

Aluminium release by water-rock interaction during hydraulic tests in a siliciclastic aquifer in Berlin (Germany)

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Abstract. Two hydraulic tests of a Triassic sandstone aquifer were performed to determine hydraulic and geochemical parameters of the reservoir formation. Samples collected during all tests showed neutral and constant pH-value of about 7.5. During the initial step rate test, the aluminium concentration of the water remained below 0.005 mM, but it increased significantly during the production phase of the following single well push-pull test to 4.8 mM. Drill cuttings of the well, collected at reservoir depth (Exter Fm. and the overlaying Tertiary sand), were additionally characterized and used for leaching experiments. These experiments evidenced a strong release of aluminium from the Tertiary, pyrite containing sand, indicating processes of pyrite oxidation being responsible for aluminium mobilization.

1 Introduction

In 2016 a research well (GtBChb 1/2015) was drilled to a depth of 259 m to investigate the possibility of using the Upper Triassic Exter sandstone as test site for aquifer thermal energy storage (ATES) in an urban area (Berlin, Germany). The Exter Fm. (Fig. 1) is represented by a grey, fine-grained to silty, poorly cemented, and well-sorted quartz sandstone interbedded with silty layers with the highest porosity of 30 % between 221.7 m and 225.7m depth [1]. This formation is separated from the hanging aquitard (Tertiary Rupelton Fm.) by a thin, sand and lignite containing, dark-brown Tertiary sand (TS) at a depth between 212.5 and 213.8 m that showed an artesian discharge during drilling [1]. Although only the section of the Exter Fm. was filtered between 220 m and 230 m, a hydraulic connection between the two formations - either in the reservoir or via the gravel pack (Fig. 1) cannot be excluded.

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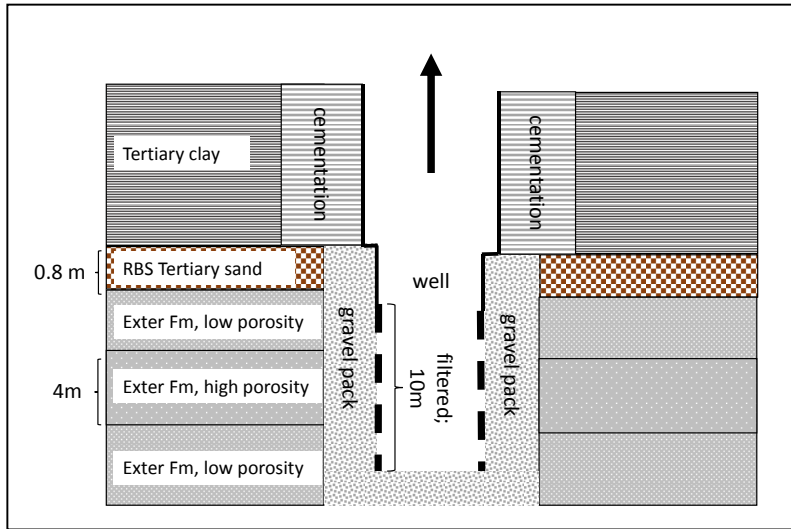


Fig. 1. Simplified scheme of the well (GtBChb 1/2015) and stratigraphic layers at near reservoir depth (~210-250 m).

2 Materials and Methods

2.1 Tests and water sampling

For intermediate water storage of the step rate test (SRT) and the single well push pull test (PPT), three 28 m³ containers (C1, C2, C3) were installed on the site. First, 37 m³ of groundwater was pumped out of the reservoir and discarded. Afterwards (27th of September 2017), C1 and partly C2 were filled by producing 35 m³ water from the reservoir. The SRT started on the 28th of September 2017 by producing over 10 h subsequently 2, 3, 5, and 6 m³/h water (altogether 38.4 m³), which was filled into C2 and C3. Finally another 19.7 m³ were produced (6 m³/h) and filled into C3. For the PPT, a tracer mixture (5992 g NaI, 160 g Eosine Y; 3396 g NaNO₃) was first dissolved in 250 L water, which was pumped into C2 and circulated there for a few hours. On the 4th of October 2017 the water was injected from the three containers into the reservoir (flow rate: 7 m³/h) starting with C1 (no tracer), followed by the tracer-yielding C2 and finally by the water of the tracer-free C3 (“chaser”). Twelve hours later, the water was extracted (6 m³/h) until 300 m³ water were removed.

During both, production and injection phase of the tests, samples were continuously collected and pH-value, redox, electric conductivity, and O₂ content were monitored. Bicarbonate (HCO₃⁻) was measured by quick tests (Merck Millipore). Samples for inorganic cations and anions as well as for dissolved organic carbon were quickly transported to the lab and frozen. Before analysis they were filtered (0.45 μm) and a subsample was acidified.

2.2 Analytics of aqueous samples

Metals (Al, Ca, Fe, K, Mg, Mn, Na,) were analysed in acidified solution by ICP-OES (inductive coupled plasma optical emission) spectroscopy and nitrate (NO₃⁻) by CFA (Continuous-Flow Analysis). Other anions and organic acids were measured by IC (ion chromatography) and dissolved organic carbon (DOC) was quantified by LC-OCD (liquid

chromatography - organic carbon detection). Isotope analyses of water isotopes ^{18}O , and ^2H were performed in selected water samples by mass spectroscopy.

2.3 Rock characterization

Cutting samples from the Triassic Exter formation and from the Tertiary Sand (collected during well drilling in 2016) were geochemically analysed by X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscopy (SEM), and by mass spectrometry for total and organic carbon (TC and TOC).

A leaching experiment was conducted to estimate metal mobilization from formation rocks. For these tests, samples (TS and Exter cuttings) were dried at 105°C and ground to a powder. Each 5 g were added to 10 mL electrolyte (0.5 M NaCl) or to electrolyte plus tracer mix (NaCl-T). The pH-values were measured before and after 24 h of continuously shaking in each sample. Afterwards, the suspensions were filtered ($0.45\ \mu\text{m}$) and acidified to $\text{pH} < 2$ for analysing Al- und Fe concentration.

3 Results

3.1 Monitoring the hydraulic tests

During the SRT the electric conductivity (EC) of the produced water increased from 40.1 to 42.0 mS/cm. Dissolved oxygen (DO) and redox values decreased from 2.6 to 1.4 mg/L and -188 mV to -200 mV, respectively and the pH value was constant between 7.48 and 7.53. Most cations and anions varied slightly over time without any clear tendencies. Dominant ions are Na and Cl (both $>320\ \text{mM}$), followed by SO_4 ($\sim 13\ \text{mM}$) and bicarbonate (5.5 to 6.9 mM). Nitrate, Al, and Mn were all at concentrations $< 0.005\ \text{mM}$ (Fig. 2). DOC varied during the step rate test between 3.2 and 5.8 mg/L, and the content of organic acids was below the detection limit.

During injection of the PPT, pH and EC, remained relatively constant within the three containers (7.4 - 7.57; 42.2 - 42.6 mS/cm). The DO ranged between 3 and 10 mg/L and redox between -60 and +174 mV. Iron was generally close to detection limit with the exception of samples from container 1, where up to 3 mM Fe were measured (Fig. 2). The Al concentration was generally low (0.01 -0.09 mM; Fig 2).

Twelve hours later, the water was back-produced from the reservoir (PPT, pull phase). The pH and EC were stable (7.3 to 7.6 and 42.6 mS/cm) and the redox decreased from +23 mV to -64 mV. The nitrate tracer was measurable from the very beginning in the samples and increased until production of $55.2\ \text{m}^3$ to a maximum of 0.89 mM. Afterwards it decreased down to 0.08 mM (after $300\ \text{m}^3$; Fig. 2). Na, Cl, Ca, Mg, and SO_4 correlated roughly with each other and the DOC was about 5 mg/L. While the Fe concentration remained constantly low (about 0.0002 mM), Al varied strongly: until production of $19\ \text{m}^3$ it remained relatively constant (0.02 mM) then increased afterwards to up to 3.9 mM (at $50.5\ \text{m}^3$) followed by an immediate decrease down again to 0.02 mM at $52.8\ \text{m}^3$, which remained constant until production of $207\ \text{m}^3$ (here, the pump was switched on again a production break), when it increased again to 4.7 mM at $225\ \text{m}^3$, dropped down to 0.9 mM at $262\ \text{m}^3$ and roughly remained at this order of magnitude until the end of the production phase.

The isotopic ratios of water of ten fluid samples collected during the tests showed very constant data of δD of about $-61\ \text{‰}$ SMOW and $\delta^{18}\text{O}$ of $-9\ \text{‰}$ SMOW.

3.2 Rock characterization and leaching test

The rock samples from the Exter Fm. are predominantly composed of quartz with traces of kaolinite, montmorillonite, and calcite. The TS contains pieces of coal, quartz and pyrite. The elemental composition of the two rock types is given in Table 1.

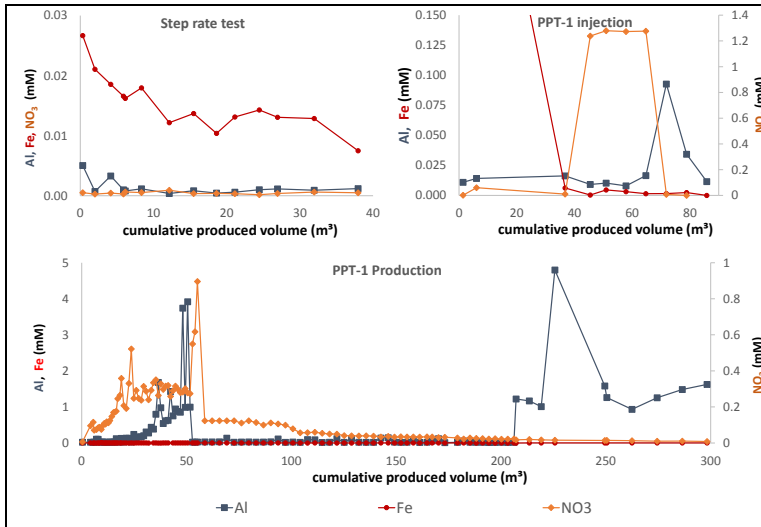


Fig. 2. Concentrations of Fe, Al, and NO₃ during SRT, PPT-injection and PPT production.

Table 1. XRF analysis of Exter (Ex) and Tertiary Sands (TS) cuttings.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	Cl
Ex₁	63.9	20.8	3.54	3.44	2.44	1.65	1.55	1.17	0.7	0.35
Ex₂	70.7	19.1	2.45	1.78	1.75	1.31		1.07	0.11	0.16
TS	42.8	17.75	23.32	0.95	3.1	2.03	1.86	0.75	5.5	1.14

The carbon content of the Exter Fm. samples was 3 to 4 % (TIC as calcite) and 0.5 to 1.8 % TOC, whereas the TS contained a TOC of 6.4 and 9 % TC (as calcite). Analysis by SEM/EDX revealed that components in the Exter Fm. are indeed mainly quartz and aluminosilicates. The TS also contained gypsum and pyrite.

The pH measured both, immediately and 24 hours after the rock cuttings were added into the electrolytes remained around neutral for the Exter Fm samples but decreased strongly for the TS (~ 4; Fig. 3). Similarly, the Fe and Al concentrations increased strongly in the TS samples but remained low after reaction with the Exter (Fig. 3). The effect of the tracer-mix on pH, Al, or Fe concentration was, however not significant.

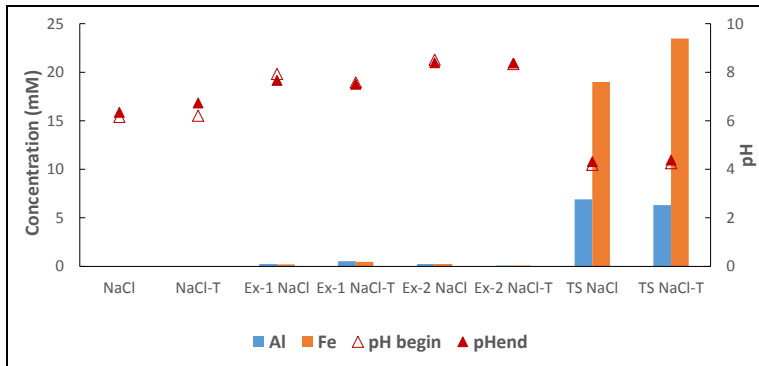


Fig. 3. Release of Fe and Al after reaction for 24 h with 0.5 M NaCl or NaCl +Tracer (T) mix.

4 Discussion and Conclusion

Since the isotopic ratios of water (δD and $\delta^{18}O$) remained constant in all collected aqueous samples, a well-mixed groundwater that was in equilibrium before well drilling and injection tests can be assumed for the site. The mobilization of Al from the reservoir during the PPT production phase can be explained by the following processes: The injected water passed - possibly via the gravel pack - into the TS (Fig.1). The pyrite (FeS_2) within this formation undergoes oxidation induced by the O_2 -rich water. This oxidation possibly began already during drilling the well in 2016. Pyrite oxidation [2] was followed by precipitation of Fe(III) hydroxides (explaining why hardly any Fe was measured) and the release of protons. The acid would be consumed by dissolution of clay minerals (explaining the neutral pH value in collected field samples), which in turn releases Al. Based on the fact that Al^{3+} is not stable at neutral pH (it precipitates either as gibbsite or as alunite) we assume the formation of colloids consisting of gibbsite ($Al(OH)_3$, alunite ($KAl_3(SO_4)_2(OH)_6$), or bound to the organic phase. The colloidal Al species are of small particle size (e.g. about 50 nm; [3]) and would thus pass the filters ($<0.45 \mu m$) but would re-dissolve after acidification before ICP analysis.

These processes and observations demonstrate the strong impact of oxygen input on water composition during hydraulic aquifer testing. The strong release of Al could result in enhanced precipitation and thus clogging of the reservoir pores during future operation of the site as ATES.

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