Experimental Modelling and Prevention of Chemical Fe-Clogging in Deep Vertical Wells for Open-Pit Dewatering

Experimentelle Modellierung und Prävention chemischer Fe-Verockerung in tiefen Vertikalfilterbrunnen zur Tagebauentwässerung

Von der Fakultät für Georessourcen und Materialtechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften

genehmigte Dissertation

vorgelegt von

Christoph Hubert Franz-Josef Guido Weidner, M.Sc.RWTH

aus Bonn-Duisdorf

Berichter: Univ.-Prof. Dr.rer.nat. Thomas R. Rüde

Univ.-Prof. Dr.-Ing. Holger Schüttrumpf

Tag der mündlichen Prüfung: 27.07.2015

Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek online verfügbar
Acknowledgements

At first, I would like to express my gratitude to all persons and institutions that supported me and my work on this topic and made the completion of this thesis possible. Many thanks to my doctoral supervisor Prof. Thomas R. Rüde of the Institute of Hydrogeology (LFH) of RWTH Aachen University for giving me the opportunity to work on this interesting topic as doctoral candidate and research assistant and his intense involvement with the project during numerous professional discussions.

My second supervisor Prof. Holger Schüttrumpf of the Institute of Hydraulic Engineering and Water Resources Management (IWW) of RWTH Aachen University is kindly acknowledged for his commitment with the project and for giving me the opportunity to realise the Fe-clogging experiments in his institute’s experimental hall.

The RWTH Aachen, Marion Heinrichs and the committee for allocation of the RWTH Scholarships for Doctoral Students According to the Guidelines for the Promotion of Young Researchers (RfwN) are kindly acknowledged for choosing me and my work to be financially supported over three years of the graduation process. Many thanks also go to Hieu Trung Ngujen for his help with the application for the RfwN-scholarship. The financial support of the Deutscher Akademischer Austauschdienst (DAAD) is very appreciated for enabling my participation at the 2013 Annual Conference of the International Mine Water Association (IMWA) in Golden, Colorado, USA.

I am very grateful to my colleague and friend Sebastian Henkel of the IWW who worked closely with me on the major part of the experimental investigations described in this thesis. The current and former personnel of the IWW, namely Dr. Sebastian Roger, Stefanie Lorke, Catrina Cofalla, Dr. Wiebke Klauder, Norbert Quast, Mario Czogallik, Manfred Kriegel, Irene Ohligschläger and Christian Vogelgesang, are acknowledged for their administrative support within the Fe-clogging project, for conceptionally planning and constructionally implementing the experimental Fe-clogging model that enabled experimental simulation of chemical Fe-clogging in the laboratory.

My current and former colleagues of the Institute of Hydrogeology Dr. Andre Banning, Dr. Thomas Demmel, Dr. Thomas Putranto, Paul Mießner, Lisa Krien, David Burs, Timm Reisinger and Norbert Cuvelier as well as the student assistants are acknowledged for their guidance and uncounted supports to my work, their friendship and for always having an open door to discuss tasks and challenges posed in the process of graduation.

Implementation of this project was supported technically and financially by the project partner RWE Power AG in a close cooperation. Dr. Wiebke Klauder, Wilhelm Schlegel, Dr. Gero Vinzelberg, Morris Reich, Dr. Martin Back and Matthias Metzger are acknowledged for numerous meetings and several hours of constructive discussions on the experiments described in this thesis. Sampling at excavated dewatering wells in the open-pit Garzweiler was only possible thanks to Volker Heinrich, Dietmar Wirtz and Heinz-Willi Hoffmann of RWE Power AG.
Several institutions furthermore supported the project by conducting and evaluating mineralogical, chemical and physical analyses or by allowing to use their measurement devices or analytical equipment. Thanks are due to:

- Dr. Markus Neuroth and Norbert Frerix from the mineralogical laboratory of the RWE Power AG and Amélie Lenders, student intern at the laboratory for conducting enrichment of dense phases in samples from the Fe-clogging model and from the field, analysing the samples with X-ray diffractometry and the investigation of thin sections with transmitted light microscopy and SEM/EDX-analyses.
- Prof. Helge Stanjek, Michel Heuser and Dennis Künkels from the research group Clay and Interface Mineralogy (CIM) of RWTH Aachen University for conducting measurements of the BET surface area and providing database extensions and assistance with processing of XRD data.
- Prof. Ralf Littke, Dr. Sabine Heim, Dr. Dirk Prinz, Kerstin Windeck and Donka Macherey from the Institute of Geology and Geochemistry of Petroleum and Coal (LEK) of RWTH Aachen University for conducting measurements of the total organic and inorganic carbon (TOC/TIC) on samples from the field and the Fe-clogging model and for allowing to use their laboratory for sample preparation.
- Prof. Peter Kukla, Dr. Lars Reuning and Philipp Binger from the Institute of Geology and Palaeontology (GIA) of RWTH Aachen University for the preparation of thin sections and allowance to use their equipment for polarisation microscopy.
- Prof. Janos Urai, Max Arndt, Werner Kraus, Alexander Raith and Susanne Hemes from the Institute of Structural Geology, Tectonics and Geomechanics (GED) of RWTH Aachen University for preparation of thin sections and allowance to use their equipment for polarisation microscopy.
- Prof. Christoph Treskatis and Dr. Georg Houben for interesting and constructive discussions during collaborative meetings in the field or at the IWW.
- Jana Milatz for her laboratory work on the topic of Fe-addition to the clogging model in her bachelor thesis and her field work on the topic of annular space dewatering in her master thesis.

I sincerely thank Jenny Weidner, Dr. Wiebke Klauder, Dr. Andre Banning and Sebastian Henkel for proof reading of this thesis.

Many thanks go to my parents, parents-in-law, siblings and friends for repeatedly encouraging and supporting me with welcome distractions from the sometimes strenuous work on the dissertation.

My deepest gratitude goes to my wife Jenny and my daughter Maya Louisa. Thank you so much for the love you bear me and your patience with me and my not always enjoyable moods during the final phase of my dissertation. I hope I can give you back some of the friendship and love I owe to you!
Contents

1 Introduction ............................................................................................................................................. 17
  1.1 Former and current studies on well loss and well ageing ......................................................... 19
  1.2 History of the MaxWell Project .............................................................................................. 21
  1.3 Aims and scope of this thesis ................................................................................................. 23

2 Theoretical Background ....................................................................................................................... 25
  2.1 Groundwater flow and hydraulics in porous media ................................................................. 25
  2.2 Design and operation of vertical filter wells ..................................................................... 26
      2.2.1 Dewatering well installation, screens and casing .......................................................... 26
      2.2.2 Gravel pack and annular filling material ................................................................. 28
      2.2.3 Flow towards vertical filter wells ............................................................................. 30
      2.2.4 Properties and operational modes of wells for different purposes ....................... 32
  2.3 Well loss ..................................................................................................................................... 34
      2.3.1 Time independent well loss ......................................................................................... 35
      2.3.2 Well ageing .................................................................................................................. 38
      2.3.3 Known countermeasures in drinking water supply wells ..................................... 43
  2.4 Build-up of Fe(III)-hydroxide-incrustations ......................................................................... 46
      2.4.1 Chemical Fe(II)-oxidation .......................................................................................... 46
      2.4.2 Thermodynamics of the Fe-H₂O-system ..................................................................... 47
      2.4.3 Kinetics of Fe(II)-oxidation ...................................................................................... 49
      2.4.4 Autocatalytic effect ...................................................................................................... 51
      2.4.5 Biological Fe(II)-oxidation ....................................................................................... 52
      2.4.6 Fe(III)-hydroxides and their formation pathways ..................................................... 55

3 Geography and Geology of the Rhenish Lignite District ................................................................. 61
  3.1 Geographical overview and tectonic and sedimentary history ............................................. 61
  3.2 Hydrostratigraphy ...................................................................................................................... 62
  3.3 Locations and sedimentary history of relevant gravel pits ..................................................... 63

4 Materials and Methods ....................................................................................................................... 67
  4.1 Materials ...................................................................................................................................... 67
      4.1.1 Aquifer material .......................................................................................................... 67
      4.1.2 Gravel pack materials .................................................................................................. 67
      4.1.3 Screen pipes ................................................................................................................ 70
  4.2 Column experiments .................................................................................................................... 71
      4.2.1 Experimental set-up ..................................................................................................... 72
      4.2.2 Tracer experiments ...................................................................................................... 72
      4.2.3 Measurements and data recording ............................................................................. 74
5 Results and Discussion .............................................................................................................. 113

5.1 Column experiments ........................................................................................................... 113
  5.1.1 Time series of hydrochemical parameters .................................................................... 113
  5.1.2 PhreeqC-calculations ................................................................................................... 114

5.2 Clogging experiments ........................................................................................................... 115
  5.2.1 Model optimisation ....................................................................................................... 115
  5.2.2 Material tests ................................................................................................................ 118
  5.2.3 Saturated screen pipe with and without air phase in the gravel pack ......................... 121
  5.2.4 Filter aeration experiments .......................................................................................... 125

5.3 Properties of Fe-incrustations in the model and in the field ................................................. 126
  5.3.1 Distribution of Fe-clogging inside the well filter ............................................................ 126
  5.3.2 Chemical and mineralogical analyses .......................................................................... 130
  5.3.3 Microscopic methods .................................................................................................... 138

5.4 Evaluation and verification of the Fe-clogging model .......................................................... 142
  5.4.1 Hydrochemistry in the field and in the model ................................................................. 142
  5.4.2 Hydrochemical model of the flow channel .................................................................... 144
  5.4.3 Comparison of hydraulic data from the Fe-clogging model ...................................... 147
  5.4.4 Application example ..................................................................................................... 150

5.5 Tracer experiments in annular space dewatering .................................................................... 151

6 Conclusions ............................................................................................................................. 153
7  Prospect ......................................................................................................................................... 161
8  Summary ....................................................................................................................................... 163
9  Literature ...................................................................................................................................... 167
10 Appendices .................................................................................................................................. 191

List of Figures
Figure 1  Open-cast lignite mining districts in Germany ................................................................. 18
Figure 2  Possible temporal progressions of the hydraulic conductivity with increasing Fe-clogging time .............................................................................................................. 24
Figure 3  Screen pipes used in dewatering wells in the Rhenish lignite mining district ......................... 27
Figure 4  Cross section through a cone of depression of the piezometric surface around a pumped well in a confined and unconfined aquifer .............................................................. 31
Figure 5  General assemblage of production water wells ..................................................................... 33
Figure 6  Possible hydraulic effects in multi-layered dewatering wells .................................................... 34
Figure 7  Different modes of operation of vertical filter wells in drinking water supply and aquifer dewatering .................................................................................................................. 34
Figure 8  Well loss in an unconfined aquifer expressed as a deeper actual drawdown in the discharge well than expected ............................................................................................................. 35
Figure 9  Well loss due to turbulent flow conditions and vertical flow components near a vertical filter well in an unconfined aquifer ......................................................................................... 37
Figure 10 Effects of suffosion .................................................................................................................. 37
Figure 11 Filtration mechanisms of particle suspensions injected in porous media ................................. 39
Figure 12 Corrosion, material degradation and fatigue of metallic screen pipes ........................................ 39
Figure 13 Screen pipe before installation and affected by iron clogging ................................................... 40
Figure 14 Shares of different well ageing processes in Germany ............................................................. 41
Figure 15 Shares of different production types for public drinking water supply and distribution of groundwater with elevated Chloride-, Sulphate and Iron-/Manganese-contents in Germany ................................................................. 41
Figure 16 Bacteria populations in a well environment .................................................................................. 42
Figure 17 Differences in entrance resistance between mechanical well bore clogging and chemical screen slot clogging ............................................................................................................. 43
Figure 18 Increased oxygen supply in the vicinity of a groundwater well in unconfined conditions due to intermittent abstraction .................................................................................................. 45
Figure 19 Phase diagram of fields of domination of dissolved Fe-species and mineral phases in the pH-pe-space for different total Fe-concentrations ......................................................... 49
Figure 20 Reaction rates of homogeneous and heterogeneous Fe(II)-oxidation ........................................ 52
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Phylogenetic relations of different microorganisms contributing to Fe-redox-cycling</td>
<td>54</td>
</tr>
<tr>
<td>22</td>
<td>Major formation pathways of Fe-hydroxides and oxyhydroxides</td>
<td>56</td>
</tr>
<tr>
<td>23</td>
<td>Tectonic overview of the Lower Rhine Embayment</td>
<td>61</td>
</tr>
<tr>
<td>24</td>
<td>Geologic profile through the Lower Rhine Embayment</td>
<td>62</td>
</tr>
<tr>
<td>25</td>
<td>Locations of the three gravel pits in the Rhenish lignite mining district</td>
<td>64</td>
</tr>
<tr>
<td>26</td>
<td>Locations of the three gravel pits in a geological context</td>
<td>65</td>
</tr>
<tr>
<td>27</td>
<td>Grain size distribution of the aquifer material applied in the model</td>
<td>67</td>
</tr>
<tr>
<td>28</td>
<td>Grain size distribution of the considered filter materials</td>
<td>68</td>
</tr>
<tr>
<td>29</td>
<td>Close-up pictures of the three considered natural gravel materials</td>
<td>70</td>
</tr>
<tr>
<td>30</td>
<td>SEM-images of the surface of glass beads and conventional gravel grains</td>
<td>70</td>
</tr>
<tr>
<td>31</td>
<td>200×200 mm section of a GRP-rod screen pipe and shortened, 200×30 mm screen section for evaluation of filter aeration effects</td>
<td>71</td>
</tr>
<tr>
<td>32</td>
<td>Experimental set-up of the long-term elution column experiments</td>
<td>72</td>
</tr>
<tr>
<td>33</td>
<td>Preparation of tracer injection and measurement of Br⁻-transport</td>
<td>73</td>
</tr>
<tr>
<td>34</td>
<td>Schematic experimental set-up of the long-term elution experiments</td>
<td>74</td>
</tr>
<tr>
<td>35</td>
<td>Schematic illustration of the well section, reconstructed in the experimental laboratory model</td>
<td>77</td>
</tr>
<tr>
<td>36</td>
<td>Schematic experimental set-up of the laboratory clogging model</td>
<td>77</td>
</tr>
<tr>
<td>37</td>
<td>Addition points and compulsory auto-mixer</td>
<td>78</td>
</tr>
<tr>
<td>38</td>
<td>Filter column for oxygen-capture, ultraviolet disinfection lamp and fine filter column</td>
<td>79</td>
</tr>
<tr>
<td>39</td>
<td>Flexible water tank</td>
<td>79</td>
</tr>
<tr>
<td>40</td>
<td>Measurement cell with probes for eC, DO, pH and Eh and flow meter</td>
<td>80</td>
</tr>
<tr>
<td>41</td>
<td>Top view of the flow channel</td>
<td>81</td>
</tr>
<tr>
<td>42</td>
<td>Front view of the gravel pack, screen pipe and outflow chamber with the three sections for analysis of hydraulic conductivity Kᵢ, Kᵢᵢ, and Kᵢᵢᵢ</td>
<td>81</td>
</tr>
<tr>
<td>43</td>
<td>Front view of the flow channel in the experimental model</td>
<td>82</td>
</tr>
<tr>
<td>44</td>
<td>Detailed top view of the outflow chamber with active air supply and measurement probes</td>
<td>82</td>
</tr>
<tr>
<td>45</td>
<td>Model operational concept for standardised, comparative investigation of clogging affinity</td>
<td>84</td>
</tr>
<tr>
<td>46</td>
<td>Idealised and actual development of the primary clogging zone in the capillary fringe of a glass bead filter pack during the Fe-clogging phase</td>
<td>85</td>
</tr>
<tr>
<td>47</td>
<td>Evaluation of the hydraulic properties of the primary clogging zone of a glass bead filter pack during the evaluation phase and development of the secondary clogging zone in the capillary fringe</td>
<td>86</td>
</tr>
<tr>
<td>48</td>
<td>Influence of chloride concentration on density and dynamic viscosity</td>
<td>90</td>
</tr>
<tr>
<td>49</td>
<td>Vertical stability of the gravel pack and cemented sample of filter gravel</td>
<td>91</td>
</tr>
<tr>
<td>50</td>
<td>Layered excavation system</td>
<td>91</td>
</tr>
<tr>
<td>51</td>
<td>Resin impregnation for undisturbed sampling of the filter pack</td>
<td>92</td>
</tr>
<tr>
<td>52</td>
<td>Sampling in the outflow chamber</td>
<td>93</td>
</tr>
<tr>
<td>53</td>
<td>Recovery tests in standard extracts with solution I or II</td>
<td>95</td>
</tr>
<tr>
<td>54</td>
<td>Wavelength-absorbance-scans of standard extracts with solution I and II</td>
<td>96</td>
</tr>
<tr>
<td>55</td>
<td>Distribution of solid and dissolved species in the Fe(II)-oxalate system</td>
<td>97</td>
</tr>
</tbody>
</table>
Figure 56 Calibration functions at $\lambda_{\text{oxalate}} = 345$ nm for the extraction steps I and II........ 98
Figure 57 Interim-experiment of chemical dissolution of the Fe-incrustations from the outflow chamber .................................................................................................................. 104
Figure 58 Probe and measurement device for the aerial oxygen percentage........ 105
Figure 59 Schematic conversion of a PhreeqC-model result from temporal to spatial consideration .................................................................................................................. 106
Figure 60 Excavated wells sampled in a 1st campaign in the open-pit Garzweiler ....... 108
Figure 61 Excavated wells sampled in a 2nd campaign in the open-pit Garzweiler ...... 108
Figure 62 Samples taken during the 2nd campaign in the open-pit Garzweiler .......... 109
Figure 63 Concepts of a conventional multi-layered dewatering well and of a well with annular space dewatering .............................................................. 111
Figure 64 Tracer tests concept, conducted at wells with annular space dewatering .... 112
Figure 65 Progression of pH and eC and difference of dissolved Al, Mn, Fe and Si at the in- and outflow of the long-term-elution-columns ........................................ 113
Figure 66 Fe-clogging zone in the capillary fringe in LTT 2 ................................ 116
Figure 67 Installation of filtration steps between LTTs 2, 3 and 4 ......................... 116
Figure 68 Reynolds-numbers depending on the water level in the outflow chamber ................................................................................................................................. 117
Figure 69 Pressure loss in the hydraulic evaluation sections during LTT 4 ............ 117
Figure 70 Development of hydrochemical parameters in the flow channel during the Fe-clogging phases of all material tests ......................................................... 118
Figure 71 Balance of Fe-measurements in the process water during the Fe-clogging phases of all material tests ................................................................. 119
Figure 72 Progression of hydraulic conductivity with increasing Fe-clogging time, compared for all tested materials .............................................................. 120
Figure 73 Change of the hydraulic conductivity $K$ after 35 h of Fe-clogging relative to the initial value for all material tests .................................................. 120
Figure 74 Hydrochemical parameters in the flow channel during the Fe-clogging phases of all long term tests ............................................................. 121
Figure 75 Balance of Fe-measurements in the process water during the Fe-clogging phases of all long term tests ............................................................. 122
Figure 76 Composition of the air inside the flexible air reservoir ....................... 122
Figure 77 Primary and secondary clogging zones at different air supply situations ...... 124
Figure 78 Hydraulic conductivity for different scenarios of $O_2$-supply .................. 124
Figure 79 Change of the hydraulic conductivity $K$ after 35 h of Fe-clogging relative to the initial value for all Fe-clogging experiments .................................................. 125
Figure 80 Conditions during the experiments of screen pipe aeration .................... 125
Figure 81 Distribution of Fe-clogging after LTT 16 with full saturation of the filter pack and after the aeration experiments .................................................. 126
Figure 82 Layered excavation of the gravel pack .................................................. 127
Figure 83 Distributions of Fe-clogging products at excavated wells in the field........ 128
Figure 84 Comparison of measured distributions of Fe-incrustations with the PhreeqC-model .............................................................. 129
Figure 85 Transmitted-light microscopic images on a sample from well 1C .......... 139
Figure 86 SEM/EDX image and elemental distributions in a sample from well 1C.... 140
Figure 87  SEM/EDX image and elemental distributions in a sample from LTT 3 .......... 140
Figure 88  Close-up SEM/EDX image and elemental distributions of a weathered orthoclase-grain in the thin section from LTT 3 ................................................. 140
Figure 89  Weathered feldspar-grain in the thin section from LTT 3 ......................... 141
Figure 90  Irregularly formed polycrystalline quartzite-grain with increased amounts of Fe(III)-hydroxide-encrustation ......................................................... 141
Figure 91  Monocrystalline quartz-grain with irregular geometry and polycrystalline quartzite grains with thicker Fe(III)-hydroxide coatings in the thin section from LTT 3 ................................................................. 142
Figure 92  Result of the PhreeqC model ................................................................ 144
Figure 93  Total mass of Fe and total volume of Fe(III)-minerals in each model cell, calculated with the PhreeqC-model ................................................................. 147
Figure 94  Initial and final hydraulic conductivities of material tests and scenarios in the Fe-clogging model ................................................................. 148
Figure 95  Fe-clogging-progressions of the different long term tests ..................... 149
Figure 96  Continuous injection of tracer and rinsing water into the piezometer in the annular space of well H 1307 with annular space dewatering and measurement of tracer passage at the top of the well ........................................ 152
Figure 97  Progression of the hydraulic conductivity with increasing influence of chemical Fe-clogging as observed in the experimental model .................... 156
List of Tables
Table 1  Lignite production by country .................................................................................................. 18
Table 2  Mean values of hydrochemical parameters in the groundwater levels
dewatered in regions of the Rhenish lignite mining district ........................................... 63
Table 3  Results of XRF analyses of the initial gravel materials ..................................................... 69
Table 4  Schedule for column experiments .................................................................................... 74
Table 5  Parameters measured in the experimental Fe-clogging model during the
individual phases of a clogging experiment .............................................................................. 88
Table 6  Poorly crystallised, well crystallised and total Fe-contents of synthetic
minerals determined by the sequential extraction method with direct
measurement in the oxalate extracts at $\lambda = 345 \text{ nm}$ compared with
theoretical stoichiometric Fe-contents ....................................................................................... 99
Table 7  Densities of relevant minerals in comparison to bromoform ....................................... 101
Table 8  Overview of the first four long term tests ....................................................................... 102
Table 9  Overview of Ikong term tests 5 to 16 ............................................................................ 103
Table 10  Overview of field samples, taken in the open-pit Garzweiler .................................... 110
Table 11  Saturation indices of relevant minerals after the second stop-flow
period in the inflow and each column’s outflow ....................................................................... 115
Table 12  Percental change of the hydraulic gradient of the gravel pack between
the reference and Fe-clogging situation ..................................................................................... 118
Table 13  Results of SEP-analyses in laboratory samples and field samples,
compared to values from synthetic hydroxidic Fe-clogging-minerals .......................... 130
Table 14  Results of BET-analyses in laboratory samples and field samples ..................... 132
Table 15  Results of XRD-analyses in field samples .................................................................... 133
Table 16  Results of XRD-analyses in initial gravel materials ..................................................... 134
Table 17  Results of XRD-analyses of samples from the Fe-clogging model ....................... 135
Table 18  Results of XRD-analyses of samples from the outflow chamber ......................... 136
Table 19  Results of TOC/TIC-analyses of samples from the field and the model.............. 137
Table 20  Hydrochemical parameters in the model process water during LTT 7,
compared to field values ........................................................................................................ 143
Table 21  Scenarios modelled with PhreeqC and results of total Fe-precipitation ......... 146
Table 22  Ranges of hydraulic conductivities in the Fe-clogging model in
comparison to literature values ................................................................................................. 147
Table 23  Hydraulic conductivities of material tests and modelled scenarios in the
Fe-clogging model ..................................................................................................................... 150
Table 24  Changes in pumping rate Q at constant pressure loss $\Delta h_{\text{cp}}$ and vice
versa on an exemplary dewatering well considering the change in K-
value over 56 h of Fe-clogging time in S II in LTT 6 .......................................................... 151
### List of Symbols

#### Roman letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>area</td>
<td>m²</td>
</tr>
<tr>
<td>A₆₀</td>
<td>cross-sectional area of the annular space</td>
<td>m²</td>
</tr>
<tr>
<td>A₈₆₇</td>
<td>circular cross-sectional area of the borehole</td>
<td>m²</td>
</tr>
<tr>
<td>A₉₀₇</td>
<td>circular cross-sectional area of the laboratory column</td>
<td>m²</td>
</tr>
<tr>
<td>A₉₀₇₈₉₉</td>
<td>cylindrical surface area with well as middle axis</td>
<td>m²</td>
</tr>
<tr>
<td>Aₑ</td>
<td>flow effective part of the cross-sectional area perpendicular to flow direction</td>
<td>m²</td>
</tr>
<tr>
<td>A₈₆₇₉₄</td>
<td>circular cross-sectional area of the well casing</td>
<td>m²</td>
</tr>
<tr>
<td>a(X)</td>
<td>activity (effective concentration) of the dissolved element X</td>
<td>mol L⁻¹</td>
</tr>
<tr>
<td>b</td>
<td>aquifer thickness</td>
<td>m</td>
</tr>
<tr>
<td>bₐₙₑ</td>
<td>breadth of the PhreeqC-model cell</td>
<td>m</td>
</tr>
<tr>
<td>Δibernate</td>
<td>breadth of the gravel pack cell</td>
<td>m</td>
</tr>
<tr>
<td>BET</td>
<td>BET-surface area</td>
<td>m² g⁻¹</td>
</tr>
<tr>
<td>bₚₙₐₗ</td>
<td>breadth of the flow channel</td>
<td>mm</td>
</tr>
<tr>
<td>bₘₚₚ</td>
<td>length of the water conducting slit perpendicular to flow</td>
<td>m</td>
</tr>
<tr>
<td>bₜₜₜₚ</td>
<td>water-filled/saturated aquifer thickness</td>
<td>m</td>
</tr>
<tr>
<td>C</td>
<td>integration constant</td>
<td>-</td>
</tr>
<tr>
<td>f₅₅₅₅</td>
<td>temporal integral of Δc(Fe(II))-values in the process water</td>
<td>g (10 h⁻¹)</td>
</tr>
<tr>
<td>cₖₖₖₖ</td>
<td>time-dependent concentration of element i</td>
<td>g L⁻¹</td>
</tr>
<tr>
<td>cₖₖₖₖ</td>
<td>time-dependent concentration</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>Σcₖₖₖₖ</td>
<td>time-dependent normalised cumulative tracer passage</td>
<td>-</td>
</tr>
<tr>
<td>cₖₖₖₖ</td>
<td>mass concentration of the dissolved element X</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>d₅₅₅₅</td>
<td>grain size at 10 % quantile of the grain size distribution</td>
<td>m</td>
</tr>
<tr>
<td>d₆₆₆₆</td>
<td>grain size at 30 % quantile of the grain size distribution</td>
<td>m</td>
</tr>
<tr>
<td>d₅₅₅₅</td>
<td>grain size at 60 % quantile of the grain size distribution</td>
<td>m</td>
</tr>
<tr>
<td>dₙₙₙₙ</td>
<td>characteristic grain size of the porous medium</td>
<td>m</td>
</tr>
<tr>
<td>dₘₘₘₘ</td>
<td>characteristic grain size of the gravel pack (GP)</td>
<td>m</td>
</tr>
<tr>
<td>dₘₘₘₘ</td>
<td>indicator grain size of the aquifer material</td>
<td>m</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>Eₐₐₐₐₐₐ</td>
<td>redox-potential measured with the Ag/AgCl-probe</td>
<td>mV</td>
</tr>
<tr>
<td>eC</td>
<td>electrical conductivity</td>
<td>mS cm⁻¹</td>
</tr>
<tr>
<td>Eh</td>
<td>redox-potential</td>
<td>mV</td>
</tr>
<tr>
<td>Eₐₐₐₐ</td>
<td>reference potential between standard-hydrogen-electrode and the Ag/AgCl-probe</td>
<td>mV</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
<td>J V⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>Feₕₕₕₕ</td>
<td>oxalate soluble Fe</td>
<td>-</td>
</tr>
<tr>
<td>Feₕₕₕₕ</td>
<td>ascorbic acid soluble Fe</td>
<td>-</td>
</tr>
<tr>
<td>fₕₕₕₕ</td>
<td>screening factor</td>
<td>-</td>
</tr>
<tr>
<td>Feₕₕ(gulp)</td>
<td>total Fe-content of the gravel sample, determined by the SEP</td>
<td>g kg⁻¹</td>
</tr>
<tr>
<td>∫∫∫ Feₕₕgulp ΔV</td>
<td>volume integral over of the Feₕₕgulp-distribution in the gravel pack</td>
<td>g</td>
</tr>
<tr>
<td>∫ΔFeₕₕ gulp Δt</td>
<td>total Fe-retardation in the FC (integral over the Fe-clogging time)</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>Feₕₕ(gulp, max)</td>
<td>Maximum Feₕₕ(gulp) in the gravel pack determined by the SEP</td>
<td>g kg⁻¹ (10 h⁻¹)</td>
</tr>
<tr>
<td>g</td>
<td>gravitational acceleration</td>
<td>m s⁻²</td>
</tr>
<tr>
<td>GP</td>
<td>total mass or volume of gravel pack</td>
<td>-</td>
</tr>
<tr>
<td>h₁₂₂₂</td>
<td>hydraulic pressure (= free water level) at the two points P1 and P2</td>
<td>mm</td>
</tr>
</tbody>
</table>
\[ \Delta h = h_2 - h_1 \] pressure difference between point 2 and 1 \( (h_2 > h_1) \) [m]

\( \Delta h \) loss of hydraulic head [mm]

\( h_{\text{cap}} \) height of water saturated capillary fringe [m]

\( h_{\text{cell}} \) height of the PhreeqC-model cell [m]

\( \Delta h_{\text{cell}} \) height of the gravel pack cell [m]

\( \Delta h_{\text{clog}} \) loss of hydraulic head after Fe-clogging [mm]

\( \Delta h_{\text{gp}} \) change in hydraulic head in the gravel pack [m]

\( h_i \) hydraulic head at point i [mmH\(_2\)O]

\( \Delta h_{\text{ref}} \) initial loss of hydraulic head during the reference test [mm]

\( h_{\text{OC}} \) water level in the outlet chamber of the flow channel [mm]

\( i \) hydraulic gradient \( (=\Delta h/\Delta x \text{ or } = \Delta h/\Delta L) \) [-]

\( \text{IAP} \) ion activity product [-]

\( k \) permeability of the porous medium (only in section 2.1) [m\(^2\)]

\( k' \) homogeneous rate constant \( [\text{mol} \, \text{L}^{-1} \, \text{s}^{-1}] \)

\( k' \) reaction constant of Fe(III)-surface-species \( [\text{mol} \, \text{L}^{-1} \, \text{s}^{-1}] \)

\( k^* \) pH-dependent overall reaction rate constant after Millero (1985) [s\(^{-1}\)]

\( K \) hydraulic conductivity of a porous medium \( [\text{m} \, \text{s}^{-1}] \)

\( k_1 \) reaction constant as defined by Stumm and Lee (1961) \( [\text{L}^2 \, \text{mol}^{-2} \, \text{atm}^{-1} \, \text{min}^{-1}] \)

\( k_0', k_1', k_2' \) oxidation reaction constant of different dissolved Fe(II) species [s\(^{-1}\)]

\( K_{\text{IL}, \text{III}} \) K-value in piezometric evaluation sections I to S III \( [\text{m} \, \text{s}^{-1}] \)

\( K_{\text{I}} \) primary hydrolysis constant \( [\text{mol} \, \text{L}^{-1}] \)

\( K_{\text{ads}} \) adsorption constant [-]

\( K_{\text{H}} \) Henry’s distribution coefficient \( [\text{mol} \, \text{L}^{-1} \, \text{atm}^{-1}] \)

\( K_{\text{S}} \) solubility product [-]

\( k_{\text{S,0}} \) specific rate constant of Fe(II)-surface-species \( [\text{L} \, \text{mol}^{-1} \, \text{s}^{-1}] \)

\( K_w \) intrinsic dissociation constant of water \( [\text{mol} \, \text{L}^2] \)

\( L \) length [m]

\( L_{\text{AS}} \) vertical length of the annular space [m]

\( L_{\text{cap}} \) length of the capillary [m]

\( L_{\text{cell}} \) length of the PhreeqC-model cell [m]

\( \Delta L_{\text{cell}} \) length of the gravel pack cell [m]

\( L_{\text{col}} \) length of the column [m]

\( L_{\text{FP}} \) total length of the filter pack in flow direction in the flow channel [m]

\( L_{\text{slit}} \) length of the slit in flow direction [m]

\( L_{\text{SP}} \) vertical length of the screen pipe [m]

\( \text{LOI} \) loss of ignition [wt.-%]

\( m(X) \) mass of element X [g]

\( M(X) \) molar mass of element X \( [\text{g} \, \text{mol}^{-1}] \)

\( m_i(PV) \) mass flow of element i per exchanged pore volumes \( [\text{g} \, \text{PV}^{-1}] \)

\( m_i(t) \) mass flow of element i per time \( [\text{g} \, \text{s}^{-1}] \)

\( m_{\text{gravel}} \) total mass of gravel in the column [g]

\( m_{\text{in}} \) total mass of tracer injected [mg]

\( n \) porosity [-]

\( n(X) \) molar amount of substance X [mol]

\( n_e \) flow effective porosity [-]

\( n_{e, H} \) flow effective porosity, calculated after Helmbold (cf. section 2.2.1) [-]

\( n_{e, M} \) flow effective porosity, calculated after Marotz (cf. section 2.2.1) [-]

\( p(X) \) partial pressure of gas phase X [atm]

\( p_e \) negative decadic logarithm of the “electron activity” \( a(e^-) \) [mol \, L^{-1}]

\( pH \) negative decadic logarithm of the proton activity \( a(H^+) \) [-]

\( p_{\text{IC}} \) pressure in the inflow chamber [mmH\(_2\)O]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pOH</td>
<td>negative decadic logarithm of the dissolved hydroxide activity ( a(\text{OH}^-) )</td>
<td>[-]</td>
</tr>
<tr>
<td>PV(t)</td>
<td>time-dependent number of pore volumes exchanged</td>
<td>[-]</td>
</tr>
<tr>
<td>q</td>
<td>specific flow rate per unit cross-sectional area</td>
<td>([\text{m s}^{-1}])</td>
</tr>
<tr>
<td>Q</td>
<td>rate of flow or groundwater abstraction</td>
<td>([\text{m}^3 \text{s}^{-1}])</td>
</tr>
<tr>
<td>( Q_{uc} )</td>
<td>rate of addition of Fe-stock solution</td>
<td>([\text{mL min}^{-1}])</td>
</tr>
<tr>
<td>( Q_{sys} )</td>
<td>system flow rate</td>
<td>([\text{L min}^{-1}])</td>
</tr>
<tr>
<td>( r )</td>
<td>radial distance from the well</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( \Delta r )</td>
<td>difference of the radial distance from the well</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( R )</td>
<td>ideal gas constant</td>
<td>([\text{J K}^{-1} \text{mol}^{-1}])</td>
</tr>
<tr>
<td>( r_{BH} )</td>
<td>radius of the borehole</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( r_{cap} )</td>
<td>radius of the capillary</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( \text{Re} )</td>
<td>Reynolds number</td>
<td>[-]</td>
</tr>
<tr>
<td>( r_{slit} )</td>
<td>width (aperture) of the slit perpendicular to flow</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( r_{ox} )</td>
<td>oxidation rate of Fe(II)</td>
<td>([\text{mol L}^{-1} \text{min}^{-1}])</td>
</tr>
<tr>
<td>( r_{SP} )</td>
<td>radius of the screen pipe</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( r_{WC} )</td>
<td>radius of the well casing</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( s(\text{FeII}) )</td>
<td>percental mass fraction of Fe(II) on Fe_total (= Fe_i + Fe_ii)</td>
<td>[%]</td>
</tr>
<tr>
<td>( s(fh) )</td>
<td>percentage of ferrihydrite (fh) of the total Fe-phases</td>
<td>[%]</td>
</tr>
<tr>
<td>( s(O_2, \text{atm}) )</td>
<td>percentage of gaseous oxygen in the air</td>
<td>[%]</td>
</tr>
<tr>
<td>( S_I )</td>
<td>saturation index</td>
<td>[-]</td>
</tr>
<tr>
<td>( t )</td>
<td>time</td>
<td>([\text{s, [h]}])</td>
</tr>
<tr>
<td>( \Delta t )</td>
<td>time step</td>
<td>([\text{s, [h]}])</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
<td>([\text{°C}])</td>
</tr>
<tr>
<td>( t_{0.5} (= t_{med}) )</td>
<td>average flow duration or median transport time</td>
<td>([\text{s}])</td>
</tr>
<tr>
<td>( t_{abs} )</td>
<td>absolute temperature</td>
<td>([\text{K}])</td>
</tr>
<tr>
<td>( \text{TC} )</td>
<td>total carbon (TIC+TOC)</td>
<td>([\text{wt.-%}])</td>
</tr>
<tr>
<td>( t_{cell} )</td>
<td>estimated residence time of the water in the model cells</td>
<td>([\text{s}])</td>
</tr>
<tr>
<td>( \text{TOC} )</td>
<td>total inorganic carbon</td>
<td>([\text{wt.-%}])</td>
</tr>
<tr>
<td>( \text{U} )</td>
<td>uniformity coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>( v )</td>
<td>flow velocity</td>
<td>([\text{m s}^{-1}])</td>
</tr>
<tr>
<td>( V )</td>
<td>volume</td>
<td>([\text{m}^3])</td>
</tr>
<tr>
<td>( V(X) )</td>
<td>total volume of element X</td>
<td>([\text{m}^3])</td>
</tr>
<tr>
<td>( V_{Air} )</td>
<td>air filled volume</td>
<td>([\text{m}^3])</td>
</tr>
<tr>
<td>( V_{cell} )</td>
<td>total PhreeqC-model cell volume</td>
<td>([\text{m}^3])</td>
</tr>
<tr>
<td>( \Delta V_{cell} )</td>
<td>total gravel pack cell volume</td>
<td>([\text{m}^3])</td>
</tr>
<tr>
<td>( V_{col} )</td>
<td>total column volume</td>
<td>([\text{L}])</td>
</tr>
<tr>
<td>( v_{d} (= v_{med}) )</td>
<td>average flow distance velocity</td>
<td>([\text{m s}^{-1}])</td>
</tr>
<tr>
<td>( V_{e} )</td>
<td>flow effective pore volume</td>
<td>([\text{L}])</td>
</tr>
<tr>
<td>( V_{m} )</td>
<td>molar volume</td>
<td>([\text{m}^3 \text{ mol}^{-1}])</td>
</tr>
<tr>
<td>( v_{med} (= v_{d}) )</td>
<td>median transport velocity</td>
<td>([\text{m s}^{-1}])</td>
</tr>
<tr>
<td>vol.-%</td>
<td>per cent by volume</td>
<td>[%]</td>
</tr>
<tr>
<td>( V_{water} )</td>
<td>saturated cell pore volume</td>
<td>([\text{m}^3])</td>
</tr>
<tr>
<td>wt.-%</td>
<td>per cent by weight</td>
<td>[%]</td>
</tr>
<tr>
<td>( x )</td>
<td>distance</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>([X])</td>
<td>dissolved molar concentration of element or species X</td>
<td>([\text{mol L}^{-1}])</td>
</tr>
</tbody>
</table>

**Greek letters**
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_2^*$</td>
<td>secondary hydrolysis constant</td>
<td>[mol$^2$ L$^{-2}$]</td>
</tr>
<tr>
<td>$2\theta$</td>
<td>diffraction angle</td>
<td>[°]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength of light</td>
<td>[nm]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity of the fluid</td>
<td>[kg m$^{-1}$ s$^{-1}$]</td>
</tr>
<tr>
<td>$\nu$</td>
<td>kinematic viscosity of the fluid</td>
<td>[m$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_{fl}$</td>
<td>density of the fluid</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_{gravel}$</td>
<td>density of the gravel grains</td>
<td>[kg m$^{-3}$]</td>
</tr>
</tbody>
</table>

**Abbreviations**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdP</td>
<td>addition point</td>
</tr>
<tr>
<td>AF</td>
<td>aquifer</td>
</tr>
<tr>
<td>AM</td>
<td>aquifer material</td>
</tr>
<tr>
<td>AT</td>
<td>aquitard</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller surface area</td>
</tr>
<tr>
<td>bpγ</td>
<td>quartz brash and sands (Pliocene unit)</td>
</tr>
<tr>
<td>CCR</td>
<td>core cutter ring for undisturbed sampling</td>
</tr>
<tr>
<td>clog</td>
<td>clogging phase</td>
</tr>
<tr>
<td>(C)PVC</td>
<td>(chlorinated) polyvinyl chloride</td>
</tr>
<tr>
<td>D</td>
<td>Dorsfeld gravel</td>
</tr>
<tr>
<td>dg</td>
<td>coarse gravel (Pleistocene unit)</td>
</tr>
<tr>
<td>d$\lambda$/dg</td>
<td>&gt; 2 m confining loess-loam over main terrace gravel (Pleistocene unit)</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
</tr>
<tr>
<td>eC</td>
<td>electrical conductivity</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>ENR</td>
<td>enrichment</td>
</tr>
<tr>
<td>eva</td>
<td>evaluation phase</td>
</tr>
<tr>
<td>F</td>
<td>Frimmersdorf gravel</td>
</tr>
<tr>
<td>FC</td>
<td>flow channel</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>ferrous iron</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>ferric iron</td>
</tr>
<tr>
<td>FeOB</td>
<td>iron oxidising bacteria</td>
</tr>
<tr>
<td>FIBC</td>
<td>flexible intermediate bulk container (big bag)</td>
</tr>
<tr>
<td>FP</td>
<td>filter pack</td>
</tr>
<tr>
<td>GB</td>
<td>glass beads</td>
</tr>
<tr>
<td>GP</td>
<td>gravel pack</td>
</tr>
<tr>
<td>GRP</td>
<td>glass fibre reinforced plastic</td>
</tr>
<tr>
<td>H</td>
<td>heavy mineral fraction</td>
</tr>
<tr>
<td>HFO</td>
<td>hydrous ferric oxide</td>
</tr>
<tr>
<td>Hz.</td>
<td>geologic horizon after Schneider and Thiele (1965)</td>
</tr>
<tr>
<td>IAP</td>
<td>ion activity product</td>
</tr>
<tr>
<td>IC</td>
<td>inflow chamber</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>inductively-coupled-plasma mass-spectrometry</td>
</tr>
<tr>
<td>ID</td>
<td>inner diameter</td>
</tr>
<tr>
<td>InP</td>
<td>inflow pump</td>
</tr>
<tr>
<td>LTT</td>
<td>long term test</td>
</tr>
<tr>
<td>LOI</td>
<td>loss of ignition</td>
</tr>
<tr>
<td>MC</td>
<td>measurement cell</td>
</tr>
</tbody>
</table>
MI main ions
NaN not a number
NDA no data available
nq not quantified
OC outflow chamber
OutP outflow pump
P1, P2, P3 pressure measurement point in the gravel pack of the flow channel
PM polarisation microscopy
PMMA Polymethylmethacrylate (colloquial term: acrylic glass)
PSD position sensitive detector
PTFE Polytetrafluoroethylene
PV pore volume
Qz. quartz
ref reference test/reference situation
S I hydraulic evaluation section S I
S II hydraulic evaluation section S II
S III hydraulic evaluation section S III
SEM scanning electron microscope
SEP sequential extraction procedure
SI saturation index
SP screen pipe
spp. biological species
SSP shortened screen pipe
TC total carbon
TIC total inorganic carbon
TNT trinitrotoluene
TOC total organic carbon
UV ultraviolet lamp
W Weilerswist gravel
WC well casing
XRD X-ray diffractometry
XRF X-ray fluorescence
2L/6L 2-line or 6-line ferrihydrite
1 Introduction

Pumping groundwater by use of vertical filter wells is widely accepted as one of the most reliable concepts to sustainably cover the daily demand for high quality drinking water. Compared to surface waters, groundwater in general can more easily be protected from anthropogenic interferences like industrial, agricultural or urban pollution (Schmoll et al., 2006). Thus, the use of groundwater for drinking water production is of equal interest to industrial and developing countries.

In 2010, a 78.1 % share of the total drinking water supply of Germany was produced by use of groundwater wells (including artificial groundwater recharge and bank storage water), corresponding to around 4 billion m³ of drinking water (German Federal Ministry of Health (BMG) & Umweltbundesamt (UBA), 2011; Hagenkort-Rieger & German Federal Statistical Office, 2012). On a world wide scale, the importance of groundwater abstraction and especially its use for agricultural irrigation purposes has increased in recent years, as several major international organisations agree (e.g. United Nations Educational, Scientific and Cultural Organization (UNESCO): van der Gun & UNESCO, 2012; Food and Agriculture Organization of the United Nations (FAO): Siebert et al., 2010; World Health Organization (WHO): Schmoll et al., 2006).

All over the world, vertical filter wells are used for a wide range of purposes, most importantly for a sustainable supply of high-quality groundwater, but also for artificial groundwater recharge, groundwater remediation and local dewatering of aquifers for huge mining facilities or small construction projects.

The German and international lignite mining industry is one example for a branch of economy that requires reliable operation of a huge number of dewatering and reinjection wells. In Germany, lignite is mined in four open- cast districts (Figure 1), all of which have a need to locally dewater aquifers to keep the open-pits dry.

Compared to the Lusatian, Central German or Helmstedt district, the Rhenish district has the highest capacity of production in respect to actual and capacitive lignite extraction as well as power generation (Deutscher Braunkohlen-Industrie-Verein e.V. (DEBRIV) – Bundesverband Braunkohle, 2013a), even though it occupies a comparatively small area (Rhenish district: 9,180 ha, Helmstedt: 1,140 ha, Lusatia: 31,200 ha, Central Germany: 11,050 ha; Statistik der Kohlenwirtschaft e.V., 2012). Operating at up to 400 m below ground surface, the open-pit Hambach in the Rhenish district is the deepest open-pit in Germany, producing 40 million tons of lignite per year (RWE Power AG, 2013). Even the open-pit Inden – the smallest of the Rhenish district – has a higher production capacity (21.3 Mt) than the open-pit Welzow-Süd (19.7 Mt) – the biggest open-pit of all the other German lignite districts (Statistik der Kohlenwirtschaft e.V., 2013).
In 2011, Germany was the world leader in lignite production with an overall production of 176.4 million tons, accounting for more than one third of the whole European production (Table 1; Statistik der Kohlenwirtschaft e.V., 2012), followed by China, the Russian federation, Turkey, the USA, Australia, Poland, Greece, the Czech Republic and India. However, when considering black coal, the situation of course is dramatically different (Table 1).

Table 1  
Lignite production by country (other countries < 50 million tons; Statistik der Kohlenwirtschaft e.V., 2012). 1) plus CIS, NDA: no data available

<table>
<thead>
<tr>
<th>Country</th>
<th>Lignite production [Mt]</th>
<th>Black coal production [Mt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>176.4</td>
<td>13.0</td>
</tr>
<tr>
<td>China</td>
<td>136.3</td>
<td>3334.7</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>77.6</td>
<td>429.2 1)</td>
</tr>
<tr>
<td>Turkey</td>
<td>74.4</td>
<td>3.7</td>
</tr>
<tr>
<td>USA</td>
<td>73.4</td>
<td>930.7</td>
</tr>
<tr>
<td>Australia</td>
<td>69.5</td>
<td>344.8</td>
</tr>
<tr>
<td>Poland</td>
<td>62.8</td>
<td>76.4</td>
</tr>
<tr>
<td>Greece</td>
<td>58.8</td>
<td>NDA</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>42.9</td>
<td>11.5</td>
</tr>
<tr>
<td>India</td>
<td>41.3</td>
<td>544.6</td>
</tr>
<tr>
<td>Indonesia</td>
<td>NDA</td>
<td>376.2</td>
</tr>
<tr>
<td>South Africa</td>
<td>NDA</td>
<td>253.1</td>
</tr>
<tr>
<td>Columbia</td>
<td>NDA</td>
<td>83.8</td>
</tr>
<tr>
<td>Europe</td>
<td>514.0</td>
<td>132.5</td>
</tr>
<tr>
<td>World</td>
<td>1071.3</td>
<td>6612.5</td>
</tr>
</tbody>
</table>
To keep groundwater from flooding the open-pits and to ensure stability of the embankment, intersected and excavated aquifers need to be continuously dewatered in the near-field of the open-pits, while keeping the effects on other uses of groundwater and on ecological systems as low as possible. As in the Rhenish lignite district, this is most often achieved by galleries of vertical filter wells that abstract groundwater in close vicinity and inside the open-pits and reinjecting the water near the ecologically or socioeconomically relevant areas, if necessary after processing. To accomplish dewatering in the surroundings of the three huge open-pits of the Rhenish district, an average of 180 boreholes for dewatering wells are drilled each year up to 700 m deep into the unconsolidated rock, reaching a cumulative length of 35,000 drilling meters with a diameter of up to 1.5 m (RWE Power AG, 2012). Additionally, 140 boreholes with a cumulative length of 25,000 drilling meters with smaller diameters (around 0.3 m) are drilled each year for exploration or to install monitoring wells (RWE Power AG, 2012). To manage the discharge of the water pumped from the aquifers, pipelines with a length of 750 km and a diameter of up to 2 m are needed. Around 1,500 dewatering wells in the Rhenish district pump around 580 million cubic meters of water up from the Tertiary and Quaternary aquifers (RWE Power AG, 2012). Of course, this huge network of water resources management exceedingly depends on the performance of all the system elements. Even small losses in efficiency of a specific kind of system element can have a huge influence on energy consumption and necessary financial expenses for operation and maintenance of the whole system. Thus, the operation of a large number of wells that are very sensitive regarding effects of well loss and well ageing poses economic risks to the mining company.

The term “well loss” summarises several phenomena that affect the performance of a well, including flow resistances in the different media (aquifer, gravel pack, screen pipe, pump inlet) as well as transition resistances between these media (skin effects) and flow velocities and conditions (turbulent vs. laminar flow) at any point along the flow path. With a higher flow and transition resistance in the filter pack, the hydraulic gradient in the vicinity of the well needs to be increased in order to maintain a constant amount of water extracted from the aquifer. This most often is accomplished by increasing drawdown in the well, which also will result in water having to be lifted up from a greater depth. In general it can be said that all these effects lead to higher expenditure of energy and thus money. While some phenomena of well loss are time independent, others deteriorate the situation over time and can be considered causes of “well ageing”. Due to these processes, the hydraulic conductivity of the flow-media decreases over time or, in other words, their flow or transition resistance and thus energetic and monetary expenditure increases. The individual phenomena of well loss and well ageing will be described in detail in section 0. This thesis will focus on chemical clogging of system elements of dewatering wells with Fe(III)-minerals, the main phenomenon of well ageing.

1.1 Former and current studies on well loss and well ageing

Considering the number of projects conducted in and around Germany during the last decades, the high importance of topics like well performance and ageing processes becomes obvious. The following listing of projects cannot be considered complete, but addresses major German and European research groups that have been working on the subject of well clogging.
in a similar environment to the one addressed in this thesis over the last few decades and tries to give a short summary of their projects’ main focus areas. Many of their results will be used in the literature review and the results and discussion chapter.

In the metropolitan area of Berlin, first considerations about biologically induced Fe-clogging of wells were published in the early 1960ies by Krems of the “Berliner Wasserbetriebe” (BWB), the public water resources management authority of Berlin (Krems, 1961, 1972, 1980). In the year 2000 the “Berliner Wasserbetriebe” was partially privatised and the Berlin Centre of Competence for Water (Kompetenzzentrum Wasser Berlin, KWB) was founded to continue their work (Strauch, 2001). Their first project regarding well ageing and clogging with ferric mineral incrustations was initiated in 2007 in the context of optimising well operation management (WellMa-1; Schwarzmüller et al., 2011). It was continued by a follow-up project in 2009 (WellMa-2; Orlikowski et al., 2010), consisting of a huge survey of 399 German companies in drinking water supply, with a questionnaire concerning well ageing, possible influencing factors, regeneration and criteria for regeneration (monitoring strategy). Besides other projects on economic optimisation of well and well field operation strategies (OptiWells-1 and OptiWells-2; Staub, 2012 and Staub et al., 2012) and oxidative removal of organic compounds from the aqueous phase in bank filtration by adjusting the redox-potential (OxiMAR; Staub, 2011), a new project concerning well ageing and especially biological clogging with Fe(III)-minerals was initiated recently. The project “ANTIOCKER” that is funded by the German Federal Ministry of Education and Research (BMBF) was initiated in 2011 and is being carried out in cooperation with a considerable number of research institutions, including the Technical University of Berlin (TUB), the Berlin Center of Competence for Water, the “Berliner Wasserbetriebe”, the Friedrich Schiller University of Jena (FSU), the University of Duisburg/Essen and the University of Applied Science of Dresden as well as an institute for scientific photography and a company for engineering consulting (Szewzyk, 2011, Schwarzmüller & Sperlich, 2011).

Well ageing processes and their prevention or restoration of well capacity were also intensely investigated by a team from the German Federal Institute for Geosciences and Natural Resources in Hanover (Bundesanstalt für Geowissenschaften und Rohstoffe, BGR) led by Dr. Georg Houben and Prof. Dr. habil. Christoph Treskatis of the consulting engineers “Bieske und Partner”, (Treskatis & Nillert, 2009). The group works in close cooperation with economic partners like the cleanwells GbR who offer commercial well regeneration measures (Houben et al., 2000a, Houben et al., 2000b, Treskatis et al., 2000a, 2000b, Weihe, 2000, Treskatis, 2003) or the Sigmund Lindner GmbH who produce glass beads for technical applications like glass bead filter packs (Treskatis et al., 2009, 2010, Treskatis, 2011, Klaus & Walter, 2011, 2012, Klaus, 2013). Besides several publications regarding spatial distribution of ochreous incrustations in groundwater wells (Houben & Weihe, 2004, Houben, 2006, Houben & Weihe, 2010), their mineralogy (Brauckmann et al., 1990, Houben et al., 1999, Houben, 2003a), their solubility in different acids (Houben 2003b) and their influence on the water quality (Houben, 2002, Houben, 2003a), this group also published two books on water well rehabilitation and reconstruction (Houben & Treskatis, 2007, Houben & Treskatis, 2012). Some of their other publications focus on modelling the near-well flow-field (Houben & Hauschild, 2011) and the build-up of Fe-incrustations (Houben, 2004).
Another recent project concerning the development of a Fe-clogging and -corrosion-sensor (FeQuan) promoted by the European Union (Ruck & Opel, 2009) was conducted at the Institute of Sustainable and Environmental Chemistry (ISEC) of the Leuphana University of Lüneburg (Opel & Liñares, 2007, Opel et al., 2008, Opel et al., 2009, Opel, 2012). One prototype of the sensor has been developed and optimised in cooperation with the Franatech GmbH Lüneburg and the Celler Brunnenbau GmbH (Ruck & Opel, 2009). The process of national, European and international patent registration was initiated in August 2010 (Leuphana University Lüneburg et al., 2010).

Maximising well yield is also of interest to other European states, like Poland (Polak et al., 2011, Polak & Kaznowska, 2010), France (Larroque & Franceschi, 2011), and especially the Netherlands. As clogging of groundwater wells is a major issue there, just like in northern Germany (Weihe, 2000), scientists from the universities of Amsterdam (van Beek et al., 2009, van Beek, 2010, Medina et al., 2013), Delft (van Beek et al., 2006, de Zwart et al., 2006, de Zwart, 2007) and Wageningen (van Beek et al., 2010, van Beek et al., 2012) are working together with the KWR Water Research Institute of Nieuwegein (KWR, formerly KIWA Water Research) and other project partners like the water utility Vitens N.V. of Lelystad and the Water Utility WMU of Maastricht (e.g. van Beek et al., 2012). In 30 years of research on the subject of well ageing and regeneration (van Beek & Kooper, 1980, van Beek & van der Kooij, 1982), the group has identified two types of well clogging in well fields distributed throughout the Netherlands – the mechanical well bore clogging and the chemical screen slot clogging (van Beek, 1984, 1995) – and has developed methods for prevention or regeneration of both of the clogging types (van Beek et al., 2006, de Zwart et al., 2006, van Beek et al., 2009).

### 1.2 History of the MaxWell Project

As this dissertation is to be considered part of the MaxWell-Project that had been initiated by the RWE Power AG in cooperation with RWTH Aachen University and as some of the results described herein have already been composed as project reports, the history of the whole project and all its contributors shall be briefly explained in this section.

The collaboration concerning well optimisation between RWTH Aachen and RWE Power AG started with the PhD project of Dr. Wiebke Klauder with her dissertation on conditions of hydraulic flow towards vertical filter wells at the Institute of Hydraulic Engineering and Water Resources Management (IWW) of RWTH Aachen University (Klauder, 2010). Here, different well assembling materials for the dewatering wells of the Rhenish lignite district like filter media and screen pipes were tested in an experimental model for their hydraulic performance and their relative contributions to overall well loss. Lots of different parameters of the assembling materials like grain size and surface condition of the filter pack medium and the type of screen tube were varied in order to characterise their influence on well loss. Apart from that, several hydraulic conditions from laminar to turbulent flow regime were also tested to find the optimal assemblage and mode of well operation, specifically for the dewatering wells of the Rhenish lignite district (Klauder, 2010).

After these explicitly technically controllable parameters of well assemblage and operation had been described holistically and their optimisation had been finished, effects of well loss
and ageing that naturally occur during drilling and well operation were yet to be considered. Thus, in 2008, the project MaxWell (Maximising Well Yield) was initiated by the RWE Power AG, in cooperation with the Institute of Hydraulic Engineering and Water Resources Management (IWW) of RWTH Aachen University.

In the first phase of the project, an extensive literature study on Fe-clogging was conducted by the IWW together with the Institute of Applied Polymer Chemistry (IAP) of FH Aachen University of Applied Sciences. The results were composed as a report of project phase I. Any results and statements in this thesis that are taken from that report will be referred to as “final report phase I, 2008”.

Based on this literature study, the IWW and RWE Power AG planned the development of a hydraulically and hydrochemically combined experimental model of a well screen section, to realistically simulate the natural processes of Fe-clogging in vertical filter wells under controlled and accelerated laboratory conditions. This is when the Institute of Hydrogeology (LFH) of RWTH Aachen University joined as a project partner to assist with hydrochemical component of the model. Conceptual development and construction of the experimental model by IWW and LFH took from June 2009 to October 2010 (Henkel, 2010, Milatz, 2010, Rüde et al., 2010). At that time, the author of this thesis joined the project team from sides of the LFH, so the optimisation of model operation was mainly conducted by Sebastian Henkel, Dr. Wiebke Klauder and Christoph Weidner. In April 2011, IWW and LFH composed a first interim report of project phase II, describing the components of the model and defining necessary cycles of measurement and regulation of hydrochemical parameters to establish a controlled progress of Fe-clogging in the model. Any results and statements in this thesis that are taken from that report will be referred to as “interim report phase II, 2011”. In the final report of phase II in December 2011, the influences of distinct hydraulic and hydrochemical parameters on the laboratory simulation of Fe-clogging were added to the interim report. The build-up and spatial distribution of the incrustations were described qualitatively and a concept for model operation to produce and quantitatively evaluate the effect of Fe-incrustations on the hydraulic situation was proposed (see also Weidner et al., 2011, Henkel et al., 2012, Weidner et al., 2012a, Weidner et al., 2012b). Any results and statements in this thesis that are taken from the final report of project phase II will be referred to as “final report phase II, 2011”.

As the model was now finally ready to produce and quantitatively evaluate the effects of Fe-clogging on well loss, different settings of well assembling materials and operation modes were tested for their clogging affinity in a third project phase from January 2012 to June 2013 (Weidner et al., 2013). The incrustations produced in the model were compared with samples, taken in the field from well, excavated in the open-pit with several analytical laboratory methods. One tested operation mode with avoiding screen pipe aeration proved successful to prevent the build-up of incrustations in the gravel pack and was transferred to the field scale in three test wells and has become a new regular construction method in the Rhenish mining district also as a result of the research shown in this thesis. Any results and statements in this thesis that are taken from the final report of project phase III will be referred to as “final report phase III, 2013”.

22
As the Fe-clogging affinity of different gravel materials could be assessed with the experimental model, their other hydrogeochemical interactions with the water (mineral dissolution and release of certain elements) still had to be evaluated. For that reason, the materials were tested for their long term elution in tap water in five simultaneous column experiments (Weidner et al., 2013). The results of these experiments were composed to a project report, so any results and statements in this thesis that are taken from this report will be referred to as “report long term elution, 2012”.

The transfer of the model results to the field was conducted by RWE Power AG and LFH in form of two master theses. Firstly, in his thesis, Matthias Metzger did a large hydrochemical and microbiological survey of wells affected or unaffected by Fe-clogging, especially focusing on different types of water and their affinity towards different types of Fe-clogging as well as the effectiveness and sustainability of methods of well regeneration (Metzger, 2011). Secondly, the functionality of the well assembling concept to prevent oxygen from entering the gravel pack in multi-layered aquifer dewatering that had been developed as a result of project phase III was evaluated with tracer tests at the three test wells by Jana Milatz in her master thesis (Milatz, 2013) and additionally composed to a project report. Any results and statements in this thesis that are taken from this project report will be referred to as “report annular space dewatering, 2013”. Especially the topic of annular space dewatering and its optimisation still is part of on-going follow-up research projects between RWE Power AG and LFH.

### 1.3 Aims and scope of this thesis

As described in section 1.1, there are a considerable number of projects and research groups focusing on topics of well loss and ageing. In all of these projects, different theories for parameters affecting the progress of clogging with Fe(III)-minerals have been proposed in the past. However, all these theories are based on hydraulic and hydrochemical measurements from the ground surface, theoretical simulations or laboratory experiments that are not consistent with the actual subsurface situation.

The project described in this thesis is the first to realistically simulate the hydraulic-hydrochemical situation in an unscaled and realistic experimental laboratory model of a well screen section, combining the hydraulic situation in several settings of well assemblage with different hydrochemical settings. As these two disciplines may interfere with each other – or are even bound to interfere with each other in the model – this combination poses extraordinary challenges on measurement and regulation in the model. Additionally, the progression of Fe-incrustation build-up in a vertical filter well was made optically visible for the first time in a realistic laboratory reconstruction of a well screen section in a transparent PMMA flow channel.

Through the cooperation with the RWE Power AG sampling the gravel pack of actual wells in the field that are affected by Fe-clogging was made possible, as wells in the field of the open-pits are excavated with advancing lignite exploitation. This offers the unique opportunity of comparing the spatial distribution, intensity and type of incrustations produced in the model to those actually found in the field as a means of validation of the Fe-clogging model.
There are several sets of questions about the development of Fe-incrustations and the progress of Fe-clogging or related subjects that were addressed within this thesis:

**Question 1** What are the relevant controlling parameters for distribution, intensity and type of Fe-incrustation in the vicinity of a well?

**Question 2** Can the naturally occurring Fe-clogging process be representatively reproduced in the laboratory by means of the proposed experimental model?

**Question 3** How will the progression of Fe-clogging develop with time? Will it decelerate, remain constant or accelerate itself (autocatalytically) with time (Figure 2)?

**Figure 2** Possible temporal progressions of the hydraulic conductivity with increasing Fe-clogging time *(final report phase III, 2013, redrawn, translated)*

**Question 4** Does the type of filter material affect the interaction with the groundwater with respect to mineral dissolution and precipitation? Will the type or intensity of Fe-incrustations depend upon initial contents of hydroxic Fe(III)-minerals or the specific surface area of the filter medium?

**Question 5** How does the aeration of the screen pipe proceed? What is the distribution and direction of flow paths of air and water? In which way and how quickly does filter aeration affect the progression of Fe-clogging?

**Question 6** Can dewatering of multi-layered aquifers be established through wells with only one deep screen pipe in the lower aquifer and dewatering the upper aquifer through the annular space between borehole and well pipe?

In the following sections, the exploration of these questions will be described after a summary of an extensive literature review. The answers to these questions will be given in the conclusions section 6.
2 Theoretical Background

2.1 Groundwater flow and hydraulics in porous media

Water in the subsurface can be classified according to its appearance. There are several types of water that do not contribute to a pressure-driven groundwater flow and thus need to be distinguished from actual groundwater. According to Zunker (1930), water in the underground may occur in form of percolating, hygroscopic (or adsorbed) water, adhesive water, capillary water, groundwater and vapour in the soil air. Hygroscopic, adhesive and capillary water is held against gravity by electrostatic attractive forces of the soil particles or the surface tension of the water. Only below the closed capillary fringe are the pores actually filled with groundwater, and contribute to hydrostatic pressure (Langguth & Voigt, 2004).

Flow of groundwater is induced by the general tendency towards compensation of the potential energy of the water. According to the Bernoulli-equation, the potential energy of incompressible, slowly moving water can be expressed by its hydraulic head above a reference altitude or a hydrostatic overpressure, when free ascension of the water is hindered by a confining layer (Langguth & Voigt, 2004).

According to Darcy (1856) the flow rate in terms of volume per time in porous media depends on the pressure (or hydraulic head) difference between two points and the hydraulic conductivity of the material in-between. This is in analogy to the flow of electrical currents, with the voltage representing the pressure difference (driving force) and the electrical resistivity representing the inverse of the hydraulic conductivity. Considering geometrical circumstances, Darcy’s law can be expressed as follows:

\[ Q = K \cdot \frac{(h_2-h_1)}{L} \cdot A = K \cdot i \cdot A = q \cdot A \] (1)

with \( Q \) = flow rate \([m^3 s^{-1}]\), \( K \) = hydraulic conductivity of the porous medium \([m s^{-1}]\), \( h_2-h_1 \) = pressure difference between point 2 and 1 \([m]\) with \( h_2 > h_1 \) and thus flow direction from point 2 to point 1, \( L \) = length of the flow path between point 2 and 1 \([m]\), \( A \) = cross-sectional area perpendicular to groundwater flow \([m^2]\), \( i \) = hydraulic gradient (inclination of the water table or the pressure head in the direction of flow) \([-]\) and \( q \) = specific flow rate per unit cross-sectional area \([m s^{-1}]\) (Sterrett, 2007). The hydraulic conductivity \( K \) ranges between \(10^0\) and \(10^3\) m s\(^{-1}\) for coarse to fine gravel, between \(10^{-4}\) and \(10^{-7}\) m s\(^{-1}\) for sandstone or coarse to fine sand, between \(10^{-6}\) to \(10^{-9}\) m s\(^{-1}\) for silt, loess and unfractured limestone and between \(10^{-9}\) and \(10^{-12}\) m s\(^{-1}\) for clay, shale and unfractured igneous and metamorphic rocks (Sterrett, 2007).

To abstract groundwater from an aquifer, the hydraulic gradient can be created artificially by means of groundwater wells. In an ideal case, the amount of groundwater abstracted (Q) is directly proportional to the hydraulic gradient i and can be increased by drawing down the pressure head \( h_1 \) in the well (cf. section 2.2.3).

Of course the hydraulic conductivity of a porous medium is still a function of the properties of the fluid, like its density and viscosity which vary due to temperature or concentrations of
dissolved compounds and types of fluid (e.g. water, gas or oil). To transfer the hydraulic conductivity of a solid/fluid-system to a technical material property of the porous medium, the permeability \( k \) of the porous medium can be calculated by:

\[
k = \frac{K \mu}{\rho g} = \frac{K_v}{g}
\]

with \( k = \) permeability of the porous medium \([\text{m}^2]\), \( K = \) hydraulic conductivity of the specific solid/fluid-system \([\text{m} \text{s}^{-1}]\), \( \mu = \) dynamic viscosity of the fluid \([\text{kg} \text{m}^{-1} \text{s}^{-1}]\) = \( \rho \nu = \) product of the density of the fluid \( \rho \) \([\text{kg} \text{m}^{-3}]\) and the kinematic viscosity of the fluid \( \nu \) \([\text{m}^2 \text{s}^{-1}]\), \( g = \) gravitational acceleration \([\text{m} \text{s}^{-2}]\) (Sterrett, 2007).

As mentioned above, these simplifications of the theories of Bernoulli and Darcy are only valid, when groundwater movement does not become too fast. At high hydraulic gradients, increased flow velocities may lead to turbulent flow resulting in an additional dissipation of energy and thus invalidating the linearity of Darcy’s law. The applicability of Darcy’s law can be checked by calculating the Reynolds number, which is commonly used to describe the current flow regime:

\[
Re = \frac{q \cdot d_{\text{char}}}{\nu} = \frac{q \cdot d_{\text{char}} \rho}{\mu}
\]

with \( Re = \) Reynolds number \([-]\), \( q = \) specific flow rate per unit cross-sectional area \([\text{m} \text{s}^{-1}]\), \( d_{\text{char}} = \) characteristic grain size of the porous medium \([\text{m}]\), \( \nu = \) kinematic viscosity of the fluid \([\text{m}^2 \text{s}^{-1}]\), \( \rho = \) density of the fluid \([\text{kg} \text{m}^{-3}]\) and \( \mu = \) dynamic viscosity of the fluid \([\text{kg} \text{m}^{-1} \text{s}^{-1}]\) (Reynolds, 1883, Hantush, 1964, Burchardt & Andersen, 1995, Langguth & Voigt, 2004, Klauder, 2010). Going back to the work of Reynolds (1883), Hantush (1964) was one of the first to apply calculation of the Reynolds number to flow in porous media (Langguth & Voigt, 2004). Above a value of around \( Re = 1…10 \) (Hantush, 1964, Bear, 1988, Şen, 1989, 1990), dependency of the flow from the hydraulic gradient starts to increasingly deviate from the linear law of Darcy (1856).

### 2.2 Design and operation of vertical filter wells

#### 2.2.1 Dewatering well installation, screens and casing

To install dewatering wells in the Rhenish lignite district, the “air lift drilling” method is commonly applied to guarantee the stability of the borehole even when drilling huge diameter boreholes (up to 1500 mm), reaching down several hundred meters through unconsolidated rock and coal layers. To accomplish this, a continuous hydraulic pressure, at all times exceeding the active earth pressure is achieved by a reversed fluid cycle with pressurised air injected into the rod, lifting the water and cuttings upward inside the drilling rod (RWE Power AG, 2012, Sterrett, 2007). In the Rhenish district, pure water without additives is commonly used as a drilling fluid.

When the borehole is completed, the actual construction of the well can begin. The main underground system elements of a vertical filter well are the screen pipe (SP) and well casing.
(WC), filter pack (FP) and fill materials for the annular space between borehole surface and casing like annular seals and annular filling material as well as the pump and rising pipe.

One of the first things to consider is the type of casing and screen tube. In a broader perspective, in the past, the casing and screen pipes often were made from ordinary steel, but soon proved very sensitive towards corrosion effects. So, chemically more inert materials were considered, ranging from low carbon steel and diverse types of stainless steel and nickel-based alloys (e.g. Mogg, 1972, McGillicuddy, 2013) over plastics like (chlorinated) polyvinyl chloride ((C)PVC) and glass fibre reinforced plastic (GRP) to PTFE-coated materials (Sterrett, 2007), polyethylene (Sass et al., 2012) or epoxy resin-glued gravel screens (“prepacked screens” Bieske et al., 1998).

There are also several variations of the filter screen design and the geometry of the slots or open area for the water to pass into the well tube. For example, slotted screens, including bridge slot or louvered screens were produced by cutting or stamping vertical or horizontal slots into a steel or GRP pipe (Sterrett, 2007, Figure 3a, b). However, as the near-well flow-field is distorted in the vicinity of such slot screens, well loss can be reduced by using continuous slot screens with horizontal slots enveloping the whole circumference of the well tube (Bieske et al., 1998). These can either be realised by welding a wire spiralling around several supporting rods arranged in a circle (Johnson screen or wire wrapped screen, Figure 3d) or by attaching discs to supporting rods (disc screen, Figure 3e, Klauder, 2010). In consideration of the amortisation period of a high quality material, the choice of well screen and associated investment costs largely depend on the purpose and planned service life of the well.

Due to their homogeneous distribution of a huge number of irregular pores, a homogeneous near-well flow-field can also be achieved by using prepacked screens, preferably omitting an inner screen tube. This can be accomplished by only supporting the stability of epoxy-resin-gravel only by vertical rods of GRP (prepacked GRP-rod screen, Figure 3c). As this type of screen pipe proved to exhibit the least degree of well loss (Klauder, 2010) and – in contrast to wire wrapped screens – to be uncritical during excavation with bucket wheel excavators (RWE Power AG), these prepacked GRP-rod screens nowadays are commonly used for installation of dewatering wells in the Rhenish lignite district and therefore for the investigations described in this thesis.

![Figure 3](image)
Figure 3 Screen pipes used in dewatering wells in the Rhenish lignite mining district; a: prepacked bridge slot screen, b: prepacked GRP-hole-tube screen, c: prepacked GRP-rod screen, d: wire-wrapped continuous slot screen, e: continuous slot disc screen (Klauder, 2010)
To prevent an increased well loss due to unnecessarily high flow resistances at the well screen, the open area of the screen should be evenly distributed over the whole length and circumference of the tube and its percentage should be as high as possible. However, many publications by Barker and Herbert (1992), Parsons (1994), Klauder (2010) and Houben and Hauschild (2011) suggest that effects of the type of screen pipe on well loss is barely measurable and plays a minor role in comparison to other well components. Still, the slot size of the well screen is important to allow for a proper development of the well and let fine particles pass the screen. While in Germany the slot size traditionally is chosen to be smaller than the smallest 5% of the filter pack grains, McGillicuddy (2013) recommends allowing the smallest 10 to 20% of the gravel pack grains to pass the screen slots in order to attain a higher permeability of the filter pack. Sterrett (2007) suggests selecting a slot size retaining 90% or more of the gravel pack.

### 2.2.2 Gravel pack and annular filling material

To ensure stability of intersected layers and the well itself, the annular space between the borehole and the casing or well screen needs to be filled up. Sections that are of no hydraulic importance and are constructed with a blank casing can either be backfilled with drill cuttings or filling material. When penetrating multiple aquifers, annular seals of impermeable clay or cement have to be installed at the depths of naturally confining layers, in order to avoid artificial hydraulic connection of two aquifers through the annular space of the well. This is especially important in areas relevant to drinking water supply or ecology, but in Germany has developed to a general rule to protect water resources of high water quality from intrusions from other aquifers. However, this is of course also relevant to dewatering wells lateral to open-pits, in the far pre-field and deep wells in the near pre-field. Only the upper layers in the near pre-field of the open-pits that will actually be excavated, installation of annular seals is not stringently necessary.

In those depth sections of the well that penetrate the aquifer and where screen pipes are installed in order to abstract water, the annular space needs to be filled with a hydraulically conductive sand or gravel (gravel pack or, more generally, filter pack). One of the most sensitive parameters to ensure this is the grain size distribution of the gravel used. To allow for a high hydraulic permeability of the gravel pack, the grain size of the gravel pack material should not be chosen too small. But the grain size distribution of the gravel pack should not exceed a certain factor in comparison to the grain size distribution of the aquifer material (Balke et al., 2000) to prevent sand from the aquifer from being transported through the gravel pack (suffosion or “sand pumping”):

\[
\text{d}_{\text{GP}} = \text{d}_\text{ind} \cdot \text{f}_s
\]

(4)

with \( d_{\text{GP}} \) = characteristic grain size of the gravel pack (GP) [m], \( d_{\text{ind}} \) = indicator grain size of the aquifer material [m], \( f_s \) = screening factor [-] (Balke et al., 2000).

There are different methods to choose the two parameters \( d_{\text{ind}} \) and \( f_s \). In Germany, the indicator grain size \( d_{\text{ind}} \) ("Kennkorn") often is identified by intersection of a grain size distribution curve of an aquifer with an empirical line that was proposed by Bieske (1961). Another German standard method, defined by DVGW W 113 of the German Technical and
Scientific Association for Gas and Water (DVGW, 2001) uses the grain size at the inflection point of the grain size distribution of the aquifer material as indicator grain size (Bieske et al., 1998). If the inflection point cannot be determined, the grain size at the 30 %-quantile of the aquifer material grain size distribution is used for $d_{\text{ind}} = d_{30}$, which is the most common standard procedure in the US (Balke et al., 2000, Sterrett, 2007, McGillicuddy, 2013).

The screening factor $f_s$ is mostly estimated by past experience. The German method after Bieske (1961) chooses the screening factor to be $f_s = 5$ (4 to 5 after Bieske et al., 1998; 4 to 5.5 after Balke et al., 2000), whereas in the US American area there is a tendency towards higher screening factors between $f_s = 4$ and 9 (Balke et al., 2000; 3 to 8 after Sterrett, 2007; 6 to 9 after McGillicuddy, 2013), to achieve a higher permeability of the gravel pack rather than to prevent sand transportation.

The German Technical and Scientific Association for Gas and Water (DVGW, 2001) in their DVGW W 113 even define the screening factor $f_s$ as dependent on the uniformity coefficient of the aquifer material, which is calculated from the grain sizes at the 10 % and 60 % quantile of the grain size distribution ($d_{60}$ and $d_{10}$):

$$U = \frac{d_{60}}{d_{10}}$$

$$f_s = 5 + U \quad \text{with} \quad 5 < f_s < 10$$

The grain size distribution of the filter pack can be constructed from the characteristic grain size of the gravel pack $d_{GP}$. For the described German methods, a grain size class defined by DIN 4924 of the German Institute for Standardization (1998, 2012), all with an $U < 2$ is chosen according to the value of $d_{GP}$. In the US, $d_{GP}$ is defined to be equal to $d_{30}$ of the gravel of choice with a uniformity coefficient of $U < 2.5$ (Sterrett, 2007).

Recently, artificially produced glass beads (GB) with a very narrow spectrum of grain sizes and thus very low coefficients of uniformity have been proposed as a substitute for natural gravel materials (Herrmann & Stiegler, 2008, Treskatis et al., 2009, 2010, Treskatis, 2011, Klaus & Walter, 2011, 2012, Schwarzmüller et al., 2013, Klaus, 2013). Even so, these technically produced glass beads consist of very well rounded grains with a low specific surface area, which is also an advantageous criterion of filter materials in groundwater wells and ensures a high hydraulic conductivity as well as good conditions for the development of the well (Sterrett, 2007). The resistance of glass beads against chemical Fe-clogging, however, has been shown to be of minor relevance in comparison to conventional gravel pack material in a semi-quantitative approach by Schwarzmüller et al. (2013).

If the grain size distribution of a gravel pack material is known, the German Technical and Scientific Association for Gas and Water (DVGW, 2001) in their DVGW W 113 also suggests application of the empirical calculation method for the hydraulic conductivity as proposed by Beyer (1964):

$$K = C \cdot d_{10}^2$$

with $K$ = hydraulic conductivity (K-value) [m s$^{-1}$], $C = 0.011$ m s$^{-1}$ mm$^{-2}$ (for $1.0 \leq U \leq 1.9$) proportionality coefficient [m s$^{-1}$ mm$^{-2}$] and $d_{10} = 10$ % quantile of the grain size distribution [mm]. With $K$ given, the flow effective porosity $n_e$ can be approximated by the formulae of

\[
\begin{align*}
    n_{e,H} &= 1.33 \cdot K^{0.22} & \text{(Helmbold, 1988)} \\
    n_{e,M} &= 0.462 + 0.045 \cdot \ln(K) & \text{(Marotz, 1968)}
\end{align*}
\]

Even though the Helmbold-equation is said to be suitable for application in the German lignite districts, this is only true for materials with \( K \leq 10^3 \text{ m s}^{-1} \), as no materials with higher conductivities were included in the Helmbold data set (which is based on the work of Golf, 1966) and the formula was primarily developed to allow calculation of \( n_e \) even for low hydraulic conductivities (Helmbold, 2012). Thus, for calculations of \( n_e \) from grain size distributions for the gravel materials used in this thesis, the Marotz-equation will be used, even though his formula is based on a few samples only. However, Marotz used manufactured grain size mixtures in the same range as the gravel materials and thus is more applicable than the Helmbold equation, which would lead to a strong overestimation of \( n_e \) when used for values of \( K > 10^3 \text{ m s}^{-1} \).

Besides the flow-mechanical properties of the filter medium, the material ought to be chemically inert to not adversely affect the quality of the water or vice versa. On the one hand, the material should not release trace elements into the water, so that water quality is maintained. On the other hand, substances dissolved in the water should not unduly precipitate on the surface of the gravel material, so that its hydraulic permeability is maintained. Traditionally, this chemical inertia of the gravel is ensured by using gravel materials that primarily consist of Quartz and silicates. In the US, Quartz-contents of 90-95 wt.-% are claimed for a material used as filter pack (Sterrett, 2007), whereas in Germany, a minimum content of SiO₂ in measurements of X-ray fluorescence (XRF) of 96 wt.-% is requested by DIN 4924 of the German Institute for Standardization (1998, 2012), which may originate from Quartz as well as silicate minerals.

In the Rhenish lignite mining district, the requirement of 96 wt.-% of SiO₂ was always strictly complied with in the past. The gravel pack grain size class after DIN 4924 of the German Institute for Standardization (1998, 2012) is chosen based on the method after Bieske (1961), but with an especially modified empirical indicator grain size curve. Until 2010, the most commonly used grain size class for dewatering wells in the Rhenish lignite mining district covered a range from 0.7 to 1.4 mm (Klauder, 2010). As a main result of her experiments, Klauder (2010) found this class to cause more than twice as much head loss as the two next coarser grain size classes 1.4-2.2 mm and 2.0-3.15 mm. Thus, the here generally applied screening factor of \( f_s = 4.5 \) was raised to \( f_s = 6.5 \) which resulted in a change of the most commonly applied grain size class to the coarser 1.4-2.2 mm class.

\[2.2.3\] Flow towards vertical filter wells

When groundwater is pumped from a vertical filter well, the piezometric surface is lowered at that specific point, causing the hydraulic gradient to increase. The surrounding groundwater starts to flow towards the well, following the laws described in section 2.1. In a homogeneous aquifer flow towards the well is radially distributed around the well, ideally functioning as an infinitesimal line sink (Kruseman & de Ridder, 1990). Thus, the cross-sectional area
perpendicular to the flow direction can be expressed as a cylindrical area with the well representing its middle axis. As this area increases geometrically with the distance from the well, the change in the hydraulic gradient does not follow a linear but a logarithmic trend with increasing distance from the well. In a three-dimensional context, the piezometric surface deforms according to a cone of depression around the vertical filter well (Kruseman & de Ridder, 1990). When discharge from the well and the drawdown do not change anymore, an equilibrium situation between flow towards the well and discharge is reached. In that stationary phase, the cone of depression in the piezometric surface or free water table also remains constant and can be used to calculate the hydraulic conductivity of the aquifer (Figure 4).

Applying Darcy’s law for the cylinder surface area described above yields:

\[ Q = K \cdot i \cdot A_{cylinder} = K \cdot \frac{\Delta h}{\Delta r} \cdot 2\pi \cdot r \cdot b_{water} \]  \hspace{1cm} (10)

with \( Q \) = flow rate [m³ s⁻¹], \( K \) = hydraulic conductivity [m s⁻¹], \( i \) = hydraulic gradient [-] = \( \Delta h/\Delta r \) = change in piezometric head \( h \) [m] with distance from the well \( r \) [m], \( A_{cylinder} = 2\pi \cdot r \cdot b_{water} \) = cylindrical surface with well as middle axis [m²], \( r \) = distance from the well [m], \( b_{water} \) = water-filled/saturated aquifer thickness [m]. As in the unconfined case the water-filled thickness is not constant with the distance from the well, rearrangement of the formula has to be distinguished for the two cases. With \( b_{water} \) equalling the piezometric surface \( h \), the formula for the unconfined case can be expressed as:

\[ \Delta h \cdot h = \frac{Q}{K \cdot 2\pi} \cdot \frac{\Delta r}{r} \]  \hspace{1cm} (11)

In the confined case, \( b_{water} \) can be exchanged by \( b \), the constant thickness of the steadily and completely water-filled aquifer:

\[ \Delta h = \frac{Q}{K \cdot 2\pi \cdot b} \cdot \frac{br}{r} \]  \hspace{1cm} (12)

For the unconfined and confined case, logarithmic functions are attained by integration:

\[ \frac{1}{2} h^2 = \frac{Q}{K \cdot 2\pi} \cdot \ln r + C \hspace{0.5cm} \text{and} \hspace{0.5cm} h = \frac{Q}{K \cdot 2\pi \cdot b} \cdot \ln r + C \]  \hspace{1cm} (13)

Subtracting the equation on one point of the cone of depression \( P_2 \) \( (r_2/h_2) \) with known distance from the well \( r_2 \) and known hydraulic head \( h_2 \) from the equation of a second point \( P_1 \) \( (r_1/h_1) \) eliminates the integration constant \( C \) from the function and leads to the Thiem-Dupuit
equations for the unconfined or confined aquifer, respectively (Dupuit, 1863, Thiem, 1906, Kruseman & de Ridder, 1990, Klauder, 2010):

\[ h_2^2 - h_1^2 = \frac{q}{k' \pi} \cdot \ln \frac{r_2}{r_1} \quad \text{and} \quad h_2 - h_1 = \frac{q}{k' \pi b} \cdot \ln \frac{r_2}{r_1} \]  \hspace{1cm} (14)

With these equations and two piezometers in the range of the cone of depression, the hydraulic conductivity of the aquifer can be calculated for a given well discharge and vice versa. The equations, however, are only valid when certain assumptions – so called Dupuit-assumptions – are approximately met (Dupuit, 1863):

- homogeneous and isotropic aquifer, evenly distributed into infinity in all directions with a constant thickness
- exclusively horizontal and linear laminar, stationary flow towards the well
- fluid and aquifer incompressible
- constant well discharge

In unconfined conditions, these assumptions are no longer applicable in the near field of a well, as the hydraulic gradients become too high here and vertical flow components can no longer be neglected (Klauder, 2010). In confined conditions, the flow direction remains horizontal, as only the piezometric surface is affected by the cone of depression (Klauder, 2010), so long as the conditions remain constant and the filter screen fully penetrates the water-filled thickness of the aquifer (perfect well).

### 2.2.4 Properties and operational modes of wells for different purposes

Vertical filter wells are used for a range of purposes, including water supply, agricultural and industrial use. In case of anthropogenic groundwater contaminations, vertical filter wells are often used to pump and treat the contaminated water or to avoid spreading of the contamination into unaffected areas. Artificial recharge of overstressed aquifers recently has developed as another major use for vertical filter wells, using the aquifer as a storage volume instead of surface water reservoirs by means of aquifer storage and recovery (ASR) wells. A huge area for the application of vertical filter wells is the local and temporal dewatering of aquifers to enable construction and mining projects even below the groundwater table. To keep the influence of dewatering on human demands as well as ecological systems as minimal and as locally limited as possible, installation of infiltration galleries of vertical filter wells for re-injection are installed in the vicinity of susceptible areas.

There are huge differences in construction and operation of wells for different purposes. These differences may affect well loss and ageing and shall be explained in the following paragraphs with a focus on wells in drinking water supply and aquifer dewatering. Figure 5 shows examples of wells in drinking water supply in unconfined and confined conditions in loose and hard rock in comparison to an exemplary multi-layered dewatering well. One main difference in well construction is the necessity to integrate seals in the annular space between borehole and casing in those parts, where layers of low hydraulic conductivity are penetrated by the borehole. This is necessary in all wells, regardless of their purpose, in order to protect water resources of high quality from intrusions and mixing with groundwater of low quality. The only exceptions are upper (soon to be excavated) layers in dewatering wells inside the
field of a prospective open-pit. As the aquifer and the wells are designed to become excavated with further progression of the open-pit, there is no need to install annular seals in these wells. In such dewatering wells, mixing of waters from different aquifers will not only be allowed inside the annular space, but inside the well tube as well. Simultaneous dewatering of multiple aquifers in a single well is often accomplished by installation of multiple filter sections, covering as much of the whole thickness of the aquifer as possible, to maximise the amount of open area for the water to enter the well (Bieske et al., 1998; Figure 5, right).

![Diagram](image)

**Figure 5** General assemblage of production water wells in an unconfined, confined and artesian well in loose rock and of a dewatering well (from left to right; Bieske et al., 1998, redrawn)

When dewatering multiple layers of aquifers with one well, the aquifers are connected hydraulically, allowing a pressure compensating flow between the several intersected aquifers (Figure 6, left). During shutdown-periods of such a well, water from an aquifer of lower hydraulic pressure will enter the well and infiltrate into another aquifer with a lower piezometric head. The flow direction must not necessarily be from top to bottom, if there happen to be lower confined aquifers exhibiting a higher pressure than upper aquifers. During operation of the well, the compensating flow may even change its direction (Figure 6, right).

Beside the construction or assemblage of the well, there are significant differences in the operational mode of wells for different purposes. Operation in a water supply well is aimed to reach a steady state in its cone of depression. The water level in the well is lowered moderately to produce as much water as can be sustainably delivered by the aquifer. As the energy necessary to abstract the water is proportional to the distance the water has to be lifted, the operation of a water production well aims at a drawdown as deep as necessary but
as shallow as possible. The discharge is held approximately constant and the drawdown reaches stationarity (Figure 7, left; Atkinson, 2013). Also drawdown must be strictly avoided to reach the depth of the well screen and to avoid aeration of the filter.

![Diagram](image)

**Figure 6** Schematic visualisation of possible undesirable hydraulic effects in inappropriately designed multi-layered dewatering wells during shutdown periods (left) and well operation (right; after an idea by Glotfelty, 2013).

This situation is completely different for dewatering wells. As such wells aim to completely abstract all water contained in the aquifer, the maximum discharge is withdrawn from the beginning by establishing the maximum drawdown in the well and thus creating the maximum hydraulic gradient possible in the vicinity of the well (Atkinson, 2013).

![Diagram](image)

**Figure 7** Different modes of operation of vertical filter wells in drinking water supply (left) and aquifer dewatering (right; Atkinson, 2013, redrawn)

With the water level held constant at maximum drawdown, the cone of depression around the dewatering well will spread, causing the hydraulic gradient and therefore the discharge to decrease continuously (Figure 7, left; Atkinson, 2013). To completely dewater the aquifer the water table inside the well has at some point to be drawn down into the well screen section. Sometimes – in multi-layered-dewatering – upper well screens will fall dry very soon after the commissioning of the well. Of course the planned service life of a dewatering well is
frequently considerably lower compared to a well in drinking water supply, especially when installed in the pre-field of an open-pit or for short term construction projects.

2.3 Well loss

2.3.1 Time independent well loss

The term of time independent well loss includes effects of energy loss during water flow in the vicinity of a well. The actual hydraulic gradient, necessary to pull a desired amount of water towards the well, then exceeds the idealised gradient calculated after the Thiem-Dupuit equations. When the hydraulic conductivity of the aquifer and the discharge of the well are known, the Thiem-Dupuit-water surface can be calculated based on one measurement of the hydraulic head someplace in the surroundings of the well (e.g. the rim of the cone of depression). This yields a theoretically ideal value for the drawdown in the well. However, the actual drawdown in the well will always be deeper than the theoretically calculated value due to the described steepening in the hydraulic gradient, necessary to compete with the increased flow friction resulting from well loss phenomena (Batu, 1998; Figure 8). After Jacob (1950), drawdown $s_w$ in a discharge well consists of a linear and a quadratic part:

$$s_w = BQ + CQ^2 \quad (15)$$

with $s_w$ = drawdown in the discharge well [m], $B$ = aquifer-related constant [$s\ m^{-2}$], $Q$ = flow rate (discharge from the well) [$m^3\ s^{-1}$], $C$ = well-related loss constant [$s^2\ m^{-5}$]. With the Thiem-Dupuit-formula, the parameter $B$ can be calculated from the well diameter, radius of the cone of depression and the aquifer hydraulic conductivity. The parameter $C$, however, summarises all effects of well loss that are related to the assemblage of the discharge well itself, several of which are described below.

![Figure 8](image)

**Figure 8** Well loss in an unconfined aquifer expressed as a deeper actual drawdown in the discharge well than expected from Thiem-Dupuit-calculation.

A deeper drawdown necessary in the well to attain the required amount of discharge results in a greater height that the water needs to be lifted and therefore increased energy...
consumption and operational costs. If now the values of drawdown from the discharge well and observing piezometer are used to calculate the hydraulic conductivity of the aquifer with the Thiem-Dupuit relationship, the aquifer hydraulic conductivity will be underestimated, when well loss is neglected in the calculation. In a cross section through a cone of depression of the piezometric water table, the actually measured water table will deviate upwards from a calculated ideal “Thiem-Dupuit-water table” (Figure 9). This phenomenon is especially crucial in aquifer dewatering, as the calculation overestimates the dewatering situation of the aquifer. Actually, there is more water left in the aquifer than estimated by the calculation.

Some well loss effects like transition resistances between aquifer and filter pack, filter pack and screen pipe and at the pump inlet occur naturally and cannot completely be eliminated by technical measures. Another phenomenon occurs in unconfined conditions at the boundary between aquifer materials and filter pack. Immediately at this boundary, the flow effective parameters like the hydraulic conductivity K and the flow-effective porosity ne change, but the rule of continuity of flow is still fulfilled:

\[
Q_{AM} = Q_{GP} = v_{AM} \cdot A_{e,AM} = v_{GP} \cdot A_{e,GP} = v_{AM} \cdot \frac{A_{AM}}{n_{e,AM}} = v_{GP} \cdot \frac{A_{GP}}{n_{e,GP}}
\]  

(16)

with Q = flow rate \([\text{m}^3 \text{ s}^{-1}]\) in the aquifer material (AM) and in the gravel pack (GP), \(v = \text{average flow velocity of water though the flow effective part of the cross-sectional area perpendicular to flow direction [m s}^{-1}]\), \(A_e = \text{flow effective part of the cross-sectional area perpendicular to flow direction [m}^2]\), \(A = \text{cross-sectional area perpendicular to flow direction [m}^2]\), \(n_e = \text{flow effective porosity of the porous medium [-]}\).

As \(n_e\) changes at the boundary between aquifer material and filter pack, the velocity of flow and/or cross-sectional area must change as well, contributing to a vertical “seepage distance”, the water has to seep down at the boundary of the porous media as an effect of a discontinuity of the cross-sectional area (Figure 9; Bieske et al., 1998). In a confined case, a change in the cross-sectional area at the boundary between aquifer material and filter pack is not possible. Here, continuity is accounted for by a change in the flow velocity only. Thus, following Bernoulli’s principle, energy loss here is expressed by a loss in kinetic energy. However, this (engineering-related) definition of the vertical “seepage distance” may not be confused with the hydrogeological definition of the vertical “seepage distance” that is commonly used in the German literature, describing the phenomenon of delayed vertical drainage as a response to pumping tests in unconfined, anisotropic (\(K_{\text{vertical}} < K_{\text{horizontal}}\)) aquifers (Batu, 1998). The higher water level and thus piezometric head in the aquifer material (at constant drawdown in the well) result in increased energy dissipation due to locally occurring vertical, turbulent flow conditions (Figure 9; Batu, 1998, Bieske et al., 1998, Langguth & Voigt, 2004, Klauder, 2010), that are not considered in the Dupuit-assumptions.

Other effects of well loss can arise from the material chosen for well construction. A deformation of the near-well flow field with zones of constriction of flow lines may cause locally increased flow velocities and therefore can result in energy dissipation by increased flow friction and maybe even turbulences (if flow velocities reach very high values). Deformations of the flow lines can be produced by the choice of screen pipe design or the occurrence of vertical flow components near imperfect wells.
Another phenomenon of well loss may arise from a poor choice of the filter pack material and/or screen slot size. If the filter pack material is chosen too coarse, different forms of suffosion or contact erosion may occur (Figure 10), causing “sand pumping” in the well. If no stability of the granular structure of filter pack and/or aquifer material is reached, particles are transported within the bailed groundwater. Beside abrasion effects to pump, rising pipe and other system elements, this also causes energetic losses due to the higher masses that have to be lifted to the ground surface.

The opposite case of suffosion effects is the formation of a so called mud cake as a result of particle filtration that can already take place during the drilling process. If the drilling fluid happens to intrude into the aquifer, fine particles accumulate on the borehole surface and build up the mud cake with a low hydraulic permeability (cf. Figure 11, left). The influence of drilling fluid intrusions and its remains on the borehole surface on the hydraulic conductivity and the productive capacity of a well were mathematically described and summarised under the term “skin effect” by van Everdingen (1953) and Hurst (1953).

As well construction in the unconsolidated rock in the Rhenish lignite district requires a permanent overpressure inside the borehole to stabilise its mechanical integrity, air lift drilling is applied. Due to the overpressure, water will constantly infiltrate into the subsurface, causing a high susceptibility of the wells towards mud cake formation. Even though only clear water without additives is used as a drilling fluid, fine clay or coal particles go into suspension in the drilling water and are filtered at the borehole surface.
2.3.2 Well ageing

Most processes of well ageing result from a change of the flow paths inside the porous medium. Of course, the hydraulic conductivity of the porous medium decreases when former flow paths are entirely blocked, but it is already strongly affected by reduction of the cross-sectional area of the individual flow paths. This phenomenon was first quantitatively described almost simultaneously by Hagen (1839) and Poiseuille (1840), who both systematically determined the flow through a capillary depending on its geometry. Both found the flow to be linearly inversely proportional to the length of the capillary as well as proportional to the fourth power of its radius:

\[ Q = \frac{g}{8\nu} \cdot i \cdot \pi r_{cap}^4 = \frac{g \cdot \rho_f \cdot l_{cap}}{8 \mu} \cdot \frac{h_2 - h_1}{l_{cap}} \cdot \pi r_{cap}^4 \quad (17) \]

with \( Q \) = flow rate \([m^3 \cdot s^{-1}]\), \( g \) = gravitational acceleration \([m \cdot s^{-2}]\), \( \nu \) = kinematic viscosity of the fluid \([m^2 \cdot s^{-1}]\), \( i \) = hydraulic gradient [-], \( r_{cap} \) = Radius of the capillary \([m]\), \( \rho_f \) = density of the fluid \([kg \cdot m^{-3}]\), \( \mu \) = \( \nu \cdot \rho \) = dynamic viscosity \([kg \cdot m^{-1} \cdot s^{-1}]\), \( h_2 - h_1 \) = difference in hydraulic head between both sides of the capillary \([m]\) and \( l_{cap} \) = length of the capillary \([m]\) (Hagen, 1839, Poiseuille, 1840). When considering an open joint or a slit rather than a capillary, the equation changes to the so-called “cubic law”:

\[ Q = \frac{g}{12 \nu} \cdot i \cdot b_{slit} \cdot \pi r_{slit}^3 = \frac{g \cdot \rho_f}{12 \mu} \cdot \frac{h_2 - h_1}{l_{slit}} \cdot \pi r_{slit}^3 \quad (18) \]

with \( b_{slit} \) = length of the slit perpendicular to flow \([m]\), \( r_{slit} \) = width (aperture) of the slit perpendicular to flow \([m]\) and \( l_{slit} \) = length of the slit in flow direction \([m]\) (Hagen, 1839, Poiseuille, 1840).

In either case of a fractured or a porous aquifer, the flow as a function of the hydraulic gradient is by the power of 3 to 4 most strongly dependent on the cross-sectional area of the flow channels as expressed by the aperture of a single fracture \( r_{slit} \) or the radius of an individual pore \( r_{cap} \), respectively. This fact makes clear, why even small changes in the flow-effective cross-sectional area of a porous medium can already strongly affect the hydraulic conductivity of the medium (Houben & Treskatis, 2007, 2012). Most of the ageing processes in vertical filter wells are therefore attributed to different processes reducing flow-effective cross-sectional areas of the pore channels in either the aquifer material, gravel pack or screen pipe. Other ageing processes may be due to material fatigue or other mechanical problems occurring in the well including the pump and rising pipe.

The most commonly discussed ageing processes can be classified into the three main categories mechanical, chemical and biological well ageing.

Most of the mechanical ageing processes in wells are attributed to a poor choice of the filter pack material (Paul, 1996). If the filter pack is chosen too coarse, increased suffosion and “sand-pumping” in the well may occur (Sterrett, 2007). This may result in energetic disprofits, mechanical abrasion on the pump and other system elements or the sedimentation of particles at the bottom of the well. If on the other hand the filter pack is chosen too fine, or remains of drilling fluid intruded the aquifer and built a mud cake on the borehole wall, mechanical colimation may occur at the material boundaries in the well filter (aquifer – filter pack; filter pack – screen pipe).
The mechanical ageing processes have been intensely investigated during the last 30 years by the Dutch research group led by van Beek and de Zwart (de Zwart et al., 2006, van Beek et al., 2006). According to their results, mechanical wellbore clogging can be induced by the three different processes of surface filtration, straining and particle bridging (Figure 11).

The fourth case illustrated in Figure 11 is a borderline case to the chemical ageing processes. The physical-chemical adsorption of fine particles of the coarse particles of the porous medium is triggered through adhesive electrochemical charges of the grain-surfaces. As these charges are controlled by the hydrochemistry of the fluid, this process represents the transition between physical and chemical reasons of well ageing.

![Diagram](image1.png)

**Figure 11** Filtration mechanisms of particle suspensions injected in porous media (by courtesy of BGR, redrawn and altered after McDowell-Boyer et al., 1986, cited after de Zwart, 2007)

The chemical reasons for well ageing are primarily attributed to dissolved ions and other physico-chemical properties of the groundwater interacting with the artificial system elements and materials of the well. Chemical well ageing processes mainly include dissolution and precipitation of minerals as well as reducing and oxidising reactions, manifested in form of material corrosion or chemical clogging. Processes of corrosion can cause material degradation of metallic system elements like screen pipes (Figure 12), whereas chemical clogging processes can lead to a total obstruction of flow paths and system elements by mineral precipitation (Figure 13).

![Image](image2.png)

**Figure 12** Corrosion, material degradation and fatigue of metallic screen pipes (left: slot screen, right: wire wrapped continuous slot screen; McGillicuddy, 2013)

Whereas chemical corrosion effects can be avoided by choosing an inert construction material like glass fibre reinforced plastic (GRP), epoxy-resin gravel, PVC or stainless steel, clogging by
mineral precipitation cannot immediately be substantially influenced by the choice of material. The main influencing factors here are chemical equilibria in the groundwater being disturbed upon exposure to the ambient air inside the well. Pressure release, temperature increase or turbulent agitation of the water in the well may trigger a gaseous release of CO₂ from the water, resulting in oversaturation and precipitation of CaCO₃ (Moll, 1959, Houben & Treskatis, 2007). These effects of calcareous sintering with scale mainly occur in aquifers containing at least several weight per cent of mineral carbonate. In slightly alkaline conditions and at concentrations of Ca²⁺ and SO₄²⁻ greater than 150 mg L⁻¹, well obstruction can be caused by gypsum formation (Sterrett, 2007, Schnieders, 2003). Other types of mineral incrustation like metallic sulphides or aluminum hydroxide precipitates only occur under special hydrochemical conditions and are generally of minor importance (Houben & Treskatis, 2007).

One of the most significant reasons for chemical well ageing is associated with precipitation of hydroxidic Fe- and Mn-minerals, which, due to their characteristic colouring, often are referred to as “ochre minerals” (Figure 14). Ochre formation generally occurs when reduced, Mn(II) or Fe(II) bearing groundwater changes from reducing to oxidising conditions. This may occur when the groundwater is exposed to the ambient air or mixed with another groundwater from a different redox-zone (Houben & Treskatis, 2007). With the content of oxidising agents like oxygen or nitrate and therefore the redox-potential rising, Mn(II) and Fe(II) are oxidised and hydrolysed to form insoluble Mn(III)-, Mn(IV)- and Fe(III)-hydroxides, respectively. Figure 14 shows the results of a survey of 347 groundwater well operators in Germany, 68 % of which appoint the formation of ochre as the dominating well ageing process (Nehues, 1999).

According to Houben and Treskatis (2007), the situation in the US-American area is similar, with 57 % of the ageing processes caused by Fe- and Mn-clogging (apart from mechanical causes like sand pumping and corrosion; Smith, 1995). In the US-American area, sulphidic incrustations as well as sand pumping and corrosion are of greater importance than Fe- and Mn-incrustations, when compared to the results found in Germany. A reason for this is the distribution of Fe- and Mn-rich groundwaters in Germany in comparison to the types of drinking water production in the German federal states (Figure 15). Especially in the northern

---

**Figure 13** Screen pipe before installation (left) and in operation, affected by iron clogging (right, camera inspection)
German federal states drinking water supply is almost solely accomplished by groundwater abstraction from aquifers with increased contents of Fe and Mn.

Besides the loss of efficiency and the subsequent energy loss, Fe-incrustations are suspected to cause changes in chemical water quality due to temporal fixation of trace elements and their remobilisation during recrystallization of the incrustations (Houben, 2002, Houben 2003a).

Fe-clogging is especially important in dewatering wells due to the necessity of applying a huge drawdown and exposing the screen pipe to the air column in the well. To ensure an economically efficient and ecologically sustainable well operation for the future, this thesis
focuses on the chemical processes of Fe-clogging in dewatering wells, their experimental simulation under controlled conditions in the laboratory and the development of simple and efficient methods and measures to reduce, decelerate or even preclude its disadvantageous effects.

Another huge factor in well ageing is the obstruction of the filter porosity by microbiological processes. According to DVGW W 130 of the German Technical and Scientific Association for Gas and Water (2007), biological Fe-clogging is the most frequent well ageing mechanism. There are three main groups of bacteria that are able to survive in a vertical filter well environment and are therefore able to interfere with well operation (Figure 16; Sterrett, 2007).

The largest group of bacteria are the so called slime formers. As populations of slime formers grow, the bacteria produce slime (also known as biofilm) to enclose and protect themselves from lethal environmental conditions. The conditions necessary for an excessive growth of biofilms, their characteristics and the various problems thereby arising in water technology are discussed by Flemming (1991, 1992a, 1992b).

The second group are anaerobic bacteria, the most common of which are sulphate reducing bacteria (SRB, van Beek & van der Kooij, 1982). SRB favour living in flow stagnant zones of the well and can produce iron sulphides that may clog the well as well as hydrogen sulphide gas, which causes a rotten-egg odour to escape from the well (Sterrett, 2007).

The third group includes oxidising bacteria that utilise the oxidation of dissolved metals as a source of energy as part of their metabolism. The most prominent metals in that respect are iron and manganese (Ehrlich et al., 1991).

Figure 16  Bacteria populations in a well environment (Schnieders, 2003, cited after Sterrett, 2007)

Biofilm growth is especially prominent in areas of slightly elevated flow velocities, where the conditions of nutrition supply are at their optimum (Paul, 1996). As the occupation of a groundwater well poses problems to microorganisms, the initial colonisation is carried out by highly specialised bacteria (Cullimore, 2000). Once the first pioneer bacteria become established, other microorganisms follow and initiate a phase of exponential growth. As the supply with nutrients with the groundwater flow is limited and part of the biofilm may be torn
off by the water current, the biofilm growth is limited to a certain degree, as expressed by a stagnant phase (Paul, 1996). The hydrochemical conditions necessary for microbiological mass growth to develop in a well and give considerations to its avoidance is also described (cf. section 2.3.3).

Several experimental investigations of bioclogging (Cullimore & Mansuy, 1987, Taylor et al., 1990, Wu et al., 1997, Seifert, 2005) and its microstructure (Hand et al., 2008) are commonly known. In their sand-packed column experiments, Taylor et al. (1990) simulated the growth of biofilms in porous media with bacteria extracted from sewage sludge and developed models of transient biofilm thickness and the resulting change in porosity and permeability. They found the biologically induced reduction of permeability of a porous medium to be limited to a minimum residual hydraulic conductivity necessary to maintain nutrition transport and supply for the bacteria.

One crucial difference between the various types of well ageing is the exact location of where the process will take place. Most types of mechanical well loss and ageing as well as some kinds of biological clogging proceed at the boundary between aquifer material and filter pack (Figure 17, left). Chemical clogging is mostly assumed to concentrate in the immediate vicinity of the screen pipe (Figure 17, right, van Beek et al., 2009), but its distribution is actually strongly dependent on the pathway of air in contact with the groundwater susceptible to chemical clogging (Houben, 2006, Schwarzmüller et al., 2011, Kuang et al., 2013, Medina et al., 2013) as well as the flow directions and velocities (Houben & Weihe, 2004, 2010, Houben & Treskatis, 2007), especially in multi-layered dewatering wells (Metzger, 2011). Due to these numerous factors, distribution of well aging phenomena or its influence on well performance cannot easily be predicted or even calculated.

![Figure 17](image)

**Figure 17** Differences in entrance resistance between mechanical well bore clogging (A) and chemical screen slot clogging (B; van Beek, 1995, cited after de Zwart, 2007)

2.3.3 Known countermeasures in drinking water supply wells

There are some possibilities to prevent well loss and ageing that are known from drinking water supply wells. Besides precautionary measures, implemented before or during well installation (special constructive adaption, disinfection, well development), there are methods to restore well performance during the well operation and maintenance periods (certain
operational patterns, regeneration, rehabilitation, reconstruction). All of these measures are specifically developed for wells in drinking water supply, and transferability of their applicability and economic expediency to dewatering wells is uncertain. Thus, a list of the different measures shall be given and evaluated from perspectives of dewatering wells.

When the formation of a mud cake cannot be avoided by choosing another drilling method or by application of certain additives in the drilling fluid, there are mechanical methods to remove or disrupt the mud cake before or during installation of the well tube. The backreamer is a special drilling tool for loose rock, developed to enlarge the borehole in the flow relevant sections. When the drilling rods are pulled back after the final depth of the borehole is reached, the drilling damage zone and the mud cake are removed (Hilker, 2003). Hilker (2003) reports an increase of the specific yield of wells, otherwise strongly affected by mud cake of up to the factor of ten. Scratchers and scrapers attached to the well tube during its installation to destroy the mud cake are primarily applied to improve the connection of intersected aquifers with a cemented annular seal. The backreamer method also has – with uncertain success – been tested in dewatering wells of the RWE Power AG to destroy drilling mud cake. However, both methods have been applied to oppose mechanical well clogging in wells for drinking water supply, but are of course unsuitable to counter chemical and mechanical well ageing.

Possibilities to antagonise mechanical (but still no chemical) well loss and ageing effects after well construction is finished are well development or intermittent well operation (van Beek, 2010).

Generally, well development measures are conducted immediately after finishing well construction and usually consist of applying flow physical agitation to wash fine particles out from the gravel pack, mud cake and aquifer in the vicinity of the well. In an optimal case, the grain size of the sediment around the well should gradually change from coarse to fine with increasing radial distance from the well axis. This ensures the pore channels to be as wide and the flow effective porosity to be as high as possible, but still stabilises the granular structure of the filter medium and the aquifer to prevent sand pumping. As the dewatering wells of the Rhenish lignite district are operated at maximum discharge from the beginning anyway, well development is not explicitly conducted here.

According to van Beek et al. (2010), mechanical well bore clogging can be opposed by intermittent groundwater abstraction in the well. By periodically disengaging groundwater flow towards the well, the hydraulic current pressure acting on the particle bridges is released and the particles can be rearranged by the water’s buoyancy. Obstructed flow paths may thus be reactivated. In the Rhenish district, intermittent well operation is currently being conducted and tested to oppose mechanical clogging. However, this method also bears the risk of enhancing oxygen supply in the surroundings of the well (Figure 18) and therefore chemical Fe-clogging processes if both mechanical and chemical clogging are present. Thus, before deciding on a method to oppose well loss or ageing, the site-specifically most probable ageing processes should be identified as best as practically possible by hydrochemical, mineralogical and biological sampling or camera inspections (Brauckmann et al., 1990). In well regeneration, mechanical, hydro-mechanical and chemical methods can be almost freely
combined (Treskatis, 2003), as soon as permittability and applicability, especially for dewatering wells is given.

Mechanical methods range from a simple brushing of the well tube (Houben & Treskatis, 2007) over temperature shifts (Cullimore, 2000) and mechanical impulses by explosion of gas or TNT to ultrasonic regeneration (Bott & Wilken, 2002, Bott et al., 2003, Houben & Treskatis, 2007) and ionising radiation methods (Wissel & Gerstner, 1974, Cullimore, 2000). Most of these methods are applied to disaggregate incrustations from the filter pack material and screen slots or to break particle bridges. The methods of ionising radiation (X-rays, gamma radiation) or temperature shifts like hot water recycling or CO$_2$-freezing are primarily applied to oppose microbiological well ageing by freeze-thaw-disruption of biofilms or killing the microorganisms. Electrochemical approaches to counter chemical or biological incrustations are described by Houben and Treskatis (2007) and Mangold and Weidlich (2009). However, many of the above mentioned methods can be problematic due to environmental hazards and would not be permitted in Germany any more (explosives, radiation methods).

Hydromechanical methods which are basically analogous to methods of well development can be applied to remove the mechanically disaggregated incrustations from the well. A series of special tools and methods are available (Paul, 1996) to direct increased flow velocities and intense pumping into the relevant areas of the porous media, to remove fine particles by suffosion and inner erosion (Houben & Treskatis, 2007).

Chemical regeneration methods include dissolution of biological or chemical incrustations with acidic or neutral regeneration solutions (Houben, 2003b) as well as chemical disinfection methods against biologically induced well ageing. Different chemical regeneration solutions are available for different types of incrustations (Houben & Treskatis, 2007). Dissolution of Fe and Mn incrustations can be conducted proton-assisted (hydrochloric, sulphuric or different organic acids), ligand-assisted (oxalate, citrate, salicylate or tartrate salt solutions) or with organic (e.g. sulphides, dithionites) or inorganic reductants (e.g. ascorbic acid, phenols, pyruvate or glycolate; Houben & Treskatis, 2007). Inorganic acids can also be applied to dissolve carbonatic scales or hydroxidic Al incrustations. The performance of different regeneration solutions is most often investigated in the field and in laboratory experiments (Paul, 1996, Cullimore, 2000, Houben et al., 2000a, 2000b, Treskatis et al., 2000a, 2000b). However, many of the mentioned chemical methods can be problematic with respect to permittability in Germany due to environmental hazards or even simply with respect to economic profitability due to a high demand on expensive chemicals (e.g. oxalate).
Of course, before applying any of the described chemical regeneration methods, the situation needs to be analysed for the predominating ageing process (e.g. chemical or biological), to choose an economically and ecologically reasonable, legally permissible and especially technically suitable regeneration method (Schiemann et al., 1997, DVGW W 130, German Technical and Scientific Association for Gas and Water, 2007). For example in chemical treatment, \( \text{H}_2\text{O}_2 \) (Schwarzmüller et al., 2011) or \( \text{NaClO} \) (van Beek & Kooper, 1980) both act as oxidative disinfectants against microbially induced well ageing (Sterrett, 2007), but may also trigger or enhance chemical Fe(II)-oxidation and -incrustation (Robinson et al., 1987, Browman et al., 1989, Houben & Treskatis, 2007). Another example is regeneration with the aciddically neutral compound AIXTRACTOR® which was found to be effective against chemical incrustations with Fe and Mn, but ineffective against calcareous incrustations and – if not removed properly again – involves the danger of infecting the well with microbiological clogging due to nitrate production (Houben et al., 2000b, Treskatis et al., 2000a, 2000b).

When well regeneration is no longer considered to achieve a sufficient improvement of the well capacity or proves not to be sustainable to further allow for profitable operation, reconstructing the well must be considered instead, for example by pulling and replacing the casing and well screen (Glotfelty, 2013) or by completely redrilling at the same spot (Houben & Treskatis, 2007). In general, groundwater wells in drinking water supply are considered to have an average lifetime of around 25 years, sometimes less, but often very much longer (Bieske et al., 1998, Glotfelty, 2013).

As the considerations and experiments in this thesis are mainly focused on chemical Fe-clogging processes, the chemistry behind Fe(II)-oxidation and precipitation of ferric iron minerals will be described in detail in the following section.

### 2.4 Build-up of Fe(III)-hydroxide-incrustations

#### 2.4.1 Chemical Fe(II)-oxidation

The first quantitative experiments on the oxidation of ferrous solutions were conducted by McBain (1901) around the turn of the 19th century. McBain determined rates of oxidation of Fe(II)-sulphate, Fe(II)-chloride and Fe(II)-acetate solutions in dependency on temperature, the exposure to light and on the concentrations of dissolved oxygen, sulphate, chloride, acetate and carbon dioxide in acidic environments. He found the rate of oxidation to be proportional to the amount of dissolved oxygen as well as to the concentration of Fe(II) and within an acidic environment almost independent from the pH. He had already found some retardation effects that were caused by the anion present in the solution. Besides that, he found a strong dependency of the oxidation rate on the temperature that increases by a factor of 3 to 4 when the temperature rises by 15°C (McBain, 1901).

On the basis of his results, McBain (1901) was still not able to define the chemical reaction equations to properly describe the principle mechanism of the oxidation process leading from ferrous solutions to the precipitation of ferric hydroxides. The first theory on these chemical mechanisms and their kinetic reaction process was finally proposed by Haber and Weiss.
(1932) who used hydrogen peroxide as an oxidising agent instead of free oxygen, so that a considerable reaction progress could even be reached in low pH-conditions:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightleftharpoons \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \]  
\[ \text{OH}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2^- + \text{H}_2\text{O} \]  
\[ \text{HO}_2^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2 + \text{H}_2\text{O} + \text{OH}^- \]  
\[ \text{OH}^- + \text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{OH}^- \] (22)

Due to their unsaturated electron, the intermediate radical molecules OH\(^-\) and HO\(_2^-\) are very reactive and immediately proceed with the reaction. Their concentrations very quickly reach a stationarity and thus do not need to be considered as rate-limiting reaction increments (Haber & Weiss, 1934). A few years later, Weiss (1935) also transcribed the process for the oxidation of Fe\(^{3+}\) with free dissolved oxygen, which today is still widely accepted and cited as the so-called Haber-Weiss-mechanism (Stumm & Lee, 1960, 1961, Millero et al., 1987, King et al., 1995, Rose & Waite, 2002, Morgan & Lahav, 2007, Opel, 2012):

\[ \text{Fe}^{2+} + \text{O}_2 \rightleftharpoons \text{Fe}^{3+} + \text{O}_2^- \]  
\[ \text{Fe}^{2+} + \text{O}_2^- + 2\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{O}_2 \]  
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightleftharpoons \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \]  
\[ \text{OH}^- + \text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{OH}^- \] (26)

Disregarding the individual reaction steps and temporary formation of the radicals, the equations sum up to the following expression:

\[ 4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}^+ \rightleftharpoons 4\text{Fe}^{3+} + 2\text{OH}^- \] (27)

At first sight, the reaction seems to consume protons and thus cause the pH to rise. But as the concentration of OH\(^-\) rises, the speciation of Fe(III) successively changes by hydrolysis from Fe\(^{3+}\) over Fe(OH)\(^{3+}\) and Fe(OH)\(_2\)\(^+\) to Fe(OH)\(_3\)\(^0\) or even Fe(OH)\(_4\)\(^-\), governing the equation:

\[ 4\text{Fe}^{2+} + \text{O}_2 + 10\text{H}_2\text{O} \rightleftharpoons 4\text{Fe(OH)}_3 \downarrow \quad \text{+} \quad 8\text{H}^+ \] (28)

This reaction now includes the whole process of fast oxidation, hydrolysis and precipitation of insoluble Fe(OH)\(_3\) from ferrous solutions and is most often cited as the reaction responsible for well clogging with Fe(III)-containing incrustations (Roden et al., 2004, Houben & Treskatis, 2007, Metzger, 2011). If the reaction is given more time, slow oxidation will instead lead to the formation of goethite (α-FeOOH) or lepidocrocite (γ-FeOOH) (Wehrli, 1990, Houben & Treskatis, 2007, Cornell & Schwertmann, 2003):

\[ 4\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} \rightleftharpoons 4\text{FeOOH} \downarrow \quad \text{+} \quad 8\text{H}^+ \] (29)

A detailed description of the different minerals that can be products of chemical and biological Fe-clogging, their conditions of formation as part of the natural iron cycle and their characteristics will be given in section 2.4.6.

2.4.2 Thermodynamics of the Fe-H\(_2\)O-system

In general, most hydrochemical processes in the groundwater can be estimated with chemical equilibrium calculations, as the groundwater movement is very slow in comparison to the
progression of the chemical processes. In the near flow field of a well, though, the increased hydraulic gradients and flow velocities result in shorter residence times of the water, so achievement of chemical equilibrium cannot necessarily be expected.

Like most aqueous thermodynamic systems, the Fe-H₂O system is primarily controlled by pH and pe (redox-potential). At higher redox-potentials, most ions will release electrons into the solution to reduce final electron acceptors (oxidising agents) like oxygen. This will for example change the species of Fe²⁺ to Fe³⁺ or S²⁻ to SO₄²⁻ (Fe(II) to Fe(III) or S(II-) to S(VI+)). At higher pH, metal ions may become hydrolysed by increased contents of OH⁻ in solution. With pH rising from acidic towards alkaline, the dominating species of Fe(III) for example changes from Fe³⁺ over Fe(OH)³⁺ and Fe(OH)₂⁺ to Fe(OH)₃⁰ or even to Fe(OH)₄⁻. Of course if there are other elements included in the system, species with mixed compositions may occur.

In order to distinguish which species dominates in which pe-pH-environment, the laws of mass action are defined for the hydrolysis or redox-reaction transferring each species into each other species. With the thermodynamic equilibrium constant known, and defining the activities of both species as equal, lines of thermodynamic equilibrium are plotted in the pH-pe-space (phase diagram, Figure 19), with the areas inbetween depicting the fields of stability or dominance of the specific phase. The upper and lower boundary of the phase diagram are defined by the redox-stability of the water itself (reduction of H₂O to H₂ and OH⁻ at low pe and pH, oxidation of H₂O to O₂ and H⁺ at high pe and pH, releasing protons; Appelo & Postma, 2005).

To express the state of a system of mineral dissolution and precipitation in relation to the reference equilibrium state, the saturation index for specific minerals is calculated. To do so, the solubility product of the equilibrium state is compared to the actual ion activity product of the water sample. The saturation index is calculated from the logarithm of the quotient between actual (IAP) and equilibrium activity product (Appelo & Postma, 2005):

\[ SI = \log_{10} \frac{IAP}{K_{eq}} \]  

(30)

with SI = saturation index [-], IAP = ion activity product of the sample [-], K_{eq} = ion activity product at equilibrium state (with dissolution-precipitation reactions: solubility product K₅ of the mineral) [-]. If SI = 0, the mineral is in equilibrium with the corresponding ions in solution. If SI < 0, the solution is undersaturated and the corresponding mineral is likely to dissolve if present in contact with the solution. If SI > 0, the solution is oversaturated and the corresponding mineral is likely to precipitate from the solution.

In thermodynamic equilibrium calculations with the hydrogeochemical modelling programme PhreeqC for Windows (version: 2.18.00, database: wateq4f.dat, Parkhurst & Appelo, 1999), the distribution of all possible species and saturation indices of all possible minerals are calculated and set into equilibrium state instantaneously (Parkhurst & Appelo, 1999). Equilibrium calculations do not consider kinetic constrains on the chemical processes and temporal delay in reaction progression that may be caused by the energy input to the reaction or the change in the educt and product concentration through the reaction itself. In all cases where other processes (e.g. groundwater movement in the near well field) may proceed faster than the hydrochemical reactions, kinetic calculations need to be conducted.
2.4.3 Kinetics of Fe(II)-oxidation

Until the 1960ies, most quantitative experimental investigations of the oxidation kinetics were conducted in low pH-ranges (McBain, 1901, Haber & Weiss, 1934, Weiss, 1935, George, 1954, Huffman & Davidson, 1956, Stumm & Lee, 1961). However, staying in an acidic environment, the Fe-oxidation rate is independent from changes in the pH. The effect of pH-dependency in alkaline environments already had been observed qualitatively by several authors (Just, 1908, Bredig & van Berneck (as locally cited in van Bohnson, 1921), Holluta & Eberhardt, 1957, Holluta & Kölle, 1964, Tödt & Stoklassa, 1954), before Stumm and Lee (1961) first empirically determined the quantitative relationship between pH and the rate of kinetic Fe(II)-oxidation that is generally accepted by most authors until today:

\[
\frac{d\text{[Fe(II)]}}{dt} = k_1 \cdot \text{[Fe(II)]} \cdot p(\text{O}_2) \cdot [\text{OH}^-]^2
\]

\[
= \frac{k_1 K_W^b}{K_H} \cdot \frac{[\text{Fe(II)}][\text{O}_2,\text{aq}]}{[\text{H}^+]^2} = k \cdot [\text{Fe(II)}] \cdot \text{[O}_2,\text{aq}] \cdot 10^{2pH}
\]

(31)

with \(r_{ox}\) = oxidation rate of Fe(II) [mol L\(^{-1}\) min\(^{-1}\)], [Fe(II)] = concentration of Fe(II) [mol L\(^{-1}\)], \(t = \text{time [s]}, k_1 = 1 \ldots 2 \times 10^{-3} \text{L}^2 \text{mol}^{-2} \text{atm}^{-1} \text{min}^{-1} = \text{reaction constant as defined by Stumm and Lee (1961),} p(\text{O}_2) = \text{oxygen partial pressure [atm],} [\text{OH}^-] = \text{concentration of dissolved hydroxide ions [mol L}^{-1}\text{],} K_W = [\text{OH}^-][\text{H}^+] = 10^{-14} \text{mol}^2 \text{L}^{-2} = \text{dissociation constant of water,} K_H = \ldots \)
\[O_{2,\text{aq}}] p(O_2)^{-1} = 1.30 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1} = \text{Henry’s distribution coefficient}, [O_{2,\text{aq}}] = \text{concentration of dissolved oxygen [mol L}^{-1}], [H^+] = \text{proton concentration [mol L}^{-1}], k = 1.28 \ldots 2.56 \times 10^{-14} \text{ mol L}^{-1} \text{ s}^{-1} = \text{rate constant considering}[O_{2,\text{aq}}]\text{ and } [H^+]\text{ or pH rather than } p(O_2)\text{ and } [OH^-] \text{ (Stumm & Lee, 1961, Davison & Seed, 1983, Applin & Zhao, 1989, Houben & Treskatis, 2007). Thus, the oxidation of Fe(II) to Fe(III) is of } 1\text{st order}\text{ with respect to Fe(II)}\text{ and } [O_{2,\text{aq}}]\text{, but } 2\text{nd order with respect to } [H^+]. \text{An increase of the } \text{pH of one unit increases the reaction rate by the factor of 100. The considerations in this thesis will be based on this simple mixed } 1\text{st}/2\text{nd order reaction defined by Stumm and Lee (1961).}

A plausible explanation for the strong dependency of the reaction rate on the pH in the range between pH = 4 and pH = 8 was given Morgan and Lahav (2007). As the pH increases, the dissolved ferrous ion gets hydrolysed step by step. As the oxidation rate of dissolved Fe(II) species increases with each hydrolysis step by 5 orders of magnitude in the order Fe^{2+} \ll Fe(OH)^+ \ll Fe(OH)_2^0, \text{ the overall oxidation rate strongly increases with pH. Thus, for comparison with the considerations based on the rate law after Stumm and Lee (1961), another rate law, defined by Millero (1985) will be tested:}

\[
\tau_{ox} = -\frac{d[Fe(II)]}{dt} = k_0' \cdot [Fe^{2+}] + k_1' \cdot [Fe(OH)^+] + k_2' \cdot [Fe(OH)_2^0] \\
= \left(k_0' + \frac{k_1' \cdot K_1^*}{[H^+]^2}ight) \cdot [Fe(II)] = k^* \cdot [Fe(II)]
\]

(32)

with \(k_0' = 1 \cdot 10^{-8} \text{ s}^{-1}\); \(k_1' = 3.2 \cdot 10^{-2} \text{ s}^{-1}\); \(k_2' = 1 \cdot 10^4 \text{ s}^{-1}\) = oxidation reaction constant of the Fe(II) species Fe^{2+}, Fe(OH)^+ and Fe(OH)_2^0, respectively, at constant oxygen partial pressure of \(P(O_2) = 1 \text{ atm}[s^{-1}], [Fe^{2+}], [Fe(OH)^+], [Fe(OH)_2^0] = \text{concentrations of the dissolved Fe-species [mol L}^{-1}], [H^+] = \text{proton concentration [mol L}^{-1}], K_1^* = 10^{-9.5} \text{ mol L}^{-1}; \beta_2^* = 10^{20.6} \text{ mol}^2 \text{ L}^{-2} = \text{hydrolysis constants of } Fe^{2+} \text{ to } Fe(OH)^+ \text{ and } Fe(OH)_2^0, \text{ respectively and } k^* = \text{pH-dependent overall reaction rate constant [s}^{-1}] \text{ (all values taken from Wehrli, 1990).}

There are several other effects that influence the kinetic rate of Fe-oxidation like concentrations of (foreign) ions (ClO_4^-, Cl^-, SO_4^{2-}; Sung & Morgan (1980), CO_3^{2-}; Carlson & Schwerdtmann (1990), SO_4^{2-}; PO_4^{3-}; Fe^{3+} and Fe(OH)^{2+}; Grundl & Delwiche (1993), CO_3^{2-}; Pham & Waite, 2008), uncertainties in existence of certain Fe-species (Pham et al., 2006), and the individual reaction rates of the single species (Morgan & Lahav, 2007, Pham & Waite, 2008). In their systematic investigations of the influence of several anions on the rate of Fe(II)-oxidation, Tamura et al. (1976a) found the rate constant k to decrease in the presence of ClO_4^-, NO_3^-, Cl^-, H_2SiO_4, Br^-, I^ and SO_4^{2-}, sorted accordingly to rising influence on the reaction rate. F^- and H_2PO_4^- were found to accelerate Fe(II) oxidation. The influence of foreign anions on the oxidation rate of ferrous iron was identified by Stumm and Lee (1960). They found Fe(II) to build complexes with the anion which are not as readily oxidised as free Fe^{2+} or the hydroxidic dissolved species mentioned above. Still in recent literature, considerations about the kinetics of Fe(II) oxidation continue, especially under low O_2-conditions (Sugimori et al., 2011, Vollrath et al., 2012, Kanazaki & Murakami, 2013).
2.4.4 Autocatalytic effect

Besides the dependency of the Fe(II)-oxidation rate on several foreign ions, Tamura et al. (1976b, 1980) also found the reaction rate to be dependent on the amount of solid ferric hydroxides in contact with the considered solution. Presumably, the presence of initial ferric hydroxides creates a secondary reaction pathway via sorption of Fe(II) onto the Fe(III)-hydroxide surface and subsequent oxidation, proceeding parallel to the oxidation of dissolved Fe(II)-to Fe(III)-species described above (see also Stumm & Sulzberger, 1991). The mechanisms and controlling parameters of sorption and crystallisation of dissolved Fe(II)-species onto the surface of different Fe(III)-hydroxides and subsequent crystallisation on a nano-scale have recently been discussed by Larese-Casanova et al. (2012). The homogeneous reaction rate law defined by Stumm and Lee (1961) can be modified to a heterogeneous rate law by adding another summand, describing the secondary reaction pathway (Tamura et al., 1976b, 1980, Sung & Morgan, 1980, Houben, 2004, Houben & Treskatis, 2007, 2012, Geroni & Sapsford, 2011, Larroque & Franceschi, 2011, Larese-Casanova et al., 2012):

$$r_{ox} = -\frac{d[Fe(II)]}{dt} = (k \cdot \frac{[Fe(II)] \cdot [O_{2,aq}]}{[H^+]^2} + k' \cdot [Fe(III)]_{s} \cdot \frac{[Fe(II)] \cdot [O_{2,aq}]}{[H^+]})$$ (33)

with \(k = 2.56 \cdot 10^{-14} \text{ mol L}^{-1} \text{ s}^{-1}\) = homogeneous rate constant considering \([O_{2,aq}]\) and \([H^+]\) as defined by Stumm and Lee (1961) (Davison & Seed, 1983), \(k' = 1.024 \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}\) = reaction constant of the secondary reaction pathway (Tamura et al., 1976b, [Fe(III)]\(_{s}\) = concentrations of solid ferric hydroxide minerals [mol L\(^{-1}\)], with

$$k' = k_{s,0} \cdot K_{ads} = 73 \frac{L}{mol \cdot s} \cdot 1.403 \cdot 10^{-5} = 1.024 \cdot 10^{-3} \frac{L}{mol \cdot s}$$ (34)

with \(k_{s,0} = 73 \text{ L mol}^{-1} \text{ s}^{-1}\) = specific reaction rate constant of the secondary reaction pathway (oxidation of surface-sorbed species) considering \([O_{2,aq}]\) and \([H^+]\) as defined by Tamura et al. (1976b), \(K_{ads} = 1.403 \cdot 10^{-5} \) = dimensionless adsorption constant of Fe(II) onto the Fe(III)-mineral-surface as defined by Tamura et al. (1976b) with

$$K_{ads} = 10^{-9.6} \frac{mol \text{ Fe(II)}}{mg \text{ Fe (III)}} \cdot 55.845 \frac{g}{mol} \cdot 1000 \frac{mg}{g} = 1.403 \cdot 10^{-5} = 10^{-4.85}$$ (35)

As the product of the reaction is thought to increase the rate of the reaction itself, this “self-reinforcing” process is commonly referred to as an autocatalytic effect. Stumm and Sulzberger (1991) found Fe(II) sorption on a surface to be a similar effect to hydrolysis as described by Millero (1985, see above). However, the secondary part of the heterogeneous rate law is only a 1\(^{st}\) order reaction with respect to \([H^+]\), whereas the primary part remains a 2\(^{nd}\) order reaction as previously described by Stumm and Lee (1961). Thus, the autocatalytic effect becomes most significant at lower pH-values (Figure 20; Sung & Morgan, 1980, Houben, 2004, Houben & Treskatis, 2007, Geroni & Sapsford, 2011).

Of course, there is a strong dependency of the heterogeneous reaction on the amount of Fe(III)-hydroxide-minerals in contact with the solution. With \(c(Fe(III))_o = 5 \text{ g L}^{-1}\), at pH 6.6 or 7.6, the heterogeneous reaction model predicts a reaction rate 1000 or 100 times as high as the homogeneous model by Stumm and Lee (1961), respectively, whereas with \(c(Fe(III))_o = 0.5 \text{ g L}^{-1}\), these factors are reduced to 100 or 10, respectively (Figure 20).
The same calculations were conducted by Houben (2004), who unfortunately converted the value of \( k_{s,0} \) from \( \text{L mol}^{-1} \text{s}^{-1} \) to \( \text{L mol}^{-1} \text{min}^{-1} \) by dividing with 60 s \( \text{min}^{-1} \) instead of multiplying. Thus, Houben (2004) used a wrong value of \( k_{s,0} = 1.217 \text{ L mol}^{-1} \text{min}^{-1} \) instead of 4380 \( \text{L mol}^{-1} \text{min}^{-1} \) and underestimated the effect of autocatalysis. Opel (2012) already suspected the printing error ([H\(^+\)] \(^2\) instead of [H\(^+\)] \(^3\) in the second summand) in the heterogeneous kinetic reaction formula in Houben (2004) to be the reason for that underestimation that has been copied by Larroque and Franceschi (2011).

However, as stated by Sung and Morgan (1980), the value of \( k_{s,0} \) is not to be considered as a fixed constant, but is used here as a fitting parameter. An increase of reaction rates of about \( 10^3 \) to \( 10^5 \) due to the autocatalytic effect is in agreement with observations in the laboratory and in the field reported by Sung and Morgan (1980) and Geroni and Sapsford (2011), respectively. Geroni and Sapsford (2011) especially mention the higher Fe(II)-contents of up to 70 mg L\(^{-1}\) to be responsible for an increased importance of the autocatalytic effect. As similarly high concentrations of Fe(II) are applied in the experiments described in this thesis, special attention needs to be paid to identify a possible autocatalytic effect.

### 2.4.5 Biological Fe(II)-oxidation

Another effect that potentially strongly accelerates Fe(II)-oxidation, precipitation and incrustation is the microbially induced Fe(II)-oxidation. Ghiorse and Ehrlich (1992) give an extensive summary of the literature published on biomineralisation of Fe and Mn until 1992 as well as an overview of the most important groups of microorganisms in relation to the Fe- and Mn-minerals formed. There is a variety of microbes, fungi, algae and protozoa that may promote Fe and Mn precipitation. Ghiorse and Ehrlich (1992) also state that biological Fe-oxidation becomes most significant at low pH (1.5 to 3.5, e.g. *Thiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, see also Nordstrom & Southam, 1997, Tuhela et al., 1997) or anaerobic conditions (c(O\(_2\)) < 0.01 mg L\(^{-1}\), e.g. *Gallionella ferruginea*, see also Sobolev & Roden, 2001), when the reaction rates of the purely chemical processes decelerate. However, according to Vollrath et al. (2012), the relative importance of microbially induced Fe(II)-oxidation at low O\(_2\)-contents is less pronounced than expected when compared to abiotic oxidation.
Descriptions of the structure, physiology and growth rates of the single iron oxidising bacteria like *Gallionella spp.* (de Vet et al., 2011), *Gallionella ferruginea Ehrenberg* (Hanert, 1968, 1970, 1973), and *Leptothrix* (van Veen et al., 1978, Vollrath et al., 2012) are numerous in biological literature. Good overviews of all Fe and Mn oxidising bacteria relevant in water wells are given by Ehrlich et al. (1991) and Tuhela et al. (1997), descriptions of the individual bacteria are given by Ellis (1919). Emerson et al. (2010) and Weber et al. (2006) recently depicted the variety of the main iron oxidising bacteria (FeOB) and their complex genetic relations with each other. Due to the complexity of the biological Fe-cycling system and the variety of influencing factors, even the diverse mechanisms of oxidation remain matters of current research (Larese-Casanova et al., 2010, Konhauser et al., 2011, Lerm et al., 2011, Schwarzmüller & Sperlich, 2011, Dippon et al., 2012, Larese-Casanova et al., 2012, Kluglein & Kappler, 2013).

Distinct species of bacteria like *Gallionella ferruginea, Leptothrix ochracea, Leptothrix discophora,* and *Sphaerotilus spp.* are likely to form morphologically recognisable structures like sheaths and stalks of extracellular Fe(II)-mineralisations, whereas there are lots of microorganisms that may not be recognised as easily, exhibiting diverse forms and morphologies (Ghirose & Ehrlich, 1992, Tuhela et al., 1997). The above named species as well as *Hyphomicrobium, Pedomicrobium spp.* and the fungi *Metallogenium* prefer circumneutral pH-conditions and primarily form poorly ordered Fe(III)-hydroxides like 2-line ferrihydrite (cf. section 2.4.6, Tuhela et al., 1992).

The oxidation of Fe(II) to Fe(III) and Mn(II) to Mn(III) or Mn(IV) are the only microbiological processes that are conducted enzymatically by autotroph bacteria that exclusively utilise CO₂ as their carbon-source. Those bacteria – like the Fe-oxidising species *Thiobacillus ferrooxidans* – are contingent upon a source of “chemical reducing power”, i.e. reducing agents like Fe(II), to endergonically reduce CO₂ and to build up organic molecules and cellular tissue (biosynthesis, polymerisation). Other parts of the Fe(II) are exergonically oxidised by O₂ rather than CO₂, to win the energy necessary to maintain the endergonic process of CO₂-reduction with Fe(II). Within both of these processes, *Thiobacillus ferrooxidans* oxidises Fe(II) to Fe(III), which is often coprecipitated with SO₄²⁻ (Ghirose & Ehrlich, 1992), leading to the formation of jarosite (pH < 3) or schwertmannite (3 < pH < 5; Tuhela et al., 1997, Nordstrom & Southam, 1997). Not much information are available on other relevant genera like *Siderocapsaceae, Toxothrix, Clonothrix* and *Crenothrix* (Tuhela et al., 1992, Walter, 1997).

Besides the enzymatic Fe(II)-oxidation, the reaction may as well be biologically mediated non-enzymatically. As a result of metabolic by-products of various microorganisms, arbitrary bacteria, fungi or algae that do not necessarily have to metabolise Fe(II) directly, the hydrochemical conditions can be shifted, for example by photosynthetic O₂-production or local changes in pH through CO₂-consumption, promoting abiotic Fe(III)-precipitation (Ghirose & Ehrlich, 1992).

Hässelbarth and Lüdemann (1967) gave examples of biological clogging at eight locations in Germany and described the hydrochemical conditions necessary for biological Fe-clogging. Another extensive case study of forty wells affected by biological Fe-incrustations in Suffolk
County, Long Island, New York was published by Walter (1997) with data about mineralogy and microbiology.

Besides microbiological oxidation, Fe(III)-minerals in the aquifer can also be biologically reduced again. For example anaerobic H₂S production or mineralisation of organic matter may lead to subsequent precipitation of pyrite or siderite, respectively. Final electron acceptors may well be Fe(III)-minerals that are reduced in the process (Ghiorse & Ehrlich, 1992), which results in a closed biological cycle of Fe in the groundwater space (Stumm & Sulzberger, 1991, Kappler & Newman, 2003, Kappler & Straub, 2005, Konhauser et al., 2011). The most prominent species known to reduce ferric iron are Geobacter metallireducens, Shewanella putrefaciens, Geospirillum and Geovibrio (Weber et al., 2006, Metzger, 2011). An extensive and comprehensively illustrated overview of bacteria, involved in Fe cycling in sediments, their taxonomic relations, relevant chemical compounds and mechanisms of the biological Fe cycling is given by Weber et al. (2006; Figure 21).

![Figure 21](image.png)

**Figure 21**  
Phylogenetic relations of different microorganisms contributing to Fe-redox-cycling; Fe-oxidising and Fe-reducing bacteria are printed in black and red, respectively (Weber et al., 2006).

The system of Fe(II) oxidation and even its pH-dependency becomes incredibly complex, when both chemical and microbiological processes are allowed in the system (Kirby et al., 1999). As is commonly known, microbial processes are capable of increasing kinetic reaction rates of
Fe(II)-oxidation by a factor of $10^5$ to $10^6$ at low pH by *Thiobacillus ferrooxidans* (Singer & Stumm, 1970, Nordstrom & Southam, 1997) up to a factor of $10^3$ at pH 6 (Kasama & Murakami, 2001, Opel, 2012) when compared to the abiotic reaction rates at the same hydrochemical conditions. As the complex interaction between chemical and biological processes are capable of strongly changing the conditions of Fe-clogging processes, the effects of biological clogging need to be excluded from the Fe-clogging model. Nonetheless, as in the field an influence of biological processes exist, those need to be taken into account when comparing the model results to field investigations.

### 2.4.6 Fe(III)-hydroxides and their formation pathways

Iron circulation in natural environments and specifically in the groundwater-bearing subsurface most often begins with the oxidative dissolution of primary geogenic reduced Fe-minerals that can either be sulphidic (FeS$_2$: pyrite, marcasite or FeS: pyrrhotine) or carbonatic (FeCO$_3$: siderite). Initial deposition of those reduced iron minerals occurs for example in suboxic zones of the shelf area with sedimentation of shallow marine sands when river water, entering the highly saline ocean water becomes oversaturated with respect to Fe(II) (Okrusch & Matthes, 2005). So long as these minerals stay covered with other geologic layers, the reduced Fe-minerals are preserved from oxygen supply, and are thermodynamically stable, even when the ocean has disappeared due to tectonic events or marine regression. As lignite forms under similar conditions of marine transgression and regression cycles, reduced Fe-minerals are often associated with lignite deposits (Evangelou & Zhang, 1995).

Dissolved Fe$^{2+}$ in the groundwater can develop into several minerals. If pH rises in the Fe-bearing groundwater under conditions of reducing pe, a green rust mineral will form, whose composition depends on the dominating anion present. Green rusts are mixed phases of ferrous and ferric iron, that exclusively develop in very low concentrations of oxygen. These bluish green double layer hydroxide salts are capable of incorporating a variety of anions in between their hydroxide layers (Cornell & Schwertmann, 2003). The two most prominent representatives are green rust I (Fe(III)$_3$Fe(II)$_2$(OH)$_6$Cl$_2$H$_2$O; Refait & Génin, 1993, Refait et al., 1998) and green rust II (McGill et al., 1976) which incorporate Cl$^-$ and SO$_4^{2-}$ in-between their Fe-hydroxide layers, respectively. Other possibilities include Br$^-$, I$^-$, CO$_3^{2-}$, NO$_3^-$ and ClO$_4^-$ (Lewis, 1997) as well as oxalate (Refait et al., 1998) and even hydroxide itself (Trolard et al., 1997). If the pH is further increased anaerobically, solid ferrous hydroxide (Fe(OH)$_2$) will form (Cornell & Schwertmann, 2003).

In the case of increasing pe and stably low pH, the ferrous iron species become oxidised. As the solubilities of the resulting ferric iron species are substantially lower than of Fe(II), mineral precipitation occurs. The formation of a specific Fe(III)-mineral is strongly controlled by the initial pH, the dominating anion present in the solution as well as the rapidity of the oxidative process. Since a low pH and a broad range of sulphate concentrations through pyrite oxidation is often associated with dissolved Fe(II), there are two commonly known minerals, precipitating from such solutions. As according to Hammarstrom et al. (2005), at very high concentrations of sulphate ($c$(SO$_4^{2-}$) $>$ 3000 mg L$^{-1}$), very low pH (pH 1.5 to 3) and in presence of a monovalent cations (K$^+$, Na$^+$, NH$_4^+$ or H$_2$O$^+$) jarosite (KFe(III)$_3$(SO$_4$)$_2$(OH)$_6$) is formed (Cornell & Schwertmann, 2003). At moderately high sulphate ($c$(SO$_4^{2-}$) = 1000...3000 mg L$^{-1}$) and
moderately acidic pH, precipitation of schwertmannite is predominant (with optimum conditions pH 2 to 4, Cornell & Schwertmann, 2003). If the dominating anion during precipitation is changed from sulphate to chloride or fluoride, akaganéite forms (pH < 5) instead of schwertmannite (Schwertmann & Cornell, 2000, Cornell & Schwertmann, 2003). At room temperature and pH 4 schwertmannite may easily transform to goethite via dissolution in an aquatic environment. However, transformation can be retarded or even inhibited by contents of chromate or arsenate, substituting sulphate in the schwertmannite structure (Regenspurg & Peiffer, 2005).

The stoichiometry and structure of schwertmannite was first described by Bigham et al. (1994). As the mineral was only discovered 20 years ago, the discussion on the exact structure and composition of schwertmannite, especially its content of water of crystallisation is still open (Yu et al., 2002, French et al., 2012). In the text, the commonly accepted structural formula \( \text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n \text{H}_2\text{O}, \) with \( y = 16-2z, \) \( 2.0 \leq z \leq 3.5 \) and \( n \approx 2 \) given in Cornell and Schwertmann (2003) will be used. For hydrogeochemical calculations, however, the thermo-dynamic and average stoichiometric information of schwertmannite \( \text{(Fe}_2\text{O}_{2.54}(\text{SO}_4)_{1.71} \cdot 2.4 \text{H}_2\text{O}) \) as defined by Yu et al. (2002) will be used to account for the sensitivity of elevated sulphate contents.

There is a series of Fe(III) oxide, hydroxide and oxyhydroxide minerals that can be formed from aqueous Fe(II)-solutions. The most frequent of these minerals and their most common pathways of formation as well as conditions necessary for their occurrence are summarised in Figure 22. One of the main factors that determine the mineral forming from an aqueous Fe(II)-system is the rate of oxidation and hydrolysis.

![Figure 22](image-url)
With pH increasing even above pH 8 (very intense hydrolysis) and suddenly occurring strongly oxidising conditions (e.g. in contact with \( \text{H}_2\text{O}_2 \) or dry oxidation of \( \text{Fe(OH)}_2 \), Glenmuer & Gwinner, 1939, Feitknecht, 1959, Misawa et al., 1974, Carlson & Schwertmann, 1980), violent oxidation will lead to the formation of ferrihydrite, which is of more or less the same degree of crystallinity as schwertmannite and akaganéite (maximum of four peaks in a diffractogram). However, the conditions for ferrihydrite precipitation do not very frequently occur in natural systems. The most common hydrochemical situation in natural aquifers leading to chemical iron clogging in groundwater wells is an anaerobic environment of circumneutral pH. Here, the dominating species of dissolved Fe(II) are Fe(II)-hydroxides. In contact with oxygen from the ambient air inside a well, pe increases, resulting in rapid, but not violent oxidation.

As according to Hammarstrom et al. (2005), at pH > 5 and \( \text{c(SO}_4^2^- < 1000 \text{ mg L}^{-1} \), ferrihydrite, a poorly ordered ferric hydroxide is formed. In the past, ferrihydrite often was referred to as “amorphous iron oxide” or “hydrous ferric oxide” (HFO), both of which are not exactly correct. In fact, the mineral possesses a crystalline short-range order (Schwertmann & Cornell, 2000), that may be well or poorly developed. With rapid hydrolysis (neutral pH) and temperatures around \( T = 20 \text{ °C} \), the mineral precipitates in a poorly ordered form exhibiting only 2 broad peaks in a diffractogram. With slower hydrolysis (moderately acidic pH) or at elevated temperatures around \( T = 80 \text{ °C} \), the well crystallised ferrihydrite precipitates exhibiting 6 to 8 peaks in a diffractogram (Schwertmann & Cornell, 2000). The products are accordingly denominated as 2- or 6-line (2L or 6L) ferrihydrite (Cornell & Schwertmann, 2003, Janney et al., 2000). According to Tuhela et al. (1992) ferrihydrite also is the preferred primary product of the enzymatic microbiological formation pathway.

Due to the varied amounts of water that can be incorporated into the crystal lattice of ferrihydrite, scientific discussion on the stoichiometry, crystal structure and ageing properties of ferrihydrite remains open until today (Michel et al., 2007, 2010, Manceau, 2011, 2012 and Gilbert et al., 2013) just as with schwertmannite. While in the past and sometimes still today, stoichiometry of ferrihydrite is often simplified as \( \text{Fe(OH)}_3 \), Cornell and Schwertmann (2003) recommend using the bulk formula \( \text{Fe}_x\text{H}_y\text{O}_z \cdot 4\text{H}_2\text{O} \) as defined by Towe and Bradley (1967), which will be used in the further texts for reasons of common convention. As Yu et al. (2002) provide statistically determined compositions of synthetic ferrihydrites from the laboratory along with solubility products of the minerals, the average compositions of 2L- and 6L-ferrihydrite according to their findings \( \text{Fe}_2\text{O}_{2.145}(\text{OH})_{1.71} \cdot 1.06 \text{H}_2\text{O} \) and \( \text{Fe}_2\text{O}_{2.465}(\text{OH})_{1.07} \cdot 0.98 \text{H}_2\text{O} \) will be used for hydrochemical modelling in this thesis only.

As structural models for ferrihydrite are thus difficult to define (Xu et al., 2011), identification and especially quantification of mineral inventory of samples containing ferrihydrite may be difficult with standard XRD-methods. However, the percentage of ferrihydrite in a sample or as the part of the total Fe-hydroxides in the sample can sufficiently accurately be determined by sequential extraction methods (cf. section 4.3.8) as the poorly crystallised percentage, dissolvable with oxalic acid in the darkness (Schwertmann, 1959b, 1964, McKeague & Day, 1966, Carlson & Schwertmann, 1981):

\[
s(fh) = \frac{m(\text{Fe})}{m(\text{Fe}_{\text{tot}})} \cdot 100 \text{ wt. } - \%
\]  
(36)
with \( s(\text{fh}) \) = percentage of ferrihydrite (fh) of the total Fe-content, \( m(\text{Fe}) \) = mass of Fe, dissolvable with oxalic acid, \( m(\text{Fe}_{\text{tot}}) \) = total mass of Fe. The validity of this formula can, however be disturbed in the presence of very fine-grained lepidocrocites, that can be dissolved by the kinetic method of oxalate extraction (Schwertmann, 1973, Chao, 1984, La Force & Fendorf, 2000).

As ferrihydrite is thermodynamically metastable, the mineral is likely to transform to more stable phases (Childs, 1992). With enough time and a pH between 7 and 8, ferrihydrite will transform to hematite by rearrangement of ferrihydrite-nuclei (Schwertmann & Murad, 1983, Schwertmann et al., 1998). At lower (or higher) pH, formation of goethite from ferrihydrite predominates via the fluid phase through dissolution and re-precipitation (Schwertmann & Murad, 1983), with the transformation rate increasing with pH. But transformation half-life at pH 7 still exceeds 100 days (Schwertmann & Murad, 1983). Instead, transformation of ferrihydrite to goethite or lepidocrocite can be strongly accelerated with higher concentrations of Fe(II) in the water (Pedersen et al., 2005). The process of transformation can be strongly decelerated or even inhibited by increased concentrations of silicate (with \([\text{Si}]/[\text{Fe}] > 0.1\) (in the experimental model: 0.01), Schwertmann & Cornell, 2000), phosphate, aluminium and organic molecules or by dry storage (Carlson & Schwertmann, 1981).

Direct precipitation of lepidocrocite (\(\gamma\)-FeOOH) rather than ferrihydrite from the aqueous solution occurs, at \(\text{pH} > 7\) and high contents of \(\text{Cl}^-\), especially when concentrations of Si and \(\text{CO}_3^{2-}\) are moderate (Cornell & Schwertmann, 2003). Even though exhibiting the same stoichiometry, other than goethite, lepidocrocite does not consist of a tunnel structure but of layered crystals. Its crystallinity and thermodynamic stability are thus lower than those of goethite. Due to the smaller crystalite size, its specific surface area is somewhat higher in comparison to goethite. Through dehydration, lepidocrocite can be transformed to maghemite or via solution to goethite (Cornell & Schwertmann, 2003).

Goethite (\(\alpha\)-FeOOH) is mostly closely associated with lepidocrocite. The conditions for transformation from ferrihydrite to lepidocrocite and goethite are very similar and lepidocrocite readily transforms to goethite via solution. With formation in aqueous Fe(II)-systems, goethite is favoured over lepidocrocite when the oxidation rates are lower and when the dominating anion is sulphate (Tamaura et al., 1981) or bicarbonate (Schwertmann, 1959a, Fey & Dixon, 1981, Carlson & Schwertmann, 1990) rather than chloride or other halogenides (Detournay et al., 1976, Taylor, 1984). Also the transformation from lepidocrocite to goethite via solution in alkaline media can be supported by sulphate and dissolved Fe(II) (Krause et al., 1934, Nitschmann, 1938, van Oosterhout, 1967, Bechinë et al., 1982) and retarded by increased Si (Schwertmann & Taylor, 1972, Cornell & Giovanoli, 1987).

Maghemite (\(\gamma\)-Fe$_2$O$_3$) can be formed via thermal de-hydroxylation from lepidocrocite at 200-280 °C as an intermediate phase of thermal hematite formation (Cornell & Schwertmann, 2003). As maghemite is isostructural with magnetite (Fe$_3$O$_4$), which contains Fe(II) besides Fe(III) in its crystal lattice, the thermal formation of maghemite is thought to proceed via magnetite. The oxidation of Fe(II) in the magnetite structure is compensated by cation vacancies in the maghemite structure (Cornell & Schwertmann, 2003). Besides the thermal transformation pathway, maghemite can also directly be precipitated from mixed...
Fe(II)/Fe(III)-solutions with very slow oxidation rates at room temperature and pH 7 (Schwertmann & Cornell, 2000).

Almost all of the other minerals can function as a precursor for hematite via thermal or hydrothermal transformation or under mechanical stress. Only with lepidocrocite as a precursor, transformation proceeds over maghemite as an intermediate phase (Cornell & Schwertmann, 2003). Hematite can also be formed from ferrihydrite via solution transformation, preferably at elevated temperatures (T > 80 °C). During the transformation, hematite formation is preferred over goethite with the pH becoming not too alkaline which would promote hydrolysis with OH⁻ and therefore goethite formation instead of hematite (Cornell & Schwertmann, 2003). Whereas transformation of ferrihydrite to goethite can be promoted by addition of goethite seeding crystals, this is not possible with hematite, indicating that the transformation mechanism of ferrihydrite to hematite is not as simple as transformation to goethite (Atkinson et al., 1968, Fischer & Schwertmann, 1975, Cornell & Schwertmann, 1979, Cornell & Giovanoli, 1987).

The minerals that are most important in well ageing by chemical Fe-clogging have been identified in several studies by measurements of field samples. They primarily consist of ferrihydrite and goethite and minor amounts of lepidocrocite and traces of hematite or maghemite (Houben et al., 1999, Metzger, 2011). So far, magnetite, ferroxyhyte, schwertmannite, jarosite and akaganéite have not been observed (Houben et al., 1999, Houben, 2003a, 2003b, Houben & Treskatis, 2007, Metzger, 2011). Nonetheless, in the mineralogical analyses and hydrochemical calculations presented in this thesis, all these minerals will be taken into account, to validate the processes of precipitations in the experimental set-up and to affirm its similarity to the processes observed in the field.
3 Geography and Geology of the Rhenish Lignite District

As the material that is used in the model originates from the Rhenish lignite mining district, a brief overview of the geological history of the region and the conditions during sedimentation of the materials applied shall be given in this section. For comparison with the situation in the field, an overview of the main hydrogeological units and their general hydrochemistry will be given as well.

3.1 Geographical overview and tectonic and sedimentary history

The Rhenish lignite mining district is located at the south rim of the Lower Rhine Embayment. The embayment is located in the westernmost part of Germany and dissects the northern rim of the Variscian (Devonian to Carboniferous) mountains into the left and right Rhenish slate mountains, the Eifel to the west and the Bergisches Land to the east (Walter, 2007).

Geotectonic subsidence of the embayment started in the late Tertiary period (Oligocene, Miocene). During that period, a series of sometimes localised marine transgression and regression sequences sedimented in the embayment (Knufinke & Kothen, 1997, Walter, 2010). The embayment is tectonically subdivided into the Cologne-block in the southeast, Krefeld-block in the northeast, Venlo-block in the central north, Erft-block in the central south and Rur-block in the west (Figure 23).

![Tectonic overview of the Lower Rhine Embayment with distributions of coal seams and locations of the open-pits of the Rhenish lignite district (Stoll et al., 2009, redrawn, translated)](image-url)
The resulting stratigraphy consists of an alternation between shallow marine sand and clay layers with marshy or swampy peat and lignite sediments (Schneider & Thiele, 1965). After the final regression of the Tertiary ocean in the late Miocene, an overburden of estuarine and deltaic terrestrial sediments was deposited until the late Pliocene. During the Quaternary period (Pleistocene and Holocene), formation of fluvial terraces of the Rhine dominated the sedimentary milieu (Walter, 2007). The thicknesses of the individual lignite seams and their overburden greatly differ between the various tectonic blocks and their paleo-tectonic rates of subsidence and sedimentation (Figure 24, Knufinke & Kothen, 1997). The Tertiary and Quaternary stratigraphy and hydro-stratigraphy of the Lower Rhine Embayment was defined in 1965 by Schneider and Thiele (1965) and implemented as technical standard DIN 21919 by the German Institute for Standardization (2001).

![Geologic profile through the Lower Rhine Embayment with horizon numbers according to Schneider and Thiele (1965) in centred numbers (Knufinke & Kothen, 1997, redrawn, translated)](image)

### 3.2 Hydrostratigraphy

To allow for a dry extraction of the Miocene lignite in the open-pits of the Rhenish lignite district, the Tertiary and Quaternary sandy and gravelly interlayers need to be locally dewatered. As several of these interlayers were deposited in anaerobic shallow marine conditions, sedimentary contents of pyrite may cause elevated contents of ferrous iron and sulphate as well as lowered pH-values in the anaerobic groundwater originating from pyrite oxidation (Bergmann, 1999).

The most important aquifers atop the coal seams to dewater in the Rhenish district are the terrestrial sediments of the Quaternary Rhine terraces (“Hauptterrasse”, Horizon 16 (Hz. 16) after DIN 21919 by the German Institute for Standardization, 2001) and Upper Miocene main gravel series (“Hauptkiesserie”, Hz. 8). The Schophoven Sand (Hz. 7E), Kirchberg Sand (Hz. 7C), Friesheim Sand (Hz. 7A), Neurath Sand (Hz. 6D/C) and Frimmersdorf Sand (Hz. 6B) are shallow marine sands that are deposited intermittently with the Miocene coal seams, continued by
the Morken Sand (Hz. 5D/B) and Kerpen Sand (Hz. 4C/B/A) which in most regions of the district form the basis below the coal seams (DIN 21919; German Institute for Standardization, 2001).

The hydrochemistry of these aquifers in general follows the geochemistry of the sediments and the effects of anthropogenic influence factors. Human interactions with the groundwater (agricultural fertilisation, road salt) in the shallow aquifers are indicated by elevated contents of Cl\textsuperscript-, NO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} (Table 2) which are more prominent in the upper Hz. 16 when compared to the lower Hz. 8, showing the human interference to decrease with depth (Bergmann, 1999). Increased Eh-values and contents of dissolved oxygen as well as low S\textsuperscript{2-} and Fe\textsuperscript{2+}-contents signify the aerobic conditions of the shallow groundwater (Bergmann, 1999).

### Table 2

Mean values of hydrochemical parameters in the groundwater levels dewatered in regions of the Rhenish lignite mining district that are undisturbed by the mining facilities (values given by Bergmann, 1999, validated and compared with Reinisch, 2009)

<table>
<thead>
<tr>
<th>Hz. stratum</th>
<th>Fe\textsuperscript{2+}</th>
<th>Ca\textsuperscript{2+}</th>
<th>DO</th>
<th>HCO\textsubscript{3}</th>
<th>Cl</th>
<th>NO\textsubscript{3}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>S\textsuperscript{2-}</th>
<th>Eh</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 Hauptterrasse</td>
<td>0.3</td>
<td>125</td>
<td>4.0</td>
<td>340</td>
<td>70</td>
<td>72</td>
<td>130</td>
<td>3</td>
<td>338</td>
<td>6.5</td>
</tr>
<tr>
<td>8  Hauptkiesserie</td>
<td>1.5</td>
<td>99</td>
<td>1.0</td>
<td>390</td>
<td>25</td>
<td>6</td>
<td>47</td>
<td>1</td>
<td>186</td>
<td>6.9</td>
</tr>
<tr>
<td>6D Neurath Sand</td>
<td>3.0</td>
<td>91</td>
<td>0.2</td>
<td>550</td>
<td>13</td>
<td>2</td>
<td>15</td>
<td>15</td>
<td>95</td>
<td>6.9</td>
</tr>
<tr>
<td>6B Frimmersdorf Sand</td>
<td>5.1</td>
<td>67</td>
<td>0.0</td>
<td>580</td>
<td>6</td>
<td>0</td>
<td>4</td>
<td>20</td>
<td>24</td>
<td>6.9</td>
</tr>
<tr>
<td>5  Morken Sand</td>
<td>1.4</td>
<td>57</td>
<td>0.0</td>
<td>460</td>
<td>6</td>
<td>0</td>
<td>3</td>
<td>8</td>
<td>163</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Since the deeper aquifers are not affected by agricultural fertilisation and street salt application, contents of Cl\textsuperscript-, NO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsubscript{2-} decrease in the deeper aquifers. Even so, the redox-milieu shifts towards more anaerobic conditions in the shallow marine and deeply buried sand layers, which can be inferred from lower Eh-values and lower contents of SO\textsubscript{4}\textsubscript{2-}, NO\textsubscript{3}\textsuperscript{-} and DO and higher contents of Fe\textsuperscript{2+} and S\textsuperscript{2-}. As the shallow aquifers are widely covered by Pleistocene loess layers and the deep aquifers are shallow marine sands (Fliegel, 1937), all groundwater levels contain substantial amounts of HCO\textsubscript{3} and Ca\textsuperscript{2+} that show an indifferent behaviour with respect to depth. However, as shown by Reinisch (2009), there can be huge local variations of the general hydrochemical distribution that may be due to anthropogenic effects of surface mining and aquifer dewatering or local geological conditions allowing interactions between the individual aquifers on the different tectonic blocks.

### 3.3 Locations and sedimentary history of relevant gravel pits

The gravel used for construction of the filter pack of vertical filter wells in the Rhenish lignite mining district is produced in gravel pits in close vicinity to the huge lignite open-pits. The material that has been used until now was produced in a Tertiary deposit in Weilerswist, 25 km SE of the open-pit Hambach (Figure 25). As it is known that the approved claim area of the Weilerswist gravel pit will soon reach depletion, search for alternative materials or deposits near the lignite open-pit began. Two possible alternatives were the Quaternary gravel pits in Frimmersdorf and Dorsfeld 2 km southeast of the open-pits Garzweiler and
Hambach, respectively (Figure 25). All three deposits consist of fluvial sediments of the Rhine. The main difference between the conventional Weilerswist gravel and the alternative gravels from Dorsfeld and Frimmersdorf is the time of their sedimentation during the geo-tectonic development of the area. Succeeding the synsedimentary subsidence and the repetitive Tertiary transgression and regression cycles, the “main gravel series” (Hauptkiesserie, Hz. 8) was sedimented 5.5 million years ago, at the transition from the Miocene to the Pliocene period. At that time, the delivery area of the sediments reached as far as the Alsace-Lorraine area via the paleo-Rhine and the Paris Basin via the Moselle. During this long way of transport, the sediments were matured mineralogically (Walter, 2010), causing the more brittle minerals to be ground to small grains that are transported away with the current of the river. The remaining bed load almost exclusively consisted of hard quartz grains that sedimented on the ground of the river to form the so-called Kieseloolith-layer (Fliegel, 1910) or “Hauptkiesserie” that today is used to produce filter gravel in the Weilerswist gravel-pit. The deep burial of the layers into the anoxic underground contributes to the white colouring of the gravel.

Figure 25 Locations of the three gravel pits Weilerswist (conventional Tertiary gravel material), Dorsfeld and Frimmersdorf (alternative Quaternary gravel materials) in the Rhenish lignite mining district (Deutscher Braunkohlen-Industrie-Verein e.V. (DEBRIV) – Bundesverband Braunkohle, 2013b, redrawn, translated, locations of gravel pits inserted Weidner et al., 2013)

Until the Pleistocene period, around 0.75 million years ago, the origin of the material sedimented by the Rhine had been shifted towards closer areas like the slowly rising Ardennes and Rhenish Massif from the “Siebengebirge” and the Eastern Eifel volcanic zone to the Lahn-Taunus and Nahe-Hunsrück area. Due to the short pathways of transport, the sediment is of lower mineralogical maturity than the Tertiary gravel and can reach quartz contents as low as 20% (Walter, 2010). The other components of the gravel are white to violet-red Taunus-quartzites, siliceous shale and iron flint from the Lahn-area (Walter, 2010). On top of that, the
Quaternary gravel materials may contain initial amounts of ferric hydroxides due to their shallow burial into the aerobic underground and relatively thin covering. The properties of the different gravel materials resulting from these geologic depositional conditions and their possible impact on the applicability of the materials for well construction are summarised in section 4.1.2.

At the western flank of the Ville (cf. Figure 23), the Tertiary Hauptkieserie is easily accessible close to the ground surface (overburden less than 10 m, often even without any cover, e.g. next to the Swistbach near Wellerswist, bpγ, Figure 26) and becomes as thick as 20 m. Compared to that, on the Erft-block, the Hauptkieserie reaches thicknesses of around 200 m, but is buried under a cover of up to 260 m. Thus, in the vicinity of the open-pits, the Tertiary gravel is not as easily available as uppermost Quaternary gravels of the youngest Rhenish terrace-sediments which cover a large area of the Lower Rhine Embayment with thicknesses between 15 and 75 m. The Quaternary gravels of the main Rhine terrace sediments are buried only under a thin layer of loess that rarely reaches a maximum thickness of 10 m (dg or dγ over dg, Fliegel, 1910) and are thus easily accessible for production in the gravel pits in Dorsfeld and Frimmersdorf.

![Fig. 26](image)

**Figure 26** Locations of the three gravel pits in a geological context (left: Fliegel, 1910; centre: Quaas, 1908; right: Krause, 1912)

In the geologic map of Frimmersdorf, the change in the landscape due to extensive mining and construction activities in the region during the last 100 years becomes obvious by the change of the deviation of the river Erft at the time of compiling the map and the current directions. At the rim of the former alluvial meadows of the Erft, the layers of the „Hauptterrasse” (dg) are accessible for gravel production.
4 Materials and Methods

4.1 Materials

4.1.1 Aquifer material

The aquifer material that was applied for all experimental simulations was taken from the open-pit Garzweiler to allow for a realistic experimental simulation of the natural conditions in a dewatering well. As the experiments were conducted under anaerobic conditions of the deeper aquifers, one big bag (flexible intermediate bulk container; FIBC) of the fine and well-sorted (Figure 27), greenish-grey Frimmersdorf Sand (Hz 6B) from the open-pit Garzweiler was provided by the RWE Power AG. According to Bergmann (1999), the Frimmersdorf Sand contains up to 0.13 wt.-% Fe_{tot} (40% in pyrite, 32% in silicates, 28% in hydroxidic minerals) and 0.2 to 0.5 wt.-% of organically bound carbon. Inorganic carbon only reaches 0.01 to 0.03 wt.-%, around half of which is bound in calcite (CaCO₃), half in siderite (FeCO₃).

![Grain size distribution of the aquifer material](image)

Figure 27: Grain size distribution of the aquifer material applied in the experimental clogging model (Klauder, 2010)

4.1.2 Gravel pack materials

The gravel pack materials were varied during the experimental investigations described in this thesis to evaluate their reaction towards long term elution in contact with tap water and their affinity towards chemical Fe-clogging. To allow for an interpretation of the results, the properties of the gravel materials applied are briefly described in the following section.

The grain size distributions of the gravel materials were determined at the IWW by sieve analyses. As Klauder (2010) found the grain size class of 1.4 to 2.2 mm to perform best for the gravel pack in the Frimmersdorf sand layers and this grain size class has become the most
commonly applied since (cf. section 2.2), grain sizes of all gravels tested in the experiments in this thesis were chosen accordingly (Figure 28).

The mineralogical inventories of the Quaternary and Tertiary gravel materials were evaluated prior to their application in the experimental columns and clogging model by X-ray diffractometric (XRD) and X-ray fluorescent (XRF) analyses in the mineralogical laboratory of the RWE Power AG (Dr. Markus Neuroth). The results of the XRD analyses showed quartz to represent the dominating mineral phase of all three gravels with contents of > 95 wt.-%. Accessory contents of feldspars (tectosilicates) like orthoclase (KAlSi₃O₈) and sanidine ((K,Na)AlSi₃O₈) were partly hidden behind the strong reflexes and peaks of the quartz contents.

According to DIN 4924 after the German Institute for Standardization (1998, 2012), in respect to mineralogy, only the relative content of silicon dioxide as determined via XRF-analysis is of relevance for the applicability of a gravel material as a filter medium. This amount of SiO₂ that is not equal to the mineralogical quartz content and does not necessarily need to originate solely from quartz, is defined to be at least 96 % (DIN 4924; German Institute for...
Standardization, 1998, 2012). The results of the XRF-analyses (Table 3) show the Dorsfeld gravel to be the only of the three gravels strictly fulfilling this requirement. Whereas the conventional Weilerswist gravel nearly reaches 96 wt.-% SiO₂, the Frimmersdorf gravel even stays below 94 wt.-%.

Besides increased Fe-contents in the Quaternary gravel materials and especially in the Frimmersdorf gravel, the XRF-data also shows a higher loss of ignition (LOI) as well as higher relative contents of Al, Mg and Na in the Frimmersdorf gravel that point to higher non-quartz-contents therein (Table 3). The elevated LOI can be due to escaping moisture from the crystal lattice of clay minerals, CO₂ from carbonates or combustion of organic ingredients. Al and Na presumably result from increased amounts of feldspars within the mineralogical inventory (orthoclase or sanidine), Mg from minor contents of dolomite (CaMg(CO₃)₂) or staurolite ((Fe(II),Mg,Zn)₂Al₉(Si,Al)₄O₂₂(OH)₂) (Yoo, 2008). The same goes for the elevated content of K in the Weilerswist gravel which is associated with – compared to the Dorsfeld gravel – increased amounts of Al and Na that also originate from increased contents of feldspar in the Weilerswist gravel (Walter, 2010).

Table 3 Results of XRF analyses of the initial gravel materials [wt.-%]. LOI: Loss of ignition at 815 °C, exceeding the temperature of 550 °C that is recommended by DIN 18128 of the German Institute for Standardization (2002; Frerix, 2012)

<table>
<thead>
<tr>
<th>Sample</th>
<th>LOI</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>MnO</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dorsfeld</td>
<td>0.34</td>
<td>96.1</td>
<td>0.59</td>
<td>1.75</td>
<td>0.25</td>
<td>0.25</td>
<td>0.19</td>
<td>0.69</td>
<td>&lt;0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Frimmersdorf</td>
<td>1.22</td>
<td>93.6</td>
<td>0.90</td>
<td>2.74</td>
<td>0.25</td>
<td>0.35</td>
<td>0.29</td>
<td>0.89</td>
<td>&lt;0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Weilerswist</td>
<td>0.53</td>
<td>95.6</td>
<td>0.25</td>
<td>2.04</td>
<td>0.25</td>
<td>0.25</td>
<td>0.24</td>
<td>1.16</td>
<td>&lt;0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>

The initial contents of ferric iron bound in hydroxidic minerals (Figure 29) were determined via a sequential extraction procedure (SEP) that is described in detail in section 4.3.8. The increased contents of initial oxidic Fe-minerals in the Frimmersdorf gravel is consistent with the optical impression and ochreous colouring of the gravel grains as well as the results of the XRF-analyses that also indicate increased contents of Fe in the Frimmersdorf gravel (Table 3). However, the results of the two analyses cannot be compared directly, as the extraction procedure does not include iron possibly bound in alumosilicates like biotite (K(Mg,Fe⁴⁺)₃(Si₂Al)O₁₀(OH,F)₂) or staurolite ((Fe(II),Mg,Zn)₂Al₉(Si,Al)₄O₂₂(OH)₂) (Yoo, 2008). Furthermore, the extraction gives the mass of Fe relative to the total mass of the gravel, whereas in the XRF-procedure the total amounts of carbon are expelled from the sample and relative percental masses of oxides of all other elements are measured.

Apart from the natural gravel materials, artificially produced glass beads with diameters between 1.25 and 1.65 mm of the company Sigmund Lindner GmbH were tested for their affinity towards chemical Fe-clogging as an alternative filter pack material. The main advantages of glass beads in comparison to natural gravel materials are their general surface properties. As glass beads exhibit a nearly perfectly spherical shape, not only the ratio of surface area per volume of a single bead but also of a filter pack made up of glass beads is at its optimum. Furthermore, due to the very narrow distribution of grain sizes (cf. Figure 28), the packing of the glass beads also exhibits a nearly highest-density close sphere packing and an optimal distribution of the flow-effective porosity. Also at the microscopic scale,
smooth surface of the glass beads does not offer many rough edges that could function as starting points for crystallisation, sorption and precipitation (Treskatis et al., 2010, Figure 30).

Disadvantages of glass beads compared to naturally available gravel materials are high financial and energetic costs in glass bead production. Amortisation of the investment costs for glass beads is conceivable in a long term view, if the clogging affinity of the filter medium and therefore reduced operating costs of a well can be substantially decreased. According to calculations of the glass bead producer Sigmund Lindner GmbH, amortisation in water wells can be expected after 25 years of use (Treskatis et al., 2010, Sigmund Lindner GmbH, 2014). However, in open-pit dewatering, the total lifetime of vertical filter wells is often planned much shorter than that, as the wells are excavated with continuing succession of the open-pit. Furthermore, the economic considerations for shallow and deep wells after Klaus and Walter (2011) only consider drinking water well with depths between 30 and 150 m and small diameters and the economic advantage after 40 years of use which are not realistic in dewatering applications of huge open-pits. The main advantage is seen in lower operating costs and in the increase of the interval of necessary regeneration measures. These economic considerations cannot without caution be transferred to the open-pit dewatering wells of the Rhenish lignite district, because they have substantially greater well depths, higher investment costs, shorter planned lifetimes and because regeneration measures are usually not conducted here at all.

4.1.3 Screen pipes

The screen pipes that were considered during the clogging experiments were also provided by the RWE Power AG. The only variable in the single clogging experiments, however, was the
lengths of the screen pipes and their state of aeration. For all experiments, a prepacked GRP-rod screen with grain sizes of the prepack-gravel of 3 to 5 mm was used which was found to exhibit the best hydraulic conditions by Klauder (2010). In the material tests, the whole 200 mm height of the flow channel was covered by the screen pipe (Figure 31, top). To allow for simulation of different situation of screen pipe aeration, a shortened screen pipe, of 30 mm height was applied in the LTs 15 and 16 (Figure 31, bottom). The upper 170 mm part of the screen pipe was replaced with a PMMA-plate with venting hole to simulate a well casing. Thus, the shortened screen pipe stayed submerged even when the low $h_{OC} = 40$ mm of the Fe-clogging phase was applied.

![Figure 31](image)

**Figure 31** 200×200 mm section of a GRP-rod screen pipe (top; final report phase II, 2011) and shortened, 200×30 mm screen section for evaluation of filter aeration effects (bottom; final report phase III, 2013, redrawn, translated)

### 4.2 Column experiments

Column experiments were conducted to evaluate and quantify the potential of the different gravel materials towards release (or capture) of different major ions or distinct (semi-)metallic substances. The column experiments were primarily conducted to evaluate the influence of the gravel material on the quality of the water as well as to observe possible dissolution processes of minerals contained in the gravel that in a long term view could affect their mechanical stability. As glass beads are known to exhibit a higher chemical inertia in comparison with natural gravel materials (Treskatis, 2011), the glass beads were not tested in
this context. The two alternative Quaternary gravel materials from Dorsfeld and Frimmersdorf were tested in two replicas each, compared with a fifth control-column filled with the conventional Tertiary Weilerswist gravel.

4.2.1 Experimental set-up

The laboratory columns consisted of 600 mm long PMMA-tubes with an inner diameter of 100 mm. At top and bottom, the various columns are covered with PTFE-obturator parts, filter plates and out- and inflow-tubes. The columns were filled with the gravel, saturated with tap water and compacted with a wooden plunger. The total mass of the equipment of each empty and filled column and the mass of gravel inserted into each column were documented to calculate the total porosity of the assembly. A constant hydraulic gradient was realised by continuously filling tap water into elevated tanks with spill-over openings (Figure 32). The elevated tanks were connected to the inflow tubes at the bottom of each column. The column outflow tubes at the top of each column were installed at a fixed height. The pressure differences, i.e. hydraulic gradients between in- and outflow were individually measured for each column and adjusted by elevating the column height, if necessary to reach a reasonable amount of discharge for each column (Figure 32). In the in-and outflow-tube, three-way valves were installed to allow tracer injection at the inflow or sampling and measuring discharge at the outflow.

![Experimental set-up of the long-term elution column experiments in the hydraulic laboratory of the LFH (Weidner et al., 2013)](image)

4.2.2 Tracer experiments

Conservative tracer experiments using a nonreactive Br⁻-tracer were conducted in each column to determine the amount of actually flow effective pore volume and to normalise the flow through the columns to the number of pore volumes exchanged (PV). The solution for tracer injection was prepared by diluting 4.336 g of LiBr in 50 mL of deionised water
(79.79 g L\(^{-1}\) Br\(^{-}\)). Five mL of this tracer solution were injected into the inflow tube during column operation, equating a total of 399 mg Br\(^{-}\). In the outflow, bromide concentrations were measured with an ion sensitive electrode (Mettler Toledo DX280-Br with reference electrode and the handheld device WTW pH 340i) in a time series after tracer injection (Figure 33). The average flow velocity was determined from the time after tracer injection at which half of the tracer had passed the column by constructing the cumulative tracer passage curve, normalised by the tracer injection mass:

\[
\sum c(t) = \frac{c(t) \cdot Q(t) \cdot t}{m_{in}}
\]  

(37)

Figure 33 Preparation of tracer injection with a syringe (left) and measurement of Br\(^{-}\)-transport (report long term elution, 2012)

with \(\Sigma c(t)\) = time-dependent normalised cumulative tracer passage [-], \(c(t)\) = time-dependent tracer concentration [mg L\(^{-1}\)], \(Q(t)\) = time-dependent rate of flow through the column [L s\(^{-1}\)], \(t\) = total time of the tracer test [s], \(m_{in} = 399\) mg = total mass of tracer injected [mg]. When the curve of \(\Sigma c(t)\) reached a value of 0.5, half of the total observed tracer mass passed the column, which gave the average flow-duration in the column \(t_{0.5}\). Due to dispersion and diffusion, half of the tracer was faster and the other half was slower. From that, the average flow distance velocity could be calculated as follows:

\[
v_d = v_{med} = \frac{l_{col}}{t_{0.5}} = \frac{l_{col}}{t_{med}}
\]  

(38)

with \(v_d = v_{med} =\) average flow distance velocity or median transport velocity [m s\(^{-1}\)], \(l_{col}\) = length of the column [m], \(t_{0.5}\) = \(t_{med}\) = average flow duration or median flow duration in the column, time between tracer injection and passage of 50 % of the total observed tracer mass [s]. The flow effective pore volume as a percentage on the total volume could then be calculated by:

\[
n_e = \frac{q}{v_d A_{col}} = \frac{Q}{v_d A_{col}}
\]  

(39)

with \(n_e =\) flow effective porosity [-], \(q = Q/A_{col} =\) specific flow rate [m s\(^{-1}\)], \(Q =\) rate of flow through the column [L s\(^{-1}\)], \(A_{col}\) = cross-sectional area of the column, perpendicular to flow
direction \([\text{m}^2]\). The normalisation of the time axis to the expression as pore volumes exchanged could then be calculated as follows:

\[
P V(t) = \frac{Q(t) \cdot t}{V_e} = \frac{Q(t) \cdot t}{V_{\text{col}} \cdot n_e}
\]

with PV\((t)\) = time-dependent number of pore volumes \((\text{PV})\) exchanged \([-]\), Q\((t)\) = time-dependent rate of flow through the column \([\text{L s}^{-1}]\), t = time \([\text{s}]\), V\(_e\) = flow effective pore volume \([\text{L}]\), V\(_{\text{col}}\) = total column volume \([\text{L}]\). The data thus became independent from the actual flow times and discharge values and could easily be adapted to different Q/t-conditions.

### 4.2.3 Measurements and data recording

Tap water was directed through the columns for 11 weeks with two shutdown periods to allow for intense reaction times of once four days and once two weeks (Table 4).

**Table 4**  **Schedule for column experiments (report long term elution, 2012)**

<table>
<thead>
<tr>
<th>Week</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>column assembly</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>initial phase until stationarity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st sampling of main ions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>conservative tracer experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st shutdown period (4 days)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>column operation period</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd shutdown period (2 weeks)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd sampling of main ions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rinsing after long shutdown period</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd sampling of main ions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During the whole period of column operation, daily samples were taken in the in- and outflow for measurements of hydrochemical parameters. As all the elevated tanks were continuously filled with the same tap water, sampling of the inflow water was only done in one of the elevated tanks. Sampling in the outflow was performed simultaneously with the measurements of the flow rate (Figure 34).

**Figure 34**  **Schematic experimental set-up of the long-term elution column experiments with numbers of columns C1 to C5 and sampling points marked with red crosses (Weidner et al., 2013)**
The samples were analysed immediately for their pH and electrical conductivity (eC), acidified with concentrated nitric acid and given to an external laboratory for analysis of the (semi-)metals Si, Al, Fe and Mn via ICP-MS (DIN EN ISO 17294-2; German Institute for Standardization, 2005a), to estimate the change in the hydrochemical parameters and (semi-)metal-contents in contact with the gravel material. Thrice during column operation, additional samples were taken to analyse the contents of Na⁺, K⁺, Mg²⁺, Ca²⁺, NO₃⁻, SO₄²⁻, Cl⁻, F⁻ and HCO₃⁻ in the in- and outflow of the columns. The first analysis of main ions was done before the tracer tests after an initial operating phase that was conducted until stationarity of flow was reached. The second sampling for main ions was done after the long shutdown period and the third immediately before final column shutdown at the end of the experiment. Samples taken after shutdown-periods were immediately taken after restarting the flow to representatively depict the effects of first flush after prolonged reaction times.

Measurement of cations was conducted via ICP-MS, whereas NO₃⁻, SO₄²⁻, Cl⁻ was conducted via ion chromatography after DIN EN ISO 10304-1 by the German Institute for Standardization (2009), F⁻ via ion sensitive electrode after DIN 38405-4 by the German Institute for Standardization (1985) and HCO₃⁻ via titration after DIN 38409-7 by the German Institute for Standardization (2005b).

The data for main ions was used in hydrochemical modelling with PhreeqC for Windows (version: 2.18.00, database: wateq4f.dat, Parkhurst & Appelo, 1999), to determine saturation indices and the distribution of species in the column in- and outflow.

### 4.2.4 Data processing and evaluation

Besides the conversion of the time axis as given above, the concentrations of the (semi-)metals were converted to the mass flow \( m_i \) per pore volume PV:

\[
\frac{m_i(PV)}{m_{gravel}} = \frac{m_i(t) \cdot V_e}{Q(t) \cdot m_{gravel}} = \frac{c_i(t) \cdot V_e}{m_{gravel}}
\]

with \( m_i(PV) \) or \( m_i(t) \) = mass flow rate of (semi-)metal \( i \) dependent on numbers of pore volumes exchanged [g PV⁻¹] or time [g s⁻¹], respectively, \( m_{gravel} \) = total mass of gravel in the column [g], \( c_i(t) \) = time-dependent concentration of (semi-)metal \( i \) [g L⁻¹]. The amount of (semi-)metals released from the gravel could therefore be expressed as mass of the specific (semi-)metal in milligrams per mass of gravel in metric tons per pore volume exchanged [mg t⁻¹ PV⁻¹]. The values in the outflow were compared to the inflow values to identify possible capture and release of the specific (semi-)metal. The time series were plotted versus pore volumes exchanged or versus time to compare with the measurements of pH and eC (report long term elution, 2012, Weidner et al., 2013).

With the hydrochemical parameters and contents of main ions, the distribution of species of the four considered (semi-)metals and saturation indices of corresponding minerals were calculated with the hydro-geochemical modelling software PhreeqC for Windows (version: 2.18.00, database: wateq4f.dat, Parkhurst & Appelo, 1999).
4.2.5 PhreeqC-calculations

The elemental species distributions and saturation indices of relevant mineral phases as well as their development during the experiments were calculated using the hydro-geochemical modelling software PhreeqC for Windows (version: 2.18.00, database: wateq4f.dat, Parkhurst & Appelo, 1999) for 7 selected times during the column experiments in the in- and outflow of the columns: initial conditions, conditions before and immediately after the first shutdown period, conditions during normal column operation, conditions before and immediately after the second shutdown period and conditions at the end of the experiments.

The data for the main ions was, if available, either taken directly from the measurements or, if not available determined from the latest and next measurements by a time-weighted average. The data for (semi-)metals and pH was taken from the daily measurements, whereas the predefined values of pe = 4 (Eh ≈ 230 mV) and T = 20 °C was used for all calculations that were based on the database phreeqc.dat (Appendix 1). The time series of the species and saturation indices (SI) were plotted element-specifically as well as column-specifically. Dissolved (semi-)metal species were plotted on the primary y-axis as a share on the total species inventory, saturation indices on the secondary y-axis (report long term elution, 2012).

4.3 Experimental clogging model

After investigating the elusive properties of the gravel materials, the affinity of the different gravels towards clogging with chemical Fe-precipitation was evaluated with a combined hydraulic-hydrochemical experimental model that was developed by the IWW in cooperation with the LFH and RWE Power AG. In this section, the experimental set-up and general concept of model operation will be explained, before the topics of the modelled scenarios are presented in section 4.4.

4.3.1 Experimental set-up

In the experimental clogging model, a section of a vertical filter well (Figure 35) was reconstructed in the laboratory as similar to the natural conditions as possible. With respect to spatial dimensions, the model was executed in an unscaled manner. The well section was constructed in a flow channel with artificially prepared process water actively pumped through the channel. The hydrochemical conditions of the process water were especially adjusted to adapt the scale of the fourth dimension in the model and to create an accelerating effect to reproduce chemical Fe-clogging and its impact on the hydraulic conditions in different well filter settings in the laboratory in an appropriate time frame.
To achieve this, after passing the flow channel the process water was regenerated in a process cycle to once again flow through the well section. The whole cycle of the experimental model is illustrated in Figure 36. Before describing the flow channel itself in section 4.3.4, an overview of the individual components of the peripheral water regenerating cycle (section 4.3.2) and of the measurement points and devices of hydraulic and hydrochemical parameters of the peripheral cycle (section 4.3.3) will be given.
4.3.2 Peripheral water regenerating model cycle

The peripheral model cycle was divided into two major parts. The primary, post-flow-channel part was oxygen-bearing, whereas the pre-flow channel part was free of oxygen. The water leaving the flow channel was actively pumped at a rate of around $1.06 \text{ L min}^{-1}$ with an outflow pump (OutP) that first passed the first addition point (AdP 1) of the model (Figure 37, top). At this point, a solution of Fe(II)Cl$_2$ with $c(\text{Fe(II)}) = 30 \text{ g L}^{-1}$ was added to the process water along with a variable amount of NaOH of three different molarities. The solutions were added by two peristaltic proportioner pumps (Ismatec Laboratoriumstechnik) and could be adjusted by changing the number and diameter of the pump hose, the frequency of the peristaltic pump and/or – in case of NaOH – the molarity of the solution. Downstream of the addition point, the added chemicals were mixed with the process water by compulsory auto-mixers (spirals in Figure 36; Figure 37, bottom).

Ferrous iron solution was added at addition point 1 for two reasons. Firstly, as the concentration of ferrous iron decreased by precipitation of ferric hydroxides in the flow channel through the clogging reaction, the Fe(II)-concentration needed to be readjusted. Secondly, Fe(II) was added in excess in order to bind oxygen remaining in the water from the active air-supply in the flow channel by oxidation of Fe(II) and precipitation as Fe(III)-hydroxides and to readjust the redox-conditions.

The Fe(III)-hydroxides, precipitated to remove remaining oxygen, were captured in a filter column of medium sand (Figure 38, left), to prevent particles from being transported into the flow channel inflow.

The next system element of the cycle was an ultraviolet disinfection lamp (“UV” in Figure 36; Figure 38, centre), which was installed to keep the system free of microbiological contaminations and to exclude effects of biological clogging from the experiments. Behind the second addition point, where pH was adjusted by NaOH-addition, the process water was directed into a flexible water tank (Figure 39), in which fluctuations in the total volume of water were compensated and peaks in the hydrochemistry (e.g. pH-peaks due to over-
regulation at AdP 1) were buffered by dilution with a huge storage volume of process water (between 50 and 80 L). Thus, the total volume of water in the flexible water tank was exchanged completely approximately once in an hour. From that reservoir, the water was pumped at a constant rate through a last fine filtration step (Figure 38, right) to remove green rusts that may have formed under conditions of locally extremely increased pH at AdP 2, before re-entering the flow channel.

4.3.3 Measurements in the peripheral water cycle

At several points in the water cycle, measurements of hydraulic and hydrochemical parameters were integrated into the model system. The hydrochemical parameters were monitored in three measurement cells (MC in Figure 36; Figure 40, left). Additionally, the pH was measured immediately behind addition point 2 to allow for immediate intervention of pH-regulation and to avoid injection of prolonged pH peaks into the water tank. Hydrochemical measurements behind the flow channel were actually conducted inside the outflow chamber. For the hydrochemical parameters, probes from WTW, Schott or Mettler Toledo were connected to WTW handheld devices that were connected to serial ports of the main control PC with an interconnected galvanic separation. In advance of each long term test, the probes were cleaned with a mixture of oxalic acid and ascorbic acid and calibrated with the respectively appropriate WTW standard solutions.

The system flow rate of the in- and outflow pump were each measured behind the respective filter columns, for O₂-removal and green rust filtration, respectively and the subsequent hydrochemical measurement cells with mechanical impeller devices (Meister Strömungstechnik; symbols between MC I and flow channel and MC III and UV in Figure 36; Figure 40, right).
The data sent by the hydrochemical and hydraulic measurement devices was decoded, displayed and stored to a file server as ASCII-files by a LabView-programme that was written by the IWW staff. From here, regulation of chemical addition and system flow were remotely possible as well.

The only measurements that required the model operator to personally take samples at four points in the model were the ones necessary for determination of the ferrous iron concentration \( c(\text{Fe(II)}) \). Depending on the current phase of model operation (cf. section 4.3.5), this was done in irregular intervals between 20 min and 3 h. Measurements before and behind the \( \text{O}_2 \)-capturing filter column were used to regulate the necessary addition of \( \text{Fe(II)Cl}_2 \)-stock solution, whereas the measurements in the in- and outflow of the flow channel were performed in order to quantify the extent of Fe-oxidation. On-site-determination of \( c(\text{Fe(II)}) \) in the samples was conducted photometrically, applying the reddish \( \text{Fe(II)} \)-phenanthroline-complex ferroine in an acetous environment after DIN 38406-1 by the German Institute for Standardization (1983) and measuring the absorption at 510 nm with the Cadas 100 spectrophotometer (Dr. Lange). The \( c(\text{Fe(II)}) \)-data was manually recorded in an MS Excel-file. Due to the high \( \text{Fe(II)} \)-concentrations of around 80 mg L\(^{-1} \) applied in the model, nearly all samples needed to be diluted by the factor of 50, raising the resolution of Fe-measurements to become \( \pm 0.50 \) mg L\(^{-1} \) on the undiluted sample concentration.

### 4.3.4 Flow channel

The flow channel was a rectangular 200 mm \( \times \) 200 mm \( \times \) 1200 mm PMMA channel with removable cover that sealed the whole channel except for the outflow chamber. The interior of the channel consisted of an inflow chamber filled with the anaerobic process water from the peripheral water cycle. Two perforated steel plates with attached wire cloth were installed perpendicular to the flow direction in order to parallelise the lines of hydraulic current. One was installed in the rearward part of the flow chamber, the other at the interface to the aquifer material. The water passed a 400 mm long pack of disturbedly embedded aquifer material, 100 mm of gravel pack and 45 mm of a screen pipe section (GRP-rod prepacked screen with 380 mm outer diameter), before entering the outflow chamber (Figure 41).
As the progression of Fe-clogging was mainly concentrated in the gravel pack material, examination of the hydraulic gradient was concentrated here by measurements of hydraulic pressure at three and later four drilled holes in the bottom of the flow channel (Figure 42). Using the distance and pressure difference in between the drillings, the flow cross-sectional area in the middle between the two measurement points and the flow rate, the hydraulic conductivity $K$ of the two (later three) sections of the well filter could be calculated by modification of Darcy’s law:

$$K = \frac{Q_{\text{Sys}}}{A \cdot i} = \frac{Q_{\text{Sys}}}{b_{FC}(h_2 + h_1)/2 \cdot (h_2 - h_1)/L} = \frac{2 \cdot Q_{\text{Sys}} \cdot L}{b_{FC}(h_2^2 - h_1^2)} \quad (42)$$

with $K =$ hydraulic conductivity of the filter gravel or screen tube $[\text{m s}^{-1}]$, $Q_{\text{Sys}} =$ system flow rate $[\text{L min}^{-1}]$, $A = b_{FC}(h_2 + h_1)/2 =$ cross-sectional area, perpendicular to flow in the middle between the two pressure measurement points P2 and P1 $[\text{mm}^2]$, $i = (h_2 - h_1)/L =$ hydraulic gradient between P2 and P1 $[-]$, $b_{FC} = 200 \text{ mm} =$ breadth of the flow channel $[\text{mm}]$, $h_{1,2} =$ hydraulic pressure (= free water level) at the two points P1 and P2, respectively $[\text{mm}]$, $L =$ length between the two points P1 and P2 $[\text{mm}]$. 

**Figure 41**  Top view of the flow channel (Weidner et al., 2012a)

**Figure 42**  Front view of the gravel pack, screen pipe and outflow chamber in the flow channel with the three sections (I to III) for analysis of hydraulic conductivity $K_i$, $K_{ii}$ and $K_{iii}$ (final report phase III, 2013)
For these calculations, the hydraulic pressure at the measurement points was continuously measured by the hydraulic pressure cell DP300-C (Mecotec). A set of electromagnetic valves were used to switch every 4 seconds between the measurement points. Hydraulic pressure data were recorded as ASCII-files by a LabView-programme and further processed with MS Excel by the IWW staff, as were the hydrochemical parameters and the values of system flow from the peripheral cycle. The hydraulic overpressure in the inflow chamber was adjusted by regulating the inflow pump (InP) of the peripheral cycle to reach a continuous system flow rate of 1.06 L min⁻¹, whereas the water level in the outflow chamber was regulated by changing the frequency of the outflow pump (OutP) to stay at a constant level during the individual phases of model operation (section 4.3.5).

The hydrochemical parameters in the flow channel were adjusted in the peripheral cycle to correspond to specified values in the channel inflow. To allow for a continuously high rate of oxidation, the inflow water was adjusted to pH ≈ 7.9 and c(Fe(II)) ≈ 80 mg L⁻¹, but DO < 0.1 mg L⁻¹, to avoid untimely precipitation of Fe(III) minerals in the channel inflow (Figure 43). In the outflow chamber, an active pneumatic air supply was installed to increase DO to roughly DO ≈ 2.0 mg L⁻¹ (Figure 44). The change of hydrochemical parameters (c(Fe(II)), DO, pH and Eh) as a result of the clogging processes was measured in the outflow chamber and recorded along with the other data (Figure 43).

![Figure 43](image1.png)  
**Figure 43**  
Front view of the flow channel in the experimental model (final report phase III, 2013, Weidner et al., 2013); the different water levels in the outflow chamber and the location of the clogging zone will be explained in section 4.3.5.

![Figure 44](image2.png)  
**Figure 44**  
Detailed top view of the outflow chamber with active air supply and measurement probes
4.3.5 Operating concept of the experimental clogging model

Based on the results of the first four clogging experiments of project phase II (section 4.4.2), a standardised experimental model operating concept was developed in order to attain comparable results from the clogging experiments of different well construction materials as well as different well operational conditions and constructional settings (Figure 45). From the beginning of project phase III, all clogging experiments were conducted following this concept.

The model system was at first prepared for the clogging test by placing the sand and gravel materials into the filter columns and the flow channel. The devices for hydrochemical and hydraulic measurements were regenerated, calibrated and put into place in advance of each new clogging experiment. The whole model system was then completely filled with previously degassed water and the air was vented from all system elements. With the flow channel excluded by a bypass tube, the water was then circulated through the system simultaneously adding moderate amounts of FeCl₂-stock solution and NaOH in order to remove residual dissolved oxygen (up to 2 mg L⁻¹) remaining in the degassed water. The addition was thoroughly controlled to prevent an increase of c(Fe(II)) in the process water but to still completely remove the dissolved oxygen from the water. The filter columns functioned as terminal sinks for both, the dissolved oxygen as well as the iron added to the system in form of Fe(III)-hydroxides.

Subsequently, the flow channel was filled, vented and rinsed with degassed water before being integrated into the system cycle and filled with the anoxic, Fe(II)-free process water. The original water from the flow channel was temporarily stored and treated with FeCl₂- and NaOH-addition before being reintroduced into the model cycle.

The first analytically relevant phase of model operation was represented by the reference test. During this phase, the flow channel was integrated into the model cycle and the initial hydraulic conditions in the gravel pack were measured without increased contents of ferrous iron. The hydraulic gradients and conductivities of the sections I, II and III were measured for the two water levels in the outflow chamber (hOC) of 40 and 100 mm that were applied in the subsequent Fe-clogging and evaluation phase of the clogging test. To ensure a statistical significance of the measured hydraulic gradients and calculated conductivities, each water level in the outflow chamber was held for at least 4 h, acquiring 780 single measurements of the piezometric head and 180 values for the hydraulic conductivities Kᵢ to Kᵢᵢ. Oxygen, diffusively added to the process water in the outflow chamber was removed by a minor addition of FeCl₂-stock solution with c(Fe(III)) always below 2 mg L⁻¹ in the whole system. Depending on the time necessary to reach stationarity of flow in the channel, the reference test could take between one and three work days.

After the reference tests, the process water could be prepared for the first Fe-clogging phase. With the flow channel disintegrated from the system once again, the water was concentrated to c(Fe(II)) = 80 mg L⁻¹ by continuously adding FeCl₂-stock solution of c(Fe(II)) = 30 g L⁻¹ at a rate of around Qₑₑ = 3 mL min⁻¹ to the model cycle with Qᵦᵦᵦᵦ = 3 L min⁻¹.
Figure 45  Model operational concept for standardised, comparative investigation of clogging affinity of specific well assemblage materials, operational modes or constructive settings (final report phase III, 2013, redrawn, translated); parameters printed in red are of major importance.
When the intended $c(\text{Fe(II)})$-value was reached, the flow channel was reintegrated into the model cycle and charged with the highly Fe(II)-bearing, pH-neutral water in order to produce incrustations of Fe(III)-hydroxides in the gravel pack, screen pipe and outflow chamber under controlled conditions. To achieve this, $c(\text{Fe(III)})$ and pH in the inflow chamber (IC), DO and the water level in the outflow chamber ($h_{\text{OC}}$) and $Q_{\text{sys}}$, needed to be kept at a constant level. $Q_{\text{sys}}$ and $h_{\text{OC}}$ were controlled by regulation of the InP and OutP, respectively, whereas DO was regulated by adjusting a valve in the pneumatic supply tube. As $c(\text{Fe(II)})$ and pH decreased as a result of the clogging reaction in the outflow chamber, FeCl$_2$ and NaOH needed to be constantly added to the system at addition point 1. Due to the active aeration of the process water in the outflow chamber, FeCl$_2$ needed to be added in excess, to remove the oxygen that was not bound by the clogging reaction in the outflow chamber. To ensure a constant ferrous iron concentration of $c(\text{Fe(II)}) = 80 \text{ ml L}^{-1}$ in the channel inflow, water samples were taken every half to full hour at four points in the system (cf. Figure 36) to estimate the necessary rate of FeCl$_2$-addition along with the addition rate of NaOH.

During the clogging phase which usually lasted about 5 h, incrustations of Fe-hydroxides primarily developed in the partly saturated zone (capillary fringe) of the filter pack. Here the DO-free, slightly alkaline, Fe(II)-bearing process water came into contact with the oxygen from the ambient air and the active pneumatic air supply, oxidising the ferrous iron to insoluble Fe(III)-hydroxides (Figure 46, left). Actually, in the vicinity of the matrix boundary between aquifer material and filter pack, the clogging zone reached higher than the optically apparent capillary fringe of the glass beads (Figure 46, right). This was due to the piezometric head as well as capillarity increasing rapidly in the aquifer material. The water slowly seeped down from the material boundary as unsaturated vertical flow components not contributing to the piezometric head, moistening the gravel with Fe(II)-bearing water and triggering Fe(III)-precipitation.

![Figure 46](image)

**Figure 46** Idealised (left) and actual (right) development of the primary clogging zone in the capillary fringe of a glass bead filter pack during the Fe-clogging phase (final report phase III, 2013); the baffle sheet in the outflow chamber was installed to smooth out the water surface from air bubbles in order to achieve accurate measurement of $h_{\text{OC}}$ with the ultrasonic device.

Main flow was concentrated in the fully saturated zone beneath the actual clogging zone and was not affected by the Fe-clogging at a constant water level. Thus, to evaluate the impact of
Fe-clogging on the hydraulic conductivity of the filter pack, the water level in the outflow chamber was raised in the evaluation phase in order to extend the flow-effective saturated zone into the area of the primary clogging zone. The change of the hydraulic conductivity with proceeding incrustation was measured in 9 evaluation steps, each succeeding another clogging step of around 5 h.

During each evaluation step of about 2.5 hours, 180 K-values were calculated to statistically and assuredly quantify the effect of Fe-clogging in the previous Fe-clogging step. During the evaluation step, the water level in the outflow chamber was kept at a constant level of 100 mm above the channel bottom, as the height of the primary clogging zone approximated 60 mm. This water level was chosen to include as many parts of the primary clogging zone as possible as well as few parts of unclogged zone as necessary. Although the pneumatic air supply was not active during the evaluation phase, a secondary clogging zone developed in the capillary fringe of the elevated water level (Figure 47, right) as the process water still contained around 80 mg L⁻¹ ferrous iron and oxygen was supplied diffusively through the open water surface. As the clogging zone only developed above the zone of the main flow relevant area, the secondary clogging zone did not interfere with evaluation of the hydraulic relevance of the primary clogging zone.

As the progress of the secondary clogging zone was not relevant for evaluating the clogging affinity of the filter material, the hydrochemistry of the process water was uncritical. The evaluation step could thus be used to adjust the hydrochemical parameters (especially $c(\text{Fe(II)})$ and pH) as preparation for the subsequent clogging step. Only the water level in the outflow chamber $h_{\text{OC}} = 100.0 \pm 0.5$ mm and the system flow $Q_{\text{SYS}} = 1.06 \pm 0.01$ L min⁻¹ were crucial for hydraulic evaluation of the primary clogging zone and had to be thoroughly regulated.

![Figure 47](image)

Figure 47 Evaluation of the hydraulic properties of the primary clogging zone of a glass bead filter pack during the evaluation phase (left) and development of the secondary clogging zone in the capillary fringe (right, final report phase III, 2013, translated)

An automatic overnight operation was impossible, because regulation of the experimental clogging model required a lot of attention and manual measurement and adjustment by the model operator. This was especially true for $Q_{\text{SYS}}$, $h_{\text{OC}}$, pH and $c(\text{Fe(II)})$. Therefore, the model
was shut down over night. To conserve the situation in the flow channel for the next day, the water level in the outflow chamber was raised to 100 mm after the afternoon clogging step to fully saturate the primary clogging zone. The flow was stopped during the shutdown periods by closing valves in the channel in- and outflow and the inflow chamber stayed fully filled with process water. Though the pneumatic air supply was also shut down over night, oxygen was still supplied diffusively over the open water surface in the outflow chamber. Nonetheless, Fe(II)-oxidation did not continue as no fresh process water was delivered to the outflow chamber and the pH in the stagnant water decreased quickly, diminishing the reaction rate and conserving the situation for the next evaluation step on the morning of the following work day.

4.3.6 Data processing and evaluation

During the different preparative and analytic phases of model operation, the various measurements of hydrochemical and hydraulic parameters were of varying importance at several points in the model. Thus, these values were phase-specifically classified into observatory, regulatory and analytical parameters (Table 5). Whilst the observatory parameters were controlled only in irregular time intervals, the regulatory parameters had to be continuously checked and regulated if necessary. These parameters, however, unlike the analytical parameters, were mostly not relevant to evaluating the intensity of the clogging process and were thus not considered in further data processing.

Most of the hydrochemical and hydraulic parameters were automatically forwarded to the control unit PC. Observatory and regulatory parameters were displayed with the LabView-programme (National Instruments) to allow immediate checking for the necessity of regulation. Analytical parameters were recorded in an ASCII-file for further processing. Some of the observatory and regulatory parameters were also recorded (e.g. addition rates of stock solutions, pump frequencies of InP and OutP) to possibly allow for automation of model regulation in the future (regulation of \( Q_{\text{in}} \), \( h_{\text{OC}} \), \( c(\text{Fe(II)}) \) and pH).

Data processing of hydrochemical parameters was conducted by importing the ASCII-files into a standardised MS Excel sheet, first eliminating values that were recorded before starting flow through the flow channel by examining the corresponding value of pressure in the inflow chamber (\( p_{\text{IC}} \)). Values, recorded as “NaN” or “0” due to timeouts of the measurement devices or manual deactivation of data recording were also eliminated from the data.

Special consideration of eC and Eh was necessary. Due to the continuous addition of FeCl₂- and NaOH-stock solutions in order to regulate \( c(\text{Fe(II)}) \) and pH, rising contents of Na⁺ and Cl⁻ caused the eC to continuously increase throughout the duration of the individual experiments. Thus, at some point during the experiment, the unit of the eC automatically changed from \( \mu \text{S cm}^{-1} \) to \( \text{mS cm}^{-1} \) and had to be converted by automatically checking the range of the value and dividing by 1000 (e.g. If value > 100, divide value by 1000).

As the redox-potential was recorded by Ag/AgCl-probes, the Eh was calculated by adding 217 mV to the redox-potential given by the electrodes (Olthoff, 1986, Schüring et al., 2000):

\[
Eh = E_{\text{Ag/AgCl}} + E_{\text{Ref}} \tag{43}
\]
with \( \text{Eh} = \) standard-potential of the hydrogen electrode [mV], \( E_{\text{Ag}/\text{AgCl}} = \) redox-potential measured with the Ag/AgCl-probe [mV], \( E_{\text{ref}} = 217 \text{ mV} \) (at \( 15^\circ \text{C} \)) = Reference potential between standard-hydrogen-electrode and the Ag/AgCl-probe [mV]. For the calculations in PhreeqC, the \( \text{pe} \) was calculated from the \( \text{Eh} \):

\[
\text{pe} = \frac{\text{Eh} - F}{2.303 \cdot R \cdot T_{\text{abs}}}
\]

(44)

with \( \text{pe} = \) negative decadic logarithm of the “electron activity” (in \( \text{mol L}^{-1} \)) [-], \( \text{Eh} = \) standard-potential of the hydrogen electrode [mV], \( F = 9.649 \cdot 10^4 \text{ J V}^{-1} \text{ mol}^{-1} = \) Faraday-constant \([\text{J V}^{-1} \text{ mol}^{-1} = \text{C mol}^{-1}]\), \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = \) ideal gas constant \([\text{J K}^{-1} \text{ mol}^{-2}]\) and \( T_{\text{abs}} = \) absolute temperature [K] (Manahan, 2000).

Table 5  Parameters measured in the experimental Fe-clogging model during the individual phases of a clogging experiment (final report phase III, 2013)

<table>
<thead>
<tr>
<th>Point</th>
<th>Parameter</th>
<th>Unit</th>
<th>Values (ranges)</th>
<th>Parameter type</th>
</tr>
</thead>
<tbody>
<tr>
<td>gravel pack</td>
<td>( h_i )</td>
<td>[mmH(_2)O]</td>
<td>ref</td>
<td>clog</td>
</tr>
<tr>
<td>inflow chamber (IC, MC I)</td>
<td>( c(Fe(II)) )</td>
<td>[mg L(^{-1})]</td>
<td>&gt; 2.0</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>DO</td>
<td>[mg L(^{-1})]</td>
<td>0.05</td>
<td>&gt; 0.05</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>[-]</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Eh</td>
<td>[mV]</td>
<td>≈ 70</td>
<td>≈ -210</td>
</tr>
<tr>
<td>outflow chamber (OC)</td>
<td>( eC )</td>
<td>[mS cm(^{-1})]</td>
<td>≈ 0.63</td>
<td>≈ 2.60</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>[°C]</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>( p_{\text{OC}} )</td>
<td>[mmH(_2)O]</td>
<td>610/675</td>
<td>625</td>
</tr>
<tr>
<td></td>
<td>Q(_{\text{OC}})</td>
<td>[L min(^{-1})]</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>before filter</td>
<td>( c(Fe(II)) )</td>
<td>[mg L(^{-1})]</td>
<td>&gt; 2.0</td>
<td>77.9</td>
</tr>
<tr>
<td>column (MC II)</td>
<td>pH</td>
<td>[-]</td>
<td>≈ 8.0</td>
<td>≈ 8.0</td>
</tr>
<tr>
<td>AdP 2</td>
<td>pH</td>
<td>[-]</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>behind filter column (MC III)</td>
<td>( c(Fe(II)) )</td>
<td>[mg L(^{-1})]</td>
<td>&gt; 2.0</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>[-]</td>
<td>≈ 8.0</td>
<td>≈ 8.0</td>
</tr>
<tr>
<td></td>
<td>DO</td>
<td>[mg L(^{-1})]</td>
<td>&gt; 0.05</td>
<td>&gt; 0.05</td>
</tr>
<tr>
<td>MC I/II/III:</td>
<td>Measurement cells /II/III</td>
<td>AdP 2:</td>
<td>behind addition point 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( h_i ):</td>
<td>hydraulic head at point i (DP300.a)</td>
<td>A:</td>
<td>analytical parameter</td>
</tr>
<tr>
<td></td>
<td>( p_{\text{OC}} ):</td>
<td>pressure in the inflow chamber (DP300.b)</td>
<td>R:</td>
<td>regulatory parameter</td>
</tr>
<tr>
<td></td>
<td>ref:</td>
<td>reference test</td>
<td>O:</td>
<td>observatory parameter</td>
</tr>
<tr>
<td></td>
<td>clog:</td>
<td>clogging phase</td>
<td>Rec:</td>
<td>recording</td>
</tr>
<tr>
<td></td>
<td>eva:</td>
<td>evaluation phase</td>
<td>auto:</td>
<td>automatic recording</td>
</tr>
<tr>
<td>7,9</td>
<td>target value</td>
<td>man:</td>
<td>manual recording</td>
<td></td>
</tr>
<tr>
<td>-230</td>
<td>resulting average value</td>
<td>none:</td>
<td>no recording</td>
<td></td>
</tr>
</tbody>
</table>

In the later experiments the probes for measurement of pH and DO showed signs of ageing especially in the outflow chamber. These values were corrected after the experiment. Before
every long term experiment, the probes were calibrated. For pH, the values given by the probe were checked after finishing the experiment. The drift of the value in time was corrected by a linear function reaching a maximum correction of ΔpH = -0.8. With the measurements of DO, ageing of the probes appeared in form of drifts in the zero-current or – particularly in the outflow chamber – underestimation of the DO as a result of Fe-incrustations precipitating on the membrane of the probe. Before each experiment, all DO-probes were tested for a drift in the zero-current with a Na₂SO₃ solution (O₂-free environment due to oxidation of sulphite to sulphate) in order to correct the values. To counter effects of membrane encrustation in the outflow chamber, the DO-probe was cleaned with a mixture of oxalic acid and ascorbic acid for 10 min every evening and stored in tap water over night.

One arithmetic mean value was calculated for each Fe-clogging step and evaluation step from the time series of hydrochemical parameters to monitor the development of hydrochemical parameters throughout the experiment. The stability of the respective value during the considered experimental step was expressed by its standard deviation.

The data for the system flow, water level in the outflow chamber, and pressure in the inflow chamber was processed simultaneously and in the same manner as the hydrochemical data and was partly used in the further processing of the hydraulic data.

The rate of addition of Fe(II)-stock solution is integrated to calculate the total input of Fe(II) to the system. The value can be compared to and balanced with the oxidation and precipitation rate that was calculated from the photometrically determined decrease in c(Fe(II)) (temporal integral of long term average values) in the flow channel as well as with the total amount of Fe(III) minerals precipitated in the filter pack and screen pipe that was determined by analysing gravel samples after model disassemblage (section 4.3.7).

All data (hydraulic and hydrochemical) was plotted depending on the cumulative time of all preceded Fe-clogging phases (representative time axis), that was relevant for the progression of clogging in the primary clogging zone.

The hydraulic data was used to calculate the hydraulic conductivities in the different sections of the well filter. The calculation was based on a modification of Darcy’s law (cf. section 4.3.4), corrected by the actual values of Qşys and also considering extensive statistical efforts including error propagation. To check for the validity of Darcy’s law, the Reynolds-numbers (cf. section 4.3.4) were calculated at the three pressure measurement points in dependence on h₀c in the fourth long term test (cf. section 4.4.2). Based on these results, the water levels in the outflow chamber for the Fe-clogging and evaluation phase for the further long term tests were chosen to maintain a laminar flow regime. The Reynolds-numbers were not allowed to exceed the upper Reynolds-number threshold towards non-linear flow (Re = 10, cf. section 2.1). With outflow water levels of h₀c = 40 mm and 100 mm, Reynolds-numbers in the model reached about 3 and 1.2 for the water levels during the Fe-clogging and evaluation phases, respectively, as a laminar flow regime was especially important during the evaluation phases. Higher outflow water levels would have resulted in even lower Reynolds-numbers, but also would have shifted the primary and secondary Fe-clogging zones towards the upper boundary of the flow channel which could probably have resulted in boundary effects. Also, the gravel pack volume encompassed in the evaluation step was defined not to include too
many parts of unclogged gravel above and below the primary Fe-clogging zone, to focus measurements of head loss on the actually clogged zone. Analysis of the hydraulic data was carried out by the IWW staff and led to one average value of the hydraulic conductivity per evaluation phase as well as its percental change compared to the initial K-value of the reference situation. To allow comparison of the change in hydraulic conductivity of all experiments, the relative difference between the initial hydraulic conductivity and hydraulic conductivity after 35 h of representative time was calculated for each experiment (final report phase III, 2013).

To exclude model effects due to a change in density and viscosity as a result of the rising content of Cl⁻ in the process water, the effect of Cl⁻ on those two parameters was estimated from the literature (Hai-Lang & Shi-Jun, 1996, Kestin et al., 1981, Figure 48) to exemplarily calculate the permeability from the hydraulic conductivity (cf. section 2.1) with these values adapted to the lowest and highest Cl⁻-concentrations appearing in the model of $50 \text{ mg L}^{-1} < c(\text{Cl}^-) < 725 \text{ mg L}^{-1}$.

![Figure 48](image)

**Figure 48** Influence of chloride concentration on density and dynamic viscosity of the fluid at $T = 25 \, ^\circ\text{C}$; calculated from Hai-Lang and Shi-Jun (1996). The two most extreme situations of $c(\text{Cl}^-)$ that appeared in the experimental model and their quite low influence on density and dynamic viscosity of the fluid are illustrated with red, blue and green lines, respectively.

As shown in Figure 48 the density and dynamic viscosity of the process water only changed on the fourth and third decimal place, respectively, even when the highest observed increase of chloride content due to addition of FeCl₂-stock solution was considered. Of course, at $15 \, ^\circ\text{C}$, the curves for density and viscosity are somewhat shifted downwards and upwards, respectively, but the slopes remain subtle in the considered range. Thus, correcting the calculated hydraulic conductivities to the permeability of the filter materials with respect to changing $c(\text{Cl}^-)$ was not necessary, especially since both of the parameters increased with rising $c(\text{Cl}^-)$, but permeability is directly proportional to dynamic viscosity, but inversely proportional to density.

4.3.7 Excavation and sampling

After finishing a long term experiment, the water was drained from the model and the filter columns and flow channel were opened and excavated. When the filter pack was excavated
after several hours of Fe-clogging phases, the material exhibited an obviously higher mechanical stability due to cementation of the gravel grains with coatings of Fe(III)-hydroxides. This effect was most obvious in the third and longest long term test (LTT 3) that was conducted to evaluate the effect of different water levels in the outflow chamber on the hydraulic conditions in the gravel pack. After this experiment, the gravel even stayed stable after removing the whole aquifer material (Figure 49).

![Figure 49](image)

Figure 49  Vertical stability of the gravel pack in long term test LTT 3 (left) and cemented sample of filter gravel (right, final report phase II, 2011)

For the later experiments with shorter experimental durations, an excavation system was developed that allowed standardised sampling in a layered system even at lower gravel pack stability. For layered excavation 10 PMMA-blocks with a height of 20 mm each were stacked behind the boundary of the filter pack after removing most of the aquifer material (Figure 50).

![Figure 50](image)

Figure 50  Layered excavation system to prevent the filter pack from collapsing (bottom left, long term test 6) and to determine a three-dimensional distribution of Fe(III)-hydroxide-incrustations by sampling and analysis (final report phase II, 2011)
The filter gravel was then cut off in horizontal layers by pushing a thin metal sheet through the gap in-between the two uppermost PMMA blocks. After lifting off a layer of gravel, the excavated surface was charted and photographed. Each layer was sampled in the zones of different incrustation intensity for determination of the total Fe-content. The sample locations were described by a coordinate system originating in the lower left front edge of the boundary between aquifer material and gravel pack with the positive z-direction pointing upwards, x-direction to the right and y-direction to the back wall of the channel. The distribution of total Fe-contents in the x-z-plane could thus be calculated by interpolation between the sampling points. The total amount of Fe(III) precipitated in the gravel pack could be calculated by a volume integral:

$$\iiint Fe_{tot} \, dV \, (SEP) = \sum [Fe_{tot} \cdot \Delta b_{cell} \cdot \Delta h_{cell} \cdot \Delta l_{cell} \cdot \rho_{gravel}]$$  \hspace{1cm} (45)$$

with $\iiint Fe_{tot} \, dV \, (SEP) =$ volume integral over of the total Fe-content distribution in the gravel pack, determined via the sequential extraction procedure (SEP) [g], $Fe_{tot} =$ total Fe-content of the gravel sample, determined by the SEP [g kg$^{-1}$], $\Delta b_{cell} \cdot \Delta h_{cell} \cdot \Delta l_{cell} =$ breadth, height and length of the gravel pack cell, represented by the individual Fe$_{tot}$-measurement (irregular cell dimensions, depending on the three-dimensional Fe$_{tot}$-distribution and sampling density) [m], $\rho_{gravel} =$ density of the gravel grains [kg m$^{-3}$].

In each long term test, a mixed sample of incrusted material was taken for enrichment of the Fe-clogging products and subsequent mineralogical analysis. Many of the mixed samples were also analysed to quantify their reactive BET surface areas and total contents of organic carbon (TOC) in comparison to fresh gravel material and samples from the field affected by Fe-clogging. To assess the distribution of the incrustations on a microscopic scale, undisturbed samples were taken in the model by impregnation with the two-component epoxide resin Körapox 439 (Sikora). The components A and B (resin and hardener) were mixed at a ratio of 2:1, optionally stained with a blue pigment (Figure 51, left) and heated in a drying cabinet for 1.5 min at 100 °C in order to decrease the viscosity of the resin.

![Resin impregnation for undisturbed sampling of the Fe-clogged filter pack; left: impregnation with blue stained resin in long term test 7 (Weilerswist gravel), centre: acceleration of resin drying with a blow-dryer in long term test 9 (Frimmersdorf gravel), right: impregnation with unstained resin in long term test 14 (glass beads; final report phase III, 2013)](image-url)
The mixture was then poured onto the filter pack and allowed to percolate into the material with maximum infiltration depths of around 30 mm. Drying of the resin could be additionally supported by directing an air flow onto its surface, for example with a customary blow dryer (Figure 51, top centre).

Fe(III)-minerals precipitated in the outflow chamber were also sampled, dried at 50 °C and stored for mineralogical analysis (Figure 52).

**Figure 52 Sampling in the outflow chamber (final report phase II, 2011)**

### 4.3.8 Sample analytics: sequential extraction procedure (SEP)

Amounts of poorly crystallised and well crystallised Fe(III)-hydroxides were determined by applying the steps 3 and 4 of the improved sequential extraction procedure (SEP) that was described by Wenzel et al. (2001). In step 3, easily soluble Fe-hydroxides were dissolved in a cold ammonium oxalate solution (Schwertmann, 1964, “solution I” in the following texts), whereas in step 4, residual Fe-hydroxides were reduced and dissolved by application of a hot mixture of ammonium oxalate and ascorbic acid solutions (Shuman, 1982, “solution II” in the following texts). Firstly, a 0.2 mol L⁻¹ NH₄⁺-oxalate buffer (solution I) was prepared by dissolving 28.422 g di-ammonium oxalate monohydrate ((NH₄)₂C₂O₄·H₂O, for analysis, Merck Millipore) and 25.214 g oxalic acid dihydrate (H₂C₂O₄·2H₂O, for analysis, Merck Millipore) in 1 L of deionised water after adjusting to pH 3.25 with a concentrated NH₃-solution. Secondly, a 0.2 mol L⁻¹ NH₄⁺-oxalate buffer with 0.1 mol L⁻¹ ascorbic acid (solution II) was prepared by dissolving 17.613 g L(+)-ascorbic acid (C₆H₇O₆, for analysis, BDH Prolabo) in 1 L of 0.2 mol L⁻¹ NH₄⁺-oxalate buffer (solution I). If other amounts of extract solutions were needed, the weighed portions of chemicals and the amounts of fluid phases were changed proportionally (e.g. a doubled amount of solution I was prepared, half of which was used for the preparation of solution II).

For the first extraction step, around 5 g of each sample taken from the clogging model or from the field were weighed for their exact mass and filled into a centrifuge tube. The tubes were then filled up with 40 mL of solution I and shaken in the darkness. After 4 h of shaking, the fluid and solid phases were separated by centrifugation and decantation. The extract was stored for determination of the Fe-content.
For the second extraction step, the solid phases were washed free of oxalate extracts with deionised water and were then quantitatively transferred into an Erlenmeyer flask with 40 mL of solution II. The Erlenmeyer flasks were placed in a pre-heated water bath and tempered at 96°C for 30 minutes. Strong evaporation and huge overpressures were avoided by loosely capping the Erlenmeyer flasks. After cooling in the ambient air, the extract was again separated from the solid by centrifugation and decantation and stored for determination of Fe-content.

Initially, the Fe-measurements in the extracts were conducted using a spectrophotometric method with 2,4,6-Tripyridyl-s-triazine (Collins et al., 1959), a derivate of triazine as a complexing agent (iron test spectroquant® by Merck Millipore). The Cadas 100 spectrophotometer, calibrated at a wavelength of $\lambda_{\text{triazine}} = 565$ nm was used. But after only a few measurements it became clear that this method underestimated the Fe-contents. In the extracts, development of the purple colour of the triazine-complex seemed to have been interfered with. This interference was confirmed by the increase of measured Fe-contents when diluting the extracts by multiples of the factor of 10 with deionised water (Figure 53).

To quantify the effect of interference, standard solutions of 10 g Fe L$^{-1}$ were prepared by dissolving 2.42 g of FeCl$_2$·6H$_2$O (Merck Millipore, p.A.) each in 50 mL of solution I and in 50 mL of solution II and a subsequent dilution series of these standard extracts with solution I and solution II. Measurements were simulated with the triazine method on these extracts and when creating an overrange-signal, were diluted by multiples of the factor of 10 – exactly the same method applied when measuring a real over range sample. Figure 53 shows the concentrations measured by the triazine method in both extract standard solution series in comparison to the real standard concentrations.

The tests with both extract solutions showed the strongest interference effects in the undiluted standards extracts. The concentrations were underestimated by a factor of around 1000. When diluting the standard extracts with deionised water by the factor of 10, 100 or 1000, the interference factor decreased to 30-40, 6-20 or 1.1-4, respectively. Obviously, decreasing the concentration of oxalate also decreased the interfering effect, which was confirmed by scanning three of the diluted and undiluted standard extracts for their absorption spectra after adding the triazine indicator (Figure 54).

In all cases, the Fe-triazine peak can be recognized with its peak at a wavelength of $\lambda_{\text{triazine}} = 565$ nm. In the samples diluted with deionised water before adding the triazine, the relative dominance of the secondary interference peak over the triazine peak decreased. In the first dilution (1:10), the amplitude of the triazine peak even increased absolutely. In the third dilution (1:1000), the dominance of the peaks changed from the interference peak to the triazine peak. This observation argues for a competition of different complexing ligands for the dissolved Fe. Diluting one of the ligands (presumably oxalate) shifts the chemical equilibrium towards the other (triazine). This implies that the interference could be avoided by further diluting the sample. But this would also result in a dilution of the Fe-content of the standards (or samples), so the spectrometric triazine method reached its lower detection limit of 0.05 mg Fe L$^{-1}$. Also, lots of dilution steps for each measurement would be very time consuming and would introduce even more uncertainties into the method.
The phenomenon of complexation of dissolved Fe with oxalate and its interference with spectrophotometric methods for determination of Fe-content has already been noticed in the past (Miller et al., 1986). This issue was described for a spectrophotometric method using a sulfosalicylic acid-complex at an absorption wavelength of $\lambda_{\text{sulfosalicylic acid}} = 436$ nm (Schwertmann, 1964). Due to this interference the search for an applicable photometric method for determination of the Fe-content in oxalate extracts remains a topic of current scientific discussion. Dominik and Kaupenjohann (2000) proposed application of an Fe(II)-ferrozine-
complex at a wavelength of $\lambda_{\text{ferrozine}} = 652$ nm, but still found the method to be interfered with by oxalate.

For the measurements in this study, another quite straightforward method of determining the Fe-content in the extracts was considered to avoid the interfering effect. As shown in Figure 54, the interfering effect is caused by the occurrence of a secondary absorption peak at a wavelength of about $\lambda_{\text{oxalate}} = 345$ nm. This peak corresponds to a yellow-greenish colouring occurring in the extracts, apparently caused by the Fe-oxalate-complex, whose intensity seemed to be proportional to the solution’s content of Fe.

![Figure 54](image)

**Figure 54**  Wavelength-absorbance-scans of different standard extracts with solution I (top) and II (bottom), diluted with deionised water before addition of the triazine reagent

Dissolution of Fe(III)-minerals with oxalate follows the mechanism described by Cornell and Schindler (1987). In a first step, the dissolved oxalate-ion gets adsorbed on the Fe(III)-surface, building a surface-complex. Thus, the covalent bond of the adsorbing Fe(III) weakens due to a shift in its polarisation. Additional protonation of the surrounding surface may promote the detachment of a dissolved Fe(III)-oxalate-complex $[\text{Fe(III)}(\text{C}_2\text{O}_4)_3]^{3-}$. The ferric iron in this complex can be photochemically reduced according to (Cornell & Schindler, 1987):

$$2 \cdot [\text{Fe(III)}(\text{C}_2\text{O}_4)_3]^{3-} \leftrightarrow 2 \cdot \text{Fe(II)}(\text{C}_2\text{O}_4) + 3 \cdot \text{C}_2\text{O}_4^{2-} + 2 \cdot \text{CO}_2$$  (46)
The reduction process can be supported by adding an electron donor or by increasing the temperature, both of which were applied in the second extraction step of the SEP in this study (ascorbic acid as electron donor, T = 96 °C).

The process of dissolution and reduction of ferric hydroxides can be accelerated by dissolved Fe(II)(C₂O₄), sorbing to an Fe(III)-hydroxide surface and transferring one electron from the Fe(III)-hydroxide to the Fe(II) of the dissolved complex, exchanging their valence states and dissolving the Fe(II) from the surface to form another ferrous oxalate complex. With photochemical reaction, the formed Fe(III)(C₂O₄)²⁻-complex can be regenerated to Fe(II)(C₂O₄). As the product of the reaction accelerates the reaction itself an autocatalytic process evolves (Cornell & Schindler, 1987).

As the pH is adjusted to pH 3.25 during the extraction procedure, the predominant species in the solutions will be Fe(II)(C₂O₄)²⁻ (Cornell & Schindler, 1987, Panias et al., 1996, Lee et al., 2007; Figure 55).

![Figure 55](image)

**Figure 55** Distribution of solid and dissolved species in the Fe(II)-oxalate system (Panias et al., 1996)

The interfering effects in the applied method and the optical impression of a yellow-greenish colouring that depends on the content of Fe was assumed to originate from the occurrence of the dissolved complex species [Fe(C₂O₄)₂]²⁻. With an excess supply of C₂O₄²⁻ compared to Fe²⁺, the intensity of the colouring was assumed to be solely dependent on the Fe-content.

To verify these assumptions, another dilution series of standard extracts was prepared analogue to the one described above. The intensity of absorbance in the standard extracts was measured with the Cadas 100 spectrophotometer at a wavelength of λ_{oxalate} = 345 nm (Figure 56).

The absorption in the samples showed a linear dependency on the predefined standard concentrations, until a maximum absorbance of about 3.4 arbitrary units was reached at Fe concentrations of about 200 mg L⁻¹. The standards below that value were used to fit a linear regression line, covering a concentration range of 0.1 to 120 mg Fe L⁻¹ for use as a calibration function for a new spectrophotometric method (Figure 56, middle). For higher concentrations, the standards above 100 mg L⁻¹ were diluted with deionised water by the factor of 10 and again measured at λ_{oxalate} = 345 nm to generate a calibration function for the upper concentration range between 100 and 1000 mg L⁻¹ (Figure 56, bottom). For these samples, the extraction solutions had to be diluted by the factor of 10 with deionised water.

In order to validate the method, a test was conducted using ferric chloride salt (FeCl₃·6H₂O, Merck Millipore, p.A.) and the following synthetic Fe(III)-minerals, kindly provided by Thomas...
R. Rüde: ferrihydrite (fh), lepidocrocite (lp), goethite (gt) and schwertmannite (sh). All of these had been synthesised between 1998 and 2002 after the methods described by Schwertmann and Cornell (2000), freeze dried and their mineralogy after synthesis verified with XRD-measurements. To exclude ageing or mineral transformations of the reference materials during the 12-16 years of dry storage, XRD-verification was repeated for the fh-, lp- and gt-reference shortly before the reference minerals were used for evaluating the proposed oxalate method. Whereas the compositions of the ferrihydrite and goethite sample were unchanged, the lepidocrocite sample apparently had somehow transformed to maghemite (Appendix 2), even though transformation usually requires temperatures of at least $T > 120$ °C (in vacuum, Cornell & Schwertmann, 2003). However, the lepidocrocite-sample could therefore not be used as a reference material.

![Spectrophotometric calibration functions at $\lambda_{\text{oxalate}} = 345$ nm for the extraction steps with solutions I (left) and II (right) for the lower (0.1-100 mg L$^{-1}$, middle) and higher (100-1000 mg L$^{-1}$, bottom) concentration range](image)

The data of total iron content and degree of crystallinity in the reference-materials that were determined by duplicate measurements of the Fe-oxalate-complex is listed in Table 6 along with theoretical stoichiometric Fe-contents of the corresponding mineral. For the schwertmannite and ferrihydrite sample, total Fe-contents were underestimated with respect to ideal stoichiometry by 23 % and 6 %, respectively. These deviations presumably result from higher contents of water in the samples and therefore small errors in initial weight. For
stoichiometric Fe, the commonly used mineral formulae given by Cornell and Schwertmann (2003) were considered, even though the exact composition of sh and fh are still subject to scientific discussion and may vary with their synthesis-pathways (cf. section 2.4.6). For goethite, less than 20 % of the stoichiometrically ideal Fe-content was determined by the method. This strong deviation may result from an inappropriately high sample/eluent-ratio or an increased degree of crystallinity in the sample, which may be due to ageing processes. However, the Fe-content of ferric chloride was determined correctly with only a slight overestimation of 2.3 %.

Table 6 Poorly crystallised, well crystallised and total Fe-contents (FeI, FeII and Fe\textsubscript{tot}, respectively) of synthetic minerals determined by the sequential extraction method with direct measurement in the oxalate extracts at \( \lambda = 345 \) nm compared with theoretical stoichiometric Fe-contents, values given in g kg\(^{-1}\) (s(FeII) in [%])

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>FeI</th>
<th>FeII</th>
<th>Fe\textsubscript{tot}</th>
<th>s(FeII)</th>
<th>Stoichiom. Fe\textsubscript{tot}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schwertmannite</td>
<td>Fe\textsubscript{1}O\textsubscript{1.5}(OH)\textsubscript{2}(SO\textsubscript{4})\textsubscript{2} \cdot 2 H\textsubscript{2}O</td>
<td>457.6</td>
<td>0.0</td>
<td>457.6</td>
<td>0.0</td>
<td>564.9</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>Fe\textsubscript{3}O\textsubscript{4} \cdot 4H\textsubscript{2}O</td>
<td>500.7</td>
<td>49.3</td>
<td>550.0</td>
<td>9.0</td>
<td>581.4</td>
</tr>
<tr>
<td>Goethite</td>
<td>Fe =FeOOH</td>
<td>6.1</td>
<td>96.3</td>
<td>102.4</td>
<td>94.0</td>
<td>628.5</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>Fe(III)\textsubscript{2}Cl\textsubscript{2} \cdot 6H\textsubscript{2}O</td>
<td>211.4</td>
<td>0.0</td>
<td>211.4</td>
<td>0.0</td>
<td>206.6</td>
</tr>
<tr>
<td>Fe-mud sample</td>
<td>-</td>
<td>425.3</td>
<td>20.2</td>
<td>445.5</td>
<td>4.5</td>
<td>-</td>
</tr>
</tbody>
</table>

The total Fe-content of a Fe-mud field sample taken by Metzger (2011) from the inside of a filter screen tube of a dewatering well near the open-pit Garzweiler was determined for comparison. The total Fe-content and percentage of well crystallised Fe-minerals (s(FeII)) were found to approximately match those of schwertmannite and ferrihydrite. Thus, the method of direct measurement of Fe-content in the oxalic extracts delivered quite reasonable values in synthetic minerals, an Fe(III)-salt and a sample from the field alike.

4.3.9 Sample analytics: mineralogical methods

Measurements of the total inorganic and organic carbon (TIC and TOC) and the specific surface area (Brunauer-Emmett-Teller- or BET-surface area) were conducted on the mixed samples of Fe-encrusted gravel material and the samples from the Fe-mud from the outflow chamber. X-ray-diffraction and -fluorescence were conducted before and after enrichment.

The TIC/TOC-measurements were conducted at the Institute of Geology and Geochemistry of Petroleum and Coal (LEK) of RWTH Aachen University with a liquiTOC device (Elementar Analysensysteme GmbH) and with an attached Solids Module. The values for TIC and TOC were determined in wt.-% with a lower detection limit of 4×10\(^{-4}\) wt.-% and an accuracy of ±1.4×10\(^{-4}\) wt.-% at a sample weight of 500 mg.

BET surface areas were measured at the research group Clay and Interface Mineralogy (CIM) of RWTH Aachen University by 5-point measurements with an Autosorb-1-MP device (Quantachrome) and nitrogen as adsorbate gas. The values for the BET surface area were determined in m\(^2\) g\(^{-1}\) with a lower detection limit of 0.04 m\(^2\) g\(^{-1}\) and accuracy (i.e. reproducibility) of ±3 % on the measured value.

The measurements of XRD were also conducted in the internal mineralogical laboratory of the RWE Power AG with a D4 Endeavor X-Ray diffractometer (Bruker AXS) with a Cu-K\(\alpha\) X-ray-
tube, a radius of the goniometer circle of 200.5 mm, an automatically adjusting primary divergence slit, primary and secondary Söller collimators and a position sensitive detector (PSD) array. The diffraction angle 2θ ranged from 5° to 70.0059° with a step size of 0.0142776° and counting times of 10 s per angle step. The data was analysed with the Rietveld refinement programme BGMN, written by Bergmann (2006). The default database of mineral structure files provided with the programme was extended by adding relevant Fe-mineral phases that were provided by the research group Clay and Interface Mineralogy (CIM) of RWTH Aachen University.

As the total contents of Fe(III)-hydroxide minerals were low compared to the original gravel grain minerals, detection and especially quantification of the Fe(III)-minerals in bulk samples was only possible in strongly encrusted samples. In order to identify the individual Fe(III)-minerals relevant to the clogging process and to quantify their relative contents, the Fe(III)-mineral phases had to be enriched in the mixed samples from the clogging model and the field samples (cf. section 4.6). After drying the samples, the Fe(III)-minerals often partly appeared as a fine-grained dust, separating easily from the gravel grains, so different enrichment methods focusing on wet grain size separation were tested in the laboratory. The gravel samples were put into deionised water and treated for several hours either in an ultrasonic bath or overhead shaking or magnetic stirring, in order to mechanically enhance disaggregation of the Fe(III)-minerals from the gravel grain surfaces. The suspension of Fe(III)-minerals was separated from the gravel grains by sieving with a 1 mm sieve and was dried over a few days in a drying oven at 50 °C. As the ultrasonic bath method performed best with respect to purity, fractionation and yield of the separated Fe(III)-minerals, this method was subsequently applied to all considered samples. The method of disaggregation was found to work even better with application of an ultrasonic probe (oral communication by Dr. Andre Banning, Institute of Geology, Mineralogy and Geophysics (GMG) of the Ruhr-Universität Bochum (RUB)).

Another enrichment method was carried out by a student apprentice of RWTH Aachen University in the internal mineralogical laboratory of the RWE Power AG after a method described by Bier (2010). Disaggregation with the ultrasonic bath was here conducted in bromoform, an organic fluid of high density rather than in deionised water. The samples were then transferred to a 1 L separating funnel and allowed to settle overnight. Due to the high density of the fluid of 2.84 ± 0.01 g cm⁻³, minerals of lower density like quartz, alkali feldspars, plagioclases (including orthoclase, anorthoclase and microcline) and clay minerals (Table 7) floated at the surface of the fluid, whereas dense minerals like all Fe(III)-oxides, oxyhydroxides and hydroxides settled at the bottom of the fluid (goethite, lepidocrocite, ferrihydrite, feroxyhyte, schwertmannite, jarosite, akaganéite, maghemite, hematite and magnetite; Table 7).

Densities of other phyllosilicates, especially micas like muscovite and biotite lie near the threshold of floating and settling and thus may easily sink to the bottom of the separating funnel, especially if a coating of Fe(III)-minerals additionally increases their weight (Table 7). This may also happen to smaller grains of the other lighter minerals, whereas large grains of filter gravel will divert coatings of Fe(III)-minerals that are imperfectly disaggregated into the lighter phase, resulting in an imperfect separation of the two density phases. Centrifuging the
mixtures of the sample and the bromoform was found to produce no further improvement of the separation. The fractions of heavy minerals were collected at the bottom outflow of the separation funnels, washed free of bromoform with ethanol, filtered from the suspension and dried for diffractometric measurement.

Table 7  

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Density $\rho$ [g cm$^{-3}$]</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>clay minerals</td>
<td>2.0-2.6</td>
<td>O&amp;M, N</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.2-2.6</td>
<td>O&amp;M, N</td>
</tr>
<tr>
<td>alkali feldspars</td>
<td>2.5-2.6</td>
<td>O&amp;M, N</td>
</tr>
<tr>
<td>Plagioclases</td>
<td>2.6-2.8</td>
<td>O&amp;M</td>
</tr>
<tr>
<td>Muscovite</td>
<td>2.77-2.88</td>
<td>O&amp;M, N</td>
</tr>
<tr>
<td><strong>BROMOFORM</strong></td>
<td><strong>2.84 ± 0.01</strong></td>
<td><strong>Lenders, 2013</strong></td>
</tr>
<tr>
<td>Biotite</td>
<td>2.8-3.2</td>
<td>O&amp;M, N</td>
</tr>
<tr>
<td>Jarosite</td>
<td>2.9-3.3</td>
<td>A</td>
</tr>
<tr>
<td>Akaganéite</td>
<td>3.6</td>
<td>S&amp;C</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>3.8-4.0</td>
<td>B</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>4.0</td>
<td>S&amp;C</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>4.0-4.1</td>
<td>S&amp;C, O&amp;M, N</td>
</tr>
<tr>
<td>Ferroxyhyte</td>
<td>4.2</td>
<td>S&amp;C</td>
</tr>
<tr>
<td>Goethite</td>
<td>4.3-4.5</td>
<td>S&amp;C, O&amp;M, N</td>
</tr>
<tr>
<td>Maghemite</td>
<td>4.9</td>
<td>S&amp;C</td>
</tr>
<tr>
<td>Hematite</td>
<td>5.2-5.3</td>
<td>S&amp;C, O&amp;M, N</td>
</tr>
<tr>
<td>Magnetite</td>
<td>5.18</td>
<td>S&amp;C</td>
</tr>
</tbody>
</table>

The undisturbed samples that were impregnated with epoxy resin were given to the Institute of Geology and Palaeontology (GIA) of RWTH Aachen University for preparation of thin sections. The thin sections were examined with polarisation microscopy at the Institute of Structural Geology, Tectonics and Geomechanics (GED) of RWTH Aachen University as well as with scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) and polarisation microscopy in the internal mineralogical laboratory of the RWE Power AG. Due to the microscopic methods, the extent and chemical composition of Fe-encrustation on the mineralogy of the individual gravel grains and their surface structure could be evaluated. Samples from the experimental clogging model were compared to samples from the field.

Not all analytic methods were applied for samples from all clogging experiments. The overview of modelled scenarios given in the following section also includes an overview of which methods were applied in what long term tests (LTTs).

### 4.4 Overview of Fe-clogging experiments

The Fe-clogging model was used to conduct a total of 16 long term tests. In the following descriptions a chronological number appended to the abbreviation “LTT” will be assigned to each test.
4.4.1 Model optimisation

LTT 1 to LTT 4 were carried out during the second phase of the clogging project and were concerned with analysing, optimising and defining the operational hydraulic and hydrochemical parameters and conditions of the model in order to reproducibly and quantifiably generate Fe-encrustations in the gravel pack in an accelerated manner under standardised laboratory conditions (Table 8). All four LTTs of the second project phase were conducted with the same gravel material and the standard screen pipe.

Table 8 Overview of the first four LTTs (final report phase II, 2011), ENR: test of enrichment methods, Time: net-Fe-clogging time, K: hydraulic conductivity, Re: Reynolds number, hOC: water level in the outflow chamber

<table>
<thead>
<tr>
<th>LTT</th>
<th>Duration</th>
<th>Sample analytics</th>
<th>Main objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 h</td>
<td>-</td>
<td>produce Fe-clogging</td>
</tr>
<tr>
<td>2</td>
<td>42 h</td>
<td>ENR, XRD, TOC</td>
<td>increase of clogging time</td>
</tr>
<tr>
<td>3</td>
<td>295 h</td>
<td>SEP, ENR, XRD, TOC, PM, SEM/EDX</td>
<td>characterise Fe(III)-minerals</td>
</tr>
<tr>
<td>4</td>
<td>176 h</td>
<td>SEP, ENR, XRD, TOC</td>
<td>quantify K &amp; Re vs. hOC</td>
</tr>
</tbody>
</table>

During LTT 1 and 2 a special focus was laid on the temporal development of hydrochemical parameters and ionic contents of the process water necessary to produce chemical Fe-clogging over longer operational durations in the clogging model. This was accomplished by varying the operating concept of the model and observing the reactions of the hydrochemical parameters. Initially, the addition of Fe(II)-stock solution was still performed at AdP 1 and 2, with the first addition to remove the DO from the water and the second one to adjust the \( c(\text{Fe(II)}) \). The fine filtration had also not yet been installed in front of the flow channel. As green rust minerals precipitated at AdP 2 and migrated into the channel inflow, the hydraulic situation in the flow channel was disturbed from the inflow side. For LTT 3, Fe(II)-addition at AdP 2 was terminated, preventing the major part of green rust precipitation and thus allowing a significantly increased experimental duration. To prevent a minor part of green rusts from precipitating due to NaOH addition at AdP 2, the modular exchangeable fine filtration column was installed in LTT 4.

In LTT 3 the layered excavation system described in section 4.3.7 was applied in order to determine the quantitative distribution and mineralogical composition of Fe(III)-hydroxide minerals for the first time.

Whereas in LTTs 1 to 3 the system flow rate \( Q_{\text{sys}} \) and the water level in the outflow chamber \( h_{\text{OC}} \) were allowed to fluctuate, \( Q_{\text{sys}} \) and \( h_{\text{OC}} \) were regulated to fixed values in LTT 4 by manually adjusting the pump frequencies of the inflow and outflow pump (InP, OutP). At constant \( Q_{\text{sys}} \), \( h_{\text{OC}} \) was lowered from the maximum of 200 mm to the minimum of 4 mm in steps of 20 mm first in a reference test without adding Fe(II) to the process water. It was then increased again in the same manner, holding each \( h_{\text{OC}} \) level for 2 to 9 h in order to statistically determine the hydraulic conductivity and Reynolds numbers in the filter pack depending on \( h_{\text{OC}} \). After the reference test, \( c(\text{Fe(III)}) \) in the process water was raised to 80 mg L\(^{-1}\) and \( h_{\text{OC}} \) was again raised from 4 mm to 200 mm in steps of 20 mm. For every applied water level, the Reynolds numbers were calculated for each pressure measurement point. The K-values of the clogging situation and the reference situation were compared (final report phase II, 2011).
4.4.2 Material tests

Based on these four experiments, the model operating concept described in section 4.3.5 was developed for standardised evaluation and quantification of clogging affinity in the different filter materials in the LTTs 5 to 14 and well constructional settings with the last two LTTs 15 and 16 (Table 9).

Table 9 Overview of LTT 5 to LTT 16 (final report phase III, 2013), time: net-clogging time, ENR: test of enrichment methods, PM: polarisation microscopy, MI: main ions

<table>
<thead>
<tr>
<th>LTT</th>
<th>Duration</th>
<th>Sample analytics</th>
<th>Filter pack material</th>
<th>Screen length</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>34 h</td>
<td>SEP, ENR, XRD</td>
<td>Weilerswist gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>6</td>
<td>56 h</td>
<td>SEP, TOC, PM</td>
<td>Weilerswist gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>7</td>
<td>38 h</td>
<td>SEP, XRD, TOC, PM, MI</td>
<td>Weilerswist gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>8</td>
<td>37 h</td>
<td>SEP, XRD, TOC, BET</td>
<td>Weilerswist gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>9</td>
<td>42 h</td>
<td>SEP, ENR, XRD, TOC, BET, PM</td>
<td>Frimmersdorf gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>(SEP), (XRD)</td>
<td>Dorsfeld gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>11</td>
<td>46 h</td>
<td>SEP, ENR, XRD, TOC, BET, PM</td>
<td>Dorsfeld gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>12</td>
<td>44 h</td>
<td>SEP, ENR, XRD, TOC, BET, PM</td>
<td>Frimmersdorf gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>13</td>
<td>52 h</td>
<td>SEP, ENR, XRD, TOC, BET, PM</td>
<td>Dorsfeld gravel</td>
<td>200 mm</td>
</tr>
<tr>
<td>14</td>
<td>45 h</td>
<td>SEP, ENR, XRD, TOC, BET, PM, MI</td>
<td>Glass beads</td>
<td>200 mm</td>
</tr>
<tr>
<td>15</td>
<td>40 h</td>
<td>SEP, TOC, BET, PM</td>
<td>Glass beads</td>
<td>30 mm</td>
</tr>
<tr>
<td>16</td>
<td>36 h</td>
<td>-</td>
<td>Glass beads</td>
<td>30 mm</td>
</tr>
</tbody>
</table>

In LTT 5 to 8, the model operating concept as defined in section 4.3.5 was applied to the standard well assembly with Weilerswist gravel and the standard length screen pipe section. Due to technical problems the LTTs 5 and 7 unfortunately did not yield any usable or comparable hydraulic data and thus were repeated (LTTs 6 and 8). But as only the hydraulic parameters were problematic in the LTTs 5 and 7, sampling in these LTTs was still useful for comparison with LTT 8, as all were carried out with the same gravel material from the Weilerswist deposit.

In LTT 6, the gravel pack unfortunately collapsed during disassemblage of the flow channel (cf. Figure 50), so only 6 samples were taken and the distribution of incrustations could not quantitatively and representatively be evaluated in this LTT. However, the method of undisturbed sampling with resin impregnation could be tested directly in the model environment for the first time and was applied and optimised during the subsequent tests.

To evaluate the clogging affinity of the alternative gravel materials in comparison to the standard gravel, LTTs 9 and 12 were conducted with the Frimmersdorf gravel and LTTs 10, 11 and 13 with the Dorsfeld gravel. LTT 10 had to be cancelled after the reference test due to persisting hydraulic instationarity in the assembly. However, at least the process water of LTT 10 could be stored and used again for LTT 11 after the disassemblage of aquifer material and Dorsfeld gravel in the flow channel had been exchanged. In LTT 12, measurement of the hydraulic conductivity of the screen pipe (hydraulic evaluation section 5 III) was possible for the first time, as an additional measurement point was installed inside the outflow chamber. This also involved daily rinsing of the drilling in the bottom of the outflow chamber that connected to the pressure transducer to prevent interference by Fe(III)-hydroxide particles clogging the drilling.
With LTT 14, the last material test, the clogging affinity of the glass bead filter pack was evaluated (cf. section 4.1.2). Hydrochemical and hydraulic data were recorded as usual. But sampling of the Fe-clogging products was only done after an interim experiment was done, trying to re-dissolve the products of Fe-clogging “in situ” with a hot mixture of ammonium oxalate, oxalic and ascorbic acid. As the upper part of the filter pack was undisturbed by this interim-experiment due to a density gradient of the acidic solution in comparison with the process water, sampling was still possible in that part (Figure 57). The total Fe-content that was dissolved during the interim-experiment could be estimated by a measurement of c(Fe) in the hot acid solution. After the interim-experiment, one evaluation phase, one Fe-clogging phase and another evaluation phase were conducted to study the effect of re-clogging. However, the approach was not further investigated as part of this thesis.

Figure 57 Interim-experiment of chemical dissolution of the Fe-incrustations from the outflow chamber; red line: lower boundary of primary clogging zone after LTT 14 (cf. also Appendix 9, final report phase III, 2013, translated)

4.4.3 Saturation conditions in screen pipe and gravel pack

Since the controlling factors of Fe-clogging in the filter pack of dewatering wells were now found and the effect of different filter pack materials was evaluated, the effect of saturation and water/air-distribution in the filter pack was identified as a primary cause of Fe-clogging. Thus, in the last two LTTs 15 and 16, a method to reduce or even prevent Fe-clogging in the filter pack was developed and optimised in the model.

To avoid contact of air and water in the filter pack, the shortened screen pipe (30 mm) was installed in the flow channel. In both experiments, aeration of the screen pipe was avoided by never lowering hOC below a minimum of 40 mm in order to keep the shortened screen pipe saturated at all times and to avoid aeration of the filter pack through the screen pipe. In LTT 15, the amount of air inside the filter pack was only restricted, whereas in LTT 16, the air supply was completely precluded and the filter pack and screen pipe fully saturated.

In LTT 15, the venting hole at the top of the shortened screen pipe was connected to a flexible air reservoir. This allowed pressure compensation in the gravel pack when changing of hOC in order to switch between the Fe-clogging phase and the evaluation phase without disturbing the hydraulic measurements in the filter pack (final report phase III, 2013). An aerial oxygen analyser was installed inside the flexible air reservoir to monitor the development of the percentage of oxygen in the air flowing between the gravel pack and the reservoir (Figure 58).
After the third Fe-clogging step of LTT 15, the addition of NaOH and FeCl₂-stock solution was unfortunately not switched off properly during overnight shutdown due to a technical error. The next morning, the Fe-concentration in the outflow chamber was strongly increased to \( c(\text{Fe(II)}) \approx 120 \text{ mg L}^{-1} \) at very high pH \( \approx 12 \). As a result of the malfunction of the model, the hydraulic data exhibited an abrupt decrease in the hydraulic conductivity between evaluation phases 2 and 3.

In LTT 16, the venting hole in the shortened screen pipe was completely closed after the glass bead filter pack had been fully saturated. To speed up the experiment, the process water from LTT 15 was used for LTT 16 and the reference test was omitted. As absolutely no Fe-clogging in the filter pack was observed after five Fe-clogging and five evaluation steps, several tests with aeration of the shortened screen pipe were conducted with the assembly of LTT 16.

Firstly aeration of the gravel pack through aeration of the 30 mm screen pipe with sustaining flow was tested applying a low \( h_{\text{OC}} \) of 4 mm. This test was conducted to check, whether the gravel pack was filled with air by diffusion of oxygen against the water flow current through the 30 mm screen pipe section. Afterwards, the venting hole in the upper part of the screen pipe was opened to check for the level of saturation in the glass bead filter pack (flow effective area plus capillarity) with sustaining flow and completely emptied outflow chamber. Finally, the gravel pack was again fully saturated, the flow through the channel was stopped and the outflow chamber was completely emptied again. The progression of air diffusing through the shortened screen pipe into the filter pack was monitored with a web cam overnight to determine how long the capillarity of the glass beads would hold the hydraulic underpressure against gravity.

### 4.5 Hydrochemical model of the flow channel

To compare the results attained in the experimental model, a simple hydrogeochemical model was set up using the hydrogeochemical modelling programme PhreeqC for Windows (version: 2.18.00, database: wateq4f.dat, Parkhurst & Appelo, 1999). For the calculation, the kinetic assumptions by Stumm and Lee (1961) and the reaction constant given by Davison and Seed (1983; cf. section 2.4.3) were used. The formula of kinetic Fe(II)-oxidation was applied to calculate the temporal Fe(II)-decay-function and temporal development of pH and DO and the mass of precipitated Fe(III)-hydroxides.
With the flow velocity in the flow channel of the experimental model, these temporal functions were then converted to spatial distributions. To accomplish this, the filter pack in the flow channel was divided into 11 model cells aligned in the direction of flow. As according to $h_{OC}$ in the Fe-clogging phase, the height of water saturation of each model cell was defined as $h_{cell} = 40 \text{ mm} = 0.04 \text{ m}$, with the breadth of the flow channel (FC) as cell breadth $b_{cell} = 200 \text{ mm} = 0.2 \text{ m}$ and the cell length $L_{cell} = 10 \text{ mm} = 0.01 \text{ m}$. With a total porosity of $n = 0.379$, the total flow effective volume of the model cell equals:

$$V_{water} = V_{cell} \cdot n = h_{cell} \cdot b_{cell} \cdot L_{cell} \cdot n \quad (47)$$

with $V_{water} = 3.032 \cdot 10^{-5} \text{ m}^3 = \text{saturated cell pore volume [m}^3\text{]}, V_{cell} = \text{total cell volume [m}^3\text{]}, n = \text{total porosity [-]}$, determined from the total filter pack volume and mass in the model and the mineral density of the gravel, $h_{cell} = \text{height of the model cell [m]}, b_{cell} = \text{breadth of the model cell [m]}, L_{cell} = \text{length of the model cell [m]}$. From the system flow, the residence time of the water in each model cell could be estimated with:

$$t_{cell} = \frac{V_{water}}{Q_{sys}} \quad (48)$$

with $t_{cell} = 1.716 \text{ s} = \text{estimated residence time of the water in the model cells [s]}, V_{water} = 3.032 \cdot 10^{-5} \text{ m}^3 = \text{saturated cell pore volume [m}^3\text{]}, Q_{sys} = 1.06 \text{ L min}^{-1} = 1.767 \cdot 10^{-5} \text{ m}^3 \text{ s}^{-1}$. Thus, the reaction progression during the first 1.716 seconds was assigned to the first model cell, between 1.716 and 3.432 s to the second cell and so on. With ten model cells in the gravel pack and an eleventh (and twelfth) in the screen pipe, the residence time of the process water in the well filter totalled 20.592 s (Figure 59).

![Figure 59 Schematic conversion of a Phreeqc-model result from temporal to spatial consideration](image)

The kinetic calculations of Fe(II)-oxidation with Phreeqc were carried out applying the water4f.dat database. In this database, the oxidation of dissolved Fe(II) to dissolved Fe(III) ($\text{Fe}^{2+}$ to $\text{Fe}^{3+}$) is automatically defined as a chemical equilibrium (Parkhurst & Appelo, 1999). But as there is a strong interdependency of the reaction rate of Fe(II) and pH, the reaction is not likely to reach chemical equilibrium during the short residence time in the filter pack. A purely thermodynamic model is thus not suitable to properly describe the reaction in the experimental model and in an actual well.

Therefore, to realistically simulate the clogging-process with Phreeqc, the oxidation from Fe(II) to Fe(III) needed to be decoupled by alternating the programme database. To accomplish this, all phases (dissolved species and minerals) that included Fe(II) or Fe(III) and their thermodynamic interrelations, except from the direct interrelation between Fe(II) and Fe(III) were copied from the database and Fe(II) and Fe(III) were exchanged with Fe_di and
Fe_tri that were defined as new master species in the input file (Appendix 2). The kinetic reaction of Fe\(^{2+}\) to Fe\(^{3+}\) was then defined in a “rates” and “kinetics” data block in the input file. The time steps for the kinetic calculation of Fe oxidation were chosen to increase from the first step of 0.1 ms over 0.4 ms, 3.1 ms, 10.8 ms, 21.6 ms, 50.4 ms, 86.4 ms for the 2\(^\text{nd}\) to 7\(^\text{th}\) time step and 172.8 ms for the last 122 time steps, totalling in a cumulative reaction time of 21.25 s in order to exceed the total residence time in the 12 model cells of 20.592 s.

As the step of Fe-oxidation from dissolved Fe\(^{2+}\) to dissolved Fe\(^{3+}\) was considered to be the rate limiting step of the total formation process of Fe(III)-precipitates from Fe(II)-solutions (Opel, 2012; Rose & Waite 2002), the subsequent reaction steps (precipitation of Fe(III)-hydroxide minerals from dissolved Fe\(^{3+}\)) could then be modelled in chemical equilibrium. For the equilibrium precipitation, the thermodynamic data of the wateq4f-database was compared, completed and updated with primary and more recent literature. Most of the solubility products of the additional minerals were found in Cornell and Schwertmann (2003). Solubility products of akaganéite and hematite were taken from Königsberger et al. (2008), those of Fe(OH)\(_2\)(a), ferrihydrite, lepidocrocite, goethite and hematite from Bonneville et al. (2004, 2009) and stoichiometry and solubility products of 2L- and 6L-ferrihydrite as well as schwertmannite from Yu et al. (2002).

The change of hydrochemical parameters over time were plotted and assigned to the particular model cells (cf. Figure 59). The sensitivity of the initial hydrochemical parameters pH, DO, c(Fe(II)), temperature and the influence of increasing contents of the dominating anion (Cl\(^{-}\) vs. SO\(_4^{2-}\)) were evaluated with the PhreeqC-model. However, effects of kinetically oxidising mixed dissolved species like FeCl\(^{+}\) could not be considered with the PhreeqC-model due to missing kinetic data.

### 4.6 Field sampling

With the RWE Power AG as a project partner, the unique opportunity of in situ observation and sampling of the gravel pack and screen pipes at dewatering wells, affected by Fe-clogging and excavated during progression of the open-pit Garzweiler was given. Of course, sampling was only possible, when the progression of the mining activities allowed access to the wells. Still, samples could be taken from 6 wells during two sampling campaigns in the open-pit Garzweiler. During the first campaign, samples were taken at three excavated wells (Figure 60). At two of the three wells, disturbed mixed samples of the gravel pack were taken. At the third well, the gravel pack was rather solidified through the Fe-clogging process, so an undisturbed sample could be taken.

During a second field campaign, the gravel packs of two additional wells in the open-pit Garzweiler were sampled (Figure 61). Both wells were located only 150 m apart from each other. Their wire-wrapped screens were laid open in Hz. 6B (German Institute for Standardization, 2001; DIN 21919). Despite similar conditions, the degree of well loss effects was considerably different in both wells. Whereas well B (WS 3120) only showed a thin mud cake on the borehole surface and was strongly encrusted with Fe-clogging products, well C exhibited a thicker mud cake and only minor clogging effects close to the screen tube.
Figure 60  Excavated wells sampled during the first campaign in the open-pit Garzweiler (wire wrapped screens in horizon (Hz.) 6D and gravel pack grain size class 0.7 to 1.4 mm). The exact location and drilling and assemblage data were only known for well 1C (RWE Power AG). Stratigraphic numbers (Hz.) according to DIN 21919 after the German Institute for Standardization (2001); gravel pack grain classes (GP) with lower and upper grain size boundary value; well casing (WC) and screen pipes (SP) backfilled.

Figure 61  Locations of excavated wells sampled during the second field campaign in the open-pit Garzweiler (wire wrapped screens in horizon (Hz.) 6B, gravel pack grain size class 0.7 to 1.4 mm). The exact location and drilling and assemblage data were only known for well 2B and 2C (RWE Power AG). Stratigraphic numbers (Hz.) according to DIN 21919 after the German Institute for Standardization (2001); gravel pack grain classes (GP) with lower and upper grain size boundary value; well casing (WC) and screen pipes (SP) backfilled.
These differences may possibly be caused by different water types north and south of the Otzenrath fault which dislocates the lower boundary of the dewatered aquifer in-between the two wells. At both wells, disturbed mixed samples of encrusted gravel pack as well as undisturbed samples were taken with core-cutter-rings (Figure 62).

Figure 62 Wells sampled and samples taken during the second campaign in the open-pit Garzweiler; A: fragments of a GRP-rod screen with Fe-clogging products on the inner tube surface; B, C: undisturbed core-cutter-ring samples taken for resin-impregnation at wells WS 3120 (only thin mud cake, but strong Fe-encrustations) and WS 3151 (thick mud cake, but weak Fe-encrustations), respectively; bottom: preparation of resin-impregnation in the field.
At a third well with a GRP-rod-screen that was also laid open in Hz. 6B only a fragment of the screen pipe could be taken as a sample (Figure 62, top). Due to intense wetness, the gravel pack could not be sampled here. Impregnation of the gravel with epoxy resin directly in the field was also tested. The two components were weighed with a battery powered letter balance and heated with a mobile blowtorch in order to lower the viscosity of the mixture and to increase its penetration depth when poured onto the gravel. As sampling was conducted in February, the temperature of the gravel was unfortunately too low for the resin to reach high penetration depths into the gravel before indurating. Therefore, the undisturbed samples taken with core-cutter rings were later used for gravel-impregnation at room temperature in the laboratory.

The field samples were included in the analytical programme of the laboratory samples that is described in section 4.3.8. Mixed disturbed samples were included in the SEP, TOC, BET, ENR and XRD analyses, whereas the solidified sample from the first campaign and the impregnated resin samples from the second campaign were used for preparation of thin sections, polarisation microscopy, and SEM/EDX analysis. An overview of the samples taken in the field and the analyses conducted on these samples are summarised in Table 10.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Well</th>
<th>RWE-Well-No.</th>
<th>Samples</th>
<th>Sample analytics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1A</td>
<td>unknown</td>
<td>MIX</td>
<td>SEP, ENR, XRD, TOC, BET</td>
</tr>
<tr>
<td>1</td>
<td>1B</td>
<td>unknown</td>
<td>MIX</td>
<td>SEP, ENR, XRD, TOC, BET</td>
</tr>
<tr>
<td>1</td>
<td>1C</td>
<td>WS 3039</td>
<td>Solid</td>
<td>SEP, ENR, XRD, TOC, BET, PM, SEM/EDX</td>
</tr>
<tr>
<td>2</td>
<td>2A</td>
<td>unknown</td>
<td>Screen</td>
<td>SEP, XRD, TOC, BET</td>
</tr>
<tr>
<td>2</td>
<td>2B</td>
<td>WS 3120</td>
<td>MIX, CCR</td>
<td>SEP, ENR, XRD, TOC, BET, PM</td>
</tr>
<tr>
<td>2</td>
<td>2C</td>
<td>WS 3151</td>
<td>MIX, CCR</td>
<td>SEP, ENR, XRD, TOC, BET, PM</td>
</tr>
</tbody>
</table>

### 4.7 Tracer experiments and annular space dewatering

When the experiments in the Fe-clogging model revealed the saturated well operation as a successful concept to prevent chemical Fe-clogging of the filter pack and screen tube of dewatering wells, the concept was transferred to the field scale in three multi-layered dewatering test wells in the pre-field of the open-pit Hambach, where installation of annular seals can be omitted for soon to be excavated upper aquifers.

Conventionally, in multi-layered dewatering each aquifer that was penetrated by the drilling got its own screen pipe and gravel pack, each aquitard its own casing and backfilling material in the annular space. Unfortunately, this most often resulted in a quick aeration of the upper screen pipe with the residual water from the upper aquifer dripping down into the water column (Figure 63, left). Apart from directly triggering Fe-clogging of the upper screen pipe, this also created two additional pathways of oxygen supply to the lower aquifer as well. Firstly, the water dripping down inside the well casing is likely to take up and transport oxygen down into the water column in the well. Secondly, when dewatering of the upper aquifer is
complete, a gas phase may intrude into the annular space through the upper screen pipe, reaching down to the lower aquifers.

Alternatively, according to the concept of annular space dewatering, the well can be constructed without the uppermost screen pipe and the whole annular space in between the aquifers filled with gravel pack instead of the hydraulically less conductive filling material (Figure 63, right). The water from the upper aquifer is then drawn down through the annular space without taking the risk of increased oxygen supply through an upper screen pipe. Ideally, these wells should be equipped with frequency-controlled pumps and automatic or telemetric regulation of the operating water level to protect the lower screen pipe from aeration.

To prevent oxygen supply of the ground water in multi-layered dewatering, the RWE Power AG constructed three of their deep dewatering wells according to the concept of annular space dewatering in the prefield of the open-pit Hambach. To check for the effectiveness of annular space dewatering, tracer tests were conducted in these three wells located in the field of the open-pit Hambach. 3 m$^3$ of Na-Naphthionate (4-Aminonaphthaline-1-sulphonacid, sodium salt, CAS: 130-13-2) input-solution were prepared with the groundwater from the well itself for each tracer test and directed into a piezometer tube that had been installed in the annular space additionally to the well tube with its screen tube at the height of the base of the upper aquifer (Figure 64). The rate of continuous tracer injection as well as the pumping rate of the dewatering well were constantly monitored with flow meters and stored with data loggers. The temporal development of tracer concentrations at the well head was determined by taking one sample every minute at the sampling valve (Figure 64). Concentrations of the
ground water before tracer injection, the samples during tracer injection, the tracer input solution, and the rinsing water were measured directly in the field with a “Cary Eclipse” fluorescence spectrophotometer (Varian Inc.). The median residence times of the tracer $t_{med}$ were then determined at breakthrough of 50 % maximum tracer concentration.

With the geometric dimensions and hydrostatic conditions in piezometer and well and the flow effective porosity of the gravel, the K-value of the annular space was determined according to Darcy’s law:

$$K = \frac{L_{AS} n_e}{t_{res} i} = \frac{L_{AS}^2 n_e}{t_{res} \Delta h}$$  \hspace{1cm} (49)

with $K = \text{hydraulic conductivity of the gravel pack in the annular space [m s}^{-1} \text{]}$, $L_{AS} = \text{vertical flow distance of the tracer in the annular space [m]}$, $n_e = \text{flow effective porosity of the gravel pack in the annular space}$, $t_{med} = \text{median residence time of the tracer in the annular space}$, $i = \text{hydraulic gradient between piezometer and well [-]}$, $\Delta h = \text{change in piezometric head between piezometer and well [m]}$. Given the annular cross-sectional area, the flow through the annular space could then be determined depending on the hydraulic situation in the annular space of the well also using Darcy’s law:

$$Q_{AS} = K \cdot i \cdot A_{AS} = K \cdot i \cdot (A_{BH} - A_{WC}) = K \cdot i \cdot \pi \cdot (r_{BH}^2 - r_{WC}^2)$$  \hspace{1cm} (50)

with $Q_{AS} = \text{downward flow through the annular space [m}^3 \text{ min}^{-1} \text{]}$, $i = \text{hydraulic gradient in the annular space [-]}$, $A_{AS} = \text{cross-sectional area of the annular space [m}^2 \text{]}$, $A_{BH} = \text{cross-sectional area of the borehole [m}^2 \text{]}$, $A_{WC} = \text{cross-sectional area of the well casing [m}^2 \text{]}$, $r_{BH} = \text{radius of the borehole [m]}$, $r_{WC} = \text{outer radius of the well casing [m]}$.  

---

**Figure 64**  Concept of the tracer tests, conducted at a well with annular space dewatering (Milatz, 2013, *report annular space dewatering, 2013, translated*)
5 Results and Discussion

5.1 Column experiments

5.1.1 Time series of hydrochemical parameters

The progression of pH and eC in the outflow of the columns generally followed the trend in the column inflow (Figure 65). During normal column operation, eC in the outflow was equal to the inflow value, whereas the pH was steadily decreased by around 0.1 units. At the beginning of the experiments as well as after the prolonged reaction times after the stop-flow-phases, pH in the outflow of all columns was decreased by 0.3 to 0.6 units, whereas eC was increased by around 20 to 60 µS cm⁻¹. At the beginning of the experiments, this originated from a first-flush-phenomenon after column assemblage.

Figure 65  Progression of pH and eC in the in- and outflow of the columns (left) and difference of dissolved Al, Mn, Fe and Si between column in- and outflow (right; negative values represent retardation of the corresponding element in the column, positive values represent release of the element from the column); yellow areas represent stop-flow-periods; the results of only one column of each gravel material is shown here, as the duplicate columns for the Frimmersdorf and Dorsfeld gravel showed similar results except from more extreme values at the beginning of the experiments (Appendix 4).
The decrease in pH presumably is a result of hydrolysis of silicate surfaces and the release of silicic acid, but buffered by minor amounts of carbonates dissolving from the gravel. The rise in eC originates from increasing aqueous mineralisation, exceptionally occurring after prolonged times of contact between water and gravel (stop-flow phases) due to dissolution of minor contents of carbonates and aluminosilicates.

Including the prolonged reaction times, release of (semi-)metals from one metric ton of gravel after 3000 to 5600 exchanged pore volumes cumulates to between a few grams for Al and Mn to tens of grams for Si. As confirmed by the hydrogeochemical calculations, dissolution of clay minerals, feldspars and quartz results in the release of Al and Si with decreasing importance. Fe tends to be captured in the columns rather than to be released from the gravel.

As was to be expected from the chemical compositions determined by the XRF analysis of the three initial different gravel materials (section 4.1.2), the Dorsfeld gravel exhibits the weakest release of Mn and Si and the least pronounced effect on the hydrochemical parameters. This is due to the lower content of feldspars and clay minerals in the Dorsfeld gravel when compared to the Frimmersdorf gravel. Only the release of Al was slightly lower in the Frimmersdorf gravel after prolonged reaction times (Weidner et al., 2013).

Even though the column experiments did not necessarily aim towards quantification of the Fe-retardation potential and Fe-clogging affinity of the materials, capture of the low Fe-content contained in the tap water could be noted. In all five columns Fe-contents were considerably lower in the column outflow than in the inflow, especially after the stop-flow phases. With 50 to 70 % retention, the strongest effect of Fe-capture was found in the Frimmersdorf gravel, which also exhibited the highest initial content of ferric hydroxides as determined by the SEP analysis (cf. section 4.1.2; e.g. goethite as sorptive mineral and terminal sink for Mn and Fe, respectively). In the Dorsfeld and Weilerswist gravel, Fe-retention averaged at around 25 %. However, in order to reliably investigate the Fe-clogging affinity of the different gravel materials and its influence on the hydraulic conductivity, the Fe-clogging experiments needed to be considered (report long term elution, 2012).

However, no strong differences in the elusive properties were found in the comparison of the three gravel materials. Elusion even seems to be strongest in the currently used conventional Weilerswist gravel, especially when compared to the Dorsfeld gravel. With respect to long term elusion, the Quaternary gravels do not show any disadvantages in comparison to the conventionally used material (Weidner et al., 2013).

**5.1.2 PhreeqC-calculations**

The distribution of Fe-species was dominated by uncharged but dissolved Fe(OH)\(_3\)\(^0\), followed by the anionic complex Fe(OH)\(_4\)^\(^-\). Saturation indices (cf. section 2.4.2) of relevant minerals show the inflow water to be slightly oversaturated with ferrihydrite (SI ≈ 2.5) and strongly oversaturated with goethite (SI ≈ 8.0). In the outflow, SI tended towards lower values for ferrihydrite (SI ≈ 2.0) and goethite (SI ≈ 7.5), indicating the general tendency of Fe to become captured in the gravel by precipitation of ferrihydrite (Fe(OH)\(_3\)) or goethite (FeOOH – stoichiometries used in the wateq4f.dat-database) rather than to be washed out of the gravel. This effect was only slightly stronger in the Frimmersdorf gravel than in the other two
materials, but, however, the Fe-clogging affinity shall be primarily evaluated using the Fe-clogging model.

Manganese species distribution was controlled by a dynamic equilibrium between uncharged but dissolved $\text{MnCO}_3^0$ and $\text{Mn}^{2+}$ with the percentage of $\text{Mn}^{2+}$ lightly increasing after prolonged reaction times due to the lowered pH. All relevant minerals exhibited continuous undersaturation in the inflow and outflow of all columns. While after the first stop-flow phase the SI were slightly increased, a decrease in SI was measured after the second stop-flow phase, so the influence of the stop-flow phases did not appear to be systematic.

Dissolved Al mainly appeared as the anionic hydroxide complex $\text{Al(OH)}_4^-$ in the inflow and outflow of each column. Silicon predominated as uncharged, dissolved silicic acid $\text{H}_n\text{SiO}_4^\ominus$. Relevant aluminosilicates mineral phases in the inflow were strongly undersaturated with respect to albite, anorthite, orthoclase and illite (SI < -3.5) and weakly undersaturated with kaolinite, gibbsite and quartz (-1.0 < SI < -0.4). In the column outflow, saturation indices of these minerals increased considerably, which was most significant after the prolonged reaction times during the stop-flow phases. The values after the second stop-flow phase (Table 11) reveal the increase in saturation between column in- and outflow to occur for all Al and Si-containing minerals except from quartz. The change in saturation indicates that the corresponding (semi-)metals went into solution by dissolving the relevant minerals inside the columns, and the solution thus became less undersaturated, or even oversaturated with respect to certain phyllosilicates.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthite</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
<td>-5.5</td>
<td>-3.7</td>
<td>-3.9</td>
<td>-3.0</td>
<td>-3.0</td>
<td>-2.7</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi$_3$O$_8$</td>
<td>-5.0</td>
<td>-3.8</td>
<td>-3.9</td>
<td>-3.5</td>
<td>-3.4</td>
<td>-3.1</td>
</tr>
<tr>
<td>Illite</td>
<td>K$<em>{0.6}$M$</em>{0.25}$Al$<em>{2.3}$Si$</em>{3.5}$O$_{10}$(OH)$_2$</td>
<td>-3.9</td>
<td>-0.8</td>
<td>-1.3</td>
<td>-0.3</td>
<td>-0.1</td>
<td>+0.4</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>KAlSi$_3$O$_8$</td>
<td>-3.5</td>
<td>-2.1</td>
<td>-2.2</td>
<td>-2.0</td>
<td>-1.9</td>
<td>-1.5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td>-1.0</td>
<td>+1.9</td>
<td>+1.5</td>
<td>+2.3</td>
<td>+2.4</td>
<td>+3.1</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al(OH)$_3$</td>
<td>-0.5</td>
<td>+0.8</td>
<td>+0.6</td>
<td>+1.0</td>
<td>+1.2</td>
<td>+1.4</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>-0.4</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.3</td>
<td>-0.2</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

Compared to the Dorsfeld gravel, the effect of aluminosilicate dissolution and therefore the changes in SI were found to be weaker in the Frimmersdorf gravel. However, both of the alternative materials revealed weaker changes in SI and therefore lower solubility of aluminosilicates than the conventionally used Weilerswist gravel. With respect to mineral dissolution, an even better performance can be expected of the alternative materials than of the conventional Weilerswist gravel.

**5.2 Clogging experiments**

**5.2.1 Model optimisation**

The development of the Fe-clogging zone in the capillary fringe of the gravel pack and its dependency on $h_{OC}$ was found during LTT 2 (Figure 66). To increase the experimental duration,
the fine filtration was installed upstream of the flow channel in LTT 3 in order to prevent clogging of the channel inflow with green rust particles (Figure 67).

![Figure 66](image1)

**Figure 66** Fe-clogging zone in the capillary fringe in LTT 2 and its dependency on the water level in the outflow chamber (final report phase II, 2011)

![Figure 67](image2)

**Figure 67** Installation of filtration steps between LTTs 2, 3 and 4 (top views)

By shifting the Fe-addition point from AdP 2 to AdP 1, most of the green rust particles were captured in the main filtration column, increasing the possible experimental duration. Still, after 295 h of Fe-clogging time (Figure 67, centre), the amount of green rust particles reached a similar level as in LTT 2 after 42 h (Figure 67, left). With installation of the fine filtration upstream of the flow channel, migration of green rust particles into the channel inflow was completely prevented in LTT 4 (Figure 67, right), so hydraulic evaluations became possible.

The Reynolds numbers calculated from the results of LTT 4 show the flow regime in the channel to exceed the lower threshold of the laminar regime (Re = 1) at h_{OC} = 120 mm (Figure 68). This trend increases significantly at h_{OC} < 60 mm, reaching the highest Reynolds numbers of Re ≈ 6.5 at the lowest possible water level of h_{OC} = 4 mm. However, this value still not reaches the upper threshold of Re = 10, also found in common literature (cf. section 2.1). Thus, the h_{OC}-values for the Fe-clogging and evaluation phase for the standardised material tests of project phase III were chosen to be h_{OC} = 40 mm and 100 mm, respectively (cf. section 4.3.5). As the hydraulic situation in the gravel pack is only relevant during the evaluation phase, the water level was chosen to exhibit an Re close to 1 and still to encompass all of the primary clogging zone, but also not too much of the upper, unlogged parts in order to achieve the best possible measurement of the change in hydraulic conductivity (cf. section 4.3.6).

The comparison of the hydraulic condition of the gravel pack in the reference situation to the Fe-clogging situation in LTT 4 shows the loss of hydraulic head in the gravel to increase at constant Q_{SYS} and flow cross-sectional area (h_{OC}). As the loss of hydraulic head between two observation points is linearly inversely proportional to the hydraulic conductivity at these
conditions, the change in hydraulic conductivity can be read from the comparison of $\Delta h_{\text{ref}}$ with $\Delta h_{\text{clog}}$ (Figure 69). The relative changes in hydraulic conductivity for the different water levels in the outflow chamber ($h_{\text{OC}}$) are summarised in Table 12.

![Figure 68](image1.png) Reynolds-numbers (Re) depending on the water level in the outflow chamber ($h_{\text{OC}}$), calculated from the reference test of LTT 4 (Weidner et al., 2012a, final report phase II, 2011)

![Figure 69](image2.png) Pressure loss in the hydraulic evaluation sections S I and S II as well as the sum of both, compared for the reference situation (dashed line) with the Fe-clogged situation (solid line) of LTT 4 (coloured areas between the lines are for illustration purposes only; Weidner et al., 2012a, final report phase II, 2011, redrawn)

The measurements show that a measurable effect of Fe-clogging on the hydraulic conductivity of the gravel pack can be produced in an appropriate model operating duration. Only the temporal development of the incrustations and resulting progression of pressure loss and hydraulic conductivity could not yet be read from the results of LTT 4. In the subsequent experiments of project phase III, model operation was thus focused on the two $h_{\text{OC}}$-levels for the Fe-clogging and evaluation phase of $h_{\text{OC}} = 40$ mm and $h_{\text{OC}} = 100$ mm, respectively. Furthermore, based on the results of the first four LTTs, the standardised experimental concept (cf. section 4.3.5) was developed and applied for all further LTTs, in order to attain multiple values of the same water level in a temporal view.
Table 12
Percental change of the hydraulic gradient in the gravel pack between the reference and Fe-clogging situation, dependent on the outflow water level \( h_{oc} \) (final report phase II, 2011)

<table>
<thead>
<tr>
<th>( h_{oc} ) [mm]</th>
<th>Change S I [%]</th>
<th>Change S II [%]</th>
<th>Change S I + S II [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>197.2</td>
<td>42.8</td>
<td>75.1</td>
<td>59.8</td>
</tr>
<tr>
<td>180.1</td>
<td>21.7</td>
<td>31.8</td>
<td>27.7</td>
</tr>
<tr>
<td>160.6</td>
<td>5.3</td>
<td>22.4</td>
<td>18.3</td>
</tr>
<tr>
<td>140.2</td>
<td>46.7</td>
<td>41.2</td>
<td>29.6</td>
</tr>
<tr>
<td>120.1</td>
<td>12.6</td>
<td>38.4</td>
<td>27.5</td>
</tr>
<tr>
<td>100.4</td>
<td>29.0</td>
<td>58.0</td>
<td>45.1</td>
</tr>
<tr>
<td>80.7</td>
<td>15.7</td>
<td>41.2</td>
<td>29.3</td>
</tr>
<tr>
<td>59.9</td>
<td>23.9</td>
<td>38.2</td>
<td>32.4</td>
</tr>
<tr>
<td>40.2</td>
<td>30.9</td>
<td>44.1</td>
<td>39.2</td>
</tr>
<tr>
<td>20.5</td>
<td>15.3</td>
<td>27.0</td>
<td>22.6</td>
</tr>
<tr>
<td>4.1</td>
<td>6.8</td>
<td>8.5</td>
<td>7.9</td>
</tr>
</tbody>
</table>

5.2.2 Material tests

A detailed overview of the relevant hydrochemical and hydraulic data as well as pictures of the progression of the Fe-clogging zone for the material tests LTT 5 to 14 are compiled in diagrams, tables and pictures from Appendix 5 to Appendix 9. The changes of the relevant analytic hydrochemical parameters inside the flow channel during the Fe-clogging phases do not show significant differences between the different material tests (Figure 70). As a result of the active air supply, DO and Eh increase in the flow channel by \( 1.3 \pm 0.5 \) to \( 1.8 \pm 0.5 \) mg L\(^{-1}\) and \( 280 \pm 30 \) to \( 320 \pm 30 \) mV, respectively. Only in LTT 9 and 14 the change in Eh in the flow channel seems to be considerably higher with \( \Delta \text{Eh} = 500 \) and \( 450 \) mV, respectively. As these differences do not correlate with any other hydrochemical values, this data is obviously due to systematic errors of the Eh-measuring instruments. In all material tests, pH decreases as a result of the proton-producing Fe-clogging reaction by \( 1.0 \pm 0.2 \) to \( 1.5 \pm 0.2 \).

![Figure 70](image.png)

Figure 70 Development of hydrochemical parameters in the flow channel during the Fe-clogging phases of all material tests as difference between channel inflow and outflow (absolute values pH: decrease, DO/Eh: increase; final report phase III, 2013).

A similar situation is found when considering the values of the Fe-balance (Figure 71). Very high standard deviations occur at the temporal integral of total Fe retention in the flow channel that is calculated from the photometrical c(Fe(II))-measurements in the process.
water. These deviations range between 50 and more than 100 % of the actual value and arise from the low measurement resolution of 0.5 mg L⁻¹ at Fe(II)-concentrations as high as 80 mg L⁻¹ as well as the high tendency of sampling and measurement to systematic errors. For example in LTTs 5 and 6, samples were taken at a wrong position inside the outflow chamber, only representing water from the saturated zone of the filter pack. In later experiments, samples were always taken directly at the drain of the outflow chamber, accounting for the mixture of water from the saturated and unsaturated zone. Another error may arise from prolonged exposition of the sample to the ambient air between sampling and measurement, as Fe(II) quickly oxidises to Fe(III).

The results of the sequential extraction show the maximum value and volume integral of incrustations, normalised with respect to the total Fe-clogging time to be relatively similar in comparison of all material tests. The maximum values vary between 1.6 and 2.1 g kg⁻¹ (10 h)⁻¹ for the gravel materials. The low value of 1.3 g kg⁻¹ (10 h)⁻¹ in the glass beads is not reliable, as sampling was done only after the interim experiment of “in-situ” dissolution of the Fe-clogging-products (cf. section 4.4.2). The volume integral showed extreme values in LTT 5 and 11, which were not confirmed by the corresponding duplicate experiment and could thus not be assigned to a specific filter pack material.

With values between 2.10⁻² and 2.6.10⁻² m s⁻¹, the glass beads and alternative Quaternary gravel materials showed higher initial hydraulic conductivities than the conventional Tertiary Weilerswist gravel with 1.2.10⁻² to 1.7.10⁻² m s⁻¹ (Figure 72). However, the change in hydraulic conductivity with increasing Fe-clogging time showed a similarly descending trend in all LTTs and all pressure evaluation sections S I to S III, regardless of the filter material considered. This impression is confirmed by the direct comparison of the relative change after 35 h (Figure 73).

Whereas the change in K in S II showed almost no difference between the filter materials, values in S I showed a broader range of variation. The lowest change for S I, found in the glass
The bead experiment, had to be interpreted carefully, considering the obvious outlier value recorded in the progression of K after 35 h (Figure 72).

![Figure 72](image)

**Figure 72** Progression of hydraulic conductivity with increasing Fe-clogging time, compared for all tested materials, including the results of the interim experiment of “in-situ” dissolution of Fe-clogging products, conducted after LTT 14 (*final report phase III, 2013, redrawn, translated*).

The material test with glass beads was not repeated as the reproducibility of the experimental results could already be demonstrated in the previous experiments. The change of hydraulic conductivity of the screen pipe (S III) was similar for all three experiments, also somewhat varying with partly outlying values after 35 h in the LTTs 12 and 14. However, there were no obvious trends favouring a specific filter material with respect to clogging affinity.

![Figure 73](image)

**Figure 73** Change of the hydraulic conductivity K after 35 h of Fe-clogging relative to the initial value in the different evaluation sections S I to S III of all material tests; evaluation in section S III was first implemented for LTT 12; GB: glass beads (*final report phase III, 2013*).

The increase in K in the last two values of LTT 14 in all three evaluation sections (light coloured parts in Figure 72 bottom right) are caused by the interim experiment of “in-situ” dissolution of Fe-clogging products in the model (cf. section 4.4.2). By cleaning the gravel material from the Fe-incrustations, the hydraulic conductivity of the gravel material was raised back to its
During FeFeFeFe of the evaluation, the progression of the hydraulic conductivity again approximately followed the progression of the original first clogging step of LTT 14. Therefore, the affinity of the glass beads towards chemical Fe-clogging apparently did not change due to the interim experiment.

5.2.3 Saturated screen pipe with and without air phase in the gravel pack

The hydraulic and hydrochemical data recorded in the process water during the experiments of the situation of saturation in the filter pack are summarised in Appendix 10. The comparison of the change in hydrochemical parameters in the flow channel with the material tests shows the saturation experiments to be comparable to the results of the material tests (Figure 74).

![Development of hydrochemical parameters in the flow channel during the Fe-clogging phases of all LTTs as difference between channel inflow and outflow (absolute values pH: decrease, DO/Eh: increase; final report phase III, 2013).](image)

During LTT 15 and 16, DO and pH change in the flow channel were in the same range as in the material tests LTT 5 to 14. With 320 to 370 mV, the change in Eh in the flow channel lay between the most frequent value and the two outliers of the material tests. The change in c(Fe(II)) in the flow channel and the resulting temporal integral for the Fe-balance also presented values similar to the average from the material tests (Figure 75). Only with the restricted air supply in the filter pack, Fe-retention in the flow channel and the results of the SEP (maximum and integral Fe(III) values) appeared somewhat below average, but in LTT 16, Fe-retention was higher again. In LTT 16 no samples were taken in the filter pack as no visible Fe-clogging had formed in the filter pack.

During LTT 15, the oxygen content in the air, contained in the gravel pack was decreased as a result of the Fe-clogging process. As the O2-content of the air could not be measured immediately in the filter pack, measurement had to be conducted in the flexible air reservoir that had been installed to allow for a gas escape in times of higher water levels in the outflow chamber. When hOC was raised in the end of the Fe-clogging phase to prepare for the next evaluation phase, the air was pushed out of the gravel pack into the flexible air reservoir (cf. 121
section 4.4.3) in about 4 min (Figure 76, right). During these 4 min, the content of oxygen in the air decreased by 1 to 2.7 vol.-%.

By mixing with the air in the reservoir and a possibly imperfect air tightness of the reservoir, the oxygen content increased again over night. All over the whole LTT, the oxygen content in the reservoir decreased stepwise with each Fe-clogging step, with an overall minimum Fe-content of 16.9 (Figure 76, left).

Consumption of oxygen from the air inside the filter pack and air reservoir as a result of the Fe-clogging reaction was calculated from an estimation of the air volume in the filter pack:

\[
V(O_2) = V_{Air} \cdot s(O_{2,atm}) = (h_{FC} - h_{capit}) \cdot b_{FC} \cdot L_{PP} \cdot n_e \cdot s(O_{2,atm})
\]  

(51)

with \(V(O_2)\) = volume of oxygen inside the filter pack during the Fe-clogging phase (initially 0.196 L \([\text{m}^3]\)), \(s(O_{2,atm})\) = percentage of oxygen in the air, measured inside the air reservoir (initially 0.209 = 20.9 vol.-%) [-], \(V_{Air} = 0.00094 \text{ m}^3\) = volume of air inside the filter pack during the Fe-clogging phase \([\text{m}^3]\), \(h_{FC} = 0.2 \text{ m}\) total height of the flow channel \([\text{m}]\), \(h = 0.04 \text{ m} =\)
piezometric head during the clogging phase [m], \( h_{\text{capill}} = 0.04 \text{ m} \) = estimated height of the water saturated capillary fringe [m], \( b_{c} = 0.2 \text{ m} \) = breadth of the flow channel [m], \( L_{f} = 0.1 \text{ m} \) = length of the filter pack in flow direction [m], \( n_{e} = 0.379 \) flow effective porosity [\( \cdot \)], determined from the total filter pack volume and mass in the model and the mineral density of the gravel.

For calculation of the molar oxygen consumption in the air, the molar volume of oxygen had to be calculated for the \( p/T \) conditions applied in the model from the ideal gas law:

\[
V_{m} = \frac{R \cdot T_{abs}}{p_{atm}} \tag{52}
\]

with \( V_{m} = 0.02365 \text{ m}^{3} \text{ mol}^{-1} \) = molar volume of oxygen [\( \text{m}^{3} \text{ mol}^{-1} \)], \( R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \) = ideal gas constant [\( \text{kg m}^{2} \text{s}^{-2} \text{K}^{-1} \text{mol}^{-1} \)], \( T_{abs} = 288.15 \text{ K} = 15 \text{ °C} \) = absolute temperature [K], \( p_{atm} = 101325 \text{ Pa} \) = atmospheric pressure [\( \text{kg m}^{-1} \text{s}^{-2} \)]. The molar amount, consumed during the first Fe-clogging step was then calculated by:

\[
\Delta n(O_{2}) = \frac{\Delta V(O_{2})}{V_{m}} = \frac{V_{\text{air}} \left( s_{\text{init}}(O_{2,atm}) - s_{\text{end}}(O_{2,atm}) \right)}{V_{m}} \tag{53}
\]

with \( \Delta n(O_{2}) \) = molar amount of oxygen consumed by the Fe-clogging reaction [mol], \( \Delta V(O_{2}) \) = change in the absolute oxygen volume in the filter pack air [\( \text{m}^{3} \)], \( s_{\text{init}}(O_{2,atm}) \) = initial percentage of oxygen in the air reservoir [\( \cdot \)], \( s_{\text{end}}(O_{2,atm}) \) = minimum percentage of oxygen in the air reservoir after the Fe-clogging step [\( \cdot \)]. Considering the values of the first Fe-clogging step \( s_{\text{init}}(O_{2,atm}) = 0.209 \) and \( s_{\text{end}}(O_{2,atm}) = 0.182 \), within 4.5 h the total amount of oxygen consumed equalled \( \Delta n(O_{2}) = 1.07 \text{ mmol O}_{2} \). As each mole of oxygen oxidises 4 mol of Fe(II), this corresponds to oxidation of 4.28 mmol Fe(II) which would correspond to a constant decrease of \( c(Fe(II)) \) of:

\[
\Delta c(Fe(II)) = \frac{\Delta n(Fe(II))}{t \cdot Q_{\text{sys}}} \cdot M(Fe) \tag{54}
\]

with \( \Delta c(Fe(II)) = 0.83 \text{ mg L}^{-1} \) = decrease of \( c(Fe(II)) \) in the filter pack, \( n(Fe(II)) \) = molar amount of Fe(II) consumed by the oxygen, \( t = 4.5 \text{ h} \) = Fe-clogging time of the first Fe-clogging step [h], \( Q_{\text{sys}} = 1.06 \text{ L min}^{-1} \) = system flow rate [\( \text{L min}^{-1} \)], \( M(Fe) = 55.845 \text{ g mol}^{-1} \) = molar mass of Fe [\( \text{g mol}^{-1} \)]. The calculated decrease in \( c(Fe(II)) \) of 0.83 mg L\(^{-1}\), however, is more than four times lower than the value usually measured in the model of \( \approx 3.5 \text{ mg L}^{-1} \) (LTT 15, but with very high standard deviations; cf. Appendix 10).

The underestimation produced by the calculation on the one hand could result from the air from the gravel pack mixing with the only roughly estimated volume of air inside the flexible reservoir before the percentage of oxygen is measured. On the other hand, the direct measurement of \( \Delta c(Fe(II)) \) in the model additionally includes the amount of Fe precipitated in the outflow chamber. The actually precipitated amount of Fe will therefore lie somewhere in between the two values.

Visual observation of the development of the primary and secondary clogging zone indicated the intensity of Fe-clogging to be about as strong as in LTT 14. But due to the shortened screen pipe that was used in LTTs 15 and 16, the primary clogging zone was in the vicinity of the screen pipe pulled down towards the open part of the screen by a distortion of the flow field (Figure 77, centre). The picture completely changed when the filter pack was fully saturated with process water from the beginning in LTT 16. With air supply in the filter pack
completely avoided, no Fe-clogging zones developed at all, even after 30 h of cumulative Fe-clogging time (Figure 77, right).

The absence of Fe-clogging in LTT 16 in comparison to LTT 15 was not only documented optically, but also by measuring the change of the hydraulic conductivity. In LTT 15, the decrease of K was found to proceed approximately as quickly as in the other LTTs (Figure 78).

Of course the effect of increased Fe-input overnight before the fourth evaluation step needs to be taken into account. After this incident, the hydraulic conductivities in all three evaluation sections exhibited a strong decrease that is not realistic under normal experimental conditions. Lying closest to the defective addition point AdP 1, the decrease is strongest in the screen pipe section S III, weaker in S II and weakest in S I. However, there also are still descending trends in the other parts of the curve, obviously resulting from the primary clogging zone that developed in the filter pack. This is not true for LTT 16 that exhibited constant values of hydraulic conductivity in all three evaluation sections (Figure 78, right). In all evaluation sections S I to S III, even a light increase in the K-value could be detected in LTT 16 (Figure 79), which may be due to flow-induced particle rearrangement like in well development. The results of the experiments show the Fe-clogging affinity to be almost independent on the choice of filter pack material and no disadvantages for the application of the two alternative Quaternary gravel materials were found. Disregarding the malfunction of addition point 1 (AdP 1) in LTT 15, limiting, or even better, completely inhibiting air supply to the filter pack appears as the method of choice to prevent development of chemical Fe-incrustations in the filter pack of dewatering wells. A possibility to transfer these results to the field scale of real dewatering wells is discussed in sections 4.7 and 5.5.
5 Results and Discussion

5.2.4 Filter aeration experiments

To understand how air supply to a saturated filter pack through an aerated filter screen would proceed in a dewatering well, filter aeration experiments were conducted with the assemblage of LTT 16 after the LTT was finished. When the filter was first aerated for several minutes ($h_{oc} = 4$ mm and $Q_{sys} = 1.06$ L min$^{-1}$), no air flow through the 30×200 mm screen pipe section back into the filter pack was observed (Figure 80 A). Then, to check for the height of the capillary fringe, air was supplied to the filter pack from a top opening of the flow channel (Figure 80 B). The capillary fringe of around 40 mm in the glass beads stayed saturated, but the hydraulic pressure in the filter pack stayed unaffected by the aeration through the top opening.

Figure 79  Change of the hydraulic conductivity $K$ after 35 h of Fe-clogging relative to the initial value in the different evaluation sections S I to S III for all Fe-clogging experiments; evaluation in section S III was first implemented for LTT 12; GB: glass beads (final report phase III, 2013)

Figure 80  Conditions during the experiments of screen pipe aeration; A: filter pack stays saturated when the screen pipe is aerated and $Q_{sys}$ continues; B, C: aeration from the top of the flow channel; D, E: aeration of the filter pack through the screen pipe occurs after 16 h when $Q_{sys}$ is stopped.
After raising $h_{\text{OC}}$ again after only 15 min and expelling the air from the filter pack, some air bubbles were captured inside the previously unsaturated zone, immediately triggering Fe-clogging.

To evaluate how long it would take for the filter pack to become aerated through the screen pipe, $Q_{\text{sys}}$ was stopped completely at $h_{\text{OC}} = 4$ mm over one weekend. Backflow of air through the screen pipe into the glass bead filter pack occurred after 16 h, as was documented by a webcam (Figure 80 D, E). After picture E was taken, a usual capillary fringe of 45 mm stayed stable in the glass bead filter pack for the rest of the weekend.

Finally, as a cumulative result of 15 min of aeration from the top, residual air bubbles and 16 h of air diffusing into the filter pack from the screen pipe, a considerable ochreous stain was visible in the glass beads (Figure 80 D, E). As documented during disassembling the flow channel, the main incrustations were concentrated near the pathways of air flow like the upper part of the 30 mm flow-effective screen-pipe-section (Figure 81, left) and the top venting hole of the screen pipe (Figure 81, centre). Of course, strong incrustations were found on the front outflow-chamber-side of the screen pipe that had been exposed to the active air supply during the whole 30 h of Fe-clogging of LTT 16 (Figure 81, right).

![Figure 81](image)

Figure 81 Distribution of Fe-clogging after LTT 16 with full saturation of the filter pack and after the aeration experiments; the venting hole in the upper part of the shortened screen pipe shows stains of oxidised iron due to the aeration experiments (centre).

The aeration experiments showed that chemical Fe-clogging can be triggered even after short periods of screen pipe aeration. Once saturation of the filter back breaks off, Fe-clogging is bound to develop and affect the hydraulic conductivity of the filter pack. As the K-value was found to decrease strongest at the beginning of the Fe-clogging progression, this emphasises the importance to avoid aeration of the filter pack as long as possible.

### 5.3 Properties of Fe-incrustations in the model and in the field

The actual spatial distribution and mineralogy of the incrustations produced in the model and found in the field could be compared to the results of the hydrogeochemical model.

#### 5.3.1 Distribution of Fe-clogging inside the well filter

The sampling locations for SEP analyses and the distributions of Fe-incrustations in comparison to the optical impression are given from Appendix 11 to Appendix 26. As the distributions attained in the model are quite similar in all LTTs, only one example from LTT 5 is
shown here (Figure 82) for comparison with the distribution patterns found in the field (Figure 83).

The spatial distribution of Fe-incrustations most strongly depends upon the pathway of O₂-supply (Houben, 2006, Houben & Weihe, 2004, 2010, Medina et al., 2013). As seen in the experimental model, zones that are saturated with anoxic water will not be affected by chemical Fe-clogging. The distributions of incrustations produced in the model correlated with those found in the field.

There are zones with incrustations only near to the boundary between aquifer material and gravel pack (well 1B in Figure 83, top row), representing zones of “fresh, Fe(II)-bearing groundwater” entering the annular space from the aquifer and flowing downwards at the boundary. This corresponds to the upper three layers when disassembling the gravel pack in the clogging model by layered excavation (Figure 82) and is consistent with simulation results of Fe-clogging by Larroque and Franceschi (2011).

![Figure 82](image)

Layered excavation of the gravel pack for determination of the spatial distribution of Fe-incrustations in the experimental model; red layer numbers count from top to bottom with layer 1 200 mm above channel bottom, layer 2 180 mm above channel bottom and so on; white dots with yellow numbers illustrate sampling locations (example from LTT 5, final report phase III, 2013)

Other zones are completely and homogeneously clogged with Fe(III)-incrustations (wells 1A and 2B in Figure 83, 2nd row) and presumably correspond to partly saturated water level fluctuations with predominantly horizontal flow like in layers 4, 5 and 6 of the layered excavation system in the model (Figure 82). Frequently, the incrustations are concentrated in close vicinity to the screen pipe, representing the locations of former water levels (well 2C in Figure 83, 3rd row). This situation is found in the model in the layers 7 to 9 (Figure 82).

Of course the exact distribution of Fe(III)-incrustations in a real gravel pack is by far more heterogeneous due to changing flow conditions, discontinuities and preferential flow paths in aquifer and gravel pack as well as irregularities of the borehole wall (sloughing and caving material; wells 2B and 3A in Figure 83, bottom row) and the mud cake distribution. Other wells did not exhibit any incrustations at all, presumably in zones of saturated flow or of low Fe-contents in the water.
Figure 83  Types of spatial distributions of Fe-clogging products found at excavated wells in the open-pit Garzweiler; top row: inhomogeneous distribution, 2nd row: nearly homogeneous distributions (asymmetrical distribution at well 2B), 3rd row: screen-pipe associated incrustations (biological Fe-clogging products only on the inner surface of well 2A), bottom row: patterns of preferential flow at irregular borehole surfaces; well numbers correspond to denominations defined in Table 10
Apart from all that, in the field there are often increased amounts of fine-grained Fe(III)-precipitations found on the inner screen pipe surface (well 2A in Figure 83, 3rd row), the area of maximum flow velocities, presumably originating from biological clogging (Paul, 1996).

The distributions of Fe-hydroxides in the gravel pack in the experimental model show the major part of incrustations to precipitate close to the boundary between aquifer material and filter pack. This trend was also observed in the PhreeqC-model. A quantitative comparison of the PhreeqC-model with an exemplary Fe-distribution in the model is shown in Figure 84. The Fe-distribution of LTT 13 was chosen for comparison, as the Fe-clogging time here was with 51.5 h close to the time of 50 h modelled with PhreeqC.

In model cells 4 to 10, the results of the PhreeqC model correspond well to the actually measured values. In the first three model cells, however, the precipitated amounts are strongly overestimated by the PhreeqC-model by the factors of 1.3, 1.6 and 3 in the third, second and first model cell, respectively. The sum of Fe precipitated in the gravel pack totalled 31.6 g (32.6 g when additionally considering the 11th model cell) in the PhreeqC model and 20.0 g from the actual data (22.3 g when additionally considering the curving in the screen pipe). The overestimation in the PhreeqC model most certainly results from the model assumption of a DO, immediately rising to 2 mg L⁻¹ in the total water volume of first model cell. More realistically, only the unsaturated part of the model cell will mix with oxygen from the air. However, when only considering the model cells 4 to 10, the sum of precipitated Fe totalled 11.15 g in the PhreeqC-model and 11.47 g in the actual data, so the overestimation seems to be limited to the first three PhreeqC-model cells.

![Figure 84](image)

**Figure 84** Comparison of measured distributions of Fe-incrustations with the PhreeqC-model (Fe-clogging time: 50 h; top right); the actual data (bottom right) was calculated from average concentrations of the model cells in the cells 1 to 10 (centre) after 51.5 h of Fe-clogging time in LTT 13.

With the mentioned exceptions, the comparison of the model results with the actual data are in good agreement so the chosen analytical and evaluative methods appear to deliver plausible results and to be suitable for evaluation of the Fe-clogging process. The same is true for the PhreeqC-model that can be applied to analyse the sensitivity of the Fe-clogging...
process towards different hydrochemical and physical parameters that could not be investigated experimentally due to the high temporal expenditure necessary for the singular long term tests (cf. section 5.4.2).

5.3.2 Chemical and mineralogical analyses

The results of the sequential extraction procedures showed the average and maximum Fe-contents observed in the field to be twice as high as the values reached in the laboratory model (Table 13). The proportions of poorly crystallised to well crystallised minerals exhibited a general trend towards higher crystallinity in the model when compared to the field data. Only when the initial contents of Fe(III)-minerals in the alternative Dorsfeld and Frimmersdorf gravels were subtracted from the final values after the LTTs, crystallinity of the laboratory precipitates was found in the same low range of crystallinity as in the field samples.

The sequential extraction applied to the synthetic minerals showed that well crystallised goethite was successfully separated from the poorly crystallised phases ferrihydrite and schwertmannite. Unfortunately, no lepidocrocite sample could be included in the above mentioned investigation. Generally, in the literature, lepidocrocite is considered a well crystallised phase (see also section 2.4.6, Schwertmann, 1959b, 1964, McKeague & Day, 1966, Carlson & Schwertmann, 1981), but it also has been reported, that especially very fine-grained lepidocrocites can be easily dissolved by the kinetic method of cold oxalate extraction (Schwertmann, 1973, Chao, 1984, La Force & Fendorf, 2000). Thus, clear assignment of

---

**Table 13** Results of SEP-analyses in laboratory samples and field samples, compared to values from synthetic hydroxic Fe-clogging-minerals; corr: values corrected with respect to initial contents of Fe(III)-minerals, W: Weilerswist gravel, F: Frimmersdorf gravel, D: Dorsfeld gravel, GB: glass beads, IE: interim experiment (values of LTT 14 are not comparable: influenced by interim experiment of “in-situ” dissolution of Fe-clogging products), SSP: shortened screen pipe

<table>
<thead>
<tr>
<th>Sample/LTT</th>
<th>t [h]</th>
<th>Fe$_{tot}$ [g kg$^{-1}$]</th>
<th>Fe$_{tot}$/t [g kg$^{-1}$ h$^{-1}$]</th>
<th>well cryst. perc. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>avg</td>
<td>max</td>
<td>avg</td>
</tr>
<tr>
<td>LTT 5.W</td>
<td>37.0</td>
<td>4.2</td>
<td>8.9</td>
<td>0.11</td>
</tr>
<tr>
<td>LTT 7.W</td>
<td>37.5</td>
<td>2.3</td>
<td>7.2</td>
<td>0.06</td>
</tr>
<tr>
<td>LTT 8.W</td>
<td>36.7</td>
<td>2.9</td>
<td>8.9</td>
<td>0.08</td>
</tr>
<tr>
<td>LTT 9.F</td>
<td>41.7</td>
<td>4.6</td>
<td>9.6</td>
<td>0.11</td>
</tr>
<tr>
<td>corr.LTT 9.F</td>
<td>41.7</td>
<td>2.7</td>
<td>7.6</td>
<td>0.07</td>
</tr>
<tr>
<td>LTT 12.F</td>
<td>44.0</td>
<td>4.7</td>
<td>10.5</td>
<td>0.11</td>
</tr>
<tr>
<td>corr.LTT 12.F</td>
<td>44.0</td>
<td>2.8</td>
<td>8.4</td>
<td>0.06</td>
</tr>
<tr>
<td>LTT 11.D</td>
<td>46.2</td>
<td>5.5</td>
<td>10.6</td>
<td>0.12</td>
</tr>
<tr>
<td>corr.LTT 11.D</td>
<td>46.2</td>
<td>4.5</td>
<td>9.5</td>
<td>0.10</td>
</tr>
<tr>
<td>LTT 13.D</td>
<td>51.5</td>
<td>4.9</td>
<td>11.2</td>
<td>0.10</td>
</tr>
<tr>
<td>corr.LTT 13.D</td>
<td>51.5</td>
<td>3.8</td>
<td>10.1</td>
<td>0.07</td>
</tr>
<tr>
<td>LTT 14.GB,IE</td>
<td>44.6</td>
<td>0.8</td>
<td>4.2</td>
<td>-</td>
</tr>
<tr>
<td>LTT 15.GB,SSP</td>
<td>39.7</td>
<td>1.1</td>
<td>3.5</td>
<td>0.03</td>
</tr>
<tr>
<td>Field samples</td>
<td>-</td>
<td>8.8</td>
<td>14.5</td>
<td>-</td>
</tr>
</tbody>
</table>

For 2A (Fe-mud) - 445.5 - - | 4.5 |

Ferrihydrite - 550.0 - - | 9.0 |
Goethite - 102.3 - - | 94.1 |
Schwertmannite - 457.6 - - | 0.0 |

---
lepidocrocite to the poorly or well crystallised phase appears difficult. All samples taken from the field or the experimental model were therefore analysed by SEP as well as XRD analyses, to classify the type (i.e. grain sizes) of the lepidocrocites precipitated in both groups of samples. Those data were then confirmed by BET surface areas, additionally giving hints towards the grain sizes of the precipitates.

When normalising the total Fe-contents, produced in the model to the experimental duration, the intensity of Fe-clogging in the different LTT-settings can be estimated. However, LTT 14 has to be excluded from that consideration, as the values attained here were disturbed by the interim experiment of “in-situ” dissolution of Fe-clogging products and could not be corrected. When considering the values observed with the alternative materials, before correcting for initial Fe(III)-mineral contents, the Fe-clogging affinity of the Frimmersdorf (Fe_{tot}/t = 0.11 g kg^{-1} h^{-1} (avg) and 0.24 g kg^{-1} h^{-1} (max)) and Dorsfeld (Fe_{tot}/t = 0.11 g kg^{-1} h^{-1} (avg) and 0.23 g kg^{-1} h^{-1} (max)) materials appear similar to the Weilerswist gravel (Fe_{tot}/t = 0.09 g kg^{-1} h^{-1} (avg) and 0.23 g kg^{-1} h^{-1} (max)). However, after correction, both alternative gravels showed lower values than the Weilerswist gravel, with the Frimmersdorf gravel (Fe_{tot}/t = 0.07 g kg^{-1} h^{-1} (avg) and 0.19 g kg^{-1} h^{-1} (max)) performing somewhat better than the Dorsfeld gravel (Fe_{tot}/t = 0.09 g kg^{-1} h^{-1} (avg) and 0.20 g kg^{-1} h^{-1} (max)). An evaluation of the glass beads is not possible in this context, as sampling of LTT 14 was disturbed by the interim experiment and LTT 15 was conducted with the shortened screen pipe. The lowest Fe-clogging intensity was found in LTT 15 (Fe_{tot}/t = 0.03 g kg^{-1} h^{-1} (avg) and 0.09 g kg^{-1} h^{-1} (max)), which emphasises the success of restricting oxygen-supply to the filter pack.

In contrast to the observations in the field, the hydrochemistry applied in the model seems to promote precipitation of higher crystallised minerals (goethite, lepidocrocite) rather than those of lower crystallinity (ferrihydrite). This certainly results from the increased contents of Cl (Cornell & Schwertmann, 2003) and dissolved Fe(II) (Pedersen et al., 2005) and moderate contents of Si in the model (cf. Figure 33). The ratio of [Si]/[Fe] = 0.01 in the model is ten times lower than ratios that would promote ferrihydrite formation over goethite and lepidocrocite ([Si]/[Fe] > 0.1; Cornell & Schwertmann, 2003). This should also presumably result in a higher compactness of the minerals in the model, so less volume of Fe-minerals is precipitated from the same amount of Fe(II) ions than in the field. The measurements of the BET surface areas (Table 14) allow comparison of the specific surface areas and may therefore give an indication towards the grain sizes, compactness and porosity of the precipitated ochre.

The change in the BET surface area in the laboratory samples generally correlated with Fe-clogging time as expressed by values of ΔBET/Δt between 0.019 and 0.027 m² g⁻¹ h⁻¹. The only exception was found in LTT 4 that was conducted over 176 h, but not under the defined standardised conditions. Within LTT 4, h_{oc} was varied in a broader range, so the comparability of the experimental duration is questionable.

The total Fe-contents in the field samples (Table 15) correlate with the optical impressions of their degree of Fe-clogging. Three of the six samples that exhibited lower crystallinity also showed high BET surface areas, as expressed by increased ratios of ΔBET/ΔFe_{tot}. This was also true for the samples taken from the glass-bead experiments which may be due to a higher availability of Si to the solution from the glass beads. This verifies the correlation of lower
crystallised percentages to more voluminous Fe-precipitates. Since no samples of the initial gravel pack of the field samples were available, the mineral contents in the final field samples were evaluated with XRD measurements (Table 15).

**Table 14**

<table>
<thead>
<tr>
<th>Sample/LTT</th>
<th>Duration [h]</th>
<th>Fe&lt;sub&gt;tot&lt;/sub&gt; [%]</th>
<th>Fe&lt;sub&gt;est&lt;/sub&gt; [%]</th>
<th>Well cryst. perc. [%]</th>
<th>BET [m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>BET [m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>BET [m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>BET/At [m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt; h&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>BET/Fe&lt;sub&gt;tot&lt;/sub&gt; [m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTT 4.W</td>
<td>176</td>
<td>8.28</td>
<td>7.90</td>
<td>62.5</td>
<td>0.3</td>
<td>1.1</td>
<td>0.8</td>
<td>0.097</td>
<td>0.005</td>
</tr>
<tr>
<td>LTT 8.W</td>
<td>36.7</td>
<td>8.91</td>
<td>8.53</td>
<td>14.1</td>
<td>0.3</td>
<td>1.3</td>
<td>1.0</td>
<td>0.112</td>
<td>0.027</td>
</tr>
<tr>
<td>LTT 9.F</td>
<td>41.7</td>
<td>7.40</td>
<td>5.37</td>
<td>51.5</td>
<td>0.8</td>
<td>1.7</td>
<td>0.9</td>
<td>0.168</td>
<td>0.022</td>
</tr>
<tr>
<td>LTT 12.F</td>
<td>44.0</td>
<td>6.81</td>
<td>4.78</td>
<td>41.2</td>
<td>0.8</td>
<td>1.7</td>
<td>0.9</td>
<td>0.188</td>
<td>0.020</td>
</tr>
<tr>
<td>LTT 11.D</td>
<td>46.2</td>
<td>6.16</td>
<td>5.06</td>
<td>38.8</td>
<td>0.9</td>
<td>1.8</td>
<td>0.9</td>
<td>0.178</td>
<td>0.019</td>
</tr>
<tr>
<td>LTT 13.D</td>
<td>51.5</td>
<td>7.28</td>
<td>6.18</td>
<td>31.2</td>
<td>0.9</td>
<td>2.1</td>
<td>1.2</td>
<td>0.194</td>
<td>0.023</td>
</tr>
<tr>
<td>LTT 14.GB</td>
<td>47.6</td>
<td>3.30</td>
<td>3.30</td>
<td>4.0</td>
<td>0.01*</td>
<td>0.9</td>
<td>0.89</td>
<td>0.270</td>
<td>0.019</td>
</tr>
<tr>
<td>LTT 15.GB.SSP</td>
<td>39.7</td>
<td>3.56</td>
<td>3.56</td>
<td>7.4</td>
<td>0.01*</td>
<td>0.9</td>
<td>0.89</td>
<td>0.250</td>
<td>0.022</td>
</tr>
<tr>
<td>Well 1A</td>
<td>-</td>
<td>11.74</td>
<td>11.74</td>
<td>16.0</td>
<td>0.3**</td>
<td>7.6</td>
<td>7.3</td>
<td>0.622</td>
<td>-</td>
</tr>
<tr>
<td>Well 1B</td>
<td>-</td>
<td>10.18</td>
<td>10.18</td>
<td>12.9</td>
<td>0.3**</td>
<td>1.4</td>
<td>1.1</td>
<td>0.108</td>
<td>-</td>
</tr>
<tr>
<td>Well 1C</td>
<td>-</td>
<td>14.53</td>
<td>14.53</td>
<td>7.0</td>
<td>0.3**</td>
<td>11.8</td>
<td>11.5</td>
<td>0.791</td>
<td>-</td>
</tr>
<tr>
<td>Well 2B</td>
<td>-</td>
<td>13.51</td>
<td>13.51</td>
<td>7.9</td>
<td>0.3**</td>
<td>3.6</td>
<td>3.3</td>
<td>0.244</td>
<td>-</td>
</tr>
<tr>
<td>Well 2C</td>
<td>-</td>
<td>4.40</td>
<td>4.40</td>
<td>18.4</td>
<td>0.3**</td>
<td>1.1</td>
<td>0.8</td>
<td>0.182</td>
<td>-</td>
</tr>
<tr>
<td>Well 2A (Fe-mud)</td>
<td>-</td>
<td>445.5</td>
<td>445.5</td>
<td>4.5</td>
<td>0.0</td>
<td>199.1</td>
<td>199.1</td>
<td>0.447</td>
<td>-</td>
</tr>
</tbody>
</table>

Except for the Fe-mud sample of well 2A, in all non-enriched samples, contents of quartz ranged between 86 and 90 % and contents of feldspars between 9.5 and 13.5 %. This leaves only low residual percentages for Fe(III)-hydroxides, that are exclusively identified as goethite. In general with XRD-measurements one cannot be certain that a mineral is actually present, if its rate is below 2 %. So the presence of goethite in the samples is uncertain, as its content was lower than 0.8 % in all cases. This is in agreement with the total Fe-contents that were determined by the sequential extraction that ranged from 0.1 % in sample 1.B1 to 1.4 % in sample 1.C.

The Fe-mud sample was found to consist of lepidocrocite to 88 %. This also approximately corresponds to the amount of FeOOH calculated from the Fe<sub>tot</sub>-content that had been determined via the sequential extraction procedure. As Fe<sub>tot</sub> equalled 44.55 % (or g (100 g)<sup>-1</sup>), FeOOH resulted in 70.9 % (or g (100 g)<sup>-1</sup>):

\[
m(FeOOH) = \frac{m(Fe)}{M(Fe)} \cdot M(FeOOH) = \frac{44.55}{55.845} \cdot 88.852 = 70.9 \ \frac{g}{100 \ g}.
\]

As the well crystallised percentage in the Fe-mud sample was almost negligible (4.5 %), this speaks for a very finely grained lepidocrocite found in the field sample that is easily dissolved in cold oxalate extraction. This assumption is confirmed by the very high specific BET-surface area in the Fe-mud-sample. Still, there is a considerable deviation between the two values that most certainly results from uncertainties in processing of XRD-data. As commonly known,
exact quantification of relatively poorly ordered Fe(III)-minerals cannot easily be accomplished with customary XRD-measurements. Especially contents of ferrihydrite that was formerly referred to as “amorphous Fe-hydroxide” in a diffractogram may result in high background values. Quantification can thus be interfered with by other, not Fe(III)-related minerals also plotting in the background of a diffractogram like certain phyllosilicates.

Furthermore, as described above, it cannot be estimated, what percentage of lepidocrocite that was identified with XRD-measurements might actually be easily dissolvable in cold oxalate extractions due to small grain sizes. In consistency with the Fe-mud sample (2A), all lepidocrocites in field samples (Table 15) were considered as poorly crystallised. However, this attribution of lepidocrocite to the poorly crystallised phase may vary with each individual sample.

This also indicates that the values of the XRD-measurements are to be understood as rough estimates rather than exact amounts of minerals. This is especially true for the poorly crystallised minerals whose quantification often leads to unrealistically high contents of 70 or 90 % in the enriched field samples if no phyllosilicates are detected and vice versa.
Only in one sample (1.B.i) the relative proportions of the different Fe(III)-minerals correlate with the crystalline percentage as determined by sequential extraction. In the samples from well 1A, the well crystallised percentage of Fe(III)-phases is overestimated by the XRD-analyses, as phyllosilicates were considered here and the poorly crystallised Fe(III)-phases were therefore underestimated. The opposite case is shown in samples 1B.i and 1B.c, where no phyllosilicates were identified, lepidocrocite and ferrihydrite were therefore overestimated and the well crystallised percentage underestimated.

There also are other possible explanations for the deviations. Firstly, the amounts of poorly crystallised schwertmannite that were qualitatively identified by characteristic XRD-peaks, could not be quantified due to missing structural information. Secondly, a fractionating effect could occur during disaggregation within the enrichment method that would favour enrichment of specific Fe(III)-phases over other Fe(III)-phases. But as even the exact mineralogical structures of several Fe(III)-minerals still remain open subjects to scientific discussion (e.g. for ferrihydrite: Gilbert et al., 2013; cf. Section 2.4.6), quantification with the Rietveld method appears to be the main reason.

Remarkably, considerable amounts of gypsum were identified in five of the nine enriched field samples. Generally, in the environment of mine water from pyritic layers, increased amounts of sulphate and calcium in the water could lead to precipitation of gypsum, especially when the aquifer falls dry and residual water is vaporised. These amounts of precipitated gypsum possibly are carried into the heavy mineral fraction by coatings of Fe(III)-minerals enclosing the gypsum grains. One of the highest amounts of gypsum was found in the sample from well 1C which exhibited the strongest solidification of the gravel pack, even allowing taking an undisturbed “hard rock” sample. Thus, solidification of the sample may even have been due to gypsum precipitation (Schnieders, 2003, Sterrett, 2007).

The mineralogies of the initial gravel pack materials applied in the Fe-clogging model show the percentage of quartz to amount 74 % for the Dorsfeld gravel, 88 % for the Frimmersdorf gravel and 87 % in the Weilerswist gravel (Table 16).

Table 16  Results of XRD-analyses in initial gravel materials applied in the Fe-clogging model; W: Weilerswist gravel, D: Dorsfeld gravel, F: Frimmersdorf gravel, F: fine-grained fraction after wet sieving (d < 1 mm, printed in bold type), nq: not quantified

<table>
<thead>
<tr>
<th>Gravel</th>
<th>Quartz [%]</th>
<th>Feldspars [%]</th>
<th>Phyllosilicates [%]</th>
<th>Gypsum [%]</th>
<th>Goethite [%]</th>
<th>Lepidocrocite [%]</th>
<th>Ferrihydrite [%]</th>
<th>Ferrioxhyte [%]</th>
<th>Schwertmannite [%]</th>
<th>ΣFe-Hydroxides [%]</th>
<th>BET [m² g⁻¹]</th>
<th>SEP Fetot [kg g⁻¹]</th>
<th>SEP cryst. perc. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>86.7</td>
<td>13.2</td>
<td>-</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0.3</td>
<td>&lt; 0.01</td>
<td>-</td>
</tr>
<tr>
<td>W,F</td>
<td>91.5</td>
<td>7.8</td>
<td>-</td>
<td>0.4</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>74.6</td>
<td>24.9</td>
<td>-</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.9</td>
<td>1.10</td>
<td>86.8</td>
</tr>
<tr>
<td>D,F</td>
<td>74.2</td>
<td>16.6</td>
<td>7.8</td>
<td>10.0</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>88.2</td>
<td>11.5</td>
<td>-</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.8</td>
<td>2.03</td>
<td>88.3</td>
</tr>
<tr>
<td>F,F</td>
<td>83.2</td>
<td>16.3</td>
<td>-</td>
<td>0.5</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>nq</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
When separating the fine fraction (d < 1 mm) from the initial gravel materials by wet sieving, the Fe-mineral phases become enriched relative to quartz and silicates. In the Dorsfeld gravel, phyllosilicates are enriched relatively to quartz and feldspars as well, whereas in the Frimmersdorf gravel, feldspars are enriched. This accounts for those mineral grains that are likely to crumble to smaller grains after the sieving process during production. Separation of a heavy mineral fraction with the bromoform method was not possible with the initial gravel materials. Enrichment only yielded smaller amounts of minerals than necessary for representative XRD-measurements.

As with the samples from the field, the samples from the Fe-clogging model before enrichment also showed quartz-contents between 74 and 90 % (Table 17). The variation in the quartz-content was not explicitly attributed to a specific gravel material and indicates towards high heterogeneities of the alternative gravel materials during sampling. The second major component was represented by feldspars. Fe-hydroxide contents again ranged from 0.4 to 1.1 % and were only identified as goethite.

Table 17 Results of XRD-analyses of samples from the Fe-clogging model; W: Weilerswist gravel, D: Dorsfeld gravel, F: Frimmersdorf gravel, GB: glass beads, H: heavy mineral fraction after bromoform enrichment (printed in bold type). The samples from LTT 14 are disturbed by the interim experiment of “in-situ” dissolution of Fe-clogging products, XRD cryst. perc. Gt: goethite content/ΣFe-Hydroxides*100 %, XRD cryst. perc. Gt+Lp: (goethite content + lepidocrocite content)/ΣFe-Hydroxides*100 %

<table>
<thead>
<tr>
<th>LTT filter</th>
<th>Quartz [§]</th>
<th>Feldspars [%]</th>
<th>Phyllosilicates [%]</th>
<th>Goethite [%]</th>
<th>Lepidocrocite [%]</th>
<th>Ferrhydrite [%]</th>
<th>Ferroxyhite [%]</th>
<th>Σ Fe-Hydroxides [%]</th>
<th>XRD cryst. perc. Gt [%]</th>
<th>XRD cryst. perc. Gt+Lp [%]</th>
<th>BET [m² g⁻¹]</th>
<th>SEP Fe₅₀₀ [%]</th>
<th>SEP cryst. perc. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.W</td>
<td>88.8</td>
<td>10.7</td>
<td>-</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>0.5</td>
<td>8.3</td>
<td>43.5</td>
<td>-</td>
<td>-</td>
<td>5.8</td>
</tr>
<tr>
<td>2.W.H</td>
<td>9.4</td>
<td>13.5</td>
<td>3.5</td>
<td>6.5</td>
<td>27.3</td>
<td>37.1</td>
<td>7.3</td>
<td>78.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>62.0</td>
<td></td>
</tr>
<tr>
<td>4.W</td>
<td>85.7</td>
<td>13.8</td>
<td>-</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>0.5</td>
<td>23.6</td>
<td>54.2</td>
<td>1.1</td>
<td>8.3</td>
<td>62.5</td>
</tr>
<tr>
<td>4.W.H</td>
<td>16.0</td>
<td>13.0</td>
<td>-</td>
<td>17.0</td>
<td>22.0</td>
<td>19.0</td>
<td>14.0</td>
<td>72.0</td>
<td>17.2</td>
<td>51.0</td>
<td>-</td>
<td>61.6</td>
<td></td>
</tr>
<tr>
<td>9.F</td>
<td>87.3</td>
<td>12.1</td>
<td>-</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>0.7</td>
<td>17.2</td>
<td>51.0</td>
<td>1.7</td>
<td>7.4</td>
<td>-</td>
</tr>
<tr>
<td>9.F.H</td>
<td>17.1</td>
<td>10.1</td>
<td>-</td>
<td>12.5</td>
<td>24.6</td>
<td>5.9</td>
<td>29.8</td>
<td>72.8</td>
<td>19.2</td>
<td>43.8</td>
<td>1.7</td>
<td>6.8</td>
<td>55.2</td>
</tr>
<tr>
<td>12.F</td>
<td>74.2</td>
<td>23.1</td>
<td>1.6</td>
<td>0.7</td>
<td>0.4</td>
<td>0.0</td>
<td>-</td>
<td>1.1</td>
<td>9.4</td>
<td>32.9</td>
<td>1.8</td>
<td>6.2</td>
<td>47.3</td>
</tr>
<tr>
<td>12.F.H</td>
<td>19.0</td>
<td>7.0</td>
<td>-</td>
<td>14.0</td>
<td>18.0</td>
<td>20.0</td>
<td>21.0</td>
<td>73.0</td>
<td>6.2</td>
<td>72.4</td>
<td>-</td>
<td>2.1</td>
<td>39.6</td>
</tr>
<tr>
<td>11.D</td>
<td>80.9</td>
<td>10.5</td>
<td>-</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>9.4</td>
<td>32.9</td>
<td>1.8</td>
<td>6.2</td>
<td>-</td>
</tr>
<tr>
<td>11.D.H</td>
<td>10.0</td>
<td>5.0</td>
<td>-</td>
<td>8.0</td>
<td>20.0</td>
<td>50.0</td>
<td>7.0</td>
<td>85.0</td>
<td>6.2</td>
<td>72.4</td>
<td>-</td>
<td>2.1</td>
<td>39.6</td>
</tr>
<tr>
<td>13.D</td>
<td>76.9</td>
<td>22.5</td>
<td>-</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>9.4</td>
<td>32.9</td>
<td>1.8</td>
<td>6.2</td>
<td>-</td>
</tr>
<tr>
<td>13.D.H</td>
<td>1.4</td>
<td>8.4</td>
<td>-</td>
<td>5.6</td>
<td>60.0</td>
<td>12.0</td>
<td>13.0</td>
<td>90.6</td>
<td>6.2</td>
<td>72.4</td>
<td>-</td>
<td>2.1</td>
<td>39.6</td>
</tr>
<tr>
<td>14.GB</td>
<td>89.3</td>
<td>10.2</td>
<td>-</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>0.4</td>
<td>3.8</td>
<td>3.8</td>
<td>0.9</td>
<td>3.8</td>
<td>16.0</td>
</tr>
<tr>
<td>14.GB.H</td>
<td>25.0</td>
<td>15.4</td>
<td>16.9</td>
<td>1.6</td>
<td>40.0</td>
<td>0.0</td>
<td>0.0</td>
<td>42.6</td>
<td>3.8</td>
<td>3.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

With bromoform enrichment, the relative quartz-contents (resp. silica within the glass bead sample) were decreased to values between 1.4 and 25 %. As observed before, feldspars and phyllosilicates were in some cases enriched relatively to quartz along with the Fe(III)-phases.
In the glass bead sample these are considered to originate from sample contamination with mineral grains from the aquifer material, as no such phases ought to be contained in the glass beads from the beginning.

The amounts of Fe(III)-minerals in the enriched laboratory samples showed predominance in lepidocrocite and ferrihydrite with considerable amounts of feroxyhyte and minor percentages of goethite. Feroxyhyte is presumed to occur due to the high pH and very quick oxidation rates applied in the model. The relative amounts of well crystallised minerals from the XRD-measurements were only found to correlate with the SEP well crystallised percentage when lepidocrocite was considered to be a well crystallised mineral. Obviously, the lepidocrocite that was produced in the model did not dissolve as easily within the first extraction step by 4 h of treatment with cold oxalate solution in the dark as the lepidocrocite found in the field. This fact again suggests that the Fe-precipitates produced in the Fe-clogging model are of higher compactness than those found in the field. The more compact (coarser-grained, low specific surface area) lepidocrocite produced in the Fe-clogging model cannot as easily be dissolved by the kinetic method of Fe-extraction with oxalate, whereas the less compact (finer-grained, high specific surface area) lepidocrocites found in the field can easily be dissolved by cold oxalate (Schwertmann, 1973, Chao, 1984, La Force & Fendorf, 2000).

Samples of Fe-mud that were taken in the outflow chamber of the Fe-clogging model allowed for an immediate determination of the mineralogy of Fe-precipitates in the model without the necessity to conduct enrichment measures beforehand (Table 18).

Table 18  Results of XRD-analyses of samples from the outflow chamber of long term tests in the Fe-clogging model; XRD cryst. perc. Gt: goethite content/2Fe-Hydroxides*100 %, XRD cryst. perc. Gt+Lp: (goethite content + lepidocrocite content)/2Fe-Hydroxides*100 %, nq: not quantified

<table>
<thead>
<tr>
<th>LTT</th>
<th>Quartz [%]</th>
<th>Feldspars [%]</th>
<th>Phyllosilicates [%]</th>
<th>Halite [%]</th>
<th>Goethite [%]</th>
<th>Lepidocrocite [%]</th>
<th>Ferrihydrite [%]</th>
<th>Σ Fe-Hydroxides [%]</th>
<th>XRD cryst. perc. Gt [%]</th>
<th>XRD cryst. perc. Gt+Lp [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>9.0</td>
<td>26.8</td>
<td>-</td>
<td>0.01</td>
<td>0.2</td>
<td>62.9</td>
<td>-</td>
<td>63.1</td>
<td>0.3</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>15.6</td>
<td>0.0</td>
<td>-</td>
<td>8.4</td>
<td>44.9</td>
<td>32.0</td>
<td>85.3</td>
<td>9.8</td>
<td>62.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>10.5</td>
<td>19.6</td>
<td>5.1</td>
<td>-</td>
<td>36.3</td>
<td>28.6</td>
<td>64.9</td>
<td>0.0</td>
<td>55.9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>65.7</td>
<td>2.7</td>
<td>0.0</td>
<td>-</td>
<td>29.5</td>
<td>2.2</td>
<td>31.7</td>
<td>0.0</td>
<td>93.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>30.1</td>
<td>7.2</td>
<td>nq</td>
<td>23.1</td>
<td>61.8</td>
<td>0.9</td>
<td>85.8</td>
<td>26.9</td>
<td>99.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>26.0</td>
<td>5.0</td>
<td>-</td>
<td>8.7</td>
<td>37.0</td>
<td>23.3</td>
<td>69.0</td>
<td>12.6</td>
<td>66.2</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>31.1</td>
<td>7.1</td>
<td>-</td>
<td>17.6</td>
<td>40.6</td>
<td>6.0</td>
<td>64.2</td>
<td>27.4</td>
<td>90.7</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>33.0</td>
<td>3.8</td>
<td>-</td>
<td>15.3</td>
<td>33.6</td>
<td>14.4</td>
<td>63.3</td>
<td>24.2</td>
<td>77.3</td>
<td></td>
</tr>
</tbody>
</table>

The measurements still showed considerable amounts of quartz and feldspars, presumably resulting from grains of aquifer or gravel pack material, transported through the screen pipe by suffosion and sedimented in the outflow chamber or contamination of the Fe-mud in the outflow chamber with grains of gravel pack or aquifer material during disassembling and
sampling the flow channel. Halite was found in one sample from LTT 3 that originated as an evaporitic residue from the highly mineralised process water after 295 h of Fe-clogging time with continuous addition of FeCl₂- and NaOH-stock solutions.

The Fe-phases in the precipitates were dominated by lepidocrocite in each case, followed by ferrihydrite in LTTs 7, 8 and 11 or by goethite in LTTs 10 and 12. The change in the secondary dominating mineral did, however, not correlate with any other factors observed in the corresponding LTTs. Due to low sample quantities, no SEP- or BET-measurements could be conducted in this group of samples, so no statement can be made as to whether or not the lepidocrocite in these samples is to be assigned to the poorly or well crystallised percentage of the total Fe-precipitates (i.e. high or low specific surface area, dissolvable or not in cold oxalate extraction).

The measurements of total carbon content (Table 19) showed nearly indifferent values of inorganic carbon in all samples from the field and from the laboratory model (variability between 0.162 % and 0.172 %, except from the Fe-mud-sample 2A with TIC = 0.222 wt.-%).

![Table 19](image)

<table>
<thead>
<tr>
<th>Set of samples</th>
<th>Gravel/Well/</th>
<th>Fe₉₅</th>
<th>SEP cryst.</th>
<th>TOC</th>
<th>TIC</th>
<th>TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial filter materials</td>
<td>Sample/LTT</td>
<td>[g kg⁻¹]</td>
<td>perc. [%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>W</td>
<td>&lt; 0.01</td>
<td>100</td>
<td>&lt; 0.0004</td>
<td>0.171</td>
<td>0.171</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1.10</td>
<td>86.8</td>
<td>&lt; 0.0004</td>
<td>0.171</td>
<td>0.171</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2.03</td>
<td>88.3</td>
<td>&lt; 0.0004</td>
<td>0.172</td>
<td>0.172</td>
<td></td>
</tr>
<tr>
<td>1A.a</td>
<td>11.74</td>
<td>16.0</td>
<td>0.219</td>
<td>0.166</td>
<td>0.383</td>
<td></td>
</tr>
<tr>
<td>1A.b</td>
<td>3.71</td>
<td>11.7</td>
<td>0.178</td>
<td>0.169</td>
<td>0.347</td>
<td></td>
</tr>
<tr>
<td>1B.i</td>
<td>8.83</td>
<td>8.3</td>
<td>0.257</td>
<td>0.163</td>
<td>0.420</td>
<td></td>
</tr>
<tr>
<td>1B.c</td>
<td>10.18</td>
<td>12.9</td>
<td>0.279</td>
<td>0.163</td>
<td>0.442</td>
<td></td>
</tr>
<tr>
<td>1B.o</td>
<td>11.42</td>
<td>11.6</td>
<td>0.215</td>
<td>0.165</td>
<td>0.380</td>
<td></td>
</tr>
<tr>
<td>Field samples</td>
<td>1B.l</td>
<td>0.98</td>
<td>42.5</td>
<td>0.169</td>
<td>0.171</td>
<td>0.340</td>
</tr>
<tr>
<td>1C</td>
<td>14.53</td>
<td>7.0</td>
<td>0.216</td>
<td>0.165</td>
<td>0.381</td>
<td></td>
</tr>
<tr>
<td>2B</td>
<td>13.51</td>
<td>7.9</td>
<td>0.239</td>
<td>0.166</td>
<td>0.406</td>
<td></td>
</tr>
<tr>
<td>2C</td>
<td>4.40</td>
<td>18.4</td>
<td>0.238</td>
<td>0.164</td>
<td>0.402</td>
<td></td>
</tr>
<tr>
<td>2A (Fe-mud)</td>
<td>445.5</td>
<td>4.5</td>
<td>4.088</td>
<td>0.222</td>
<td>4.310</td>
<td></td>
</tr>
<tr>
<td>Laboratory Samples</td>
<td>2.W</td>
<td>5.38</td>
<td>60.2</td>
<td>0.188</td>
<td>0.162</td>
<td>0.350</td>
</tr>
<tr>
<td>4.W</td>
<td>8.28</td>
<td>62.5</td>
<td>0.163</td>
<td>0.170</td>
<td>0.333</td>
<td></td>
</tr>
<tr>
<td>4.W</td>
<td>6.27</td>
<td>75.4</td>
<td>0.174</td>
<td>0.167</td>
<td>0.341</td>
<td></td>
</tr>
<tr>
<td>6.W</td>
<td>5.27</td>
<td>73.3</td>
<td>0.175</td>
<td>0.166</td>
<td>0.341</td>
<td></td>
</tr>
<tr>
<td>7.W</td>
<td>7.22</td>
<td>18.7</td>
<td>0.168</td>
<td>0.169</td>
<td>0.337</td>
<td></td>
</tr>
<tr>
<td>8.W</td>
<td>7.93</td>
<td>14.3</td>
<td>0.169</td>
<td>0.167</td>
<td>0.335</td>
<td></td>
</tr>
<tr>
<td>9.F</td>
<td>3.18</td>
<td>51.3</td>
<td>0.171</td>
<td>0.171</td>
<td>0.342</td>
<td></td>
</tr>
<tr>
<td>11.D</td>
<td>9.14</td>
<td>36.0</td>
<td>0.169</td>
<td>0.166</td>
<td>0.335</td>
<td></td>
</tr>
<tr>
<td>11.D</td>
<td>8.18</td>
<td>72.6</td>
<td>0.169</td>
<td>0.167</td>
<td>0.336</td>
<td></td>
</tr>
<tr>
<td>12.F</td>
<td>6.81</td>
<td>55.2</td>
<td>0.182</td>
<td>0.164</td>
<td>0.346</td>
<td></td>
</tr>
<tr>
<td>13.D</td>
<td>7.28</td>
<td>39.6</td>
<td>0.173</td>
<td>0.163</td>
<td>0.335</td>
<td></td>
</tr>
<tr>
<td>14.GB</td>
<td>3.30</td>
<td>4.0</td>
<td>0.190</td>
<td>0.168</td>
<td>0.358</td>
<td></td>
</tr>
<tr>
<td>15.GB</td>
<td>3.56</td>
<td>7.4</td>
<td>0.189</td>
<td>0.167</td>
<td>0.356</td>
<td></td>
</tr>
</tbody>
</table>
The total organic carbon, however, showed different ranges of values in the different sets of samples, but also a comparatively low variability within these sample sets. The initial filter materials that were applied in the Fe-clogging model showed TOC-values below the detection limit of 0.0004%. TOC in the field samples generally ranged between 0.215 and 0.279% with two samples of lower Fe_{tot}-content also showing lower TOC-values of 0.169 and 0.178%. The Fe-mud could be identified as a microbiological clogging product by its extremely high TOC content of 4.088%, which correlated with a very low percentage of well crystallised Fe(III)-minerals as determined by the sequential extraction and an extremely high BET surface area. As enzymatic Fe(II)-oxidation predominantly leads to formation of poorly crystallised ferrihydrite or, as in this case, very fine-grained lepidocrocite as its transformation product (cf. section 2.4.6), these findings indicate towards the assumption of the Fe-mud to be a product of a microbiological Fe-clogging. This impression already emerged during sampling of well 2A which exhibited plume-like Fe-mud, primarily concentrating on the inner surface of the screen pipe, where the highest flow velocities and therefore highest nutrition supply could be expected (cf. section 4.6). In general, increased contents of organic carbon above 0.2% only occurred in samples of lower crystallinity (<20% well crystallised percentage on the total contents of Fe(III)-minerals).

The samples from the experimental model showed only low contents of organic carbon, ranging between 0.168 and 0.190%. This verified the success of the UV-disinfection that was implemented in the model in order to prevent mass development of Fe-bacteria and related microbiological Fe-clogging. The highest TOC values were found in the two glass bead experiments that also exhibited the lowest crystallinity of the Fe-precipitates. This indicated that Fe-clogging in the glass beads developed differently than in the natural gravel materials.

5.3.3 Microscopic methods

Overviews of all thin sections prepared during the whole project in polarised as well as unpolarised light are given from Appendix 27 to Appendix 33. Comparison of the micro-scale distribution of Fe-clogging products in the pore volume between the gravel grains revealed differences between samples from the model and from the field. Whereas the pores in the field sample were almost totally obstructed (Figure 85, top left), only coatings of Fe(III)-minerals were found on the surface of the gravel grains in the laboratory sample (Figure 85, top right).

However, the field sample from well 1C that was taken for comparison here, was extraordinarily solidified compared to other field samples and therefore had obviously been most strongly affected by Fe-clogging. The same is true for the laboratory sample that was taken from LTT 3, the long term test with the longest experimental duration of almost 300 h Fe-clogging time. The field sample still exhibited a higher degree of Fe-clogging than the laboratory sample.

In the field sample, only a small percentage of the initial porosity of the gravel remained between the Fe-precipitates, so its hydraulic conductivity must also have been decreased to a minimal fraction of its initial value. In the close-up view (Figure 85, bottom left), the Fe(III)-precipitates in the field sample exhibited smaller crystallite sizes than in the sample from the
model, flocculating to larger aggregates, completely blocking the pore channels. The micro-scale porosity between the aggregates most certainly did no longer significantly contribute to the flow-effective porosity and hydraulic conductivity of the gravel. In the sample from the model, more compact, larger crystallites (Figure 85, bottom right) were found. Even though the precipitates only concentrated in crotches, voids and contact points between the gravel grains or formed as thin coatings on the grains, an effect on the hydraulic conductivity was already measurable.

These findings confirm the results of the BET, SEP and XRD analyses that all indicated towards formation of more compact Fe(III)-hydroxide minerals of higher crystallinity in the Fe-clogging model. This is certainly a result of the hydrochemistry in the model that differed from the hydrochemical conditions found in the field especially with respect to the dominating anion (cf. section 5.4.1). Another reason for these differences could be the exclusion of biological Fe-clogging processes in the model. As can be assumed from the TOC data, this may play a role in the field samples.

These assumptions are supported by the elemental distributions as determined by SEM/EDX-analyses on the same thin sections. In the sample from the field, the voids in between the gravel grains were primarily filled with iron, oxygen and sulphur (Figure 86). Carbon in the pores, however, originated from the sample preparation technique with graphite and cannot be interpreted from the SEM/EDX-analyses. Gravel grains with decreased contents of Si and
elevated contents of Al and K indicate feldspars (orthoclase). In the surroundings of at least one of these feldspar grains, the contents of Fe and S appeared to be further increased, indicating a higher Fe-clogging-affinity of at least one of these minerals.

![Image 1](image1.png)

**Figure 86** SEM/EDX image and elemental distributions of the field sample from well 1C (cf. section 4.6, final report phase III, 2013, translated).

In the laboratory sample, only Fe and oxygen are found to accumulate in the intergranular spaces, primarily concentrating on the surfaces of the gravel grains (Figure 87) and only partly filling the pore spaces. In the upper left edge of the image a top view onto a gravel grain surface with Fe(III)-hydroxide coating was found. The area of the thin section shown in Figure 87 did not contain any feldspar gravel grains. A close-up view of a weathered orthoclase-grain in the same thin section is shown in Figure 88.

![Image 2](image2.png)

**Figure 87** SEM/EDX image and elemental distributions of the laboratory sample from LTT 3 (final report phase III, 2013, translated).

![Image 3](image3.png)

**Figure 88** Close-up SEM/EDX image and elemental distributions of a weathered orthoclase-grain in the thin section from LTT 3 (final report phase III, 2013, translated).

The spatial distribution of Fe relative to the orthoclase-grain shows the Fe(III)-incrustations to even reach the porosity of the singular weathered mineral grains. Thus, the weathered orthoclase grain appeared to be more affected by Fe(III)-precipitation than the quartz grains.
However, as the inner porosity of weathered gravel grains does not even initially (before Fe-clogging) significantly contribute to the all-over hydraulic conductivity of the gravel, this phenomenon does not appear problematic.

Similar observations were made with transmitted polarised light microscopy. Here, weathered feldspars often exhibited thicker Fe-coatings on their jagged surfaces, when compared to the smooth surfaces of monocrystalline quartz grains (Figure 89) which, however, could have an increased effect on the hydraulic conductivity $K$.

However, the type of mineral was not necessarily decisive for the thickness of the coatings, but their surface structure was. There also were polycrystalline quartzite (Figure 90) or chert grains and irregularly formed monocrystalline quartz grains (Figure 91) found in the LTT 3 sample that exhibited increased amounts of Fe(III)-encrustations. In general, this argues for the application of either glass beads or pure, sedimentary quartz sands with a high mineralogical maturity and delivery areas of igneous rather than metamorphic rocks to avoid polycrystalline quartzite grains.

When comparing the three considered natural gravels, the percentage of feldspar grains appeared similar in all materials, whereas a higher percentage of polycrystalline quartzites
was found in the Quaternary gravels than in the Weilerswist gravel. However, in the Quaternary gravel materials, the surface structure of the polycrystallites was often found much smoother than those observed in the Weilerswist gravel. In all three materials, approximately equal amounts of weathered feldspar grains and polycrystalline quartzites with rough surface structure (both of which exhibit higher susceptibilities towards Fe-clogging) were found. Thus, regarding the surface structure of the gravel grains, no huge differences of the Fe-clogging affinity can be expected from the comparison of the materials. Of course, the thin sections only showed small fractions of the gravel pack materials and are not necessarily representative of the whole gravel deposit at the considered location.

![Monocrystalline quartz-grain with irregular geometry (upper left edge) and polycrystalline quartzite (or chert) grains with thicker Fe(III)-hydroxide coatings in the thin section from LTT 3 under parallelised (left) and crossed polarising filters (right).](image)

**Figure 91**

5.4 Evaluation and verification of the Fe-clogging model

5.4.1 Hydrochemistry in the field and in the model

The hydrochemical data of the process water was measured to compare situations in the model to the actual situations observed in the field. The measurements were also needed as input data for the hydrogeochemical Phreeqc-model. However, the main ion data that is given in Table 20 only represents one momentary value from LTT 7 for each parameter. Thus, the ion balance delivered quite satisfying relative differences between ±2 % and -7 % error. The same is true for the momentary values of the three dewatering wells, whose ion balance errors range from -1 % to -7 %. The error in the ion balance of the data given by Bergmann (1999) for Hz. 68, however, is quite high with -47 % which is due to the single values of ionic concentrations representing average values of a number of samples rather than concentrations in a singular sample. For the parameters of major sensitivity for the Fe-clogging reaction (c(Fe(II)), DO, pH, Eh, T and c(Cl⁻)), long term average data was used to account for the variations observed in the Fe-clogging model. Moreover, a sensitivity analysis of the model result was conducted by varying these values in the input data.

The initial values in the inflow chamber corresponded to the background values of the degassed tap water used to prepare the process water. The initial outflow values were influenced by the contact of the process water with material in the filter columns and the flow channel (aquifer material and gravel pack) in the reference test. At the time the sample was
taken, the dissolved oxygen already had been chemically removed from the water with simultaneous adjustment of pH by adding small amounts of FeCl₂ and NaOH. This caused c(Fe(II)), eC, c(Na⁺) and c(Cl⁻) to rise and Eh to decrease slightly. Due to its low Eh, nitrate was chemically reduced and therefore automatically gradually removed from the process water during the LTT. The values in the final samples were strongly influenced by the described chemical addition of stock solutions during the 38 h of the whole LTT. Whereas the concentrations of sulphate, calcium, magnesium and potassium remained unchanged during the LTT, manganese was increased in contact with the assembly in the flow channel, dissolved silicon in the process water decreased, presumably as a result of precipitation of polymeric silicic acids at pH-values around 8. Finally, as a result of acid production in the outflow chamber the equilibrium of bicarbonate was shifted towards H₂CO₃. Disintegration to H₂O and CO₂ lead to degassing of CO₂ in the outflow chamber.

Table 20  Hydrochemical parameters in the process water during LTT 7, compared to mean values of Hz. 68 (Frimmersdorf Sand) as determined by Bergmann (1999; cf. Table 2) and to own measurements in three multi-layered dewatering wells near the open-pit Hambach (mixed water from layers Hz. 7A, 7C & 8); IC: inflow chamber; OC: outflow chamber

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>LTT 7 initial</th>
<th>LTT 7 final</th>
<th>Hz. 68</th>
<th>Dewatering Well No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>IC</td>
<td>OC</td>
<td>IC</td>
<td>OC</td>
</tr>
<tr>
<td>c(Fe(II))</td>
<td>[mg L⁻¹]</td>
<td>0.104</td>
<td>1.81</td>
<td>74.1</td>
<td>77.7</td>
</tr>
<tr>
<td>c(Fe_total)</td>
<td>[mg L⁻¹]</td>
<td>0.104</td>
<td>1.88</td>
<td>74.3</td>
<td>107</td>
</tr>
<tr>
<td>DO</td>
<td>[mg L⁻¹]</td>
<td>4.84</td>
<td>0.21</td>
<td>0.03</td>
<td>0.60</td>
</tr>
<tr>
<td>Eh</td>
<td>[mV]</td>
<td>282</td>
<td>249</td>
<td>-162</td>
<td>174</td>
</tr>
<tr>
<td>pH</td>
<td>[⁻]</td>
<td>8.0</td>
<td>7.81</td>
<td>7.83</td>
<td>7.15</td>
</tr>
<tr>
<td>eC</td>
<td>[mS cm⁻¹]</td>
<td>258</td>
<td>621</td>
<td>3100</td>
<td>3100</td>
</tr>
<tr>
<td>T</td>
<td>[°C]</td>
<td>16.0</td>
<td>15.4</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>c(Na⁺)</td>
<td>[mg L⁻¹]</td>
<td>14.5</td>
<td>56.6</td>
<td>516</td>
<td>520</td>
</tr>
<tr>
<td>c(Cl⁻)</td>
<td>[mg L⁻¹]</td>
<td>17</td>
<td>71</td>
<td>962</td>
<td>976</td>
</tr>
<tr>
<td>c(NO₃⁻)</td>
<td>[mg L⁻¹]</td>
<td>6.1</td>
<td>4.9</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>c(SO₄²⁻)</td>
<td>[mg L⁻¹]</td>
<td>22</td>
<td>24</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>c(Ca²⁺)</td>
<td>[mg L⁻¹]</td>
<td>26.9</td>
<td>13.4</td>
<td>35</td>
<td>35.6</td>
</tr>
<tr>
<td>c(K⁺)</td>
<td>[mg L⁻¹]</td>
<td>1.6</td>
<td>2.2</td>
<td>3.6</td>
<td>4.8</td>
</tr>
<tr>
<td>c(Mg²⁺)</td>
<td>[mg L⁻¹]</td>
<td>5.9</td>
<td>4.6</td>
<td>7.0</td>
<td>6.8</td>
</tr>
<tr>
<td>c(Mn_total)</td>
<td>[mg L⁻¹]</td>
<td>0.004</td>
<td>0.011</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>c(Si_total)</td>
<td>[mg L⁻¹]</td>
<td>1.65</td>
<td>1.05</td>
<td>0.79</td>
<td>0.7</td>
</tr>
<tr>
<td>c(HCO₃⁻)</td>
<td>[mg L⁻¹]</td>
<td>86.6</td>
<td>81.8</td>
<td>17.7</td>
<td>8.5</td>
</tr>
<tr>
<td>Ion Balance</td>
<td>[%]</td>
<td>1.9</td>
<td>-7.7</td>
<td>-1.1</td>
<td>-0.9</td>
</tr>
</tbody>
</table>

The data for c(K⁺), c(Ca²⁺), c(Mg²⁺), c(Mn_total), c(NO₃⁻) and c(SO₄²⁻) in the process water correspond quite well to the values found in the field. Of course, major differences occurred in the parameters that were intentionally or necessarily altered in order to achieve acceleration of the chemical Fe-clogging process. Parameters that were changed intentionally included a raise in c(Fe(II)) by a factor of 15 to 40 and pH by around 1.5, as well as a decrease in Eh, whereas parameters that were necessarily changed included rising eC, c(Na⁺) and c(Cl⁻).

However, the values measured at dewatering wells in the field may already have been influenced by the ambient air coming into contact with the groundwater inside the well. Even when measured immediately in the field, turbulent flow of the groundwater in the pump and ascending main will already promote oxygen to become dissolved in the groundwater. This
caused the Eh to rise, Fe to oxidise and precipitate and therefore the pH to decrease. Thus, their comparability to the values measured in the outflow chamber of the model is at least questionable.

Major differences were found within the c(HCO₃⁻) and c(Si₉) data. In the model, c(Si₉) was ten times lower than in the field. As stated in section 2.4.6, this may have changed the type of mineral precipitated as a result of the Fe-clogging reaction. The model fell short of the threshold molar ratio of [Si]/[Fe] > 0.1 that favours formation of ferrihydrite over lepidocrocite and goethite by the factor of 10 due to the high contents of Fe. Whereas [Si]/[Fe] in the model equals 0.018 mol mol⁻¹, in the field samples the ratio yields 14.6 mol mol⁻¹. Therefore, in the field, precipitation of ferrihydrite was anticipated, whilst in the model, precipitation of goethite and lepidocrocite was to be expected. This is in good agreement with the results that were attained with the sequential extraction and the mineralogical analyses (cf. section 5.3.2). In the field, c(HCO₃⁻) was around 4 times higher than in the model which results in a lower capacity to buffer acid production in the Fe-clogging model and would thus decrease the amount of precipitates by a quicker decrease of the pH and therefore of the kinetic reaction rate of the Fe-oxidation. The effects of changing silicon and bicarbonate concentrations therefore were included in the sensitivity analysis within the hydrogeochemical model of the flow channel that is described within the following section.

5.4.2 Hydrochemical model of the flow channel

The result of the PhreeqC-model that was based on the hydrochemistry of the process water listed in Table 20, showed the pH to decrease in the gravel pack from 8 to only 7 (Figure 92). c(Fe(II)) also changes from 80 mg L⁻¹ to ≈ 70 mg L⁻¹. To compare the amounts of precipitated minerals, the cumulative mass of FeOOH precipitated over the modelling duration was calculated for all modelled scenarios (purple lines).

![Figure 92](image)

**Figure 92** Result of the PhreeqC model calculated after Stumm and Lee (1961) with the reaction constant by Davison and Seed (1983)

The thermodynamic preference of the different hydroxidic Fe(III)-minerals to precipitate followed the order goethite > (hematite) > lepidocrocite > ferrihydrite2L > Fe(OH)₃ > ferrihydrite6L > schwertmannite > akaganéite. This was determined by successively excluding the precipitating mineral from the model, causing the next likely mineral to precipitate in the following step. However, hematite is only thermodynamically stable, but not to be expected from a kinetic point of view.
To simulate application of an FeSO₄-stock solution rather than the FeCl₂ solution, the contents of chloride and sulphate were changed in the model from c(Cl⁻) = 970 mg L⁻¹ and c(SO₄²⁻) = 20 mg L⁻¹ to c(Cl⁻) = 25 mg L⁻¹ and c(SO₄²⁻) = 1300 mg L⁻¹. However, the series of mineral priority did not change, except for ferrihydrite₆L and schwertmannite exchanging their positions in priority. The changes in reaction rate with changing concentration of chloride and sulphate were subtle, with a slight decrease in reaction rate with sulphate as the dominating anion (Appendix 34). As already stated by Tamura et al. (1976a), Sung and Morgan (1980) and Millero (1985), a strong chemical effect of the chloride concentrations applied in the model on the oxidation rates of Fe can thus be ruled out. A similar behaviour of the PhreeqC-model was observed when changing the concentrations of dissolved Si. Even assuming the [Si]/[Fe] ratio as found in the field did not at all change the amount of Fe-precipitations or the priorities of precipitating Fe-minerals. This may be owing to the simplifications of the model approach with kinetic oxidation and thermodynamic precipitation which are necessary due to the limited availability of kinetic input data.

Stronger sensitivities were observed when considering changes in c(Fe(II)) and DO (Appendix 36), but especially pH (Appendix 37), c(HCO₃⁻) (Appendix 35) and the temperature (Appendix 38). The results show that the reaction rate decreased with decreasing DO, and decreasing c(Fe(II)), as can be seen by the purple lines in the diagrams (cumulative precipitated mass of Fe(OH)₃). By quartering the DO from 2 to 0.5 mg L⁻¹, the total mass of precipitated minerals was about halved. Using only one eighth of the c(Fe(II)) (i.e. 10 rather than 80 mg L⁻¹) only produced around one third of the actually precipitated minerals. Lowering the initial pH from 7.83 to 7 lead to almost quartering the amount of precipitation, whereas a change in temperature from 15 to 25 °C produced 60 % more precipitates. Raising c(HCO₃⁻) from 150 to 300 mg L⁻¹ will increase precipitation by ca. 50 %, whereas decreasing c(HCO₃⁻) to 20 mg L⁻¹ will reduce precipitation by 73 %.

The results given in the diagrams only refer to exchanging the total saturated pore volume exactly once. Thus, to balance the total amount of Fe(III)-minerals precipitated during a complete LTT, the precipitation in each model cell was calculated from the difference of c(Fe(II)) after each 1.77 s from the previous value and converting the unit from mg L⁻¹ (1.77 s)⁻¹ to g (31 mL⁻¹) (50 h)⁻¹. The time of 1.77 s refers to the residence time of the water in one model cell, 31 mL to the total flow effective water volume in the model cell and 50 h to an exemplary cumulative Fe-clogging time of a complete LTT. Cumulated over the 11 model cells, this yields the total amount of Fe precipitated in the gravel pack during the whole LTT. The balances for all different modelled scenarios are given in Table 21.

The results confirm that changing the concentrations and dominance of the anions Cl⁻ and SO₄²⁻ had the smallest effect on the precipitation rate. The effects of c(Fe(II)) and DO were the second strongest effects, whereas already small changes in pH and HCO₃⁻ changed the precipitation rate strongly. This is understandable when considering the kinetics of the reaction that is of a 1st order dependency with respect to c(Fe(II)) and DO and of 2nd order dependency with respect to [H⁺]. The strong effect of HCO₃⁻ is explained by its pH-buffering capacity. As already described by McBain (1901), a strong effect was found to arise from raising temperature by 10 °C, increasing the precipitation rate by 60 %. Of course, a temperature of 25 °C is unrealistic in a real aquifer, but the simulation was done to emphasise
that temperature regulation that was done in the experimental model was a necessary measure.

Another crucial factor in the Fe-clogging model was the concentration of bicarbonate in the process water. As observed in the field, bicarbonate concentrations can be as high as 300 mg L\(^{-1}\). In a real dewatering well, these concentrations of bicarbonate account for a pH buffering effect that continued as long as HCO\(_3^−\) was continuously delivered with the fresh groundwater. Buffering the pH will maintain a high rate of iron oxidation and thus enhance chemical Fe-clogging. In the Phreeqc-model, if the initial c(HCO\(_3^−\)) was assumed to be 300, 150 or 20 mg L\(^{-1}\), the ratio of species distribution of dissolved carbon changed within only 20 s from an initially clear dominance of bicarbonate HCO\(_3^−/\)CO\(_2\) \(\approx 30:1\) to ratios of 7:1, 5:1 or 2:1, respectively. With the acid production through Fe oxidation, bicarbonate will be completely consumed, especially in the water cycle of the Fe-clogging model. The capacity of the process water to produce Fe-precipitates will decrease with reduced bicarbonate, which is not the case in a real well. In the Phreeqc-model, the continuous renewal of HCO\(_3^−\) was considered correctly during upscaling the modelled Fe-clogging time from 20 s to 50 h. Unfortunately, bicarbonate concentrations were not further considered in the experimental Fe-clogging model (even though pH itself was of course still regulated). However, as this effect was neglected in all conducted LTTs, comparison of the progressions of Fe-clogging for the different materials and scenarios is still valid.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>(\Sigma (\Delta c(\text{Fe(II)}) \text{ [g GP}^{-1} \text{ (50 h)}^{-1}])</th>
<th>relative change</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 7.0</td>
<td>6.58</td>
<td>- 80 %</td>
</tr>
<tr>
<td>c(HCO(_3^−)) = 20 mg L(^{-1})</td>
<td>8.92</td>
<td>- 73 %</td>
</tr>
<tr>
<td>c(Fe(II)) = 10 mg L(^{-1})</td>
<td>11.34</td>
<td>- 65 %</td>
</tr>
<tr>
<td>DO = 0.5 mg L(^{-1})</td>
<td>19.81</td>
<td>- 39 %</td>
</tr>
<tr>
<td>pH = 7.5</td>
<td>22.32</td>
<td>- 32 %</td>
</tr>
<tr>
<td>c(Fe(II)) = 50 mg L(^{-1})</td>
<td>26.15</td>
<td>- 20 %</td>
</tr>
<tr>
<td>c(Cl(^{-})) = 970 mg L(^{-1}), c(SO(_4^{2-})) = 1300 mg L(^{-1})</td>
<td>30.85</td>
<td>- 5 %</td>
</tr>
<tr>
<td>c(Cl(^{-})) = 25 mg L(^{-1}), c(SO(_4^{2-})) = 1300 mg L(^{-1})</td>
<td>31.24</td>
<td>- 4 %</td>
</tr>
<tr>
<td>DO = 2 mg L(^{-1}), c(Fe(II)) = 80 mg L(^{-1}), pH = 7.83, c(HCO(_3^−)) = 150 mg L(^{-1}), T = 15 °C, c(Cl(^{-})) = 970 mg L(^{-1}), c(SO(_4^{2-})) = 20 mg L(^{-1})</td>
<td>32.60</td>
<td>± 0 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c(Cl(^{-})) = 25 mg L(^{-1}), c(SO(_4^{2-})) = 20 mg L(^{-1})</td>
<td>33.53</td>
<td>+ 3 %</td>
</tr>
<tr>
<td>pH = 8.0</td>
<td>38.05</td>
<td>+ 17 %</td>
</tr>
<tr>
<td>DO = 4 mg L(^{-1})</td>
<td>40.67</td>
<td>+ 25 %</td>
</tr>
<tr>
<td>c(HCO(_3^−)) = 300 mg L(^{-1})</td>
<td>48.57</td>
<td>+ 49 %</td>
</tr>
<tr>
<td>T = 25 °C</td>
<td>51.60</td>
<td>+ 60 %</td>
</tr>
</tbody>
</table>

The total mass of Fe precipitated in each model cell decreased from 12.6 g Fe in the first cell to 1.0 g in the eleventh cell (Figure 93). The total volume of Fe(III)-minerals precipitated in each model cell was then calculated considering the density of lepidocrocite after Schwertmann and Cornell (2000) of 4.0 g cm\(^{-3}\). The values of precipitated minerals ranged from 5 to 0.4 cm\(^{3}\) in the 1\(^{st}\) and 11\(^{th}\) model cell, respectively. In relation to the total cell pore
of 156 cm³ or the cell pore volume that was saturated during the Fe-clogging phase of 31.2 cm³; this yielded a maximum of 16 to 3.2 % of the respective pore volume being filled up with Fe(III) minerals during 50 h of Fe-clogging in the model.

![Figure 93](image)

**Figure 93** Total mass of Fe and total volume of Fe(III)-minerals (calculated with the density of lepidocrocite of 4.0 g cm⁻³) in each model cell, calculated with the Phreeqc-model

Of course, the simple model approach chosen here only considered the saturated zone with a constant saturated water level of 40 mm throughout the filter pack during the Fe-clogging phases and disregarded the secondary clogging zone of the evaluation phases as well as the exact processes in the unsaturated zone and capillary fringe. Instead, the whole process water in all model cells was immediately set to a constant supply of O₂ in order to achieve a constant DO = 2 mg L⁻¹ throughout the gravel pack. These model assumptions are necessary for the Phreeqc input file, but also introduce considerable model uncertainties.

### 5.4.3 Comparison of hydraulic data from the Fe-clogging model

The absolute values of hydraulic conductivities measured in the clogging model were found to range between 1.0 and 2.7·10⁻² m s⁻¹ (Figure 94). These values were found to be in good agreement with hydraulic conductivities determined by Klauder (2010) in the dewatering well optimisation model (linear Ergun-coefficients, simplified by disregarding the quadratic fractions) as well as via analyses of grain size distributions after DVGW W 113 of the German Technical and Scientific Association for Gas and Water (DVGW, 2001; Table 22).

**Table 22** Ranges of hydraulic conductivities in the Fe-clogging model in comparison to values given by Klauder (2010) (final report phase III, 2013)

<table>
<thead>
<tr>
<th>K-values [·10⁻² m s⁻¹]</th>
<th>W</th>
<th>D</th>
<th>F</th>
<th>GB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dewatering well model (Klauder, 2010)</td>
<td>1.2 ... 1.7</td>
<td>-</td>
<td>-</td>
<td>1.9 ... 2.0</td>
</tr>
<tr>
<td>Analyses of grain size distributions</td>
<td>1.3 ... 2.4</td>
<td>1.1 ... 2.5</td>
<td>1.4 ... 1.8</td>
<td>1.9 ... 2.0</td>
</tr>
<tr>
<td>Fe-clogging model initial value</td>
<td>1.2 ... 1.8</td>
<td>2.0 ... 2.7</td>
<td>1.9 ... 2.4</td>
<td>2.1 ... 2.7</td>
</tr>
<tr>
<td>Fe-clogging model final value</td>
<td>1.0 ... 1.4</td>
<td>1.6 ... 2.4</td>
<td>1.5 ... 2.0</td>
<td>1.7 ... 2.5</td>
</tr>
</tbody>
</table>

The K-values of the Weilerswist gravel even yielded an almost identical range, whereas the glass beads exhibited somewhat higher values in the Fe-clogging model than predicted by the grain size distributions and the dewatering well model by Klauder (2010). The hydraulic conductivities of the alternative filter materials were always slightly underestimated by the grain size distributions method. Nonetheless, the comparison with other methods showed that the results of the calculation method chosen for the Fe-clogging model are feasible.
A scattering in the initial K-values was even found when comparing two different long term tests with the same filter material. This scattering most certainly resulted from random microscale differences in the assembly of the filter pack. The distribution of hydraulic conductivities between the two different piezometric evaluation sections of the gravel pack, however, appeared to exhibit systematic deviations. The conductivity close to the boundary between aquifer material and filter pack (S I) was higher than in the vicinity of the screen pipe (S II) in almost all cases. This was caused by vertical flow components occurring close to the interface between aquifer and filter pack, resulting in an overestimation of the hydraulic conductivity by underestimating the cross-sectional area in Darcy’s law. Therefore, the values attained in section S II were considered to be more reliable than the values from section S I. To allow for a direct comparison of all relevant long term tests, their K-value progressions with proceeding Fe-clogging time were additionally plotted distinguished by piezometric evaluation section due to these systematic differences (Figure 95).

The strongest effect on the conductivity in all cases was found after the first Fe-clogging step of around 5 h. Subsequently, the slope decreased, but only became positive in a few cases, possibly due to flow-induced material rearrangement (like in well development), corresponding to an increase in K. The influence of Fe-clogging on the hydraulic conductivity in S II of the alternative materials from Dorsfeld and Frimmersdorf proceeded very similarly with increasing Fe-clogging time. When disregarding the different initial conductivities, even the K-progression of the Weilerswist gravel develops similarly to the alternative materials. K-progression with the glass beads lacked the strong decrease after the first Fe-clogging step, but exhibited a more continuous slope, resulting in a similar relative decrease after 35 h of Fe-clogging time (Table 23). In LTT 15 and 16, the piezometric evaluation section S II was also influenced by vertical flow components as the flow field became deformed by the shortened screen pipe, thus causing a considerably lower initial hydraulic conductivity found in S II. In LTT 16 the conductivity did not at all decrease with proceeding Fe-clogging time. The conductivity of the screen pipe was found to develop similarly in the three experiments with the standard screen pipe. Of course, the hydraulic conductivity in the shortened screen pipe
was significantly lower than that of the standard screen pipe. As no experiments were conducted with different types of screen pipe, comparative evaluation of its Fe-clogging affinity was not possible, but the curves’ progressions behaved similarly to those measured inside the gravel pack.

![Graphs showing Fe-clogging progressions](image)

**Figure 95** Fe-clogging-progressions of the different long term tests, distinguished by piezometric evaluation section S I to S III; S I: filter pack section close to the aquifer material; S II: filter pack section close to the screen pipe, S III: screen pipe itself, W: Weilerswist gravel, F: Frimmersdorf gravel, D: Dorsfeld gravel, G: glass beads, SSP: shortened screen pipe (final report phase III, 2013)

Except for LTT 16, the relative decrease in hydraulic conductivity was in a similar range in all modelled scenarios (Table 23). Whereas the decrease of hydraulic conductivity in section S I again showed a broader range of variability, the values in S II only ranged from 20.1 % to 22.4 % with the exceptions of LTT 6 and LTT 15. However in LTT 15 the malfunction of AdP 1 was the reason for the strong decrease in section S II. In LTT 6 K-decrease in S I was significantly lower than in the other tests, so only the distribution and not the total amount of Fe incrustations and their effect on the hydraulic conductivity seemed to be spatially shifted.

Even though the changes in hydraulic conductivity appeared to be very small at first glance, their impact on a real dewatering well can be stronger than expected. To illustrate this, the following application example will depict the impact of changes in the hydraulic conductivity as subtle as observed in the Fe-clogging model during only short periods of chemical Fe-clogging.
Table 23: Hydraulic conductivities of material tests and modelled scenarios in the Fe-clogging model; the final K-values represent the conductivity after 35 h of Fe-clogging time. S I to S III: piezometric evaluation sections I through III, W: Weilerswist gravel, F: Frimmersdorf gravel, D: Dorsfeld gravel, GB: glass beads, SSP: shortened screen pipe (final report phase III, 2013)

<table>
<thead>
<tr>
<th>LTT</th>
<th>Initial K-value [10^-2 m s^-1]</th>
<th>Final K-value [10^-2 m s^-1]</th>
<th>Decrease [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S I</td>
<td>S II</td>
<td>S III</td>
</tr>
<tr>
<td>6 (W)</td>
<td>1.21</td>
<td>1.55</td>
<td>-</td>
</tr>
<tr>
<td>8 (W)</td>
<td>1.69</td>
<td>1.56</td>
<td>-</td>
</tr>
<tr>
<td>9 (F)</td>
<td>1.99</td>
<td>1.95</td>
<td>-</td>
</tr>
<tr>
<td>11 (D)</td>
<td>2.56</td>
<td>2.12</td>
<td>-</td>
</tr>
<tr>
<td>12 (F)</td>
<td>2.28</td>
<td>2.12</td>
<td>2.34</td>
</tr>
<tr>
<td>13 (D)</td>
<td>2.24</td>
<td>2.09</td>
<td>2.15</td>
</tr>
<tr>
<td>14 (GB)</td>
<td>2.57</td>
<td>2.23</td>
<td>1.93</td>
</tr>
<tr>
<td>15 (SSP)</td>
<td>1.93</td>
<td>1.03</td>
<td>1.35</td>
</tr>
<tr>
<td>16 (SSP)</td>
<td>2.15</td>
<td>1.09</td>
<td>1.28</td>
</tr>
</tbody>
</table>

5.4.4 Application example

In order to demonstrate the impact of the changes in the hydraulic conductivity as observed in the Fe-clogging model, an exemplary calculation of increasing energy loss or decreasing pumping rate is conducted based on the Thiem-Dupuit equation (cf. section 2.2.3).

\[ Q = \frac{K \cdot 2\pi \cdot L_{SP} \cdot \Delta h_{GP}}{\ln(r_{BH}/r_{SP})} \]  \hspace{1cm} (56)

with \( Q \) = pumping rate of the exemplary well [m³ s⁻¹], \( K \) = hydraulic conductivity of the gravel pack [m s⁻¹], \( L_{SP} \) = vertical length of the screen pipe [m], \( \Delta h_{GP} \) = change in piezometric head between borehole surface and screen pipe [m], \( r_{BH} \) = radius of the borehole [m], \( r_{SP} \) = radius of the screen pipe [m]. \( Q \) and \( \Delta h_{GP} \) represent variables that can be influenced by a change in the hydraulic conductivity, whereas the geometric factors \( L_{SP}, r_{BH}, r_{SP} \) remain constant:

\[ \frac{Q}{\Delta h_{GP}}(K) = \frac{2\pi \cdot L_{SP}}{\ln(r_{BH}/r_{SP})} \cdot K \]  \hspace{1cm} (57)

A decrease in \( K \) is thus directly proportional to the factor \( Q/\Delta h_{GP} \). The energy loss due to a decreasing \( K \)-value can therefore either be expressed as a decrease in the pumping rate at constant \( \Delta h_{GP} \) or – in consistency with Klauder (2010) – as an increase in \( \Delta h_{GP} \) (increasing loss of hydraulic head in the gravel pack) at constant \( Q \):

\[ Q(K) = \frac{2\pi \cdot L_{SP} \cdot \Delta h_{GP}}{\ln(r_{BH}/r_{SP})} \cdot K \]  \hspace{1cm} with \( \Delta h_{GP} = \text{const.} \) \hspace{1cm} (58)

or

\[ \Delta h_{GP}(K) = \frac{Q \cdot \ln(r_{BH}/r_{SP})}{2\pi \cdot L_{SP}} \cdot \frac{1}{K} \]  \hspace{1cm} with \( Q = \text{const.} \) \hspace{1cm} (59)

To illustrate the change in the pumping rate or the loss of hydraulic head in the gravel pack with the changes of \( K \) observed in the experimental Fe-clogging model, an exemplary dewatering well with \( r_{BH} = 0.6 \text{ m}, r_{SP} = 0.295 \text{ m (DN 500-pipe)} \) and \( L_{SP} = 88 \text{ m} \) was calculated with the initial and resulting \( K \)-value of LTT 6 in pressure evaluation section S II. The realistic geometry of the exemplary well was chosen according to Klauder (2010), who used a similar
example to illustrate her results concerning time independent well loss in her dissertation. The results of the application example are listed in Table 24.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Initial</th>
<th>Final</th>
<th>Rel. change</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>[m s⁻¹]</td>
<td>0.0155</td>
<td>0.0108</td>
<td>-30.3 %</td>
<td>-</td>
</tr>
<tr>
<td>Q/Δh₉₉₉</td>
<td>[m² min⁻¹]</td>
<td>724</td>
<td>505</td>
<td>-30.2 %</td>
<td>Δh₉₉₉, const = 3 mm</td>
</tr>
<tr>
<td>Q</td>
<td>[m³ min⁻¹]</td>
<td>2.17</td>
<td>1.52</td>
<td>-30.0 %</td>
<td></td>
</tr>
<tr>
<td>Δh₉₉₉</td>
<td>[mm]</td>
<td>2.07</td>
<td>2.97</td>
<td>+43.4 %</td>
<td>Q, const = 1.5 m³ min⁻¹</td>
</tr>
</tbody>
</table>

When K decreased by 30 %, due to the linear dependency, the factor Q/Δh₉₉₉ also decreased by 30 % from 724 to 505 m² min⁻¹. Or more intuitively at constant Δh₉₉₉ = 3 mm, the pumping rate decreased from 2.17 to 1.52 m³ min⁻¹. This is equivalent to a 43 % increase of pressure loss from 2.1 to 3.0 mm. In a real well, both phenomena of increasing well loss Δh₉₉₉ and decreasing Q will most certainly occur simultaneously.

For comparison, the increase of Δh₉₉₉ = 0.90 mm observed in the filter pack of the Fe-clogging model was equivalent to decreasing the flow effective porosity from 0.4 to 0.25, decreasing the inner screen tube diameter by 100 mm or changing from a coarser grain size class (2.0 to 3.15 mm) to the next finer class (1.4 to 2.2 mm). So, even increasing the well loss by less than one millimetre as a result of Fe-clogging is equivalent to major changes in well assemblage.

### 5.5 Tracer experiments in annular space dewatering

As prohibiting air supply to the filter pack of dewatering wells was found to be the method of choice to prevent Fe-clogging with LTT 16 of the experimental model, the concept was transferred to the field scale. To accomplish this, three multi-layered dewatering test wells were constructed without an upper screen pipe which in conventional multi-layered dewatering wells was commonly quickly aerated and became subject to chemical Fe-clogging. The water of the upper aquifers was instead drawn down through the annular space of the well. To quantify the hydraulic conductivity and the capacity of the annular space to conduct water down to the lower screen pipe, tracer experiments were conducted in the three test tubes.

The results of the tracer experiments in the wells with annular space dewatering all yielded total residence times in the wells between 30 and 60 minutes, until half the concentration of the plateau was reached. Figure 96 exemplarily shows the resulting tracer passing curve of the well with the longest residence time of 59 min. The other two wells H 1301 and H 1712 yielded similar curves but with residence times of 28 and 35 min, respectively (Milatz, 2013, report annular space dewatering, 2013, cf. Appendix 39). From this total time, the times of downward flow in the piezometric pipe (around 6 min for a distance of 280 m) and in the ascending pipe (around 5 min for a distance of 330 m) were subtracted to estimate the total residence time of the tracer in the annular space.
Continuous injection of tracer and rinsing water ($Q_{rin}$) into the piezometer in the annular space of well H 1307 with annular space dewatering and measurement of tracer passage at the top of the well (normalised to the maximum concentration); the red and black arrows mark the times of arrival of half the maximum tracer concentration and of the change from tracer solution to rinsing water, respectively (report annular space dewatering, 2013).

Depending on the assumption of the flow effective porosity, the $K$-values in the annular space of the three dewatering wells ranged between $0.6 \cdot 10^{-2}$ m s$^{-1}$ and $1.6 \cdot 10^{-2}$ m s$^{-1}$, representing quite high hydraulic conductivities. The calculated flow rates through the annular space that were calculated from these values with the horizontal cross-sectional area of the annular space ranged from 0.3 to 0.9 m$^3$ min$^{-1}$, accounting for approximately 15 to 50 % of the total well yield. These values show that a sufficient dewatering effect can be attained by dewatering the upper aquifers through the annular space of multi-layered dewatering wells (Milatz, 2013, report annular space dewatering, 2013).

Generally, these results can be seen as a successful approach to transfer the results of LTT 16 to the field scale and to prevent chemical Fe-clogging in the filter pack of multi-layered dewatering wells. Since the dewatering effect was sufficient in the test wells, the concept of annular space dewatering was implemented by the RWE Power AG into their future well construction plans in the surroundings of their three lignite open-pits in order to investigate the long-term-performance of the concept (RWE Power AG).
6 Conclusions

In the context of this work, the properties of different well filter pack materials were assessed with respect to long term elution and chemical Fe-clogging affinity. The processes and consequences of Fe-clogging within the different materials were evaluated by the progression of the hydraulic conductivity with increasing influence of chemical Fe-clogging, and numerous analytical approaches of chemical, physical and mineralogical character. The results gained from samples taken in the laboratory experiments were compared to actual samples taken from the filter pack of excavated wells in the open-pit Garzweiler that were actually affected by different types of Fe-clogging. Apart from the tests of different filter materials, two different concepts of well operation regarding the aeration of screen pipe and filter pack were simulated in the laboratory. Transferring the results of the filter aeration experiments to field scale multi-layered dewatering wells required omitting the upper screen sections and conducting the water of the upper aquifers downwards inside the annular space towards the lower filter screen. Thus, the capacity of the annular space to conduct the required amount of water was evaluated by means of tracer experiments in three test-wells that had been installed by the mining company.

As a final result of all experiments conducted and evaluated in this thesis, the research questions that were posed in the introducing chapter can be answered as follows:

Question 1  What are the relevant controlling parameters for distribution, intensity and type of Fe-incrustation in the vicinity of a well?

As was already known from the literature review the main factors influencing the kinetic reaction of chemical Fe-clogging are a high pH, high dissolved oxygen concentrations and therefore increased Eh. For classically operated dewatering wells (with screen pipe aeration) the experiments in the simplified Fe-clogging model showed these conditions to exclusively occur in the unsaturated (aerated, but wet) zone of the filter pack and screen pipe as well as at the open water surface in the outflow chamber. Both the experimental model and the computed hydrogeochemical model found the effect to develop the strongest impact in close vicinity to the borehole surface, the interface between aquifer material and filter pack.

Interestingly, in the experiments as well as in the open-pit Garzweiler, Fe-clogging always concentrated solely in the gravel pack and screen pipe, whereas no indications of Fe-clogging were found in the aquifer material whatsoever. This may be due to the comparatively high capillarity and saturation conditions of the fine aquifer sands, slow oxygen-diffusion as compared to strong groundwater flow in the opposite direction, quick pH-decrease as a result of the Fe-clogging reaction and quick oxygen-consumption in the filter pack (and by pyrite-oxidation in the first millimeters of the aquifer material at the latest).

Of course, in a realistic dewatering well, and especially in multi-layered dewatering, additional factors may change the locations of increased Fe-clogging activity. For example, water
trickling downwards inside the well tube from an upper, already aerated screen pipe takes up oxygen on its way down and is finally turbulently mixed with the water column inside the well. This will cause an increased oxidation rate inside the well. Even when the water from the upper aquifer is not exposed to enhanced oxygen-supply inside the well tube, mixing of groundwater from different aquifers may lead to increased Fe(III)-precipitations, if a reduced, Fe-bearing groundwater is mixed with an oxic groundwater. If the hydraulic conditions between the multiple aquifers, dewatered in one well, induces infiltration of groundwater from one aquifer into another, this may lead to dislocation of Fe-clogging-zones or -products into the intruded aquifer.

Furthermore, turbulences due to pump operation may amplify mixing of the water inside the well and with the surrounding air. Other flow paths for oxygen may occur as a result of specific geologic conditions (nearby ground surface or infiltrating surface water; e.g. Medina et al., 2013) or well operation conditions (air supply through the filter pack from the surface or from an upper, aerated screen pipe, especially when intermittent operation is applied; cf. Figure 18). Also, no conclusions can be drawn on effects of biological Fe-clogging as these were intentionally excluded from the experimental model.

Finally, another influencing factor is the dominating anion in the reduced ground water. Changing the contents of sulphate or chloride only changes the type of Fe(II)-mineral that will form from reduced Fe(II)-bearing groundwater, but the content of bicarbonate in the water has a major influence on the reaction rates due to its pH-buffering effect.

**Question 2** Can the naturally occurring Fe-clogging process be representatively reproduced in the laboratory by means of the proposed experimental model?

Generally, the chemical process of Fe-clogging could be reproduced with the experimental model. Its influence on the hydraulic conductivity of the well filter could be quantified within only 35 h to a maximum of almost 300 h of net-Fe-clogging time. This was only possible by accelerating the process with increased c(Fe(II)) and pH to achieve results of the material tests and well operation scenarios in an appropriate time frame. Still, due to a high intensity of manual measurements and regulation during model operation, one complete long term test of 40 h net-Fe-clogging time required a total model-operation time between six and seven weeks, including preparation of the flow channel, filter columns and process water, conducting the reference test, Fe-clogging phases and evaluation phases as well as disassembling, sampling and cleaning the model and subsequent laboratory analyses and data evaluation.

In order to keep the experimental model simple, certain “micro-scale” hydrochemical condition still somewhat differed from actual conditions in a realistic situation in a dewatering well of the Rhenish lignite district. For the same reason, biological aspects were also intentionally excluded. Nonetheless, applying the proposed experimental model, the Fe-clogging affinity of the different well assembling materials could reliably be compared with each other.
The impact of these micro-scale hydrochemical differences on type and intensity of the precipitated Fe oxide minerals could be identified by means of the kinetic PhreeqC Fe(II)-oxidation-model. The most prominent differences were found to originate from the dominating anion (chloride used in the model instead of sulphate or bicarbonate). Whereas changing the dominating anion from chloride to sulphate will only change the positions of two minerals in their rank of precipitation probability, the amounts of bicarbonate found in the field due to its pH-buffering effect resulted in a continuously higher rate of Fe-oxidation. Applying an Fe(II)SO₄-stock solution rather than Fe(II)Cl₂ would presumably allow biologically induced Fe-clogging in the experimental model. As found in the field samples, this would result in more voluminous precipitates with a lower compactness, lower percentage of well crystallised Fe(III)-hydroxides, higher specific surface areas and porosities (BET) and higher total contents of organic carbon (TOC) or even gypsum precipitation. In order to avoid complex uncontrollable effects and interferences of voluminous precipitates with the hydrochemical measuring probes, the Fe(II)Cl₂-stock solution was chosen for the experimental model.

The rate of Fe(II)-oxidation in the model was primarily controlled by the HCO₃⁻ and Fe(II)-content in the process water as well as temperature and pH. Increasing one of these parameters would further increase the amount of precipitated Fe(III)-minerals, but would also affect the type of Fe-minerals precipitated. In the model, ferrihydrite was precipitated only due to the already strongly accelerating conditions. Decreasing the reaction rate to a more realistic naturally occurring situation would lead to precipitation of the more realistic, low-density, voluminous ferrihydrite with higher BET (like found in the field), but would also dramatically increase the necessary experimental time towards impractical durations.

“Macro-scale” differences between the model and the realistic situation that were primarily hydraulic (mixing of different groundwater types, infiltration from one aquifer into the other, geologically or technically altered pathways of air flow) were approached by field investigations. Inspection and sampling the gravel pack of wells excavated in the open-pit Garzweiler revealed the clogging zones to be distributed more irregularly than in the model, especially due to the higher importance of vertical flow components.

**Question 3** How will the progression of Fe-clogging develop with time? Will it decelerate, remain constant or accelerate itself (autocatalytically) with time?

In the laboratory experiments, the main impact of the clogging process on the hydraulic conductivity of the filter medium used as gravel pack appeared immediately after aeration of the screen pipe. In all subsequent steps, the loss in hydraulic conductivity per time step was lower than in the first clogging step (Figure 97). No autocatalytic effect was observed in the experimental model. It is, however, uncertain whether the progression of the K-value will experience a further decrease at prolonged Fe-clogging times, as a maximum of about 300 h of Fe-clogging was accomplished in the model. Even though the progress of Fe-oxidation was accelerated in the model (by factor of 10 on c(Fe(II))), real well operation times still by far exceed the effective Fe-clogging times attained in the model, even when assuming an
acceleration factor of 10. This assumption gains special importance when considering the microscopically discovered extent of Fe-incrustations that were still limited to coatings of up to 50 μm on the individual gravel grains (compare with “initial phase B of slow well ageing with beginning incrustations” as defined by Houben, 2004, see also Houben & Treskatis, 2007).

![Graph](Image)

Figure 97 Progression of the hydraulic conductivity with increasing influence of chemical Fe-clogging as observed in the experimental model (green, solid line). With the Fe-clogging time further increasing, a secondary acceleration is possible (blue, dashed line; final report phase III, 2013, redrawn, translated).

Furthermore, the progression of Fe-clogging might well change when exchanging the dominating anion in the process water, especially when considering a continuous pH-buffering effect that could arise from increased amounts of bicarbonate in the process water. The same is true for biological Fe-clogging processes that could also completely change the development of the K-value with proceeding Fe-clogging time.

**Question 4** Does the type of filter material affect the interaction with the groundwater with respect to mineral dissolution and precipitation? Will the type or intensity of Fe-incrustations depend upon initial contents of hydroxidic Fe(III)-minerals or the specific surface area of the filter medium?

In the column experiments, no substantial differences between the two alternative Quaternary gravel materials and the conventional Tertiary material were observed with respect to long term elution. The strongest, but still subtle release of the (semi-)metals Al, Si and Mn was found in the alternative Frimmersdorf gravel, but the alternative Dorsfeld gravel performed even better than the conventional comparative Weilerswist gravel.

With respect to Fe-clogging affinity, again no substantial differences were found between these three gravel materials and a glass bead filter pack, as observed from the progressions of the K-value with proceeding Fe-clogging time. The only differences were obtained from the chemical, mineralogical and microscopic analyses. The initial contents of Fe(III)-minerals were highest in the Frimmersdorf gravel, 2<sup>nd</sup> highest in the Dorsfeld gravel, 2<sup>nd</sup> lowest in the Weilerswist gravel and lowest in the glass beads. The amounts of Fe-precipitation per time unit determined by the SEP analyses were found to decrease in the order Dorsfeld gravel > glass beads > Weilerswist gravel > Frimmersdorf gravel, whereas the maximum concentrations descended in the order Weilerswist gravel > Dorsfeld gravel > Frimmersdorf gravel > glass beads.
As determined by the SEP, XRD, BET and TOC analyses, the well crystallised percentage in the filter materials after chemical Fe-clogging in the experimental model were found to increase in the order glass beads < Dorsfeld gravel < Frimmersdorf gravel < Weilerswist gravel. However, as precipitates of low crystallinity and low compactness take up more space of the total pore volume, but are more easily removed by chemical or mechanical regeneration measures, it is unclear, whether their formation is of advantage or disadvantage. On a microscopic level, individual grains of polycrystalline quartz and weathered feldspars with irregular surface areas showed to be more strongly affected by encrustations of Fe-clogging products and to function as more effective crystal nuclei. Contents of feldspars, however, appeared similar in all gravel materials, whereas polycrystalline quartzite grains were primarily found in the alternative Quaternary gravel materials. This would speak for the application of preferably pure and monocrystalline quartz grains with a plain surface, or even glass beads. However, all these differences between the various gravel materials were always subtle, if not even barely noticeable and sometimes not systematically reproducible. Especially considering the temporal development of the K-value with proceeding Fe-clogging time, all filter materials performed quite similarly.

Regarding the Fe-clogging affinity, no strong advantages for an application of a glass bead filter pack in the dewatering wells of the Rhenish lignite district were found in the single experiment that was conducted in the Fe-clogging model that would let amortisation of their comparatively high investment cost appear realistic. As the main advantage of glass bead filter packs is believed to lie in a better performance during regeneration measures, which generally are not conducted in the Rhenish lignite district anyway, application of glass beads cannot be recommended here. This situation may be different for wells in drinking water supply that in general feature smaller dimensions (less glass beads required), are more likely to be regenerated and have a longer planned lifetime and therefore may reach amortisation of the investment costs.

On the other hand, no strong arguments were found that would speak against application of the alternative Quaternary gravels as filter pack materials for dewatering wells. In some respects, the alternative gravels performed even better than the conventional Tertiary Weilerswist gravel. The Dorsfeld gravel for example exhibited the best properties with respect to long term elution, whereas the Frimmersdorf gravel performed somewhat better than the other materials with respect to the amounts of Fe-precipitates in the Fe-clogging model. Finally, even though the relative decrease of the hydraulic conductivity was similar in all gravel materials, both Quaternary gravels showed higher initial and final absolute K-values.

**Question 5** How does the aeration of the screen pipe proceed? What is the distribution and direction of flow paths of air and water? In which way and how quickly does filter aeration affect the progression of Fe-clogging?

In the case of the standard screen pipe, the air was supplied to the filter pack directly through the upper part of the well screen. When the shortened screen pipe was used in LTT 15 and 16, no air was exchanged between the outflow chamber and the filter pack so long as the screen section stayed submerged. In LTT 15, the air in the filter pack was expelled from the filter pack
into the flexible reservoir when the water level in the outflow chamber was raised, whereas in LTT 16 the filter pack stayed fully saturated at any time. Only when aerating the screen pipe with stopped flow over night, the capillarity in the filter pack broke within only 16 h. The filter pack was then filled with air flowing back through the screen pipe and immediately started the progress of Fe-clogging.

In the model, an only 200 mm high water column was held against gravity for 16 h of aerating a 200×30 mm screen pipe (width×height). In a realistic dewatering well, the water columns to be held against gravity as well as the lengths of aerated screen pipe are significantly higher, so the time of 16 h will diminish to a few seconds to minutes. Therefore, aeration of the well screen for only short durations may cause the gravel pack to immediately become filled with air. In the field, wells with their screen being aerated for the first time are often even reported to suck increased amounts of air from the surface (e.g. when using an inert gas).

These findings clearly imply the necessity to strictly avoid screen pipe aeration as long as possible.

Question 6  Can dewatering of multi-layered aquifers be established through wells with only one deep screen pipe in the lower aquifer and dewatering the upper aquifer through the annular space between borehole and well pipe?

Three multi-layered dewatering wells that were constructed according to the concept of annular space dewatering (omitting an upper screen pipe and conducting the water down to the lower screen pipe through the annular space) in the pre-field of the lignite open-pit Hambach showed a satisfying effectiveness of dewatering the lower and upper aquifers. The relative share of the upper aquifer on the total well production rate depended on the residual water content of the upper aquifer and therefore ranged between 15 and 50 %. The affinity towards chemical Fe-clogging in such wells is assumed to be minimal, considering the findings of long term test 16 with the Fe-clogging model, so long as the lower well screen pipe stays fully saturated. Even though the long term stability of the determined flow rates has not yet been investigated especially for unsaturated flow conditions due to progressed dewatering situation, Fe-clogging is expected not to affect dewatering wells with annular space dewatering within their relatively short planned lifetime.

Of course, air supply to the upper aquifer from the ground surface through the annular space, needs to be inhibited by installation of an upper annular seal, especially when the well is operated intermittently. Special attention also needs to be paid if the groundwaters, mixing in the annular space exhibit oppositional redox-conditions. E.g. if the upper and lower aquifer deliver an oxidising and reduced (i.e. Fe(II)-bearing) groundwater, respectively, this would lead to accelerated chemical Fe-clogging of the annular space, where the two types of groundwater mix.

However, until now it is unknown how saturated and unsaturated zones are distributed inside the filter pack of a well with annular space dewatering. Possibilities for the origin and pathway of air supplied to the filter pack are soil air, aeration through the annular space from an upper
screen pipe or from the ground surface, leakage of pipe joints, or gas phase release from the ground water. The origin of the air and its composition are the decisive parameters for the gas phase whether or not it poses a risk to trigger chemical Fe(II)-oxidation.
7 Prospect

As the approach, chosen in this study to evaluate the applicability of filter pack media regarding their long term elution behaviour as well as their tendency towards chemical Fe-clogging proved successful. With the proposed approach, further tests of filter material and hydraulic and chemical conditions are possible. However, further optimisation of the concept is thinkable to enhance its performance and its effectivity to produce usable results in a shorter period of model operation. To allow for an automatic regulation of $Q_{sys}$ and $h_{oc}$ and therefore the addition rate of FeCl$_2^-$ and NaOH-stock solutions, a weir in the outflow chamber of the flow channel is necessary to desensitise the water level in the outflow chamber. Automatisation of Fe(II)-addition, however, would also require automatic measurement of Fe(II), which cannot be easily accomplished. Integrating a second flow channel into the water cycle parallel to the first one would allow for simultaneous execution of an experiment and its reproduction at the same time and with the exactly same hydrochemical conditions.

Exact comparability of the model results with actual situations in the field was not relevant to the material tests and scenario experiments in this thesis, but could help to further understand the hydrochemical processes of Fe(II)-oxidation and precipitation. As revealed by the PhreeqC-model of the flow channel, a change in the dominating anion would result in a different mineral precipitating in the gravel pack, whereas increasing c(Fe(II)) or the temperature would result in an increase of the amount of mineral precipitation. Other changes in model operation that could be of interest include a variation in the flow velocities and the experimental duration. Decreased flow velocities (longer residence time of the process water in the gravel pack) and prolonged experimental durations are suspected to result in higher amounts of Fe and possibly to increase the change in the hydraulic conductivity of the filter pack. Apart from chemical changes in the process water, biological clogging aspects could be considered for investigation in an Fe-clogging model similar to the proposed one. As to keep the Fe-clogging model simple and controllable, biological aspects were excluded from the described experiments.

Further questions that could be assessed by application of an experimental Fe-clogging model approach include testing the chemical Fe-clogging affinity of different grain size classes of the gravel pack or types of screen pipes. Different measures to oppose Fe-clogging that already are commonly applied in the field like inert gas treatment and different chemical and mechanical regeneration methods can be optically and quantitatively investigated and optimised.

Innovative methods for prevention of chemical Fe-clogging like electrokinetic polarisation could also be tested with the proposed Fe-clogging model. As chemical Fe-precipitation in filter packs and screen pipes of wells is a process of electrostatic attraction and adhesion of ions and particles to the grain surfaces of these porous media (Narayan et al., 1997), the electrical charge of the grain surfaces plays an important role in the process. The application of electrochemical methods to manipulate the dynamics of Fe-oxidation and -precipitation mechanisms were already discussed in the 1990ies (Fischer et al., 1990, Reißig et al., 1990,
Fischer et al., 1991, Daffner et al., 2004). Induction of electrical currents is used to enhance the process of Fe-precipitation in treatment of acid mine waters (Florence & Morgan, 2013) still today, implying that inverting polarity of the electrical current should prevent Fe(III)-hydroxides from precipitating. With a constructional method of artificially changing the polarity of the electrical surface charge of the well construction materials and therefore their sorptive properties, a permanent clogging protection or intermittent repulsion periods as part of regeneration measures could be possible. Optimisation of such methods and their relevance for practical application could be accomplished by testing with the proposed experimental clogging model.

The most promising result that was found using the experimental model was the influence of filter aeration. To avoid the aeration of screen pipes especially in multi-layered dewatering, the concept of annular space dewatering of multiple aquifers was developed together with the RWE Power AG. As these wells were found to work satisfyingly in wells in the pre-field of the open-pit Hambach with respect to K-values and flow rates in the annulus downwards from the upper aquifer, the concept was implemented in the future mining plans of the mining company. Long term stability of the dewatering effect is still being investigated in collaboration of LFH and RWE Power AG.

To better understand the near-well hydraulics and the origin and pathways of air-flow, further experimental investigations could be helpful to accompany the experiments conducted in the field. Dewatering of confined aquifers is known to produce underpressures in the top of the confined aquifer (Kuang et al., 2013), it would be interesting to evaluate the distribution of pressure and composition and distribution of air inside a conventional multi-layered dewatering well compared to one with annular space dewatering in the field or in a laboratory model (e.g. similarly to Kuang et al. (2013)). This could be accomplished by application of fully grouted piezometers that are capable of distinguishing between air and water as well as over- and underpressure (Yungwirth et al., 2013).
8 Summary

Chemical Fe-clogging is a major factor strongly interfering with the performance of vertical filter wells. All over the world, groundwater is pumped by means of vertical filter wells to locally dewater aquifers for mining or construction purposes or to reliably meet daily demand for drinking water. Especially considering the increase in global population, rising production of natural soil resources and rapidly increasing demand for high quality drinking water, a sustainably high performance of vertical filter wells is essential from an economic as well as ecological point of view.

Within this study, the influence of different gravel materials and well operation concepts on the performance of open-pit dewatering wells in the Rhenish lignite mining district in Germany was assessed in an experimental laboratory approach. Special focus was laid on long-term elution and chemical Fe-clogging affinity of different filter pack materials and the distribution of chemical Fe-clogging products, when aeration of the screen pipe in a dewatering well is avoided.

Long-term elution and release of different (semi-)metals from different gravel materials were evaluated with column experiments, whereas for evaluation of the affinity towards chemical Fe-clogging, a combined hydraulic and hydrochemical experimental model of a well filter section was developed and optimised as part of the described project.

Three different natural gravel materials were evaluated for their long-term elution in five column experiments. One conventionally used gravel from a Tertiary deposit near Weilerswist was compared to two alternative gravel materials from Quaternary deposits near Dorsfeld and Frimmersdorf.

With the experimental Fe-clogging model the relevant parameters that controlled the progression of chemical Fe-clogging were identified in the first four long term tests (LTTs) and a standardised model operating concept was developed. In the LTTs 5 to 13 the same gravel materials as in the column experiments were evaluated for their affinity towards chemical Fe-clogging and additionally compared to that of artificially produced glass beads in LTT 14. Apart from these material tests, the influence of screen pipe aeration was evaluated by application of a shortened screen pipe in the LTTs 15 and 16.

The spatial distribution and temporal development of Fe(III)-precipitation was calculated by a computed hydrochemical model of kinetic Fe(II)-oxidation with the hydrogeochemical modelling programme PhreeqC in a simple approach for comparison with results of the experimental model. Varying the input data of the computed model allowed for a sensitivity analysis of the hydrochemistry applied in the experimental model.

Three multi-layered dewatering test wells had been installed by RWE Power AG without an additional screen pipe in the upper aquifer but with the annular space filled with gravel pack material in order to avoid screen pipe aeration and turbulent mixing by water trickling down inside the well casing. With this concept, the results of the filter aeration experiments were
transferred to the field scale. The annular space was then tested for its vertical hydraulic conductivity by tracer experiments.

The type and spatial distribution of the Fe-clogging products produced in the experimental model was compared to incrustations in samples from the gravel pack of wells in the field that had been excavated during succession of the open-pit.

Chemical Fe-clogging in the model was found to exclusively develop in the unsaturated zone of the gravel pack and the screen pipe. In rough agreement with the hydrogeochemical PhreeqC-model, the highest Fe-clogging-intensity in the gravel pack was concentrated close to the boundary of the aquifer. This was due to unsaturated, vertical flow components in the vicinity of the material boundary. Similar distributions of the Fe-clogging zones were observed during sampling of dewatering wells excavated in the open-pit Garzweiler. Intense Fe-clogging was found to be heterogeneously distributed in presumed zones of unsaturated vertical flow that allowed mixing with the gaseous phase, as well as homogeneously distributed in presumed zones of water level fluctuations. Fine-grained muddy or dusty plumes of Fe-precipitations on the inner surface of screen tubes in the field were found to be products of biological Fe-clogging that had been strictly excluded in the experimental model.

The mineralogical analyses revealed the Fe-encrustations produced in the experimental model to be of higher crystallinity than those sampled in the field. Whereas in the model goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) were primarily formed, the percentage of ferrihydrite (Fe₃(OH)₉·4H₂O) was higher in the field samples. Quickly precipitated ferrihydrite (δ'-FeOOH) was found in the laboratory samples only. With the XRD-measurements a gypsum phase was identified in the field samples, presumably originating from evaporation of residual mine water in the gravel pack of the sampled wells. The, however subtle, differences in mineralogy of the Fe-precipitates in the model occurred as a result of deviations in the hydrochemistry of the process water, especially the dominating anion (chloride in the model rather than sulphate or bicarbonate in the field) and the amount of dissolved silicon. As discovered with the computed hydrogeochemical model, apart from pH, the strongest effects on the reaction rate of Fe(II)-oxidation and Fe(III)-precipitation were the amount of dissolved oxygen in the process water as well as its pH-buffering content of bicarbonate.

The microscopic analyses showed the surface structure of the gravel grains to be responsible for the thickness of Fe(III)-hydroxide coatings. Especially irregularly formed monocrystalline quartz grains, weathered feldspar grains and polycrystalline quartzite grains were found to develop a higher thickness of Fe(III)-hydroxide coatings, when their surface area was uneven.

All of the different gruels and filter pack materials were found to perform similarly with respect to long-term elution as well as Fe-clogging affinity. Despite initial contents of ferric iron minerals in the Quaternary gravel materials, no significant autocatalytic effect of Fe(II)-oxidation and Fe(III)-precipitation was observed. Application of the alternative Quaternary gravel materials should therefore be possible without having to expect any substantial drawbacks or disadvantages when compared to the Tertiary Weilerswist gravel. However, application of the glass bead filter pack in the model did not result in a significantly higher performance with respect to Fe-clogging-affinity, when compared to the natural gravel.

164
materials. Therefore, amortisation of the high investment cost of a glass bead filter pack during the relatively short lifetime of a dewatering well is uncertain and can thus not be recommended for the dewatering wells in the Rhenish lignite district, where no regeneration methods are applied.

A promising concept for multi-layered dewatering was found in dewatering upper aquifers through the annular space and the screen pipe of the lower aquifer. Improved hydraulic conductivities and flow rates in the annular space – filled with gravel pack material instead of the usual filling material – were confirmed by tracer experiments in the field. The decreased Fe-clogging affinity of such wells was confirmed in the Fe-clogging model. Avoiding aeration of a shortened screen pipe in the last two LTTs lead to preclusion of Fe(II)-clogging, so long as the filter pack stayed fully saturated and the screen pipe submerged.

Further optimisation and automatisation of model operation could allow quicker evaluation of the Fe-clogging affinity of further well assembling materials and operating concepts. A more realistic situation could be simulated when considering sulphate or bicarbonate as the dominating anions. Matters that could be investigated by application of the proposed Fe-clogging model include optimising the screen pipe material and geometry, inert gas treatment and electrochemical methods for preventing chemical Fe-clogging, optimisation of regeneration measures, biological aspects of Fe-clogging and identification of relevant air-flow pathways.
9 Literature


German Institute for Standardization (DIN) [Ed.] (1983): *DIN 38406-1: German Standard methods for the examination of water, waste water and Sludge; cations (group E); determination of iron (E 1).* – Beuth, Berlin, 9 pp.

German Institute for Standardization (DIN) [Ed.] (1985): *DIN 38405-4: German standard methods for the examination of water, waste water and sludge; anions (group D); determination of fluoride (D 4).* – Beuth, Berlin, 16 pp.


German Institute for Standardization (DIN) [Ed.] (2005b): *DIN 38409-7: German standard methods for the examination of water, waste water and sludge - Parameters characterizing effects and substances (group H) - Part 7: Determination of acid and base-neutralizing capacities (H 7).* – Beuth, Berlin, 28 pp.


182


10 Appendices

Appendix 1  Exemplary PhreeqC-input file for the inflow water (1) and the five experimental columns (2-6) for scenario 1 (initial conditions) of the column experiments

DATABASE C:\Programme\USGS\Phreeqc Interactive 2.18.5570\database\phreeqc.dat
TITLE Scenario_1_02.04.12
SOLUTION_SPREAD
-units mg/l
No Temp pH pe C(4) Cl N(+5) S(6) Ca K Mg Na Al Fe Si
1 20 8.45 4 91.5 18.0 7.1 23 31.2 2.18 6.78 15.7 0.01 0.122 2.04
2 20 8.43 4 92.7 18.0 7 23 30.4 1.82 6.61 15.6 0.03 0.021 2.13
3 20 8.42 4 95.8 19.0 6.8 24 31.4 1.83 6.96 16.2 0.03 0.026 2.07
4 20 8.44 4 95.8 19.0 7.1 24 31.8 1.84 6.95 16.5 0.02 0.028 2.05
5 20 8.42 4 92.1 19.0 7.4 25 30.4 1.87 6.59 16 0.02 0.018 2.01
6 20 8.42 4 92.1 19.0 7.2 24 30.4 1.78 6.62 15.9 0.02 0.038 2.06

SELECTED_OUTPUT
-file Szenario_1.sel
-si Fe(OH)3(a) Goethite Siderite Gibbsite Calcite Albite Anorthite K-Feldspar Quartz Kaolinite Illite Manganite Rhodochrosite
-molarities Al(OH)4- Al(OH)3 Al(OH)2+ AlOH+2 Al3+ AlSO4+ Al(SO4)2- AlHSO4+2
-molarities Fe(OH)3 Fe(OH)4- Fe(OH)2+ FeOH+2 Fe3+ Fe2+
-molarities Mn+2 MnCO3 MnHCO3+ MnSO4 MnOH+ MnCl+ Mn+3
-molarities H4SiO4 H3SiO4- H2SiO4-2
END

Appendix 2  XRD scans of mineralogical reference materials (synthetic Fe(III)-hydroxides) provided by Prof. Thomas R. Rüde
Appendix 3  Exemplary PhreeqC-input file for the Fe-clogging experiments with kinetic Fe(II)-oxidation

**TITLE** Kinetically controlled oxidation of ferrous iron. Decoupled valence states of iron.

**SOLUTION_MASTER_SPECIES**

\[
\begin{align*}
\text{Fe}^{\text{di}} & \quad \text{Fe}^{\text{di}+2} \quad 0.0 \quad \text{Fe}^{\text{di}} \quad 55.847 \\
\text{Fe}^{\text{tri}} & \quad \text{Fe}^{\text{tri}+3} \quad 0.0 \quad \text{Fe}^{\text{tri}} \quad 55.847
\end{align*}
\]

**SOLUTIONSPECIES**

\[
\begin{align*}
\text{Fe}^{\text{di}+2} + \text{H}_2\text{O} & = \text{Fe}^{\text{di}+2} \quad \text{log}_k \ 0.0; \ \gamma \ 6.0 \quad 0.0; \ \text{-dw} \ 0.719e-9 \\
\text{Fe}^{\text{tri}+3} & = \text{Fe}^{\text{tri}+3} \quad \text{log}_k \ 0.0 \\
\text{Fe}^{\text{di}+2} \ + \ \text{H}_2\text{O} & = \text{Fe}^{\text{di}+2} \ + \ \text{H}^+ \quad \text{log}_k \ -9.5; \ \text{delta}_h \ 13.20 \quad \text{kcal} \\
\text{Fe}^{\text{di}+2} \ + \ \text{Cl}^- & = \text{Fe}^{\text{di}+2} \ + \ \text{Cl}^- \quad \text{log}_k \ 0.14 \\
\text{Fe}^{\text{di}+2} \ + \ \text{CO}_3^{\text{2-}} & = \text{Fe}^{\text{di}+2} \quad \text{log}_k \ 4.38
\end{align*}
\]
Fe\textsubscript{di}+2 + HCO\textsubscript{3}- = Fe\textsubscript{di}HCO\textsubscript{3}+; \quad \log_k \quad 2.0
Fe\textsubscript{di}+2 + SO\textsubscript{4}-2 = Fe\textsubscript{di}SO\textsubscript{4}; \quad \log_k \quad 2.25; \quad \delta_e \quad 3.230 \quad \text{kcal}
Fe\textsubscript{di}+2 + HS\textsubscript{O}4- = Fe\textsubscript{di}HS\textsubscript{O}4+; \quad \log_k \quad 1.08
Fe\textsubscript{tri}+3 + 2 HS\textsubscript{S} = Fe\textsubscript{di}(HS)\textsubscript{2}; \quad \log_k \quad 8.95
Fe\textsubscript{tri}+3 + 3 HS\textsubscript{S} = Fe\textsubscript{di}(HS)\textsubscript{3}--; \quad \log_k \quad 10.987
Fe\textsubscript{di}+2 + HPO\textsubscript{4}2- = Fe\textsubscript{di}HPO\textsubscript{4}; \quad \log_k \quad 3.6
Fe\textsubscript{di}+2 + H\textsubscript{2}PO\textsubscript{4} = Fe\textsubscript{di}H\textsubscript{2}PO\textsubscript{4}+; \quad \log_k \quad 2.7
Fe\textsubscript{di}+2 + F = Fe\textsubscript{di}F+; \quad \log_k \quad 1.0
Fe\textsubscript{tri}+3 + H\textsubscript{2}O = Fe\textsubscript{tri}OH+2 + H+; \quad \log_k \quad -2.19; \quad \delta_e \quad 10.4 \quad \text{kcal}
2 Fe\textsubscript{tri}+3 + 3 H\textsubscript{2}O = Fe\textsubscript{tri}2(OH)\textsubscript{2}+4 + 2 H+; \quad \log_k \quad -2.95; \quad \delta_e \quad 13.5 \quad \text{kcal}
3 Fe\textsubscript{tri}+3 + 4 H\textsubscript{2}O = Fe\textsubscript{tri}3(OH)\textsubscript{4}+5 + 4 H+; \quad \log_k \quad -6.3; \quad \delta_e \quad 14.3 \quad \text{kcal}

**PHASES**

**Melanterite** \(\text{Fe}_\text{di}SO_4:7\text{H}_2\text{O} = 7 \text{H}_2\text{O} + \text{Fe}_\text{di}+2 + \text{SO}_4-2\)
- \log_k \quad -2.209; \quad \delta_e \quad 4.910 \quad \text{kcal}

**Siderite** \(\text{Fe}_\text{di}CO_3 = \text{Fe}_\text{di}+2 + \text{CO}_3-2\)
- \log_k \quad -10.89; \quad \delta_e \quad -2.480 \quad \text{kcal}

**Ca-Siderite** \(\text{Ca}_0.1\text{Fe}_\text{di}0.9\text{CO}_3 = 0.1\text{Ca}+2 + 0.9\text{Fe}_\text{di}+2 + \text{CO}_3-2\)
- \log_k \quad -11.2

**Pyrite** \(\text{Fe}_\text{di}S_2 + 2 \text{H}+ + 2 \text{e}^- = \text{Fe}_\text{di}+2 + 2 \text{HS}^-\)
- \log_k \quad -18.479; \quad \delta_e \quad 11.300 \quad \text{kcal}

**Jarosite-K** \(K\text{Fe}_\text{tri}3(\text{SO}_4)2(\text{OH})6 + 6 \text{H}+ = 3 \text{Fe}_\text{tri}+3 + 6 \text{H}_2\text{O} + K+ + 2 \text{SO}_4-2\)
- \log_k \quad -9.21; \quad \delta_e \quad -31.280 \quad \text{kcal}

**Hematite** \(\text{Fe}_\text{tri}2O3 + 6 \text{H}+ = 2 \text{Fe}_\text{tri}+3 + 3 \text{H}_2\text{O}\)
- \log_k \quad 1.69; \quad \delta_e \quad -21.055 \quad \text{kcal}

**Goethite** \(\text{Fe}_\text{tri}OOH + 3 \text{H}+ = \text{Fe}_\text{tri}+3 + 3 \text{H}_2\text{O}\)
- \log_k \quad -1.0; \quad \delta_e \quad -14.48 \quad \text{kcal}

**Lepidocrocite** \(\text{Fe}_\text{tri}OOH + 3 \text{H}+ = \text{Fe}_\text{tri}+3 + 2 \text{H}_2\text{O}\)
- \log_k \quad 1.1225; \quad \delta_e \quad -14.93

**Schwertmannite** \(\text{Fe}_\text{tri}2O2.54(S\text{O}_4)0.46:2.4\text{H}_2\text{O} + 5.08 \text{H}+ = 2 \text{Fe}_\text{tri}+3 + 0.46 \text{SO}_4-2 + \frac{1}{494} \text{H}_2\text{O}\)
- \log_k \quad 2.01

**Akaganeite-Cl** \(\text{Fe}_\text{tri}(\text{OH})2.7\text{Cl}0.3 + 2.7 \text{H}+ = \text{Fe}_\text{tri}+3 + 2.7 \text{H}_2\text{O} + 0.3 \text{Cl}^-\)
- \log_k \quad 3.04

**Fe\textsubscript{tri}(\text{OH})3(a)** \(\text{Fe}_\text{tri}(\text{OH})3 + 3 \text{H}+ = \text{Fe}_\text{tri}+3 + 3 \text{H}_2\text{O}\)
- \log_k \quad 4.891

**Fe\textsubscript{tri}2L** \(\text{Fe}_\text{tri}2O2.145(\text{OH})1.71:1.06\text{H}_2\text{O} + 6\text{H}+ = 2\text{Fe}_\text{tri}+3 + 4.915 \text{H}_2\text{O}\)
- \log_k \quad 8.46

**Fe\textsubscript{tri}6L** \(\text{Fe}_\text{tri}2O2.465(\text{OH})1.07:0.89\text{H}_2\text{O} + 6\text{H}+ = 2\text{Fe}_\text{tri}+3 + 4.425 \text{H}_2\text{O}\)
-log_k 10.12

END

SOLUTION 1

-units mg/L  
-temp 15  
-pH 7.83  
-pe -2.83  
Fe_di 80  
Fe_tri 0.16  
Na 516  
Cl 962  
S(6) 20 as SO4-2  
Cl(4) 151.92 as HCO3-  
Si 0.79  
Ca 35  
Mg 6.96  
K 3.61  
Mn 0.274

EQUILIBRIUM_PHASES 1             #priority
O2(g) -1.39 1.0  #Cl  #SO4  
Goethite_tri 0.0 0.0  #1  #1  
Lepidocrocite_tri 0.0 0.0  #2  #2  
Schwertmannite_tri 0.0 0.0  #6  #5  
Akaganeite-Cl_tri 0.0 0.0  #7  #7  
Fe_tri(OH)3(a) 0.0 0.0  #4  #4  
Ferrhydrite_2L_tri 0.0 0.0  #3  #3  
Ferrhydrite_6L_tri 0.0 0.0  #5 #5, 5 - 6

RATES

Fe_di_ox -start

10 Fe_di = TOT("Fe_di")
20 if (Fe_di <= 0) then goto 200
30 p_o2 = SR("O2(g)")
40 moles = 2e13 * (ACT("OH-"))^-2 * p_o2 * Fe_di * TIME
200 SAVE moles -end

KINETICS 1

Fe_di_ox

-formula Fe_di -1.0 Fe_tri 1.0
-steps 0.0001 0.0004 0.0031 0.0108 0.0216 0.0504 0.0864 122*0.1728

INCREMENTAL_REACTIONS true

SELECTED_OUTPUT

-file ex9.sel  
-reset false

USER_PUNCH

-headings Cellno.[-] Fe(2)*10mg/L] pH[-] m_goethite[mg/cell] m_Fe(III)[mg/cell] O2[mg/L]
10 PUNCH SIM_TIME/1.76582, TOT("Fe_di")*1e2*55.845, -LA("H+"), /
   EQUI("Goethite_tri")*88.855*1e3*0.031196131, /
   EQUI("Goethite_tri")*1e3*55.845*0.031196131, TOT("O(0)")*1e3*16

USER_GRAPH

-headings Cellnumber[-] Fe(2)*10mg/L] pH[-] m_goethite[mg/cell]/
m_Fe(III)[mg/cell] O2[mg/L]
-chart_title "Oxidation of Ferrous Iron"
-axis_titles "Cellnumber [-]" "pH [-], Fe(2) [\times 10 \text{ mg/L}]" "O2 [\text{ mg/L}]",
m(Goethite, Fe(III)) [mg/cell]"
-axis_scale x_axis 0 12 1.0 0.5
-axis_scale y_axis 0 8 1.0 0.5
-axis_scale sy_axis 0 2 0.25 0.05
-start
10 GRAPH_X TOTAL_TIME/1.76582
 20 GRAPH_Y TOT("Fe_di")*1e2*55.845, -LA("H+"),
 30 GRAPH_SY EQUI("Goethite_tri")*88.855*1e3*0.031196131,/
    EQUI("Goethite_tri")*1e3*55.845*0.031196131, TOT("O(0)")*1e3*16
-end
END

Appendix 4
Progression of pH and eC in the in- and outflow (left) and difference of dissolved Al, Mn, Fe and Si between column in- and outflow of the duplicate columns for the Frimmersdorf and Dorsfeld gravel (right; negative values represent retardation of the corresponding element in the column, positive values represent release of the element from the column); yellow areas represent stop-flow-periods.
Appendix 5
Parameters during LTT 5 and 7: average hydrochemical parameters for each Fe-clogging step; average hydraulic parameters for each evaluation step (black bars: one standard deviation); average parameters over the whole LTT (MC I: measurement cell upstream of the flow channel, IC/OC: inflow/outflow chamber, $F_{\text{stock}}$: total input volume of Fe-stock solution (30 g L$^{-1}$), $\Delta F_{\text{total}}$: total Fe-retardation in the flow channel (integral over the Fe-clogging time)); optical progression of the clogging zones (*final report phase III*).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Unit</th>
<th>LTT 5</th>
<th>LTT 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>MC I</td>
<td>[mg L(^{-1})]</td>
<td>0.02 ± 0.01</td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td>DO</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>1.70 ± 0.47</td>
<td>1.67 ± 0.33</td>
</tr>
<tr>
<td>pH</td>
<td>MC I</td>
<td>[-]</td>
<td>8.05 ± 0.04</td>
<td>8.00 ± 0.03</td>
</tr>
<tr>
<td>pH</td>
<td>OC</td>
<td>[-]</td>
<td>6.54 ± 0.16</td>
<td>6.75 ± 0.15</td>
</tr>
<tr>
<td>Eh</td>
<td>MC I</td>
<td>[mV]</td>
<td>-151 ± 8</td>
<td>-235 ± 10</td>
</tr>
<tr>
<td>Eh</td>
<td>OC</td>
<td>[mV]</td>
<td>140 ± 28</td>
<td>79 ± 25</td>
</tr>
<tr>
<td>eC</td>
<td>MC I</td>
<td>[mS cm(^{-1})]</td>
<td>2.40 ± 0.05</td>
<td>2.44 ± 0.03</td>
</tr>
<tr>
<td>T</td>
<td>MC I</td>
<td>[°C]</td>
<td>15.2 ± 0.1</td>
<td>15.4 ± 0.1</td>
</tr>
<tr>
<td>h(_{OC})</td>
<td>OC</td>
<td>[mm]</td>
<td>39.2 ± 5.2</td>
<td>40.4 ± 2.3</td>
</tr>
<tr>
<td>Q(_{sys})</td>
<td>MC I</td>
<td>[L min(^{-1})]</td>
<td>1.054 ± 0.003</td>
<td>1.055 ± 0.014</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>IC</td>
<td>[mg L(^{-1})]</td>
<td>83.2 ± 3.0</td>
<td>83.5 ± 3.0</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>81.4 ± 3.1</td>
<td>80.9 ± 2.5</td>
</tr>
<tr>
<td>Fe(_{total})</td>
<td>Input</td>
<td>[L]</td>
<td>7.87</td>
<td>4.32</td>
</tr>
<tr>
<td>∫ΔFe(_{total}) ∆t</td>
<td>IC-OC</td>
<td>[g]</td>
<td>4.19 ± 4.36</td>
<td>6.39 ± 3.61</td>
</tr>
<tr>
<td>duration</td>
<td>-</td>
<td>[h]</td>
<td>41.8</td>
<td>40.2</td>
</tr>
</tbody>
</table>
Appendix 6 Parameters during LTT 6 and 8: average hydrochemical parameters for each Fe-clogging step; average hydraulic parameters for each evaluation step (black bars: one standard deviation); average parameters over the whole LTT (MC I: measurement cell upstream of the flow channel, IC/OC: inflow/outflow chamber, \( \Delta F_{\text{total}} \): total input volume of Fe-stock solution (30 g L\(^{-1}\)), \( \Delta F_{\text{total}} \Delta t \): total Fe-retardation in the flow channel (integral over the Fe-clogging time)); optical progression of the clogging zones (final report phase III)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Unit</th>
<th>LTT 6</th>
<th>LTT 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>MC I</td>
<td>[mg L⁻¹]</td>
<td>0.03 ± 0.01</td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td>DO</td>
<td>OC</td>
<td>[mg L⁻¹]</td>
<td>1.56 ± 0.43</td>
<td>1.50 ± 0.37</td>
</tr>
<tr>
<td>pH</td>
<td>MC I</td>
<td>[-]</td>
<td>7.85 ± 0.05</td>
<td>7.79 ± 0.04</td>
</tr>
<tr>
<td>pH</td>
<td>OC</td>
<td>[-]</td>
<td>6.58 ± 0.15</td>
<td>6.42 ± 0.06</td>
</tr>
<tr>
<td>Eh</td>
<td>MC I</td>
<td>[mV]</td>
<td>-213 ± 7</td>
<td>-217 ± 7</td>
</tr>
<tr>
<td>Eh</td>
<td>OC</td>
<td>[mV]</td>
<td>116 ± 26</td>
<td>111 ± 26</td>
</tr>
<tr>
<td>EC</td>
<td>MC I</td>
<td>[mS cm⁻¹]</td>
<td>2.84 ± 0.06</td>
<td>2.94 ± 0.04</td>
</tr>
<tr>
<td>T</td>
<td>MC I</td>
<td>[°C]</td>
<td>15.3 ± 0.1</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>hOC</td>
<td>OC</td>
<td>[mm]</td>
<td>40.1 ± 2.5</td>
<td>40.4 ± 3.7</td>
</tr>
<tr>
<td>Qsys</td>
<td>MC I</td>
<td>[L min⁻¹]</td>
<td>1.055 ± 0.019</td>
<td>1.051 ± 0.040</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>IC</td>
<td>[mg L⁻¹]</td>
<td>79.3 ± 3.9</td>
<td>82.1 ± 3.0</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>OC</td>
<td>[mg L⁻¹]</td>
<td>79.2 ± 3.9</td>
<td>77.8 ± 3.8</td>
</tr>
<tr>
<td>Fe_total</td>
<td>Input</td>
<td>[L]</td>
<td>7.38</td>
<td>5.02</td>
</tr>
<tr>
<td>∫ΔFe/Δt</td>
<td>IC-OC</td>
<td>[g]</td>
<td>2.11 ± 8.41</td>
<td>10.22 ± 5.20</td>
</tr>
<tr>
<td>duration</td>
<td>-</td>
<td>[h]</td>
<td>56.1</td>
<td>36.7</td>
</tr>
</tbody>
</table>
Appendix 7 Parameters during LTT 9 and 12: average hydrochemical parameters for each Fe-clogging step; average hydraulic parameters for each evaluation step (black bars: one standard deviation); average parameters over the whole LTT (MC I: measurement cell upstream of the flow channel, IC/OC: inflow/outflow chamber, $F_{\text{retal}}$: total input volume of Fe-stock solution (30 g L$^{-1}$), $\Delta F_{\text{total}} \Delta t$: total Fe-retardation in the flow channel (integral over the Fe-clogging time)); optical progression of the clogging zones (final report phase III)
### Parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Unit</th>
<th>LTT 9</th>
<th>LTT 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>MC I</td>
<td>[mg L(^{-1})]</td>
<td>0.02 ± 0.00</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>DO</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>1.35 ± 0.45</td>
<td>1.83 ± 0.27</td>
</tr>
<tr>
<td>pH</td>
<td>MC I</td>
<td>[-]</td>
<td>7.89 ± 0.03</td>
<td>7.84 ± 0.03</td>
</tr>
<tr>
<td>pH</td>
<td>OC</td>
<td>[-]</td>
<td>6.43 ± 0.13</td>
<td>6.60 ± 0.18</td>
</tr>
<tr>
<td>Eh</td>
<td>MC I</td>
<td>[mV]</td>
<td>-289 ± 12</td>
<td>-174 ± 13</td>
</tr>
<tr>
<td>Eh</td>
<td>OC</td>
<td>[mV]</td>
<td>215 ± 34</td>
<td>106 ± 38</td>
</tr>
<tr>
<td>eC</td>
<td>MC I</td>
<td>[mS cm(^{-1})]</td>
<td>2.62 ± 0.05</td>
<td>2.49 ± 0.06</td>
</tr>
<tr>
<td>T</td>
<td>MC I</td>
<td>[°C]</td>
<td>15.3 ± 0.1</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>h(_{OC})</td>
<td>OC</td>
<td>[mm]</td>
<td>40.2 ± 2.9</td>
<td>40.1 ± 2.3</td>
</tr>
<tr>
<td>Q(_{sys})</td>
<td>MC I</td>
<td>[L min(^{-1})]</td>
<td>1.053 ± 0.014</td>
<td>1.057 ± 0.016</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>IC</td>
<td>[mg L(^{-1})]</td>
<td>85.1 ± 3.3</td>
<td>78.1 ± 3.7</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>82.4 ± 3.1</td>
<td>74.2 ± 6.2</td>
</tr>
<tr>
<td>(\text{Fe}_{\text{total}})</td>
<td>Input</td>
<td>[L]</td>
<td>5.38</td>
<td>6.39</td>
</tr>
<tr>
<td>(\Delta\text{Fe}_{\text{total}})</td>
<td>IC-OC</td>
<td>[g]</td>
<td>7.10 ± 4.87</td>
<td>11.58 ± 8.63</td>
</tr>
<tr>
<td>duration</td>
<td>-</td>
<td>[h]</td>
<td>41.7</td>
<td>44.0</td>
</tr>
</tbody>
</table>
Appendix 8

Parameters during LTT 11 and 13: average hydrochemical parameters for each Fe-clogging step; average hydraulic parameters for each evaluation step (black bars: one standard deviation); average parameters over the whole LTT (MC I: measurement cell upstream of the flow channel, IC/OC: inflow/outflow chamber, $F_{\text{total}}$: total input volume of Fe-stock solution (30 g L$^{-1}$), $\Delta F_{\text{total}} \Delta t$: total Fe-retardation in the flow channel (integral over the Fe-clogging time)); optical progression of the clogging zones (final report phase III)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Unit</th>
<th>LTT 11</th>
<th>LTT 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>MC I</td>
<td>[mg L(^{-1})]</td>
<td>0.03 ± 0.00</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>DO</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>1.89 ± 0.20</td>
<td>1.86 ± 0.34</td>
</tr>
<tr>
<td>pH</td>
<td>MC I</td>
<td>[-]</td>
<td>7.82 ± 0.04</td>
<td>7.75 ± 0.04</td>
</tr>
<tr>
<td>pH</td>
<td>OC</td>
<td>[-]</td>
<td>6.48 ± 0.18</td>
<td>6.81 ± 0.12</td>
</tr>
<tr>
<td>Eh</td>
<td>MC I</td>
<td>[mV]</td>
<td>-206 ± 5</td>
<td>-160 ± 6</td>
</tr>
<tr>
<td>Eh</td>
<td>OC</td>
<td>[mV]</td>
<td>103 ± 25</td>
<td>127 ± 19</td>
</tr>
<tr>
<td>eC</td>
<td>MC I</td>
<td>[mS cm(^{-1})]</td>
<td>2.67 ± 0.03</td>
<td>2.37 ± 0.04</td>
</tr>
<tr>
<td>T</td>
<td>MC I</td>
<td>[°C]</td>
<td>15.2 ± 0.1</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>(h_{OC})</td>
<td>OC</td>
<td>[mm]</td>
<td>40.2 ± 2.2</td>
<td>40.3 ± 3.1</td>
</tr>
<tr>
<td>(Q_{sys})</td>
<td>MC I</td>
<td>[L min(^{-1})]</td>
<td>1.058 ± 0.026</td>
<td>1.056 ± 0.019</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>IC</td>
<td>[mg L(^{-1})]</td>
<td>79.9 ± 4.7</td>
<td>77.4 ± 4.1</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>76.2 ± 6.0</td>
<td>74.3 ± 3.8</td>
</tr>
<tr>
<td>(\Delta F_{total})</td>
<td>IC-OC</td>
<td>[g]</td>
<td>11.45 ± 7.62</td>
<td>11.09 ± 8.28</td>
</tr>
<tr>
<td>duration</td>
<td>-</td>
<td>[h]</td>
<td>46.2</td>
<td>51.5</td>
</tr>
</tbody>
</table>
Appendix 9

Parameters during LTT 14: average hydrochemical parameters for each Fe-clogging step; average hydraulic parameters for each evaluation step (black bars: one standard deviation); average parameters over the whole LTT (MC I: measurement cell upstream of the flow channel, IC/OC: inflow/outflow chamber, \( F_{\text{total}} \): total input volume of Fe-stock solution (30 g L\(^{-1}\)), \( \Delta F_{\text{total}} \): total Fe-retardation in the flow channel (integral over the Fe-clogging time)); optical progression of the clogging zones during the Fe-clogging test and the re-clogging after the interim experiment of “in-situ” dissolution of Fe-clogging products (*final report phase III*).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Unit</th>
<th>LTT 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>MC I</td>
<td>mg L⁻¹</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>DO</td>
<td>OC</td>
<td>mg L⁻¹</td>
<td>1.84 ± 0.21</td>
</tr>
<tr>
<td>pH</td>
<td>MC I</td>
<td>-</td>
<td>8.06 ± 0.03</td>
</tr>
<tr>
<td>pH</td>
<td>OC</td>
<td>-</td>
<td>6.91 ± 0.12</td>
</tr>
<tr>
<td>Eh</td>
<td>MC I</td>
<td>mV</td>
<td>-303 ± 7</td>
</tr>
<tr>
<td>Eh</td>
<td>OC</td>
<td>mV</td>
<td>145 ± 14</td>
</tr>
<tr>
<td>EC</td>
<td>MC I</td>
<td>mS cm⁻¹</td>
<td>2.67 ± 0.04</td>
</tr>
<tr>
<td>T</td>
<td>MC I</td>
<td>°C</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>h_OC</td>
<td>OC</td>
<td>mm</td>
<td>40.4 ± 3.8</td>
</tr>
<tr>
<td>Q_sys</td>
<td>MC I</td>
<td>L min⁻¹</td>
<td>1.059 ± 0.016</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>IC</td>
<td>mg L⁻¹</td>
<td>76.2 ± 4.0</td>
</tr>
<tr>
<td>c(Fe)</td>
<td>OC</td>
<td>mg L⁻¹</td>
<td>73.6 ± 4.2</td>
</tr>
<tr>
<td>Fe_total</td>
<td>Input</td>
<td>L</td>
<td>5.06</td>
</tr>
<tr>
<td>∫ΔFe_total Δt</td>
<td>IC-OC</td>
<td>g</td>
<td>8.72 ± 6.13</td>
</tr>
<tr>
<td>duration</td>
<td></td>
<td>h</td>
<td>47.6</td>
</tr>
</tbody>
</table>
Appendix 10 Parameters during LTT 15 and 16: average hydrochemical parameters for each Fe-clogging step; average hydraulic parameters for each evaluation step (black bars: one standard deviation); average parameters over the whole LTT (MC I: measurement cell upstream of the flow channel, IC/OC: inflow/outflow chamber, Fe$_{\text{total}}$: total input volume of Fe-stock solution (30 g L$^{-1}$), $\Delta$Fe$_{\text{total}}$ $\Delta$t: total Fe-retardation in the flow channel (integral over the Fe-clogging time)); optical progression of the clogging zones (final report phase III)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Unit</th>
<th>LTT 15</th>
<th>LTT 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>MC I</td>
<td>[mg L(^{-1})]</td>
<td>0.05 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>DO</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>1.62 ± 0.30</td>
<td>1.70 ± 0.23</td>
</tr>
<tr>
<td>pH</td>
<td>MC I</td>
<td>[-]</td>
<td>7.76 ± 0.08</td>
<td>7.68 ± 0.08</td>
</tr>
<tr>
<td>pH</td>
<td>OC</td>
<td>[-]</td>
<td>6.49 ± 0.30</td>
<td>6.21 ± 0.36</td>
</tr>
<tr>
<td>Eh</td>
<td>MC I</td>
<td>[mV]</td>
<td>-210 ± 19</td>
<td>-204 ± 8</td>
</tr>
<tr>
<td>Eh</td>
<td>OC</td>
<td>[mV]</td>
<td>120 ± 38</td>
<td>170 ± 38</td>
</tr>
<tr>
<td>eC</td>
<td>MC I</td>
<td>[mS cm(^{-1})]</td>
<td>2.30 ± 0.08</td>
<td>3.07 ± 0.02</td>
</tr>
<tr>
<td>T</td>
<td>MC I</td>
<td>[°C]</td>
<td>15.1 ± 0.2</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>(h_{OC})</td>
<td>OC</td>
<td>[mm]</td>
<td>40.6 ± 5.0</td>
<td>41.2 ± 3.7</td>
</tr>
<tr>
<td>(Q_{SYS})</td>
<td>MC I</td>
<td>[L min(^{-1})]</td>
<td>1.058 ± 0.022</td>
<td>1.060 ± 0.017</td>
</tr>
<tr>
<td>(c(Fe))</td>
<td>IC</td>
<td>[mg L(^{-1})]</td>
<td>81.1 ± 4.5</td>
<td>82.2 ± 4.2</td>
</tr>
<tr>
<td>(c(Fe))</td>
<td>OC</td>
<td>[mg L(^{-1})]</td>
<td>78.3 ± 4.4</td>
<td>79.0 ± 6.7</td>
</tr>
<tr>
<td>(Fe_{total})</td>
<td>Input</td>
<td>[L]</td>
<td>4.22</td>
<td>2.64</td>
</tr>
<tr>
<td>(\int \Delta F_{total} \Delta t)</td>
<td>IC-OC</td>
<td>[g]</td>
<td>7.80 ± 6.46</td>
<td>5.92 ± 4.29</td>
</tr>
<tr>
<td>duration</td>
<td>-</td>
<td>[h]</td>
<td>39.7</td>
<td>30.6</td>
</tr>
</tbody>
</table>
Appendix 11  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 4 (Weilerswist gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 12  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 5 (Weilerswist gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 13  Spatial distribution of Fe$_{tot}$-contents in LTT 5 as determined by the SEP analysis
Appendix 14  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 7 (Weilerswist gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 15  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 8 (Weilerswist gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 16  Spatial distribution of Fe_\text{tot}-contents in LTTs 6, 7 and 8 as determined by the SEP analysis
Appendix 17  
Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 9 (Frimmersdorf gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction; because no picture existed for layer 5 (resin impregnation layer), the relatively similar picture of layer 6 was copied.

Appendix 18  
Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 12 (Frimmersdorf gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 19  
Spatial distribution of Fe\textsubscript{tot}-contents in LTTs 9 and 12 as determined by the SEP analysis
Appendix 20  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 11 (Dorsfeld gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 21  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 13 (Dorsfeld gravel); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction; because no picture existed for layer 8, the similar picture from LTT 11 was copied.

Appendix 22  Spatial distribution of Fe* Contents in LTTs 11 and 13 as determined by the SEP analysis
Appendix 23  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 14 (Glass beads after “in-situ”-dissolution of Fe-clogging products and re-clogging); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 24  Spatial distribution of Fe\textsubscript{tot}-contents in LTT 14 (glass beads after “in-situ”-dissolution of Fe-clogging products and re-clogging) as determined by the SEP analysis, values in upper left corner of the right diagram were corrected as if this corner had been reached by the “in-situ”-dissolution of Fe-clogging products during the interim experiment.
Appendix 25  Sampling points (white dots with yellow numbers) in the layered excavation system of LTT 15 (glass beads with shortened screen pipe); height above channel bottom (z [mm]) printed below the individual pictures; x positive in flow direction

Appendix 26  Spatial distribution of Fe_{tot}-contents in LTT 15 (glass beads with shortened screen pipe and restricted air supply) as determined by the SEP analysis
Appendix 27  Thin section of a field sample taken at well 1C in transmitted polarised (left) and unpolarised (right) light

Appendix 28  Thin section of a field sample taken at well 2B in transmitted polarised (left) and unpolarised (right) light
Appendix 29  Thin section of a laboratory sample taken after LTT 3 (Weilerswist gravel) in polarised (left) and unpolarised (centre) transmitted light; coatings in impinging light (right)

Appendix 30  Thin section of a laboratory sample taken after LTT 6 (Weilerswist gravel) in transmitted polarised (left) and unpolarised (right) light
Appendix 31  Thin section of a laboratory sample taken after LTT 9 (Frimmersdorf gravel) in transmitted polarised (left) and unpolarised (right) light

Appendix 32  Thin section of a laboratory sample taken after LTT 11 (Dorsfeld gravel) in transmitted polarised (left) and unpolarised (right) light
Appendix 33

Thin section of a laboratory sample taken after LTT 14 (glass beads) in transmitted polarised (left) and unpolarised (right) light

Appendix 34

Sensitivity of the reaction rates modelled with PhreeqC on the dominating anion and its concentration, considering chloride and sulphate.

Appendix 35

Sensitivity of the PhreeqC-model with respect to temperature; red: actual situation in the flow channel.
Appendix 36  Sensitivity of the PhreeqC-model with respect to DO (top) and c(Fe(II)) (bottom) compared to the actual conditions in the flow channel (centre, red)

Appendix 37  Sensitivity of the PhreeqC-model with respect to pH; red: actual situation in the flow channel

Appendix 38  Sensitivity of the PhreeqC-model with respect to temperature; red: actual situation in the flow channel
Appendix 39  Continuous injection of tracer and rinsing water ($Q_w$) into the piezometer in the annular space of wells H 1301 and H 1712 with annular space dewatering and measurement of tracer passage at the top of the well (normalised to the maximum concentration); the red and black arrows mark the times of arrival of half the maximum tracer concentration and of the change from tracer solution to rinsing water, respectively (report annular space dewatering, 2013).