General Report

Geochemical compatibility
Of
Schoonebeek oil field production water with Zechstein-reservoirs

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CONTENT

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Dit rapport beschrijft de uitkomsten van de studie naar de geochemische compatibiliteit van het productiewater uit het Schoonebeek olieveld met de in het Zechstein-reservoirs voorkomende reservoirwater (ook wel formatiewater genoemd) en reservoirgesteente (ook wel mineralen genoemd).

Het productiewater bestaat voornamelijk uit ionen afkomstig uit het Schoonebeek-olieveld-reservoir, welke verdund zijn vanwege de aldaar toegepaste stoominjectie. Daarnaast bevat het productiewater kleine hoeveelheden mijnbouwhulpstoffen.

Om na te gaan of er een negatieve impact is te verwachten van het productiewater uit het Schoonebeek olieveld op het Zechstein-formatiewater en -gesteente is gekeken naar de volgende aspecten:

- Incompatibiliteit van de mijnbouwhulpstoffen met het Zechstein-formatiewater;
- Mogelijke reactie van mijnbouwhulpstoffen met het Zechstein-reservoirgesteente;
- Incompatibiliteit tussen het productiewater uit het Schoonebeek olie veld en Zechstein formatie water;
- Incompatibiliteit tussen het productiewater uit het Schoonebeek olie veld en Zechstein-reservoir gesteente.

De volgende, in het productiewater uit het Schoonebeek olie veld voorkomende, mijnbouwhulpstoffen zijn onderzocht met betrekking tot impact op het Zechstein-reservoirgesteente en formatiewater:

- Anti-corrosievloeistof
- Biocide
- Anti-bariumsulfaataanslagvloeistof
- Zuurstofbinder
- Zwavelwaterstofbinder
- Waterreiniger
- Emulsiebreker
- Anti-schuimmiddel
- Mono-ethyleen glycol
- Di-ethyleen glycol
- Tri-ethyleen glycol

Conclusie van het onderzoek is dat de mijnbouwhulpstoffen in de toegepaste concentraties in het Schoonebeek olie veld geen negatieve impact hebben op het Zechstein formatie water en gesteente.

Naast het onderzoek naar de impact van mijnbouwhulpstoffen is ook onderzocht of er mogelijk een negatieve impact is te verwachten van het productiewater uit het Schoonebeek olie veld op het formatiewater en gesteente van een Zechstein-reservoir. Het formatie water uit het Schoonebeek olie veld reservoir heeft een met het Zechstein-reservoir overeenkomstige samenstelling (zie appendix 1), waardoor er geen gevaar bestaat voor reacties met het Zechstein-reservoir gesteente. Ook de pH van het productiewater uit het Schoonebeek olie veld is zodanig hoog dat het Zechstein-reservoirgesteente niet zal oplossen.

Incompatibiliteit van productiewater met het Zechstein-formatiewater zou kunnen leiden tot het neerslaan van onoplosbare zouten, wat vergelijkbaar is met bijvoorbeeld de vorming van ketelsteen in een theeketel. Neerslag van onoplosbare zouten kan ontstaan wanneer de oplosbaarheidsgrens van bepaalde ionen wordt overschreden. Dit verschijnsel kan plaatsvinden wanneer twee waterstromen worden gemengd en/of verandering van condities zoals bijvoorbeeld pH, druk en/of temperatuur optreedt. Mogelijke gevormd neerslag heeft geen negatieve impact op het Zechstein-formatiewater en reservoirgesteente; wel kan het leiden tot verminderde injectiviteit doordat gesteenteporiën verstopt kunnen raken.

Doordat deze neerslagvorming gebaseerd is op fysische en chemische eigenschappen, kunnen deze door thermodynamische modellen worden voorspeld. De hiervoor gebruikte software wordt overal in de olie- en gasindustrie toegepast om op basis van watersamenstellingen en reservoircondities (pH, temperatuur, druk) de neerslagvorming in het reservoir bij verschillende condities te voorspellen. De uitkomsten van de modellering worden door experts gebruikt om de waarschijnlijkheid en impact van de neerslagvorming te beoordelen. Deze beoordeling is gebaseerd op wereldwijde ervaring in de industrie en specifieke kennis binnen NAM/Shell.

Op basis van het onderzoek naar mogelijke neerslagvorming kan geconcludeerd worden dat het risico van neerslagvorming in het Twente en Drenthe Zechstein-reservoir laag is. Mogelijkerwijs kunnen kleine hoeveelheden bariumsulfaat neergeslagen worden. Dit is te voorkomen door een antibarium-sulfaataanslagvloeistof toe te passen. Daarnaast kunnen kleine hoeveelheden calciumcarbonaat neerslaan omdat de oplosbaarheidsgrens wordt overschreden doordat de reservoir temperatuur hoger is dan die van het productiewater in het Schoonebeek olie veld. Het mogelijkerwijs gevormde calciumcarbonaat zal van nature weer oplossen doordat het Zechstein formatiewater enigszins zuur is vanwege het daarin opgeloste kooldioxide, welke van nature in het reservoir voorkomt.

1 Introduction

A study has been performed to review the geochemical compatibility of produced water from the Schoonebeek oil field with formation water and minerals in a Zechstein-reservoir where the produced water will be injected. Production water consists in majority of ions originating from the Schoonebeek oil field reservoir, which are diluted due to steam injection. Additionally the production water also contains small amounts of mining additives (mijnbouwhulpstoffen).

To assess if there is a negative impact of the Schoonebeek oil field production water on Zechstein-reservoirs the following has been taken into account:

- Incompatibility of mining additives with reservoir water;
- Mining additives reacting with reservoir minerals;
- Incompatibility between Schoonebeek production water and reservoir water;
- Incompatibility between Schoonebeek production water and reservoir minerals.

The following chapters describe these compatibility aspects.

2 Impact of mining additives

NAM has a chemical selection policy in place and is ISO 14001 certified showing that policies are working with the aim to constantly strive for the minimum use of chemicals and where possible use chemicals that have the least impact on health, safety and the environment. Furthermore the use of mining additives complies with Dutch (Arbowet) legislation, European Union legislation (REACH) and applicable permits, which all contain obligations to minimize the usage of chemicals and limit their impact on health, safety and the environment. By the Dutch mining act (Mijnbouwwet) State Supervision of Mines (SodM) supervises the application of mining additives.

Although the detailed composition of the mining additives is not given by the chemicals supplier to NAM (SodM has access to more detailed information from the chemical suppliers), they have the legal obligation by REACH to provide NAM with Safety Data Sheets (SDS) describing the health, safety and environmental aspects of the mining additive as delivered. This includes an overview of the dangerous components included in the mining additive. The information from the SDS has been used as a base for reviewing the impact of the mining additives.

2.1 Impact assessment in the industry

Assessing the impact of mining additives on produced water, reservoir minerals, installation materials and other mining additives is done industry wide every time new chemicals are introduced. In the past decades a lot of knowledge has been gained in the Oil and Gas industry (operators and chemical suppliers) based on chemical laboratory studies, core flow studies, practical knowledge, simulations etc. Examples are:

- Reservoir souring due to bacteria when injecting seawater for reservoir pressure maintenance
  Not applicable for Zechstein-reservoirs; no sea water injected and reservoir is already sour by origin.
- Clay swelling when fresh water is injected into reservoirs containing minerals sensitive for this phenomenon. Leads to plugging of reservoir pores and hence injectivity.
  Not applicable for Schoonebeek oil field production water as it contains enough ions to prevent clay swelling.

2.2 Impact assessment within NAM

First off all NAM will only consider chemicals for use in its operations after they have been approved against European standards (REACH) to be suited and allowed for use in the mining industry. On top of that NAM will only approve a new chemical after it has been subjected to a chemical selection process in which it is tested for technical and Health, Safety & Environment (HSE) aspects. Apart from technical & performance aspects this process includes screening of:

- HSE impact , including compliance with permits such as water injection permits;
- Compatibility with existing mining chemicals, to prevent unwanted reactions, solids forming or performance issues;
- Compatibility with reservoir minerals to prevent negative impact on rock stability;
- Compatibility with produced waters, to prevent scaling leading to plugging of equipment/reservoir;
- Compatibility with installation materials, to prevent negative impact on installation integrity;
- Operating conditions encountered, such as pH, pressure and temperature in the facilities and reservoirs, versus operating window of the chemical itself. This to prevent solids being formed due to chemical degradation reduced chemical performance, etc.

The mining additives currently used in the Schoonebeek oil field, which are also foreseen to be used in the future, have followed this process and are as such REACH compliant and approved for use in the Schoonebeek oil field system.

The table below lists the impact assessment of each Schoonebeek oil field mining additive on the reservoir rock and reservoir water (formation water). As explained earlier this assessment is based on common knowledge within the oil and gas industry and chemical suppliers combined with experience over decades within NAM itself.

Functionality	Background	Compatibility with reservoir water	Impact on reservoir rock stability
Corrosion Inhibitor	▪ Corrosion inhibitor used is organic with intention to form a very thin molecular film layer on metals to protect against corrosion. This happens also on solids etc. This thin film layer does not impact reservoir rock composition/strength. ▪ Similar corrosion inhibitors have been injected for decades in gas fields downhole without impacting the reservoir rock. ▪ No incompatibility with Twente reservoir water (outcome of chemical selection process).	Good	None
Biocide	▪ Quaternary amines (organic substance) is used in Schoonebeek. ▪ Surface-acting biocides (like quaternary amines) can be absorbed on high-surface area solids, like some proppants and silt layers of the formation. ▪ Neat product has pH of 6.5 – 7.5, but is used in such a low concentrations that it has no impact on the pH of the Twente injection water (around pH 6). ▪ Biocide does not change the reservoir rock properties. ▪ No incompatibility at applied dose rate with Twente reservoir water (outcome of chemical selection process).	Good	None
$BaSO_4$ scale Inhibitor	▪ Scale inhibitor prevents crystal growth of barium sulphate and hence scaling. ▪ Neat product has pH of 3.2, but is used in such a low concentrations that it has no impact on the pH of the Twente injection water (around pH 6). ▪ Product has been selected to work in Schoonebeek injection water / Twente reservoir water composition.	Good	None
Oxygen Scavenger	▪ Oxygen scavenger applied is commonly used in the oil and gas industry; ammonium bisulphite. ▪ Ammonium bisulphite is inorganic salt. ▪ Does not change reservoir rock properties. ▪ Bisulphite ion reacts with oxygen forming a sulphate ion. ▪ Both bisulphite and sulphate anions can react with cations which could form scale. This can be seen as incompatibility with injection water/reservoir water but dosage levels applied are low and do not lead to increased scaling risk.	Good if dosage is kept under control	None
H_2S Scavenger	▪ Assessment based on new developed H_2S scavenger to be used in future. ▪ H_2S scavenger reacts with H_2S to neutralize the impact of H_2S on installation materials. ▪ Laboratory tests combined with the molecular structure of the neat product and its reaction products do indicate there is very good compatibility with injection water/reservoir water and no impact on reservoir rock properties. ▪ No neat product will end up in the injection water as the purpose of the H_2S scavenger injection is to stay below operating limit of H_2S gas for the materials and not to aim for zero H_2S levels. So all H_2S scavenger will react.	Good	None
Water clarifier	▪ Water clarifier (surface active) goes with the oil phase. We use in water injection reporting a partitioning of 0.1% to water phase (worst case) as we cannot be 100% sure all goes to oil export as some tiny amounts of mineral oil ends up in the injection water (13 mg/l mineral oil for example in 2015). This mineral oil would then have tiny amounts of water clarifier included. ▪ High concentrations of water clarifier in the water phase could lead to emulsions. Emulsions have no impact on the reservoir rock neither reacts with the reservoir water. ▪ In 2015 0.005 mg/l water clarifier was reported to end up in injection water to Twente. ▪ Amounts are so low that there is no impact on reservoir rock neither an incompatibility with the Twente reservoir water.	Good	None

Continued on next page

Functionality	Background	Compatibility with reservoir water	Impact on reservoir rock stability
Demulsifier	▪ Demulsifier goes with the oil phase. We use in water injection reporting a partitioning of 0.1% to water phase (worst case) as we cannot be 100% sure all goes to oil export as some tiny amounts of mineral oil ends up in the injection water (13 mg/l mineral oil for example in 2015). This mineral oil would then have tiny amounts of demulsifier included. ▪ High concentrations of demulsifier in the water phase could lead to emulsions. Emulsions have no impact on the reservoir rock neither reacts with the reservoir water. ▪ In 2015 0.05 mg/l demulsifier was reported to end up in injection water to Twente. ▪ Amounts are so low that there is no impact on reservoir rock neither an incompatibility with the Twente reservoir water.	Good	None
Antifoam	▪ Antifoam goes with the oil phase. We use in water injection reporting a partitioning of 0.1% to water phase (worst case) as we cannot be 100% sure all goes to oil export as some tiny amounts of mineral oil ends up in the injection water (13 mg/l mineral oil for example in 2015). This mineral oil would then have tiny amounts of antifoam included. ▪ High concentrations of antifoam in the water phase could lead to emulsions. Emulsions have no impact on the reservoir rock neither reacts with the reservoir water. ▪ In 2014 0.001 mg/l (not used in 2015) antifoam was reported to end up in injection water to Twente. ▪ Amounts are so low that there is no impact on reservoir rock neither an incompatibility with the Twente reservoir water.	Good	None
Mono ethylene glycol, Diethylene glycol, Tri ethylene glycol *	▪ Glycols are used as solvent for some chemicals ▪ In gas production fields glycol is used as hydrate inhibitor in the LTS train / flowlines and end up partly in production water which is injected for decades on several injection wells within NAM without an impact on the reservoir rock. ▪ Glycols are sometimes used to remove hydrate plugs inside wells without impact on reservoir rocks ▪ Glycols are compatible with reservoir waters. Only if very large amounts end up they can impact the scaling of salts due to impact on solubility. But in practice this will never be the case.	Good	None

** Glycols are not separately injected, but could be part of the solvent package of the mining additives injected.*

Table 1 *Impact of mining additives in injection water on reservoir rock & reservoir water*

2.3 Conclusion

The Schoonebeek oil field mining additives:

1. are compatible in the applied concentrations with the Zechstein-reservoir water. The ammonium-bisulphite based oxygen scavenger can form scale with components in the reservoir water, but the amount is very low (traces) and in practice negligible.
2. have no negative impact on the reservoir rock properties by for example dissolution or reaction with reservoir minerals.
3. are not expected to undergo degradation in the reservoir as this will directly have impact on their performance and as such has been evaluated as part of the chemical selection process.

3 Impact of Schoonebeek production water

The Schoonebeek production water originates from the Schoonebeek oil field reservoir and contains similar ions as the Zechstein-reservoir in which it is injected. Due to steam injection in the oil field these ions become diluted. No dissolution of the Zechstein carbonate reservoir minerals is expected as the composition of the Schoonebeek reservoir water is roughly similar to the Zechstein-reservoir water and the pH of the Schoonebeek production water shows it is not acidic.

Incompatibility between Schoonebeek production water and Zechstein-reservoir water could lead to formation of insoluble salts, which is called scaling (similar phenomena as scale formed in a teakettle). Scaling in a reservoir might occur if the injected water has a different composition than the water already present in the reservoir. If the composition difference is such that the concentration of salts is above the solubility limit, precipitation (scaling) of these mineral scales will occur. These salts might block pores in the reservoir and/or clog the tubing of the well. Scaling by itself does not affect the reservoir rock properties, but might impact the reservoir injectivity if pores get blocked by scale. As scaling is based on chemical/physical phenomena it can be modelled with thermodynamic modelling tools.

Thermodynamic modelling tools are widely applied in the Oil and Gas industry and allow to simulate scale formation based on reservoir conditions and injection water composition. The models calculate the thermodynamic driving forces for precipitation of scale minerals either due to pH, temperature and/or pressure changes or as a result of mixing incompatible waters.
The model results are used to assess the likelihood and severity of any significant scale formation. However, scaling mechanisms are complex and hence the model results are reviewed by experts. The expert judgement combines worldwide experience in the industry & NAM/Shell experience with the modelling results to arrive at an overall scaling risk assessment.

The scaling risk has been assessed for the currently used Twente reservoir (Zechstein) and for Zechstein-reservoirs in Drenthe which may be used in the future. The Zechstein formation water composition for Twente and Drenthe, which are similar, in comparison with the Twente injection water composition is shown in figure 1 in Appendix 1.

The expected injection water composition is expected to change over time given the mixing of the formation water with condensed steam in the Schoonebeek field. Therefore in addition to the current injection water composition the expected injection water composition in 2022 is also predicted (see appendix 2). These different injection water compositions are analyzed and tested for potential scaling.

3.1 Twente reservoir

The scaling risk of Schoonebeek oil field production water with the Twente reservoir water can be split into three periods:

a. Schoonebeek field restarted in 2011 and the production water was injected for the first time in the Twente reservoir;
b. Current situation where the reservoir around the injection wells contains already Schoonebeek production water injected since 2011;
c. Future injection from 2022 onwards with either a more by steam diluted production water stream or a more concentrated production water stream (depending on future concept chosen).

The scaling risk for these 3 periods is described in the next sections.

3.1.1 Restart of Schoonebeek oil field in 2011

During the re-development of the Schoonebeek oil field scale assessments have been performed[1]. These scale assessments concluded a low scaling risk for the Rossum-Weerselo reservoir. The scale risk identified was linked to the formation of barium sulphate close to the injection well in the early phase of injection. Over time the injection and reservoir water will mix and the mixing front will move away from the well, thus reducing the risk for scaling on reservoir injectivity.

To mitigate the possible barium sulphate risk a scale inhibitor was advised for the initial injection phase only. This barium sulphate scale inhibitor was applied from the start-up in 2011 till September 2014. Thereafter no negative impact on injectivity was seen, showing that either there was no significant scaling in the beginning or that the scaling region had moved sufficiently far away from the well into the reservoir to not negatively affect injectivity.

3.1.2 Current situation

The water in the Twente reservoir around the injection wells contains essentially only Schoonebeek injection water. Continuation of injecting Schoonebeek water will not lead to a scaling risk as the additional injected Schoonebeek water will not get into direct contact with the original Twente reservoir water.

[1] MER Herontwikkeling olieveld Schoonebeek, 31 maart 2006

3.1.3 Future injection

From 2022 onwards two water injection options can be envisaged depending on the outcome of the Schoonebeek Long Term Water Disposal project, i.e. injection of Schoonebeek production water which:

1. is more diluted than the current water composition due to increased mixing with condensed steam;
2. is a concentrated version of Schoonebeek production water due to pre-treatment with the aim to reduce the overall injection water volume.

For both scenarios no scaling is expected when injected in the Twente reservoir based on:

a. Scale assessments done for the re-development of the Schoonebeek field (for restart in 2011)[1];
b. Scale assessments done for the pipeline Schoonebeek – Twente when concentrated injection water would be transported through the pipeline;
c. The Twente reservoir contains already Schoonebeek water. If injection water is pre-treated the concentrated injection water in 2022 will only be 2 times more concentrated compared to the 2015 composition. I.e. the water will not become over saturated which will prevent scaling to occur.

Be aware that even after a treatment and concentration step, the injection water is expected to be significantly less salty than the original Twente reservoir water. This implies that the scaling risk remains low. For example seawater has an average of 21000 mg/l chloride and Dead Sea water 212000 mg/l chloride, while concentrated production water will contains 60000 mg/l chloride at maximum. The original Twente formation water has a salinity of about 172000 mg/l chloride

3.2 Drenthe reservoir

The scaling risk assessment for the Drenthe reservoirs (Zechstein) has been carried out using the thermodynamic modeling tool as earlier described using the predicted water composition from 2022 onwards for diluted and concentrated Schoonebeek production water (see also point 1 and 2 in §3.1.3 "Future injection").

A series of scaling scenarios were modelled incorporating a range of conditions for each of the target reservoirs. In each case Schoonebeek oilfield production water was mixed with reservoir water at reservoir conditions in ratios from 0 - 100%. For each set of conditions, the type, likelihood and the potential mass of scale was calculated.

The overall scaling risk was assessed by combining the outcome with experience within NAM/Shell leading to the conclusion that the overall scaling risk is low. The identified low overall risk is linked to a few target reservoirs, which could encounter some small amounts of Barium Sulphate and/or Calcium Carbonate scales due to their reservoir conditions.

The calcium carbonate scales might form from the Schoonebeek produced water due to temperature increase in the hot reservoirs, however in gas reservoirs the tendency to form scale disappears due to the low pH caused by dissolved CO_2 gas. Hence the risk of Calcium Carbonate scale would cease to exist. Barium Sulphate scale can be prevented by the injection of a Barium Sulphate scale inhibitor as has been successfully done in the Twente reservoir.

With the natural available mitigation for Calcium Carbonate scale and the injection of the Barium Scale inhibitor the overall scaling risk is managed and low.

4 Document versions

Version	Date	Author	Modifications
1	07-Dec-2016	W.M.J. Kruse	Initial version.

Appendix 1 Comparison Zechstein formation water composition Twente & Drenthe reservoir with Twente injection water

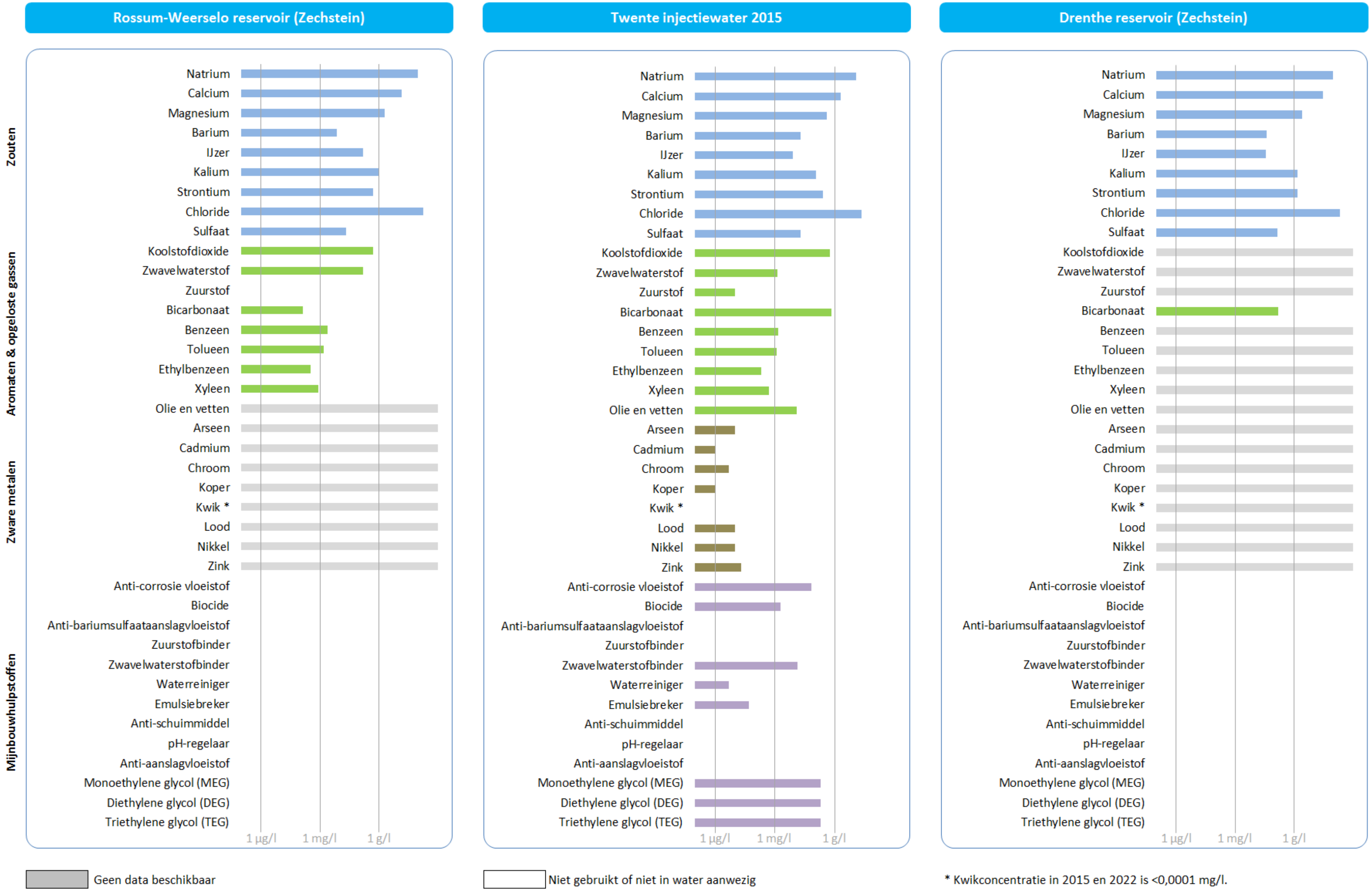

Figure 1 *Comparison Zechstein formation water composition of Twente (Rossum Weerselo) & Drenthe reservoirs with Twente injection water composition. The grey bars indicate that data is not available.*

Appendix 2 Expected water composition in 2022

The table below[1] lists the expected water composition in 2022, which is diluted due to steam injection compared with the water composition from 2015. From 2022 onwards steam injection will even lead to more dilution of this Schoonebeek oil field production water.

Parameter	Eenheid	Verwachte jaargemiddelde (2022)
pH (eenheden)	-	4 – 9
Temperatuur	°C	50
Total Dissolved Solids	mg/l	25.000
Total Suspended Solids	mg/l	46
Natrium (Na+)	mg/l	7.800
Magnesium (Mg2+)	mg/l	282
Barium (Ba2+)	mg/l	13
Arseen (As) [4]	mg/l	<0,01
Kwik (Hg) [4]	mg/l	<0,0001
Zwavelwaterstof (H2S) [1]	mg/l	18
IJzer (totaal Fe2+ en Fe3+)	mg/l	6
Kalium (K+)	mg/l	78
Strontium (Sr2+)	mg/l	168
Chloride (Cl-)	mg/l	15.000
Sulfaat (SO42-) [4]	mg/l	<14
Bicarbonaat (HCO3-)	mg/l	545
Koolstofdioxide (CO2)	mg/l	565
Zuurstof (O2) [4]	mg/l	<0,01
Olie en vetten	mg/l	10
Cadmium (Cd) [4]	mg/l	<0,001
Koper (Cu) [4]	mg/l	<0,01
Monoethylene Glycol (MEG) [4]	mg/l	<200
Diethylene Glycol (DEG) [4]	mg/l	<200
Triethylene Glycol (TEG) [4]	mg/l	<200
Ethylbenzeen (C8H10)	mg/l	0,25
Tolueen (C6H5CH3)	mg/l	1,5
Waterreiniger [2]	mg/l	6,5
Zuurstofbinder [2]	mg/l	9
Anti-schuimmiddel [2]	mg/l	0,02
Chroom (Cr) [4]	mg/l	<0,005
Benzeen (C6H6)	mg/l	2
Lood (Pb) [4]	mg/l	<0,01
Nikkel (Ni) [4]	mg/l	<0,01
Zink (Zn) [4]	mg/l	<0,02
pH- regelaar [2]	mg/l	0,06
Biocide [2, 3]	mg/l	400
Anti-aanslagvloeistof [2]	mg/l	0,05
Anti-bariumsulfaataanslagvloeistof [2]	mg/l	30
Calcium (Ca2+)	mg/l	1.320
Xylenen (C6H4C2H6)	mg/l	0,7
Zuurstofbinder [2]	mg/l	9
Anti-corrosievloeistof [2, 3]	mg/l	60
Zwavelwaterstofbinder [2, 3]	mg/l	120
Emulsiebreker [2]	mg/l	4

[1] Verwachte concentratie indien geen gebruik wordt gemaakt van H2S binder. De verwachte concentratie overschrijdt de maximaal verwachte waarde uit de vergunning.
[2] Concentraties van mijnbouwhulpstoffen (in blauwe rijen) zijn berekend op basis van verdelingscoëfficienten tussen olie en water
[3] De concentratie van Biocide/ Anti-corrosievloeistof/ Zwavelwaterstofstofbinder is afhankelijk van het alternatief en varianten binnen het alternatief, dit wordt geminimaliseerd voor bepaalde alternatieven/varianten (beschreven in detail in dit rapport).
[4] De verwachting is dat de concentratie van deze stoffen onder de bepalingslimiet blijft (deze is afhankelijk van de analysemethode)

[1] The table is in Dutch as it originates from the report "Herafweging verwerking productiewater Schoonebeek - Tussenrapport alternatievenafweging" as published by Royal haskoning DHV on 28-Jun-'16.