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Hydrogeochemistry of prolonged deep well injection and subsequent aquifer storage in pyritiferous sands; DIZON pilot, Netherlands

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ABSTRACT: A deep well injection experiment was conducted at the DIZON pilot plant in the Southern Netherlands, using pretreated canal water. It consisted of 2 phases: (a) a flushing phase during the first 938 days, with continuous injection by one well and continuous pumping by a 98 m distant well; and (b) an aquifer storage phase during the next 106 days (no injection, no pumping). The oxidized zone around the injection well, which developed during the flushing phase, vanished during the aquifer storage phase by slowly reacting pyrite and organic material (OM). Subsequently iron, manganese and ammonium dissolved from the aquifer. Analyses of water pumped out of the injection well demonstrate that significant amounts of iron(hydr)oxide and OM accumulated around the injection well (< 5m). The iron(hydr)oxides were, partly, residues from the coagulation process in the pretreatment, and OM was composed of biological inputs from the activated carbon filtration step in the pretreatment.

1 INTRODUCTION

The water supply companies WOB and WML, investigated with Kiwa the feasibility of deep well recharge of canal water for preparation of drinking or industrial water in the Southern Netherlands.

The pilot plant comprised an intake, a pretreatment facility, an injection well, 4 multilevel observation wells, a 98 m distant pumping well, and a discharge of the recovered water to a storage pond.

The deep well experiment started on July 8, 1996 and ended on May 20,1999. This period consists of 2 phases: (a) a flushing phase during the first 938 days, with continuous injection (30 m^3/h) and continuous pumping by the other well (30 m^3/h); and (b) an aquifer storage phase during the next 106 days (no injection, no pumping).

The flushing phase simulates a recharge scheme with separate, distant injection and recovery wells. The aquifer storage phase simulates a single well ASR system as defined by Pyne (1995).

The various tests, measurements and results, including those on well clogging, well regeneration and pathogen transport in the aquifer, have been summarized by Stuyfzand *et al*. (2001). The focus is here on the water-sediment reactions which transform water quality and thereby necessitate post-treatment in case of drinking water production. These reactions may render the technique of deep well injection or ASR cost ineffective.

2 THE TARGET AQUIFER

The sandy target aquifer is situated at 273-312 m below land surface, below a 50 m thick clay layer, and above a 3 m thick clay layer. This aquifer is composed of Upper Miocene sands (200 - 380 μm). The stratification within the aquifer is shown in cross section in Fig.1. The total transmissivity is 510 m^2/d, with horizontal permeability of the main strata varying from 4 to 25 m/d (Fig.1).

The sediment is deep anoxic, pyritiferous, near-neutral (pH 6.7) and very poor in $CaCO_3$ (<0.001 - <0.3 % d.w.). The geochemical reactivity of the sands is dictated by: pyrite (230-4640 mg S/kg d.w.), natural organic material (NOM 0.1-0.4% d.w.), and exchangeable cations (CEC 4-50 meq/kg d.w.). The bulk of the sands is inert quartz (>90% d.w.). Of the 5 aquifer zones, the upper zone contains most NOM and the lower zone has the highest pyrite content, which is more reactive than pyrite in the other zones. The chemical composition of native groundwater in the target aquifer is shown in Table 1.

3 THE INJECTION WATER

Water from the canal Zuid-Willemsvaart was pretreated in 7 steps, including a.o. coagulation (using $FeCl_3$), active carbon filtration and, as the last step, slow sand filtration. The latter was questioned and disconnected after 1 year of operation.

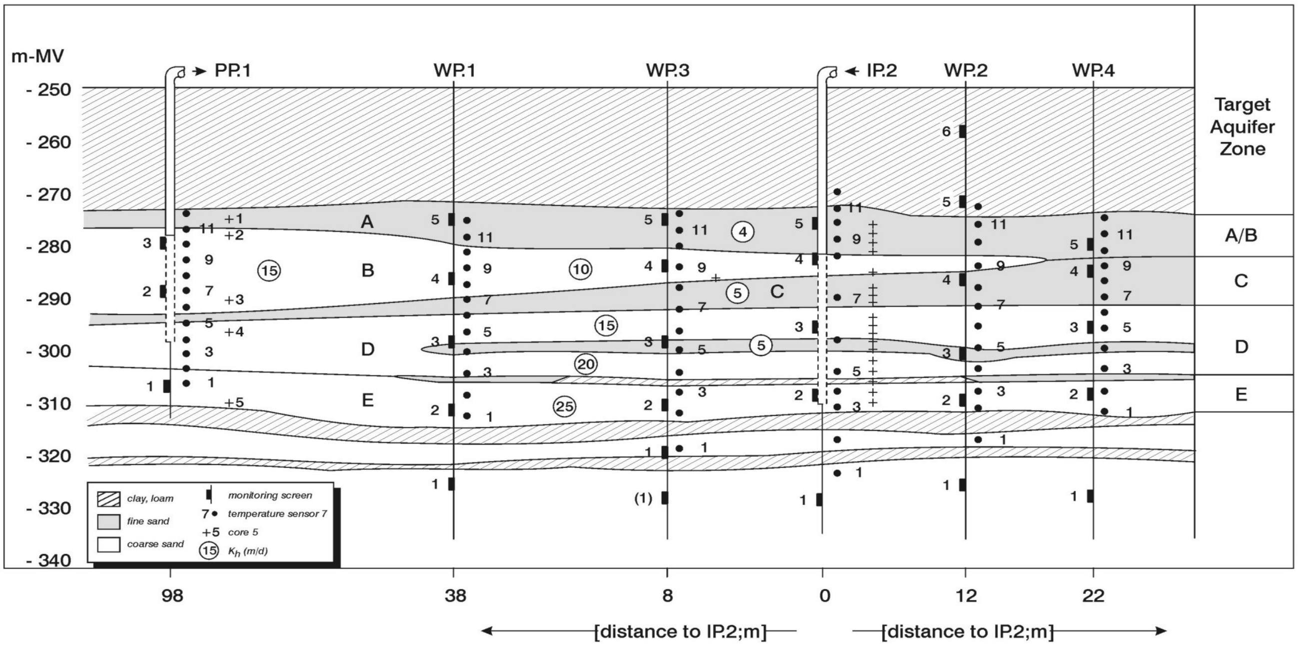

Figure 1. Position of the injection well (IP.2), monitoring wells (WP.1-4) and recovery well (PP.1) in cross section, showing well screens, temperature sensors, stratification of target aquifer, permeability distribution (K_h in m/d) and aquifer cores.

The mean composition of the effluent of pretreatment is given in Table 1. The best tracers of this infiltration water were: Cl^- (60-100 mg/l versus 6 mg/l), HCO_3^- (117 versus 330 mg/l) and temperature. Strong seasonal fluctuations in the input (2-23 ^{o}C) could be recognized by the temperature sensors shown in Fig.1. Temperature fronts moved 50% slower than Cl-fronts, so that its frequent measurements could be easily transformed into travel times. Results of tracing are shown in Fig.2.

4 QUALITY CHANGES DURING FLUSHING

The oxic influent changed, in the initially deep anoxic aquifer, mainly by redox reactions and cation exchange. Acid was formed during the redox reactions, and was buffered by HCO_3^- already present in the canal water. This showed that $CaCO_3$ was inaccessible for reaction or was absent.

Pyrite oxidation was the predominant redox reaction, followed by the oxidation of natural organic matter (NOM). Arsenic, cobalt and zinc were not mobilised, probably due to their scavenging by neoformed iron(hydr)oxides.

The resulting nitrate consumption and sulphate production showed a clear increase with travel time in the aquifer, suggesting that the kinetics of the redox reactions are slow. Oxygen was used in each aquifer zone within 3 days, whereas nitrate needed 10-20 days in the most reactive zones (A and E) and >50 days in the less reactive zones (B and D). Denitrification was dominated by unstabilized NOM in zone A, and by labile pyrite in zone E.

Table 1. Mean composition of the native groundwater, influent (input), the infiltrate as sampled from 4 observation wells, and the raw water from the recovery well. Mean values for the first year of injection, recovery well PP.1 after 2.3 years.

	unit	INPUT	AFTER 8 m IN AQUIFER (WP.3)				RECOVERY	NATIVE
		IP.2	276 m (f5)	285 m (f4)	299 m (f3)	311 (f2)	PP.1	PP.1
aquifer zone			**A**	**B**	**D**	**E**	**A – E**	**A – E**
travel time	**d**	**0**	**4**	**2.5**	**3**	**3**	**253 – 800**	**-**
pore flushes	**n**	**-**	**2 - 84**	**2 – 146**	**2 – 121**	**2 - 112**	**3.4**	**0**
pH-field	**-**	**7.12**	**6.74**	**6.79**	**6.77**	**6.71**	**6.45**	**6.55**
O_2-field	**mg/L**	**9.9**	**0.3**	**0.4**	**1.6**	**<0.3**	**<0.5**	**<0.5**
Cl^-	**mg/L**	**82.6**	**80.8**	**81.1**	**81.2**	**82.3**	**56**	**6**
SO_4^{2-}	**mg/L**	**62.4**	**76.4**	**76.1**	**75.2**	**83.7**	**53**	**5**
HCO_3^-	**mg/L**	**118**	**106**	**106**	**102**	**102**	**180**	**330**
NO_3^-	**mg/L**	**19.4**	**13.2**	**16.8**	**17.4**	**14.0**	**<0.5**	**<0.5**
Fe	**mg/L**	**0.02**	**0.55**	**0.38**	**0.30**	**0.56**	**4.3**	**5.6**
Mn	**mg/L**	**0.006**	**0.38**	**0.19**	**0.04**	**0.06**	**0.18**	**0.24**
NH_4^+	**mg/L**	**0.07**	**0.08**	**0.10**	**0.08**	**0.08**	**0.25**	**0.30**
SI-calcite	**-**	**-0.60**	**-1.09**	**-0.97**	**-1.02**	**-1.15**	**-0.93**	**-0.55**

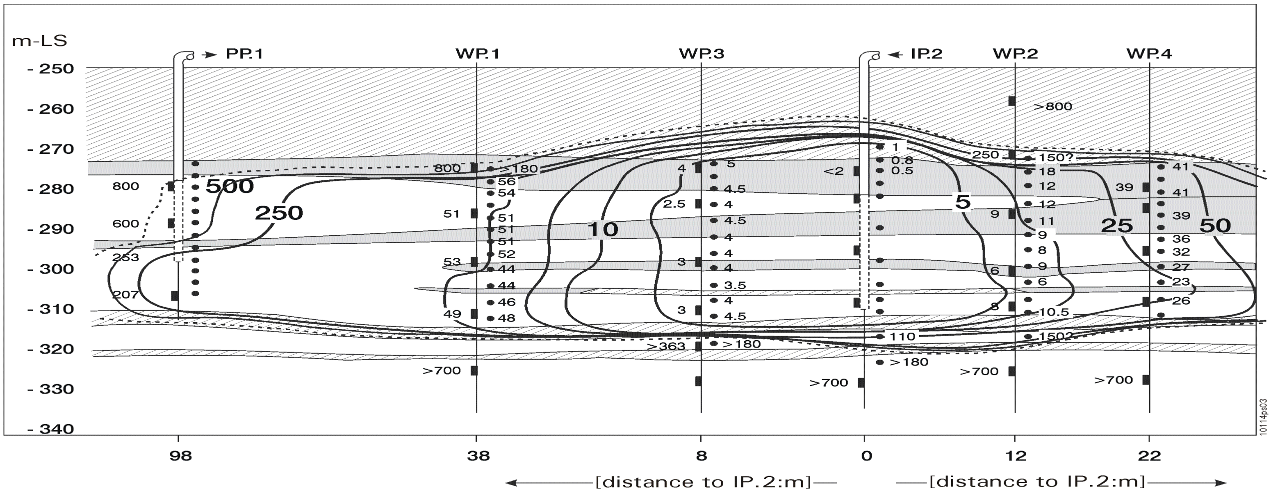

Figure. 2. Spatial distribution of the infiltrate in the target aquifer after 826 days of injection (on October 13, 1998), with isochrones (in days) and indication of the observed travel time to the observation points.

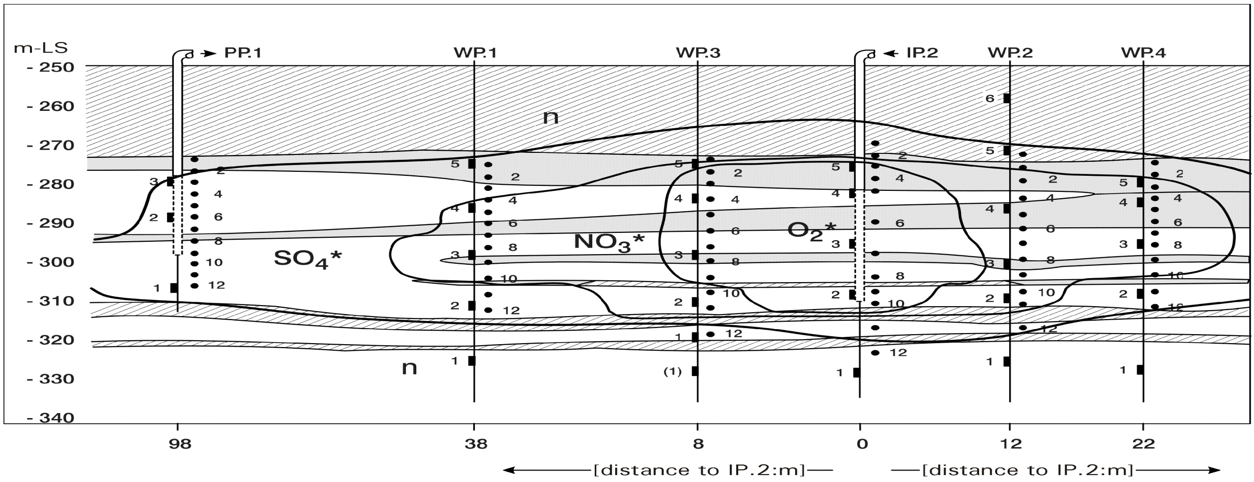

Figure 3. Redox zoning of the canal water injected into the Miocene sand aquifer, in October 1998 after 2.3 years of practically undisturbed recharge operation. O_2* = containing oxygen (decreasing from 10 to 0 mg/L with distance from the injection well) and nitrate; NO_3* = containing nitrate (decreasing from ca. 20 to 0 mg/L with distance); SO_4* = containing sulphate (higher concentration than in input, due to pyrite oxidation); n = native groundwater.

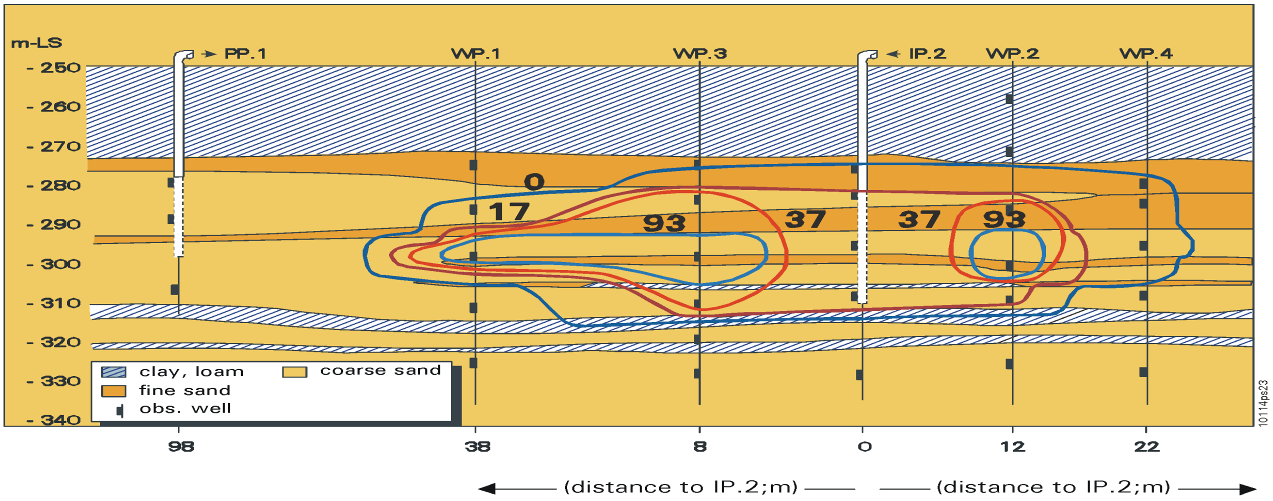

Figure. 4. Shrinkage of the (sub)oxic zone in the target aquifer during stand still (storage), directly after 938 days of continuous injection of oxic surface water. Isolines indicate position of NO_3 front 0, 17, 37, 93 days after injection stopped.

5 QUALITY CHANGES DURING STORAGE

After flushing, during storage, the (sub)oxic zone around the injection screen vanished (Fig.4), by reaction of O_2 and NO_3^- with slowly reacting pyrite and NOM. Subsequently iron, manganese and ammonium dissolved from the aquifer (Fig.5). Anoxic conditions returned first in zone A containing much labile NOM, second in zone E with much labile pyrite, third in zone B, and ultimately in zone D (lowest in FeS_2 and NOM content).

In zone A (WP.3-f5 in Fig.1) concentrations of HCO_3^-, Fe^{2+}, Mn^{2+} and NH_4^+ clearly increased, while O_2 and NO_3^- remained <0.5 mg/l (Fig.5). This indicates, in combination with constant SO_4^{2-} levels and a pH increase (not shown), that $Fe(OH)_3$ oxidized organic matter. This involves neoformed $Fe(OH)_3$ from pyrite oxidation during the injection phase or from the input, and NOM in the aquifer or freshly introduced organic matter from the input.

Denitrification during storage was slower than during injection: it was 10-20 times slower at 8 m (WP.3), 2-4 times slower at 12 m (WP.2) and 2 times slower at 38 m (WP.1). This is explained by leaching of FeS_2 and NOM during injection, especially close to the injection well, and by stagnant conditions during stand-still, which lower reaction rates.

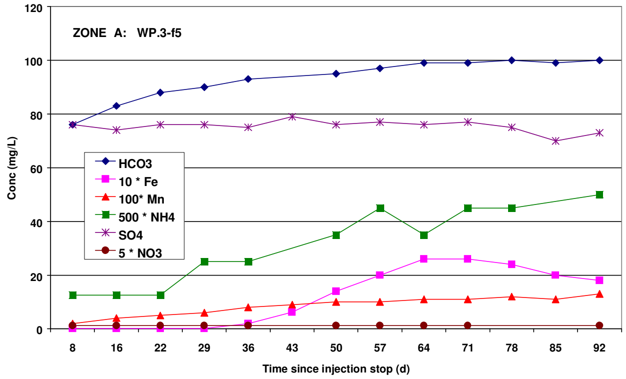

Figure 5. Quality changes in the injected bubble in zone A at 8 m from the injection well during stand-still (storage).

6 QUALITY AFTER REGENERATION

The injection well was mechanically regenerated 5 times during the flushing phase, and once after the storage phase. On each occasion water was pumped out at 215 m^3/h for at least 20 minutes.

During regenerations 1 to 5 high concentrations of tiny invertebrates, oxidized iron and manganese particles, and dissolved iron were measured in the water that was pumped out. The water that was pumped out after the storage phase showed higher concentrations of dissolved Fe^{2+}, Mn^{2+}, NH_4^+ and TOC (Fig.6), about 2-10 times higher than the native groundwater and 3-400 times more than observed in the closest observation well (WP.3) at the end of the storage phase monitoring. This is explained by oxidation of deepbed-filtrated organic matter (from the input) first through O_2 and NO_3^- and then through iron(hydr)oxides (either the oxidation product of pyrite or deepbed-filtered iron flocs). The water pumped back during regenerations 1 and 2 did not show these extremes (Fig.6).

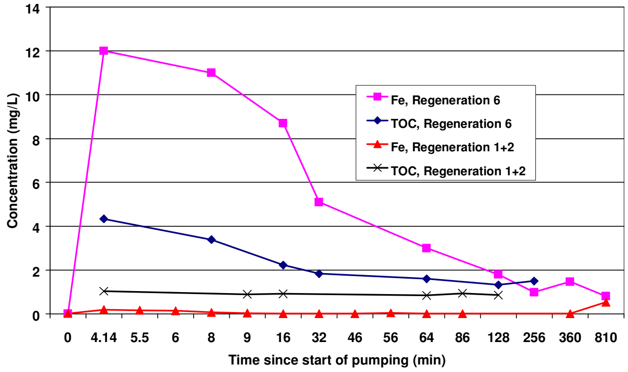

Figure 6. Quality of water pumped out during regenerations 1 and 2 (injection phase) and 6 (after storage phase).

7 CONCLUSIONS

The relatively rapid return to anoxic conditions in the injected bubble, in aquifer zones A and E, after 2.5 years of uninterrupted flushing with oxic infiltration water may affect the feasibility of single well Aquifer Storage and Recovery in this type of reactive aquifer. The very high concentrations of dissolved iron, manganese and ammonium in water pumped out after 106 days of storage are also discouraging.

Measures to raise the feasibility of ASR should focus on eliminating iron(hydr)oxide flocs and biological inputs by proper pretreatment. The activated carbon filtration (ACF) considerably reduced the concentrations of most organic micropollutants, but also generated biological problems when the polished of its effluent by slow sand filtration (SSF) ceased. Without SSF many invertebrates which develop in active carbon filters, passed the pretreatment system and were injected. These organisms contributed to the plugging of the well and immediate aquifer surroundings. In addition iron(hydr)oxides which formed during coagulation were only partially removed by flotation and ACF. SSF helped to further reduce their load and thereby their contribution to well clogging.

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