

ADDRESSING THE MOBILIZATION OF TRACE METALS IN ANAEROBIC AQUIFERS

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REFERENCE: *Proceedings of the 2011 Georgia Water Resources Conference*, held April 11–13, 2011, at the University of Georgia.

Abstract. The mobilization of trace metals such as arsenic during Aquifer Storage and Recovery (ASR) activities has hindered the growth in the implementation of ASR technology. A discussion of this issue is provided that outlines the manner in which arsenic is mobilized within the subsurface, methods that have been proposed or implemented to minimize arsenic mobilization, and a more robust chemical solution that reduces or eliminates the mobilization of arsenic in anaerobic aquifers. The chemical solution is designed to prevent the dissolution of pyrite based on Le Chatelier's Principle and the reaction between dissolved oxygen and sulfides. Finally, the discussion will address the operational and cost effectiveness of this process.

INTRODUCTION

While conducting aquifer storage and recovery (ASR) or aquifer recharge projects, it has been observed that the concentration of trace metals such as arsenic have increased above regulatory standards at some sites. The injection of water containing dissolved oxygen (DO) and other oxidants into anaerobic aquifers containing pyrite has been identified as the cause (Stuyfzand, 1998). The mobilization of trace metals in aquifers that are potential sources of drinking water has raised regulatory concerns throughout the country (Llewellyn, 2008). Many groups have studied the cause and extent of mobilization, and have developed pilot programs designed to prevent the mobilization of these trace metals during ASR operations. The proposed and implemented methods include: 1) running large numbers of recharge and recovery cycles in anticipation that arsenic levels will eventually fall below regulatory levels (CH2MHill, 2007); 2) removal of DO prior to recharge

(Kohn,2009); 3) catalytic removal of oxygen (Entrix, 2009), or 4) chemical removal of DO while chemically opposing the dissolution of pyrite by adding sulfides (sodium bisulfide, NaHS) to the injected water (Pearce et al, 2010).

It is important to note that arsenic in the recovered water is not the critical issue since arsenic can be removed at the surface after injected water is recovered. The critical issue is the mobilization of arsenic at levels above the drinking water standard in an aquifer deemed to be an underground source of drinking water (USDW). The increase of the arsenic or other trace metal concentrations above the drinking water standard in an USDW is a violation of EPA regulations, whether or not the mobilization poses a threat to human health and the environment (Llewellyn, 2008).

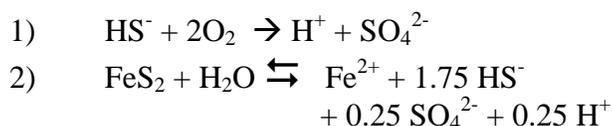
Arsenic Minimization Using Multiple Cycles of Injection and Recovery. Early data from ASR sites indicated that arsenic mobilization was only temporary and that arsenic concentrations declined below regulatory levels after only a few cycles of injection, storage, and recovery (Pyne et al, 2004). Based on the reduction in arsenic concentrations over only a few cycles at some sites, the concept was formulated that arsenic could be readily leached from an ASR storage zone. Simple calculations show that this expectation is unlikely (Pearce et al, 2010) if formation arsenic concentrations approach mg/l levels.

Physical and Catalytic Methods for the Removal of Oxidants. A brief review of systems designed to remove DO from water prior to injection shows that most methods suffer from either high cost or operational issues. A membrane degassing system, which, is currently being tested in Florida suffers from issues that cause membrane plugging

and potentially higher than anticipated operating costs (Kohn, 2009).

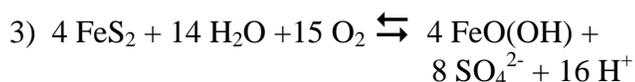
Catalytic removal of dissolved oxygen from injected water using a palladium surface and hydrogen gas was investigated in a pilot test program. The initial test results indicated that the oxygen removal efficiency of the palladium catalyst, although initially high, declined rapidly. These tests, which were performed for the Saint Johns River Water Management District (SJRWMD) and the City of DeLand Florida, did not indicate long-term reliability at this time ENTRIX, 2009).

Sulfide Treatment Method. The sulfide treatment method is based on the following principles. First, as indicated in Reaction 1, sulfides and oxygen are known to react with each other to form sulfate ions. Thus, the sulfides are able to remove the oxidants from solution. Sulfides also provide a second line of defense against trace metal release in anaerobic aquifers as indicated by Reaction 2. In this case, sulfides are able to suppress the dissolution of pyrite based on Le Chatelier's principle of equilibrium. Although there are many chemicals that can be added to remove DO, only sulfides provide the added benefit of resisting pyrite dissolution at low dosages.



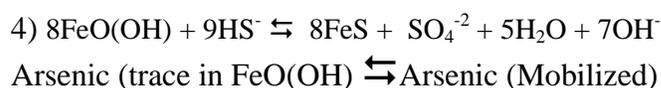
Reaction 2 also represents the natural equilibrium that occurs in the subsurface between sulfides, sulfates, iron, pH, and pyrite.

In order to evaluate the ability of sulfides to prevent arsenic from being mobilized, it is relevant to review the potential pathways leading to the major 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 after the introduction of oxygen into a native formation.



A secondary reaction that is indicated below Reaction 3 is that arsenic, which is bound to pyrite as a trace metal, is oxidized and then adsorbed by the iron oxyhydroxide formed during the reaction of pyrite with oxygen. In this case, arsenic is not mobilized to any significant extent if the reaction occurs within a zone where the water is not moving rapidly (flow through a porous media).

Reaction 4 occurs when sulfides contact iron oxyhydroxide during recovery as water, mixed with formation water, approaches the wellbore.



In this case, sulfides react with iron to produce iron sulfide, which allows arsenic to move into solution (Fendorf et. al. 2008) .

Sulfide and Oxygen Reaction Kinetics. The rate of dissolved oxygen depletion in the presence of low concentrations of sulfides was investigated using laboratory size samples (1 liter volumes) followed by testing using an approximate 300 gallon system with four sampling ports. The laboratory tests were performed by adding approximately 6 ppm sulfides as NaHS to one liter of tap water containing DO. The DO levels and the Oxidation/Reduction Potential (ORP) values were monitored for a period of 12 to 16 hours using standard field meters. For the 300 gallon system, flow rates through the system were set at 0.5, 1.0, and 2.0 gpm, which equate to retention times of 600, 300, and 150 minutes. ORP and DO 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. 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 lower in the presence of limestone. However, the

limestone was not characterized or conditioned sufficiently to allow for such a conclusion.

The conclusions that can be made, based on the kinetic results for the decline of DO, are that: 1) sulfides react to remove DO; 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 with the sulfides alone.

The 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 -280 mV even though the DO concentration had not changed. These results show that ORP values may not represent the final chemical environment of the water at equilibrium or the actual ORP level that will exist once equilibrium is established.

Mini Pilot Testing of Sulfide Pretreatment. The next phase in the evaluation of the sulfide chemistry was to run several mini pilot tests by injecting water into a target ASR storage zone while altering the sulfide concentration for each test. The testing was accomplished during start up of a new, potable water ASR system for the City of DeLand, Florida. In order to establish a base line, two mini tests were performed without treating with sulfides, two mini tests were performed using 2 ppm sulfides, and two mini cycles were performed using 6 ppm sulfides. Finally, the last two test cycles, 7 and 8, were performed using 4 ppm sulfides. 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.

Table 1. Mini Test Results

Test Run	Cycle Volume (gal)	Sulfide Concentration (mg/l)	Average Arsenic Concentration in Recoverd Water (ug/l)	Maximum Arsenic Concentration (ug/l)
1	214000	0	7.20	8.40
2	220000	0	6.00	7.30
3	336000	2	4.90	6.00
4	336000	2	2.55	4.50
5	336000	6	1.90	3.20
6	104000	6	1.68	2.00
7	750000	4	0.90	1.28
8	5,000,000	4	0.56	0.78
9	20,000,000	3.2	<0.5	1.30

The data in Table 1 show that more arsenic was mobilized when sulfides were not introduced than occurred when sulfides were introduced. It is recognized that the arsenic levels in the cycles that were not treated with arsenic 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.

Because of the potential that high levels of arsenic might be captured in the iron hydroxides that would be formed due to the injection of oxygenated water, only small volumes were used in the mini-cycles. It is also worth noting that the stoichiometric concentration for the removal of oxidants from the DeLand potable water ranged between 2 and 3.5 ppm sulfides.

Preliminary Large Scale Testing. Based on the success of the mini scale tests and the 5-MG cycle test, a preliminary large scale test was designed. This test was designed to inject, store, and recover 20 MG. The results of 20-MG test are also presented in Table 1, line 9. The highest arsenic concentration measured during this test was 1.3 ug/l at the beginning of recovery. All other recovered water samples did not indicate the presence of arsenic at concentrations above the detection limit of 0.5 ug/l.

Estimated Implementation and Operating Costs: Since the use of sulfides is in the early stag-

es of testing, only approximate capital and operating costs are provided. The basic capital costs are associated with operating a small metering pump capable of pumping at a rate of 10 to 30 gallons per day, a covered or ventilated storage area in which to store the liquid sulfide material (NaHS), and safety equipment, such as safety showers, alarms, and spill containment, and metering equipment to control sulfide injection rates. The cost of this equipment, depending on the site is estimated to fall between \$150,000 and \$450,000.

Operating costs, including operations and maintenance, chemical, and chemical transport is estimated to range between \$0.20 and \$0.30 per 1000 gal or \$20,000 to \$30,000 per 100 million gallons of water stored. For sites injecting larger volumes, it is likely that operating costs could be significantly lower per 1000 gallons, while there would be little change in the capital cost.

CONCLUSIONS

Based on the data obtained during the testing performed during this project, it is concluded that the addition of sulfides to injected water can limit the arsenic mobilization to levels that remain far below regulatory requirements. It is also relevant to note that no significant problems were encountered while implementing this treatment approach with the exception that the recovered water contained low levels of residual sulfides. Although recovered iron levels were in the 0.6 to 0.8 ppm range and mimic native aquifer concentrations, an additional test is currently being conducted to develop a deeper understanding of the higher than anticipated iron levels.

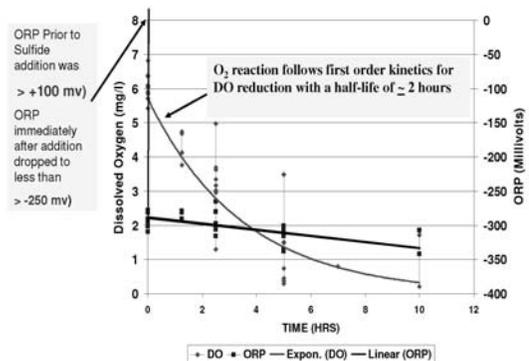


Figure 1: Dissolved oxygen and ORP levels measured during DeLand de-oxygenation testing.

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