

# In situ Arsenic removal using redox condition alteration: Visualization experiments

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## Abstract

Adsorption/co-precipitation with iron oxyhydroxides is the most commonly adopted method for arsenic removal from contaminated water because the method is both effective and cheap compared with other methods. The main idea of this in-situ treatment method of groundwater is to transfer the physical, chemical and biological processes of conventional above ground treatment plants into the aquifer.

Due to the lack of technological methods to detect the Fe(II) while flowing in a porous medium, visualization techniques were adapted. Green Rust (GR) precipitates were used as a representative of the in-situ iron precipitates. In a visualization flat cell, the change in color of GR into orange, due to oxidation, was monitored by digital camera and the images were analyzed giving the spatial and temporal distribution of Fe(II). Moreover, both oxygen and pH changes, in time, were recorded in two sections along the flow direction in the cell. The measured concentration profiles were compared with calculated ones and actual reaction rates were predicted. The reaction rate constant measured in this study was under well defined mass transport conditions and its average value agrees with that found in literature.

*Keywords:* Arsenic remediation; ferrous iron oxidation; visualization techniques.

**1- Introduction** In recent years, the presence of dissolved arsenic in contaminated groundwater from both natural and anthropogenic sources has emerged as a major concern on a global scale (AWWA, 2001). Arsenic (As) is a ubiquitous element present in various compounds through out the earth's crust. Natural geochemical contamination through soil leaching is the primary contribution of dissolved arsenic in groundwater around the world.

During the in situ arsenic remediation, the aquifer carries the function of natural subterranean reactor where oxidation and filtration processes for the removal of arsenic and other constituents take place. The injection of oxygenated water displaces the original groundwater containing iron, arsenic and other water constituents. Thus, an oxidation zone is built up in the aquifer where Fe(II) will be converted to Fe(III) compounds, which largely precipitate on the soil grains. During the following production phase, flow is reversed and groundwater flows through the oxidation zone towards the well. Consequently, Fe(II) and As(III) are adsorbed to the soil grains, which are partially coated by previously deposited oxidation products e.g. Fe(III) oxyhydroxides. Through the next oxygenated water injection period, the adsorbed Fe(II) is oxidized to ferric hydroxides.

In this paper, we deal specifically with the first stage of the remediation process where the oxygenated water is first introduced in the well vicinity and Fe(II) compounds are oxidized.

In the field, there exist many types of iron compounds depending mainly on oxidation intensity and pH. Under partially oxidizing circumstances, part of the dissolved ferrous iron will be oxidized to ferric iron which leads to the formation of GR that precipitates as sedimentary species that form coatings for the soil grains. Current thinking is that GR occurs in many soil and sediment systems (Randall, 2001). Naturally occurring GR was proved for the first time by Trolard et al. (1997) using Mossbauer and Raman spectroscopies.

For our experiments, we choose GR as a representative of the in situ iron precipitates because it exists naturally, has a color that changes due to oxidation thus it can be used to monitor the oxidation process using visualization technique and the ferrous and ferric iron percentage is well defined. GR is iron hydroxide compound occur under reducing and weakly acid to weakly alkaline conditions as an intermediate phase in the formation of iron oxyhydroxides such as lepidocrocite, goethite and magnetite by oxidation of ferrous iron aqueous solution (Schwertmann, 1994, Vins, 1987). They are known as layered double hydroxides (LDH), wherein  $[Fe_{(1-x)}^{II}Fe_x^{III}(OH)_2]^{x+}$  layers alternate with interlayers made of anions (most commonly  $CO_3^{2-}$ ,  $SO_4^{2-}$  or  $Cl^-$ ) and water molecules. The green rust that is used in this research is GR II, with the chemical formula  $[Fe_4^{II}Fe_2^{III}(OH)_{12}]^{2+} \cdot [SO_4 \cdot 2H_2O]^{2-}$  (Genin, 1998). Upon exposure to air; GR is oxidized to either lepidocrocite, goethite or magnetite depending on the rate of oxidation and pH value.

## 1.1 Theoretical background

During oxygenated water injection, Fe(II) oxidation in the interlayer will take place. The general oxidation rate of ferrous iron in aquatic ecosystem was defined by Barry et al. 1994 as follows:

$$R = -\frac{dFe(II)}{dt} = \left\{ k_o \left\{ Fe^{2+} \right\} + k_1 [Fe(OH)^+] + k_2 [Fe(OH)_2^0] \right\} pO_2 + k'_3 A [Fe(II)] [OH^-]^2 pO_2 + k_4 [Bacteria] [Fe(II)] [OH^-]^2 pO_2 + R_{other}$$

where  $k_o - k_2 =$  first order rate constants in water, in homogeneous oxidation process [ $s^{-1} atm^{-1}$ ].  $k'_3 =$  overall rate constant for heterogeneous abiotic processes [ $mol^{-2} m^{-2} s^{-1} atm^{-1}$ ].  $k_4 =$  rate constant for some bacteria.  $R_{other} =$  the oxidation rate attributed to processes not considered explicitly.

In our study, we focused on the heterogeneous oxidation because during injecting the oxygenated water oxidation will happen for the adsorbed and dissolved iron in groundwater (Wolthoorn et al., 2004).

The mass balances for the three most important elements, namely oxygen, hydrogen, and iron II, can be written as follows with their initial and boundary conditions:

$$\frac{\partial [O_2]}{\partial t} + v \frac{\partial [O_2]}{\partial x} = -\frac{1}{4} k'_3 A [Fe(II)] [OH^-]^2 pO_2 ; [O_2](x=0, t=0) = 8, [O_2](0 < x < L, t=0) = 0 \text{ g / m}^3$$

$$\frac{\partial [H^+]}{\partial t} + v \frac{\partial [H^+]}{\partial x} = k'_3 A [Fe(II)] [OH^-]^2 pO_2 ; [H^+](x=0, t=0) = 1 \cdot 10^{-5}, [H^+](0 < x < L, t=0) = 1 \cdot 10^{-5} \text{ g / m}^3$$

$$\frac{\partial [Fe(II)]}{\partial t} = -k'_3 A [Fe(II)] [OH^-]^2 pO_2 ; [Fe(II)](x=0, t=0) = 0, [Fe(II)](0 < x < L, t=0) = 50 \text{ g / m}^3$$

where  $A$  is the available surface area, and  $L$  is the total length of the cell.

## 2 Experimental

Due to the lack of an achievable technology to detect the heterogeneous oxidation of iron compounds in porous medium, visualization technique was adopted to make use of the different colours for ferric and ferrous compounds. The green rust precipitates were used as the representative of the adsorbed ferrous iron compounds at the field.

In literature the iron (II) oxidation reaction rate constants are measured mostly using the batch experiments (Barry et al. 1994, Sharma et al. 2001). In these experiments the iron (II) solution and the selected solids are put together in a beaker while stirring. Thus the reaction rates calculated in this way are not intrinsic since they contain mass transport which is in fact not very well defined and the proper dispersion of the solid particles in solution is not guaranteed. Therefore we choose to measure the oxidation reaction rates under well defined mass transport conditions using flow in visualization cell.

### 2.1 Experimental set-up

The main components of the experimental set-up are: transparent Perspex cell (0.8x 10x 20 cm) packed with glass beads (1.9-2.1mm diam.) and Clark-style pH and oxygen microelectrodes inserted into the cell, at 8.5 and 15 cm from the inlet. The set-up is installed inside a glove box in which the anaerobic conditions are mimicked.

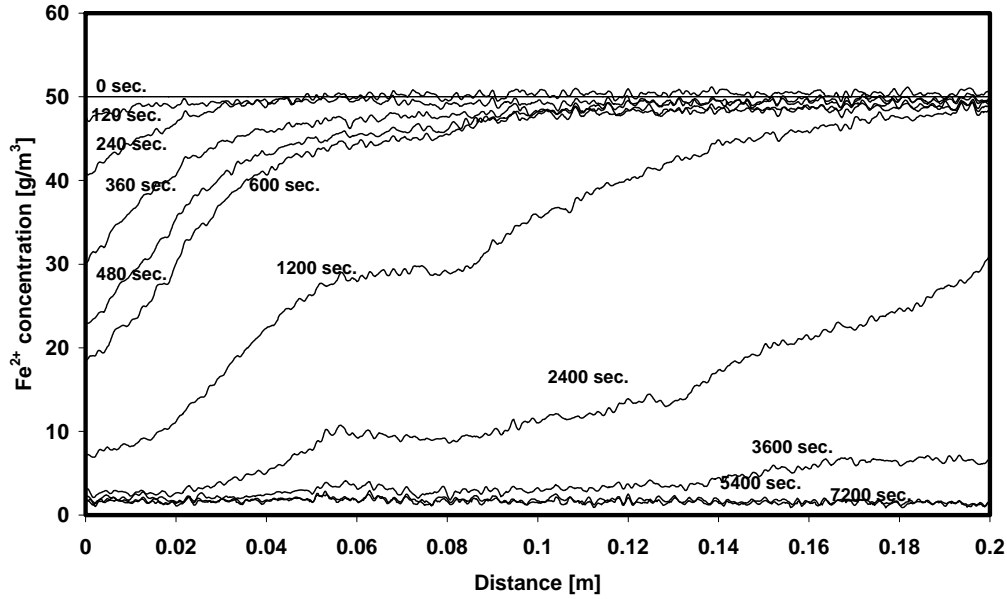
### 2.2 Methodology

- The cell was put in the glove box under anaerobic conditions. Oxygen free distilled water was injected at very low rate while the cell was aligned vertically to avoid having gas entrapment.
- The GR solution was prepared by coprecipitation and injected inside the cell. The injection of the GR solution was stopped when the green color in the cell was homogeneously distributed and a break through curve indicated equilibrium between the injected solution and adsorption to the glass beads.
- Oxygenated water ( $\approx 8 \text{ g/m}^3$ ) was injected inside the cell at 0.06ml/s. pH and dissolved oxygen concentration changes inside the cell were monitored in time. Moreover, the oxidation of GR to Lepidocrocite was recorded via the changes in colors analysing the images of the cell taken with the digital camera.

## 3 Results and discussions

### 3.1 Image analysis

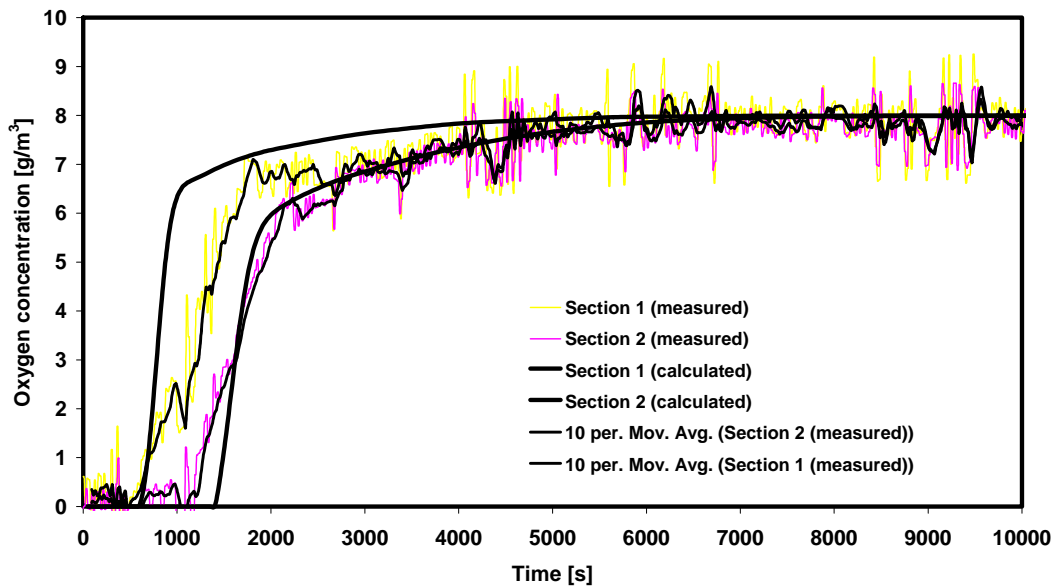
From the image analysis using RGB system, the width-averaged temporal and spatial ferrous iron concentration were calculated and plotted as shown in figure (1).



**Figure 1:** the width-averaged temporal and spatial concentration of ferrous iron, in side the cell, during the injection of oxygenated water.

### 3.2 Dissolved oxygen profiles

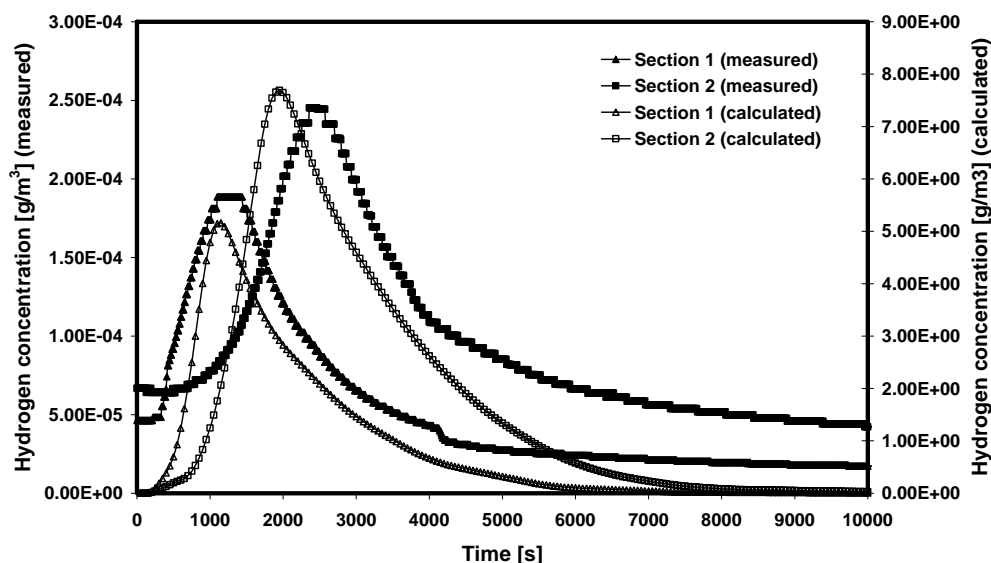
The measured and calculated oxygen concentrations in the cell at two different cross sections are shown in figure (2). There is an acceptable agreement between the calculated and measured concentration except the fact that the measured concentration in the first section is slower than the calculated one and this could be due to some small scale heterogeneity in the GR distribution towards the inlet.



**Figure 2:** the dissolved oxygen concentration in two different sections along the cell at 0.085 and 0.15 m from the inlet.

### 3.3 Hydrogen profiles

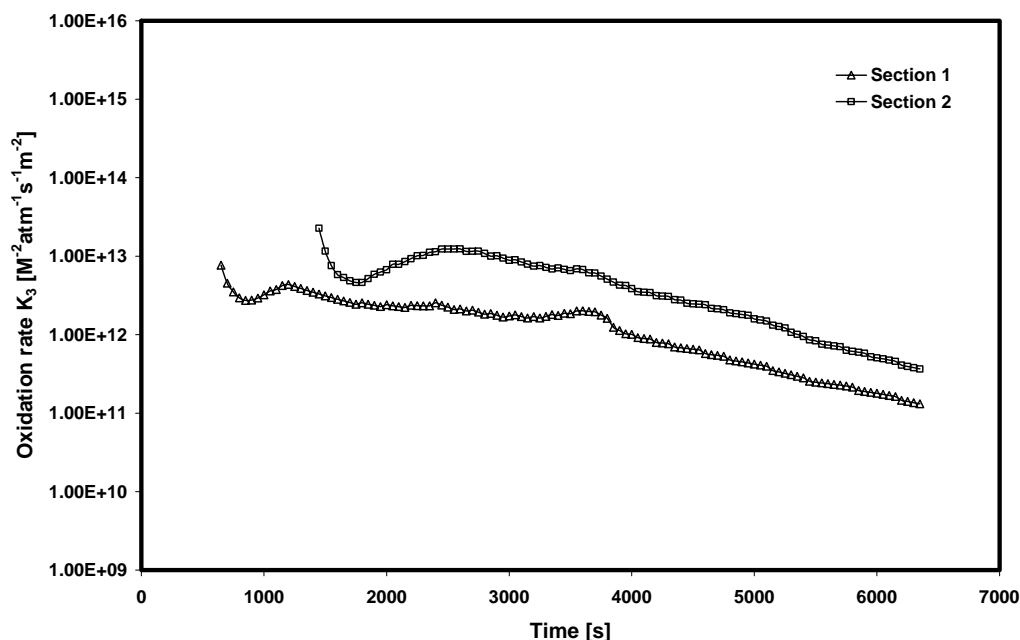
The measured and calculated hydrogen concentrations at two sections along the cell are shown in figure (3). From the figure a qualitative agreement is shown while there is a difference in the order of magnitudes of concentrations. This difference could be attributed to the buffering capacity of the glass beads present in the cell.



**Figure 3:** the measured and calculated hydrogen concentrations at two different sections along the cell.

### 3.4 Overall heterogeneous oxidation rate constant

Figure (4) shows the calculated values of the overall heterogeneous oxidation rate constant, adjusted for the surface area, at two different sections in time. The values are calculated using the ferrous iron mass balance equation knowing the concentrations of oxygen, hydrogen and ferrous iron in time. In the beginning the values are high and decrease except after a short time from the beginning the values increases slightly. The reason for the general decrease in the values could be attributed to the fact that ferrous iron is scattered in the GR interlayers which result in the occurrence of passivation phenomenon (the formed Fe(III) compounds in outer layer delays the oxidation of Fe(II) in inner layer Amaral et al. 1999). The slight increase is associated to the lowest pH values since the passivation is less with lower pH values. This explanation requires some further investigations in a future work. The values at the two sections are equal but that in the second section take place later in time due to flow conditions. The average value is in agreement with the values found in literature (Barry et al., 1994).



**Figure 4:** values of the overall heterogeneous oxidation rate at two sections in time.

## 4 Conclusions

- Visualization techniques make it possible to determine the in-situ Fe(II) profiles and oxidation rates as a function of space and time.

- In this research the oxidation reaction rate constants were measured under well defined mass transport conditions compared to that prevail in batch experiments usually used.
- The measured reaction rates are actual and not intrinsic rates since they include mass transport effects, due to passivation phenomenon, and not only due chemical events
- The hydrogen concentration profiles calculated using the measured Fe(II) oxidation rates agrees qualitatively with that measured. While the calculated oxygen concentration profiles agrees rather quantitatively.
- Average values of the actual heterogeneous oxidation rate agree with that found in literature.
- The oxidation rate values are decreasing in time which could be explained with the fact that ferrous iron is scattered in the interlayers of the GR and the occurrence of the passivation phenomenon.

## 5 References

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