remains constant at 50 ug/l and that the formation contains 3 mg of arsenic per kg of formation (Pearce and Waldron, 2010). The potential to leach all of the arsenic from a formation based on this analysis appears to be an unrealistic expectation.

**Physical Methods for Removing Oxygen**

In the event that either arsenic levels do not fall below regulatory levels in the recovered water after a few ASR cycles, or the performance of several cycles does not appear to be a viable approach for minimizing arsenic mobilization at a given site, then it is reasonable to expect that other methods for limiting arsenic mobilization would be reviewed. Since oxidants in the injected water appear to play a major role in arsenic mobilization, then methods designed to remove the oxidants from the injected water might be expected to reduce the amount of arsenic that may be mobilized at new sites or sites experiencing continued elevated arsenic concentrations. A brief review of generally available information indicates there are two physical systems available to remove oxygen from the injected water. These methods include: 1) nitrogen de-gasification systems to remove oxygen from water as used by the off-shore oil and gas industry; and 2) a membrane de-gasification system as used by the food and beverage industry, the semiconductor industry, and other industries including those concerned with corrosion due to dissolved oxygen. Although both methods can successfully remove oxygen to very low levels, cost and operational issues must also be considered.

The nitrogen de-gasification system was reported to cost approximately $1,000,000 in capital equipment for the construction of a 1-MGD system (Pearce, personnel communication from vendor, 2005). This cost was considered beyond the budget tolerance of most utilities for this type of system and was not pursued. The membrane system provided by Membrana, Inc. to remove oxygen appears to provide adequate oxygen removal, but suffers from plugging of the membranes (Kohn, 2009).

**Chemical Removal of Oxygen Using Sulfide**

Due to the capital costs and operational issues associated with the previously mentioned treatment options, a sulfide treatment was developed for recharge water based on the following principles: 1) As indicated by Reaction 1 provided below, sulfides and oxygen can react to form sulfate ions. Therefore, the introduction of sulfides into the injected water would diminish the amount of oxygen available to react with pyrite in the target storage formation; and 2) Sulfides provide a second line of defense against arsenic release in anoxic aquifers as indicated (Reaction 2). In this case, sulfides are able to suppress the dissolution of pyrite based on Le Chatelier’s principle of equilibrium.

\[
\begin{align*}
1) \quad & \text{HS}^{-} + 2\text{O}_2 \rightarrow \text{H}^{+} + \text{SO}_4^{2-} \\
2) \quad & \text{FeS}_2 + 1.75 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 1.75 \text{HS}^{-} + 0.25 \text{SO}_4^{2-} + 0.25 \text{H}^{+}
\end{align*}
\]
Reaction 2 also represents the natural equilibrium condition in the subsurface involving sulfides, sulfates, iron, pH, and pyrite.

In order to evaluate the ability of sulfides to prevent the mobilization of arsenic, it is relevant to review the potential pathways leading to the release of arsenic within the subsurface and to establish a reaction rate between sulfides and dissolved oxygen within the injected water. Reaction 3 provides an indication of the chemical reactions occurring in the subsurface when oxygenated water is introduced into a formation containing pyrite.

3) \[4 \text{FeS}_2 + 14 \text{H}_2\text{O} + 15 \text{O}_2 \rightleftharpoons 4 \text{FeO(OH)} + 8 \text{SO}_4^{2-} + 16 \text{H}^+\]

Arsenic bound to pyrite \[\rightleftharpoons\]
Arsenic bound to FeO(OH)

It is instructive to note that the iron in the above equation is oxidized from the +2 oxidation state to the +3 oxidation state (Usher et. al, 2004), whereas, the written reaction between dissolved oxygen and pyrite often suggests that only the sulfides in pyrite are oxidized during this reaction (Price and Pichler, 2005).

A secondary reaction that is indicated immediately below Reaction 3 is that arsenic, which is bound to the pyrite as a trace metal, is oxidized and then adsorbed by the iron oxyhydroxide formed during the reaction of pyrite with the oxygen. In this reaction, the arsenic is unlikely to be mobilized to any significant extent if the reaction occurs within a zone where the water is not moving rapidly (flow through a porous media). However, in zones of fast moving water such as along fractures, arsenic may not have time to bind to the newly formed iron oxyhydroxides. Reaction 4 illustrates the reaction that occurs during groundwater recovery when naturally occurring sulfides in the native water contact the iron oxyhydroxide formed during the injection of water containing dissolved oxygen.

4) \[8\text{FeO(OH)} + 9\text{HS}^- \rightleftharpoons 8\text{FeS} + 8\text{SO}_4^{2-} + 5\text{H}_2\text{O} + 7\text{OH}^-\]

Arsenic (trace in FeO(OH)) \[\rightleftharpoons\] Arsenic (Mobilized)

In this case, the sulfides in the native water react with the iron oxyhydroxides to produce iron sulfide. As the iron oxyhydroxides are reduced by the sulfides, the formerly bound arsenic moves into solution (Fendorf and Tufano, 2008).

**Performance Of A Test Sulfide Injection System**

When the catalytic process failed to produce positive results for deoxygenating the water in the mini-test, the SJRWMD was interested in pursuing other options for preventing arsenic release. At this point, Cardno-ENTRIX (2009a), proposed the use of sulfide compounds (NaHS or other soluble Group I or Group II metals) to prevent arsenic mobilization based on preliminary testing and theoretical concepts for deoxygenation that they had been evaluating.

The basic premise was that the addition of low concentrations of sulfides would make the injected water more chemically similar (chemical and oxidation/reduction conditions) with the native water in the target storage zone. In turn, the sulfides would prevent or limit the formation of iron oxyhydroxides and therefore limit arsenic mobilization.

Two major technical issues needed to be evaluated under field conditions to confirm that sulfides would limit arsenic mobilization. The required information concerned the kinetic reaction rate between sulfides and dissolved oxygen and the actual attenuation of arsenic mobility under operating conditions. The first step was to perform a pilot test to evaluate the chemical rate of reaction.

**Reaction Kinetic Testing**

The rate of dissolved oxygen depletion in the presence of low concentrations of sulfides was investigated using an approximate 300-gallon system with four sampling ports. The flow rates through the system were set at 0.5, 1.0, and 2.0 gallons per minute (gpm), which equate to retention times of 600, 300, and 150 minutes. Oxidation/Reduction potentials and oxygen concentrations were measured for samples recovered from four sampling ports. The ports were located just prior to the introduction of sulfides, just after the introduction of sulfides, after 150 gallons of system volume, and at the end of the 300-gallon pathway (Pearce and Waldron, 2010).

Although somewhat crude, the data, as presented in Figure 1, suggest that the decline in dissolved oxygen follows first order kinetics with a half-life of approximately 2 hours. The data also indicated that the half-life may be significantly lower in the presence of limestone. However, since the limestone was not characterized, such a conclusion would be premature (Pearce and Waldron, 2010).

The conclusions that were drawn, based on the kinetic results for the decline of dissolved oxygen, were: 1) sulfides react to remove dissolved oxygen; 2) the reaction is not sufficiently rapid to prevent dissolved oxygen from entering the formation; and 3) dissolved oxygen will be reduced to insignificant levels within 24 hours after entering the formation based on the reaction half-life of 2 hours at a sulfide concentration of 6 mg/l in the absence of any formation material.

The oxidation reduction potential (ORP) data were somewhat clearer. Prior to the addition of sulfides, the ORP values were greater than 100 millivolts (mv). However, immediately after the sulfides were added, the ORP value dropped to below -250 mv even though the dissolved oxygen concentration had not changed (Pearce and Waldron, 2010). These results show that ORP values do not represent the final chemical environment of the water at equilibrium or the actual ORP level that will exist once equilibrium is reached.

**Mini Pilot Testing**

Based on the favorable results from the kinetics testing, the SJRWMD approved the construction and testing of a full-scale sodium bisulfide (NaHS) injection system at the DeLand Florida site. The NaHS storage and chemical feed building was installed with secondary containment and simple metering equipment to control the NaHS concentration in the injected water.

After the installation of the NaHS handling equipment, several mini pilot tests were performed by injecting water into the target ASR storage zone while varying the sulfide concentration for each test. In order to establish a base line, two mini-tests were performed without treating injected water with NaSH, two mini tests were performed using 2 ppm NaHS in the injected water, and two mini cycles were performed using 6 ppm NaHS. Finally, the last two test cycles, 7 and 8, were performed using 4 ppm NaHS. Cycle 7 was completed using an injected volume of 750,000 gallons and the 8th cycle was performed using 5 million gallons. Testing results are provided in Table 1.

The data in Table 1 show that more arsenic was mobilized when no sulfides were introduced than occurred when...
sulfides were introduced. It is recognized that the arsenic levels in the cycles that were not treated with NaHS remained below the regulatory limit, but it should be recognized that the cycle volumes were small and were only utilized to provide some insight into the potential for arsenic release at this site. Overall, the data indicated that sulfides could minimize arsenic mobilization and that further testing was warranted.

It is also relevant to note that the potential for capturing high levels of arsenic in the iron hydroxides, by injecting a large volume of water prior to running the testing with sulfides, warranted the use of lower volumes in the mini-cycles. It is worth noting that the stoichiometric concentration for the removal of oxidants was approximately 3.3 to 3.5 mg sulfides per liter of injected water.

### Preliminary Large Scale Testing

Based on the success of the mini scale and 5-MG cycle testing, a preliminary large-scale test was performed. This test was designed to inject, store and recover 20 MG. The results of 20 MG test are also presented on line 9 of Table 1. It should be specified that the high value of 1.3 ug/l arsenic observed in this test was recorded in the initially recovered sample. No other samples indicated the presence of arsenic at concentrations above the detection limit of 0.5 ug/l.

### Conclusions

Based on the data obtained during the testing performed during this project and presented in Table 1, it is reasonable to conclude that the addition of sulfides can limit the potential to mobilize arsenic during ASR and aquifer recharge projects.

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