**Master Thesis, Department of Geosciences**

# Iron and Manganese removal from groundwater

## *Geochemical modeling of the Vyredox method*

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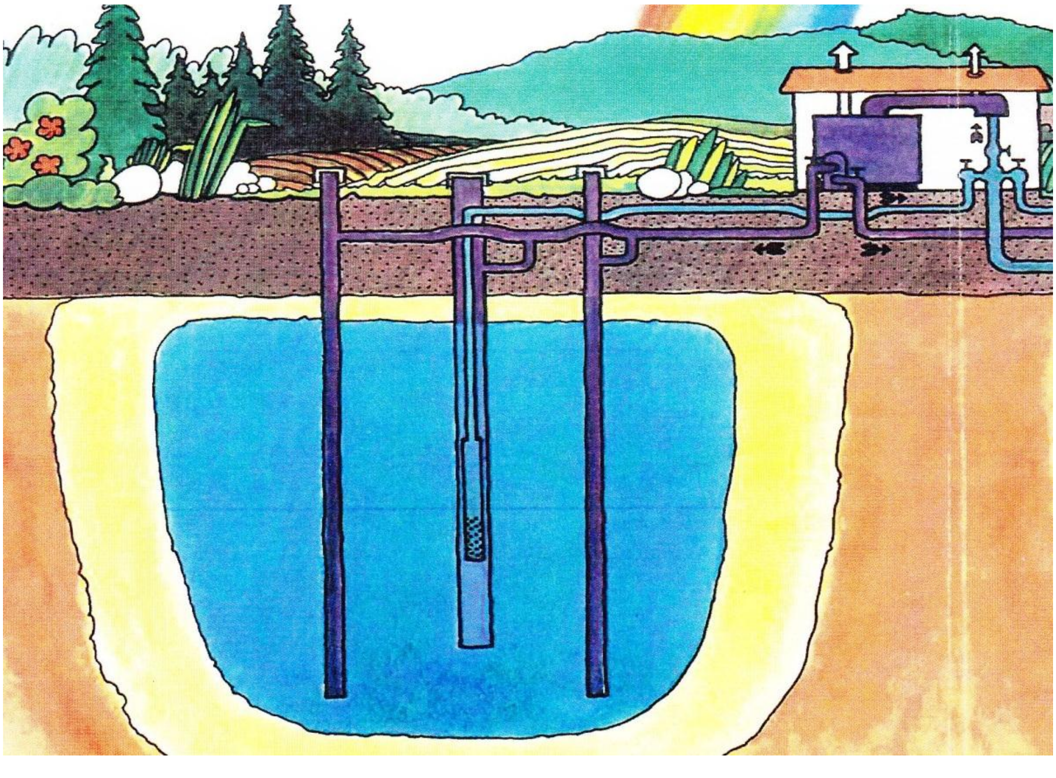

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Discipline: Environmental Geology and Geohazards
Department of Geosciences
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# *Abstract*

*Drinking water supplies are based on ground water resources all over the world. At some localities problems with higher concentrations of iron and manganese found in ground water. These higher concentration of these metals result in metallic taste of water, effect color and flavor of food and cause staining of different products like paper, cloths, and plastics. Therefore World Health Organization has approved the treatment of water if concentrations of iron and manganese are higher than 0.3mg/L and 0.1 mg/L. Several techniques have been applied to remove iron and manganese from groundwater.*

*The issue of higher concentrations of iron and manganese in groundwater wells at Grindalsmoen in Elverum Municipality in the south eastern part of Norway has been investigated by a PHREEQC geochemical model. The aim of this investigation was to analyze the relationships between oxygen levels and precipitation rates of iron and manganese. For this purpose geochemical simulations were performed with PHREEQC model with radial and linear flow. Results proved that concentration of oxygen at the water works (at its corresponding partial pressure) is high enough to precipitate the level of iron and manganese found in groundwater. The concentration of oxygen in equilibrium air at our desired temperature of 6 degree centigrade was 12.3 mg/l calculated by PHREEQC.*

*Geochemical simulations were performed by the one dimensional column flow and radial flow towards well. The phenomenon of sorption was also included in model to see the adsorption behavior of iron and manganese. Overall this geochemical study has provided satisfactory results.*

## Table of Contents

# Chapter 1: Introduction

Groundwater resources play a vital role in the production of clean and adequate drinking water supply all around the world. In European countries, like Denmark, Austria and Iceland, more than 95 percent of their water supplies originate from groundwater reservoirs (NGU, 2008). In the United States, groundwater is used to supply potable water for more than 96 percent of their population in rural areas (Biswas, 1997) cited in (Sharma, 2001). In Asia, groundwater is also used extensively for their water supplies e.g. 80 percent in (rural) india, 80 percent in Maldives and more than 60 percent of water supply in Philippines and Nepal originates from groundwater resources (Das Gupta, 1991) cited in (Sharma, 2001). The extensive use of groundwater can be explained by the ease of access, better protection from pollution sources, higher water quality as compared to surface water (Hallberg and Martinell,1976) less subject to seasonal and perennial changes, uniformly spreading over large areas (UNESCO, 2004) and also lower capital cost of production (Sharma, 2001). These benefits have resulted in groundwater use for water supply at large scale (UNESCO, 2004).

In light with the Millennium Development Goals (MGD), water supply in rural areas is being researched and applied with great importance to achieve the desired (MDG) goals which puts lot more pressure and emphasis to consider groundwater as resource (Tredoux et al., 2004).

With such extensive use, depletion and contamination of groundwater is wide spread and their impacts are realized gradually e.g. (Das et al., 2002; Nazari et al., 1993; Momodu and Anyakora, 2009; Macfarlane et al., 1982). Groundwater contamination has major complications on the environment and can pose serious threat to human health. The major contaminants found the groundwater include sulphates, nitrogen compounds (such as ammonia and nitrates, petroleum products, phenols and heavy metals (UNESCO, 2004). Sources of groundwater contamination may include infiltration of untreated storm water, accidental leakage of municipal wastewater and private septic tanks and/or other industrial waste products. Groundwater can be contaminated by more than 30 different general sources related to human activities that include point and non-point sources. The most common sources include waste disposal practices, storage and handling of materials and waste, saline water intrusion and agricultural activities (Moody, 1996). Mining practices and waste water irrigation can also cause groundwater contamination (Muhammad et al., 2011). Since the industrial revolution, one of the major concerns regarding the contamination of groundwater is the precipitation and accumulation of heavy metals. Heavy metals are natural elements with a specific gravity at least five times the gravity of water. Natural sources of heavy metal may include weathering and erosion of bedrocks and ore deposits. Some heavy metals like lead, chromium and mercury may impose acute toxicity even in lower concentrations. Other metals like magnesium, calcium, iron and manganese however are necessary to sustain the vital body function in trace amounts (Salem et al., 2000). Iron and manganese are occurring naturally in groundwater (Tredoux et al., 2004) where both elements are present in anoxic environment (Ebermann et al., 2010). Iron and manganese have been causing problems for regulatory authorities in connection to industrial and main water supplies for a long time. (Olthoff, 1985) cited in (Jaudon et al., 1989). Higher dissolved concentrations of iron and manganese do not have any serious harm to human or animal health (Ebermann et al., 2010), but these can cause aesthetic problems (Tredoux et al., 2004).

## 1.1 Objective

In this MSc thesis, I will investigate different methodologies (especially in-situ removal, Vyredox method) that are in use to remove iron and manganese from groundwater. I will apply the geochemical model, PHREEQC to investigate the relation between oxygen levels and precipitation and sorption of iron and manganese by linear and radial flow simulations.

Then I will develop PHREEQC model with the specific level of oxygen to investigate the solubility and binding mechanisms of iron and manganese in aquifer, and will simulate the Vyredox treatment plant at the Grindalsmoen, Elverum municipality.

# Chapter 2: Iron and manganese in groundwater

## 2.1 Sources of iron and manganese

Iron and manganese are common metallic elements that occurs together naturally especially in deeper wells with little or no oxygen present. Natural sources of iron and manganese may include weathering of iron and manganese bearing minerals like amphibole, iron sulfide and iron rich clay minerals. In areas where groundwater flows through an organic rich soil, iron and manganese will also dissolve in the groundwater. Iron and manganese can also have anthropogenic sources including industrial effluents, landfill leakages and acid mine drainage. Well casing, pump parts, piping and storage tank can also contribute iron and manganese to groundwater (Nova Scotia, 2008).

In natural conditions, water percolates through the organic soil where dissolved oxygen is consumed by the decomposition of organic matter and microbes in the soil. The decomposition process reduces the pH due to the microbial action. In combination with the lack of oxygen, , the iron and manganese atoms are also reduced from $Fe^{3+}$ and $Mn^{4+}$ to $Fe^{2+}$ and $Mn^{2+}$. The most dominant form of dissolved iron is the soluble $Fe^{+2}$ under the pH range of 5 to 8. When groundwater is pumped up to the surface it gets into contact with air ($O_2$) which enters the solutions and starts the oxidation process that releases carbon dioxide ($CO_2$) from the groundwater to the atmosphere. When this happens, the pH values are increased and hence the $Fe^{2+}$ and $Mn^{2+}$ are changed into the insoluble $Fe^{3+}$ and $Mn^{4+}$ minerals.

## 2.2 Origins of iron and manganese in groundwater

### 2.2.1 Origins of iron in groundwater

Iron can be originated by the weathering of iron minerals such as pyrite. During the Weathering of pyrite in heaps of pit coal, reduced groundwater with a content of $Fe^{+2}$ originates

$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO4^{2-} + 4H^+$ ***Eq. 2.1***

$5FeS_2 + 14NO_{3-} + 4CO_2 + 2H_2O = 5Fe^{2+}\ 10SO_4{}^{2-} + 7N_2 + 4HCO_3^-$ ***Eq. 2.2***

These reactions can induce $SO_4^{2-}$ in pumped raw water.

Iron carbonate reacts with $CO_2$ and get Fe into the solution.

$FeCO_3 + CO_2 + H_20 = Fe^{2+} + 2HCO3^{-}$ **_Eq. 2.3_**

If there is enough CO2 present and H donors then it will be possible to remobilize the wide spread $Fe^{+3}$ oxyhydrates.

$FeO(OH) + (H^+) + 2CO_2 = Fe^{2+} + 2HCO_3^- + e^-$ **_Eq. 2.4_**

Table 2.1 is showing the different minerals that are found in soil and subsoil that can generate the iron by the process of weathering. The soils can have iron content of 0.5% to 5% depends upon the rocks from where soil was derived, mechanism of transport and geochemical history (Vance, 1994).

**Table 2.1:** Important Iron minerals (Wegner, 1991) cited in (Rott and Lamberth, 1993).

| | | |
|---|---|---|
| Pegamatic | Olivin | $(Mg, Fe)_2 SiO_4$ |
| | Magnetit | $Fe_30_4$ |
| | Chromit | $FeCrO_4$ |
| | Ilmenite | $FeTiO_3$ |
| Pegmatitic and hydrothermal | Pyrrhotit | FeS ( in meteorites Troilit) |
| | Pyrite | $FeS_2$ |
| Hydrothermal | Hamatit | $Fe_2O_3$, $Fe_20_3$-hydrate |
| | Geothit | $\alpha$-FeOOH |
| | Lepidokrokit | $\gamma$-FeOOH |
| | Iron Carbonate | $FeCO_3$ |
| | Vivianit | $Fe_3(PO_4)_2.8H2O$ |
| | Strengit | $FePO_4.2H2O$ |

### 2.2.2 Origin of Manganese

Geological states of soil and subsoil are important factor in determination of content of manganese in groundwater. Manganese in soil can be founded in different phases that are given below (Rott and Lamberth, 1993).

- As manganese- oxides, -silicates and carbonates

- Adsorbed on iron oxide
- In organic compounds
- In exchanging ($Mn^{+2}$) and soluted condition.

## 2.3 Chemistry of iron and manganese

### 2.3.1 Chemistry of iron

Iron in water supplies can exist in either of the following states:

a) divalent ferrous iron $Fe^{+2}$ (soluble form),

b) trivalent ferric iron $Fe^{+3}$ ( insoluble form).

The process of oxidizing divalent ferrous ion ($Fe^{+2}$) to trivalent ferric ions ($Fe^{+3}$) can be described by (Eq.2. 5)

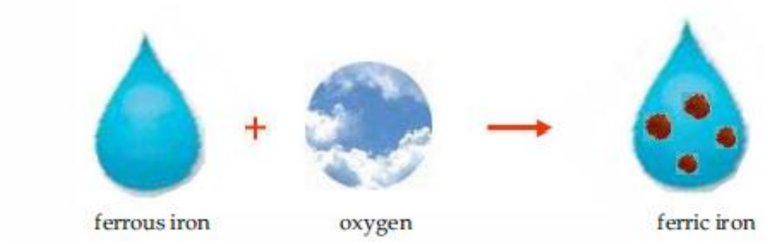


**Figure 2.1:** Oxidation of ferrous iron into ferric iron under influence of oxygen (Teunissen 2007)

$Fe^{+2} = Fe^{+3} + e^{-}$ ***Eq. 2.5***

In circumstances where high concentration of dissolved oxygen occurs, the trivalent ferric ion can further react with hydroxyl groups to precipitate in solid form (Eq. 2.6).

$Fe^{+3} + 3OH^{-} = Fe(OH)_3$ ***Eq. 2.6***

The whole sequence of oxidation-reduction reaction can be written as (Eq.2.7)

$Fe^{+2} + 3H_2O = Fe(OH)_3 + 3H^{+} + e^{-}$ ***Eq.2. 7***

The stability of iron ion depends not only on pH but also on activity of electrons which is represented by a redox potential pE. High positive value of pE indicates oxidizing conditions where iron is insoluble and the low values of pE indicates reducing conditions where iron is soluble (Silveira, 1988).

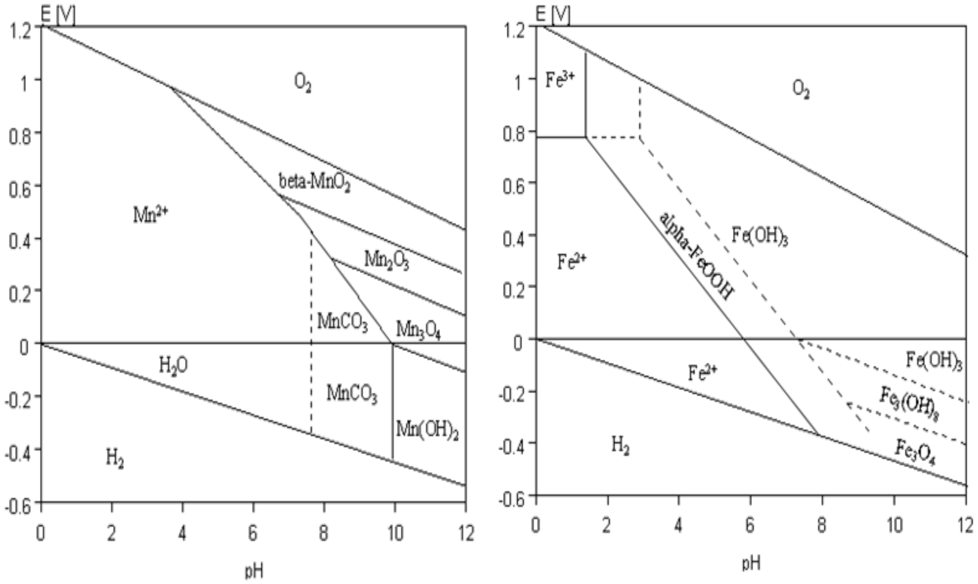


**Figure 2.2:** Eh-pH stability diagram iron and manganese (Scheffer et al., 1989).

### 2.3.2 Chemistry of manganese in water

In water, manganese exists in two forms:

(a) $Mn^{2+}$ manganous oxide (soluble)

(b) $Mn^{4+}$ magnic oxide (stable)

The occurrence and behavior of manganese is not similar to iron. (Eq. 2.8) shows how one state of manganese is converted into other (Silveria, 1988)

$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$ ***Eq.2.8***

## 2.4 Implications of iron and manganese in water supply

The relationship between iron and manganese under increasing pH and redox potential (pE) suggests that ferrous iron ($Fe^{2+}$) normally occurs in the area with lower redox potential and within the pH range of 5.5 to 8.2. This also means that $Fe^{+2}$ is more easily and rapidly oxidized than $Mn^{+2}$. The latter is often occurring with $Fe^{+3}$ under pH values larger than 8 and redox potentials between 420 to 790 millivolts. Above this redox potential, the stable form of $MnO_2$ is found (Silveira, 1988).

When iron and manganese are present in water as soluble form in drinking water supplies, then we will come across many objectionable problems related to their presence. The World Health Organization (WHO) has approved the removal of iron and manganese when concentrations are higher than 0.3 mg/L and 0.1 mg/L respectively (World Health Organization, 1996). European Union has recommended the levels of 0.2mg/L and 0.05mg/L for iron and manganese respectively (European Union, 1998).The Environmental Protection Agency (EPA) has established secondary standards of 0.30 mg/l for iron and 0.05mg/l for manganese(U.S.EPA, 2001). So if concentrations are higher than these standards, then water must be treated before using it for drinking purposes. If water is not treated then there can be different problems for water consumers and also for that municipality that delivers drinking water to consumers.

Iron and manganese can cause different types of nuisance problems. The color and flavor of food and water can be affected by iron and manganese, because they can react with tannins in coffee, tea and alcoholic beverages which result in production of black sludge. Iron can cause reddish- brown staining of laundry, utensils, dishes and glassware (Wilson et al., 1999). The excessive concentrations of Mn will result in metallic taste in water, staining of different products like clothes, paper and plastics (Homoncik et al., 2010).

The clogging of home softeners can take place and softening efficiency will be reduced by the precipitation of iron and manganese (Takerlekopoulou and Vayenas, 2006). Iron and manganese can also cause build up in pipelines, water heaters and pressure tanks. This build up is linked with a decrease in pressure and amount of available water and also increase in cost of water-using appliances. Buildup can be expensive when it results in repairing of water softener or plumbing (Wilson et al., 1999). The deposition of iron and manganese in the distribution systems can cause reduction of diameter of pipe and eventually clogging of pipe will take place (Takerlekopoulou and Vayenas, 2006).

There is another problem associated with iron and manganese in water is iron and manganese bacteria. These bacteria are not posing any health threat, but they can cause red brown (iron) and black brown (manganese) slime in toilet tanks and can cause clogging of water systems. The growth of iron and bacteria takes place on iron and manganese present in water in either light or dark conditions (Wilson et al., 1999).

## 2.5 Factors affecting the removal of Iron and Manganese

The removal of dissolved iron and manganese from groundwater is generally accomplished by the oxidation and precipitation. The removal process is affected by the different chemical and physical characteristics of water including pH, temperature, total organic carbon (TOC) and concentration of dissolved oxygen (Filtronics, 1993).

The oxidation rates are faster at high pH values and slow at low pH values. The oxidation by aeration demands a pH greater than 6.3 for iron and more than 9.3 for manganese (Filtronics 1993).Carbonic acid lowers the pH value of water and hence slows down the oxidation rate. Increased temperature also enhances the oxidation reactions while lower temperature slows down the oxidation process. In general, the rate of reaction will double for every 10 degree Celsius temperature increase. In the presence of higher concentrations of total organic carbon, the oxidation of iron and manganese is reduced due to less available oxygen. In totality, the time factor also plays a crucial role. The precipitation of manganese will take a longer time than precipitation of iron. Normally, precipitation of iron can take place within minutes but the precipitation of manganese can take more than hours (Filtronics, 1993).

## 2.6 Removal of iron and manganese

The treatment of iron and manganese is possible by two different ways.

- Ex-situ removal of iron and manganese
- In-situ removal of iron and manganese

### 2.6.1 Ex-situ removal of iron and manganese

In this method groundwater is purified on the surface (after abstraction) by different processes like chemical oxidation followed by filtration, aeration followed by filtration, iron exchange method in treatment systems and raising the pH with neutralizing filter (Wilson et al., 1999). Conventional iron and manganese treatment plants depend on the different physical and chemical reactions by using manganese greensand, aeration and chemical oxidation accomplished by ozone, Potassium permanganate or chlorine oxide. These processes can pose different operating problems (Gage et al., 2001).

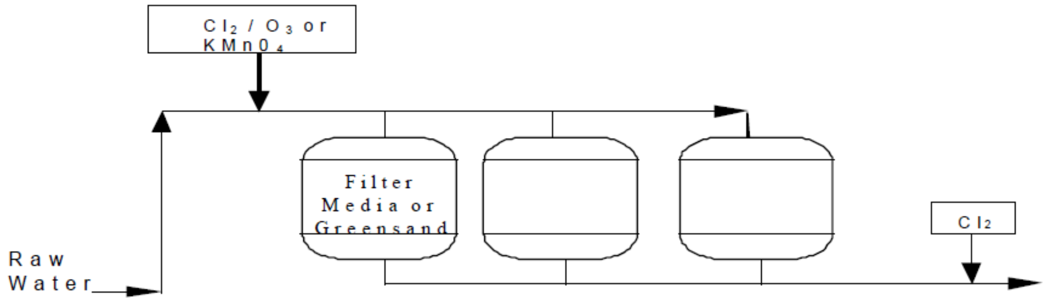


**Figure 2.3:** Conventional treatment plant (Gage et al. 2001).

### 2.6.2 Oxidation followed by filtration

Before the process of filtration of iron and manganese, it is required to oxidize them to a state in which they turn into insoluble products. The process of oxidation involves the transfer of electrons from iron and manganese to oxidizing agent that we are using. By the process of oxidation the ferrous ion ($Fe^{+2}$) will change into ferric ion ($Fe^{+3}$), which readily forms insoluble hydroxide $Fe\,(OH)_3$. Same case will be with manganese, like $Mn^{+2}$ will oxidize into $Mn^{+4}$ which will form insoluble products $MnO_2$. In the process of oxidation we use different type of oxidants which include chlorine, chlorine dioxide and potassium permanganate. Small groundwater systems often use chlorine or potassium permanganate in the process of oxidation because dosing is very easy, demands simple equipment and also fairly inexpensive (Tech Brief, 1998).

The process of chlorination is used at large scale for the oxidation of iron and manganese. Oxidation of divalent iron and manganese by chlorine can cause a problem that is formation of trihalomethanes (THMs) in highly colored waters. As compared to others, potassium permanganate (KMnO4), as an oxidant is expensive than others. The dosing of potassium permanganate should be controlled carefully. If we use too little permanganate, it will not be enough to oxidize all the iron and manganese and if we use too much, then it will enter in distribution systems and will cause a pink color. There is another problem that is associated with the use of permanganate is that it can form precipitates that can form mud balls on the filters (Tech Brief, 1998).

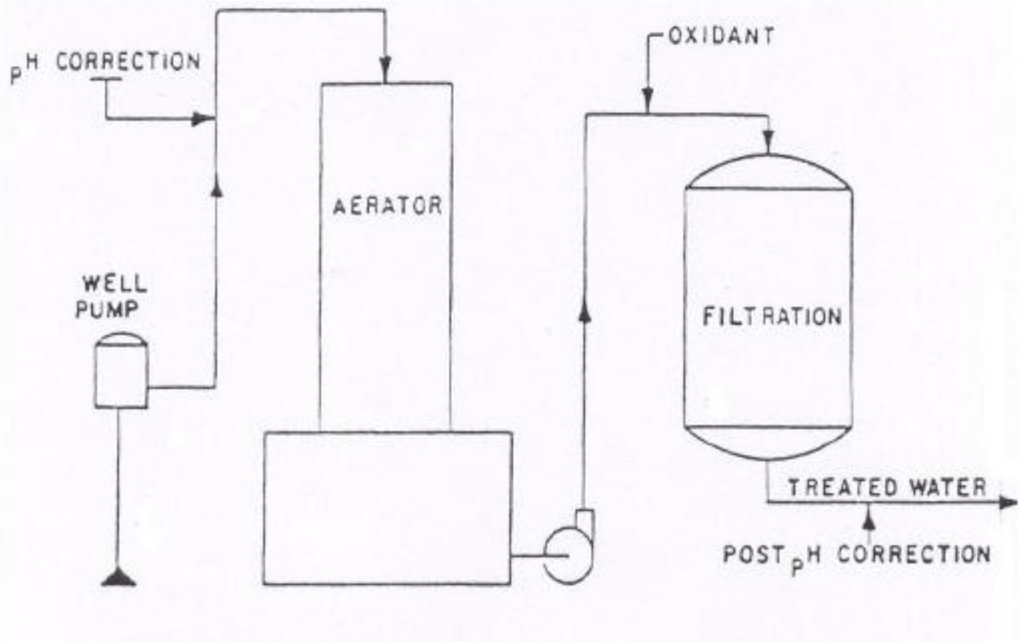


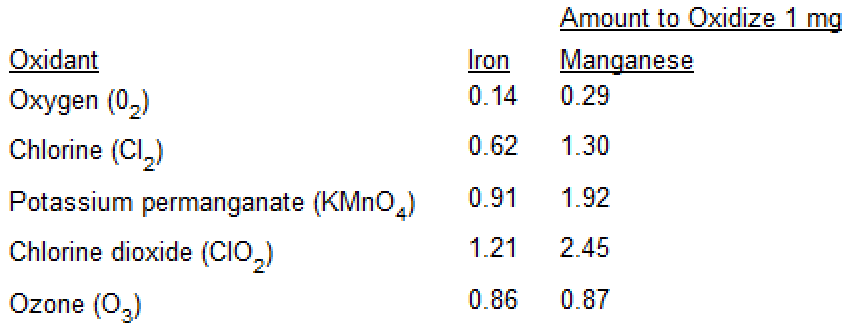
**Figure 2.4:** Aeration, additional oxidation followed by Filtration (McPeak and Aronovitch, 1983).

A flow diagram for a plant using the process of oxidation followed by filtration is shown in (fig 2.4). The water can be aerated with or without adjustment of pH values. The increase in pH will help in the oxidation of iron and if it is raised high enough it will favor the oxidation of manganese. Very high pH is required for the oxidation of soluble manganese (without adding any strong oxidant). For the complete oxidation of manganese the pH value needed to be increased to 9.5 or more but for oxidation of iron 7.0 to 8.0 pH range are enough in the process of aeration. For iron the oxidation reaction as ferrous bicarbonate by aeration is given below, and 0.14 milligrams of oxygen is required to oxidize each milligram of ferrous iron (McPeak and Aronovitch, 1983).

$4Fe\ (HCO3)_{2}{}_{+}\ O_2 + 2H_20 = 4Fe\ (OH)_3 + 8CO_2$ ***Eq. 2.9***

After aeration a strong oxidizing agent like ozone, chlorine, potassium permanganate, chlorine dioxide can added to oxidize the remaining iron and manganese. Amounts of oxidants are given in table 2.2 that are required to oxidize the 1 milligram of soluble iron and manganese.

Table 2.2: Stoichiomatric amount of various oxidizing agents required for oxidation of iron and manganese (McPeak and Aronovitch, 1983).



|  | Amount to Oxidize 1 mg |  |
|---|---|---|
| Oxidant | Iron | Manganese |
| Oxygen ($0_2$) | 0.14 | 0.29 |
| Chlorine ($Cl_2$) | 0.62 | 1.30 |
| Potassium permanganate ($KMnO_4$) | 0.91 | 1.92 |
| Chlorine dioxide ($ClO_2$) | 1.21 | 2.45 |
| Ozone ($O_3$) | 0.86 | 0.87 |

Ozone is also used for the oxidation of iron and manganese, but if humic or fulvic materials are present then it may not be effective. The dosing must be controlled very carefully because ozone can also oxidize reduced manganese to permanganate which can result in formation of pink water (Tech Brief, 1998). Ferrous iron can be oxidized by ozone according to following reaction;

$$2Fe^{2+} + O_{3\,(aq)} + 5H_20 = 2Fe\,(OH)_{3\,(s)} + O_{2\,(aq)} + 4H^+ \qquad \textbf{\textit{Eq. 2.10}}$$

Oxidation of $Mn^{2+}$ needs more oxidizing power than oxidation of iron. The oxidation reaction of manganese by ozone is given below;

$$Mn^{2+} + O_{3\,(aq)} + H_20 = Mn0_{2\,(s)} + O_{2\,(aq)} + 2H^+ \qquad \textbf{\textit{Eq. 2.11}}$$

Lately there has been more attention towards the use of ozone for the treatment of various water quality problems (Araby et al., 2009).

Manganese greensand is considered as the most common medium used for the removal and manganese through the pressure filtration. This filtration medium is a processed material that consists of nodular grains of the clay mineral glauconite. The material is coated with manganese oxide. The glauconite will facilitate the bonding of coating because it is having ion exchange properties. This treatment will provide a catalytic effect in the chemical oxidation reactions that is necessary for iron and manganese removal. This coating is maintained by the continuous feed of potassium permanganate. “Anthra/sand”, also called iron man sand, is also an available material that can be used for the iron and manganese removal (Tech Brief, 1998).

Oxidation of iron and manganese is followed by the process of filtration that is accomplished by using sand or anthracite. With the help of these filtration media insoluble oxides of iron and manganese are removed. Manganese greensand can also be used as filtration media (McPeak and Aronovitch 1983).Manganese greensand is considered as the most common medium used for the removal and manganese through the pressure filtration.

### 2.6.3 Ion Exchange

We can use the ion exchange method if we want to remove small quantities of iron and manganese, because it will be having risk of rapid clogging (Tech Brief, 1998). The process of removing iron and manganese by ion exchange is accomplished by using of sodium from strong acid cation (McPeak and. Aronovitch, 1983).

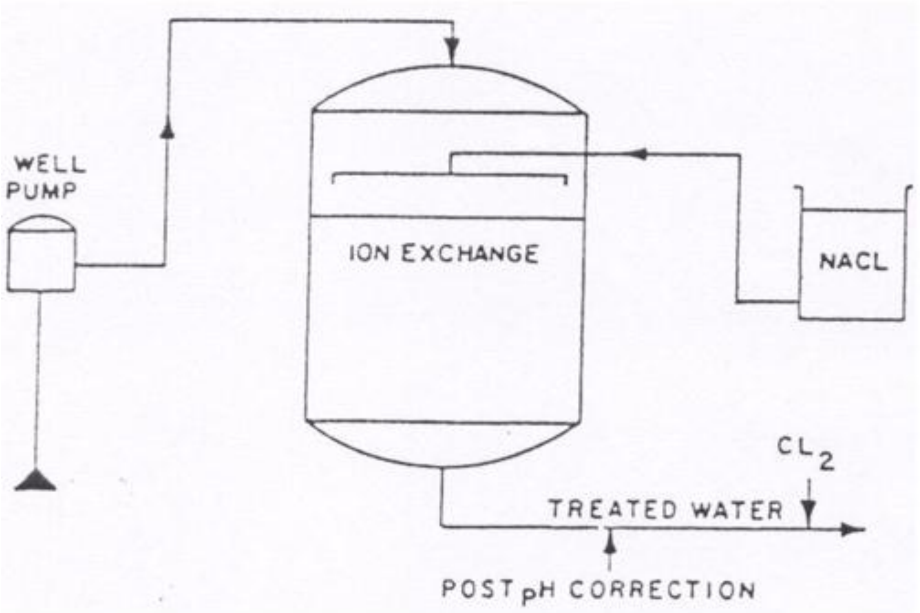


**Figure 2.5:** Ion exchange method for removal of iron and manganese **(**McPeak and Aronovitch, 1983).

The cycle of sodium with iron and manganese in iron exchange reaction is similar to the exchange of calcium and magnesium in the process exchange softening. Following reaction with R representing the fixed exchange site on resin will occur **(**McPeak and Aronovitch 1983).

$Fe^{+2} + 2\ NaR_2 = Fe\ R_2 + 2Na^{+}$ ***Eq. 2.12***

### 2.7 In-situ removal of iron and manganese

In-situ removal is a useful technique, which consists of elimination of dissolved iron and manganese in groundwater before pumping. This technique includes the use of Vyredox method in which highly oxidized zone is created around the well to be treated by the injections of oxygen rich water (Hallberg and Martinell 1976). . In 1969 first operational Vyredox plant was built and more than 100 treatment plants had been constructed in more than 10 countries until 1988 (Braester and Martinell, 1988) cited in (Tredoux et al., 2004). The principle and scope of this method is explained in detail in next chapter.

# Chapter 3: The Vyredox method and subsurface reactions affecting iron and manganese

## 3.1 Background

In the previous times, water with higher levels of iron and manganese was treated by addition of oxidant to the water after abstraction in a water treatment plants. By this technique impurities were precipitated and filtered out to leave clean water behind. For the purpose of oxidation, oxygen was added as an oxidant in the form of pure oxygen or by aeration with the use of cascade aerator. Operation costs and capital investments are so high for this type of treatment plant because the sand layers which work as filter were required to renew from time to time to increase the removal efficiency of iron and manganese (Hallberg and Martinell 1988).

The Vyredox method was discovered by Yrjo Reijonen and Veli and it was developed in Finland at the end of 1960s (Seppanen, 1992). Since the first application of this method in 1969, several countries e.g. Sweden, Norway and China chose to apply the Vyredox method. Today some 150 plants have been reported, from which 70-80 exist in Finland and Sweden (Vestland, 2010). Also, other similar in-situ technique (i.e. NITREDOX- method) has been developed on the basis of this method is used to remove nitrate (Bokalders and Block, 2012). This chapter provides a detailed description of the Vyredox treatment process.

## 3.2 Introduction of Vyredox process

The technique is based on elimination of dissolved iron and manganese before pumping by achieving the higher degree of oxidized zone around the well to be treated (Jaudon et al., 1989). The oxidized zone can be achieved by the periodic injections of aerated water through the injection wells situated around the supply well in a ring (Fig 3.1).The number of injection wells may depend on geochemical and hydrogelogical conditions. The water that is used to inject through injection wells must be degassed and oxygen enriched. This can be performed in special aerator, which is called an oxygenator (Hallberg and Martinell 1976).

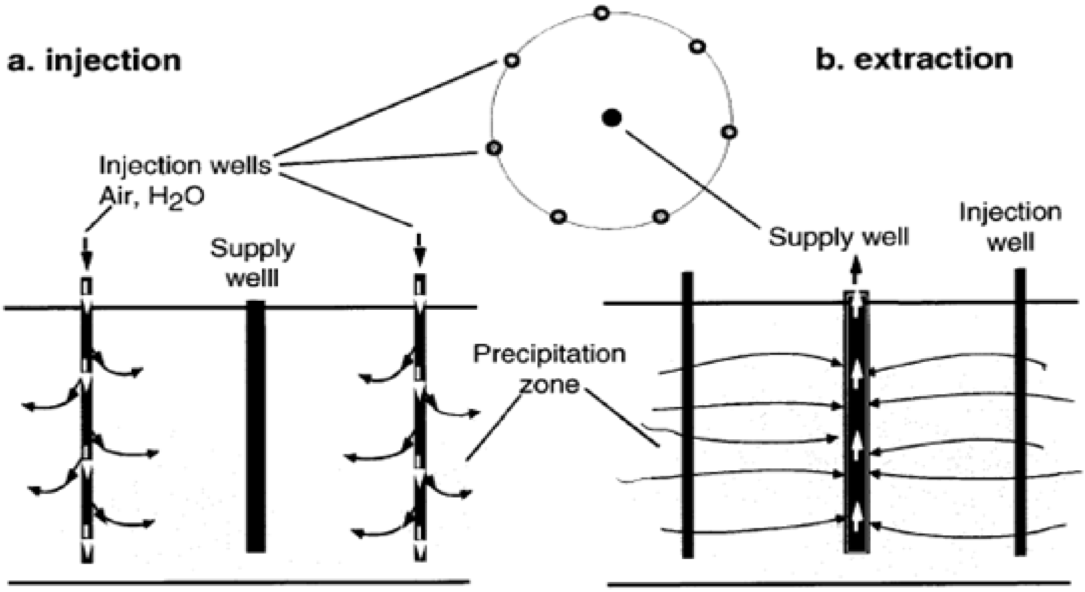


**Figure 3.1:** Location of one supply and several injection wells (Mettler, 2002).

### 3.2.1 Oxidation of iron and manganese

The application of the subsurface iron and manganese removal is based on the characteristic reaction of oxidation. The injection of $O_2$ rich water starts the oxidation of iron and manganese present in subsurface environment around the well (Van Halem et al., 2011). The process of oxidizing divalent ferrous ion ($Fe^{+2}$) to trivalent ferric ions ($Fe^{+3}$) can be described by following equations.

$Fe^{+2} = Fe^{+3} + e^{-}$ ***Eq. 3.1***

$O_2 + 4H^+ + 4e^- = 2H_2O$ ***Eq. 3.2***

The whole process can be written as

$4Fe^{+2} + O_2 + 2H_2O = 4Fe^{+3} + 4OH^-$ ***Eq. 3.3***

In circumstances where high concentration of dissolved oxygen occurs, the trivalent ferric ion can further react with hydroxyl groups to precipitate in solid form.

$Fe^{+3} + 3OH^- = Fe(OH)_3$ **Eq. 3.4**

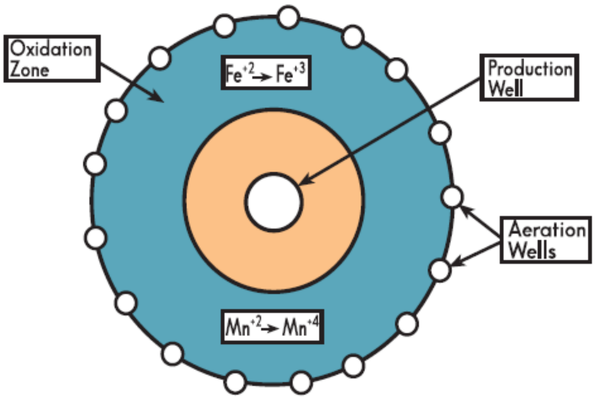


**Figure 3.2:** Oxidation of iron and manganese in oxidation zone (Ferro pure, 2012)

The oxidation reaction of manganese can be written as following.

$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$ ***Eq. 3.5***

On oxidation dissolved iron and manganese results in $Fe^{+3}$ and $Mn^{+4}$ which are highly insoluble and precipitates as oxyhrdroxides. In comparison to conventional treatment, the precipitates of Mn and Fe are not thrown away and remain underground (Mettler, 2002).

### 3.2.2 Iron and manganese content of Aquifer

The strata of soil and bed rock does not remain same at all the places, it changes from place to place due to which composition of groundwater also changes. The amount of dissolved oxygen is greater in rain water, melted ice and melted snow. . When this water seeps into ground very rapidly then this water will having low amount of iron and manganese. . In some cases surface water doesn’t seep into groundwater directly because of the less impermeable strata. Then in this case groundwater usually contains less dissolved oxygen and iron and manganese in large quantities. Such conditions can be found under the clayey soils (Hallberg and Martinell 1976).

(Fig 3.3) is describing the fluctuations in oxygen content of groundwater that relates to iron and manganese content. In (Fig 3.3) the man on left will be having low concentration of iron and manganese because he is pumping the aerated water, while the man on right side will find more iron concentration in water because of the lack of oxygen in groundwater. The governing conditions of groundwater flow are also important. Physical, biological, and chemicals factors are also very important in determine the composition of groundwater along with geology and hydrology of the area (Hallberg and Martinell 1976).

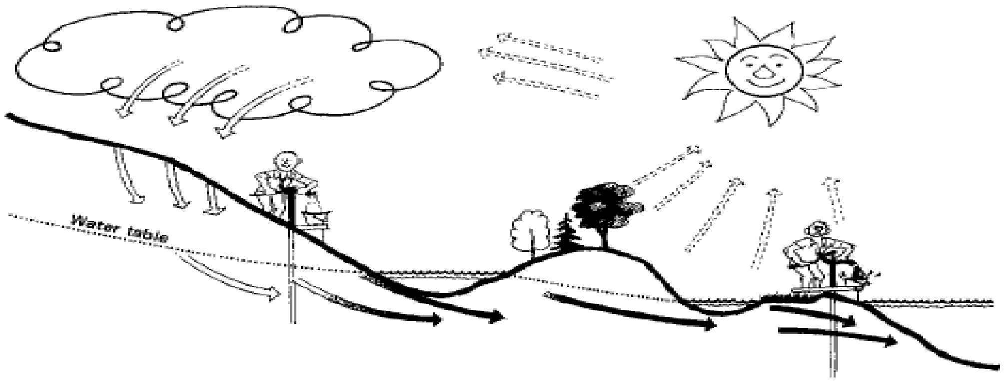


**Figure 3.3:** Schematic diagram of the hydrologic cycle (Hallberg and Martinell 1976).

### 3.2.3 Transitions between oxidized and reduced phase of iron and manganese

Transition between the reduced and oxidized forms of iron and manganese can be seen in the (Fig 3.4).Eh has been expressed in millivolts (mV). Balance between ferrous ($Fe^{+2}$) and ferric ($Fe^{+3}$) is shown by lower sloping line and the concentration of both states is equal at the every point of line. While the concentration of ferrous ions are greater than ferric ions below the line for all the values of pH and Eh. Balance between divalent manganese ($Mn^{+2}$) and tetravalent manganese ($Mn^{+4}$) is shown by lower sloping line. So if the values of Eh and pH are higher than upper sloping line then all the iron and manganese will be precipitated. The sloped lines are not hard, and can vary depending on the concentration of some other substances (Hallberg and Martinell 1976).

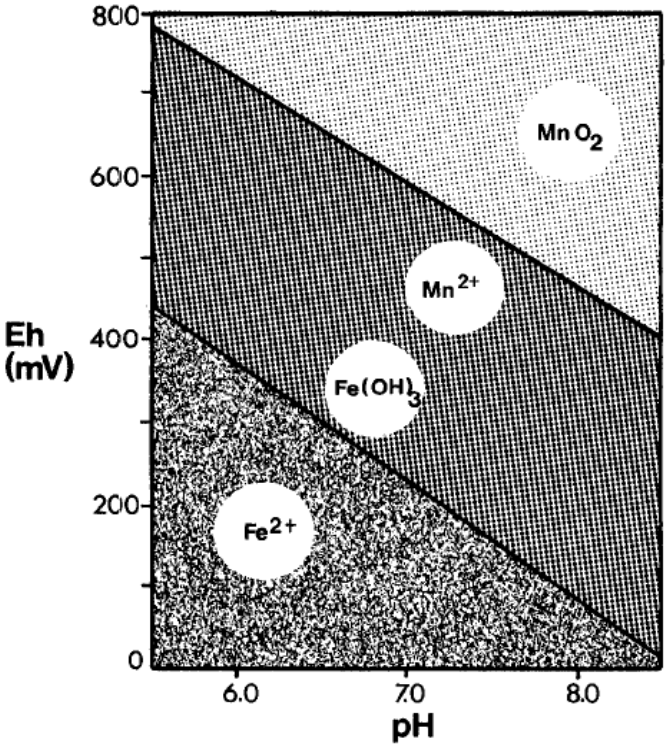


**Figure 3.4:** Iron and manganese precipitation as the function of Eh and pH.

### 3.2.4 Role of Iron and manganese bacteria

The higher values of pH and Eh are achieved by bacteria in natural waters often called iron and manganese bacteria. They are having the ability to make use of oxidation of iron and manganese by absorbing the electrons as source of energy for their metabolism. Oxidation of manganese as a source of energy about sixth as compare with the oxidation of iron so they have to oxidize six times as much manganese as iron to get the same amount of energy. The growth and reproduction of bacteria require source of carbon, so it can resulted that the greater their preference for manganese, the more they require organic carbon rather than carbonates and carbon dioxide. (Hallberg and Martinell, 1976). (Gage et al., 2001) called these bacteria as iron bacteria and concluded that wherever there is detectable amount of iron and manganese in water, these bacteria are present there. According to Seppanen (1992) the biological activity of living bacteria is responsible for iron and manganese removal from water and many applications of biological iron and manganese system are being used in groundwater engineering. But the mechanism of iron and manganese removal by bacteria is not totally understood (Sharma et al., 2001)

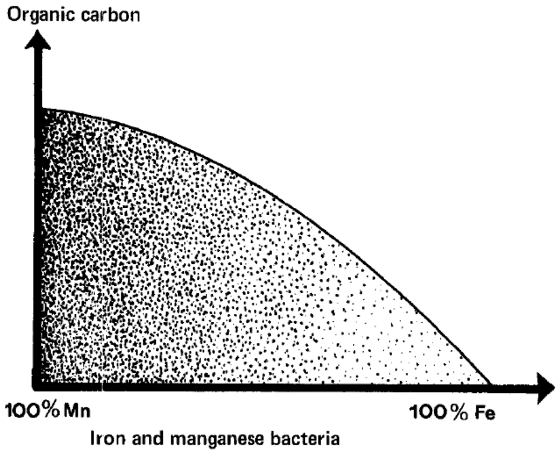


Figure 3.5: more manganese the bacteria have to oxidize, more organic carbon is needed

### 3.3 Aim of Vyredox method

The aim of Vyredox process is to create highly oxidized zone around the well, which means to achieve to higher values of pH and Eh at which iron and manganese are precipitated and retained in aquifer. The water that enters in the pumping well will be free of iron and manganese. Vyredox method is more efficient to remove iron than manganese because the precipitation of iron takes place earlier than manganese in zone furthest from the well. The amount of living and dead bacteria increases and some of them contain the organic matter that follows the flowing water towards the well. This organic matter becomes the source of carbon for the other bacteria that give preference to oxidize manganese and this process happens near the well where the Eh is higher (Hallberg and Martinell, 1976).

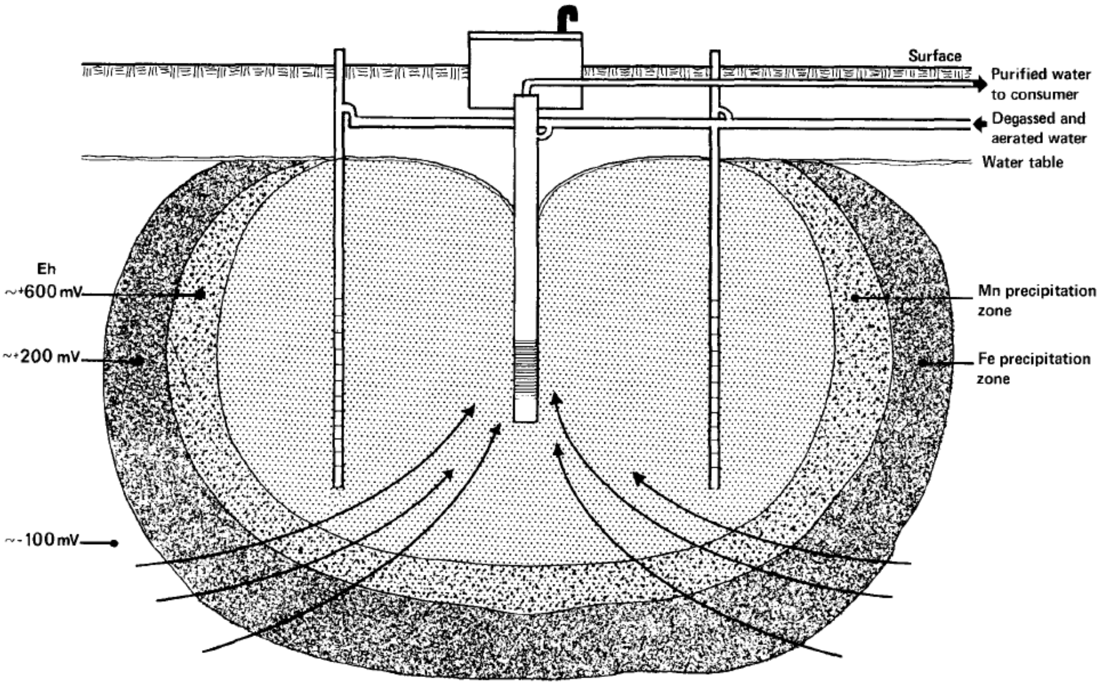


**Figure 3.6:** Iron and manganese precipitation zone achieved in aquifer, Groundwater is filtered through this zone before it is pumped up to the surface (Hallberg and Martinell 1976).

### 3.4 Principle of Vyredox method

1. Pumping is stopped in the well to be treated
2. Aeration of water from another well by mixing it with atmospheric air.
3. Elimination the non-dissolved oxygen and other gases by degassing the aerated water in a tank.
4. The water that is oxygen saturated is then returned by gravity to the aquifer through the well to be treated through satellite wells. This operation will continue for 20 hours.
5. The process is stopped for the 4 hours in order to follow the establishment of a high potential redox zone in the aquifer.
6. After a recharging sequence, we can pump the water that will be having iron and manganese in lower concentration, and it can be sent directly to water main. We can use this water until dissolved iron and manganese concentration comes to their normal levels (Jaudon et al., 1989).

### 3.5 Layout of Vyredox Plant

In past times treatment plants were having one borehole which functioned as injection well and also as supply well alternatively (Olthoff, 1986; Rott and Meyerhoff, 1993; Waldburger, 1994) (Mettler, 2002).In result no groundwater was available to supply in such treatment plants. The formation of precipitation zone takes place near to extraction well that leads to bigger risk of clogging of well (Mettler, 2002).But in present installations of Vyredox plants, several wells work, 5-23 injection wells are located in a circle around the supply well (Braester and Martinell, 1988) in (Mettler, 2002). The precipitation of iron of manganese is having very slight effect on the permeability of the aquifer and clogage should not occur for a period many times longer than the life period of typical well(Knox et al., 1986).

The layout of Vyredox is shown in the (Fig 3.7) is explaining the layout of Vyredox plant which consists of following units (Hallberg and Martinell, 1976).

**1-5** Supply wells and aeration wells
**2-** Aerator
**3-** Degassing tank
**4-** Pump for aerated water

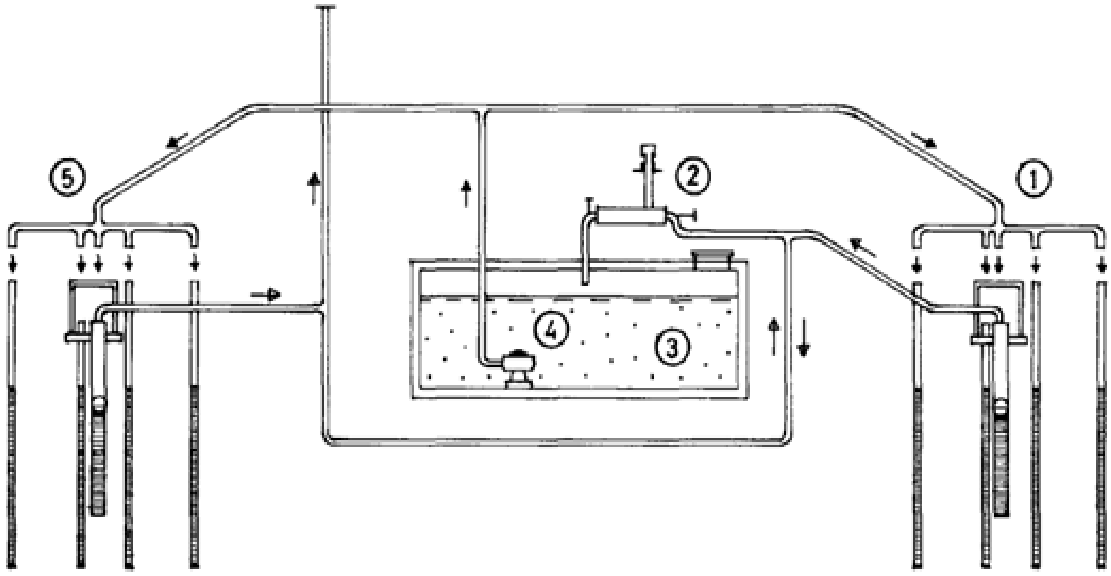


**Figure 3.7:** Vyredox plant with two supply wells complete aeration wells and oxygenator building (Hallberg and Martinell 1976).

## 3.6 Efficiency of Vyredox Method

The output of Vyredox treatment plant is explained by efficiency ratio, Er, which is ratio between volume of pumped water, $V_{out}$ divided by volume of aerated injected water, $V_{in}$ (Hallberg and Martinell 1976).

$Er = V_{out}/V_{in}$

Efficiency increases by increasing the cycles of withdrawal of groundwater, aeration and injection should be repeated many times. (Fig 3.8) is describing that efficiency can be increased by increasing the number of cycles.

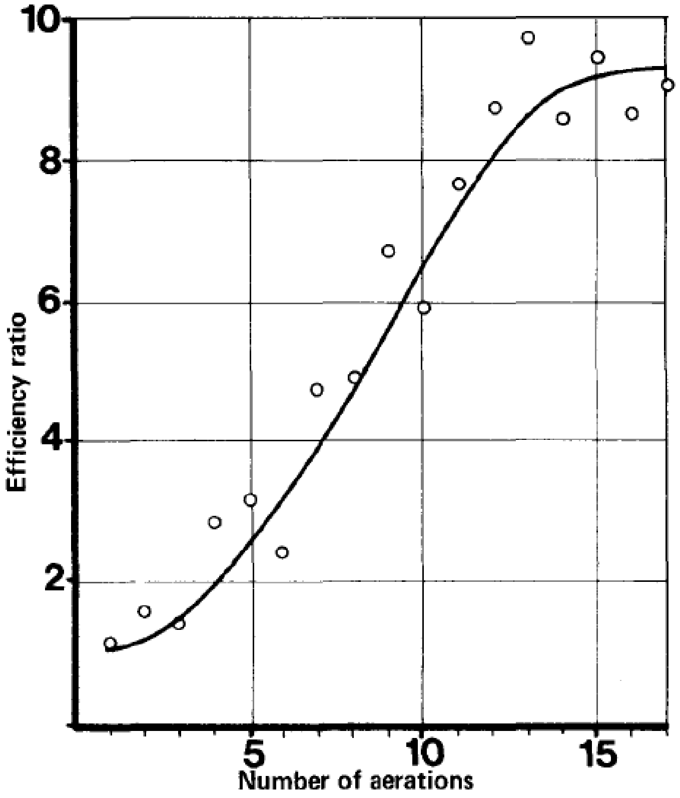


**Figure 3.8:** The efficiency ratio increasing with the number of aerations (Hallberg and Martinell 1976).

## 3.7 Advantages of Vyredox method

According to Hallberg and Martinell (1976), there are many advantages of using Vyredox method.

- The process of filtration is more efficient because it takes place slowly as compared with any conventional type of sand bed used at water works.

- It is not always required to increase the pH, which means that there is no need to use any type of expensive chemical.
- There is no need of continuous supervision a Vyredox plant because time and extent of aeration cycles are controlled automatically.
- The application of subsurface iron and manganese from groundwater is a very simple method as compared with other methods considering need of component, installation size , special experiences and constructions works (Karakish 2005)

Large investments are required to install the expensive facilities at the surface. Like Enclosed or open filters and sedimentation basins are used. Sometimes chemicals are required to help in precipitation if the iron and manganese are present in higher concentration. This means that it will be extra finances are required by the industry or municipality (Hallberg and Martinell, 1976).

### 3.8 Expected disadvantage of Vyredox method

By using this technique there will a risk of filling the aquifer pores and blockage of well. The risk of blockage of well is very small because permeability is not reduced even after many years. It is fact that reaction takes place in groundwater around the well and underneath it at a very large volume. The precipitation only occurs when the equilibrium is displaced towards the oxidative side because of addition of oxygen-enriched water. This precipitated iron has to be deposited in large pore volume in ground. Because the deposits of iron accumulated under the natural conditions take very long time, this fact is describing that there is no risk of blockage of well.

To support this fact, following discussion has been included. In a Vyredox plant the amount of water that is injected into the ground to aerate the ground water is equal to that average amount that is pumped out from the well per 24 hours. If this quantity is $q_m$ cubic meter. And the aerated pore volume is equal to $q_m$.

Now assume that the iron is precipitating only in 50 percent of the pore volume. So then volume of pores that is receiving precipitated iron will be 0.5 * qm. If it is assumed that well be abandoned when its capacity has finished because of its 50 percent blocked pore volume. If the precipitated iron is having the density of 1 gram per cubic centimeter then the amount of iron that will precipitate before the blockage of well will be $0.25*q_m*1.0*10^6$ grams of iron.

It can calculated that how long time it will take to precipitate this amount of iron.

$= 0.25*q_m*1.0*10^6 / 365*q_m*Fe$ years and Fe is the concentration of iron in mg/L.

This will be equal to

$25*1*10^4 / 3.65*Fe*10^{2 =} 6.9X10^2 X1/Fe$ Years.

So if the groundwater is containing the 5 mg/liter iron then well will take 140 years to get blocked. Here by “blocked” is meaning deposits of iron oxide has blocked the 50 percent of pore volume.

This could be highly conservative estimation. If the 100 percent of pores are taking part in the process and that the density of the iron salts that are precipitating is 2.8 grams per cubic centimeter. This means that it could take 750 years for a well to get blocked (Hallberg and Martinell 1976). The above calculations is giving the idea about the times that in which Vyredox plant can work efficiently and can provide water.

The application of In-situ treatment method at the site of La Neuveville that is located in Switzerland has revealed that highest concentration of precipitates of iron and manganese is expected on the smallest sized particles of a coarse aquifer, so no long term risks of clogging of aquifer is expected. (Mettler et al., 2001).

### 3.9 Application of Vyredox method in China

In some parts of china, the concentration of iron have found so high that it is should be removed before using it for drinking purposes according to Chinese standards. In China Vyredox method have been in use by some waterworks since 1980. Vyredox method is used ad pretreatment method where the concentration of iron is very high, and rest of the iron is removed by Conventional surface treatment plants (Mao gong, 1988).

There are three methods of recharging. In internal recharge oxygen enriched water is injected through supply well. In external recharge oxygen enriched water is injected by several injection wells situated around supply well, the distance between the injection and supply well is about 7m. In Combined recharge supply well and satellite recharge wells are used to inject the oxygen enriched water (Mao gong, 1988). Table 3.1 is showing the different characteristics of 5 different Vyredox plant.

**Table 3.1:** Characteristics of Vyredox plants working in China (Mao gong, 1988)

| **Characteristics** | **Panshi waterworks** | **Yitong waterworks** | **Harbin waterworks** | **Waterworks of Daqing oil field** | **East lake waterworks in Wuhan city** |
|---|---|---|---|---|---|
| Constitution of aquifer | Sand, coarse-grained with gravel; sand, medium grained | Sand, medium and coarse-grained with gravel | Sand, coarse-grained. | sandstone | Coarse-grained sand with gravel |
| Supply well production | 36m$^3$/h | 40m$^3$/h | 36m$^3$/h | 65m3/h | 30m3/h |
| depth | 32m | 32m | 65m | 120m | 51m |
| diameter | 0.3m | 0.3m | 0.4m | 0.3m | 0.3 |
| Recharge method | combined | external | Internal(treated surface water) | internal | internal |
| Time of recharge | 12-13 h | 3h | 5 days | 28-51 h | 7 percent daily recharge |
| Rate of Recharge | 30-36m$^3$/h | 72.4m$^3$/h |  | 40-50m3/h |  |
| Efficiency Ratio | 4 | 9 | 9 | 8 | 13 |
| Ripening period | 8 cycles | 7 cycles | 8 cycles | 8 cycles | 12 |
| Water quality | Fe$^{+2}$ = | Fe $^{+2}$= | Fe$^{+2}$= 6.1 mg/l | Fe$^{+2}$= | Fe$^{+2}$ = 0.9 |

| | | | | | |
|---|---|---|---|---|---|
| before<br>Vyredox | 3.2mg/l<br>Mn$^{+2}$ = 1.2mg/l<br>pH =6.7<br>Eh = 230mV | 20mg/l<br>Mn$^{+2}$ = 1mg/l<br>pH = 6 | Mn$^{+2}$ =1.3mg/l<br>pH =7.1 | 2.7mg/l<br>Mn$^{+2}$ = 0.4mg/l<br>pH = 7.3 | mg/l<br>Mn+2= 0.15 mg/l<br>pH = 6.8 |
| Water quality After Vyredox | Fe$^{+2}$ ≤ 0.3mg/l<br>Mn$^{+2}$ = 0.4 mg/l | Fe$^{+2}$= 14mg/l<br>Mn$^{+2}$ not removed | Fe$^{+2}$ ≤ 0.3mg/l<br>Mn$^{+2}$ not removed | Fe +2= 0.3mg/l<br>Mn+2 not removed | Fe$^{+2}$ = 0.2mg/l<br>Mn$^{+2}$ not removed |

Ripening period (i.e the number of cycles recharge and discharge for establishing a stable oxidation zone).

### 3.10 Application of Vyredox method at Beaucaire Site

An experiment was carried out at the Beaucaire site by using the P1 and P2 wells (Fig 2.9).The groundwater was pumped out from well P1, it was aerated, degassed and then injected into well P2. After a short interval, the same operation was reversed groundwater from P2 was pumped out and injected into P1. During the initial trials, it looked possible to treat both wells at the same time by this scheme without boring any satellite wells. The device of treatment was located at an equal distance from wells, full size oxygenation station and a flow similar to that of works (150m$^3$/h). 2500m$^3$ was the volume of aerated injected water for every 24 hour cycle, divided as follows:

- Pumping from P1 and injection into P2 for 18h
- Interruption of pumping and pause for P2 (6h)

The operation was reversed during the next cycles and so on.

Evolution of concentrations of iron, manganese and dissolved oxygen was followed to specify the pumped volume beyond which concentration of manganese will be above the level for drinking water.

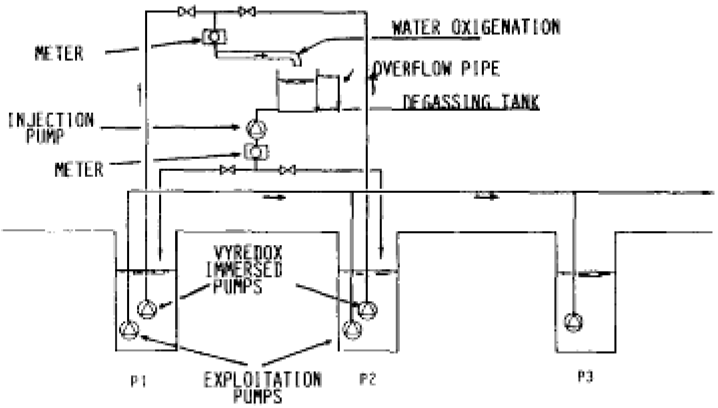


**Figure 3.9:** Application of Vyredox method (Jaudon et al., 1989).

Regular decrease in concentrations of iron and manganese was noticed from one cycle to another owing to recharged water injections that was less and less loaded with elements and to creation of dissolved oxygen enriched zone around the treated wells. After 4 injections normal concentrations of manganese for drinking water was achieved. The value of pH and concentration of dissolved pH was decreased in pumped water during a given cycle. The returning of system to its initial state accompanied by the increase of iron and manganese concentration. Long lasting pumping (cycle 6) (Table 3.2) showing that concentrations of iron and manganese are first increasing slowly, while the pH and dissolved oxygen are decreasing. The latter stabilized at the low value of 1.3 mg/L characteristic of the aquifer. The manganese concentration then increased quickly. The ratio of pumped water volume (concentration ≤ manganese limit for drinking water) to injected aerated water volume was 3.5.

Table 3.2 Main results for P2 after recharging sequence (Cycle No 6) (injection of 2120m3 aerated water and a 18h pause).Pumping flow 135m$^3$/h (Jaudon et al., 1989).

| **Voulme ( m3)** | **Fe** | **Mn** | **pH** | **O2** |
|---|---|---|---|---|
| 171 | 0.09 | 0.03 | 7.6 | 8.5 |
| 467 | 0.02 | 0.03 | 7.6 | 7.4 |
| 2530 | 0.02 | 0.03 | 7.6 | 2.5 |
| 2972 | 0.025 | 0.03 | 7.6 | 2.2 |
| 3538 | 0.017 | 0.03 | 7.3 | 1.9 |
| 3983 | 0.04 | 0.035 | 7.3 | 2.0 |

| | | | | |
|---|---|---|---|---|
| 6007 | 0.015 | 0.045 | 7.3 | 1.8 |
| 6533 | 0.02 | 0.045 | 7.4 | 1.8 |
| 7103 | 0.02 | 0.045 | 7.4 | 1.7 |
| 7549 | 0.01 | 0.055 | 7.4 | 1.6 |
| 9658 | 0.01 | 0.065 | 7.4 | 1.5 |
| 10105 | 0.03 | 0.07 | 7.4 | 1.4 |
| 10676 | 0.03 | 0.075 | 7.4 | 1.4 |
| 11123 | 0.02 | 0.08 | 7.4 | 1.3 |
| 13235 | 0.02 | 0.085 | 7.4 | 1.3 |
| 13682 | 0.02 | 0.09 | 7.4 | 1.3 |
| 14253 | 0.02 | 0.12 | 7.4 | 1.3 |
| 14699 | 0.03 | 0.12 | 7.8 | 1.3 |
| 16810 | 0.03 | 0.10 | 7.8 | 1.4 |
| 17257 | 0.02 | 0.1340 | 7.8 | 1.3 |
| 17828 | 0.02 | 0.16 | 7.8 | 1.3 |
| 18275 | 0.025 | 0.11 | 7.8 | 1.3 |
| 18381 | | ***stop*** | | |

### 3.11 Limitations of Vyredox method

The technique of Vyredox method is limited to that situation where pH of groundwater is found neutral. The condition where low pH is reported than high level of oxygen is required. The oxidisable species like methane and hydrogen sulphide are present often in reduced waters with low pH, due to which desired redox gradient for precipitation is difficult to achieve. Treatment of iron is easy as compared with manganese at low pH. The rate of removal for iron and manganese is not constant over time and some optimum conditions for removal may be required by the system. The precipitated iron and manganese accumulate in aquifer and favour the adsorption of dissolved iron and manganese by providing the suitable surfaces under neutral pH conditions. The iron and manganese are removed more quickly with time with two phase process of oxidation and adsorption (Tredoux et al., 2004).

The proper development of precipitation zone is very important to get iron and manganese removal efficiency by the technique of Vyredox method. Development of this zone may take ten or more injection cycles. The size and shape of the zone may need to be controlled by changing the arrangements of the injection boreholes and altering pumping and injection routines for each and every production borehole in the well field (Tredoux et al., 2004).

Many practical applications of Vyredox method has proved that clogging of aquifer is not the problematic. A claim by Braester and Martinell (1988) disclosing that rather than the clogging of aquifer with precipitation of iron and manganese, the borehole efficiency may be increased by the Vyredox method in first few months of operation. The borehole treated by Vyredox method is protected by a oxygenated water shield effectively that block the transport of reduced iron and manganese to the borehole, means preventing the clogging of pumping equipment and screens. The loss of pore volume will happen slowly by the proper development of oxygenation zone and running of plant correctly. With time, the precipitated iron may settled to more stable forms, such as hematite, which have a small volume than the hydrated forms (e.g. ferrihydrite) first precipitated (Tredoux et al., 2004). According to (Jaudon et al., 1989) many authors proposed theoretical model according to which, the system of Vyredox method results in precipitation at the extent of zone of enriched oxygen due to which and filling of pore of aquifer would be the expected.

### 3.12 Subsurface reactions affecting iron and manganese concentrations

Vyredox process is an in-situ method used to remove higher concentrations iron and manganese in subsurface (Tredoux et al., 2004). The Vyredox method has been discussed in detail in chapter 2. Although the technology of in-situ iron removal have been in use since many years, but the processes responsible for its effectiveness have not been been studied in details and evaluated (Van Halem, 2011). According to Der Laan (2008) there are many different types of processes that can affect the concentration of iron in subsurface including oxidation/precipitation and sorption. (Fig 3.10) describes the processes that are responsible to effect of influence the concentration of iron.

X and y are stoichiometric coefficients for Fe+2 sorption and $H^+$ release.

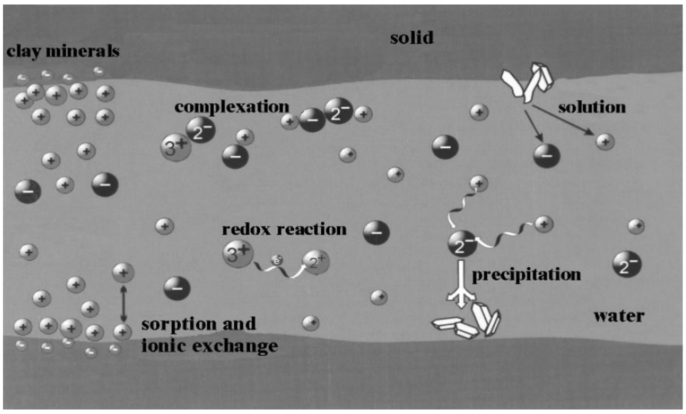


**Figure 3.10:** Different processes influencing the iron concentration in subsurface (Merkel and Freidrich, 2008).

### 3.13 Sorption

Sorption is general term that is used to describe the three different processes that includes adsorption, absorption and ion exchange. In the process of adsorption the chemical adheres to the surface of solid, while in absorption chemical specie penetrates into the solid, and replacement of ions of one chemical for another one at surface of solid is called as ion exchange.(Fig 3.11 ) is showing the all these three machanism(Appelo and Postma, 2005).

Different types of material present in soils and aquifers like clay minerals, oxy- hydroxides and organic matter, all of which are capable to sorb the chemicals. Hydrologists consider these sorption processes very important because they regulate the transport of pollutents in soils and aquifers (Appelo and Postma, 2005). Partition of contaminats takes place between solid phase and solution as the result of sorption process. Retardation of chemicals is also takes place by the sorption process due to which contaminants move slowly than the groundwater(Bedient et al.,1999) cited in in (Taylor and Aral, 2011).This process will be considered as an equilibrium reaction if the process of sorption is faster than the velocity of flow of water, but if the sorption process is slower than the process will be called as non-equilibrium reaction (Taylor and Aral, 2011).

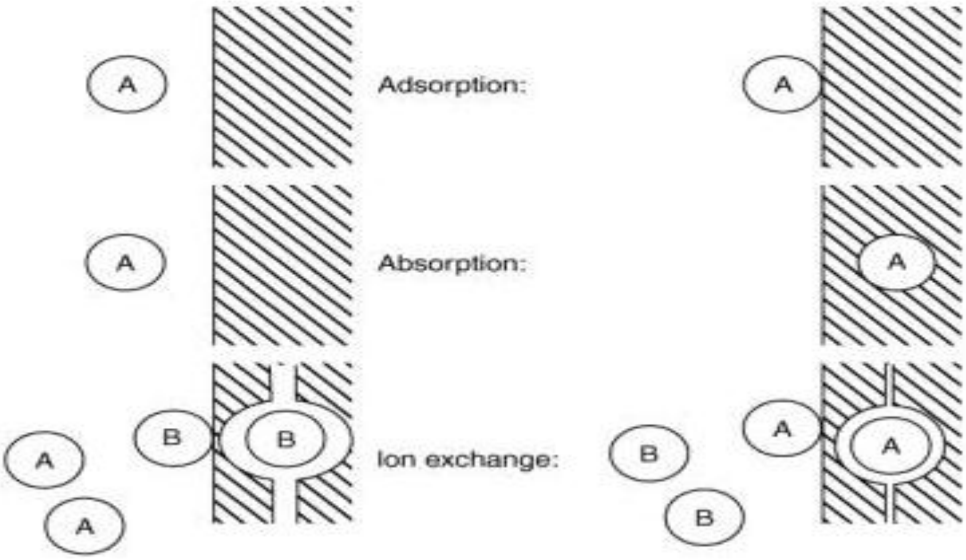


**Figure 3.11 :** Pictorial demonstration of three sorption processes (Appelo and Postma 2005).

In the process of sorption, a pollutent e.g heavy metal ions are binded to surfaces of oxides and organic matter that have variable charge. These variable charged solid surfaces sorb ions without delivering other ions in equal quantity in solution. The charge on the solid surface can be negative or positive depends on the composition of solution and pH, however these variable charge solids regulate the mobility of both negatively charged heavy metals as well as positively charged. Oxides and hydroxides surfaces achieve a charge that depends on pH because they sorb protons and others ions from solution. A potential difference is created between the solution and surface due to surface charge which influences the moving forward of ions towards the surface (Appelo and Postma, 2005).

### 3.13.1 Theoretical Background of Adsorption

The phenomenon of adsorption includes the separation of an element from one substance and adherence on the surface on another substance. The substance that is adsorbed is called as adsorbate and surface on which it adsorbs is called as adsorbent. Chemical Adsorption includes a reaction between adsorbate and adsorbent that results in change in the chemical form of the adsorbate. Electrons are shared between adsorbent and adsorbate occurs at adsorptive site of adsorbent (Buamah 2009).

According to principle of in situ iron removal, aerated water through a tube well is injected into an anaerobic aquifer due to which iron will be oxidized and precipitates. Formation of oxidation / precipitation zone takes place around the well where oxidized iron precipitates to form an adsorbent (Fig 3.12). This newly formed adsorbent helps to increase the sorption capacity of the soil (Der Laan, 2008). The precipitate adsorbs $Fe^{+2}$ according to following reaction (Appelo et al., 1999).

$XFe+^{2} + FeOOH = FeOOH_{1-Y}\,Fe_{x}^{(2x-y)+} + yH^{+}$

When injection is stopped and flow is reversed, the water will be iron free or having low iron concentrations. This is performed until an iron breakthrough is observed at the well. Consequently the injection starts again and the process continues (Der Laan, 2008).

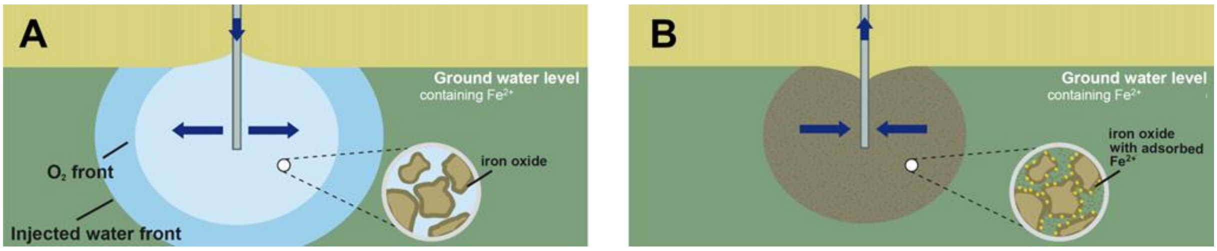


**Figure 3.12:** Principle of subsurface iron removal with (A) injection of aerated water and (B) abstraction of groundwater (van Halem et al., 2010).

### 3.13.2 Mechanism of Adsorption

In the mechanism of adsorptive iron removal ferrous ion is adsorbed on the surface of adsorbent. In the presence of oxygen ferrous ion is oxidized that forms a new surface for adsorption (Fig 3.13) (Der Laan 2008).

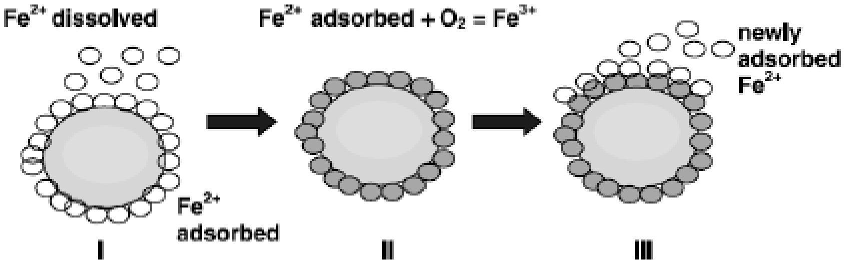


**Figure 3.13:** Adsorption-oxidation mechanism (Der Laan 2008).

Many studies have been conducted onto adsorption of metal cation on iron oxide (Davis and Leckie 1978) in (Sharma 2001). (Davis and Leckie 1978) in (Buamah 2009) explained that adsorption on hydrous oxide includes surface ionization and surface complexation of metals ions with the hydrous metal oxide. In aqueous systems hydroxyl group covers the surfaces of the metal oxide (Buamah 2009).An acid base equilibrium including the hydroxylated oxide surface is set up as following.

$$\mathbf{\equiv S\text{-}OH_2^+\ H^+ = \equiv S\text{-}OH_2^+} \qquad K_{a1} \qquad \textit{Eq. 3.6}$$

$$\mathbf{\equiv S\text{-}OH = \equiv S\text{-}O^- + H^+} \qquad K_{a2} \qquad \textit{Eq. 3.7}$$

Where �S-$OH_2^+$, �S-OH and �S-O- representing positively, neutral and negatively charged surface hydroxyl respectively and $K_{a1}$ and $K_{a2}$ are acidity constants.

$$K_{a1} = \frac{[\equiv S - OH][H^+]}{[\equiv S - OH_2^+]}$$

*Eq. 3.8*

$$K_{a2} = \frac{[\equiv S - O^-][H^+]}{[\equiv S - OH]}$$

*Eq.3.9*

The adsorption of a metal cation on a hydrous oxide includes the creation of bonds of the metal ion with the surface oxygen atoms and release of protons from the surface (Sharma 2001).

$$\mathbf{\equiv S\text{-}OH + M^{2+} = \equiv S\text{-}OM^+ + H^+} \qquad K_M \qquad \textit{Eq. 3.10}$$

Where $M^{2+}$ is a divalent cation and $K_M$ is surface complexation constant.

$$K_M = \frac{[\equiv S - OM^+][H^+]}{[\equiv S - OH][M^{2+}]}$$

*Eq.3.12*

The surfaces in aqueous solutions that are having low pH values is more positively charged due to supplementary complexed hydrogen ions producing $\equiv\!-OMOH_2^+$and loss of $OH^-$

$\equiv$S-OH + $M^{2+}$ + $H_2O$ = $\equiv$S-OMO$H_2^+$ +$H^+$/$OH^-$ ***Eq.3.13***

The surfaces are negatively charged in higher pH solutions due to the loss of H+ from surfaces and afterwards surface becomes more favorable for the cation adsorption.

$\equiv$S-OH + $M^{2+}$ + $H_2O$ = $\equiv$S-OM$O^-$ +3$H^+$ ***Eq.3.14***

This proves that increase in pH increases the adsorption of cations on to hydrous oxides. Dzombak and Morel (1990) also told that percentage of adsorption of cations onto hydrous oxides goes from 0 to 100 within narrow pH range that gives typical adsorption “pH range” (Buamah 2009).

The $Fe^{+2}$ adsorption occurs during the abstraction phase in the absence of oxygen, which can be formulated as follows (van Halem et al 2011).

S _ $OH^o$ + $Fe^{+2}$ =S _ OFe $^{+2}$ +$H^+$ ***Eq. 3.15***

An electron will be transferred from the adsorbed $Fe^{+2}$ to the solid, that will create trivalent ion that will hydrolyze and equivalent to Fe $(OH)_2$ (Hiemstra and van Riemsdijk, 2007) in (van Halem 2012). The adsorptive capacity of soil changes with the different forms of iron hydroxide present in the soil. Amorphous $Fe^{+3}$ hydroxides have the large adsorption capacities as compared with low surface area crystalline mineral structures which can include Goethite and lepidocrocite. The injection of oxygen rich water into $Fe^{+2}$ saturated groundwater causes oxidation of adsorbed $Fe^{+2}$ heterogeneously.

S-O$Fe^{+2}$ + 0.25 $O_2$ +1.2 $H_2O$ = S + O$F^{+3}(OH)_2$ +$H^+$ ***Eq. 3.16***

The reaction of oxidation releases a proton per oxidized S-O$Fe^{+2}$ complexes at near neutral pH like during the adsorption of $Fe^{+2}$.The two protons will be released in the result of combined reaction of adsorptive – catalytic oxidation. The injected water front will leave behind oxygen front due to the more consumption of oxygen during the reaction that will have effect on the penetration of the oxygen into the aquifer. The presence of Fe+3 hydroxides will catalyze the rate of heterogeneous oxidation (Tamura et al., 1980) in (Van

Halem 2012). Groundwater containing manganese can also be purified by adsorption processes (Piispanen and Sallanko., 2010).

Van Beek and Vaessen (1979) were the first who suggested that $Fe^{+2}$ that sorbed on iron-oxyhydroxide in the aquifer can be oxidized by injecting the oxidant. This will result in the formation of $Fe^{+3}$ that will precipitate and it form a new layer on the already existing layer of iron-oxyhydroxide, which will sorb $Fe^{+2}$ from the ground water in the reversed flow (Appelo et al.,1999 ).

First of all, cations which are present in injected water will exchange with $Fe^{+2}$ from the exchange sites. Then $Fe^{+2}$ present in the solution with react with oxygen, oxidation will take place means $Fe^{+2}$ will be converted into $Fe^{+3}$ which will precipitate as iron-oxyhydroxide. Oxygen is retarded since it is consumed by the reaction due to which oxygen front remains behind the front of injected water, and $Fe^{+2}$ remains in the solution between the fronts of oxygen and injected water flow (Fig 3.14 a& b) (Appelo et al., 1999).

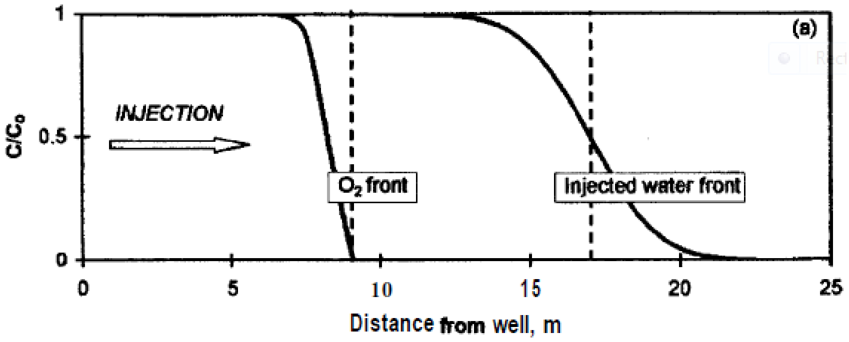


**Figure 3.14 a:** $O_2$ front and extent of injected water at the end of injection (Appelo et al., 1999).

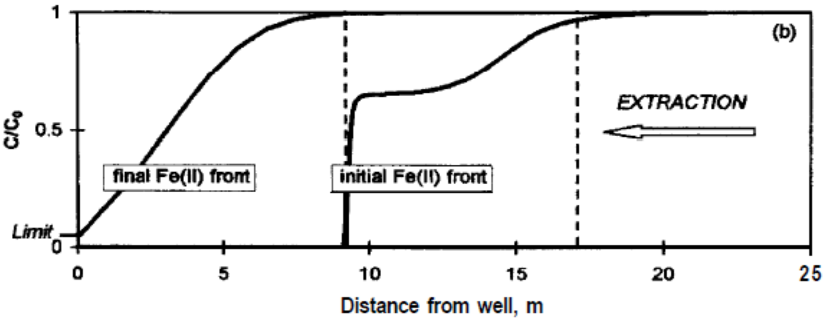


**Figure 3.14 b:** Solute $Fe^{+2}$ fronts at the beginning and end of extraction (Appelo et al., 1999).

The exchanger becomes totally free from $Fe^{+2}$ where oxygen is present in the ground water. When groundwater containing $Fe^{+2}$ is pumped, the $Fe^{+2}$ will be sorbed again by depleted exchanger. So iron front will remain behind groundwater front, the pumping water will be free of iron until $Fe^{+2}$ front reaches at the well flow (Appelo et al.,1999).

According to this theory ratio of sorbed concentration of iron and concentration of solute iron is at least equal to efficiency. But these calculations were not performed by Van Beek and Vaessen (1979) to assure that this can be case, and only considered iron-oxyhydroxide as a sorber of $Fe^{+2}$. (Eichhom 1985) in (Appelo et al 1999) proposed that a sediment which can includes clay minerals and other different type of exchanger can also have the cation exchange capacity and is also available for exchange of $Fe^{+2}$. Calculation of exchangeable $Fe^{+2}$ was also not calculated by him flow (Appelo et al., 1999).

Van Beek and Vaessen relates the increase in efficiency with initial concentration of consumed oxidant by reductants other than $Fe^{+2}$ and to the increase in concentration of iron-oxyhydroxide during consecutive cycles. The observed increase in efficiency during successive cycles is shown in (Fig 3.15) (Appelo et al., 1999).

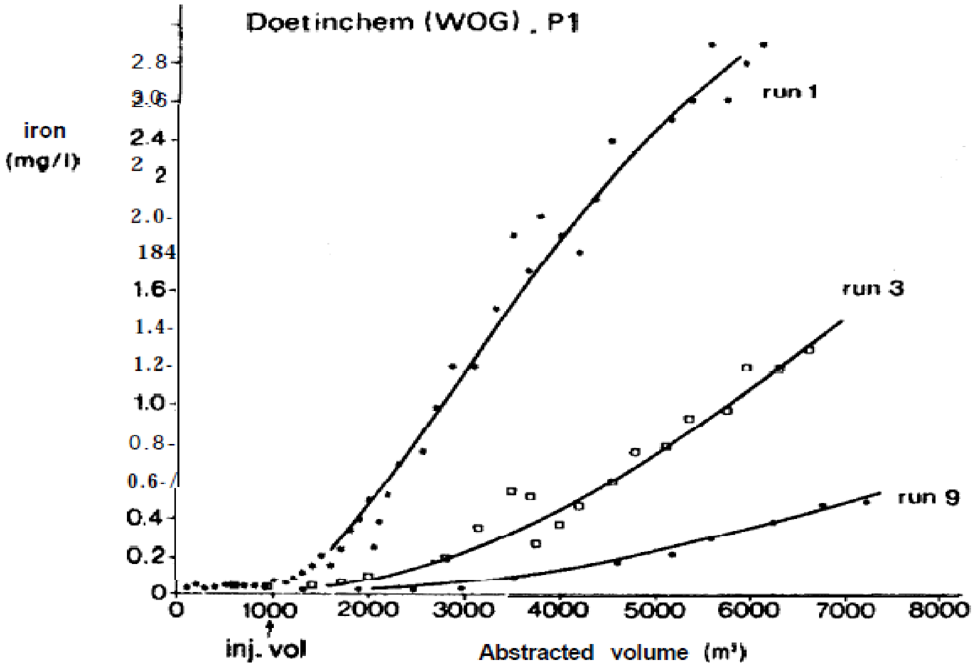


**Figure 3.15:** Iron concentration in ground water as function of pumped volume and number of injections of oxygenated water (Appelo et al., 1999) (modified from Van Beek 1980).

When injection of oxygenated water starts again before the concentration of iron in the groundwater attains the level of foregoing run, the exchanger in not refilled with Fe$^{+2}$ to the previous level. It means that small amount of exchangeable Fe$^{+2}$ will allow the oxygen to penetrate deeply into the aquifer, that results in creation of large oxidized zone to sorb the Fe$^{+2}$ from a bigger volume of water (Appelo et al.,1999).

Figure3.16 is illustrating the process, where concentration of sorbed Fe$^{+2}$ is shown against the distance to well during the first two cycles.(fig3.6 a)is showing that aquifer exchanger is containing the 1.05mmol Fe$^{+2}$ /L in pore water uniformly in this example.

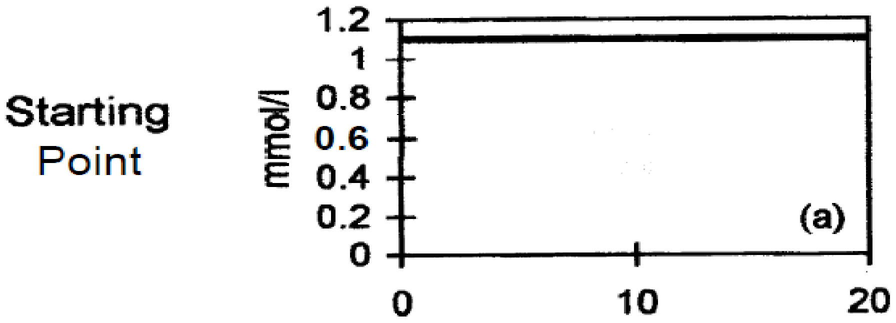


**Figure 3.16 a:** Concentration of sorbed Fe$^{+2}$ in the pristine aquifer

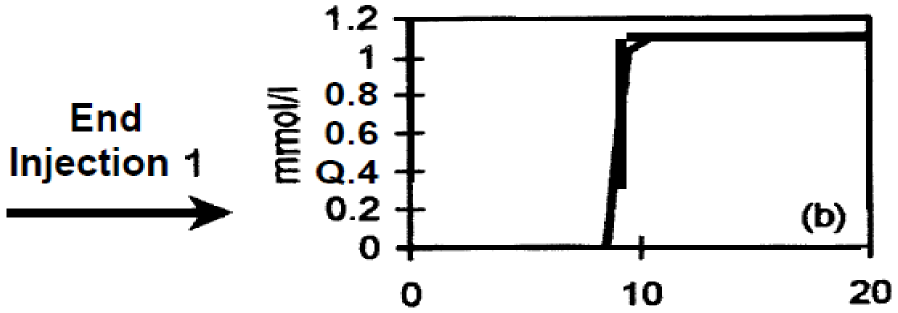


**Figure 3.16 b:** Concentration profile after the first injection of oxygynated.

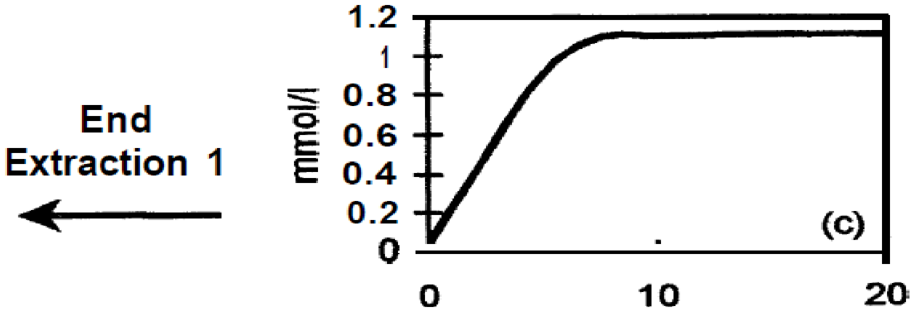


**Figure 3.16 c**: The exchange complex is not completely refilled with Fe$^{+2}$ at the end of the first extraction.

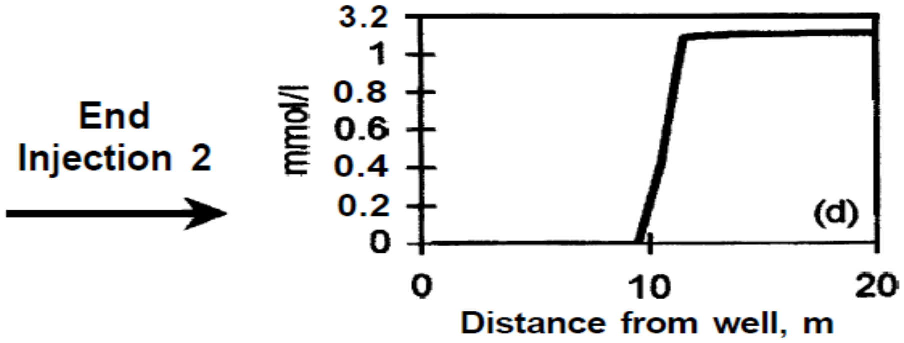


**Figure3.16 d:** less sorbed Fe$^{+2}$ near the well permits the oxygen to enter the aquifer further with the second injection (Appelo et al., 1999).

In this example at the beginning the aquifer exchanger containing the 1.05mmol Fe$^{+2}$/L pore water (Fig 3.16 a). When first injection finished the sorbed Fe$^{+2}$ concentration becomes zero in the oxidized zone near the well. The concentration of sorbed Fe$^{+2}$ is zero in the oxidized zone near the well at the end of first injection (Fig 3. 16 b).The groundwater will be extracted untill the concentration of iron reached a limiting value and then first cycle ends.(Figure3.17 c) is giving the profile of the sorbed iron, and it is different from the initial profile in which less iron is sorbed near the well. In the second injection oxygen will enter few meters further into the aquifer and it will create large oxidized zone (Fig 3.16 d).The larger oxidized zone in aquifer will allow the sorption of iron at bigger scale that will result in extraction for a long period of time until the concentration of iron attains the limit. The transient character of the operation in the initial stages is connected to the increase in efficiency. In (Figs 3.16 a, b), it can be observed that shapes of profile of solute and sorbed concentration of Fe$^{+2}$ are not similar at the end of injection stage. The concentration of solute Fe $^{+2}$ is lower between the front of oxygen and injected water than in pristine groundwater (Fig 3.14). In that part the concentration of exchangeable remains equal to original concentration in the aquifer. Because the concentration of Ca$^{+2}$ has decreased in the oxidized zone due to the exchange with Fe$^{+2}$. Thus less competition is offered by Ca$^{+2}$ for the exchange sites and Fex2 concentration is not even increasing  after oxygen front regardless the lower concentration of Fe$^{+2}$ in solution( Appelo et al., 1999).

## 3.14 Cation Exchange

The following example is explaining the principle of this process. When $Na^+$ present in injected water displaces $Fe^{+2}$ form the exchange site of clay mineral (Der Laan 2008). The reaction is given as following

$$Na+ + 1/2Fe\text{-}X_2 = Na\text{-}X + 1/2Fe^{2+} \qquad \log K = -0.22 \qquad \textbf{\textit{Eq. 3.17}}$$

Where, X is indicating the cation exchanger, with a charge of X.

All the solid surfaces present in the soils and aquifers can act as adsorbents. The adsorption capacity depends on the grain size, that's why the solid surfaces with big specific surface area will be having the most adsorption capacity. Solids having the large specific surface area located in clay fraction (≤2um), and coarser grains in sediments are covered with iron oxyhydroxide and organic matter. The adsorption is directly related to clay minerals, clay content (fraction ≤ 2), organic matter (%C) and oxide and hydroxide content.

An empirical formula which is relating cation exchange capacity to the percentage of clay (≤2um) and organic carbon at the neutral pH is given follow. (Breeuwsma et al., 1986) in (Appelo and Postma., 2005).

$$\text{CEC (meq/kg)} = 7.(\%\ \text{clay}) + 35.(\%\text{C}) \qquad \textbf{\textit{Eq. 3.18}}$$

For clay minerals CEC depends upon mineral structure and specific surface area, while for iron oxides and organic matter CEC is a function of pH.

Where (% clay) and (% C) are representing the weight percentages of clay < 2_m and organic carbon, respectively (Appelo and Postma, 1993). The recalculation of CEC to capacity per liter of groundwater by multiplication with bulk density $\rho_b$ (kg/$dm_3$) and dividing by water filled porosity $\varepsilon_w$ (Appelo and De Vet, 2003).

$$X\ (\text{mmol /l}) = \text{CEC (mmol /kg)} \cdot \rho_b / \varepsilon_w \qquad \textbf{\textit{Eq. 3.19}}$$

When the conditions are steady state, then the cation exchanger composition will be in equilibrium with the resident groundwater. When pollution or acidification will cause the composition to change, then composition of cation exchanger will be readjusted according to new groundwater concentrations. By doing this exchanger act as temporary buffer which can change the concentrations in the water through a process called as ion-chromatography (Appelo and Postma 2005).

The process of cation exchange in groundwater is multicomponent in which all the solute cations take part. The recalculation can be done easily with geochimecal models such as PHREEQC-2 (Parkhurst and Appelo, 1999) cited in in (Appelo and vet, 2003) which have database with representative values of the exchange constant.

### 3.14.1 Mechanism of ion exchange

(Appelo and Postma, 2005) proposed that injection of oxidized water will begin the exchange of adsorbed $Fe^{+2}$ with some other cations like Na and Ca.

$XCa + Fe^{2+} = XFe + Ca^{2+}$ or $2XNa + Fe^{2+} = X_2Fe + 2Na^{+}$ ***Eq. 3.20***

Where X represents exchange sites and exchange coefficients, following the Gaines-Thomas Convention, of KCa\Fe ¼ 0.7 and KNa\Fe ¼ 0.6 (Appelo and Postma, 2005).

(Fig 3.17) is explaining the process of cation exchange during the subsurface iron removal for a simple system containing $Fe^{+2}$ during extraction and $Ca^{+2}$, Na+ and $O_2$ injection. Both soluble and adsorbed $Fe^{+2}$ are present before the beginning of injection. (Fig 3.18 A) During the injection the cations present in injected water Ca+2 and Na+ will exchange with the adsorbed $Fe^{+2}$ on the soil grains (Fig 3.18 B). The deadsorption takes place and de adsorbed $Fe^{+2}$ is flushed deeper into the aquifer , where it partially mix with O2 present injected water that results in hydrolyzed $Fe^{+3}$ precipitates $Fe(OH)_3$, (Figure 3.18 C). On beginning of extraction when flow is reversed the $Fe^{+2}$ in groundwater is retained on $Fe^{+3}$ hydroxide and on mineral surface, either through cation exchange or adsorption (Van Halem et al .,2011).

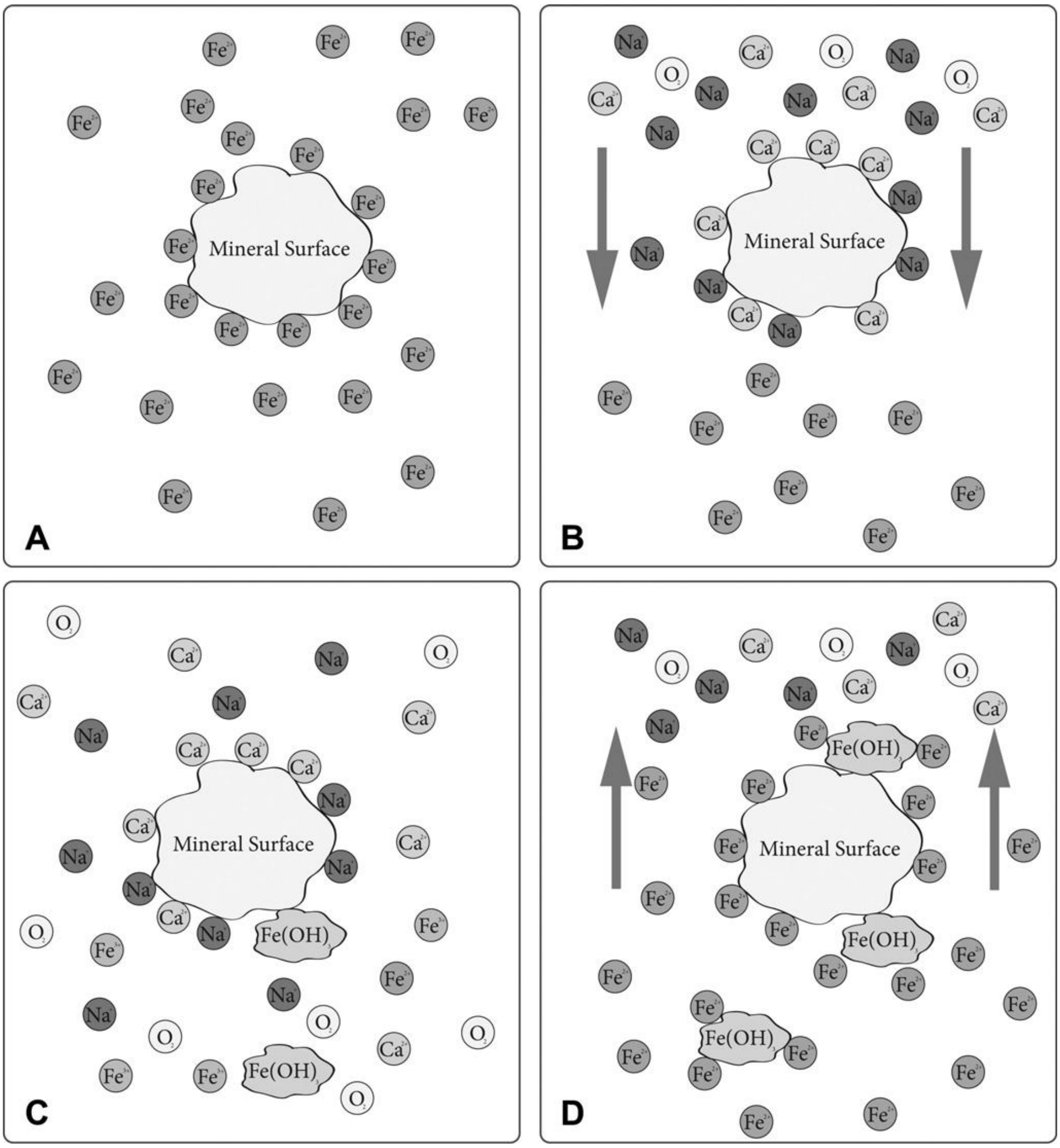


**Figure 3.17:** Schematic presentation of cation exchange during subsurface iron removal on the sand grain surface (Van Halem et al 2011).

The extent to which cation exchange cation exchange contribute to efficiency of system depends upon the composition of groundwater and injection water, but it also depends on exchangeable $Fe^{+2}$ on the material of aquifer. The cation exchange capacity (CEC) of the soil depends on the clay, organic carbon and iron hydroxide content (Appelo and Postma, 2005) in (Van Halem et al. 2011). Clay minerals have the wide range in CEC that depends upon mineral structure, specific surface of the mineral that is accessible to water and structural substitutions. For organic matter and iron oxides the cation exchange capacity CEC is also a function of pH because the surface oxygen acts as amphoteric acids (Appelo and Postma, 2005).

### 3.15 Factors Influencing Sorption

The properties of a contaminant have a profound impact on its sorption behavior. Some of these include:

- Water Solubility
- Polar/Ionic Character
- Octanol/Water Partition Coefficient
- Acid/Base Chemistry
- Oxidation/Reduction Chemistry (Keeley and Piwoni, 1990).

### 3.16 Measurement of Sorption

Batch experiments are often used to determine the sorption, where solute aliquots in varying amounts are mixed with the solid, and the amount of solute removed is determined by the difference between the initial concentration and the equilibrium concentration. The plot that shows equilibrium solute concentration against concentration of sorbed solute onto solid is known as isotherm. According to Appelo and Postma (2005) isotherm is a relation at a fixed temperature between the dissolved solute and sorbed solute.

### 3.17 Kinetic sorption isotherm

It is needed when the sorptive process is slow compared with the rate of fluid flow.

### 3.18 Equilibrium sorption isotherm

It can be used when the sorption process is rapid compared to the flow velocity. There are following types of equilibrium sorption isotherm

- Linear Sorption Isotherm
- Freundlich Sorption Isotherm
- Langmuir sorption Isotherm

### 3.18.1 Linear sorption isotherm

According to linear sorption isotherm, the sorbed concentration (S,mg/kg) of solute is directly proportional to the solute concentration (C,mg/L) in the solution and the plot results in straight line (Fig 3.18) .

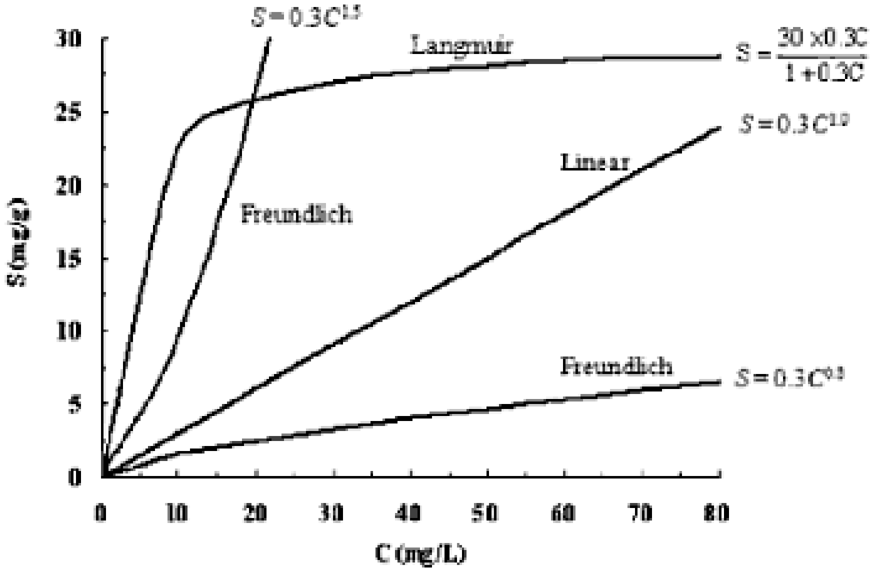


**Figure 3.18:** Example of linear, Langmuir and Freundich isotherms

Following equation is describing the linear sorption isotherm (Taylor and Aral, 2011).

$$S = K_dC \qquad \textbf{\textit{Eq.3.21}}$$

The slope of linear isotherm is shown by $K_d$ .The high value of Kd is the indicator of high tendency for sorption. Retardation of contaminants is also caused by sorption; a retardation factor can be described as

$$R = 1 + \frac{\rho_b}{n} K_d \qquad \textbf{\textit{Eq.3.22}}$$

Where R is retardation factor, bulk density of aquifer is shown by $P_b$ , n is the porosity and $K_d$ is distribution coefficient. The value of $K_d$ can range from 0 to $10^3$ mL/g (Bedient et al., 1999) cited in (Taylor and Aral, 2011).

By retardation the velocity of contaminant becomes slower than velocity of groundwater, so reatardation factor can relate the two velocities by retardation equation.

$$v_c = \frac{v_w}{R} = \frac{v_w}{1 + \frac{\rho_b}{n} K_d}$$

***Eq. 3.23***

Velocity of water is indicated by $V_w$ and $V_c$ is velocity of contaminant. Position of the advective front can be predicted by this equation when equilibrium sorption using the linear isotherm is considered. The ratio $V_w/V_c$ predicts that how fast groundwater is flowing in relative to the contaminant being sorbed. When $K_d$ is equal to zero, then $V_w = V_c$, therefore retardation factor of R suggest that plume of contaminant is moving R times slower that the velocity of groundwater (Bedient et al., 1999) cited in (Taylor and Aral, 2011).

(Fig 3.19) is showing the retardation effect on breakthroug curve of a solute that is described by dashed line and comparing it with breakthrough curve with no retardation that is shown by solid line. In conclusion it can be written that the retarded substance is having the lower maximum concentration in comparison with non retarded.In addition retarded substance is taking more pore voulmes to attain the maximum concentration (Taylor and Aral, 2011).

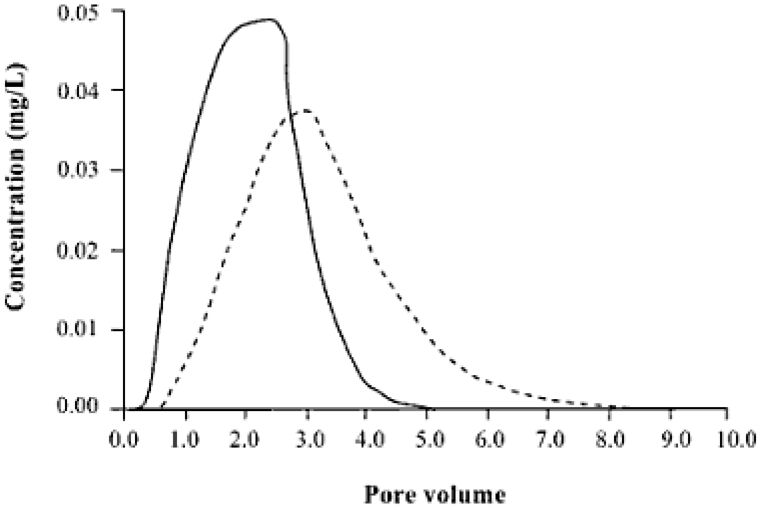


**Figure 3.19:** Comparison of the breakthrough curves for non retarded and linearly retarded solute. Dashed curve is for the retardation curve.

Linear sorption isotherm has become most popular approach in modeling sorption because of its simplicity. But Domenico and Schwartz (1990) cited in (Taylor and Aral 2011) told that it is very complex to model sorption process by linear isotherms using only Kd, which is not easy to describe because the value of $K_d$ changes from place to place according to the physical and chemical characteristics of porous medium and chemical properties of contaminant.

### 3.18.2 Freundlich sorption isotherm

The Freundlich sorption isotherm can be described by the following nonlinear relationship

$$S = KC^N \qquad \textbf{\textit{Eq. 3.24}}$$

Where S is concentration of sorbed solute, C is concentration of solute in solution, K and N are constant. Where (Fig 3.19) is showing Freundlich sorption isotherm for N = {0.8, 1.5}. In conclusion If N is greater than 1, the sorbed concentration for a given solute is bigger in comparison with when N is smaller than 1. Addtionally when N is smaller than 1 the ratio of sorbed concentration to solute concentration will decrease with increase in solute concentration (Appelo and Postma, 1996 ) cited in (Taylor and Aral, 2011). When N becomes equal to 1 then Freundlich sorption isotherm becomes linear sorption isotherm.The retardation coefficient for a Freundlich isotherm $R_F$ can be written as following (Fetter 1999) cited in (Taylor and Aral 2011).

$$R_F = 1 + \frac{\rho_b K N C^{N-1}}{n} \qquad \textbf{\textit{Eq. 3.25}}$$

### 3.18.3 Langmuir sorption isotherm

The Langmuir sorption isotherm can be described as following equation.

$$S = \frac{\alpha\beta C}{(1+\alpha C)} \qquad \textbf{\textit{Eq. 3.26}}$$

Where α describes the partition coefficient that indicates the extent of sorption and β shows the maximum sorptive capacity for the solid surface. (Fig 3.18) shows Langmuir sorption isotherm for α = 30 L/g and β = 0.3 mg/g. The retardation factor for the Langmuir sorption isotherm $R_L$ is shown by following equation (Fetter 1999) cited in (Taylor and Aral, 2011).

$$R_L = 1 + \frac{\rho_b}{n}\left(\frac{\alpha\beta}{(1+\alpha C)^2}\right) \qquad \textbf{\textit{Eq. 3.27}}$$

According to Langmuir sorption isotherm, the process of sorption will stop when all the sorption sites on the solid surface are occupied (Taylor and Aral, 2011).

# Chapter 4: Geochemical Modeling with PHREEQC

The version 2 of Software PHREEQC was used to perform the Geochemical modeling in this study. It is a computer program that can be used to simulate different type of transport processes and chemical reactions in natural or polluted waters. This program is based on equilibrium chemistry of aqueous solutions that interacts with minerals, solid solutions, exchanger, gases and sorption surfaces and can also treat Kinetic reactions (Parkhurst & Appelo, 1999).

PHREEQC is a computer program written in C language and it is derived from the Fortran program PHREEQE (Parkhurst, 1995). PHREEQE (Parkurst et al, 1980) has been used as geochemical program for nearly 30 years and it was capable to simulate a wide range of geochemical reactions that includes mixing of waters, addition of net irreversible reactions to solution, dissolving and precipitating phases to achieve equilibrium with the aqueous phase, and effects of changing temperature. But along with all these advantages PHREEQE was lacking with some of functions, and showing some deficiencies due to which it was considered as inconvenient and time consuming (Parkhurst, 1995).

## 4.1 Input Data in PHREEQC

Keyword data blocks are used to arrange the input for PHREEQC. Every data block starts with a line having the keyword. This keyword is followed by additional lines representing the data related to keyword. Data base files are used to read keywords and their associated data at the beginning of a run to define the elements, mineral phases, gas components, exchange reactions, surface complexation reactions and rate expressions. A simulation is a set of calculations defined by keyword data blocks and finished by an END. A run can include a series of one or more than one simulations that are performed by using the same input data file and calculated during the same command of the program PHREEQC (Parkhurst & Appelo, 1999).

## 4.2 Output data in PHREEQC

The Keyword data block selected_output is used to produce a file that is convenient to process by spreadsheets and other data management software like Microsoft Excel. It allows the printing of specified entities form the composition of solution, exchange assemblage, surface assemblage and solid solution assemblage after completing the each type of calculation. The selected_output file will have a column for each data item defined by the identifiers of selected_output. All names of elements, names of species, and names of phases should be spelled correctly in the input of selected output. The keyword Print is used to select the results that are written to output file. In print data block selected_output identifier can be used to selectively resume and suspending to write results in the selected_output file. While doing the transport simulations the option of reset false is important and punch_cells and punch_ frequency can be used to further control the results written in selected_output file (Parkhurst & Appelo, 1999).

## 4.3 Equilibrium Reactions and Solubility of minerals

The solubility of a mineral is maximum concentration of its components in water. By doing the solubility calculations, concentration ranges can be predicted in groundwater. Some minerals react very fast on the contact with water, while some minerals like silicates react slowly that equilibrium is never attained at low temperatures (Appelo and Postma 2005). Equilibrium reactions can be performed by PHREEQC.

## 4.4 Sorption

The process of sorption depends upon the surface area, amount of sorption sites, and the relative attraction of aqueous species to sorption sites on mineral/water interfaces. Sorption can take place on the permanent charge surface that includes ion exchange, and this mainly occurs in clay and also on variable charge surfaces that includes surface complexation. It mainly occurs on Fe, Mn oxides, hydroxide.

### 4.4.1 Surface Complexation

The processes of surface-complexation are included in the model through the equations of mass-action and mole balance for surface sites, and relations of charge potential relations for each surface. PHREEQC allows multiple surfaces and surface-site types, termed a “surface assemblage”, to exist in equilibrium with the aqueous phase.

The thermodynamic data is contained by default data bases for a surface named “Hfo” (Hydrous ferric oxide) driven from Dzombak and Morel (1990). Two types of sites are defined in database that includes a weak binding site Hfo_w and strong binding site Hfo_s. Dzombak and Morel (1990) used 0.005 strong sites per mol and 0.2 mol weak sites per mole Fe, a gram-formula weight of 89 g Hfo/mol Fe and surface area of a surface area of 5.33e4 $m^2$

/mol Fe. The relative number of weak and strong sites should remain constant to be consistent with their model as the total number of sites varies.

Surface complexation reactions for iron and manganese are given below

$Hfo\_wOH + Fe^{+2} = Hfo\_wOFe^{+} + H^{+}$  log_ *K*  -2.5  ***Eq 4.1***

$Hfo\_sOH + Fe^{+2} = Hfo\_sOFe^{+} + H^{+}$  log _k  0.7  ***Eq 4.2***

$Hfo\_sOH + Mn^{+2} = Hfo\_sOMn^{+} + H^{+}$  log_k  -0.4  ***Eq 4.3***

$Hfo\_wOH + Mn^{+2} = Hfo\_wOMn^{+} + H^{+}$  log_k  -3.5  ***Eq 4.4***

### 4.4.2 Ion Exchange

PHREEQC calculates the ion exchange in terms of association reactions of ions and exchanger with constriction that all exchange sites ate always covered up by the ions means that there is no existence of free $X^{-}$. (Appelo et al., 1997).But the ion exchange part is not included in model.

$X^{-} + Na^{+} = Na\text{-}X$;  LogK Nax = 0.0  ***Eq 4.5***

## 4.3 Reactive transport simulations with radial flow

The PHREEQC input file for calculation of data was prepared by splitting the column into 15 cells of different lengths to model the radial flow. (Fig 4.1) is showing the radial flow towards well. According to Appelo and Postma (1993) radial flow can be modeled in well injections by adapting the cell lengths in agreement with the radial extension of the injection front. The column is representing the modeled aquifer which contains $Fe^{+2}$ and $Mn^{+2}$ in solution and where the in-situ treatment is taking place. Different keywords have been used to define the data. Solution 0 is the injected water in cell 1. 15 Cells are representing the solutions 1-15. Different levels of oxygen have been introduced in cell 4 under the Keyword of Equilibrium phases. The sorbing surfaces have been defined to be in equilibrium with the given solution. The parameters of transport identify 15 cells, cell lengths and the boundary conditions. The time step associated with the each shift is 3600 sec (1 hour). The number of times the solution in each cell shifted to next higher numbered cell is known as shift (Appelo and Postma., 1999). Total shifts were 155 and total time can be calculated by shifts*time step.

Since the column consists of 15 cells and solution 0 has been transported 155 times, it means that 10.3 pore volumes are injected.  The following section describes the effects of injection of different levels of oxygen into the cell no 4 the column of 15 cells on iron and manganese removal.

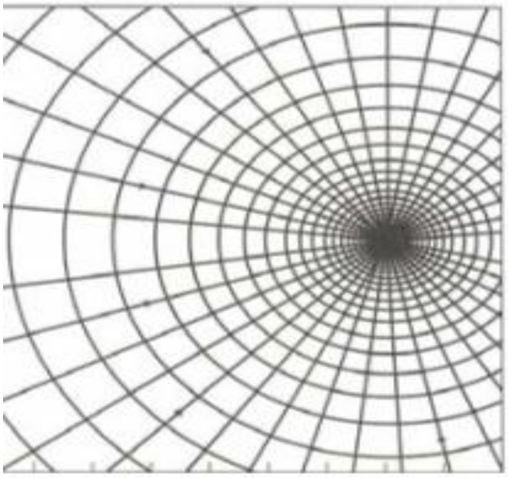


**Figure 4.1:** Radial flow towards well.

### 4.4 Results in Cell no 15

The process of in situ oxidation seems to be simple in which given amount of oxidant is injected and consumed by the reduced substances in the aquifer. Oxidation /precipitation zone is achieved by the using the different level of oxygen.  In oxidation zone the dissolved $Fe^{+2}$ and $Mn^{+2}$ use oxygen as electron acceptor to get oxidize and turn into $Fe^{+3}$ and $Mn^{+4}$ which are insoluble forms of Iron and manganese. The $Fe^{+3}$ ferric iron precipitate as oxyhydroxide like goethite and $Mn^{+4}$ also precipitate as oxyhydroxide such as pyrolusite

The increased amount of dissolved oxygen can increase the removal rate of iron and manganese at a certain range of amount. (Fig 4.2) is showing the removal of iron at the different levels of log PO2 in cell no 15. The concentration of dissolved iron is going down certainly at different log PO2 levels especially at 0 and -1 and removing all the dissolved ions very fast. At log PO2 level of -2 the concentration has decreased suddenly until step 16-18 but after then decreasing slowly with time. At at log PO2 of -3 and -4 concentrations suddenly decrease, then start to increase for a very short time after that start decreasing. Overall the removal of iron is seems to be very effective in cell no 15.

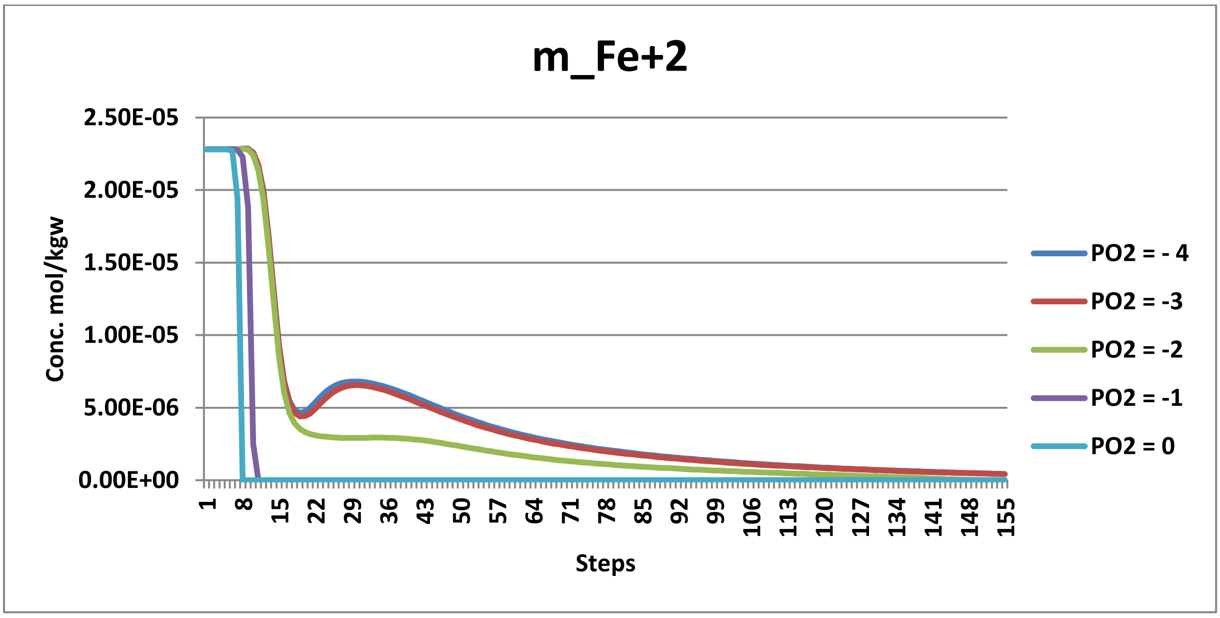


**Figure 4.2:** Concentration of soluble iron at different log PO2 levels in cell 15.

It seems that more concentration of oxygen is required to remove the manganese than iron. (Fig 4.3) is showing the behavior of manganese in cell no 15 at different log PO2 levels at all the steps. The log PO2 levels of 0, -1 and -2 are looking very effective to remove the manganese very early from solution. But on decreasing the amount of oxygen the concentration of manganese starts to increase again after 20 steps. So removal of manganese is not effective if oxygen is lower than below to -2 log PO2, because the -3 and -4 log PO2 levels are not helping to remove the manganese.

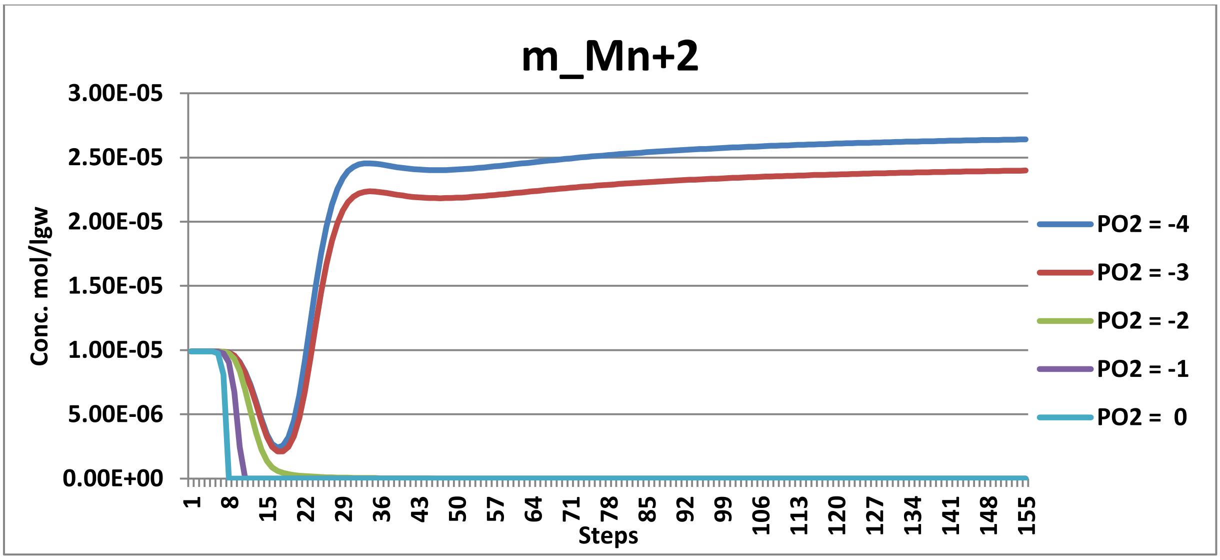


**Figure 4.3:** Concentration of manganese at different log PO2 levels in cell 15.

Fig 4 .4 & 4.5 is showing the fluctuations in pH and pe values at different log PO2 levels in cell no 15.

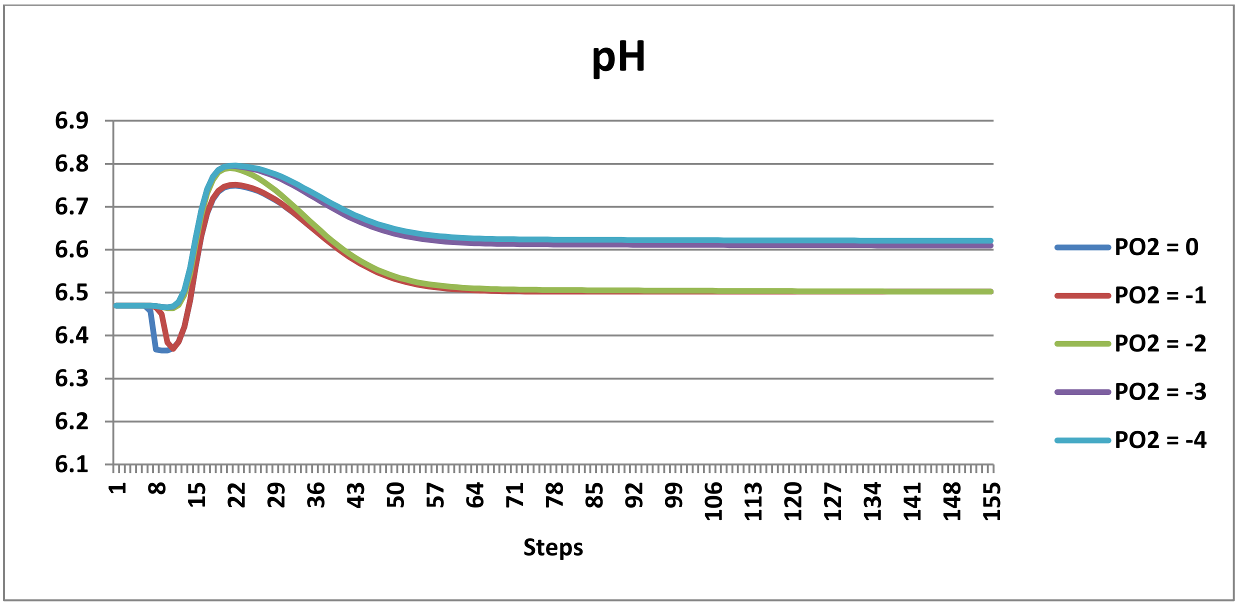


**Figure 4.4:** Fluctuations in pH along all steps in cell no 15 at different log PO2 levels.

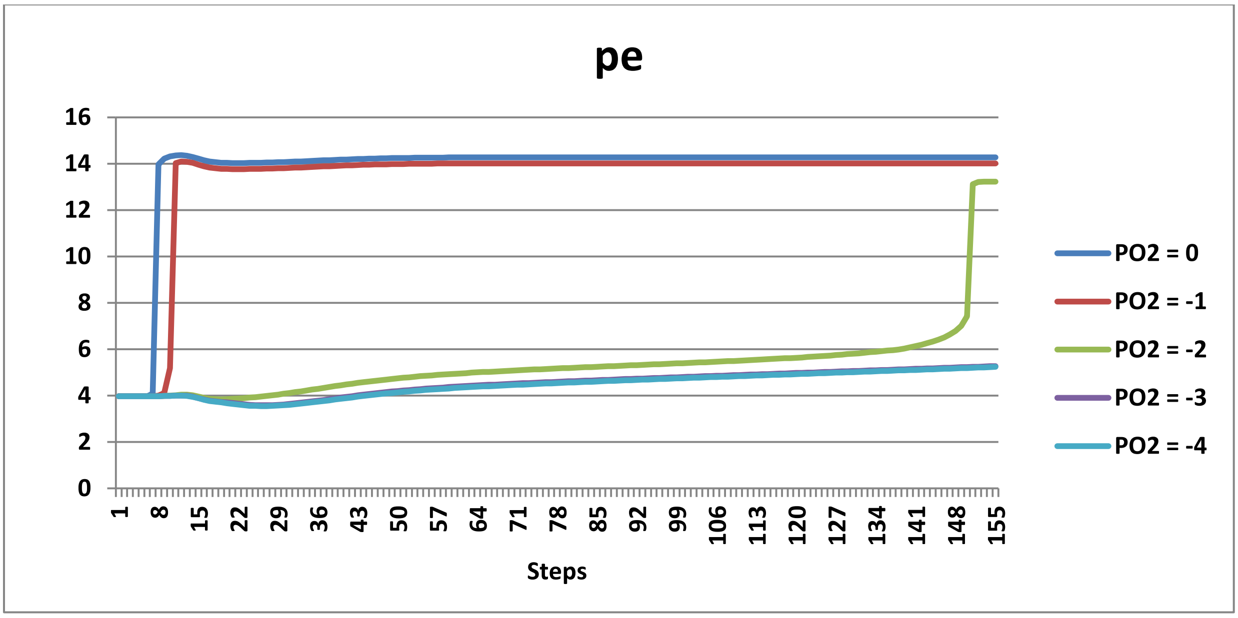


**Figure 4.5:** Fluctuations in pe along all steps in cell no 15 at different log PO2 levels.

### 4.4.1 Concentration of iron at different steps in different cells

The removal of iron has proved to be very effective even by the low log PO2 levels. Different log PO2 levels have been introduced in the cell no 4, the concentration is decreasing considerably in cell no 5. (Figure 4.6) is suggesting that log PO2 level of -3 sufficient to remove all the iron from the solution at steps 10-40 in cell no 5.

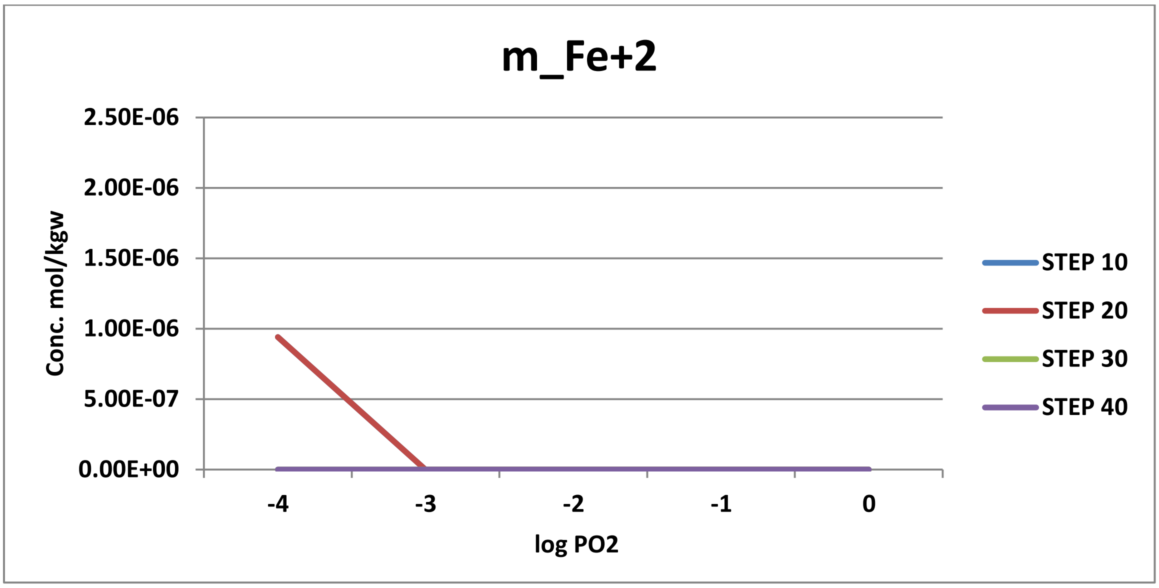


**Figure 4.6:** concentration of iron in cell no 5 at different log PO2 levels at steps 10-40.

As compared to cell 5 higher level of oxygen is required is to remove all the iron from the solution in cell no 6. In cell no 5, log PO2 level of -3 was sufficient to remove all the iron, but in cell no 6, log P02 level of -2 is required to remove all the iron. (Fig 4.7) is suggesting that log PO2 level of -2 is required to remove all the iron in cell no 6 from the solution.

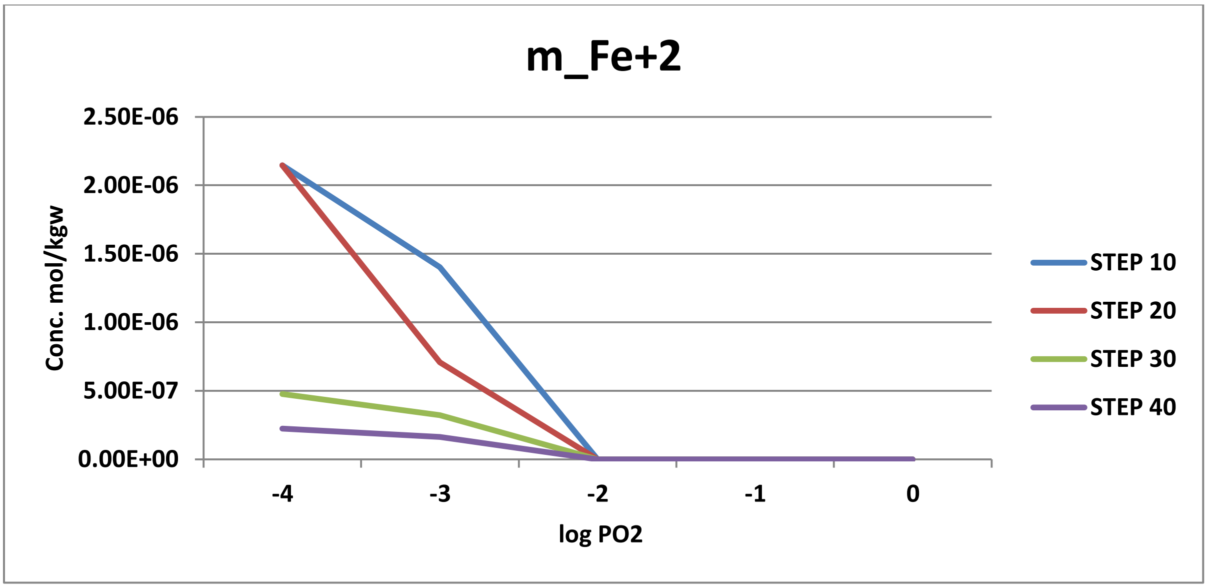


**Figure 4.7:** concentration of iron in cell no 6 at different log PO2 levels at steps 10-40.

The concentrations of dissolved iron are going down in solution as concentration of oxygen is increasing in cell no 15. At step 10 concentrations of iron have been finished from solution when amount of oxygen is reached to 0. However at step 10 it seems that concentration of iron has been decreased considerably also when amount of oxygen is -1 log PO2. Also At step 20, 30, 40 iron concentrations have removed totally from solution at log PO2 level of -1 (Fig 4.8).

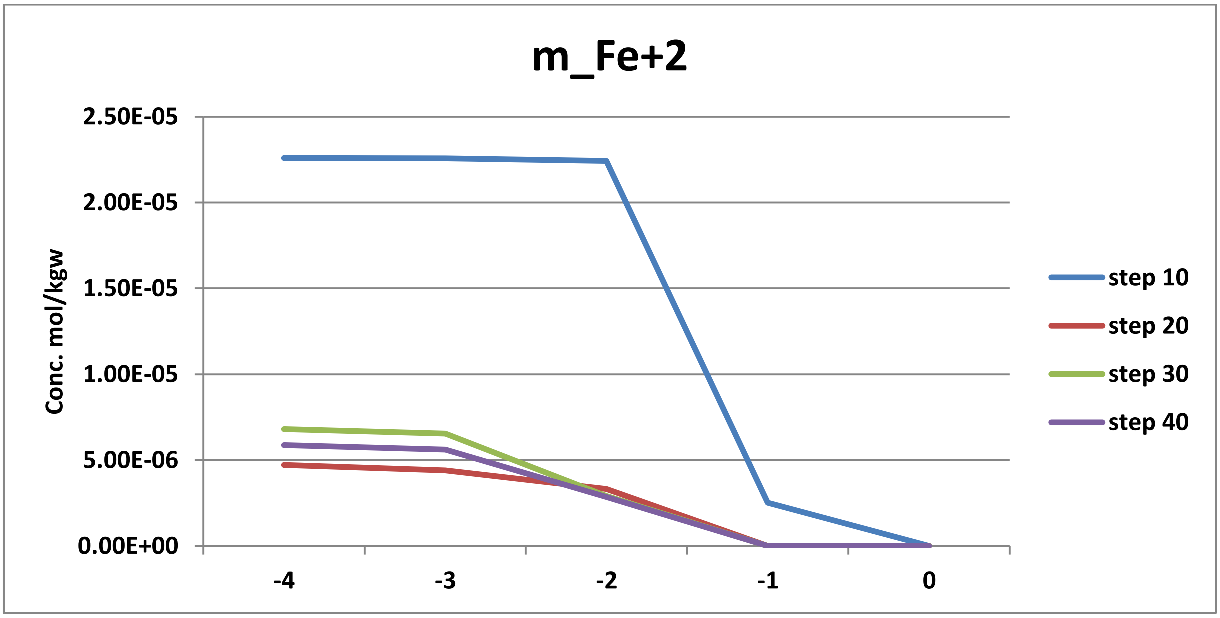


**Figure 4.8:** Concentration of iron at different log PO2 levels in cell no 15 at steps 10-40.

### 4.4.2 Concentration of manganese at different steps in different cells

As compared to iron higher levels of oxygen are required to remove the manganese from the solution in cell no 5. For iron log PO2 level of -3 was required in cell no 5, while to remove manganese in cell no 5, log PO2 level of -2 is required. (Fig 4.9) is showing that log PO2 level of -2 is high enough to remove all the manganese from the solution in cell no 5.

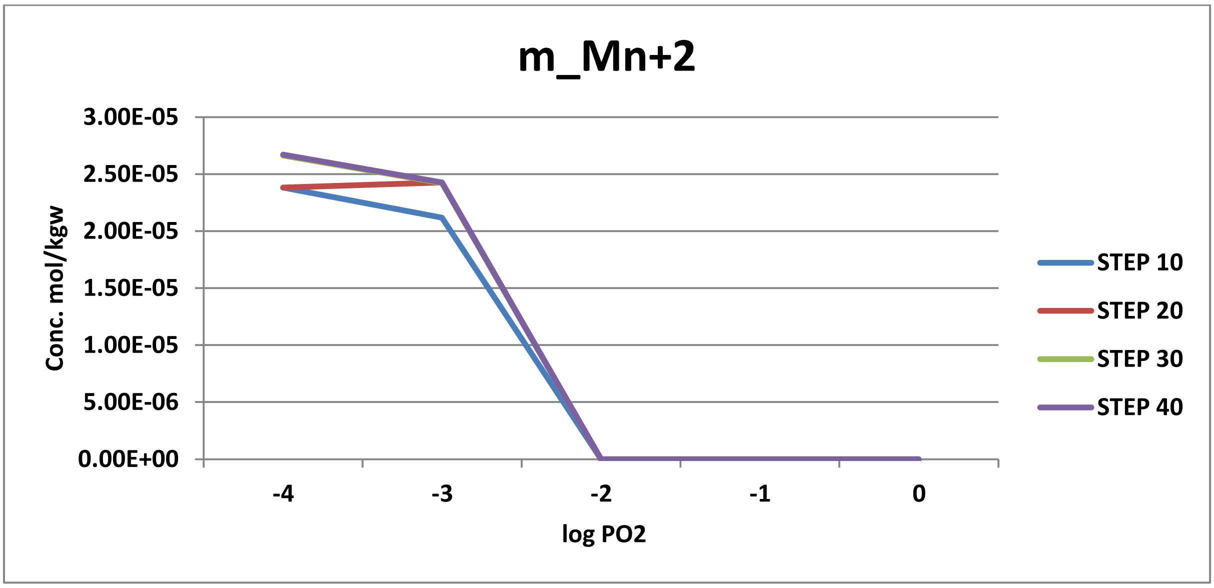


**Figure 4.9:** Concentration of manganese at different log PO2 levels in cell no 5 at steps 10-40.

Same level of log PO2 is required to remove manganese in cell no 6 as it was in cell no 5.(Fig 4.10) is showing that log PO2 of -2 is required to remove manganese from solution in cell no 6.

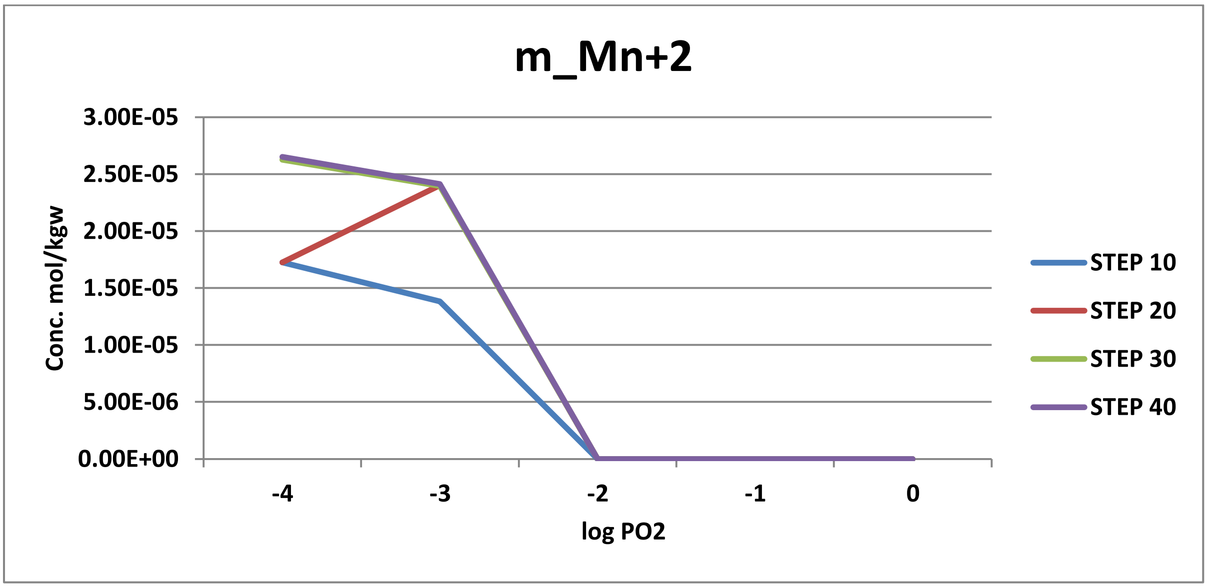


**Figure 4.10:** Concentration of manganese at different log PO2 levels in cell no 6 at steps 10-40

The removal of manganese is looking very effective at log PO2 level of -2 at all the steps other than step 10. At step 10 more amount of oxygen is required to remove all the concentration of manganese from solution. But at all other steps log PO2 Level of -2 is high enough to remove all the dissolved concentration of manganese from solution in cell no 15.

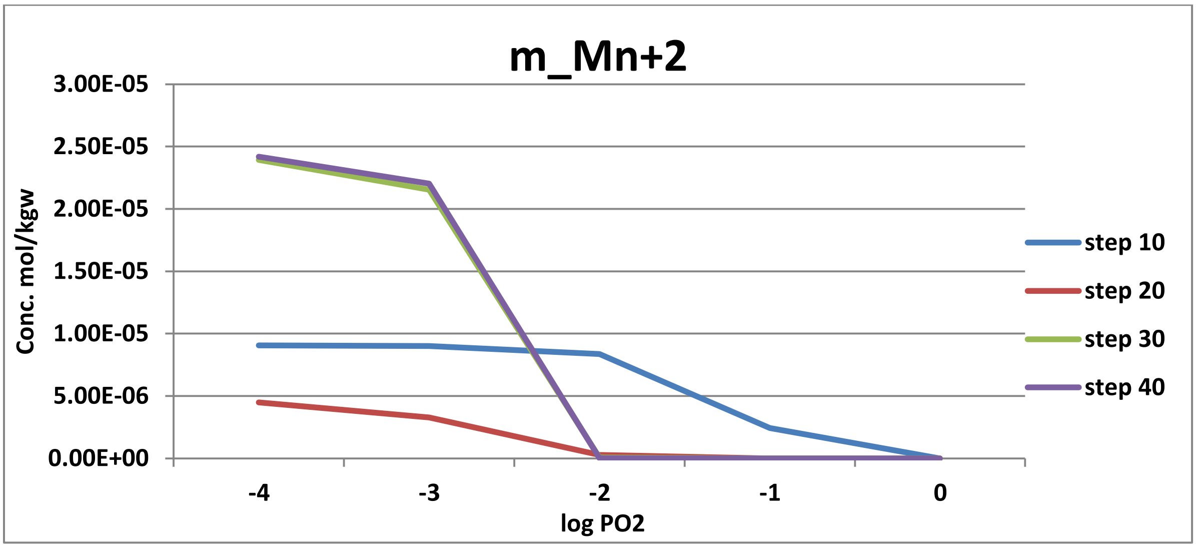


**Figure 4.11:** Concentration of manganese at different log PO2 levels in cell no 15 at steps 10-40.

### 4.4.3 Concentration of Fe (OH)3 at different steps in different cells

The concentrations of $Fe(OH)_3$ are increasing in cell no 5 very slowly as the amount of oxygen is increasing. But the concentration of $Fe(OH)_3$ is increasing as steps are increasing. (Fig 4.12) is showing that the concentration of $Fe(OH)_3$ is maximum at the higher level of oxygen and at step 40.

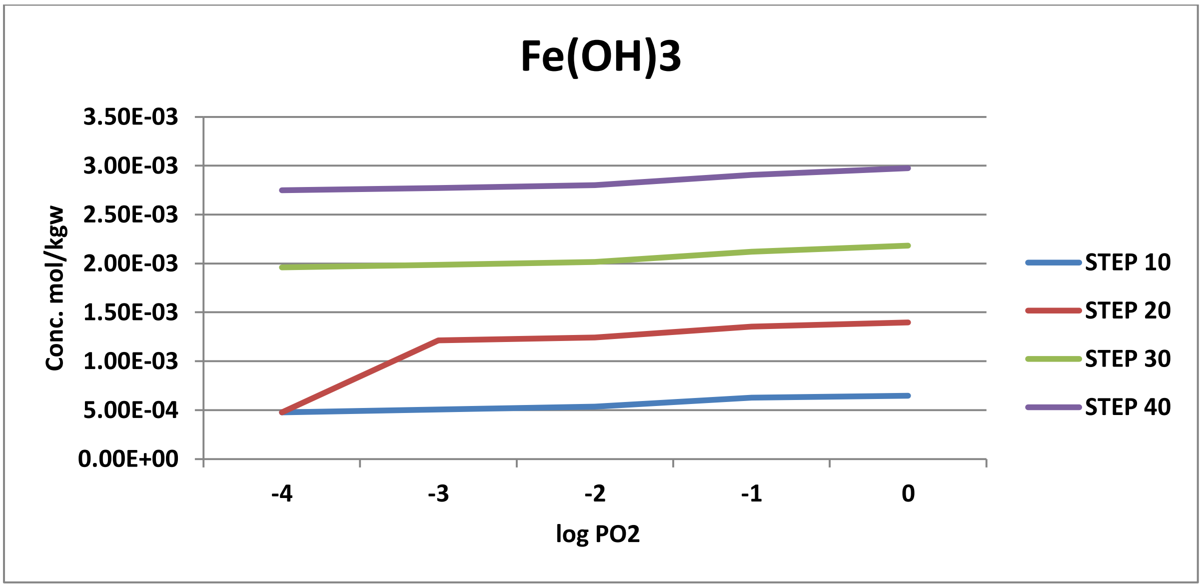


**Figure 4.12:** Concentration of Fe $(OH)_3$ at different log PO2 levels in cell no 5 at steps 10-40.

The concentration of Fe (OH) $_3$ starts increasing from log PO2 level of -3 at all the steps in cell no 6. (Fig 4.13) is showing that concentration of Fe (OH) 3 is maximum where the highest amount of oxygen is available at all steps.

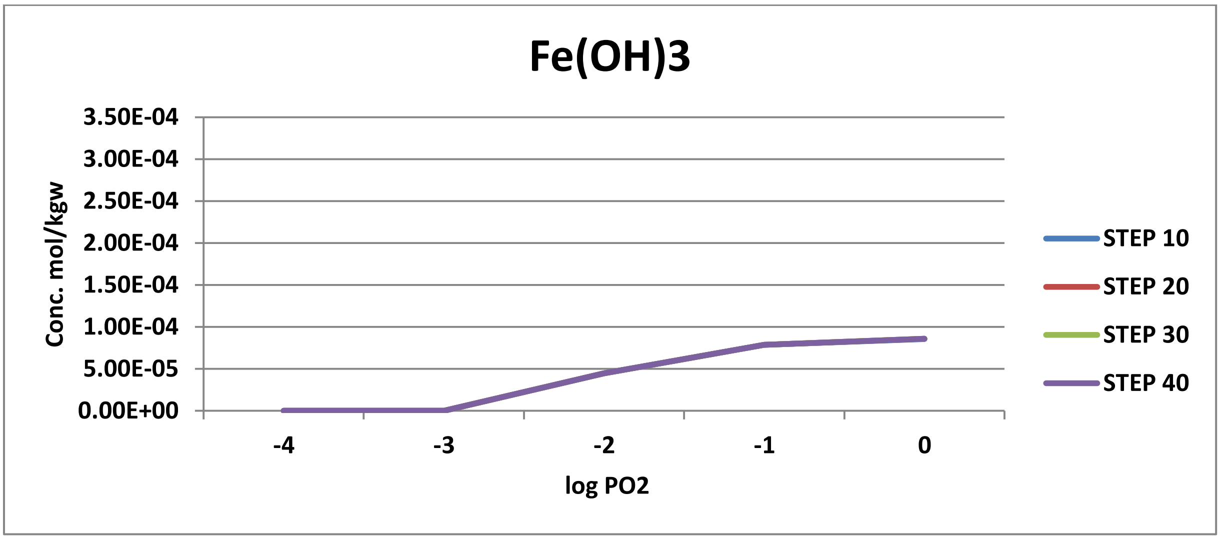


**Figure 4.13:** Concentration of Fe (OH) $_3$ at different log PO2 levels in cell no 6 at steps 10-40.

### 4.4.4 Concentration of Pyrolusite at different steps in different cells

The concentration of pyrolusite starts increasing from log PO2 level of -3 to -2 after which it is stabilizing till the end. (Fig 4.14) is explaining the trend of the precipitation of manganese as pyrolusite at the different levels of oxygen, and -2 level of log PO2 is proved to be good to precipitate the manganese.

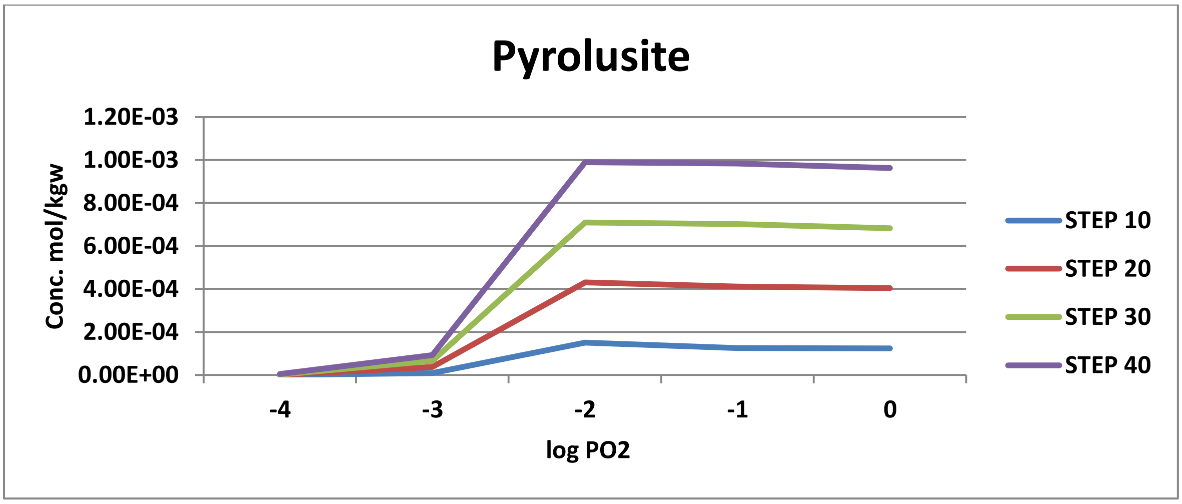


**Figure 4.14:** Concentration of pyrolusite at different log PO2 levels in cell no 5 at steps 10-40.

In cell no 6 the concentration of pyrolusite is lower than cell no 5 at different PO2 levels. The concentrations start increasing from PO2 level of -3 until PO2 level of 0 at all steps. (Fig 4.15) is showing the trend of precipitation of manganese as pyrolusite in cell no 6 at different PO2 levels.

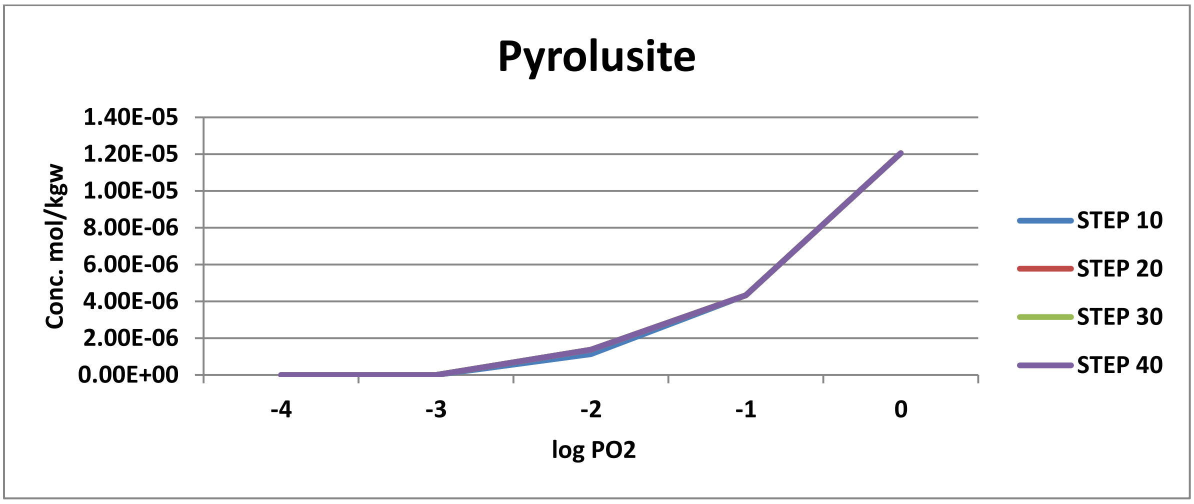


**Figure 4.15:** Concentration of pyrolusite at different PO2 levels in cell no 6 at steps 10-40.

### 4.5 Reactive transport PHREEQC simulation with linear flow

To investigate the relationship between concentration of oxygen and iron and manganese precipitation, linear flow simulations by PPHREEQC model were also performed. The column is divided into 15 cells, each having a length of 5m (Fig 4.16). The remaining parameters and keywords were same as we used in radial flow simulation. The same concentrations of dissloved iron and manganese were used and results also were found very much same.

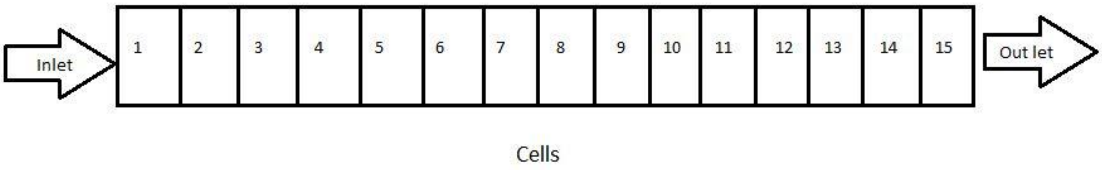


**Figure 4.16:** One dimensional flow in PHREEQC

#### 4.5.1 Results in cell no 15

(Fig 4.17) is showing the results in cell no 15 of iron removal. The results are very much like (Fig 4.2). The difference is that level -2 of log PO2 is removing the iron at steps between 50 and 60, while with the radial flow simulation level -2 of log PO2 was taking much long time to remove all the iron from solution.

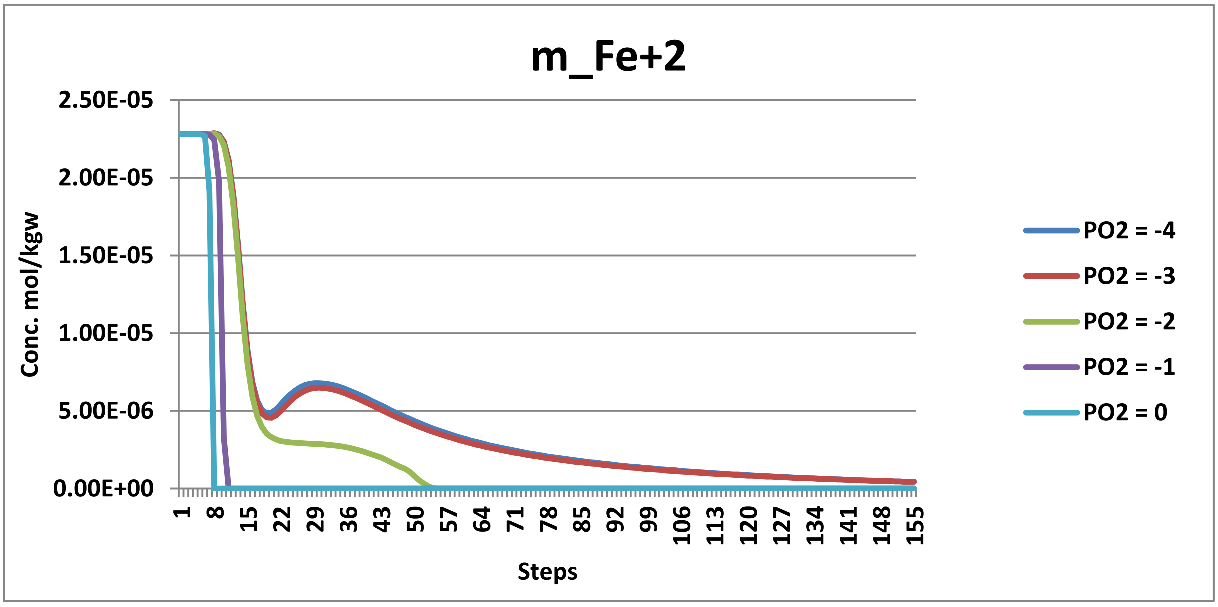


**Figure 4.17:** Concentration of iron in cell no 15 at different log PO2 levels along all steps.

The behavior of removal of manganese is totally same as it was with radial flow simulations (Fig 4.18) is showing the results of manganese removal in cell in 15.

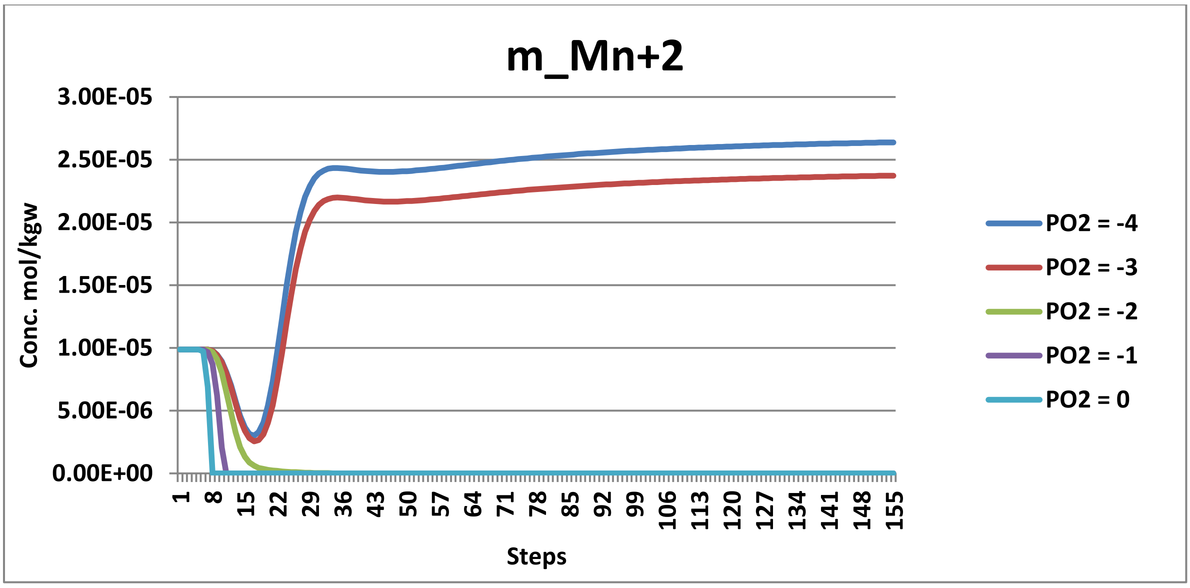


**Figure 4.18:** Concentration of manganese in cell no 15 at different log PO2 levels along all steps.

### 4.5.2 Results in Cell no 4

Cell no 4 is the cell where oxygen was introduced, it seems like log PO2 level of -4 is also very effective to remove iron from solution, because concentrations have been decreased considerably. With increasing steps and level of oxygen iron concentrations are further decreasing. (Figure 4.19) is showing the results of iron removal in cell no 4.

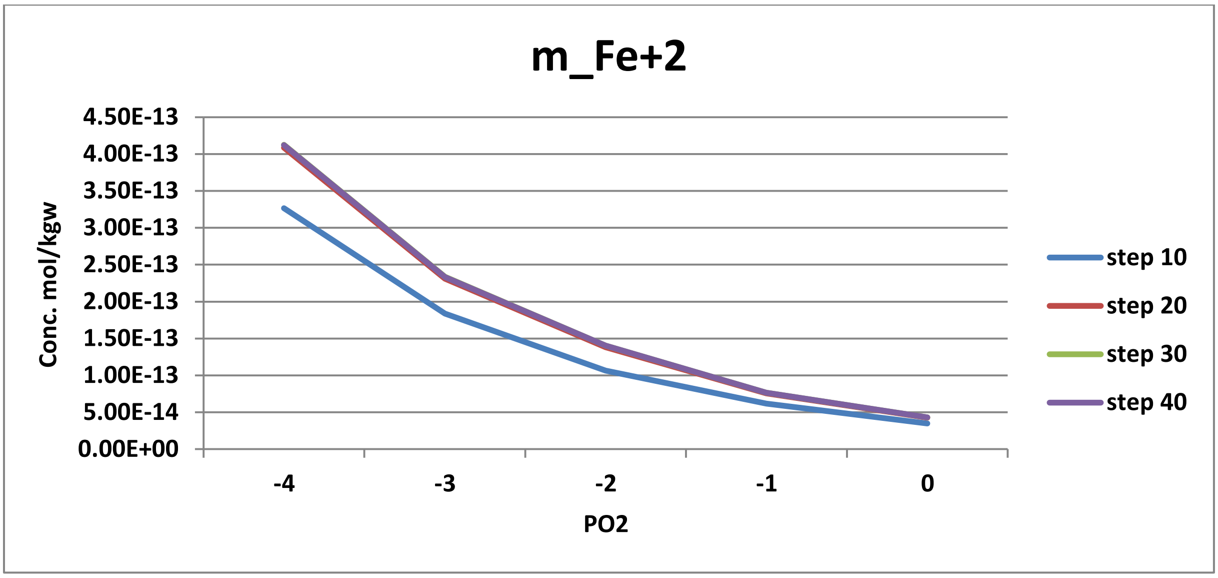


**Figure 4.19:** Concentration of iron at different log PO2 levels at steps 10-40 in cell no 4.

In cell no 4, the behavior of manganese is found to be different than iron. Because the concentrations of manganese are not decreasing even at higher level of oxygen neither by increasing the steps. (Fig 4.18) is showing the results of manganese removal in cell no 4.

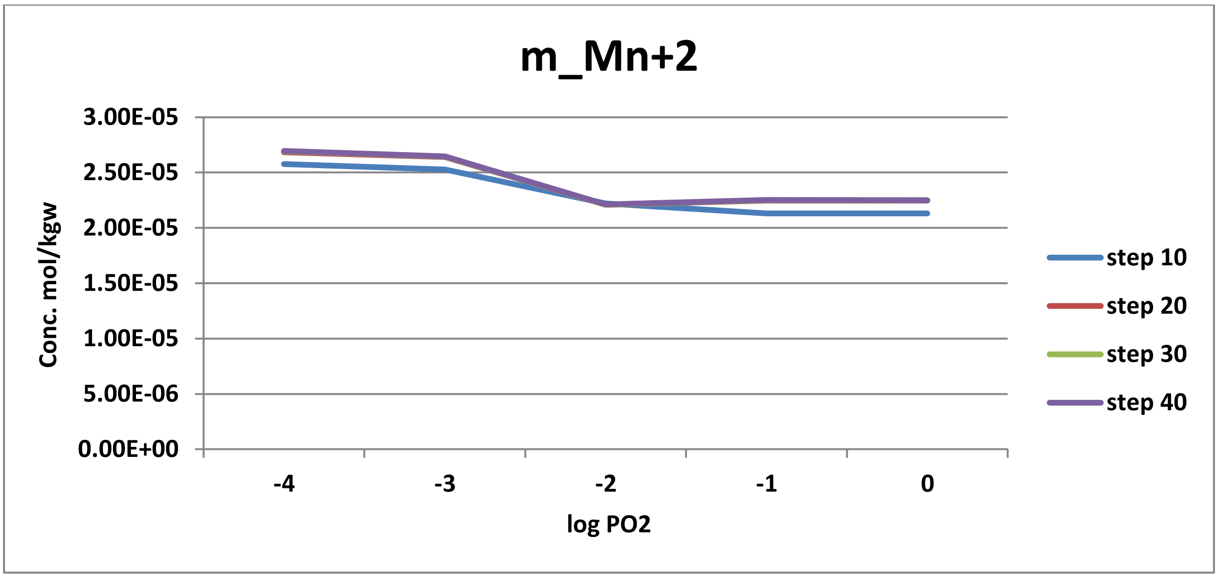


**Figure 4.20:** Concentration of manganese at different log PO2 levels at steps 10-40 in cell no 4

### 4.5.3 In Cell no 5

The log PO2 level of -3 was found to be sufficient to precipitate iron and log PO2 level of -2 is working for the manganese removal (Fig 4.22). The concentration of Fe (OH)3 is increasing with increasing the steps in cell no 5 (Fig 4.23). The concentration of pyrolusite is increasing until the log PO2 level of -2 and then remaining constant by further increase in log PO2 level. But concentration is increasing with steps (Fig 4.24).

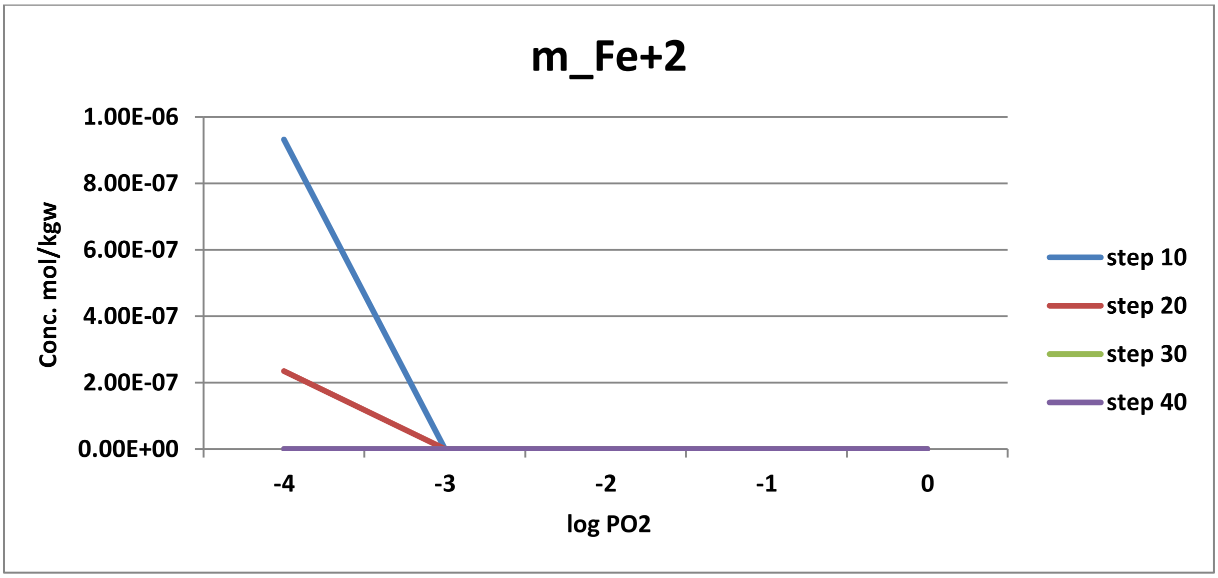


**Figure 4.21:** Concentration of iron at different log PO2 levels at steps 10-40 in cell no 5.

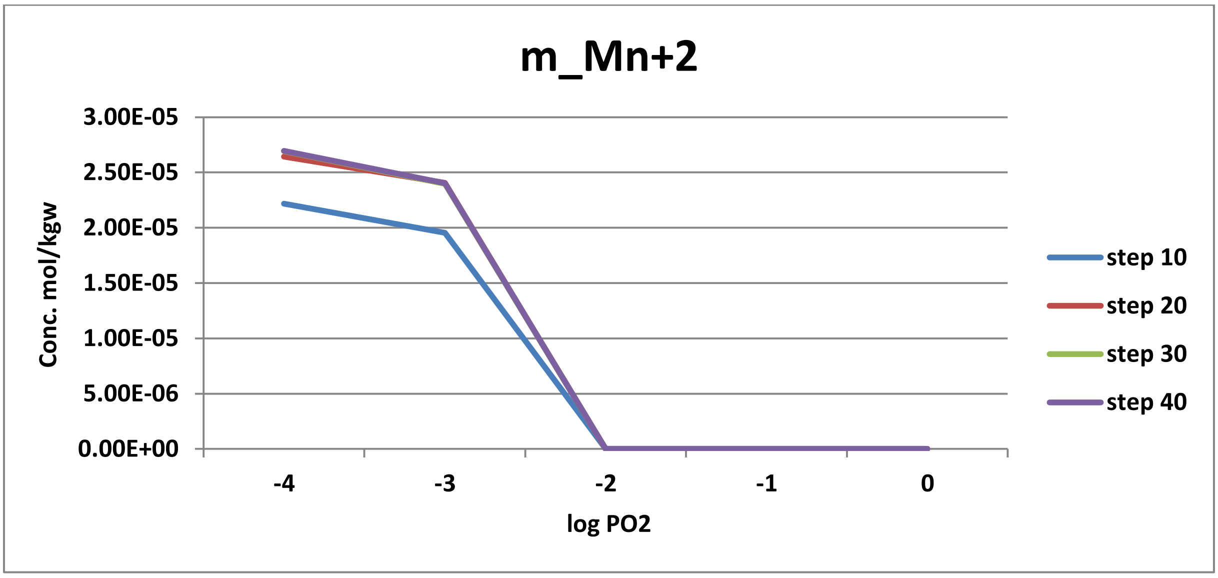


**Figure 4.22:** Concentration of manganese at different log PO2 levels at steps 10-40 in cell no 5.

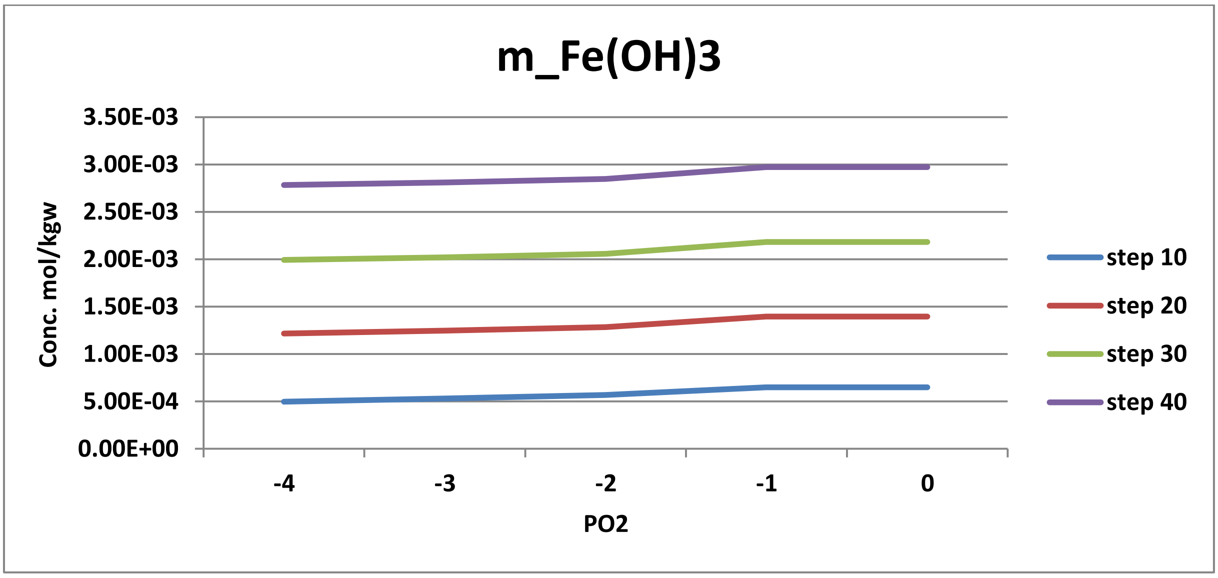


**Figure 4.23:** Concentration of iron hydroxide at different log PO2 levels at steps 10-40 in cell no 5.

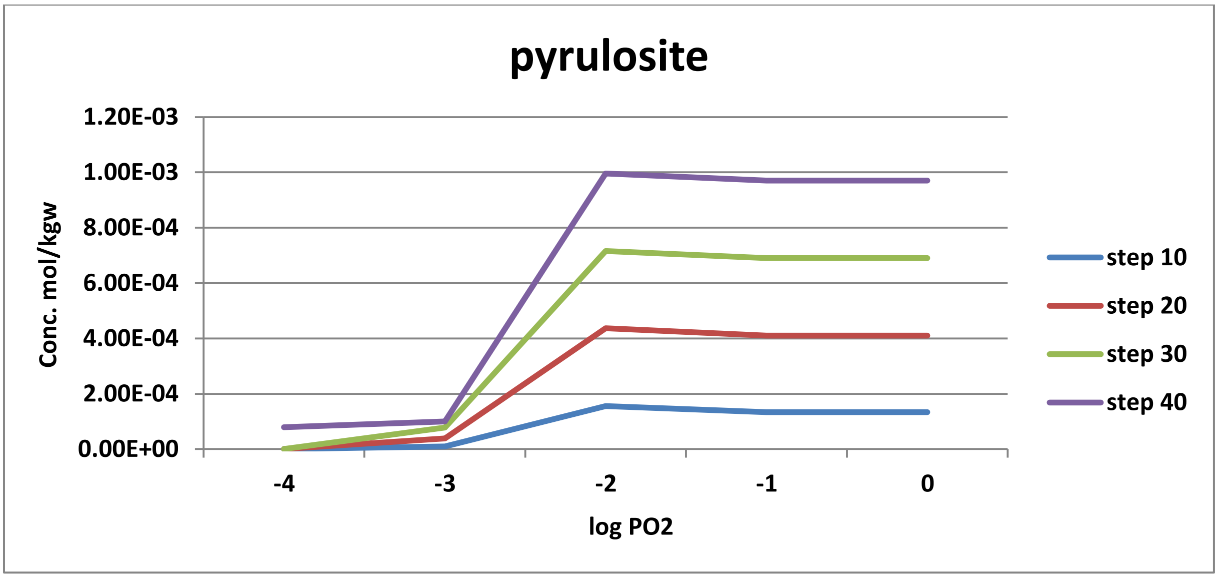


**Figure 4.24:** Concentration of pyrulosite at different log PO2 levels at steps 10-40 in cell no 5

So all the above results prove that the concentration of oxygen at log of its partial pressure which is -0.7 is sufficient to remove the higher concentrations of iron and manganese from solution.

# Chapter 5: Grindalsmoen water works, Elverum municipality

## 5.1 Elverum

Elverum is a town located in Hedmark county in the district Østerdalen in Southeast of Norway. It is situated on the banks on longest river of Norway called Glomma. The municipality of Elverum covers 12293Km$^2$ and having the population of 19500 approximately. The subsurface of Elverum area consists of highly permeable glacio-fluvial deposits with good hydraulic connection to upstream of the highland and downstream of the Glomma River. The groundwater storage is therefore rapidly recharged when it is pumped, and large outtakes are possible.

## 5.2 Water Supply by Grindalsmoen water works at Elverum municipality

The Municipality of Elverum has two municipal waterworks, includes Grindalsmoen waterworks which is main source of water supply at Elverum town and Church Circle waterworks which covers the area around the church in Sørskogbygda (Barseng 2011). Grindalsmoen waterworks supplies to approximately 14,500 people in Elverum with water from 4 groundwater wells. Each well has a capacity of 60 l /sec (Hias IKS 2009). The Grindalsmoen plant was designed and built by Vyrmetoder AB jointly with Elverum municipality.The groundwater in that area is having the problems with high concentration of iron and manganese. To purify this water in-situ treatment method has been applied which is called Vyredox method, which has shown great success in removing iron and manganese.

There are mainly 4 production wells located at Grindalsmoen water works, but only the production well 4 is surrounded by the satellite wells. The 4 production wells can be seen from the (Fig 5.1) which are located at some distance from each other.

**Figure 5.1:** Location of the Grindalsmoen water works alongside the Glomma river.

## 5.3 Method in use by Grindalsmoen water works

The main abstraction well 4 (Hovedbrønn 4) is located in center and other 9 injections wells are located in a ring around the main pumping well (Fig 5.2). The 9 wells are used to inject water to aquifer as well as to abstract water from the aquifer. These wells are also referred as satellite wells. These wells are named as SB1, SB2 so on to SB9. The system is that water is abstracted from two wells e.g. (SB1 and SB3) at a same time at the rate of 6L/sec for 2 hours. This abstracted water is kept on the surface for next 3 hours to mix with oxygen at its partial pressure. Then this aerated water is injected to ground through the well locating between these two wells (SB2). For next time water is abstracted from (SB2 and SB4) for two hours at the same rate, abstracted water is aerated with oxygen, and this aerated water is injected through the well locating between these two wells which is (SB3). Then this process is repeated with all other wells means everytime outer two wells are abstracted and aerated water is injected through the well locating between these two. This aerated or oxygen enriched water creates the oxidized zone in aquifer which forces the iron and manganese to precipitate and purified water is pumped through the main abstraction well. The pumping rate of main well is 60L/sec (0.06 $m^3/s$), which is supplied to municipality. The facility is equipped with instruments that continuously measure, adjust pH, and maintain the quality of water by adding water purification chemicals etc. of the outgoing water.

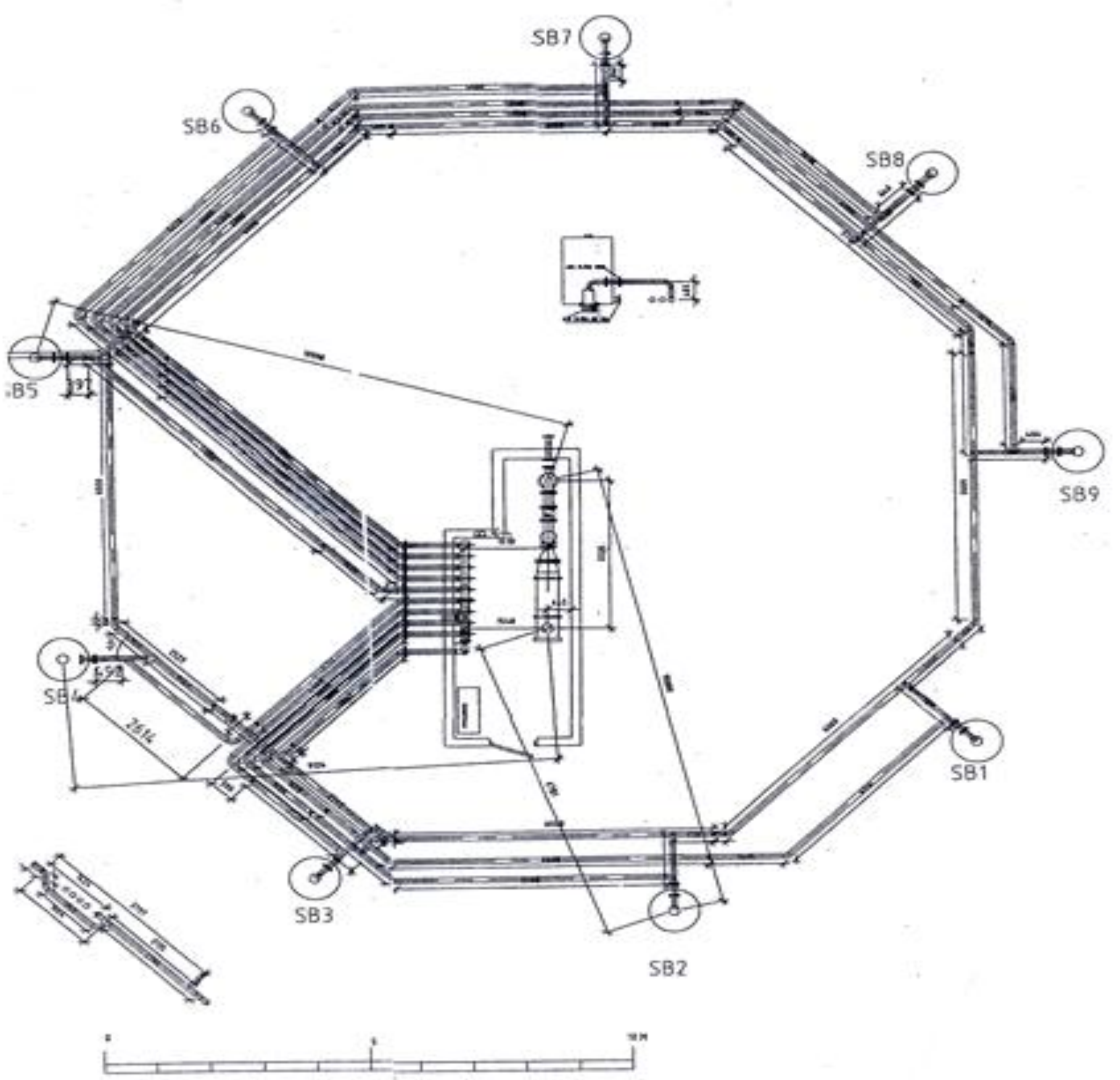


**Figure 5.2:** Grindalsmoen water works production 4 surrounded by 9 satellite wells.

At a time 3 wells are in use for the purpose of pumping and injection of aerated water. Figures 5.3 and 5.4 are explaining this fact.

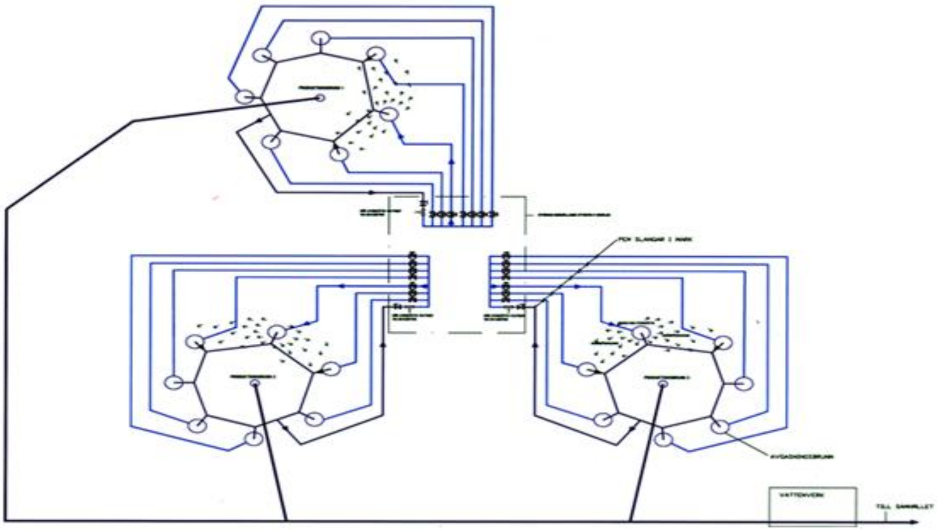


**Figure 5.3:** Satellite wells in use at the same time at Grindalsmoen water works.

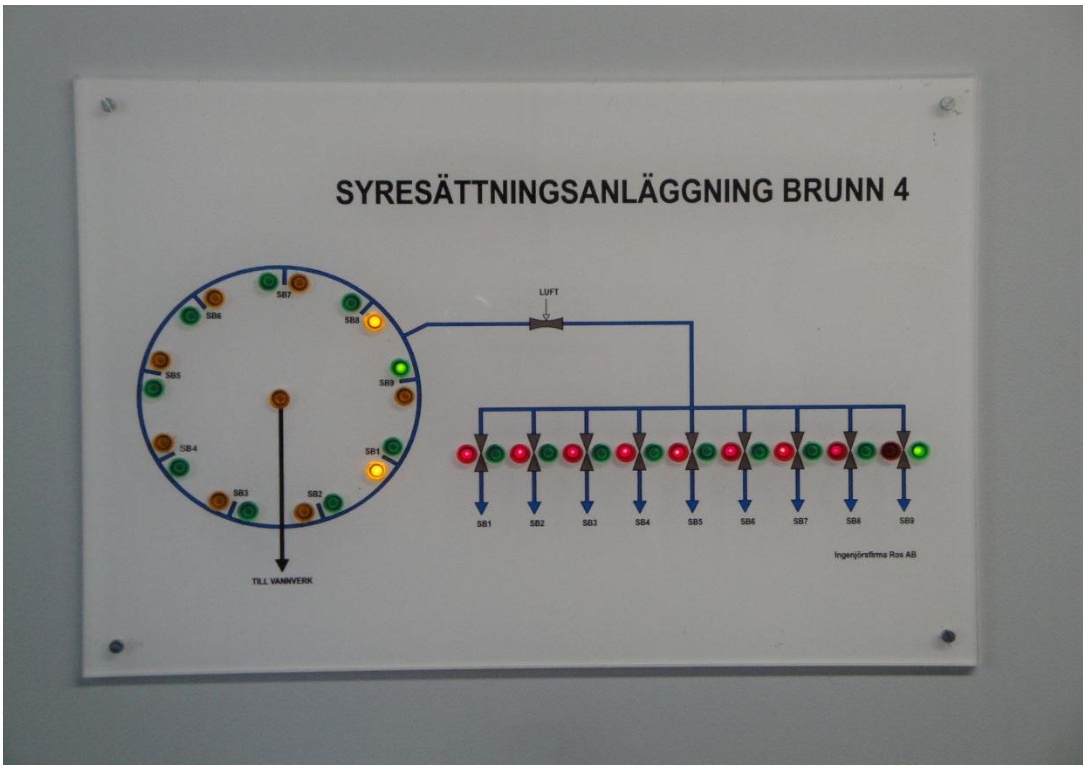


**Figure 5.4:** Wells with yellow signal are being pumped and green one is injected.

Fig 5.5 is showing the 3 wells that are in use at the same time, two wells are used for abstraction and 3rd which is locating between those two is used for injection of oxygen rich water. The oxygen rich water helps to achieve the oxidation level which causes iron and manganese to precipitate.

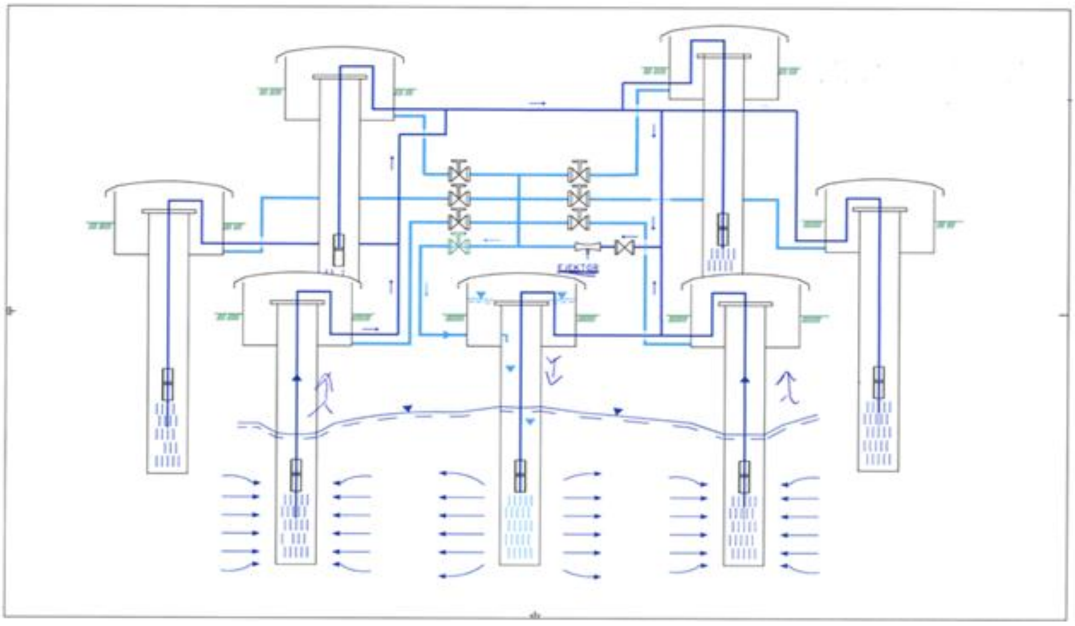


**Figure 5.5:** Scheme of Pumping and injecting oxygenated water in aquifer.

The depth of bore hole - of the main abstraction/production is well 4 is 30 m and the depths of injection/ satellite wells are also in range of 30-35 m. (Fig 5.6) is showing the depth depths of all wells, satellite wells are slightly deeper than the main abstraction well.

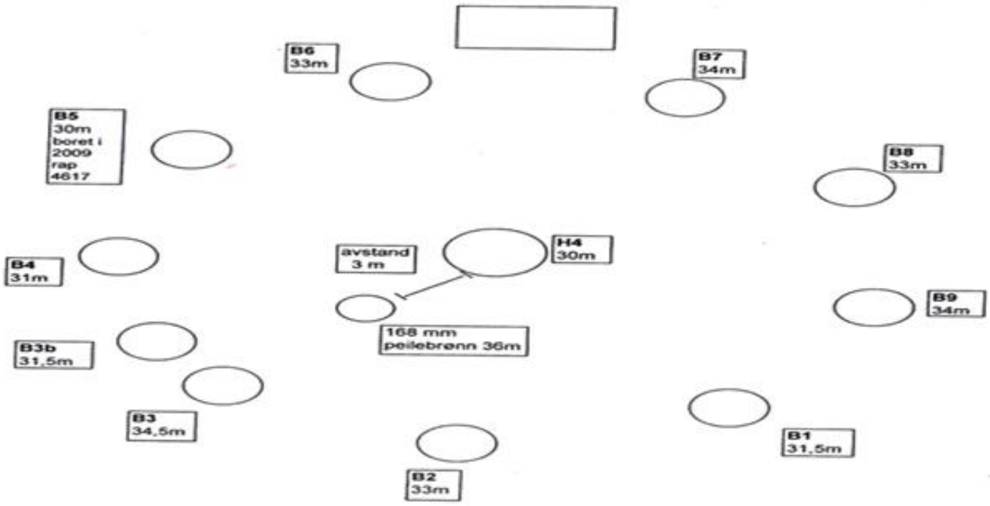


**Figure 5.6:** Depths of injection well and satellite wells.

Figures 5.7 to 5.10 are photographs taken at the Grindalsmoen water works showing the wells and system.

**Figure 5.7:** Location of satellite wells.

**Figure 5.8:** One of the satellite well with close view.

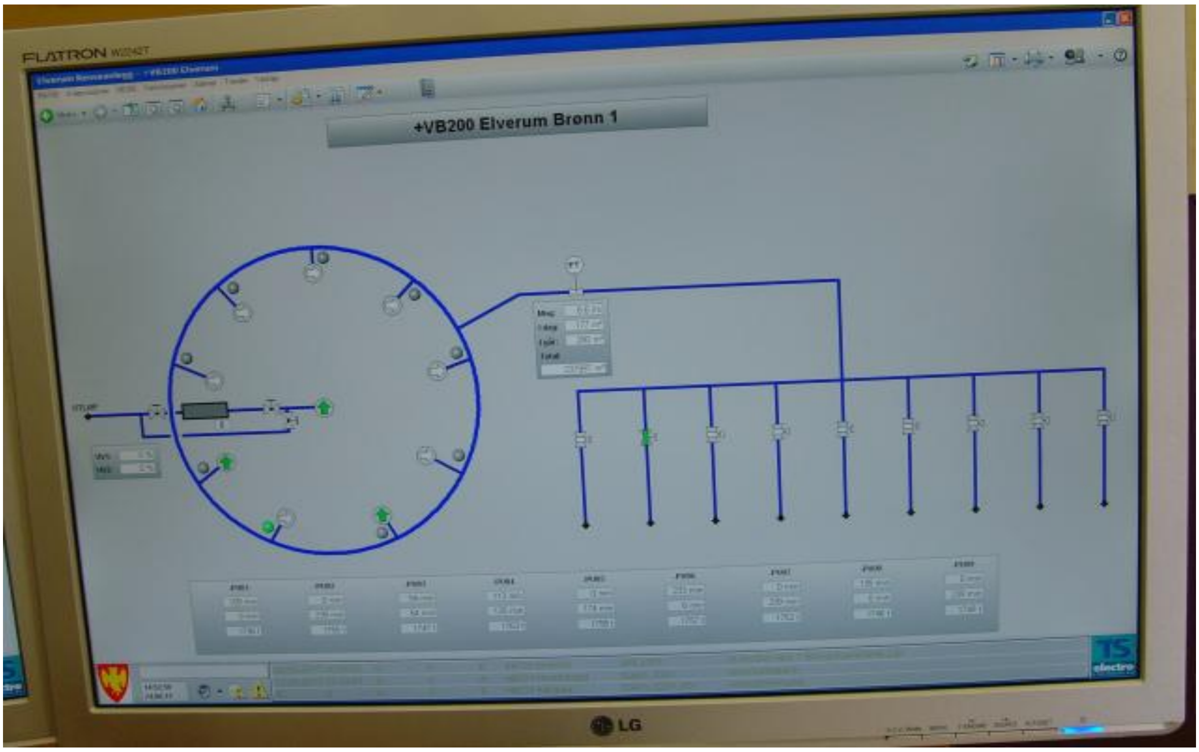


**Figure 5.9:** Online monitoring of pumped and injected water for each well.

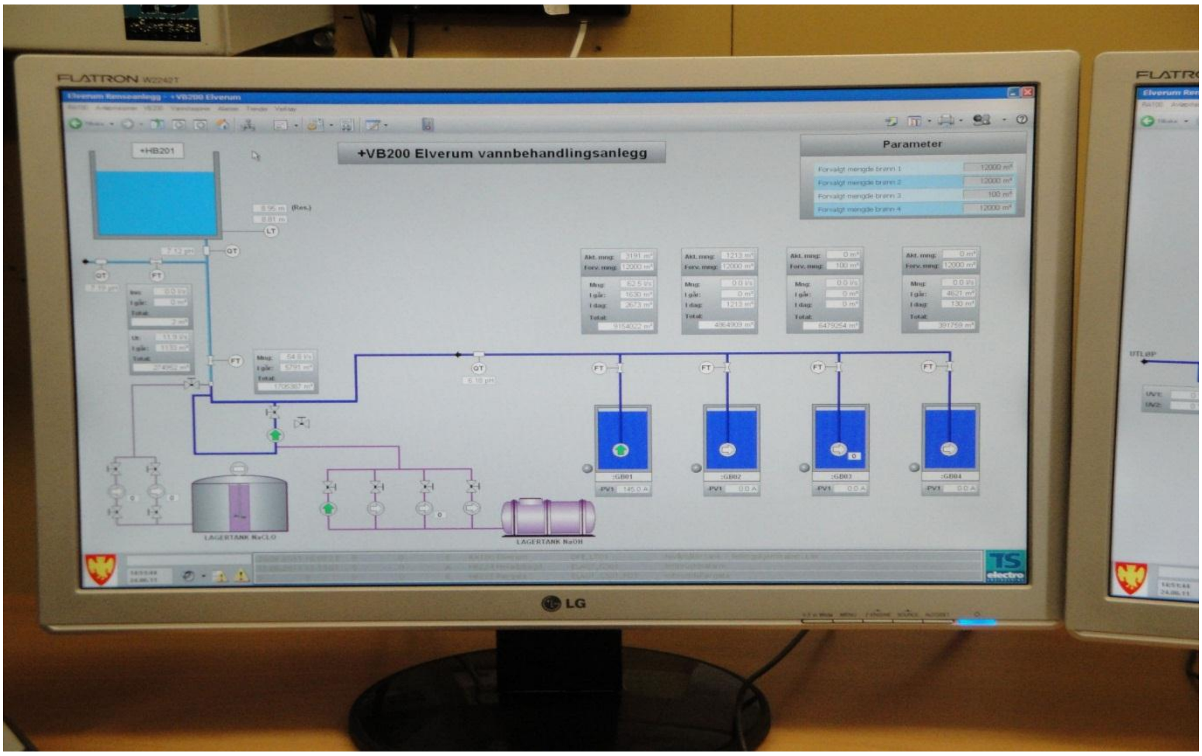


**Figure 5.10**: Processes after removing iron and manganese to adjust pH before distribution of water to municipality.

Fig 5.11 is showing the sketch of main abstraction well 4 being used at Grindalsmoen water works. The total depth of bore hole is 30m and water level is at 5m. The length of filter is 8m with 350 mm radius.

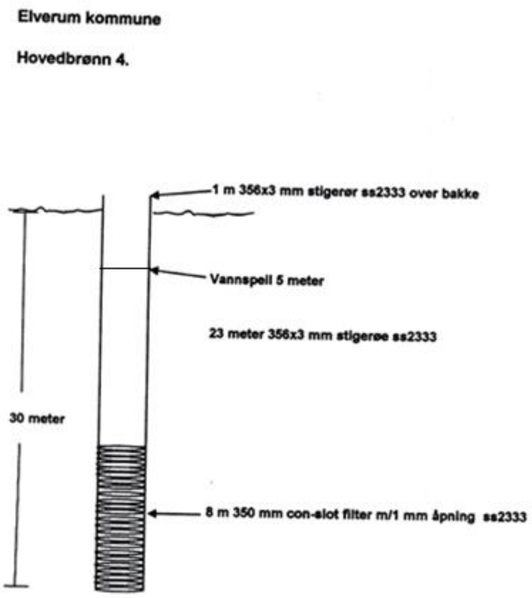


**Figure 5.11:** Layout of production well 4 working at Grindalsmoen water works.

The water that is pumped out from the main production well passes through the filter of 8 m.

## 5.4 Calculation of the concentration of Injected oxygen at Grindalsmoen

Total amount of injected water in 1 hour were calculated 8.64$m^3$ that becomes 207.3 $m^3$ in one day. The O2 saturation was estimated by PHREEQC at log PO2 at our desired temperature of 6 degree C and it was 12.3 mg/l. So the total amount of injected oxygen is 2.5kg/day. As we need 0.14 mg/l of oxygen to precipitate 1 mg/l of iron and 0.29 mg to precipitate 1 mg/l of manganese. So the calculation shows that, total amount of precipitated iron and manganese in one day will be 18.2 kg and 8.7kg respectively. It seems that huge concentrations of iron and manganese can be precipitated by injected amount of oxygen. Comparatively more amount of oxygen is required to precipitate manganese than iron.

## 5.5 PHREEQC model for Grindalsmoen water works

In PHREEQC model the concentrations of iron and manganese were considered same in native and injected solutions. Iron and manganese were considered as 0.05 and 0.004 mmol/kgw respectively. If they are converted to mg/l then iron and manganese becomes 2.79 mg/l and 0.21 mg/l respectively. These concentrations are showing the reducing conditions of the aquifer. The concentration of oxygen at its partial pressure is introduced in cell 5 of the column. To obtain the concentrations in effluent the last cell 15 is punched. The detailed description and results have been presented in next chapter.

# Chapter 6: Results and Discussions of Geochemical simulations of iron and manganese removal at Grindalsmoen waterworks

## 6.1 Description of input data

The PHREEQC input file for calculation of data was prepared by splitting the column into 15 cells of different lengths to model the radial flow. According to Appelo and Postma (1993) radial flow can be modeled in well injections by adapting the cell lengths in agreement with the radial extension of the injection front. The cell lengths are increasing from cell 1 to cell 15. The column is representing the aquifer with reducing conditions and containing $Fe^{+2}$ and $Mn^{+2}$ in solutions. Different keywords have been used to define the data in PHREEQC input file. Solution 0 is the injected water in cell 1. 15 Cells are representing the solutions 1-15. The sorbing surfaces have been defined to be in equilibrium with the given solution. The parameters of transport identify 15 cells, cell lengths and the boundary conditions. The time step associated with the each shift is 3600 sec (1 hour). The number of times the solution in each cell shifted to next higher numbered cell is known as shift (Appelo and Postma., 1999).Total shifts are 105 and total time can be calculated by shifts*time step. Since the column consists of 15 cells and solution 0 has been transported 105 times, it means that 7 pore volumes are injected.

The partial pressure of oxygen has been introduced in cell 5 in PHREEQC model. The PHREEQC model is also able to investigate the conditions, e.g. where it might good to increase the amount of oxidant and where the phenomenon of sorption is taking place. Following section describes the results of geochemical simulations by PHREEQC at Grindalsmoen water works to remove iron and manganese from groundwater. The assumed concentration of Iron and manganese in groundwater are 2.79mg/l and 0.21mg/l respectively.

## 6.2 Results in cell no 15

High positive value of (pe) indicates oxidizing conditions where iron and manganese is insoluble and the low values of (pe) shows reducing conditions where iron and manganese is soluble (Silveria 1988). Higher (pe) values have been achieved by the introduction of concentration of oxygen at its partial pressure. The (pe) values are stable at 14 from step 8 to 105, while pH values are stable between 6 and 8.

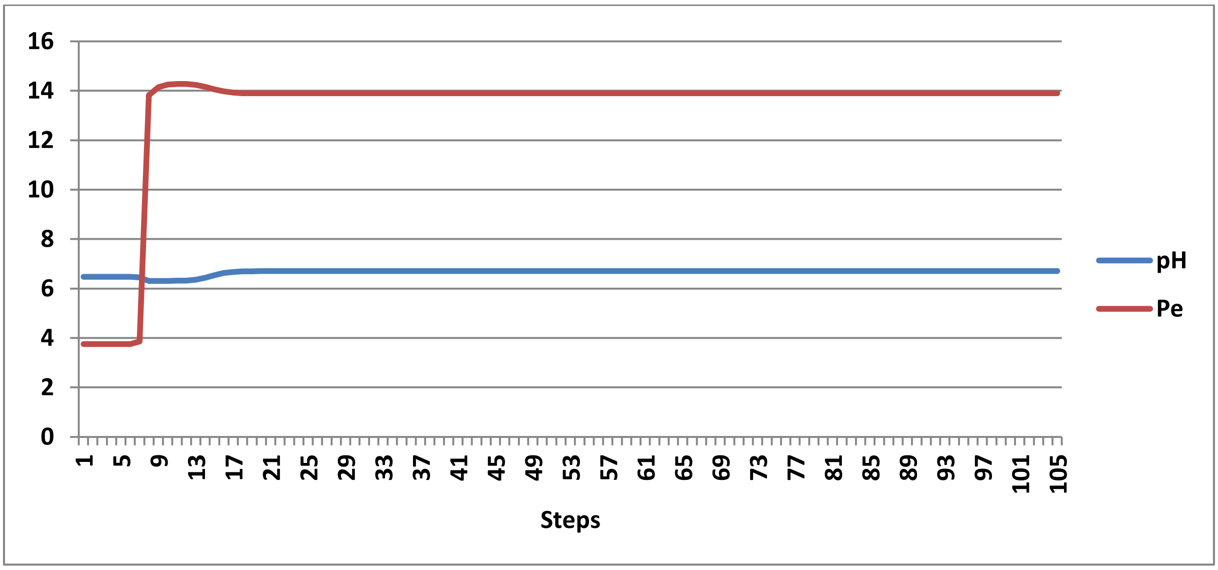


**Figure: 6.1:** Values of Pe and pH in cell no along 105 steps.

The concentrations of soluble iron and manganese have decreased considerably in cell no 15. (Fig 6.2) is showing the result in cell no 15 along all the steps. It can be seen that the concentrations of iron and manganese have gone down very early just after the 7-8 steps. These concentrations of iron and manganese are much lower than the desired concentrations so the results are satisfactory. This shows that concentration of oxygen at its partial pressure is sufficient to remove iron and manganese from solution.

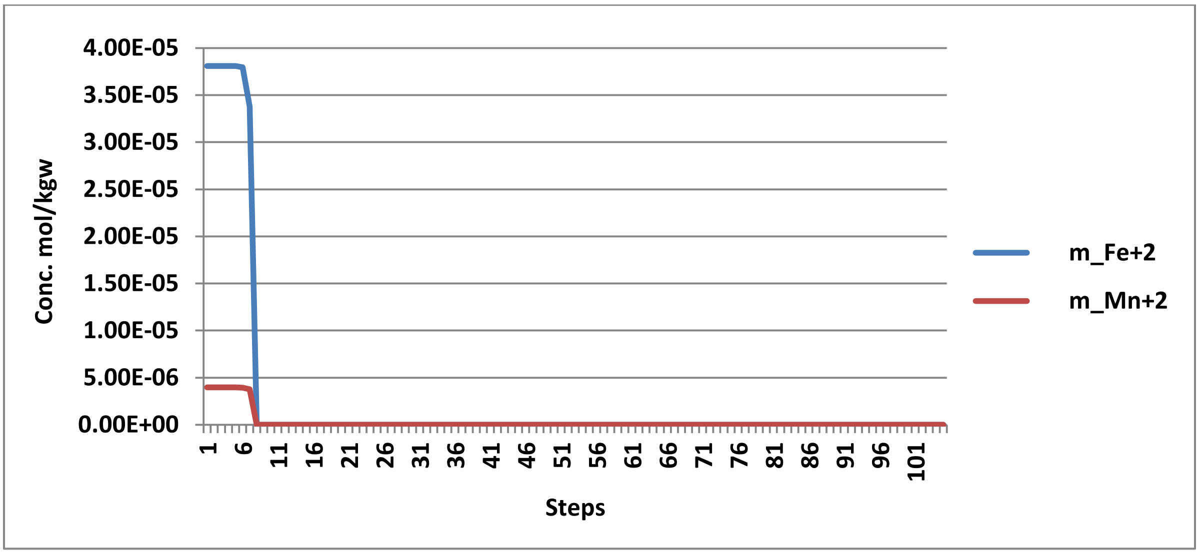


**Figure 6.2:** Concentration of iron and manganese in cell no 15 along all steps.

The concentration iron and manganese depends upon the dissolved concentration of oxygen in groundwater. Under the reducing conditions, higher concentrations of iron and manganese can dissolved and transported into the aquifer (Rott 1990). (Fig 6.3) is showing the concentration of dissolved oxygen in cell no 15. As the introduced amount of oxygen was 12.3 mg/l in cell no 5. In cell no 15 there is still nearly 4mg/l of oxygen is present, which can help to precipitate more concentrations of iron and manganese.

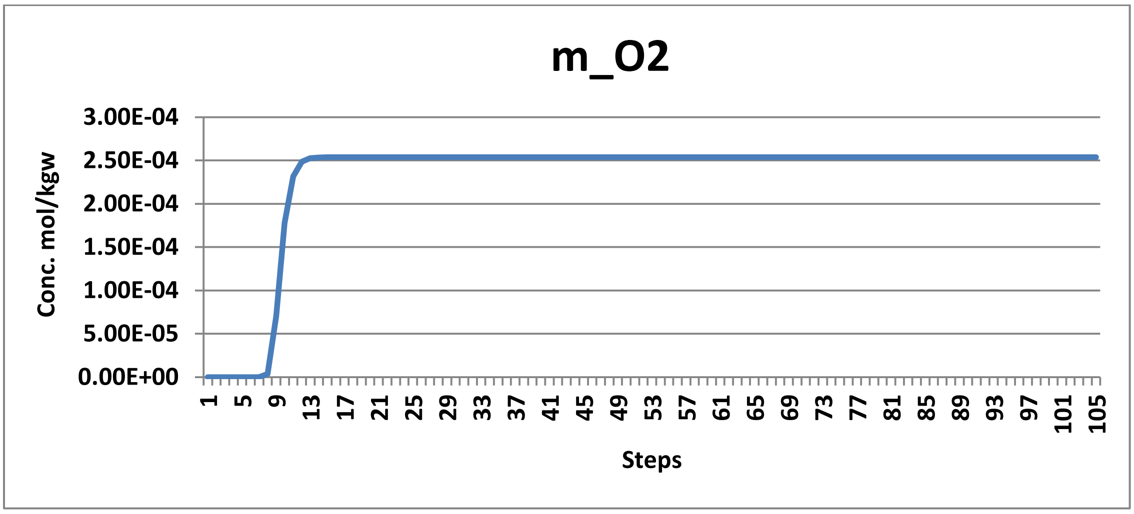


**Figure 6.3:** Concentration of oxygen in cell no 15 along all steps.

### 6.3 Results in Cell 1-15

The concentration of iron is decreasing at considerable amount in cells 1-15. The oxygen was introduced in cell no 5, and concentration starts decreasing from cell no 4. At step 5 the concentrations starts increasing again in cell no 12. But after increasing the steps, concentration of soluble iron is not increasing any more. (Fig 6.4) shows that iron has been removed from solution very effectively.

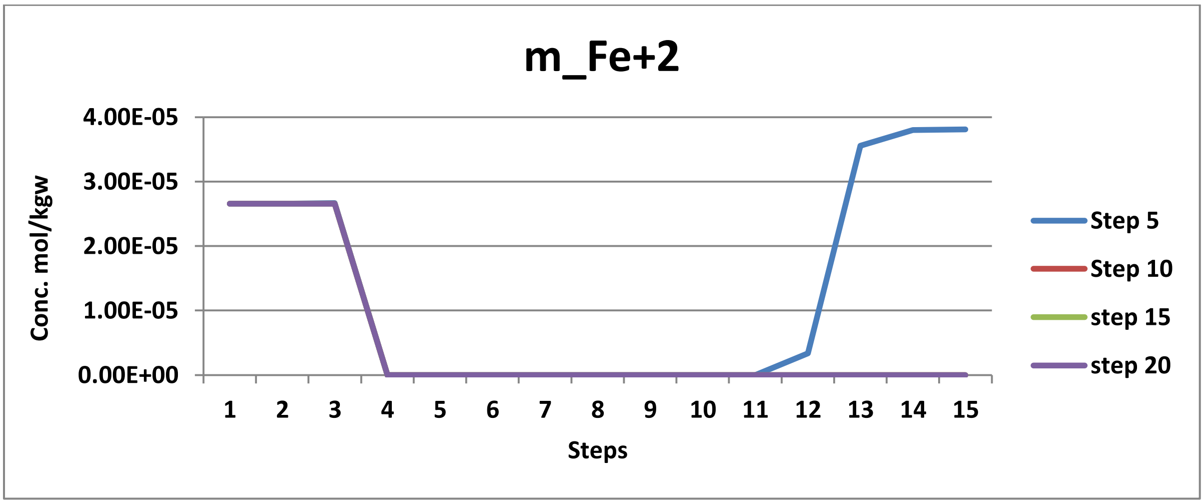


**Figure 6.4***:* Concentration of iron in cells 1-15 at steps 5-20.

The concentration of manganese also starts decreasing from cell no 4, but this is not a considerable decrease. There is only a little decrease in concentration from cell 4 to cell 5. But in cell no 6 the concentrations is going down very fastly due to oxidation. At step no 5 the concentration of manganese starts to increase again in cell no 11 because the concentration of oxygen is decreasing in cell no 12 (Fig 6.6). After step 5, the concentrations of manganese are not increasing again, and removal of manganese is also seems to be very effective along with iron.

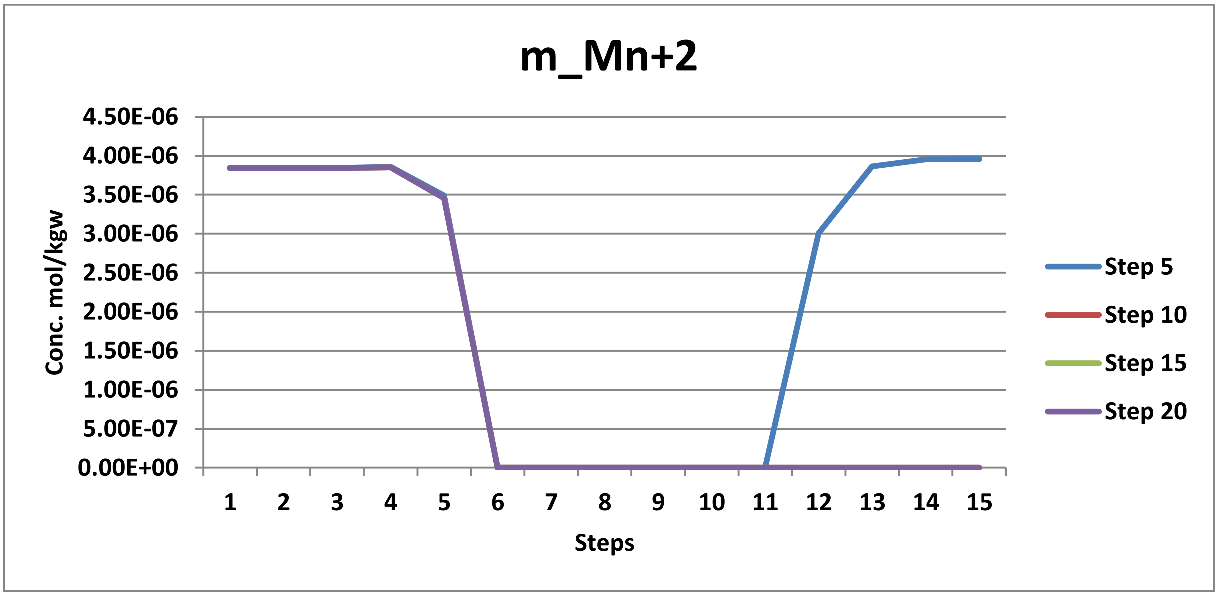


**Figure 6.5:** Concentration of manganese in cells 1-15 at steps 5-20.

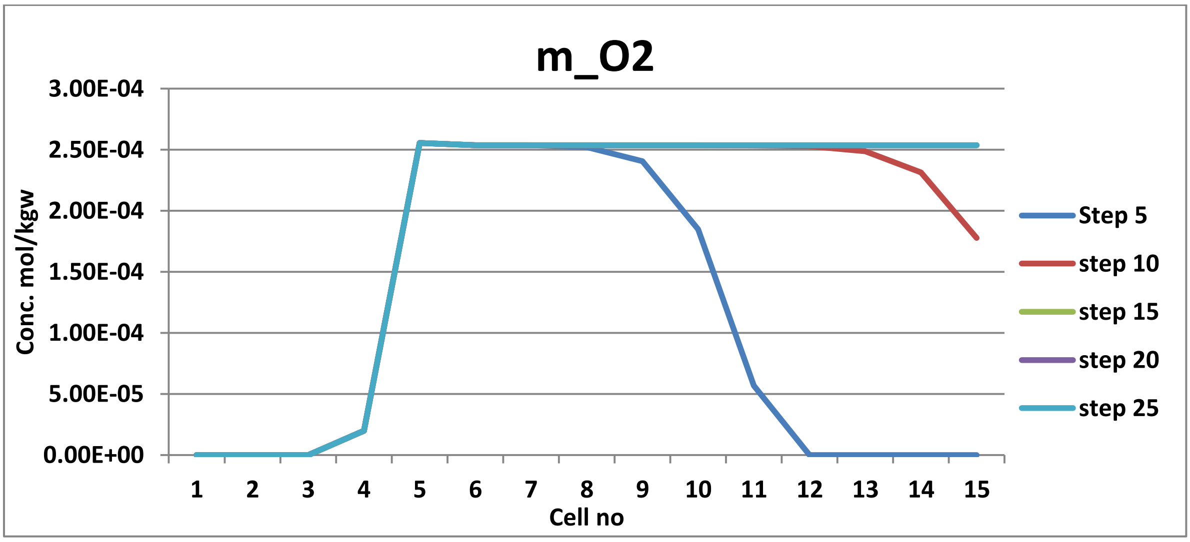


**Figure 6.6:** Concentration of oxygen in cells 1-15 at steps 5-25.

Only at step 5, the value of redox potential is going down, may be due to amount of oxygen is decreasing, But after step no 5, the values of redox potential is well maintained which is symbol of oxidizing conditions.

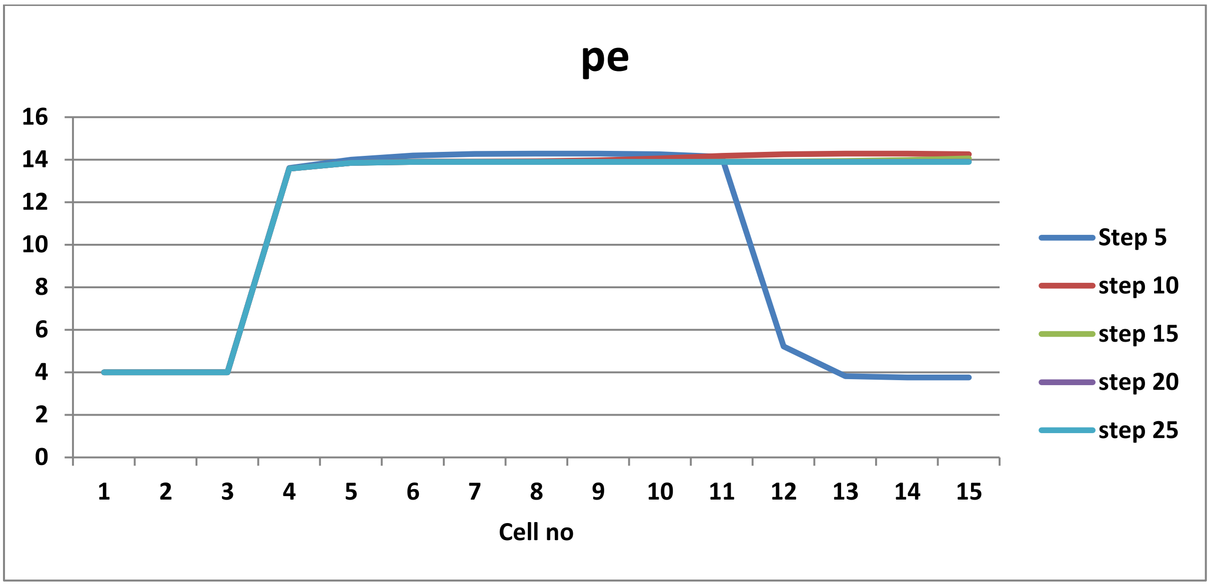


**Figure 6.7:** pe values in cells 1-15 at steps 5-25.

The concentration of Fe (OH) 3 is increasing in cell no 6. Because the oxygen was introduced in cell no 5, in cell no 5 the concentration of Fe (OH) 3 is found to be zero, it is increasing from cell no 6. The concentration of Fe (OH) 3 in cell no 6 is higher than all other cells. One possibility can be the precipitation of higher quantities in cell no 6, and no considerable concentration left to precipitate in other cells. This newly precipitated iron hydroxide will provide the adsorption sites for the remaining concentration of iron in solution. Oxygen can oxidize the adsorbed iron, thus new hydroxide will be created that will provide the adsorption sites for soluble iron. This process can be called as adsorptive- catalytic oxidation (Rott 1990).

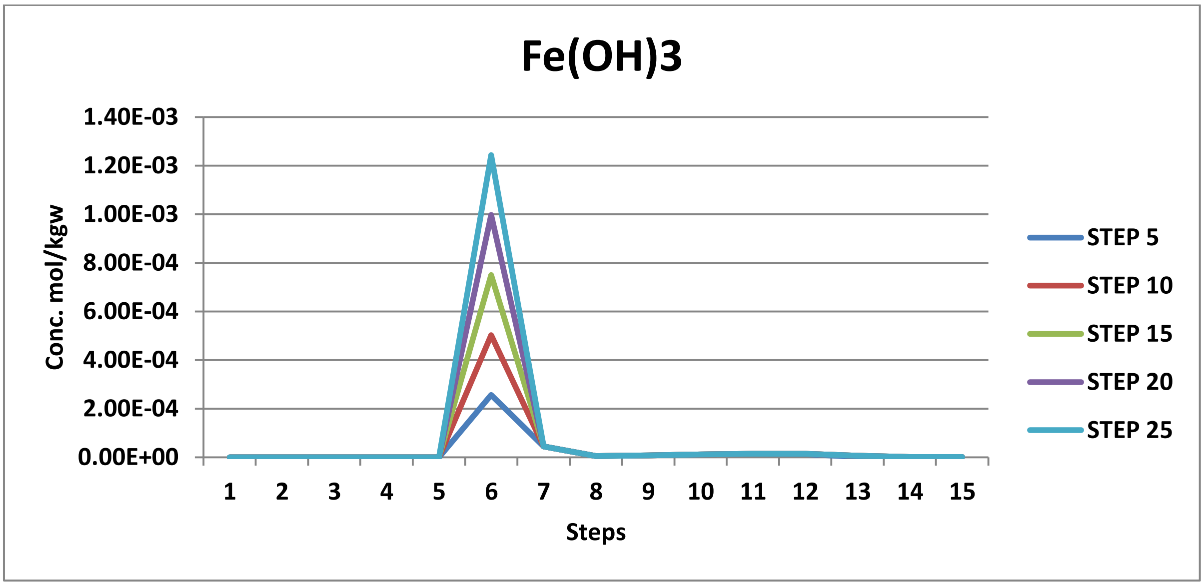


**Figure 6.8:** Concentration of Fe (OH)3 in cells 1-15 at steps 5-25.

Pyrolusite is also showing the same trend shown by the iron hydroxide. The concentrations are increasing in cell no 6 only. There is a little amount can be found in cell no 13. Pyrolusite can also provide the new adsorption sites for the soluble manganese.

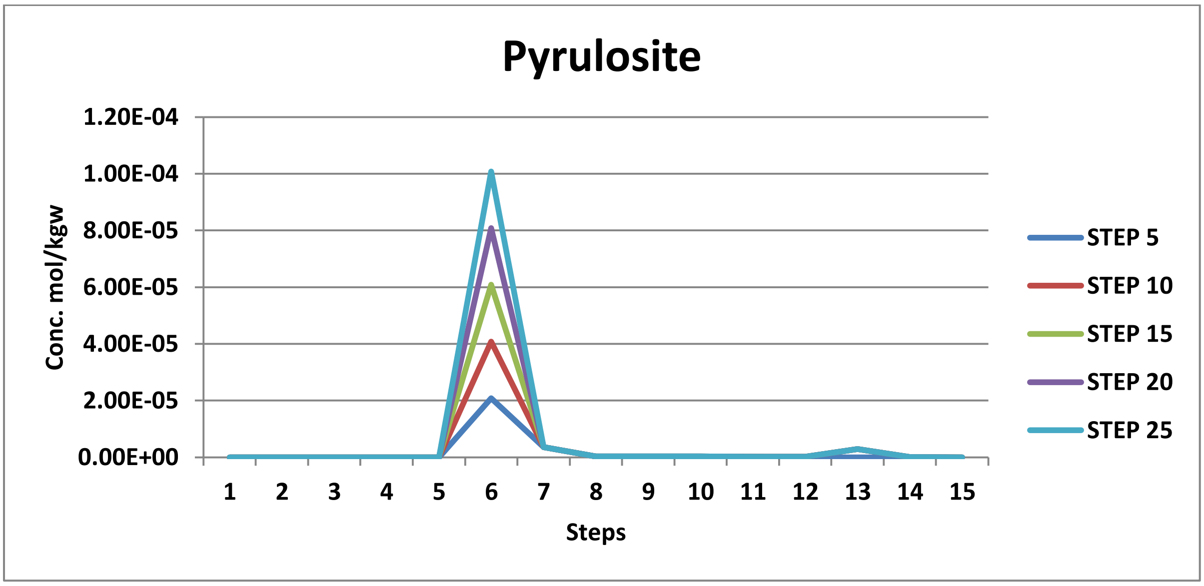


**Figure 6.9:** Concentration of pyrolusite in cells 1-15 at steps 5-25.

Fig 6.10 is showing the increasing concentration of iron hydroxide and pyrolusite in cell no 6. Higher concentration of iron and manganese are precipitating in cell no 6, so the concentrations of Fe(OH)3 and pyrolusite is increasing along with steps. But the concentration of iron hydroxide is increasing more rapidly than pyrolusite.

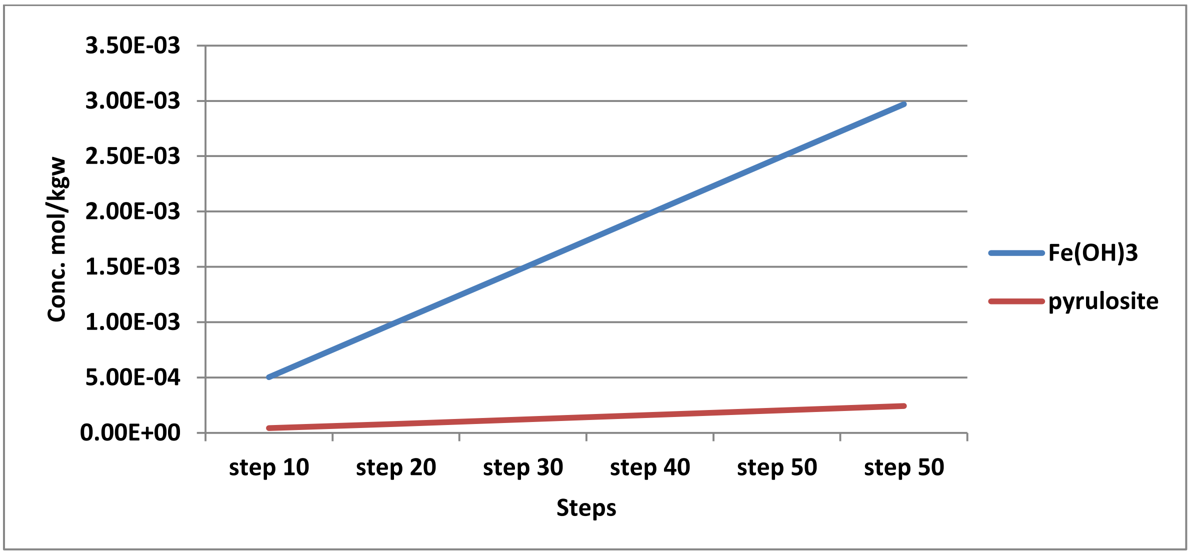


**Figure 6.10:** Concentration of Fe (OH) 3 and pyrulosite in cell no 6.

As it is shown in (Fig 6.9) that there is some concentration of pyrolusite in cell no 13. So (Fig 6.11) is showing that there is some adsorption is taking place in cell no 13 at step 5. There is also a little amount of iron hydroxide in cell no 13 as shown in (Fig 6.8). So that little concentrations of iron hydroxide and Pyrolusite helping to adsorb some concentration of iron and manganese.

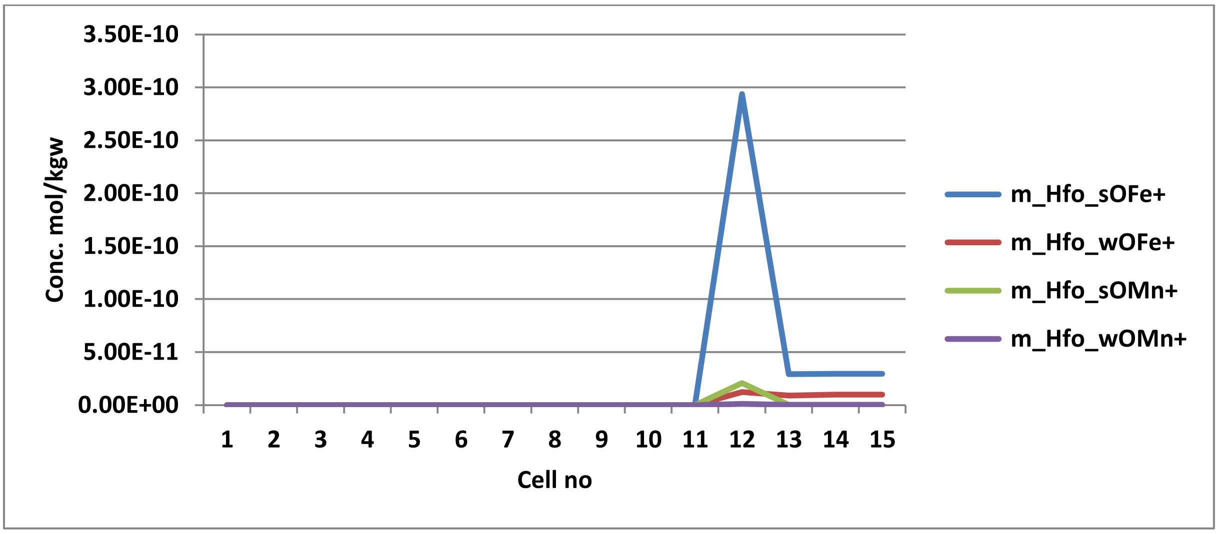


**Figure 6.11:** sorption of iron and manganese in cell 1-15 at step 5.

The scale is missing on the y-axis because these values were too lower for Micro soft Excel to show. According to (Fig 6.12) only a little amount of manganese is sorbed on the strong binding sites of hydrous ferric oxide. Else all of the concentration has been removed by the oxidation.

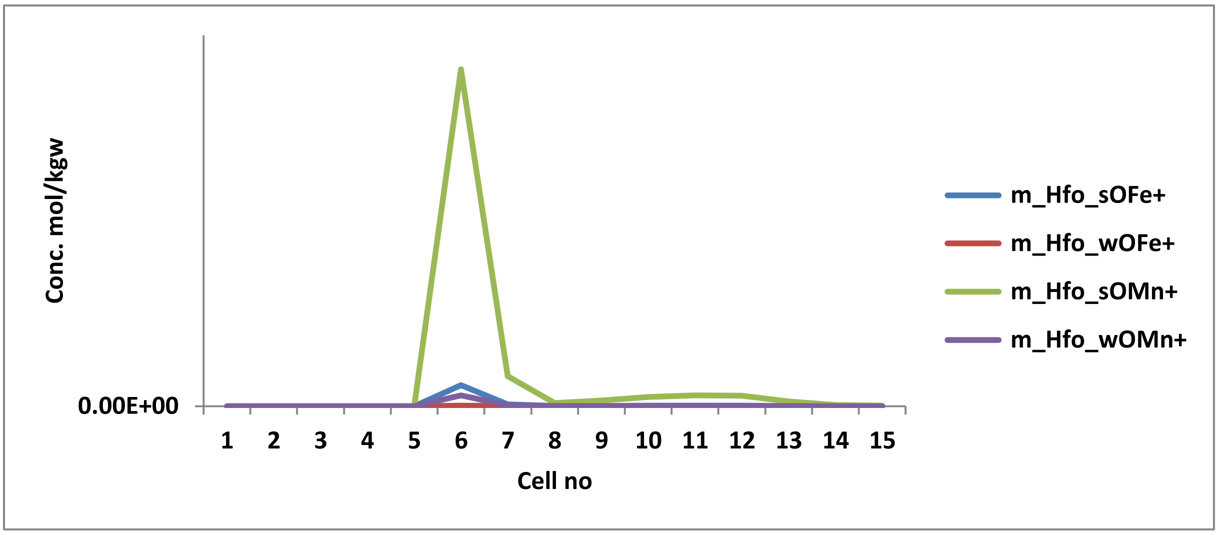


**Figure 6.12:** sorption of iron and manganese in cell 1-15 at step 5.

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Although the sorbed concentration of iron and manganese in cell no 6 is very low, in comparison of both weak and strong binding sites, strong binding sites are sorbing more concentration. Maximum sorption is taking place in cell no 6 in comparison with all other cells. From here it can be estimated that almost all concentration of iron and manganese is removed by oxidation.

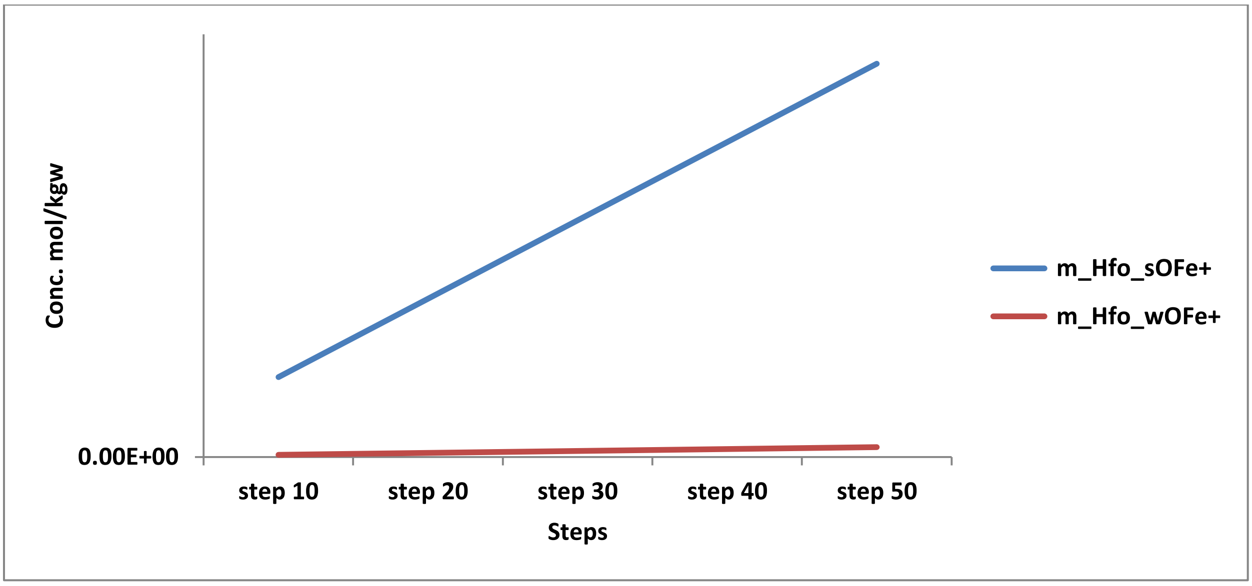

**Figure 6.13:** sorption of iron in cell no 6 by of hydrous ferric oxide.

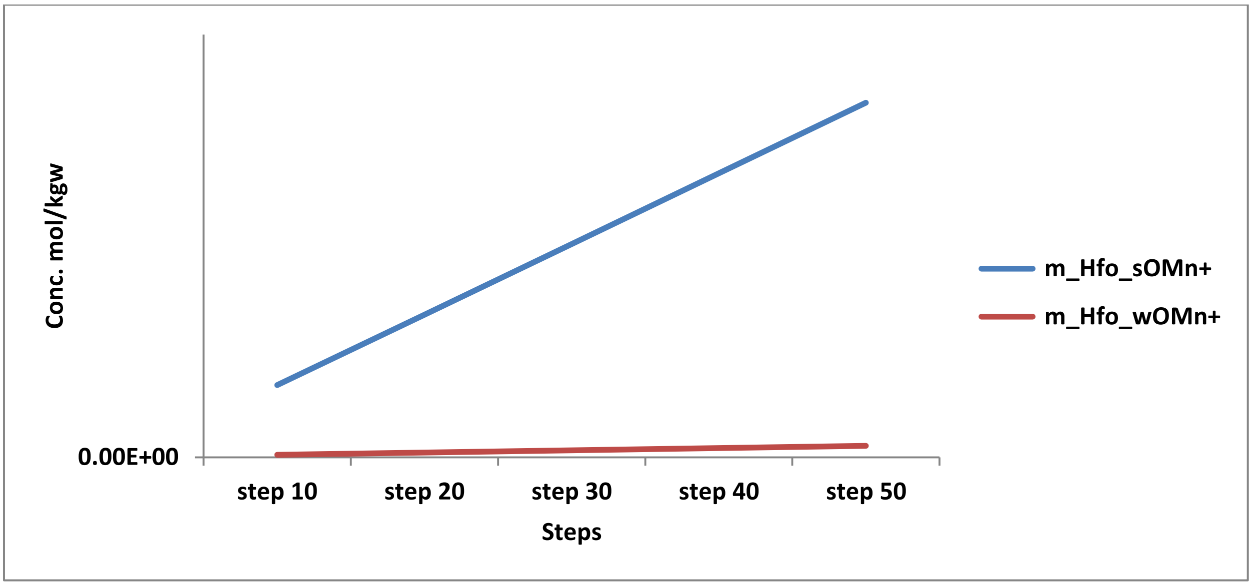

**Figure 6.14:** Sorption of manganese in cell no 6 by of hydrous ferric oxide.

Figures 6.15 and 6.16 are showing the sorption of iron and manganese by the weak and strong binding sites of hydrous ferric oxide in cell no 15. There sorbed concentrations of ieron and manganese are negligible. In comparison of both strong binding sites are sorbing higher concentrations. The scale is missing on y-axis because these values were too small for Microsoft Excel to show.

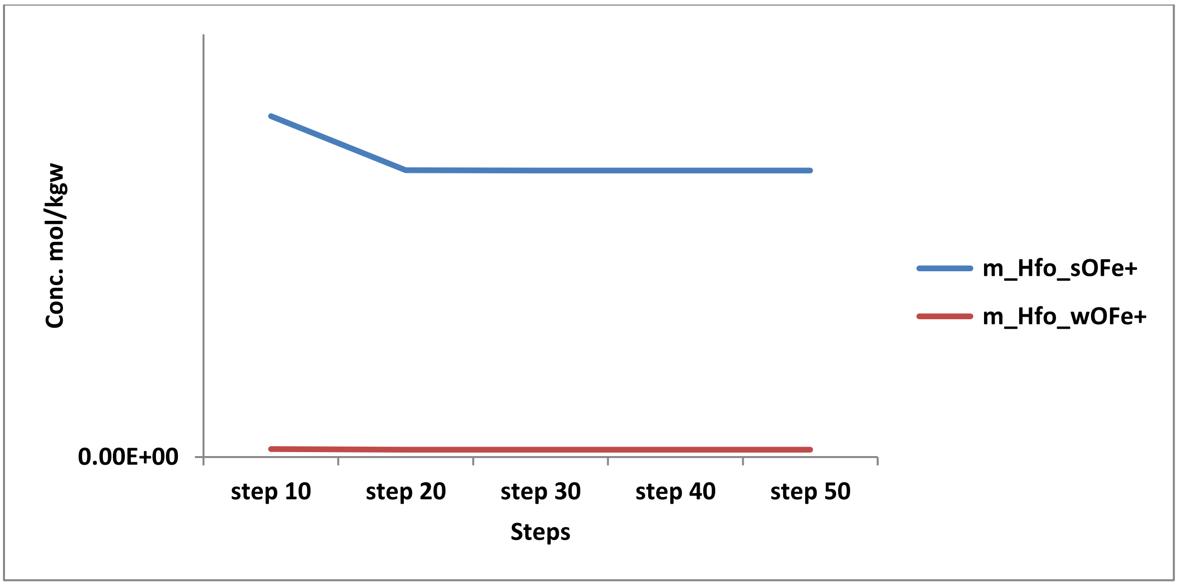

**Figure 6.15:** Sorption of iron and iron by hydrous ferric oxide in cell no 15.

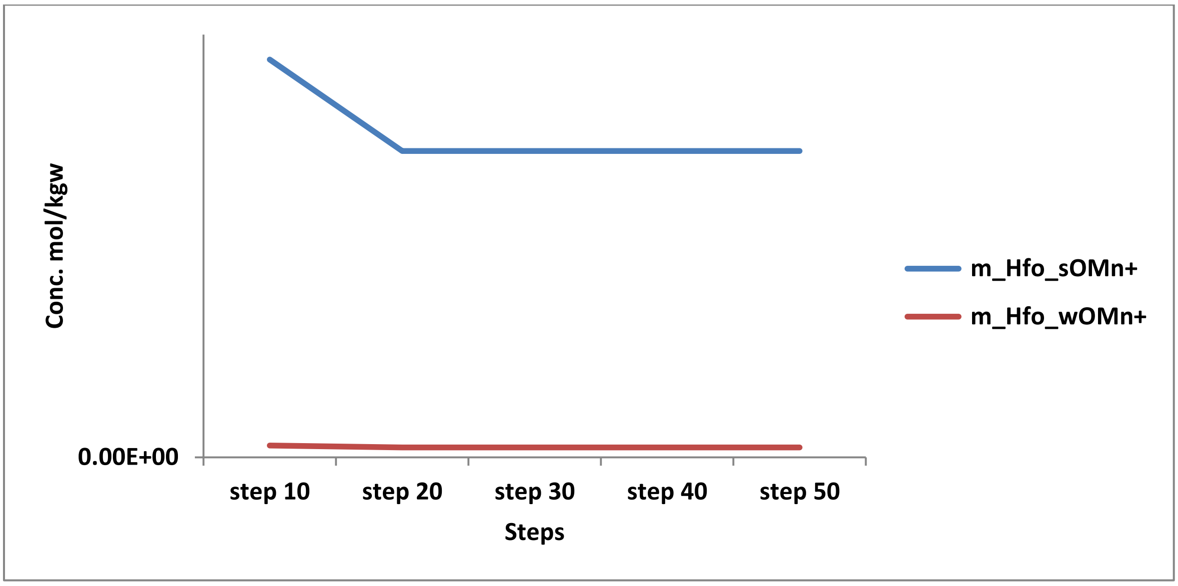

**Figure 6.16:** Sorption of iron and manganese by hydrous ferric oxide in cell no 15.

## 6.4 Surface Complexation model

PHREEQC model was prepared to calculate the sorption of iron and manganese as the function of pH. Solution was defined by the concentrations of iron and manganese 0.08 and 0.028mm/kgw respectively. Keyword of surface is used to define the weak and strong surfaces for the sorption. The oxides surfaces carry a charge that depends on pH and composition of solution. The charge increases the sorption of counter-ions (with a charge opposite to the surface), and resist co-ions (with the same charge as the surface). Many heavy metals are sorbed on oppositely charged surface. Complexation models can be used to calculate the sorption on charged surfaces (Appelo and Postma 2005).

The sorption of manganese is increasing as the pH is increasing (Fig 6.17). 50% of manganese has been sorbed at the pH of 7.2 while the 50 % of iron have been sorbed at the pH of 6.5. It means that the sorption of iron is faster than manganese on hydrous ferric oxide.

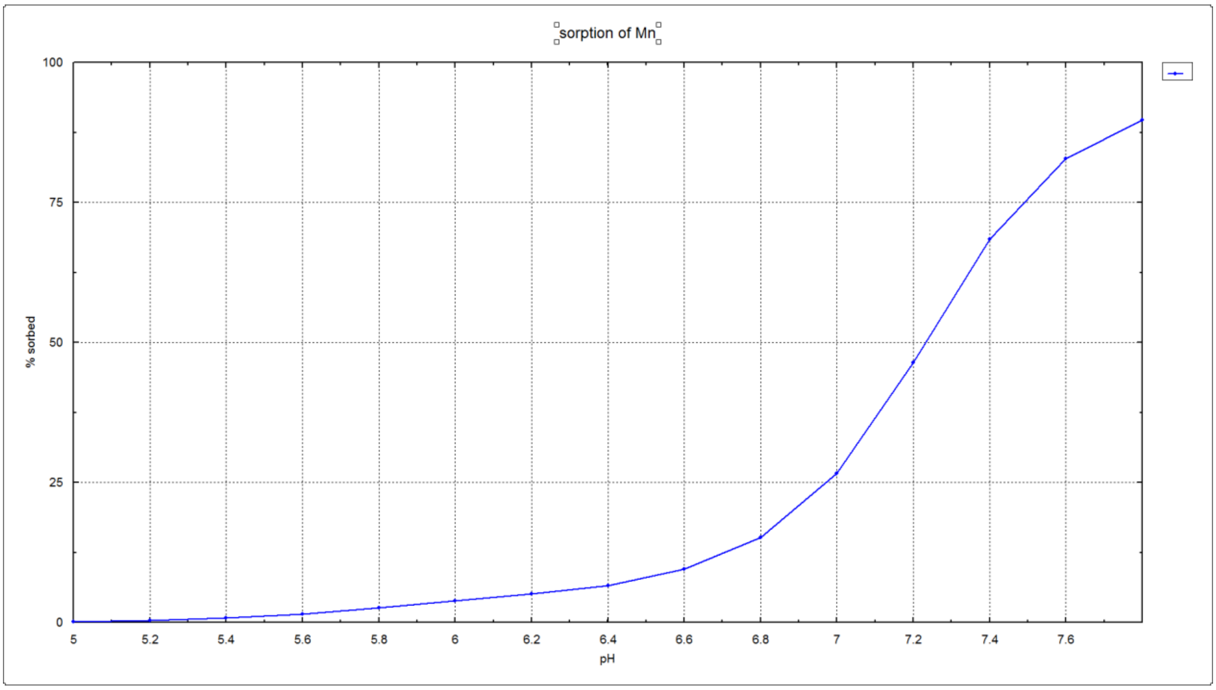

**Figure 6.17:** Sorption of manganese as the function of pH on hydrous ferric oxide.

After the pH of 7.2 the sorption of iron is reducing. It may be due the input data error in our model. But the sorption behavior of iron can be seen up to pH of 7.2.

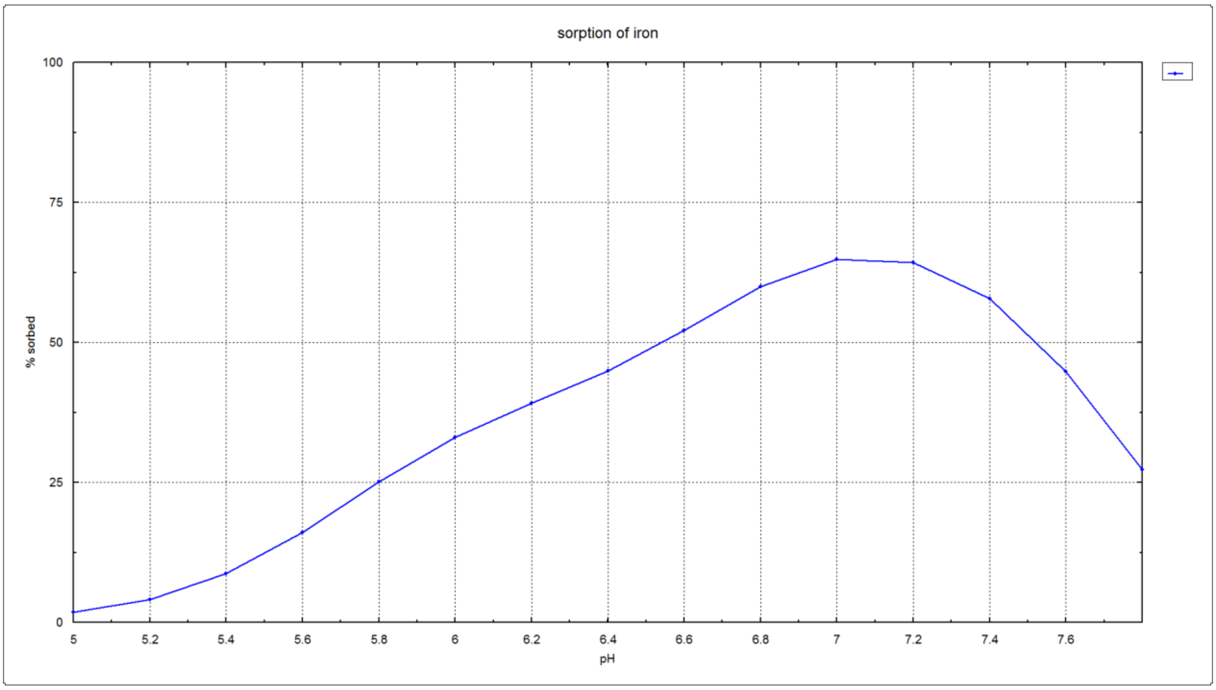

**Figure 6.18:** Sorption of iron as the function of pH on hydrous ferric oxide.

## Chapter 7: Conclusions

The concentration of iron and manganese in groundwater depends upon the amount of oxygen present in water. Considerable concentrations of iron and manganese are found in aquifer under the reducing condition. The in–situ treatment of iron and manganese contaminated water by injection of oxygenated water (Vyredox method) is a cost effective and efficient way to get rid of these metals.

Linear and radial flow simulations were performed by using PHREEQC model to examine the level of oxygen and precipitation rates of iron and manganese in groundwater. The results showed that precipitation rates increases by the increasing the level of oxygen. Manganese requires more concentration of oxygen for its precipitation as compared to iron.

The concentration of oxygen in water in equilibrium with air at 6 degree centigrade is 12.3mg/L. This concentration of oxygen is higher enough for removal of iron and manganese present in groundwater at Grindalsmoen water works. It is calculated that this (12.3mg/l) concentration of oxygen can precipitate 87.mg/l of iron and 42.4 mg/l of manganese which is way more than our assumed concentrations which is 2.79mg/l and 0.21mg/l for iron and manganese respectively.

Due to high level of oxygen, the removal of iron and manganese has taken place before their adsorption, but the adsorption capacities of iron and manganese can play significant role in their removal when the oxygen concentration is insufficient.

The PHREEQC surface complextaion model has shown that iron has more sorption capacity as manganese at same value of pH on hydrous ferric oxide.

In-situ treatment can be adopted as the best recommended treatment method, where so ever, the concentrations of metals in general and of iron and manganese in particular, are higher than the permissible limits.

## 7.1 Recommendations for further study

Although this geochemical study reveals satisfactory results for Grindalsmoen water works, but this study and modeling can be enhanced with proper geochemical and analytical data taken on site.

This work concerning the baseline parameter study may be carried out in field and more precisely in the laboratory facilities. The analysis of key parameters will not only help in understanding the geochemical modeling more properly but also will improve the working efficiency by lowering the operational cost and increasing the treatment performance of the Grindalsmoen water works.

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# Appendices

## Appendix A (Grindalsmoen geochemical model with radial flow)

```
Surface_Species

Hfo_sOH + Fe+2 = Hfo_sOFe+ + H+
          log_k    0.7
Hfo_wOH + Fe+2 = Hfo_wOFe+ + H+
      log_k   -2.5
Hfo_sOH + Mn+2 = Hfo_sOMn+ + H+
      log_k   -0.4
Hfo_wOH + Mn+2 = Hfo_wOMn+ + H+
      log_k   -3.5

Solution 0   # inlet
units          mmol/kgw
# O(0)              0.31
 pH                 6.91
Alkalinity          0.70
Cl                          0.070
S                   0.18
Na                  0.10
K                           0.029
Mn                  0.004
Mg                  0.090
Fe                   0.05
Ca                  0.30
Solution 1-4

units          mmol/kgw
pH                  6.47
#O(0)               0.20
Alkalinity          0.64
Cl                  0.6
S                   0.026
Na                  0.4
K                   0.077
Mn                  0.004
Mg                  0.1
Fe                  0.05
Ca                  0.42

Solution 5

units          mmol/kgw
pH                  6.47
#O(0)               0.20
Alkalinity           0.64
```

```
S               0.026
Na              0.4
K               0.077
Mn              0.004
Mg              0.1
Fe               0.05
Ca               0.42


EQUILIBRIUM_PHASES 5
O2(g)     -0.7

Solution 6-15
units        mmol/kgw
pH              6.47
#O(0)            0.20
Alkalinity      0.64
Cl              0.6
S               0.026
Na               0.4
K                0.077
Mn              0.004
Mg              0.1
Fe              0.05
Ca              0.42

EQUILIBRIUM_PHASES 6-15
        Fe(OH)3    0.0 0.0
        Pyrolusite  0.0 0.0

Transport
        -cells 15
        -shift 105
        -time_step 3600              # 1 hour
        -flow_direction forward      # forward from sol. 1-15
        -dispersivities  0.05
        -boundary_conditions                 flux flux
        -lengths 0.39 0.41 0.42 0.44 0.46 0.49 0.51 0.55 0.59 0.64 0.71 0.80 0.95 1.24 3.00
        -punch_cells 15
        -punch_frequency 1

SURFACE  6-15

 Hfo_w  Fe(OH)3  equilibrium_phase   2.1e-3   600
 Hfo_s  Fe(OH)3  equilibrium_phase   5.4e-5   600
 PRINT
-reset false
SELECTED_OUTPUT
```

```
-file M:\GEO\pawan i poora.out
 -selected_out true
 -molalities Cl- SO4-2 Na+ K+ Mn+2 Mg+2 Fe+2 Ca+2 O2  Hfo_sOFe+ Hfo_wOFe+ Hfo_sOMn+
Hfo_wOMn+
 -Equilibrium_phases Fe(OH)3 Pyrolusite
```

## Appendix B (PHREEQC model to check sensitivity of oxygen with linear flow)

```
Surface_Species
Hfo_sOH + Fe+2 = Hfo_sOFe+ + H+
     log_k    0.7
Hfo_wOH + Fe+2 = Hfo_wOFe+ + H+
       log_k  -2.5
Hfo_sOH + Mn+2 = Hfo_sOMn+ + H+
       log_k   -0.4
Hfo_wOH + Mn+2 = Hfo_wOMn+ + H+
       log_k   -3.5
Solution 0   # inlet
units          mmol/kgw
pH                  6.91
Alkalinity        0.70
Cl                  0.070
S                   0.18
Na                  0.10
K                   0.029
Mn                  0.028
Mg                  0.090
Fe                  0.08
Ca                  0.30
Solution 1-3
units          mmol/kgw
pH                  6.47
Alkalinity        0.64
Cl                  0.6
S                   0.026
Na                  0.4
K                   0.077
Mn                  0.01
Mg                  0.1
Fe                  0.03
Ca                  0.42
Solution 4
units          mmol/kgw
pH                  6.47
#O(0)               0.20
Alkalinity        0.64
S                   0.026
Na                  0.4
K                   0.077
Mn                   0.01
Mg                  0.1
Fe                   0.03
Ca                  0.42
```

```
EQUILIBRIUM_PHASES 4
O2(g)       -2 #          -1 0 1 2
Solution 5-15
units        mmol/kgw
pH              6.47
Alkalinity      0.64
Cl              0.6
S               0.026
Na              0.4
K               0.077
Mn               0.01
Mg              0.1
Fe              0.03
Ca              0.42

EQUILIBRIUM_PHASES 1-15
Fe(OH)3     0.0 0.0
Pyrolusite  0.0 0.0
Transport
        -cells 15
        -shift 155
        -time_step 3600                 # 1 hour
        -flow_direction forward         # forward from sol. 1-15
        -dispersivities  1
        -boundary_conditions                    flux flux
        -lengths 5
        -punch_cells 1-15
        -punch_frequency 5

SURFACE  1-15
 Hfo_w                  2.1e-3 600 0.6      # size area and mass of sorbent
 Hfo_s                   5.4e-5
-equil 1-15
PRINT
-reset false
selected_output
-file M:\GEO\H.out
 -selected_out true
-molalities Cl- SO4-2 Na+ K+ Mn+2 Mg+2 Fe+2 Ca+2 O2  Hfo_sOFe+ Hfo_wOFe+ Hfo_sOMn+
Hfo_wOMn+
 -Equilibrium_phases Fe(OH)3 Pyrolusite
-totals Fe Mn Mg Fe Ca
```

## Appedix C (PHREEQC model to check the level of sensitivity of oxygen with radial flow)

```
Surface_Species
Hfo_sOH + Fe+2 = Hfo_sOFe+ + H+
   log_k   0.7
Hfo_wOH + Fe+2 = Hfo_wOFe+ + H+
    log_k  -2.5
Hfo_sOH + Mn+2 = Hfo_sOMn+ + H+
    log_k  -0.4
Hfo_wOH + Mn+2 = Hfo_wOMn+ + H+
    log_k  -3.5
Solution 0  # inlet
units        mmol/kgw
pH              6.91
Alkalinity      0.70
Cl              0.070
S               0.18
Na              0.10
K               0.029
Mn              0.028
Mg              0.090
Fe              0.08
Ca              0.30
Solution 1-3
units        mmol/kgw
pH              6.47
Alkalinity      0.64
Cl              0.6
S               0.026
Na              0.4
K               0.077
Mn              0.01
Mg              0.1
Fe              0.03
Ca              0.42
Solution 4
units        mmol/kgw
pH              6.47
#O(0)           0.20
Alkalinity      0.64
S               0.026
Na              0.4
K               0.077
Mn               0.01
Mg              0.1
Fe               0.03
Ca              0.42
```

```
EQUILIBRIUM_PHASES 4
O2(g)       -2   #        -1 0 1 2
Solution 5-15
units         mmol/kgw
pH                6.47
Alkalinity        0.64
Cl                0.6
S                 0.026
Na                0.4
K                 0.077
Mn                 0.01
Mg                0.1
Fe                0.03
Ca                0.42

EQUILIBRIUM_PHASES 1-15
Fe(OH)3     0.0 0.0
Pyrolusite  0.0 0.0
Transport
        -cells 15
        -shift 155
        -time_step 3600                # 1 hour
        -flow_direction forward        # forward from sol. 1-15
        -dispersivities  1
        -boundary_conditions                   flux flux
        -lengths 11.62 11.22 10.80 10.39 9.95 9.49 9.00 8.49 7.94 7.35 6.71 6.00 5.20 4.24
3.00
        -punch_cells 1-15
        -punch_frequency 5

SURFACE  1-15
 Hfo_w                 2.1e-3 600 0.6      # size area and mass of sorbent
 Hfo_s                  5.4e-5
-equil 1-15
PRINT
-reset false
selected_output
-file M:\GEO\H.out
 -selected_out true
-molalities Cl- SO4-2 Na+ K+ Mn+2 Mg+2 Fe+2 Ca+2 O2  Hfo_sOFe+ Hfo_wOFe+ Hfo_sOMn+
Hfo_wOMn+
 -Equilibrium_phases Fe(OH)3 Pyrolusite
-totals Fe Mn Mg Fe Ca
```

## Appendix: D (Sorption edge of iron and manganese)

```
Solution 1
pH  8
Fe  0.08
Mn  0.028
Surface 1
Hfo_w 2.1e-3 600 0.6
Hfo_s   5.4e-5
-equil 1
User_Graph
  -chart_title sorption edge
  -axis_titles "pH"  "% sorbed"
  -axis_scale x_axis 5 7.8 0.2
  -axis_scale y_axis 0 100 25
 -connect_simulations true
 -initial_solutions false
 -start
10 sor  = mol("Hfo_sOMn+") + mol("Hfo_wOMn+")
20 graph_x -la("H+") # pH on x-axis
30 graph_y 100 * sor /(sor +tot("Mn"))
end
SOLUTION 1 ; pH 8.0; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 7.8; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 7.6; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 7.4; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 7.2; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 7.0; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 6.8; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 6.6; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 6.4; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
```

```
End
SOLUTION 1 ; pH 6.2; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 6.0; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 5.8; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 5.6; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 5.4; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 5.2; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
SOLUTION 1 ; pH 5.0; Fe 0.08; Mn 0.028
Surface  1 ; Hfo_w      2.1e-3 600 0.6 ; Hfo_s 5.4e-5; -equil 1
End
```

## Appendix E (O2 saturation at PO2 at 6 degree centigrade)

**Solution 1**

```
temp 6
O(0)  1   O2(g)    -.69
end
```