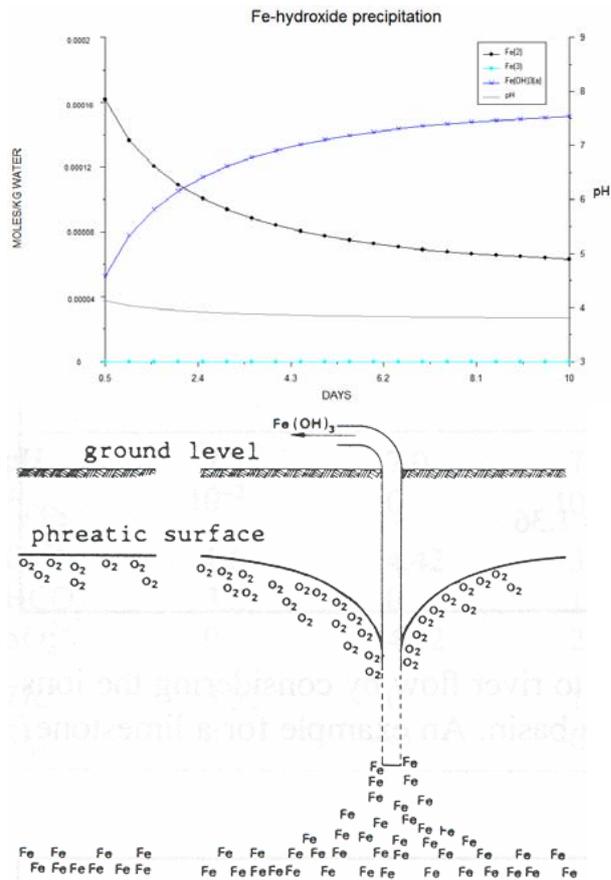


Chemical clogging processes in the filter slots of pumping wells and drains in unconsolidated aquifers



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Chemical clogging processes in the filter slots of pumping wells and drains in unconsolidated aquifers

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Chemical clogging processes in the filter slots of pumping wells and drains in unconsolidated aquifers

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Preface

This report is based on a research done Kiwa Water Research which was conducted during April 2006 - to September 2006 at Utrecht University for a Master's Degree in environmental hydrogeology. The main supervisor was professor P. J. Stuyfzand (Frije Universiteit van Amsterdam) and the co-supervisor was associate professor dr. R. J. Schotting (Utrecht University).

I would like to thank ir. Kees van Beek Kiwa Water Research, who has provided laboratory data from field. Without this data it would not have been possible to meet the objectives of this research.

I appreciate the support of dr. Henning Prommer (Centre for Groundwater Studies, CSIRO Land and Water, Australia and Delft University of Technology) who I was unfortunately never able to meet personally during the research period. Despite the distance, all my questions about modelling and PHREEQC were answered accurately and quickly.

I also like to thank Ruud Schotting and Piter Stuyfzand for their supervision during this research.

Ultimately, I like to thank all staff members and students at Kiwa Water Research for making my stay at KIWA very pleasant.

Summary

Well clogging is important because of decreasing capacity of wells due mechanical or chemical forces. In this study the focus is directed on chemical well clogging. Some chemical processes were considered in case of a real well to investigate their contribution to the clogging process.

A literature review revealed that chemical reaction and biochemical activity in the well can be a reason of clogging. The most widespread precipitations are iron hydroxide, manganese oxide and aluminum hydroxide. The iron and manganese incrustations are the result of mixing two water types: oxic water (which contains oxygen, Fe(III), Mn(III), Mn(IV)) and anoxic water (without oxygen, but containing Fe(II) and Mn(II)). Aluminum hydroxide is a result of mixing of waters with different pH. Microbiological activity plays an important role in chemical clogging. Bacteria speed up the iron hydroxide oxidation and produce slime, which clog the filter slots. All possible rehabilitation and prevention methods were analyzed in case of chemical clogging.

Field site Vierlingsbeek was studied to investigate the reason of clogging processes. Microscopic analyses of incrustation from the well screen indicate that they are mainly composed of iron hydroxide (ochre).

Chemical analysis by PHREEQC (beaker experiment) and PHT3D (steady-state pumping) revealed that two processes are needed: mixing and precipitation, kinetics. Result of models is the same as a result of microscopic analysis: ochre deposition due to mixing of oxic and anoxic water is a reason of clogging well.

Calculations to evaluate the chemical clogging rate were done for four scenarios:

- 1) well pumped 16 hours during day; followed by 8 hours rest per day.
- 2) well pumped 12 hour during day; followed by 12 hours rest per day.
- 3) well pumped 8 hour during day; followed by 16 hours rest per day.
- 4) well pumped 24 hour during day.

The result of this calculation shows that little precipitation occurs if the pump runs for station works 24 hours per day and that the most precipitation occur if the pump works 8 hours per day.

Results of calculation show that with increasing the no-pumping period the rate of clogging is increasing too. The time, which is needed to decrease the capacity of the well, was calculated. Five years appear enough to clog a well with long periods without pumping.

PHT3D model shows, that the precipitation is decreasing with increasing depth. Simulation results indicate that the concentration of iron-hydroxide precipitation increases with time.

1 Introduction

1.1 Origin of this project

The abstraction of groundwater is a great benefit to society, amongst others waterworks abstract groundwater for drinking water purpose, constructors to keep their building docks dry, and to engineers to prevent tunnels from floating and to hold dams stable. A well known problem with respect to the abstraction of groundwater is a gradual clogging of the wells.

Well clogging is a serious problem for, for instance, Water Supply Company Hydron Middle Holland and in the north of the Brabant. Pumping stations: Boxmeer, Macharen and Vierlingsbeek suffer from chemical clogging. Only a few years after their construction, the specific capacity of most wells decreases to 50% or less of the original value. This relatively rapid decrease in well capacity threatens drinking water production and disrupts the purification process (Timmer et al. 2004).

Typically, in the Netherland, well clogging occurs at two locations in the well: in the filter slots, including the interface of the well screen and gravel pack; and at the interface between the gravel pack and the aquifer. The latter is also called clogging of the borehole wall. Clogging of the filter slots is mainly a chemical process. Clogging near the borehole wall is mainly a physical process. This research focuses at the chemical type of well clogging.

1.2 Aims of this research

This research of well clogging focuses at understanding the role of chemical reactions in groundwater in and around pumping wells. This project aims to characterize the chemical influences on clogging processes.

The research questions are:

- 1) Which are the processes (chemical reactions) occurring in the well during pumping?
- 2) Will some precipitation occur during well pumping in case of mixing water from the top (oxygen) and bottom (no oxygen) parts of the aquifer?
- 3) Which the minerals will deposit?
- 4) What is the influence of the intervals without pumping?
- 5) When will minerals precipitate after pumping start?
- 6) How can clogging wells be rehabilitated?
- 7) Which preventive methods are possible?

Mineral precipitation including the kinetics is investigated as main reason of the well clogging and is modeled by PHT3D.

1.3 Field site Vierlingsbeek

The well field Vierlingsbeek is located in the southeast of the Netherlands within the municipality of Vierlingsbeek. The well field is located on originally poorly drained sandy soils close to the valley of the river Meuse (Figure 1-1).

The well field has been in operation since 1965. The production amounts to $3 \cdot 10^6$ m³/year, and it is supplied by 12 wells. These wells are about 30m deep, with screens extending from 15 to 30m.

The well field is located on windblown sands, in woods consisting mainly of conifers showing poor growth. To the south anthropogenic soils are present. The depth of the groundwater table is about 2m below surface.

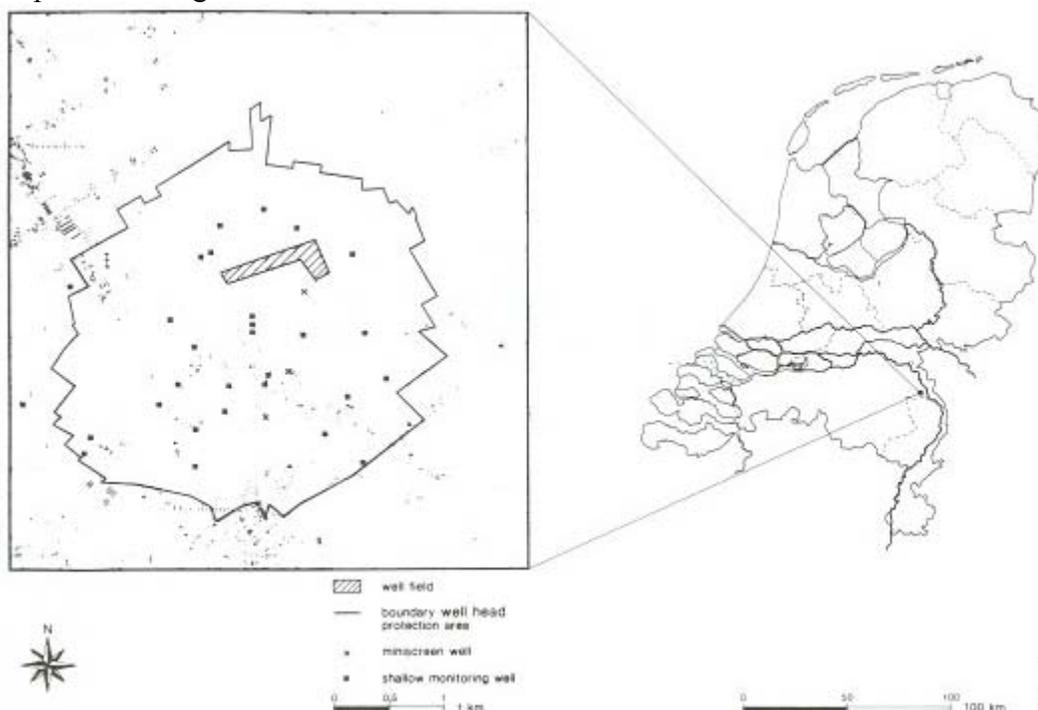


Figure 1-1 Location of the well field Vierlingsbeek.

1.4 Structure of this report

The project is divided into the following major sub-tasks that will result into the separate chapters of the thesis.

In Chapters 4-7, the backgrounds of well clogging are given. Possible chemical reactions which can result in chemical well are clogging considered. Processes of precipitation and composition of precipitation, including the microbiology and fungi are described. The determinations of rehabilitation processes due to different chemical clogging mechanisms are given and possible choices how to avoid the chemical clogging in the well are described.

In Chapters 8 field data observations, which include microscopic analysis of clogging material and chemical composition of groundwater, are given.

In Chapter 9 model construction is present. Two different programs are use to determine the relevance of chemical clogging processes. “Model construction” describes how to implement the programs PHREEQC and PHT3D in case of chemical clogging processes. Calculations of clogging processes are predicting

the clogging rate and distribution of clogging deposits. Calculations for 4 pumping scenarios were done.

2 Backgrounds of well clogging

2.1 Introduction

Well clogging is characterized by a continuous decrease in the specific capacity of the well per meter of drawdown, where drawdown is the difference between the water level in the well during operation and inaction (the undisturbed water level, i.e. in the absence of a well pumping). Well clogging is mostly indicated by an increase of the drawdown (C.G.E.M. van Beek, 1985).

As a general rule, clogging will affect all pumping wells. Chemical clogging is generally caused by geohydrochemical and/or geomicrobiological processes. If clogging is occurring, the velocity of the groundwater to be abstracted will increase around the unclogged part of the well, and the sand content of the extracted water may increase, which is considered the final stage of clogging.

In this section the chemical causes of well clogging are discussed. The main focus is on clogging problems due to iron and/or manganese incrustation and biofouling excluded limestone formation.

The formation of incrustations seriously affects the performance of wells, piezometers and drains. Their economic relevance must not be underestimated. Oxides of Fe(III) represent the most common incrustation type. Their formation via oxidation of dissolved Fe(II) is enhanced at zones of elevated flow velocities. During formation, Fe oxide incrustations take up large amounts of trace elements from groundwater if these are present in water. Trace element concentrations influence the rate of transformation and the solubility of Fe oxide incrustations.

Ferrous iron is much more soluble than ferric iron. Oxidation of ferrous iron to ferric iron, by bacteria and by oxygen, results in the formation of ochre (also called ferrihydrite) and/or bacterial slimes. These can clog the intake screens of wells, and the filters, laterals and emitters of a drip irrigation system.

2.2 Chemistry of iron and manganese.

Iron and manganese exist in many different chemical forms. The presence of a given form of iron or manganese in geologic materials or water depends on many different environmental factors. We can often anticipate iron and manganese problems in water by observing a few general principles that affect water chemistry.

An important principle to remember with respect to chemical reactions is that, if allowed enough time, they will reach equilibrium with the surrounding environment. When the conditions of that environment are changed, such as pumping water from an aquifer, the chemical equilibrium is disturbed. This will lead to either solution of certain elements such as iron and manganese or their precipitation.

Waters that do not have regular contact with the atmosphere tend to be low in oxygen (oxygen poor). Iron and manganese carbonates in an oxygen poor environment are relatively soluble and can cause high levels of dissolved iron and manganese. However, if iron is associated with sulfur as iron sulfide rather than iron carbonate, dissolved iron remains low. Dissolved oxygen generally decreases with depth, so these types of conditions are more likely to occur in deep wells. Iron and manganese problems are most likely to develop in water from wells with high carbonate and low oxygen as shown in the middle well in Figure 2-1. Problems occur when this type of water is pumped to the surface. The chemical equilibrium is changed upon exposure to the atmosphere. The end result is precipitation of iron and manganese compounds in the well only if mixing with oxygen-containing water occurs.

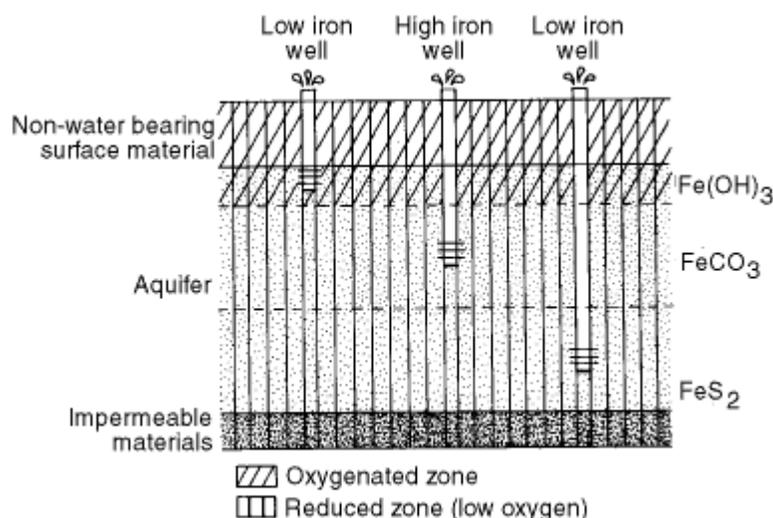
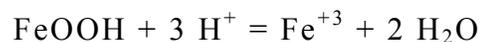


Figure 2-1. The amount of iron and manganese dissolved in water often follows a trend of low to high back to low again as depth of the well increases. (Snoeyink, and Jenkins, 1980)

Iron-rich incrustations can be subdivided into subtypes. Iron oxides occur in two varieties with little overlap. They can be distinguished into low (ferrihydrite) and high crystallinity Fe oxides (goethite – α -FeOOH and lepidocrocite – γ -FeOOH) (Figure 2-2). The metamorphose crystallisation process (ferrihydrite to lepidocrocite) involves a decrease in surface area, solubility and reactivity.

Goethite – high crystallinity



Fe(OH)3(a)-amorphous iron-hydroxide (ferrihydrite)

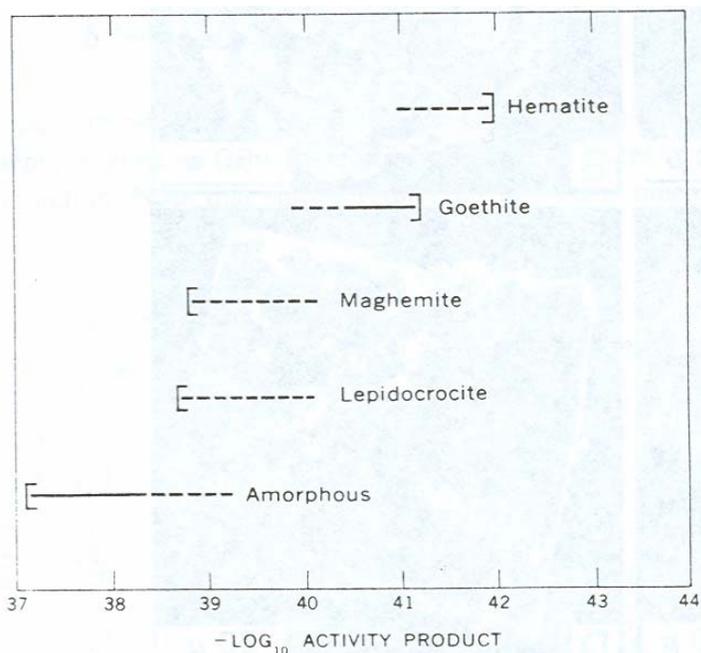
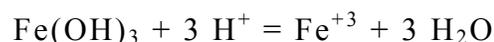


Figure 2-2 The stability ranges of common Fe-oxyhydroxides, hematite (α -Fe₂O₃), goethite (α -FeOOH), maghemite (γ -Fe₂O₃), lepidocrocite (γ -FeOOH) and amorphous Fe(OOH)₃. The activity product are expressed as $\text{IAP}=[\text{Fe}^{3+}][\text{OH}^-]^3$ and are given for 25°C and 1 atm. (Langmuir, in Appelo & Postma, 2005).

Iron can only be in solution under reducing conditions in near the pH neutral ground water, and encountering aerobic conditions provides the opportunity to initiate the iron oxidation processes of both a pure chemical and microbiologically mediated nature.

2.3 Process of ochre deposition

Most incrustations are of the ochreous type. Among them Fe and Mn oxide incrustations can be distinguished with the former being much more abundant than the latter. They rarely occur together in one well. This is due to different redox potentials required for formation (Fe: Eh: 0.0–0.5 V; Mn: Eh: 0.6–1.2 V) as shown in Figure 2-3 (G. J. Houben, 2002).

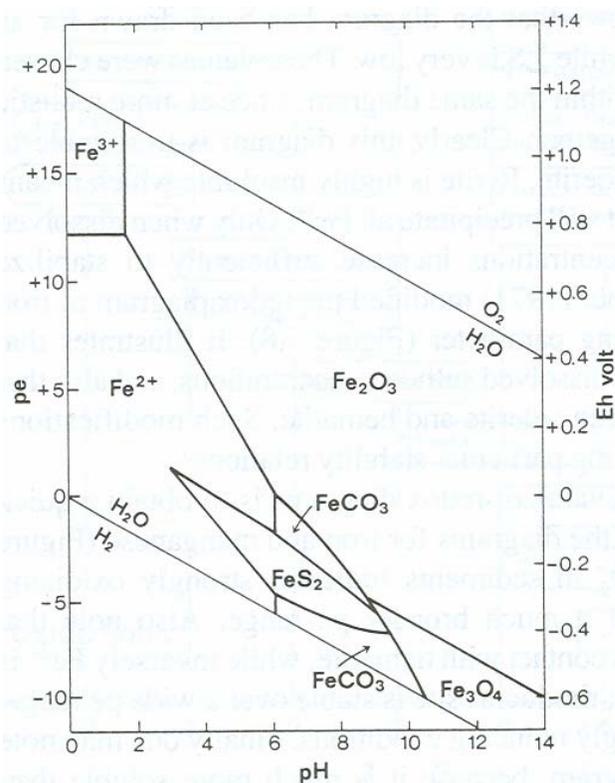
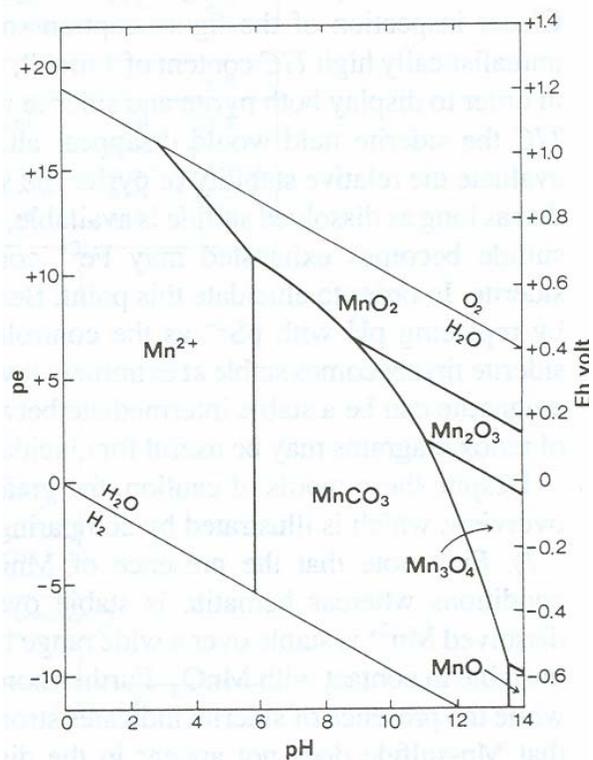
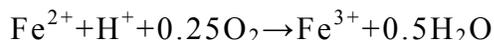


Figure 2-3. Stability relationship for iron and manganese at 25°C, $\Sigma S=10^{-6}$. Solid-solution boundaries are drawn for $Fe(II)=10^{-6}$ (Appelo, 2001)

Based on controlled studies, the minimum ferrous iron concentrations that can stimulate ochre formation are between 0.15 and 0.22 mg/l (parts per million)

(Ford, 2005). These data depend on pH, Eh, but the author does not mention the experimental conditions. Iron-precipitating bacteria must be present for extensive clogging to occur, even when other conditions are just right for chemical precipitation of the iron.

Iron-oxidizing bacteria promote the oxidation of ferrous ions, which are usually soluble under reducing conditions to the ferric state, but no oxidation without oxygen:



The ferric ions produced tend to form insoluble iron oxyhydroxides:



The rate of precipitation/dissolution reaction is described by:

$$\frac{\partial \text{Fe}}{\partial t} = k_{11} [\text{Fe}^{2+}] [\text{OH}^-]^2 P_{\text{O}_2} \quad [1]$$

where

$\frac{\partial \text{Fe}}{\partial t}$ - change in concentration of Fe^{2+} with time (mol/ L/d),

k_{11} – reaction coefficient at 11°C

$[\text{Fe}^{2+}]$ – concentration of iron (mol/L)

$[\text{OH}^-]$ – concentration of hydroxide (mol/L)

P_{O_2} – pressure of oxygen (atm)

It is the formation of ferric oxyhydroxides that produces the characteristic orange color.

Iron-oxidizing bacteria may be considered to be “interface organisms”, living at the boundary of an anaerobic, iron rich subsurface and an aerobic surface. Drilling a borehole and abstracting groundwater can create conditions in which anaerobic iron-containing groundwater and oxygen meet in the borehole environment, initiating the development of an iron-oxidizing bacteria population.

There are several kinds of processes involved in ochre deposition:

1) Oxidation of the iron by certain bacteria predominantly on the outside of the organisms

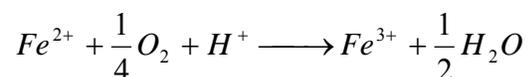
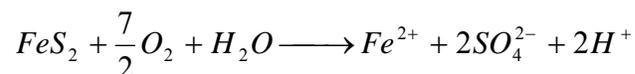
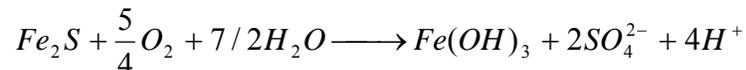
2) Auto-oxidation (chemical change) and precipitation with subsequent accumulation of the colloidal iron on the sticky surfaces of bacterial slimes.

3) Bacterially precipitated iron from complexed soluble organic-iron compounds. The soluble complex before precipitation may be either ferrous or ferric iron.

The most effective iron-precipitating bacteria are Gallionella, Leptothrix, and Sphaerotilus. The hydrochemical processes of Fe and Mn precipitation are strongly mediated by them. (Ivarson and Sojak, 1978; Hanert, 1981). These bacteria's have a name as filaments.

There are certain rod bacteria, such as Pseudomonas and Enterobacter, that also can precipitate iron, but the volumes of ochre produced are not as large as with the filamentous types.

Ochre deposits can be formed under low pH conditions. Pyritic soils, often called acid sulfate soils, are found most frequently in coastal agricultural areas, like northwestern Europe and the Scandinavian countries. The pyrites first oxidize to ferrous iron and sulfates. The sulfates change to sulfuric acid, which lowers the soil pH below 3.5. The rod-shaped bacterium Thiobacillus ferrooxidans, which can function only in an acid environment, then converts the soluble iron into ochre.



Organo-iron complexation is a complicating factor that makes it difficult to predict rates of precipitation. Iron will complex with a large number of organic compounds, such as humic, tartaric, lactic, ascorbic, and citric acids and forms ochre deposition.

As mentioned above, iron precipitation can have two causes:

1) Precipitation due to chemical oxidation in case of mixing between oxygenated and no-oxygenated water

2) Precipitation due to bacterial activity leading to Fe(II) oxidation in the aquifer, in the presence of oxygen.

2.4 Composition of incrustation

In the well, there are four known types of sludge deposits that are associated with bacterial activity. These are ochre, manganese deposits, sulfur containing

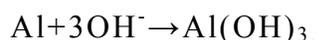
slime, and iron sulfide. Iron deposits, collectively named ochre, are the most serious and widespread. Ochre deposits and associated slimes are usually red, yellow, or tan in color. Ochre is filamentous (from bacterial filaments), amorphous (more than 90% water), and has a high iron content (2 to 65% dry wt.). It is a sticky mass combined with an organic matrix (2 to 50% dry wt.) that can clog drain entry slots, drain envelopes, and the valleys of the corrugations between envelope and inlet slots.

Elements like aluminum, magnesium, sulfur, and silicon are often present (Ford, 2002; Houben, 2002).

Well incrustations commonly exhibit elevated concentrations of heavy metals, if these metals are present, due to a high surface area and a high surface-charge density (Walter, 1997). Re-crystallization of ferrihydrite to goethite involves a drastic decrease of surface area and loss of sorption capacity. Hydroxyl groups can be replaced by sorption of anionic ligands or cations. For the wide spread anions such as phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) sorption increases with decreasing pH reflecting the increasing positive charge. Phosphate adsorption can diminish the dissolution rates of Fe-oxides. Cation sorption, especially of heavy metals, occurs via deprotonation of the surface hydroxyl groups.

Very low concentrations of arsenic in the groundwaters would suggest that the level of arsenic in the deposits is due to bioaccumulation as part of the iron biofouling process. The subject of heavy-metal bioaccumulation by iron bacteria has been reviewed by Banks (1992) and discussed by Thompson & Watling (1987). Bacteria such as *Thiobacillus* and *Leptothrix* are able to convert the soluble form of arsenic into a relatively stable, less toxic precipitate. This information indicates that the simple biological iron removal process discussed above could potentially be effective in removing arsenic from groundwater required for drinking water supplies.

Aluminium hydroxide incrustations are restricted to areas that suffer from soil and groundwater acidification. The Al is mobilized from the soil through acid dissolution of gibbsite and clay minerals. Mixing of near-surface acidified Al-rich water with deeper, less acidic water in the well causes the precipitation through:



The time scale of incrustation ageing is difficult to quantify. Laboratory experiments by Schwertmann and Murad (1983) indicate that the transformation rate from ferrihydrite to goethite increases strongly with rising pH. In the normal pH-range of groundwater (pH 6–7) the reaction has a half-life of 110–160 days (Schwertmann and Murad, 1983). Small amounts of adsorbed phosphate can significantly retard the process. Paige et al. (1997) found that 1 mol% phosphate results in an order of magnitude decrease of re-crystallisation at pH 12. Elevated concentrations of divalent metals such as Co, Ni, Cu and Zn in the crystal structure have a similar effect (Giovannoli and

Cornell, 1992; Martinez and McBride, 1998). In the field, the re-crystallization process may thus take several years.

2.5 Biofouling of the well

The ability of the bacterial biomass to change hydraulic properties of a saturated porous medium has been observed in laboratory studies (Baveye et al, 1998). This phenomenon is called bioclogging.

Biofouling is a term used to describe water well deterioration caused by microbiological activity (i.e. bacteria). Well deterioration can take the form of:

- 1) deterioration water quality in time
- 2) reduced well yield due to clogging of well screens or the aquifer itself
- 3) red or black slime on pumps, well screens, or in the distribution system

The nature of biofouling is variable, but appears to fall into two categories. The first type of biofouling occurs in the sand or gravel pack surrounding the well screen or within the aquifer adjacent to the borehole and usually arises as the result of wide spread accumulation of biomass and metabolic by-products. The second type of biofouling occurs at or near the well screen and on the (submersible) pump itself, and reflects an intensification of biological activity due to changes in the local geochemical environment as a result of ground water extraction.

Iron-oxidizing bacteria play a role in the second type of clogging (van Beek, 1984). These bacteria oxidize dissolved ferrous iron producing hydrated iron oxide precipitate as a metabolic product. The extraction of ground water from an anaerobic aquifer creates an ideal environment for the proliferation of iron oxidizing bacteria (Chapelle, 1993). Dissolved oxygen is supplied to the well from the atmosphere or from the oxygenated ground water originating near the water table (Figure 2-4), (van Beek, 1984). Dissolved ferrous iron is supplied to the well from the anaerobic ground water. Biomass and iron hydroxide compounds accumulate at the resulting aerobic-anaerobic interface, which is usually located at the well screen. The physiology of these bacteria makes them particularly troublesome (Chapelle, 1993).

Iron oxidation yields relatively little energy per mole of substrate utilized, requiring iron oxidizing bacteria to turn large amounts of Fe(II) to Fe(III) in order to sustain growth. The oxidation of 1 mole of ferrous iron produces 40kcal of the free energy (Sean F. Tyrrel and al, 1997). The insoluble oxyhydroxides formed from Fe(III) can quickly clog a well.

Iron bacteria are much more intended. A very small percentage of the slime in the well and pipeline is actually composed of iron bacteria. Most of this debris is due to slime formation by naturally occurring soil bacteria, not iron bacteria. (Hanson, 2003).

2.6 Fungi

This part is not always considered as an autonomous type of biofouling. Fungi produce slime, which is much more stable, than the slime bacteria. It is often multicolored and has a smell. It is necessary to distinguish two types of slime in a laboratory, because of different rehabilitation methods (Dave Hanson, 2003).

3 Well cleaning

The goal of a well-cleaning program is to remove materials or obstructions that are reducing the capacity of the well. Two mechanisms typically cause well clogging: inorganic chemical precipitation and bacterial growth.

If clogging process occurs in the screen slots, there are question how to rehabilitate the well. There are three possibilities: mechanical, chemical methods or combinations of both.

Rehabilitation are always starts with using mechanical methods. Common used methods like brushing, jetting and jutting. But those methods are useful only if slime exists.

The chemical way of rehabilitation uses acids or reductants for the removal of iron hydroxides, or an oxidant for the removal of manganese oxides and/or biomass. Rehabilitation methods only remove clogging material, but not the source of it. It has to be noticed that after rehabilitation clogging process will take place again, because the source of clogging still remains.

3.1 Iron and Manganese Removal

3.1.1 Mechanical methods

1) Pressure cleaning

Low pressure removal of ochre is feasible provided the ochre in the pipe is fresh and gelatinous. Care must be taken so that too much pressure isn't applied to the system as pipe joints could blow out. This method is useful where laterals are connected to a main and are not accessible from an open ditch.

High pressure cleaning is required if the ochre has aged and become firmly encrusted onto the tile. Too high a pressure will cause considerable damage to the envelope of material surrounding the pipe causing sand and gravel to be swept into the tile.

2) Brushing, jetting

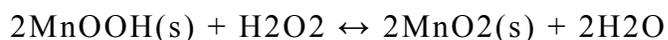
Simple mechanical processes include brushing, whereby a ware brush, is lowered and rotated on the end of a drill string inside the well lining. It is a simple and effective process for removing soft to medium encrustations but becomes much less so where internal casing/screen diameters vary or are not precisely known.

3.1.2 Chemical methods

1) Chlorination (Oxidation) Plus Filtration

Strong oxidizing agents are often used to battle microbial slimes that sometimes accompany ochreous deposits. Hydrogen peroxide and hypochlorite are commonly used for this purpose, with the aim of mineralizing the organic material.

Hydrogen peroxide is also often applied to detach Mn incrustations that primarily contain Mn(III), e.g. as MnOOH.



An additional advantage of using the chlorination system is its bactericidal effect. Iron and manganese bacteria, along with other bacteria, are destroyed.

The application of strong oxidizing agents has some disadvantages. The first is a possible oxidation and thus precipitation of dissolved Fe and Mn. The second is that Cl-containing oxidizing agents can lead to the formation of unwanted chlorinated hydrocarbons when organic carbon is present.

Shock chlorination will fail to remove slime or iron bacteria. Sulfamic acid does not work against iron, manganese, or sulfate scales. Hydrochloric acid may contain several heavy metals (lead arsenic, zinc) or VOC such as benzene.

Sometimes polyphosphate treatment is useful in chemical methods of rehabilitation.

This treatment is not suitable as such for well rehabilitation. However, polyphosphate can be used as a complexation agent in a chemical well treatment, using chlorination, to raise the solubility of the Fe(III) and Mn(III) or Mn(IV).

Polyphosphates react with dissolved iron and manganese by trapping them in a complex molecule that is soluble in water (Figure 3-1). As a result the iron and manganese are not available to react with oxygen and precipitate. Polyphosphates can be fed into the water system with controlled injection equipment. Polyphosphates are not stable at high temperatures. If water is treated prior to heating in a water heater, the polyphosphates will release iron and manganese in the heater as they break down. The released iron and manganese will then react with oxygen and precipitate.

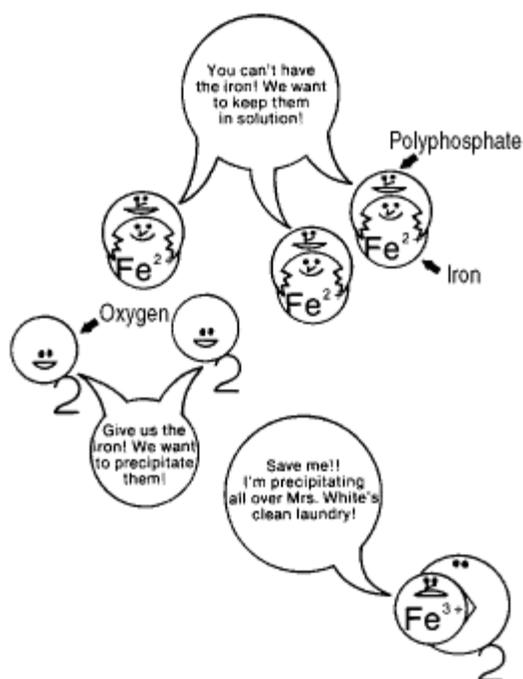
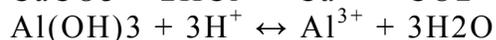
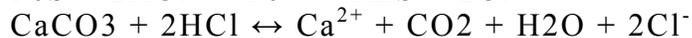
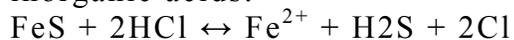


Figure 3-1 Polyphosphates protect dissolved iron and manganese from reacting with oxygen and precipitating on household appliances, bath/plumbing fixtures, and laundry.

2) Acidification

Monosulphides, carbonates and Al hydroxides which sometimes appear as additional constituents of ochreous deposits dissolve more or less readily in inorganic acids:



Acids, which useful for chemical rehabilitation are: HCl, H₂SO₄, HNO₃, etc.

The principal reaction with, for instance HCL is:



Sulphuric acid is more efficient although not for goethite. Sulphamic and citric acid performed rather poorly, NaOH is essentially useless at the pH studied (Figure 3-2) (Houben, 2001).

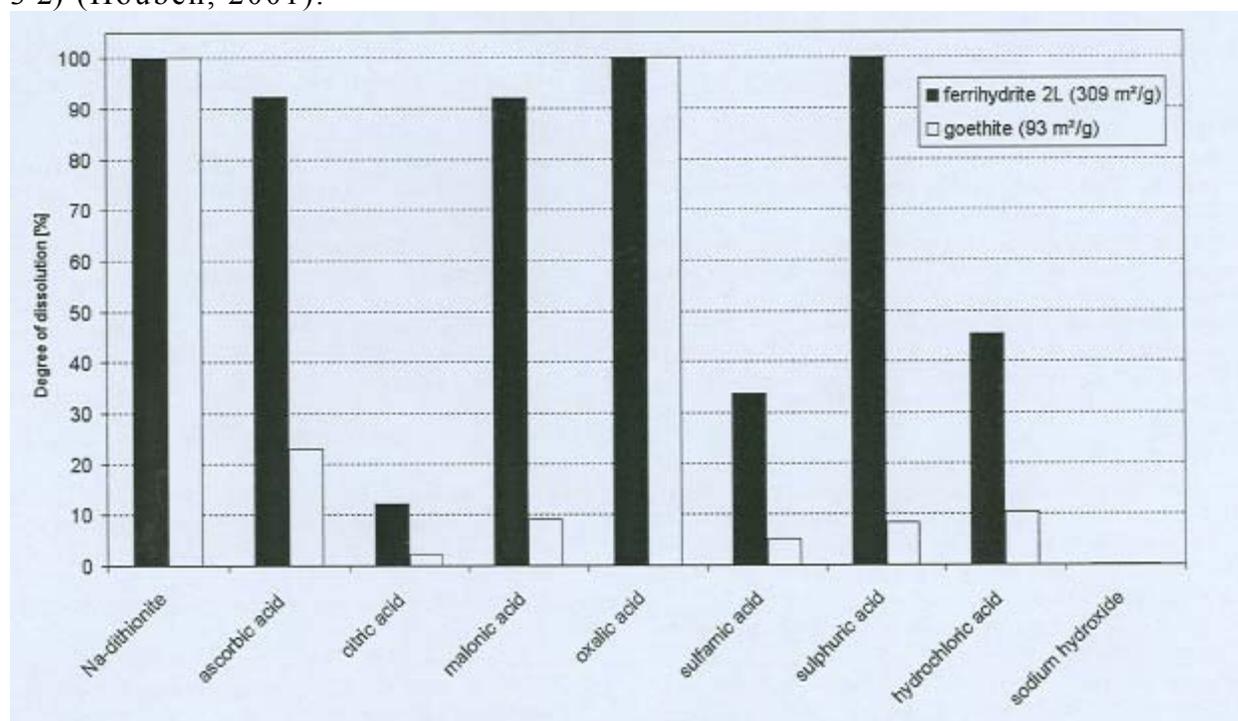
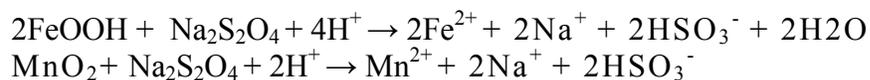


Figure 3-2 Comparison of the efficiency of the chemicals used (after 7 h). (Houben, 2002)

Acidification method can be used only on sites that have temporary clogging hazard and clay contents of about 30%. It is quite possible that iron precipitated in the soil could, under reducing conditions, become soluble again.

3) Reduction processes

Reduction processes transform practically insoluble Fe(III) into soluble Fe(II), or in case of Mn: Mn(III) or Mn(IV) → Mn(II). Reducing agents comprise reduced metal species, e.g. Fe(II), organic acids, e.g. ascorbic acid and inorganic chemicals, e.g. sodium dithionite, Na₂S₂O₄,



The efficiency of ascorbic acid can be enhanced by adding a complexing agent, e.g. oxalate ($\text{C}_2\text{O}_4^{2-}$). Experiments on natural incrustations at low solute (ascorbic acid plus oxalate) to solid ratio showed fast and efficient dissolution during the first few hours, but was followed by precipitation of the bright yellowish mineral humboldtine.

Na-dithionite and oxalic acid turned out to be the most effective chemicals. They both are able to quickly dissolve ferrihydrite as well as goethite. Dithionite has some additional disadvantages at surface areas lower than $70 \text{ m}^2/\text{g}$. (Houben, 2001).

4 Prevention of clogging process

Retardation of the clogging process in a drain attempts to deal with the ochre problem through a better design of the drainage system. This approach is required on sites where it has been determined that the clogging problem is serious. (van Beek, 2005)

Ochre becomes more adhesive as it ages and with lowered temperatures. Cleaning of drains in ochre areas should be done yearly as aged ochre becomes more difficult to remove.

New wells are constructed from plastic (PVC) to reduce chemical and biochemical corrosion. Iron ochre will stick to plastic drainpipe with about 20% more force than to a fired clay tile. Most synthetic filters installed as a sock around the pipe to prevent sand clogging are subject to clogging themselves. Clogging in the pipe will occur first in the slots and valleys of the perforations, and later, bacterial growth will plug the voids of the socks.

A great deal of ochre is produced through bacterial action. Control of the bacteria may be a means of controlling the ochre problem. Bactericide, a compound which will kill bacteria, has been soaked into the porous clay tiles before installation in the ground. Tests have shown that this technique is largely ineffective because the bactericide cannot be retained in the tile for extended periods of time.

Unconsolidated aquifers include dune sands, alluvial and marine deposits of sand and gravel. The challenges in drilling and completing wells in these types of formations are to keep the borehole open and prevent caving, and to avoid reducing the hydraulic conductivity of the near-well formation by introducing irrecoverable mud or smearing clay at the well/aquifer interface during the drilling process.

Driscoll (1986), Todd (1960), Walton (1970) and Hancock and MacPherson (1987) describe eight vertical and one horizontal drilling techniques that may be employed in unconsolidated formations. These are summarized below. The advantages and disadvantages of these techniques, their relative penetration rates and an estimation of their “clogging potential” are given in Table 4-1, which provides advantages and disadvantages of horizontal drilling, compared to vertical drilling.

Table 4-1: Comparison of different drilling techniques used in unconsolidated aquifers (Segalen, et al. 2005),

| Drilling technique | Advantages | Disadvantages | Relative penetration rate | Clogging potential | Case reference |
|--------------------------|---|---|---------------------------|--------------------|--|
| Cable tool | <p>This method enables accurate sampling of the material being drilled and generally allows sampling of water as encountered. The borehole is stabilized during drilling operation. It is possible to drill in areas where little make-up water exists. The risks of contamination of the constructed wells are minor. It is possible to drill in formations where lost circulation is a problem. Bailing is possible at any time to determine the approximate yield at that depth.</p> | <p>In unconsolidated sand and gravel, the loose material slumps and caves around the bit. Casing should be maintained to near the bottom of the hole to avoid caving.</p> | Very slow | X + | Bergambacht, West Holland |
| Direct rotary with fluid | <p>This method provides effective development of water bores. This type of drilling is fast and convenient to operate. Well screens can be set easily as part of the casing installation. Drilling fluid management requires knowledge and experience.</p> | <p>Generally sampling is not accurate and no factual information is available during drilling operation. Continuous operation from commencement of cutting the hole until completion of the hole is essential for efficient and safe work. Special care has to be taken throughout the construction of the water bore to avoid loss of performance through clogging of the aquifer with drilling mud.</p> | Rapid | ++ | Berkheide dunes, South-Holland Amsterdam Dune Area |

*Qualitative index of clogging, based on the studied cases: compare + with ++

(see Kortleve, 1998) and x with xx

(see Timmer et al., 2003) ++ or xx means more clogging than + or x; N/A: Not Available

Table 4-1 (continuous): Comparison of different drilling techniques used in unconsolidated aquifers (Segalen, et al. 2005),

| Drilling technique | Advantages | Disadvantages | Relative penetration rate | Clogging potential | Case reference |
|--|--|---------------------------------------|---------------------------|--------------------|--|
| Rotary scraping | Very clean boreholes are drilled | | | + | Rotary scraping |
| Direct Rotary drill trough casing hammer | Well-drilling is made possible in unconsolidated materials that may be difficult with cable tool or direct rotary methods. The borehole is stabilized during drilling. Penetration rates are rapid. Lost-circulation problems are eliminated. Formation and water sampling can be accurate. No water-based drilling fluid is required in unconsolidated materials. | Noise of operation. Additional costs. | Very rapid | N/A | Direct Rotary drill trough casing hammer |

*Qualitative index of clogging, based on the studied cases: compare + with ++ (see Kortleve, 1998) and x with xx (see Timmer et al., 2003) ++ or xx means more clogging than + or x; N/A: Not Available

Table 4-1 (continuous): Comparison of different drilling techniques used in unconsolidated aquifers (Segalen, et al. 2005),

| Drilling technique | Advantages | Disadvantages | Relative penetration rate | Clogging potential | Case reference |
|----------------------------|--|---|---------------------------|--------------------|---|
| Reverse Rotary with fluids | <p>This technique is particularly well suited to drilling large diameter holes in soft, unconsolidated formations. The porosity and permeability of the formation near the borehole are relatively preserved when comparing with other techniques. It is possible to drill quickly and economically largediameter holes. No casing is needed during the drilling operation. Well screens setting can be easily done as part of the casing installation. There are little opportunities for washouts in the borehole because of the low velocity of the drilling fluid.</p> | <p>The water table should be several feet below ground surface to obtain an effective head differential between well and aquifer. Large water supply is generally necessary. Large mud pits are required.</p> | Rapid | XX | <p>Bergambacht, West Holland Glendale, Arizona Palo Alto Baylands, California Mannheim, Ontario</p> |

*Qualitative index of clogging, based on the studied cases: compare + with ++ (see Kortleve, 1998) and x with xx

(see Timmer et al., 2003) ++ or xx means more clogging than + or x; N/A: Not Available

Table 4-1 (continuous): Comparison of different drilling techniques used in unconsolidated aquifers (Segalen, et al. 2005),

| Drilling technique | Advantages | Disadvantages | Relative penetration rate | Clogging potential | Case reference |
|---------------------------|---|--|---------------------------|--------------------|----------------|
| Reverse Rotary: Dual Wall | It is possible to obtain continuous representative samples of the formation and water. Aquifer yield can be estimated at many depths in the formation. Problems of lost circulation are either eliminated or considerably reduced. Washout zones are reduced or eliminated. | This technique is limited to rather slim holes (less than 229 to 254 mm) and in depth (approximately 366 to 427 m) in alluvial deposits. | Very rapid | N/A | |
| Hydraulic Percussion | Accurate samples can be obtained. | This system is generally limited to Drilling small diameter wells through clay and sand formations | Rapid | N/A | |
| Jetting | Jet-percussion drilling is commonly used for drilling in water-bearing sand. | This technique is generally limited to small diameter wells. | Rapid | N/A | |

*Qualitative index of clogging, based on the studied cases: compare + with ++ (see Kortleve, 1998) and x with xx

(see Timmer et al., 2003) ++ or xx means more clogging than + or x; N/A: Not Available

Table 4-1 (continuous): Comparison of different drilling techniques used in unconsolidated aquifers (Segalen, et al. 2005),

| Drilling technique | Advantages | Disadvantages | Relative penetration rate | Clogging potential | Case reference |
|--------------------|---|--|---------------------------|--------------------|----------------|
| Horizontal | <p>Horizontal wells are claimed to be more effective in recovering water than vertical wells where the target aquifer is unconfined with a small saturated thickness or highly heterogenous (Kaback, 2002). Permeability is generally greater in the horizontal, rather than the vertical direction and well-positioned horizontal wells can capitalise on this. This may allow more efficient recovery of groundwater via horizontal wells. Directionally drilled horizontal wells can be installed in areas with subsurface obstructions (e.g., vertical wells, utility lines) and can be used where there are surface obstructions. Sites with vertical fractures and thin aquifers are especially appropriate for horizontal well applications.</p> | <p>Horizontal wells must be considered carefully at some sites where the water table fluctuates greatly. If a horizontal well is installed at such a location, the well may change from saturated to unsaturated conditions. Horizontal wells are generally drilled to limited depths (about 15m) but some horizontal wells drilled up to 60m have been reported. A lack of drilling contractors experienced in horizontal techniques is also reported. The amount of time required to thoroughly clean a horizontal well may be much longer than that required to clean a vertical well. The total length of screen in the horizontal well is often many times greater than that utilized in vertical wells. Physical and chemical methods of treatment are usually recommended to ensure successful development. Recommended actions may include acid wash, water flush, water jet, surge block/suction head, and air lift/overpumping (Kaback, 2002 and Miller 1996).</p> | | | |

*Qualitative index of clogging, based on the studied cases: compare + with ++ (see Kortleve, 1998) and x with xx (see Timmer et al., 2003) ++ or xx means more clogging than + or x; N/A: Not Available

Well rehabilitation requires time, patience, and effective development to be effective. Maintenance, monitoring and preventive treatment is both effective and less costly than waiting for failure and rehab. From experience in England and the USA (Gottlieb, 1988; Handson, 2003) it is noted that the maintenance policy saves a lot of money over a well field life cycle.

5 Monitoring

During the pumping period it is necessary to include monitoring of the clogging processes. The monitoring of the chemical and microbiological variables should be carried out regularly and the results checked for trends which may indicate the onset of iron biofouling. The following monitoring frequency is suggested:

- 1) pumping and rest water level (monthly)
- 2) yield (monthly)
- 3) standard TOC, nitrogenous compounds, phosphate, ferrous and total iron (monthly)
- 4) bacteria plate count (monthly)

6 Field data

The field data was taken from the pumping station Vierlingsbeek, North Brabant. The clogging process exists in the filter slots due to chemical and biochemical reactions. The Figure 6-1 shows the presence of the clogging material in the well.

The thickness of the aquifer is 20 meters, hydraulic conductivity is 50 m/d. Top part of the aquifer contains oxic water (oxygen, Fe(III) are present), on the bottom anoxic water (no oxygen, Fe(III) is present) is located. During pumping the mixing process between oxygenated and no-oxygenated water takes place.



Figure 6-1. Iron sediments from the pump station Vierlingsbeek.

In our model we assume that all reactions are equilibrium reactions.

6.1 Chemical composition of the groundwater

Chemical composition of the oxic and anoxic water are illustrated in the Table 6-1.

| Component | unit | oxic | anoxic |
|------------------------------|------|--------------------|---------------------|
| NO ₃ ⁻ | mg/l | 225 | 0.3 |
| NH ₄ | mg/l | 0.17 | 0.17 |
| Ca | mg/l | 75 | 70 |
| Cl | mg/l | 27 | 50 |
| Fe | mg/l | 0.12 | 12 |
| K | mg/l | 21.5 | 9.5 |
| Mg | mg/l | 13.1 | 24.9 |
| Mn | mg/l | 0.48 | 0.6 |
| Na | mg/l | 20 | 22 |
| P | mg/l | 0.03 | 0.03 |
| SO ₄ | mg/l | 130 | 300 |
| HCO ₃ | mg/l | 3 | 8 |
| pH | | 4.2 | 5.4 |
| pe | | 16 (calculated) | 4.0 (calculated) |
| O ₂ | mg/l | 0.96 | 0 |

Table 6-1. *Chemical composition of the groundwater.*

6.2 Composition of clogging material

As we had limited time to study the samples, only one sample per field site was analyzed using the SEM (stereo electronic microscope). Sample were taken from the well screen.

As can be seen in the picture (Figure 6-2) the precipitated material is rather homogeneous. Backscattering electron microscopy, which has been used in this method, provides elemental composition variations, generating images which are dependent of the mean atomic number: higher atomic numbers are brighter

than lower atomic material. That means that a particle with similar atomic number looks similar.

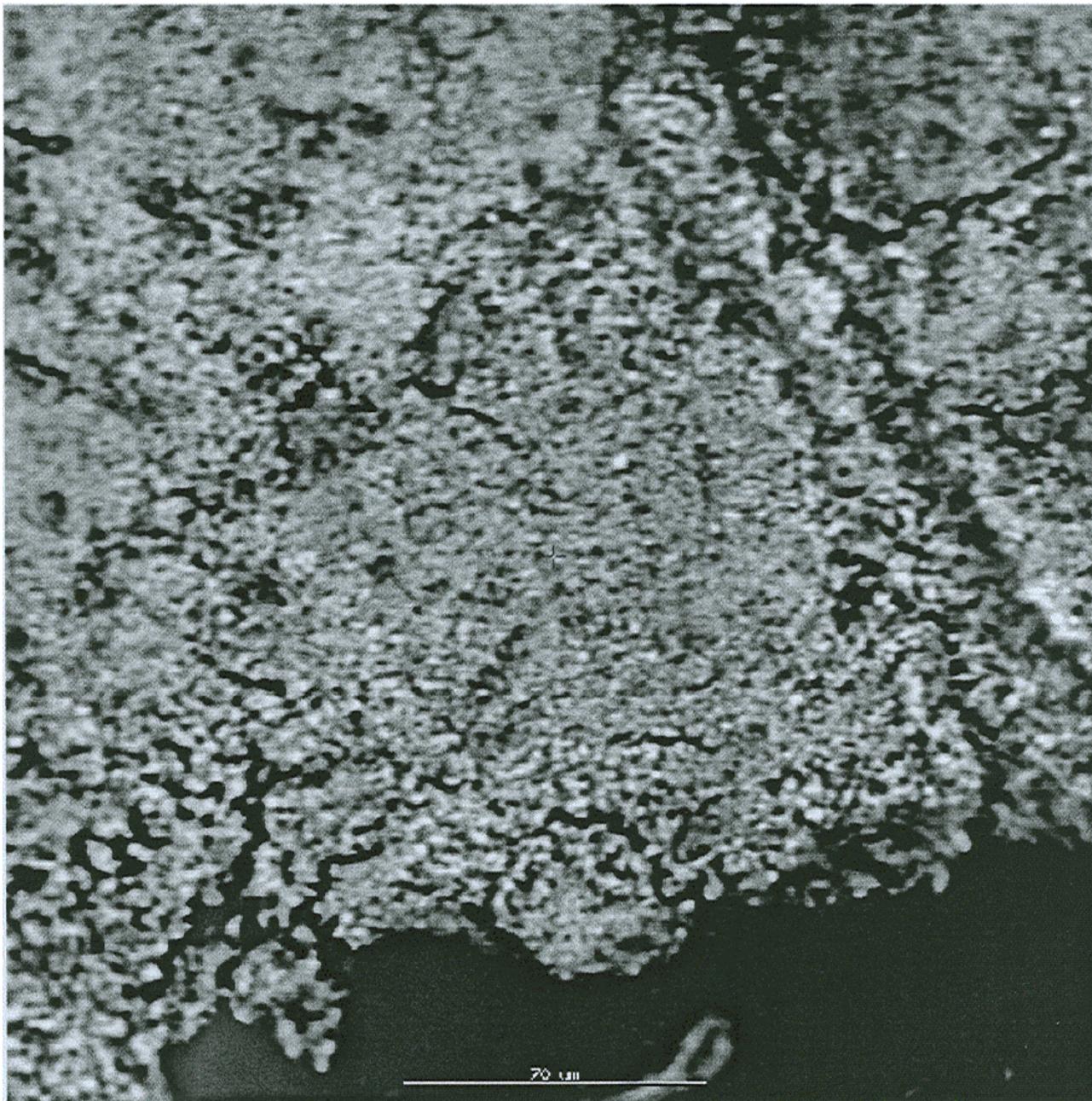


Figure 6-2. Stereomicroscopic picture of a sample of clogging material from a well in a well field Vierlingbeek.

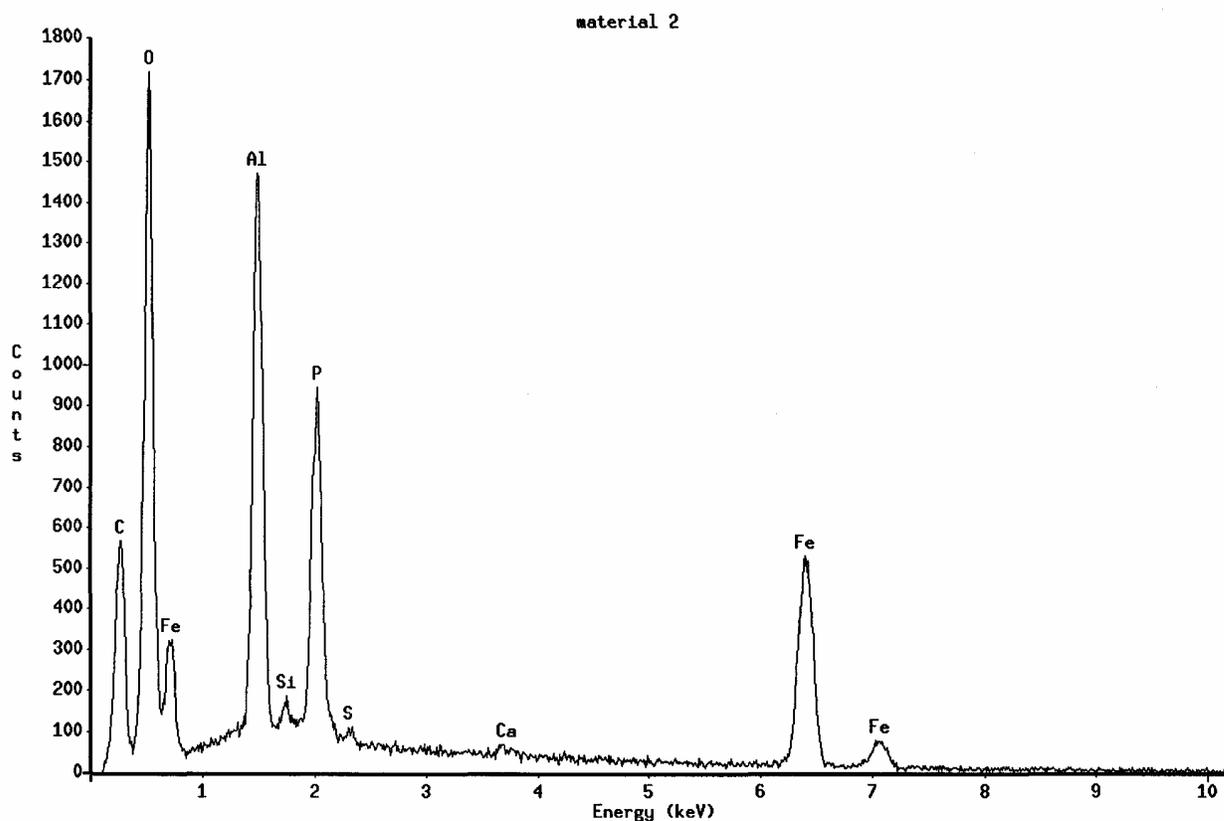


Figure 6-3. Sample composition spectra.

Organic material has always the same gray scale, so the differences in gray scale between the organic material and the well screen, which has an organic composition are not visible and we cannot distinguish the organic particles present in the sample.

Figure 6-3 shows the spectral composition of the material by using EDS technique. The spectrum allows us to see the elements that form the particles and the relative proportion in which they are present. This plot shows the distribution of *total* chemical elements, which are present in the clogging material. For example, Al can be a part of any clay mineral as well as gibbsite. By comparing this information to the proportion of the elements from the minerals we are able to distinguish the kind of particles.

Electron microscopic observations on the incrustation samples, taken from the well screen, showed accumulation (coatings) containing a lot of iron, phosphorus and oxygen (Figure 6-3). The total amount of compounds from the coating material is shown in a Table 6-2. From these analysis data we can see that the precipitation is mainly composed of iron-hydroxide accumulation (90%) and the other 10% consists of clay material.

| Material 2. NP-39-40 | | | |
|-----------------------------|------------------|-------------------|------------|
| Time 30/06/2006 11:05 | | | |
| | element(Wt%) | compound (Wt%) | |
| Si | 1.23 | 2.631 | Fe(OH)3 |
| Al | 4.017 | 7.59 | 90.0307321 |
| Fe | 44.617 | 63.79 | |
| Ca | 0.204 | 0.285 | |
| Na | 0.22 | 0.297 | |
| P | 2.743 | 6.286 | |
| O | 27.938 | *** | |

Table 6-2. Chemical composition of the filter clogging material.

7 Model construction

Iron precipitation is a widespread problem for water well companies. Modeling is needed in order to determine the scenario of precipitation, including the kinetic rate and pumping rate. The spatial distribution of clogging material notably with depth is also investigated.

Under natural conditions oxic water (containing oxygen, no Fe(II)) is in the upper parts and anoxic water (without oxygen, but containing Fe(II)) is in the lower parts of the aquifer, but precipitation of iron hydroxide does not take place there. During well pumping anoxic water flows upward, mixes with oxic water, which results the precipitation of iron. The position of the mixing area is shown in Figure 7-1A. During pumping in a phreatic aquifer the water level decreases, and the free pore space in the cone of depression is filled up by air. When pumping stops, water flows upward again and laterally, also through the well screen and gravel pack, and the water level rises again. Due to heterogeneous aquifer material and differences in hydraulic heads between aquifer layers some water is going downward. As a result the mixing area is moving downward and may spread laterally. Due to a regional flow component the mixing zone may spread in the same direction as flow. Consequently, the mixing zone will expand as shown in Figure 7-1-B.

7.1 Assumptions

In our model we assume the presence of two water types in the aquifer. At the top of the aquifer the oxic water is located, and at the bottom anoxic water is present. In nature there four redox zones contains:

- 1) the oxic zone is saturated by oxygen
- 2) the suboxic zone contains oxygen below saturation and NO_3^-
- 3) the anoxic zone, which contains Fe(II), Mn(II), NH_4 , but no SO_4^{2-} reduction, no CH_4 , and no oxygen
- 4) a deep anoxic zone, which show a SO_4^{2-} reduction and contain CH_4 .

In order to simplify modeling process we assume the presence of only two zones: oxic and anoxic.

During pumping waters with different chemical composition are mixed and some chemical reactions take place. This mixing occurs during abstraction in the well and after termination of abstraction also in the surroundings of the well. Two main processes were modeled by PHT3D: mixing and precipitation, which include not only chemical reactions but also hydrodynamic processes in the aquifer.

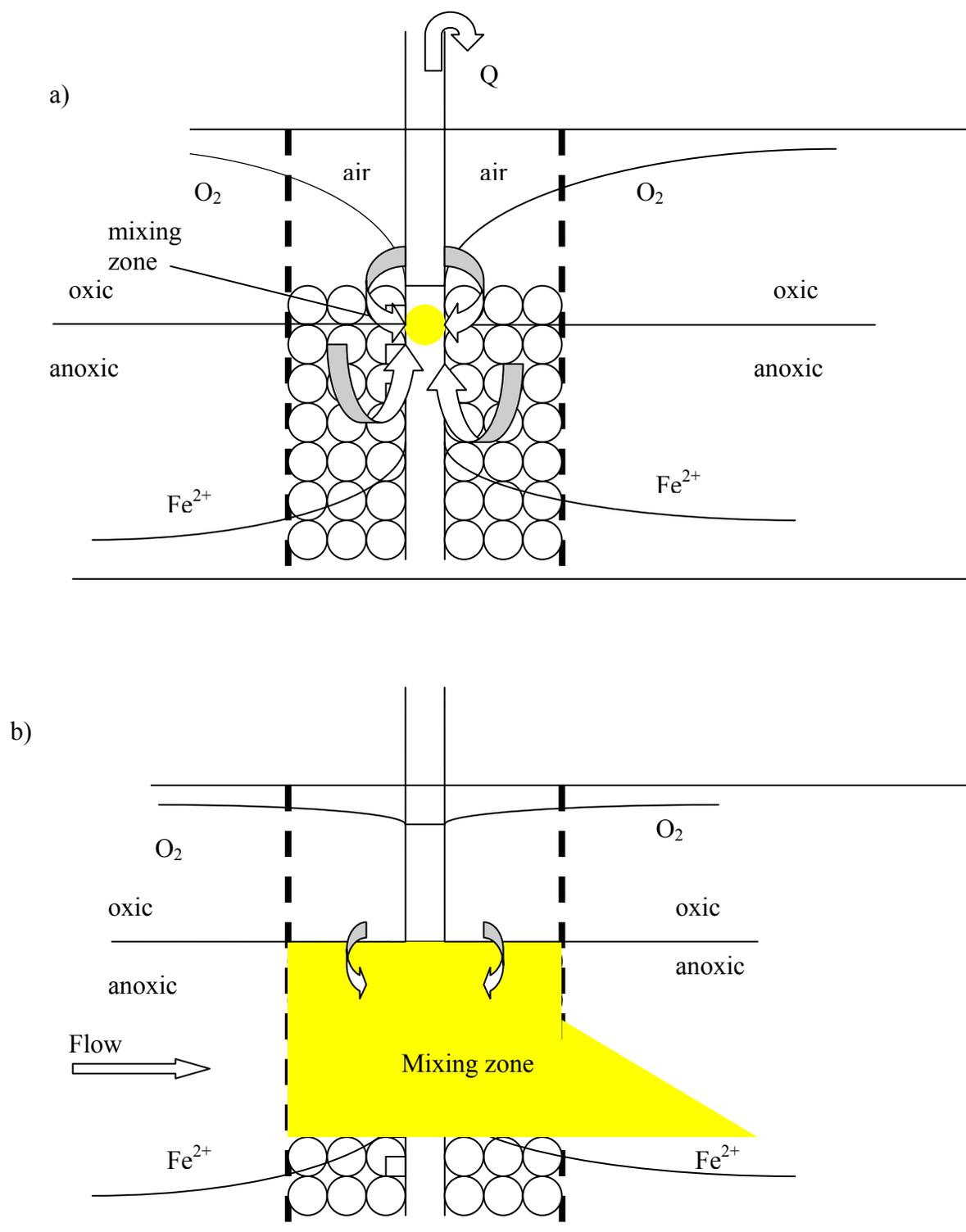


Figure 7-1. Position of mixing area during pumping period (a) and inactive period (b).

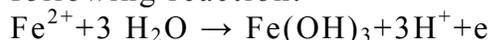
7.2 PHREEQC modeling.

Before using the PHT3D modeling, chemical reactions were tested by PHREEQC. PHREEQC simulations include only chemical aspects of the aquifer. To determine the possibility of iron-hydroxide precipitation 15 water samples at the different depths from the main aquifer were taken (Van Beek, 2006). All samples were mixed and as a result iron-hydroxide precipitation takes place. The initial chemical concentration used in a calculation is shown in a Table 7-1. The initial temperature was assumed 10°C. The PHREEQC file is given in the Appendix #2.

The next step in PHREEQC modeling was the inclusion of a kinetic rate of precipitation. For this task mixed water from the output results of previous simulation was taken and the kinetic rate was added. The initial chemical concentration used in a calculation is shown in a Table 7-1. The PHREEQC file is in the Appendix.

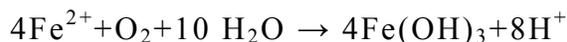
Three calculations were done: 1, 10, 40 days. Results of the one day simulation are the base for the rate of the clogging prediction in Table 7-3. These estimates are described in 9.4.

The result of a 10 days simulation is presented in Table 7-2. Figure 7-2 shows the concentration of total Fe(2), total Fe(3), and pH in the reaction vessel over the 10 days of simulation. It can be seen that the pH rapidly decreases at the beginning of the reaction. The slope of Fe(OH)₃ against time is initially very steep, but lessens as the reaction progresses, which is consistent with theory. The concentration of Fe(III) is decreasing because of iron-hydroxide formation. The boundary between the Fe(II) and Fe(OH)₃ is described by the following reaction:



$$\text{where } \log K = -3\text{pH} - \text{pe} - \log[\text{Fe}^{2+}] = -16.8$$

The rate of Fe(OH)₃ precipitation in water, including oxidation and hydrolysis is given by (Houben, 2002):



$$\frac{d[\text{Fe}^{2+}]}{dt} = k_1[\text{Fe}^{2+}][\text{O}_2][\text{H}^+]^{-2} + k_2[\text{Fe}^{3+}][\text{Fe}^{2+}][\text{O}_2][\text{H}^+]^{-1}$$

where

$$k_1 = 3 * 10^{-12} * 0.0464e^{0.1535T} \{ \text{mol} / \text{l} / \text{min} \}, T = \text{water} - \text{temperature}$$

$$k_2 = 1.71 * 10^{-5} \{ \text{mol} / \text{min} \}$$

$$T_1 = 0.693 / (k_1[\text{O}_2][\text{H}^+]^{-2}) \{ \text{min} \}$$

The temperature dependency derives from Stuyfzand (in press).

Fe³⁺ forms solute complexes with OH⁻ and it may also precipitate as iron oxyhydroxides, so that pH decreases during oxidation. Because the rate has quadratic dependence on the activity of H⁺, the oxidation rate rapidly diminishes as pH decreases.

| Aqueous Component | Unit | Original data | | Data input for PHT3D | |
|-------------------------------|--------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | Oxic water | Anoxic water | Oxic water | Anoxic water |
| pH | | 4.2 | 5.4 | 4.2 | 5.4 |
| pe | | | 4.0 | 16.3644 | 4.0 |
| Al | mmol/l | $3.370 \cdot 10^{-2}$ | $1.111 \cdot 10^{-3}$ | $3.370 \cdot 10^{-2}$ | $1.11 \cdot 10^{-3}$ |
| C | mmol/l | $4.918 \cdot 10^{-2}$ | 0.131 | $4.918 \cdot 10^{-2}$ | $1.311 \cdot 10^{-1}$ |
| Ca | mmol/l | 1.875 | 1.75 | 1.875 | 1.750 |
| Cl | mmol/l | 0.761 | 1.408 | $7.606 \cdot 10^{-1}$ | 1.408 |
| Fe | mmol/l | $2.142 \cdot 10^{-3}$ | 0.214 | $2.143 \cdot 10^{-3}$ | $2.143 \cdot 10^{-1}$ |
| K | mmol/l | 0.549 | 0.2429 | $5.499 \cdot 10^{-1}$ | $2.43 \cdot 10^{-1}$ |
| Mg | mmol/l | 0.539 | 1.0246 | 5.391e-04 | 1.025 |
| Mn | mmol/l | $8.727 \cdot 10^{-3}$ | $1.091 \cdot 10^{-2}$ | $8.727 \cdot 10^{-3}$ | $1.091 \cdot 10^{-2}$ |
| Na | mmol/l | 0.869 | 0.9565 | $8.696 \cdot 10^{-1}$ | $9.565 \cdot 10^{-1}$ |
| N(+5) | mmol/l | 3.629 | 0.0042 | 3.629 | $4.225 \cdot 10^{-3}$ |
| SO ₄ ²⁻ | mmol/l | 1.354 | 3.125 | 1.354 | 3.125 |
| NH ₄ ⁺ | mmol/l | $1.111 \cdot 10^{-2}$ | $6.296 \cdot 10^{-3}$ | $1.111 \cdot 10^{-2}$ | $6.296 \cdot 10^{-3}$ |
| P | mmol/l | $3.157 \cdot 10^{-4}$ | $3.157 \cdot 10^{-4}$ | $3.158 \cdot 10^{-4}$ | $3.158 \cdot 10^{-4}$ |
| O | mmol/l | 0.3 | 0 | $3 \cdot 10^{-1}$ | 0 |

Table 7-1: Chemical composition of groundwater aquifer of Vierlingsbeek. Based on 15 samples reported by Van Beek.

| Time (days) | Unit | Fe(2+) | Fe(3+) | Fe(OH)3(a) | pH |
|-------------|----------|-----------------------|-----------------------|-----------------------|--------|
| 0.5 | (mmol/l) | $1.618 \cdot 10^{-1}$ | $1.108 \cdot 10^{-7}$ | $5.246 \cdot 10^{-2}$ | 4.1326 |
| 1 | (mmol/l) | $1.365 \cdot 10^{-1}$ | $1.075 \cdot 10^{-7}$ | $7.775 \cdot 10^{-2}$ | 4.0407 |
| 1.5 | (mmol/l) | $1.204 \cdot 10^{-1}$ | $1.024 \cdot 10^{-7}$ | $9.383 \cdot 10^{-2}$ | 3.9857 |
| 2 | (mmol/l) | $1.090 \cdot 10^{-1}$ | $9.736 \cdot 10^{-8}$ | $1.052 \cdot 10^{-1}$ | 3.9480 |
| 2.5 | (mmol/l) | $1.004 \cdot 10^{-1}$ | $9.282 \cdot 10^{-8}$ | $1.138 \cdot 10^{-1}$ | 3.9204 |
| 3 | (mmol/l) | $9.379 \cdot 10^{-2}$ | $8.883 \cdot 10^{-8}$ | $1.204 \cdot 10^{-1}$ | 3.8992 |
| 3.5 | (mmol/l) | $8.844 \cdot 10^{-2}$ | $8.536 \cdot 10^{-8}$ | $1.258 \cdot 10^{-1}$ | 3.8824 |
| 4 | (mmol/l) | $8.407 \cdot 10^{-2}$ | $8.235 \cdot 10^{-8}$ | $1.302 \cdot 10^{-1}$ | 3.8689 |
| 4.5 | (mmol/l) | $8.045 \cdot 10^{-2}$ | $7.975 \cdot 10^{-8}$ | $1.338 \cdot 10^{-1}$ | 3.8578 |
| 5 | (mmol/l) | $7.742 \cdot 10^{-2}$ | $7.749 \cdot 10^{-8}$ | $1.368 \cdot 10^{-1}$ | 3.8485 |
| 5.5 | (mmol/l) | $7.486 \cdot 10^{-2}$ | $7.552 \cdot 10^{-8}$ | $1.394 \cdot 10^{-1}$ | 3.8408 |
| 6 | (mmol/l) | $7.268 \cdot 10^{-2}$ | $7.381 \cdot 10^{-8}$ | $1.416 \cdot 10^{-1}$ | 3.8342 |
| 6.5 | (mmol/l) | $7.082 \cdot 10^{-2}$ | $7.232 \cdot 10^{-8}$ | $1.434 \cdot 10^{-1}$ | 3.8286 |
| 7 | (mmol/l) | $6.922 \cdot 10^{-2}$ | $7.102 \cdot 10^{-8}$ | $1.450 \cdot 10^{-1}$ | 3.8238 |
| 8 | (mmol/l) | $6.664 \cdot 10^{-2}$ | $6.888 \cdot 10^{-8}$ | $1.476 \cdot 10^{-1}$ | 3.8161 |
| 9 | (mmol/l) | $6.470 \cdot 10^{-2}$ | $6.723 \cdot 10^{-8}$ | $1.495 \cdot 10^{-1}$ | 3.8103 |
| 10 | (mmol/l) | $6.322 \cdot 10^{-2}$ | $6.596 \cdot 10^{-8}$ | $1.510 \cdot 10^{-1}$ | 3.8059 |
| 20 | mmol/l | $6.186 \cdot 10^{-8}$ | $5.856 \cdot 10^{-2}$ | $1.557 \cdot 10^{-1}$ | 3.7922 |
| 30 | mmol/l | $6.151 \cdot 10^{-8}$ | $5.816 \cdot 10^{-2}$ | $1.561 \cdot 10^{-1}$ | 3.7911 |
| 40 | mmol/l | $6.148 \cdot 10^{-8}$ | $5.813 \cdot 10^{-2}$ | $1.561 \cdot 10^{-1}$ | 3.7910 |

Table 7-2. PHREEQC simulation results of the iron-hydroxide precipitation during 10 days simulation.

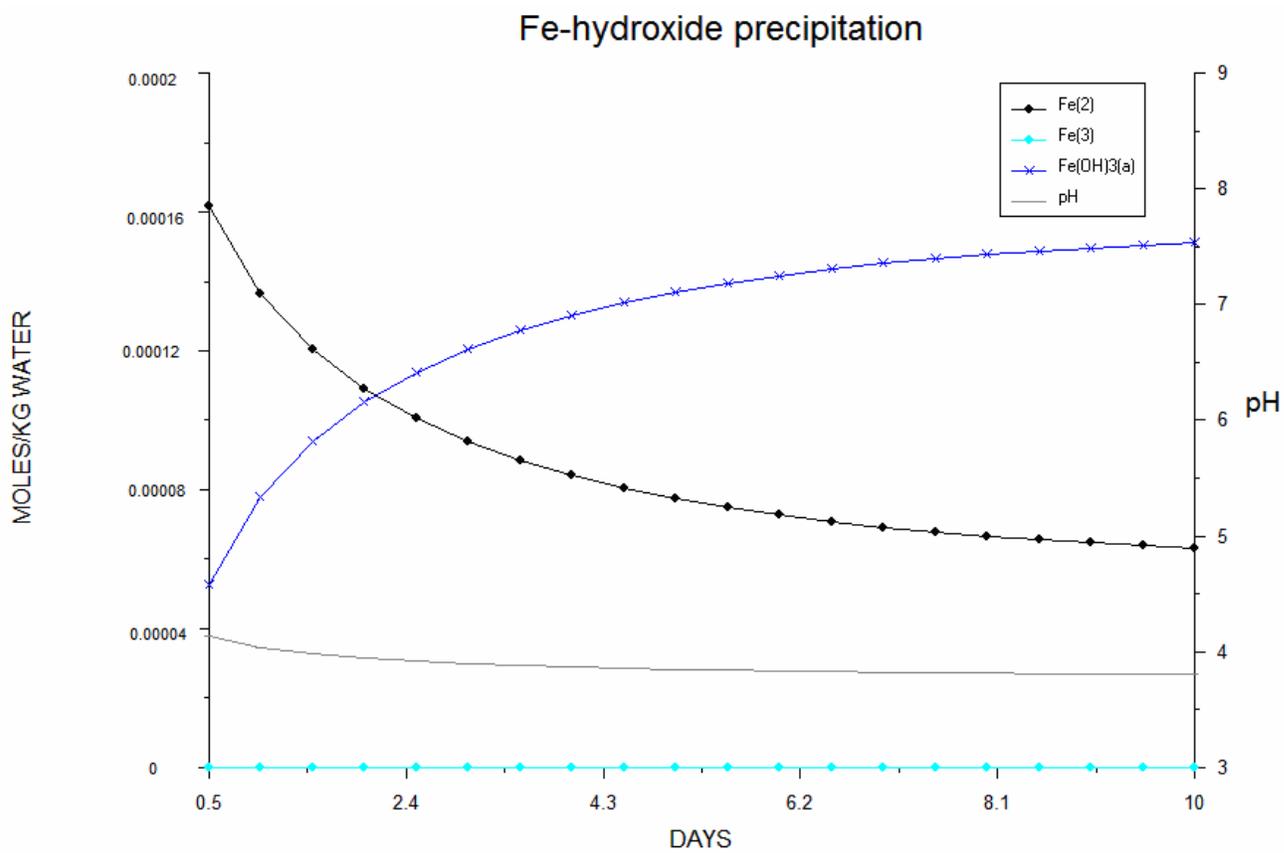


Figure 7-2. Plot of the iron-hydroxide precipitation during 10 days. PHREEQC simulation.

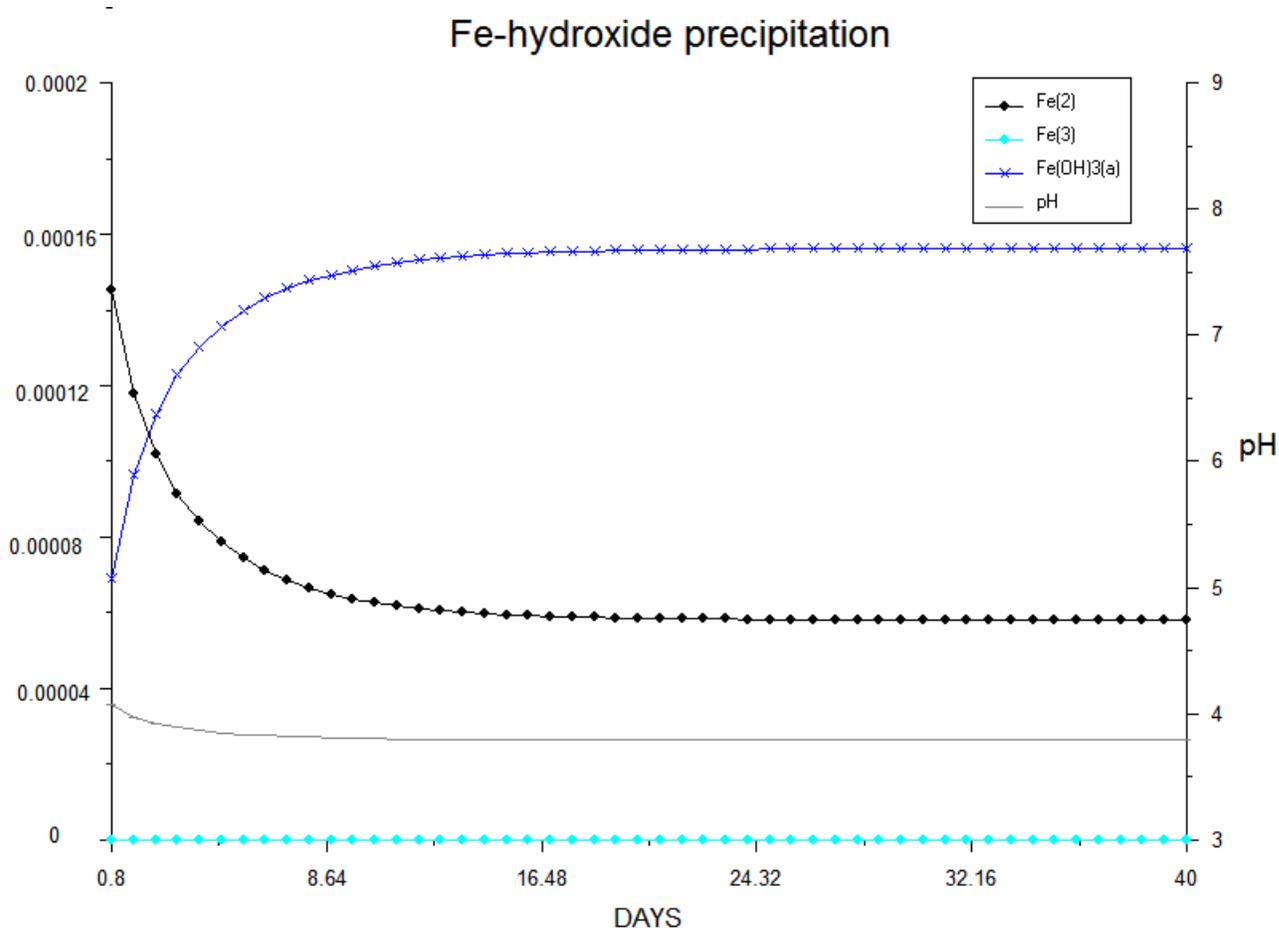


Figure 7-3. Plot of the iron-hydroxide precipitation during 40 days. PHREEQC simulation.

The result of 40 days simulation shows the time, when the mixed solution reaches equilibrium (Table 7-2). The concentration-time plot indicates iron-hydroxide stability after 20 days of simulation (Figure 7-3).

7.3 Calculation of clogging processes.

The clogging rate depends on the kinetics of iron precipitation, the pumping rate, operation time of the well, volume and porosity of the gravel pack, length of the well screen and the area of the mixing zone. Clogging can occur in filter slots and in the gravel pack. During pumping water mixing occurs within 1 sec in the filter slots. This time is too short for iron precipitation; therefore prediction of clogging processes was done for the stop-pump period. To prove the insignificance of iron precipitation during the active period in comparison to the in active period, the calculation for continuous pumping (24 hours per day) was done.

Calculations were done for 4 scenarios:

- 1) well is pumped during 16 hour; followed by 8 hour rest per day.
- 2) well is pumped during 12 hour; followed by 12 hour rest per day.
- 3) well is pumped during 8 hour; followed by 16 hour rest per day.

4) well is pumped during 24 hour; no rest.

Pump works 8, 12, 16 hour per day.

It is assumed, that during pumping mixing processes lasts within 1 second and during the inactive period the mixing process 8 hours continuously during one day. By using PHREEQC simulation for 1 day we can calculate how many moles can precipitate in time. The resulting data is shown in Table 7-3. To simplify our calculation we ignored the iron precipitation during pumping, because the time for precipitation is too small as compare 8 hours inactive period.

The pumping rate was set at $40\text{m}^3/\text{hour}$. Conversion to l/y yields $2.3 \cdot 10^8$ l/y. The area of the mixing zone is difference in the stable period derives from the one during pumping. It was assumed that mixing zone during the in inactive period is located at the top part of the aquifer: in the well screen, gravel pack and aquifer material. The volume is 3770 liters. The mixing zone in the active period is located in the well screen. The volume is 377 liters.

To calculate how many kg of iron-hydroxide will precipitate after 1 year if pumping stops we have to multiply the area of the mixing zone with the concentration of iron-hydroxide. In that case we have 3.04 kg/y in the inactive period.

One additional assumption was made. When pumping starts some amount of iron precipitation is removed from the well, because of the high flow velocity. We assumed that only 50% of the ochre deposition remains in the well and our calculated value thereby decreases to 1.52 kg/y. After 5 years of water extraction with 16 work hours per day we will have 7.6 kg of ochre sediments.

Now, the pump station works 12 hours continuously per day, time for iron precipitation is increasing up to 12 hours per day. The resulting data is shown in Table 7-3. The total amount of iron-hydroxide that can precipitate in a stable period is 4 kg/y. If 50% of total deposits remain in a well our value is decreasing to 2 kg/y. After 5 years of water extraction with 12 work hours per day we will have 10 kg of ochre precipitation.

Now, the pump station works 8 continuously hours per day, time for iron precipitation is increasing up to 16 hour per day. The resulting data is shown in Table 7-3. The total amount of iron-hydroxide that can precipitate in a stable period is 4.74 kg/y. After 5 years of water extraction including 50% residuary deposits we will have 12.85 kg of iron-hydroxide.

From this calculation we can see that precipitation of iron increases within increasing the stop-period of the well.

| Time (hour) | Fe(OH)3(a) | Time (hour) | Fe(OH)3(a) |
|-------------|-------------------|-------------|-------------------|
| 1 | 6.9305e-06 | 9 | 4.3415e-05 |
| 2 | 1.3081e-05 | 10 | 4.6615e-05 |
| 3 | 1.8609e-05 | 11 | 4.9623e-05 |
| 4 | 2.3625e-05 | 12 | 5.2465e-05 |
| 5 | 2.8215e-05 | 13 | 5.5156e-05 |
| 6 | 3.2443e-05 | 14 | 5.7710e-05 |
| 7 | 3.6359e-05 | 15 | 6.0138e-05 |
| 8 | 4.0006e-05 | 16 | 6.2451e-05 |

Table 7-3. Amount of iron-hydroxide precipitation during 16 hour stable period (no pumping).

Pump works 24 hour.

It was assumed, that during pumping the mixing process occurs for only 1 second and that, in this scenario, mixing occurs during 24 hours continuously. The time for precipitation is too small and can be disregarded, but the volume of extracted water with the pumping rate 40m³/h is huge. Due to that fact, the amount of iron-hydroxide that can precipitate is 1.35 kg/y. But owing to very high pumping rate all flocculated ironhydroxide is removed from the well. That means that the clogging process only proceed when the pump is inactive.

Next, we try to estimate how many kilograms we need to clog all pores. The well screen and borehole well were represented as a two cylinders with radius of respectively 0.2m (R₁), 0.4m (R₂) and length of 25m (h). The volume that has to be filled up can be calculated using:

$$V = (R_2^2 - R_1^2) * \pi * h,$$

where V- volume of the annual space between the borehole wall and well screen. The pore volume can be calculated using the formula $V_{pore} = n * (V_1 - V_2)$, where n is porosity, V-volume of cylinders.

Thus, the mass of the clogging material is $M_{sed} = \rho * V_{pore}$, where ρ =density of the clog material. Assuming $\rho=1000\text{kg/m}^3$, M becomes 377kg. This amount of ochre deposits is needed to fill up the tube and all the pores in a gravel pack.

Clogging material is initially deposited at the top part of the aquifer and during time ochre deposition goes downward and fills up free space. As a result the pores are closed. In reality, to decrease the specific capacity of well we need much less amount of clogging material than 377 kg. If we exclude the well screen from the calculation and assume that only part of the aquifer contains the clog material, our amount of sediments is decreasing to 62.2 kg. This amount of ochre deposition fills up *all* pores in a gravel pack in the part of the aquifer. In practice there are only 1-2 cm of well screen fill up by clogging material. With assumptions that 20 % of pores are clogged and this percent is enough to decrease the specific capacity of well, our calculations result age in 12.44kg of ochre deposition. Thus, 12.5 kg is a mass of clog material, which can clog the well. From this calculations and PHRREQC simulation results we deduce that 5 years are enough time to clog a pumping well.

7.4 PHT3D modeling

7.4.1 Spatial discretisation and flow problem.

In order to generate the 3-dimensional flow field underlying the reactive transport problem a simple MODFLOW model needs to be set up. Of course, the desired parameters can be obtained through different combinations of boundary conditions and other parameters. A flow field can be created by a domain of 10 m length, 20 m width and 20 m height which is then discretized into a model with 40 columns, 20 rows and 12 layers. With a fixed head boundary at the upstream (first column) and at the downstream end (last column) and a given hydraulic conductivity and given pumping rate, the desired pore-water velocity v can be obtained by placing an extraction well from the 2 to 11 layers. The flux in that well can be computed from:

$$Q_{well} = v * n * A$$

where Q_{well} is the extraction rate of the well at the inflow boundary and A is the cross-sectional area of the model grid cell perpendicular to the flow direction, i.e., 1 m². Before a reactive transport simulation is set up in the next step, it is worthwhile to make sure that the simulated flow field indeed agrees with the desired one. In the (likely) case that the MODFLOW model was set up with a preprocessing tool, this can be either verified using a path-line-creating advective transport simulation or, alternatively, with a simple single-species transport simulation in which the breakthrough curve of a non-reactive chemical is used to evaluate the correct travel times. To generate the flow-transport link file `mt3d.o`, this is needed by PHT3D, a MODFLOW version with an appropriate MT3D interface package needs to be used. The total simulation time is 0.1 days. It is divided into 20 time steps. A steady-state regime was assumed.

A summary of the parameters that define the flow field and non-reactive transport is given in a table:

| | |
|------------------------------|------------------------|
| Total simulation time (days) | 0.1 |
| Stress period | 1 |
| Time steps | 20 |
| Grid spacing (m) | 0.01 |
| Model length (m) | 10 |
| Porosity | 0.35 |
| Dispersivity (m) | 1 |
| Density | 2650 kg/m ³ |
| hydrostatic pressure | 24m |
| hydraulic conductivity | 50 m/d |

Flow simulation steady state.

7.4.2 Data input for the database file.

All of the aqueous species, components and minerals are already included in the original PHREEQC-2 database. The list of them is in an Appendix 1.

The file pht3d ph.dat contains the records which define that the reaction network contains 10 equilibrium aqueous components (including pH and pe) and one equilibrium minerals (being amorphouse Fe(OH)₃). The order in which the components are listed determines which species number will be allocated to each entity included in the simulation. The correct simulation of pe is generally achieved by including all possible valence-states for each chemical that possibly occurs in different redox states. The interface package file carries the information that in total 10 aqueous components (all assumed to be in chemical equilibrium) are included in the simulation.

7.4.3 Data input for the basic transport package file.

The basic transport package file pht3dbtn.dat contains, among other information, the starting, i.e., initial concentrations for each of the entities that are handled by the MT3DMS part of the simulator. Aqueous concentrations are always defined in units of mol/l and a mineral concentration

is defined as a mass per bulk volume, i.e. mol/l-volume. The analytical data always have errors. To reduce the calculation errors during simulation, input data has to be equilibrated with PHREEQC modeling. Table 7-1 shows the analytical data from the field and data after PHREEQC modeling.

The longitudinal dispersivity of the aquifer was fixed at 1m.

The inlet (inflow) water composition is defined by providing the component concentrations for the injection well located at the top layer. List of the inlet water concentrations is in Table 7-1.

8 Model results

PHT3D modeling simulates the chemical reactions in a particular hydrological situation, here including a steady pumping well, hydraulic conductivity ($K=50\text{m/d}$), dispersivity ($\alpha_L=1\text{m}$), etc.

Figure 8-1 shows the concentration distribution of iron-hydroxide at 0.1 day at different depths. From these plots we can see that the amount of incrustation decreases with increasing depth. The maximum value ($3,75 \cdot 10^{-5} \text{ mol/l}$) of the iron-hydroxide concentration is reached half way of the well screen. Results of microscopic analysis are the same as those of the model simulation: the clogging material consists of ochre deposition.

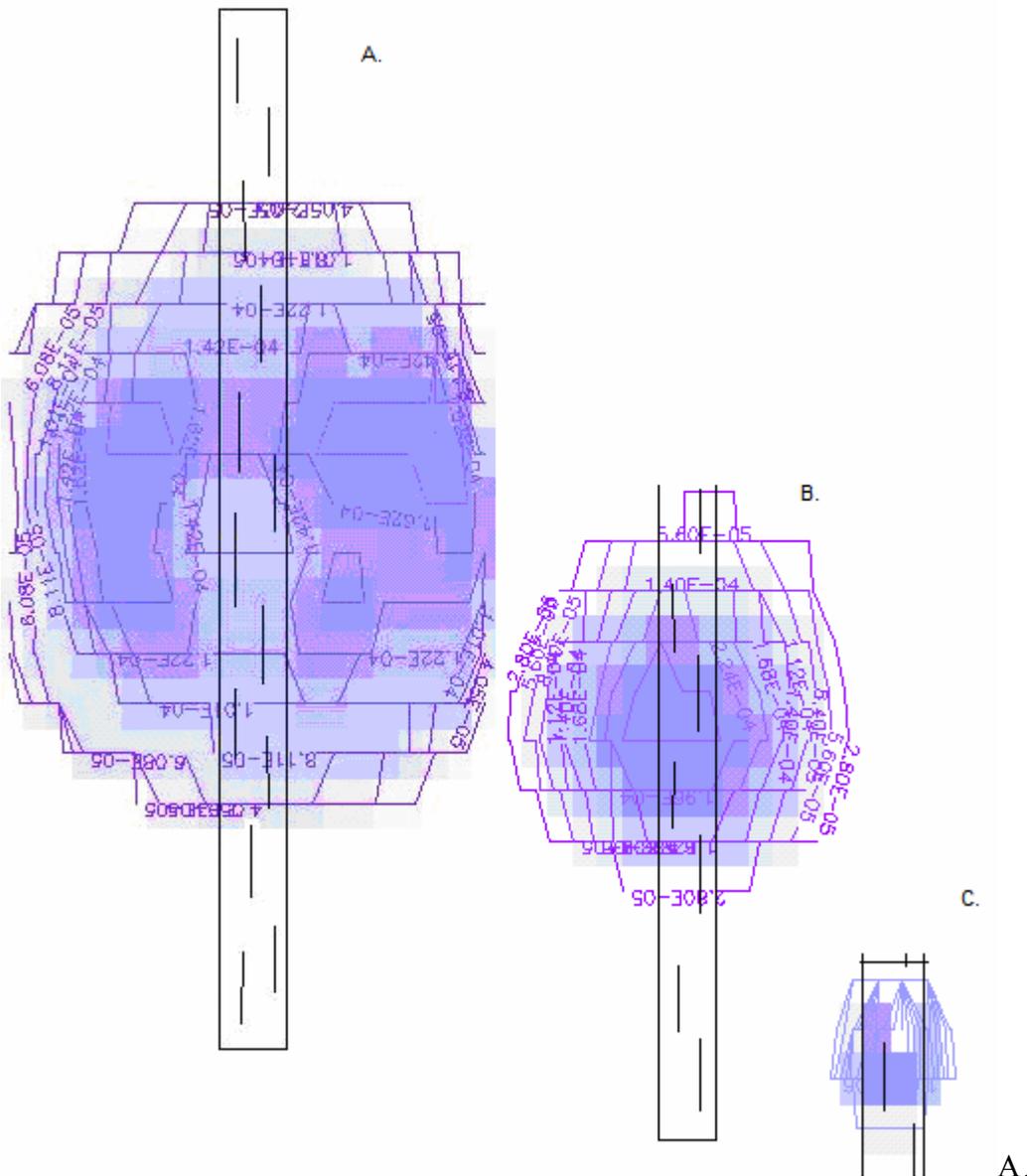


Figure 8-1. . Plot showing the iron-hydroxide concentrations at different depths. A: after 0,1 day simulation at 1m (left side). B: after 0,1 day simulation at 3m. C: after 0.1 day simulation at 4m.

9 Conclusions

Some chemical processes were considered in case of a real well to investigate their contribution in clogging process.

Two processes: mixing and precipitation were tested by PHREEQC and PHT3D program. The PHREEQC model calculated the mixing process of 15 water samples. Result shows that during mixing precipitation of iron hydroxide takes place. Next step of this research was simulation the kinetic rate of precipitation in the PHREEQC. Simulation was done for 1, 10, 40 days. Results from the 1 day simulation are a base for calculation of chemical clogging rate.

PHT3D model provides the chemical reactions in the hydrodynamic system with hydrodynamic parameters, including flow velocities, hydraulic conductivity, dispersivity, etc. Kinetic rate of chemical reactions were also included in PHT3D modeling. As a result the iron-hydroxide precipitation occurs. PHT3D model shows, that the precipitation is decreasing with increasing depth. Simulation results indicate that the concentration of iron-hydroxide precipitation increases within time.

Microscopic analysis of sediments from the well screen indicates the iron hydroxide deposits. This precipitation is result of mixing oxygenated and no-oxygen water. The modeling by using the PHREEQC and PHT3D programs are simulated this process. Result of models is the same as a result of microscopic analysis: ochre deposition due to mixing of oxic and anoxic water is a reason of clogging well.

Calculations to evaluate the chemical clogging rate were done for four scenarios:

- 1) well is pumped during 16 hour; followed by 8 hours rest per day.
- 2) well is pumped during 12 hour; followed by 12 hours rest per day.
- 3) well is pumped during 8 hour; followed by 16 hours rest per day.
- 4) well is pumped during 24 hour.

The result of this calculation shows that the less precipitation occurs if pump station works 24 hour per day and the most precipitation exist if pump station works 8 hour per day.

During constantly water extraction the time for iron precipitation is too short, but the volume of produced water is huge. As a result, in that case, the iron precipitation takes place. Due to high rate of the water extraction all clog sediments goes away. That means, the mass of sediments that can precipitate during pumping period is disregarded in compare to mass of iron hydroxide that can precipitate during inactive (no pumping) period. Result of calculation show that with increasing the stop-period of the pumping station the rate of the clogging process is increasing too. Time, which is needed to decrease the capacity of the well, was calculated. Five years is enough period to clog well.

10 Recommendations

In this research the chemical clogging process was modelled by PHREEQC and PHT3D.

- 1) The modelling was done in case of continuous pumping. By calculation it was archive that the most chemical precipitation occurs in case of inactive period of well (no pumping). To predict the clogging rate in the stop period the simulation by PHT3D (with helps of PHREEQC) has to be done.
- 2) Same exercises, now with high pH (7-8) waters, which results 1000 times more rapid iron hydroxide precipitation.
- 3) PHT3D has to be done for unsteady state modelling of well with a stop-periods and including a heterogeneous aquifer with vertical pressure graduets.

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12 Appendix

1) Input data for simulation of iron-hydroxide precipitation including kinetic rate.

```

RATES
#####
Fe(OH)3(a)
#####
-start
5 rem Transition state theory (Lasaga, 1998)
30 rate=parm(1)*(1-SR("Fe(OH)3(a)"))
40 moles=rate*TIME
50 save moles
-end
SOLUTION 3 Definition water mixing water
  units mol/kgw
  pH 5.4
  temp 10.0
  Ca 0.00175
  Mg 0.001024691358
  Na 0.000956521739
  K 0.000242966752
  Cl 0.001408450704
  Alkalinity 0.000131148 as HCO3
  S(6) 0.003125
  N(+5) 0.000004225352
  Fe(+2) 0.000214286
  Mn(+2) 1.09091E-05
  Amm 6.2963E-06
  P 3.15789E-07
  Al 1.11111E-06
EQUILIBRIUM_PHASES 3
O2(g) 0.0003
KINETICS 3
Fe(OH)3(a)
-parms 1e-10
-m 0.
-steps 57600 in 16 steps
USER_GRAPH
-headings days Fe(2) Fe(3) Fe(OH)3(a) pH
-chart_title "Fe-hydroxide precipitation"
-axis_titles "DAYS" "MOLES/KG WATER" "pH"
-axis_scale secondary_y_axis 3.0 9.0 1.0 0.5
-initial_solutions false
-start
10 GRAPH_X TOTAL_TIME/3600/24
20 GRAPH_Y TOT("Fe(3)"), TOT("Fe(2)"), KIN("Fe(OH)3(a)")
30 GRAPH_SY -LA("H+")

```

-end
END

2) Mixing of 15 water samples.

SOLUTION 1 Top water 6 meters deeptie

| units | mol/kgw | |
|------------|----------------|---------------------|
| pH | 4.45 | |
| temp | 10.0 | |
| Ca | 0.001475 | |
| Mg | 0.000646090535 | |
| Na | 0.000782608696 | |
| K | 0.000716112532 | |
| Cl | 0.000873239437 | |
| Alkalinity | 4.91803E-05 | as HCO ₃ |
| S(6) | 0.001302083333 | |
| N(+5) | 0.002323943662 | |
| Fe(+3) | 1.07143E-06 | |
| Mn(+2) | 2.54545E-06 | |
| Amm | 1.11111E-05 | |
| P | 3.15789E-07 | |
| Al | 2.14815E-05 | |
| O(0) | 0.0003 | |

end

SOLUTION 2 Top water 7 meters deeptie

| units | mol/kgw | |
|------------|-------------|---------------------|
| pH | 4.25 | |
| temp | 10.0 | |
| Alkalinity | 4.91803E-05 | as HCO ₃ |
| Cl | 0.000704225 | |
| S(6) | 0.001510417 | |
| Na | 0.000869565 | |
| K | 0.000677749 | |
| Ca | 0.00155 | |
| Mg | 0.000526749 | |
| N(+5) | 0.002822581 | |
| Al | 2.88889E-05 | |
| Fe(+2) | 1.96429E-06 | |
| Mn(+2) | 3.09091E-06 | |
| Amm | 1.11111E-05 | |
| P | 3.15789E-07 | |
| O(0) | 0.0003 | |

end

SOLUTION 3 Top water 8 meters deeptie

| units | mol/kgw | |
|------------|-------------|---------------------|
| pH | 4.2 | |
| temp | 10.0 | |
| Alkalinity | 4.91803E-05 | as HCO ₃ |
| Cl | 0.000760563 | |

| | |
|--------|-------------|
| S(6) | 0.001354167 |
| Na | 0.000869565 |
| K | 0.000549872 |
| Ca | 0.001875 |
| Mg | 0.000539095 |
| N(+5) | 0.003629032 |
| Al | 3.37037E-05 |
| Fe(+2) | 2.14286E-06 |
| Mn(+2) | 8.72727E-06 |
| Amm | 1.11111E-05 |
| P | 3.15789E-07 |
| O(0) | 0.0003 |

end

SOLUTION 4 Top water 9 meters deeptie

units mol/kgw

pH 4.2

temp 10.0

Alkalinity 4.91803E-05 as HCO3

Cl 0.000816901

S(6) 0.00125

Na 0.000956522

K 0.00044757

Ca 0.002025

Mg 0.000576132

N(+5) 0.004032258

Al 3.62963E-05

Fe(+2) 2.32143E-06

Mn(+2) 1.09091E-05

Amm 1.11111E-05

P 3.15789E-07

O(0) 0.0003

end

SOLUTION 5 Top water 12 meters deeptie

units mol/kgw

pH 4.45

temp 10.0

Alkalinity 4.91803E-05 as HCO3

Cl 0.001042254

S(6) 0.001197917

Na 0.000782609

K 0.000485934

Ca 0.002275

Mg 0.000831276

N(+5) 0.003709677

Al 7.40741E-06

Fe(+2) 7.67857E-06

Mn(+2) 1.72727E-05

```

Amm      1.11111E-05
P        3.15789E-07
O(0)    0.0003
end
SOLUTION 6 Top water 13 meters deeptie
units mol/kgw
pH      4.7
temp    10.0
Alkalinity 4.91803E-05 as HCO3
Cl       0.001098592
S(6)    0.001458333
Na       0.000826087
K        0.000434783
Ca       0.0022
Mg       0.000893004
N(+5)   0.003467742
Al       2.55556E-06
Fe(+2)  3.57143E-06
Mn(+2)  1.63636E-05
Amm     2.59259E-05
P       3.15789E-07
O(0)    0.0003
end
SOLUTION 7 Top water 14 meters deeptie
units mol/kgw
pH      4.75
temp    10.0
Alkalinity 4.91803E-05 as HCO3
Cl       0.001380282
S(6)    0.001614583
Na       0.000869565
K        0.000294118
Ca       0.001925
Mg       0.001020576
N(+5)   0.002419355
Al       0.000003
Fe(+2)  3.21429E-06
Mn(+2)  1.27273E-05
Amm     1.11111E-05
P       3.15789E-07
O(0)    0.0003
end
SOLUTION 8 Top water 15 meters deeptie
units mol/kgw
pH      4.7
temp    10.0
Alkalinity 4.91803E-05 as HCO3
Cl       0.001408451

```

| | |
|--------|-------------|
| S(6) | 0.00171875 |
| Na | 0.000956522 |
| K | 0.000294118 |
| Ca | 0.001875 |
| Mg | 0.001020576 |
| N(+5) | 0.002177419 |
| Al | 2.33333E-06 |
| Fe(+2) | 1.42857E-06 |
| Mn(+2) | 1.27273E-05 |
| Amm | 1.11111E-05 |
| P | 3.15789E-07 |
| O(0) | 0.0003 |

end

SOLUTION 9 Top water 18 meters deeptie

units mol/kgw

pH 4.95

temp 10.0

Alkalinity 8.19672E-05 as HCO3

Cl 0.001380282

S(6) 0.00171875

Na 0.001

K 0.000255754

Ca 0.001925

Mg 0.001102881

N(+5) 0.002258065

Al 1.40741E-06

Fe(+2) 1.42857E-06

Mn(+2) 1.27273E-05

Amm 1.11111E-05

P 3.15789E-07

O(0) 0.0003

end

SOLUTION 10 Top water 19 meters deeptie

units mol/kgw

pH 4.9

temp 10.0

Alkalinity 4.91803E-05 as HCO3

Cl 0.001380282

S(6) 0.0021875

Na 0.001

K 0.000956522

Ca 0.001775

Mg 0.001028807

N(+5) 0.000870968

Al 1.88889E-06

Fe(+2) 1.42857E-06

Mn(+2) 1.09091E-05

Amm 4.81481E-06

```

P      3.15789E-07
O(0)   0.0003
end
SOLUTION 11 Top water 20 meters deeptie
units  mol/kgw
pH     5.1
temp   10.0
Alkalinity  9.83607E-05  as HCO3
Cl      0.001380282
S(6)    0.00234375
Na      0.001
K       0.000956522
Ca      0.001775
Mg      0.001037037
N(+5)   0.000870968
Al      1.88889E-06
Fe(+2)  2.32143E-06
Mn(+2)  1.09091E-05
Amm     2.59259E-05
P       3.15789E-07
O(0)    0.0003
end
SOLUTION 12 Top water 21 meters deeptie
units  mol/kgw
pH     5.25
temp   10.0
Alkalinity  0.000131148  as HCO3
Cl      0.001380282
S(6)    0.003125
Na      0.001
K       0.000956522
Ca      0.001775
Mg      0.001041152
N(+5)   4.83871E-06
Al      2.55556E-06
Fe(+2)  0.000205357
Mn(+2)  1.18182E-05
Amm     3.33333E-05
P       3.15789E-07
O(0)    0.0
end
SOLUTION 13 Definition water of 22 meters deeptie
units  mol/kgw
pH     5.4
temp   10.0
Ca      0.00175
Mg      0.001024691358
Na      0.000956521739

```

| | | |
|------------|----------------|---------------------|
| K | 0.000242966752 | |
| Cl | 0.001408450704 | |
| Alkalinity | 0.000131148 | as HCO ₃ |
| S(6) | 0.003125 | |
| N(+5) | 0.000004225352 | |
| Fe(+2) | 0.000214286 | |
| Mn(+2) | 1.09091E-05 | |
| Amm | 6.2963E-06 | |
| P | 3.15789E-07 | |
| O | 0 | |
| Al | 1.11111E-06 | |
| O(0) | 0.0 | |

end

SOLUTION 14 Definition water of 23 meters deeptie

| | | |
|------------|-------------|---------------------|
| units | mol/kgw | |
| pH | 5.3 | |
| temp | 10.0 | |
| Alkalinity | 0.000114754 | as HCO ₃ |
| Cl | 0.001380282 | |
| S(6) | 0.003333333 | |
| Na | 0.000956522 | |
| K | 0.000255754 | |
| Ca | 0.001925 | |
| Mg | 0.001131687 | |
| N(+5) | 4.83871E-06 | |
| Al | 0.0000003 | |
| Fe(+2) | 0.000141071 | |
| Mn(+2) | 1.09091E-05 | |
| Amm | 6.2963E-06 | |
| P | 3.15789E-07 | |
| O(0) | 0 | |

end

SOLUTION 15 Definition water of 27 meters deeptie

| | | |
|------------|-------------|---------------------|
| units | mol/kgw | |
| pH | 6.9 | |
| temp | 10.0 | |
| Alkalinity | 0.001196721 | as HCO ₃ |
| Cl | 0.001267606 | |
| S(6) | 0.00125 | |
| Na | 0.000782609 | |
| K | 8.69565E-05 | |
| Ca | 0.00145 | |
| Mg | 0.000600823 | |
| N(+5) | 4.83871E-06 | |
| Al | 2.7037E-07 | |
| Fe(+2) | 0.0000875 | |
| Mn(+2) | 1.81818E-05 | |
| Amm | 5.92593E-06 | |

```

P      3.15789E-07
O(0)   0
end
SOLUTION 16 Definition water of 28 meters deeptie
units mol/kgw
pH     6.4
temp   10.0
Alkalinity 0.00057377 as HCO3
Cl      0.001183099
S(6)    0.001197917
Na      0.00073913
K       7.92839E-05
Ca      0.0009
Mg      0.000485597
N(+5)   4.83871E-06
Al      0.0000003
Fe(+2)  0.000148214
Mn(+2)  0.00001
Amm     4.81481E-06
P       3.15789E-07
O(0)    0
end
TITLE --Mix 50% top water, 50% bottom water.
MIX 1
1  0.05
2  0.05
3  0.05
4  0.05
5  0.05
6  0.05
7  0.05
8  0.05
9  0.05
10 0.05
11 0.05
12 0.05
13 0.1
14 0.1
15 0.1
16 0.1
SAVE solution 5
END
TITLE --Equilibrate mixture with ironhydroxide
EQUILIBRIUM_PHASES 1
Fe(OH)3(a) 0.0 0.0
USE solution 5
END
TITLE --Equilibrate mixture with ironhydroxide and pyrolusite.

```

```
EQUILIBRIUM_PHASES 2
  Fe(OH)3(a)      0.0 0.0
  Pyrolusite      0.0 0.0
USE solution 5
END
```