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(Environmental) Impact Of Inhibitors Applied In The Geothermal Sector In The Netherlands

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ABSTRACT

At this moment there are 18 geothermal sites in operation in the Netherlands. Nearly all sites dose corrosion inhibitor at the bottom of the production well to protect the carbon steel based production and injection wells from corrosion. Though these corrosion inhibitors are considered effective as they significantly reduce the corrosion rates, the environmental impact can also be significant as these chemicals have a biocide capacity. Three leakage routes of inhibitors into the environment were found that had an average risk level or higher after a Hazard Operability (HAZOP) analysis. These three leakage routes were all found on the injection side, as the injection side has overpressure and is not monitored continuously.

The first leakage route is to the production aquifer after re-injection in the injection well. It is unknown how much residual inhibitor will reach the production aquifer as monitoring of the injection well (including inhibitor concentration) is not performed on a continuous basis.

The second and third risk are also situated in the injection well. Again, as no online monitoring is performed in the injection well and as this well is operating under pressurized conditions (2 - 50 bar) there is the risk of unnoticed leakages for a period of up to three years to fresh and brackish aquifers. Therefore, both ecosystems and other extractions (e.g. drinking water extraction) in these aquifers might be influenced. In case of leakages not only the inhibitor itself is considered toxic but also the production fluid. However, the relative concentration of inhibitor compared to other toxic components in the production fluid, applying the signalling values in the Dutch drinking water guideline (Drinkwaterbesluit), can be up to twenty times higher.

1. INTRODUCTION

The use of geothermal energy for heat supply purposes has developed tremendously in the recent 10 years in the Netherlands. The first geothermal site was taken in operation in 2007 and at this moment there are already 18 geothermal sites active. Even more, the Netherlands have developed a masterplan geothermal energy. (1) This masterplan describes the strong ambition to increase the amount of sites to ~175 in 2030 and ~700 in 2050. This exponential increase corresponds to an overall energy production of 200 petajoule per year in 2050. As the sector is relatively young, it is important to learn the lessons now and mitigate any upcoming risks such that a sustainable future can be build.

One of the risks in the geothermal sector is the decrease of integrity of the geothermal installations, which can, among other measures, be mitigated by the use of inhibitors. Inhibitors are chemicals that protect against corrosion, scaling and/or biological growth. In our research, both the technical and the environmental impact of these inhibitors in the geothermal sector in the Netherlands are investigated.

2. PROCESS CONFIGURATION

In order to understand how inhibitors can have an impact on the environment, first knowledge on the geothermal installation and components present in the geothermal fluid has to be obtained. In Figure 1 a schematic representation of a geothermal installation is shown. On the left side the production well is drawn and on the right side the injection well; the reservoir depth is between 1500 - 3000 m. As the static water level is 50 - 240 m below ground level, an electric submersible pump (ESP) is used to pump the fluid to the surface, resulting in under pressure at the production site. After the hot fluid is pumped to the earth surface it is filtered and passed through a heat exchanger where the heat to the environment is released via a separate fluid stream. Downstream of the heat exchanger the cooled geothermal fluid is filtered through a second set of filters, after which it is pumped back into the injection well. This results in overpressure at the injection site. The production fluid reaches temperatures between 60 - 100 °C and the injection temperature is between 20 - 40 °C (Table 1). (2)

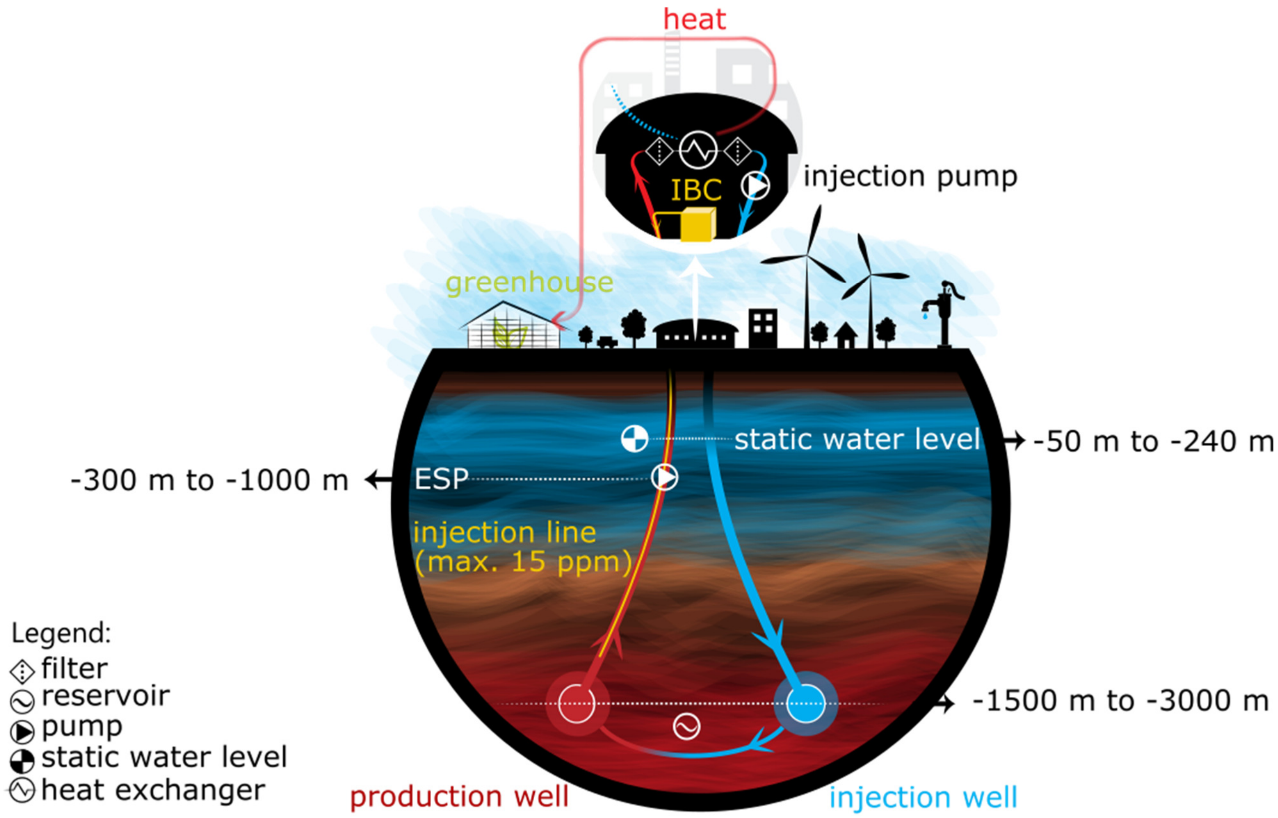


Figure 1: process configuration of geothermal installation in the Netherlands.

Table 1: Properties of geothermal fluid in the Netherlands. (2)

Property	Value	unit
Temperature producer	60 - 100	°C
Temperature injector	20 - 40	°C
Pressure producer	3.5 - 25	bar
Pressure injector	2 - 50	bar
pH	5.3 - 6.7	
TDS (total dissolved solid)	81 - 240	g/L
carbon dioxide	0 – 57	Mol%gas
methane	5.6 – 93	Mol%gas
oxygen	0 – 0.065	Mol%gas

At almost all locations, an intermediate bulk container (IBC) of 1 m^3 is present above ground, containing inhibitor. This inhibitor is continuously dosed in the production well, just above the reservoir level. (3) Just before the filters above the ground the geothermal fluid is continuously monitored on pH, temperature and oxidation reduction potential (ORP). Additionally, also coupons, Linear Polarization Resistance probes (LPR) and water analysis are used to monitor the corrosion rate of the geothermal fluid. (4) (5) Baker Hughes, one of the inhibitor suppliers, also detects the concentration of inhibitor above ground. Downstream of the second filters no monitoring of (components in) the system is performed. The only indication on if corrosion is taken place is when the ESP is pulled for maintenance purposes and visual inspections to both the production as injection sides are performed. This so called “logcampaign” is performed every 3-5 years. Thus, it may take 3 years before corrosion on the injection side is detected. In addition, the whole Dutch geothermal sector does not have a structural sector wide corrosion management plan. Therefore we recommend to draft such a corrosion management plan and evaluate outcomes via an external audit.

The fluid is slightly acidic (pH: 5.3 - 6.7) and contains high amounts of salt. The total dissolved solids (TDS) are in fact 2 - 7 times the concentration of seawater (81 - 240 g/L). Both carbon dioxide (0 - 57 mol%gas) and methane (5.6 - 93 mol%gas) are present at almost all of the locations, which at some locations results in degassing to harvest methane. In principle there is no oxygen present in the whole system and oxygen intake is prevented by the addition of a nitrogen blanket. (2) These above mentioned properties have a high potential for corrosion and scaling, which both cause decrease of well integrity. Corrosion can cause e.g. decrease of thickness of the piping material and leakages to the surrounding layers, decrease of heat capacity and precipitation of radioactive lead. Additionally, scaling can result in blockage or higher corrosion rates. (2)

The geothermal fluid consists of both high amounts of salts as substantial concentrations of metals (calcium, sodium and chloride, but also cadmium, iron, (radioactive) lead and nickel) (Table 2). All of these components make that the geothermal fluid is toxic for human, aquatic organisms and soil life in sweet aquifers (see further, Figure 5). (2) (3)

Table 2: Components in the geothermal fluid in the Netherlands. (2)

Component	Value	unit
Cadmium	<0,001 – 0,05	mg/L
Calcium	2,7 – 16	g/L
Chromium	<0,005 – 2,6	mg/L
Iron	5,6 – 190	mg/L
Lead	<0,05 – 13	mg/L
Sodium	17 – 32	g/L
Nickel	<0,01 – 2,4	mg/L

For a long term sustainable utilization of geothermal heat, it is necessary to control/limit the above mentioned corrosion processes. For this purpose, also the geothermal sector makes uses of the MOC-method, which states that mitigation actions should be taken in the following order: Mechanical (e.g. choice of (corrosion resistant) materials), Operational (e.g. nitrogen blanket to prevent oxygen inlet), Chemical (e.g. dosing of inhibitors). This research focusses on the chemical protection: the use of inhibitors (corrosion, scaling, biological growth) in the geothermal sector in the Netherlands.

3. APPLICATION OF INHIBITORS IN GEOTHERMAL ENERGY

Currently, only corrosion inhibitors are dosed in the geothermal sector in the Netherlands which also have a biocidal activity. Scaling inhibitors are not used anymore, as scaling is mitigated partially operationally by reinjection of carbon dioxide and partially as result of corrosion inhibitor dosing. Since the addition of corrosion inhibitors to geothermal wells in the Netherlands, both the rate of corrosion of the piping material and the precipitation of radioactive lead have decreased substantially. (9). The corrosion inhibitors are supplied by either Nalco Water or Baker Hughes. In tests a 88,5% - 90% corrosion protection level was found at dosing levels of 10 ppm. However the conditions in these tests were not in all cases similar to the process conditions in the Dutch geothermal wells (e.g. water from other geological reservoirs, different conditions). (4) (5)

These corrosion inhibitors are continuously dosed at the bottom of the production well with a concentration between 4 - 15 parts per million (ppm). However, the average concentration used is 10 ppm. The right concentration of dosage currently is selected via an empirical approach, where both the manager of the geothermal site as well as the inhibitor supplier together define the right concentration. The geothermal sector is moving towards site specific dosage concentration to have the best protection against corrosion, while the amount of unnatural substance inside the system is minimalized. Corrosion inhibitors are a cocktail of multiple compounds, but currently all contain a quaternary amine as the active component. The concentration of this amine in the whole cocktail is <5 wt.%.

To understand the principle of corrosion inhibitors, first corrosion has to be understood. Currently, all wells in the Netherlands are constructed of carbon steel: a combination of carbon (C) and iron (Fe). (6) (7) As at most locations carbon dioxide (CO_2) is present in the geothermal fluid the pH of the fluid is decreased to 3.5 - 6 (8): carbon dioxide reacts with water forming protons (acid; H^+) and carbonate (HCO_3^-) (1). (4) (8) It is this acid that oxidizes the iron, after which dihydrogen gas (H_2) is formed and the iron dissolves in the aqueous fluid (2). Alternatively, lead (Pb^{2+}) can oxidize the well material as well, resulting in the same dissolution of iron and precipitation of lead. Lead has the disadvantage of being a naturally occurring radioactive material (NORM), which in several cases already led to the unwanted precipitation of radioactive lead (Pb^{210}) in the installations above ground. Both of these oxidation reactions are catalyzed (accelerated) by high temperatures and chloride content. The combination of the low pH with these "catalyzing conditions" make that the geothermal fluid is very corrosive in the Netherlands.

$$CO_2 + H_2O \rightleftharpoons H^+ (aq) + HCO_3^- (aq) \quad (1)$$

$$Fe^0 (s) + 2\,H^+ \longrightarrow Fe^{2+} (aq) + H_2 \quad (2)$$

$$Fe^0 (s) + Pb^{2+} (aq) \longrightarrow Fe^{2+} (aq) + Pb^{210} (s) \quad (3)$$

To protect the, in the Netherlands used, carbon steel well material against corrosion, inhibitors are dosed. As stated before, these inhibitors are a cocktail of compounds, with one main active component: a nitrogen based polar head on one side, and a apolar carbon based hydrophobic tail on the other side (Figure 2). (7) (9) This filming amine covers the piping material with a thin layer, which protects against corrosion. (6) (11) (12)

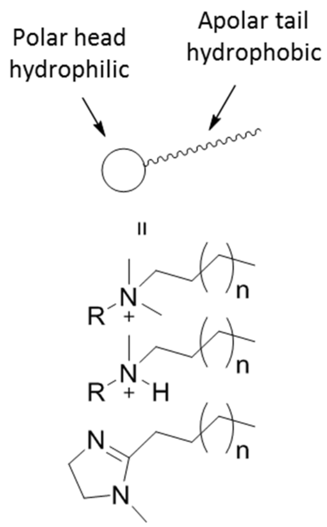


Figure 2: Active component in corrosion inhibitor cocktail. Such a filming amine often has an amine-based polar head and a carbon-based apolar tail. (7) (9)

Without any corrosion inhibitor present, the acidic water is in close contact with the carbon steel, which leads to corrosion. Upon addition of inhibitors, these filming amines compete with the acidic water, by adsorbing at the metal surface via their polar heads. Once more inhibitors bind to the surface, a strong layer (film) is formed, as a result of strengthening (ionic and van der Waals) interactions between the filming amines (Figure 3). (7) (9) Depending on the dosed concentration and properties of the inhibitor, either a monolayer or a double layer is formed. These layers cannot be penetrated by the acidic water anymore, resulting in a reduced corrosion rate.

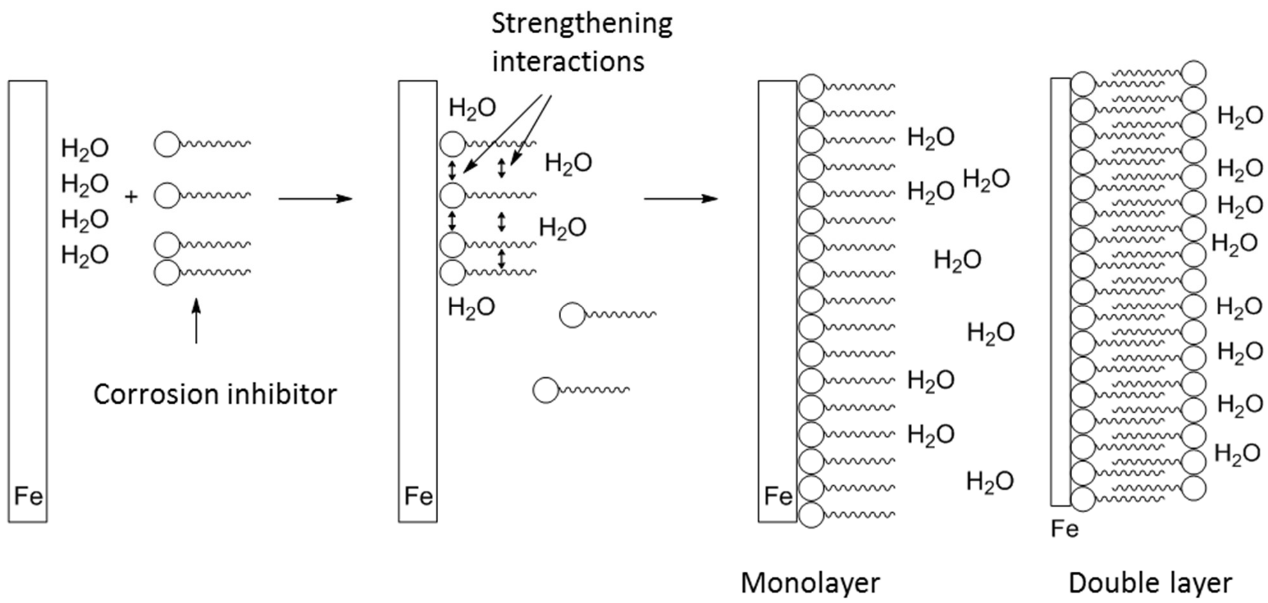


Figure 3: Principle of protection against corrosion by the use of a corrosion inhibitor. (6) (11) (12)

Desorption of inhibitors can occur in four ways:

- Due to bad properties of the inhibitor components
- Through competition with other components present in the water stream
- Through shear stress which is dependent on temperature and flow
- Due to low coverage of the surface as a result of too low concentration or insufficient mixing

As all geothermal systems have different properties, which can all contribute to desorption it is important to work with the earlier mentioned site specific dosage of inhibitors to have best protection against corrosion, while the amount of unnatural substance inside the system is minimalized.

4. RISK ANALYSIS TO DETERMINE LEAKAGE ROUTES OF INHIBITORS

Once that the effects and impact of corrosion inhibitors towards corrosion were identified, we continued our investigation to determine the environmental impact.

We conducted a Hazard Operability analysis (HAZOP) to determine possible pathways through which leakage of inhibitor towards the environment could occur.

During this risk analysis session, focusing on operational risks, it became clear that there is a small chance of leakage on the production side, because this site has vacuum pressure induced by the ESP. Next, it was discovered that it is not known what the concentration of inhibitor is throughout the whole installation. Thus, it is unknown if there is still inhibitor present and protecting against corrosion at the injection side. The installation above ground is in almost all cases completely built on a liquid proof floor where spills are automatically transferred to a waste basin, which is deposited to a chemical waste company. As a result, the main risks of leakage of inhibitor into the environment that were found during the HAZOP-session have been identified at the injection side (Figure 4):

1 Injection into the geothermal reservoir (very high-risk level)
2 Discharge along trajectory injection well into drinking water layer (average risk level)
3 Discharge along trajectory injection well into brackish water layer (average risk level)

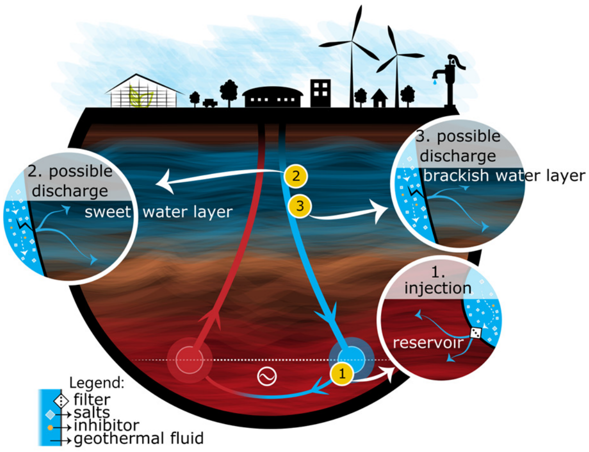


Figure 4: Three identified risks of leakage of inhibitor into the environment.

5. IMPACT OF INHIBITORS ON THE ENVIRONMENT

For the three risks identified above, the impact on the environment of identified discharge / injection risks has been evaluated in different aquifers.

Both inhibitor suppliers state that the inhibitors are relatively stable under the geothermal conditions in the Netherlands. Information is not available regarding the stability of inhibitors under the geothermal conditions in time or information on toxicity of (degradation products of) inhibitors under anaerobic conditions. (4)

In addition, commonly used classifications for chemicals as cefas and Wassergefährdungsklasse are contradictory (Table 3). For example cortron CK990-G has the least toxic classification in cefas, where it scores a 2 in WGK, where CRW93133 has silver classification in cefas where it is marked least toxic in WGK.

Table 3: Cefas and Wassergefährdungsklasse (WGK) classifications of corrosion inhibitors. (5) (4)

Product name	Cefas	WGK
Cortron CK990-G	gold (least toxic)	2
CRW83133	silver	1 (least toxic)
CGW80007	-	3

Thus, at this stage it is unknown what the degradation products and environmental impacts are of the used inhibitors in the Dutch geothermal systems. We therefore strongly recommend the drafting of European guidelines for inhibitors under anaerobic conditions. For this reason we decided to use the signaling value of the Dutch drinking water guideline (drinkwaterbesluit) as reference. (14) The signaling value for unknown substances is 0.001 ppm. Plotting the signaling value of the inhibitor (both total cocktail dosed and the 5% active compound) and other components in the geothermal fluid versus the actual concentration of the components results in the graph displayed in Figure 5. It can be seen that the relative concentration (compared to drinking water signaling value) of the total inhibitor is 20 times higher than the next compound (Pb) in the production fluid.

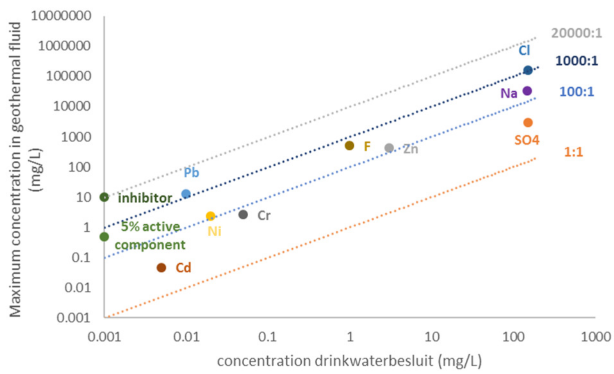


Figure 5: Relative concentrations of components present in the geothermal fluid (x-axes: concentration drinking water guideline (drinkwaterbesluit); y-axes: maximum concentration of component in geothermal fluid). (8)(14)

Next, we modelled the transport of inhibitors for the three identified risks on leakage. For this modelling we used Modflow and MT3DMS and the following worst-case assumption:

- No retardation of inhibitor
- No biodegradation

- 25 m^3/d leakage flow
- 3 years before detection
- Active use of groundwater layers

Risk 1: leakage of inhibitors in the geothermal reservoir

If the formations of the geothermal reservoir are considered as a receptor, then injection of the inhibitors trough the injection well can have a direct effect on the geothermal reservoir. In this reservoir, a concentration of 0.001 ppm (dosed inhibitor concentration of 10 ppm) spreads radially from the injection well into the geothermal reservoir over a distance of circa 740 meters. It must be stated that the concentration of 0.001 ppm does not reach the extraction well. There is neither sufficient knowledge of the biology and hydrochemistry of the geothermal reservoir nor of the behaviour of the inhibitors to say something on the environmental impact of the inhibitors on the reservoir.

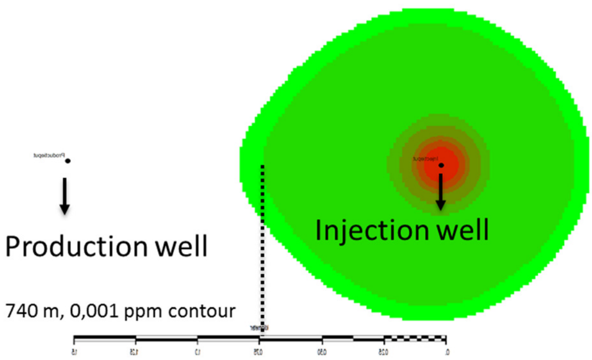
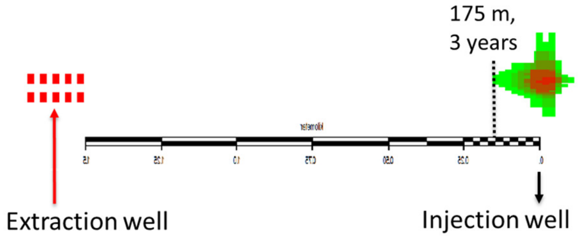


Figure 6: Modelling result of risk 1 where the transport of inhibitor from the injection well towards the production well is shown. The production well is not reached with a concentration of ≥ 0.001 ppm within 30 years.

Risk 2 and 3: discharge of inhibitors in fresh drinking water and brackish water aquifers.

For calculations of the inhibitor spread without other injection or extraction wells inside a fresh/brackish aquifer, but with a natural gradient in hydraulic heads a spread of 175 meters was calculated after simulated time of 3 years (dosed inhibitor concentration 10 ppm, contour line spread at 0.001 ppm).

The spread of inhibitors through leakage in a fresh water aquifer close to a freshwater extraction well will not directly reach the extraction well because wells cannot be placed within the 25 years zone. The 25 years zone is the contour surrounding a freshwater extraction, where the travel path of groundwater to the well is 25 years or less. After 25 years the inhibitor reaches the extraction well and in the calculated worst case scenario a concentration of 0.35 ppm (starting concentration of 10 ppm) reaches the freshwater extraction well. It must be noted that the most toxic component is only for < 5 % present in the inhibitor cocktail, which corresponds to a concentration of 0.0175 ppm. The same can be said of the release of liquid with inhibitors in a brackish water layer. Because extractions are more abundant in fresh water than brackish water, the possible impact of leakage of inhibitors in fresh water extraction wells is larger.



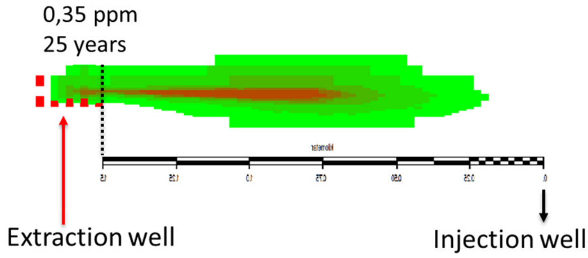


Figure 7: Modelling result of risk 2/3 where the transport of inhibitor from the injection well towards the extraction well is shown. The inhibitors can travel up to 175 meters with a concentration of 0.001 ppm towards the extraction well within three years (top). Worst case simulations show that the inhibitor reaches the extraction well with a concentration of 0.35 ppm in 25 years.

There are plausible effects of inhibitors on ecology in both fresh and brackish groundwater. It is known that inhibitors have a negative effect on biological growth. Also the salinity and heavy metal concentrations affect the biological growth. The order and magnitude of these effects are relatively unknown.

6. CONCLUSIONS

Inhibitors, as applied in the existing Dutch geothermal facilities, have a positive effect on the environment considering the currently used carbon steel based materials, because of their protective effect against corrosion, resulting in a reduced risk of leakage. In addition, precipitation of radioactive lead in the above-ground installations is also reduced.

However, there are three risks identified of possible leakage of inhibitors on the injection side. We performed simulations with a worst case approach, which makes that the simulations are overrated. The simulations for the first risk, leakage of inhibitor in reservoir, shows that the inhibitor travels 740 m with a concentration of 0.001 ppm and does not reach the production well over a period of 30 years. For the other two scenario's, leakage to sweet or brackish water layer, inhibitors can be found with a maximum concentration of 0.35 ppm of inhibitor (0.0175 ppm toxic component) at a drinking water well after 25 years. This value is higher than the signaling value of the Dutch Drinkwaterbesluit and the risk should therefore be monitored and/or mitigated. It should be noted that the degradability of (breakdown products of) inhibitors under geothermal conditions in reservoirs or aquifers is unknown and that this should be better investigated. However, corrosion inhibitors have a biocidal activity and therefore impact on the subsurface biology is expected.

Based on the generic geohydrological modelling it can be stated that there is no effect of injection of inhibitors in the geothermal reservoir on other geothermal extraction wells. Other extractions such as fresh or brackish can be effected through leakage of inhibitors in the reservoirs.

7. RECOMMENDATIONS

The following recommendations are made from the analysis of mitigating measures:

1 Drafting of a structural used corrosion management plan for the whole geothermal sector and processing in a risk-based inspection plan.
2 Quality control on the corrosion management plan (audit).
3 Set up monitoring to determine the integrity of injection wells.
4 Drafting of European guidelines for inhibitors under anaerobic conditions
5 To conduct research on the following inhibitor-related topics: the optimal concentration of inhibitor throughout the installation, the amount of inhibitor that reaches the reservoir, the degradation of inhibitors (incl. toxicity of degradation products), the diffusion rate of inhibitors and the effect of (degradation products of) inhibitors on the environment.
6 In addition, research into the use of more corrosion-resistant materials is recommended, as a result of which the dosage of inhibitors can be expected to be reduced.

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