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Aquifer pre-oxidation using permanganate to mitigate water quality deterioration during aquifer storage and recovery

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ABSTRACT

Water quality deterioration is a common occurrence that may limit the recovery of injected water during aquifer storage and recovery (ASR) operations. This limitation is often induced by the oxidation of the reduced aquifer components by the oxygenated injection water. This study explores the potential of aquifer pre-oxidation using permanganate to improve the quality and volume of the recovered water during ASR. An experimental ASR column setup was developed to simulate the oxygenated water injection and recovery cycles. Undisturbed sediments from an anoxic brackish aquifer at a pilot ASR site were used. A series of 4 conventional ASR cycles injecting oxygenated tap (drinking) water was initially performed. These experimental trials showed a persistent Mn(II) production due to the dissolution of a Mn-containing carbonate that was triggered by pyrite oxidation reactions, as shown by the observed sulfate production. The rise in the Mn(II) concentrations above the drinking water standards would limit the recovery to 15–30% of the injected water without treatment of the recovered water. To a lesser extent, arsenic production resulting from the oxidative dissolution of pyrite posed a water quality threat to the ASR operation. Consequently, a second series of experiments was performed with an oxidation cycle using a dilute (5%) potassium permanganate ($KMnO_4$) solution, aimed at deactivating the reactive phases responsible for the acidity-triggered Mn(II) production. This pre-treatment cycle improved the net recovery ratio to 84% during a conventional ASR cycle using oxygenated tap water. The extent of pyrite oxidation was decreased by 63% after the permanganate treatment. The increased competition for oxygen by the adsorbed Fe(II) and Mn(II) on the newly precipitated Mn-oxides combined with the pyrite "deactivation" by removal of the most reactive iron-sulfide crystals during the permanganate flush were primarily responsible for the observed decrease in the pyrite oxidation. The stability of the Mn-oxide precipitates was tested by flushing the columns with native groundwater before performing a final ASR cycle, simulating an increase in the reducing conditions during static periods in the ASR system. The Mn-oxide reduction by ferrous iron in the native groundwater released substantial amounts of Mn(II), which adversely affected the ASR operation in the subsequent cycle. In these cases, repeating the permanganate treatment should be considered.

1. Introduction

Aquifer storage recovery (ASR) is a water resource management tool used to balance the water supply with the demand. During periods of excess water supply, water is injected and stored in an aquifer for subsequent recovery and use in times of water demand (Pyne, 2005). ASR can result in water quality improvements, including denitrification, biodegradation of organic micropollutants, such as chlorination byproducts (Pavelic et al., 2005) and pharmaceuticals (Overacre et al., 2006), and removal of pathogens (Page et al., 2010). However, water quality deterioration may also occur during ASR, for example, when oxygenated (surface) water is injected into an anoxic environment containing reactive phases, such as pyrite, carbonates and sedimentary organic material (SOM). The water quality may further deteriorate during an extended storage or recovery phase due to the migration of the stored water or due to the reducing conditions triggered by anaerobic degradation of the organic material (Vanderzalm et al., 2002; Stuyfzand et al., 2005). This process may result, at least during the initial ASR cycles, in elevated concentrations of released Fe(II), Mn(II), arsenic and other trace elements, such as nickel and cobalt (Stuyfzand, 1998; Pyne,

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2003). These elevated concentrations may limit the recovery efficiency of each ASR cycle, defined as the percent recovery by volume (Pyne, 2005).

Arsenic release from pyritiferous aquifer material during ASR is problematic at well fields in different parts of the world (Stuyfzand, 2001; Mirecki, 2004; Price and Pichler, 2006; Arthur et al., 2007; Jones and Pichler, 2007; Vanderzalm et al., 2007; Stuyfzand and Pyne, 2010). Persistent manganese release, typically derived from the dissolution of carbonates, has also been observed during ASR operations (Ibison et al., 1995; Pyne, 2005; Antoniou et al., 2012). A common aspect of these studies has been that the manganese mobility was influenced by the pH, which controlled the solubility of a Mn-containing siderite. Chronic exposure to manganese in drinking water above the WHO guideline of 7.3 μmol/L (WHO, 2011) may have neurological effects. Concentrations above the aesthetic guideline of 0.91 μmol/L are related to a water color that is black to brown, black staining, and a bitter metallic taste (USEPA, 2009). The removal of Fe(II) and Mn(II) requires further treatment of the recovered water, thus increasing the costs of the ASR system operation. Conventional treatment techniques for the removal of iron and manganese during drinking water production include aeration and rapid sand filtration, occasionally supported by chemical oxidation and sedimentation (Buamah, 2009).

To minimize the negative effects of the aquifer reactivity on the water quality, oxygen removal prior to injection has been attempted. Physical removal using a membrane degassing system has been tested in Florida but suffered from high costs and operational issues (Kohn, 2009). Catalytic removal of dissolved oxygen from the injected water using a palladium surface and hydrogen gas has not shown long-term reliability (ENTRIX, 2009). Pearce and Waldron (2010) have successfully limited arsenic production during ASR by the addition of hydrosulfide ($NaHSO_3$ and NaHS) in the injected water and the chemical removal of the dissolved oxygen. However, the addition of hydrosulfides resulted in significant iron production during ASR cycle testing, and the system is currently inactive. Moreover, oxygen removal from the injection water is a process that must be repeated prior to every ASR cycle.

Rather than removing oxygen and possibly other electron acceptors (notably NO_3) from the water prior to the ASR injection, extensive pre-oxidation of the aquifer to remove or inactivate the reactive phases might prevent or decrease the water quality deterioration during the ASR operation. This approach is based on evidence that water quality deterioration, especially regarding iron, diminishes with successive cycles (Pyne, 2005; Antoniou et al., 2012). In this approach, the injection water is enriched with oxygen or nitrate to accelerate the oxidation of the reactive phases in an aquifer (Antoniou et al., 2012). A significant pH decline (from 7.6 to 6.7) in the subsequent storage phase due to the increased oxidation reactions caused an enhanced Mn(II) production. The source of Mn(II) is due to the increased carbonate dissolution buffering the induced acidity and due to inadequate sorptive removal. Additionally, even with oxygen-enriched water, a sufficient, therefore, beneficial decrease in the aquifer reactivity may require an impractical amount of treatment cycles.

Aquifer pre-treatment using "stronger" chemical electron acceptors could allow the removal of aquifer reactivity while minimizing the number of treatment cycles required. The use of these electron acceptors has previously been well established in the field of in-situ chemical oxidation (ISCO) to minimize groundwater organic contaminant concentrations (Cavé et al., 2007; Mahmoodlu et al., 2013). Because oxygen can achieve a maximum saturation of 5 times (100% oxygen) compared with air, the use of "strong" electron acceptors for aquifer pre-treatment during ASR allows a significantly greater oxidation capacity per injected water volume, particularly for highly soluble ionic electron acceptors, such as permanganate (MnO_4^-) (Cavé et al., 2007). An additional advantage of permanganate for aquifer pre-treatment is the increase in the sorption capacity through the generation of Mn-oxide precipitates. Mn-oxide precipitates are a by-product of the MnO_4^- reaction with the reduced aquifer phases, such as sedimentary organic matter and pyrite. These precipitates may coat the aquifer minerals and could effectively sequester a range of trace metals, including manganese (Buamah, 2009). Finally, the oxidation of the sedimentary electron donors with MnO_4^- consumes protons and increases the pH, thereby buffering the negative side effects related to the lower pH values that occur during aquifer treatment with other electron acceptors, such as oxygen.

The goal of this study is to test the feasibility of the permanganate pre-oxidation to minimize the water quality deterioration during ASR operations using bi-directional ASR column experiments to simulate the evolution of the water quality in an anoxic aquifer. The specific objectives include the following: (1) evaluation of the effect of the aquifer treatment with an aqueous permanganate solution on the water quality and comparing it with the injection of conventional oxygenated (air-saturated) water; (2) evaluation of whether the permanganate treatment of the aquifer sediments improves the recovery efficiency; and (3) evaluation of the water quality development after resaturation with native groundwater, reflecting the situation during static conditions in the ASR system.

2. Materials and methods

2.1. Aquifer sediments

Anoxic cores (1 m length and 0.1 m diameter) were obtained during the installation of an ASR well in a confined, brackish and anoxic aquifer at 14–41 m below sea level in Nootdorp, the Netherlands, using a reverse-circulation rotary method (Zuurbier et al., 2014). The sediments consist of fine to coarse Pleistocene fluvial sands that contain organic-rich clay lenses. The cores were sealed in PVC liners and stored at 4 °C until the following analyses: (1) grain size; (2) organic matter (reactive and bulk); (3) total carbonate content by thermogravimetry (TGA in a CO_2 atmosphere at 330, 550, 1000 °C); (4) total carbon and sulfur using a combustion analyzer (LECO Induction Furnace Instruments); (5) total elemental composition using X-ray fluorescence (XRF). The pyrite content and the reactive iron (non-pyrite) were calculated using the following equations (Griffioen et al., 2012):

- $$FeS_2 = 0.5 * S * M_{FeS_2}/M_S \tag{1}$$
- $$Fe_{reactive(non\text{-}pyrite)} = 2 * M_{Fe}/M_{Fe_2O_3} * [Fe_2O_3 - (0.225Al_2O_3 - 0.91\%)] - 0.5 * S * M_{Fe}/M_S \tag{2}$$

where M_{FeS_2}, M_s and $M_{Fe_2O_3}$ are the molar masses of FeS_2, S, and Fe_2O_3, respectively. S represents the total sulfur content by weight (% dry weight) as measured by the carbon/sulfur combustion analyzer, and Fe_2O_3 and Al_2O_3 represent their content by weight (% d.w.), as determined by XRF. This formula assumes that the silicate-bound Fe_2O_3 amounts to approximately 22.5% of the total Al_2O_3 content and that the total reactive Fe could be regarded as enrichment on top of the silicate-bound Fe (Huisman and Kiden, 1997; Dellwig et al., 2001; Griffioen et al., 2012). The cation exchange capacity (CEC) was calculated using the following empirical equation (Stuyfzand et al., 2012):

$$CEC = 5.6 * L + 5.1 * (pH - 1.16) * C_{org} \tag{3}$$