ZERO BRINE

D7.2 Report on the evaluation of the results from the demonstration activities

February 2022

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Deliverable lead	Delft University of Technology (TUD)
Author(s)	Gijsbert Korevaar (TUD) Steve Harris (IVL) Nilay Elginoz Kanat (IVL)
Contact	g.korevaar@tudelft.nl
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[1] **R**=Document, report; **DEM**=Demonstrator, pilot, prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other

[2] **PU**=Public, **CO**=Confidential, only for members of the consortium (including the Commission Services), **CI**=Classified

Executive Summary

The ZERO BRINE project demonstrates new configurations to recover resources from saline impaired effluents (brines) generated by various process industries, while minimising environmental impact of industries by minimizing saline wastewater discharge. The water treatment system consists of both commercially available technologies, and recently developed technologies. In the ZERO BRINE project in several deliverable reports, the environmental, economic, and social impacts of its technologies are presented and discussed.

The aim of this Deliverable 7.2 is to provide a comparison between the demonstration locations and to provide a technical assessment across the various setups. In order to do so, a set of indicators is designed to make the comparison transparent and fair. After the technical assessment, a discussion and reflection is provided. All locations show that a treatment configuration consisting of various technologies can deal with several types of brine water. This shows that ZERO BRINE systems have the potential to act as utility providers to different kinds of industry and also act as an intermediate between industries to make industrial symbiosis happen. The differences in outcomes also show that for each new waste water type, process designs need to be made and optimization is necessary to adapt ZERO BRINE systems to other industrial contexts.

Contents

List of figures

List of tables

1 Introduction

The ZERO BRINE project focuses on developing innovative recovery solutions to close the loop of saline impaired effluents (brines) generated by the process industry. It aims to eliminate wastewater discharge and minimise environmental impact of industrial operations through the integration of several existing and innovative technologies. These technologies are targeted to recover high quality end products with high purity to provide optimum market value.

ZERO BRINE therefore aims to close the loop of these problematic effluents through the recovery of water and valuable components of the effluents that include minerals (e.g. sodium chloride, sodium sulphate), regenerated acids, caustics, and magnesium. ZERO BRINE consists of four case study projects to develop and demonstrate the ZERO BRINE systems under different industrial circumstances:

a. Demineralized water effluent in The Netherlands.
b. Coal mine effluent in Poland.
c. Textile industry effluent in Turkey.
d. Silica industry effluent in Spain.

In Deliverable 7.1, the Unified approach is presented in which the approach to the demonstration locations is presented, in Deliverables 7.3 and 7.7 the results of the case studies are presented in detail. This reports takes the results of the following work packages:

- Deliverable 2.6: Report on the operation and optimization process of the pilot plants at Botlek.
- Deliverable 3.5: Report on the operation and optimization of the pilot system for treatment of coal mine water.
- Deliverable 3.8: Report on the operation & optimization of the pilot systems for the treatment of textile effluents.
- Deliverable 4.5: Innovative circular economy process in the precipitated silica industry: design and performance.

The rest of this report consists in a short description of the demonstration activities and their main outcomes, based on the documents mentioned above. This description is used to create a technology assessment overview. From that a reflection is given on the common elements within the case studies and the transfer of that insight to the other deliverables of Work Package 7

The objectives of this report are:

1. Collect the technical achievements of the four demonstration locations.
2. Assess and compare these achievements and discuss limitations and potential.
3. Deliver input for further sustainability assessment in other Deliverables of ZEROBRINE.

2 Methodology and approach

This report compares the ZERO BRINE systems of four demonstration locations that require different configurations of technology that depend on the composition of the individual brines, as well as the elements targeted for recovery. This comparison should lead to insight on how ZERO BRINE technologies perform under different circumstances. This demands a technology assessment that can address variations in context, and the overlap and the differences between the locations. In order to do this in a methodological way, a technology assessment is chosen described by Harris et al. in the context of the Industrial Symbiosis inspired Centre for Sustainable Resource Processing (Harris, Corder, Beers, & Berkel, 2006), see Figure 1.

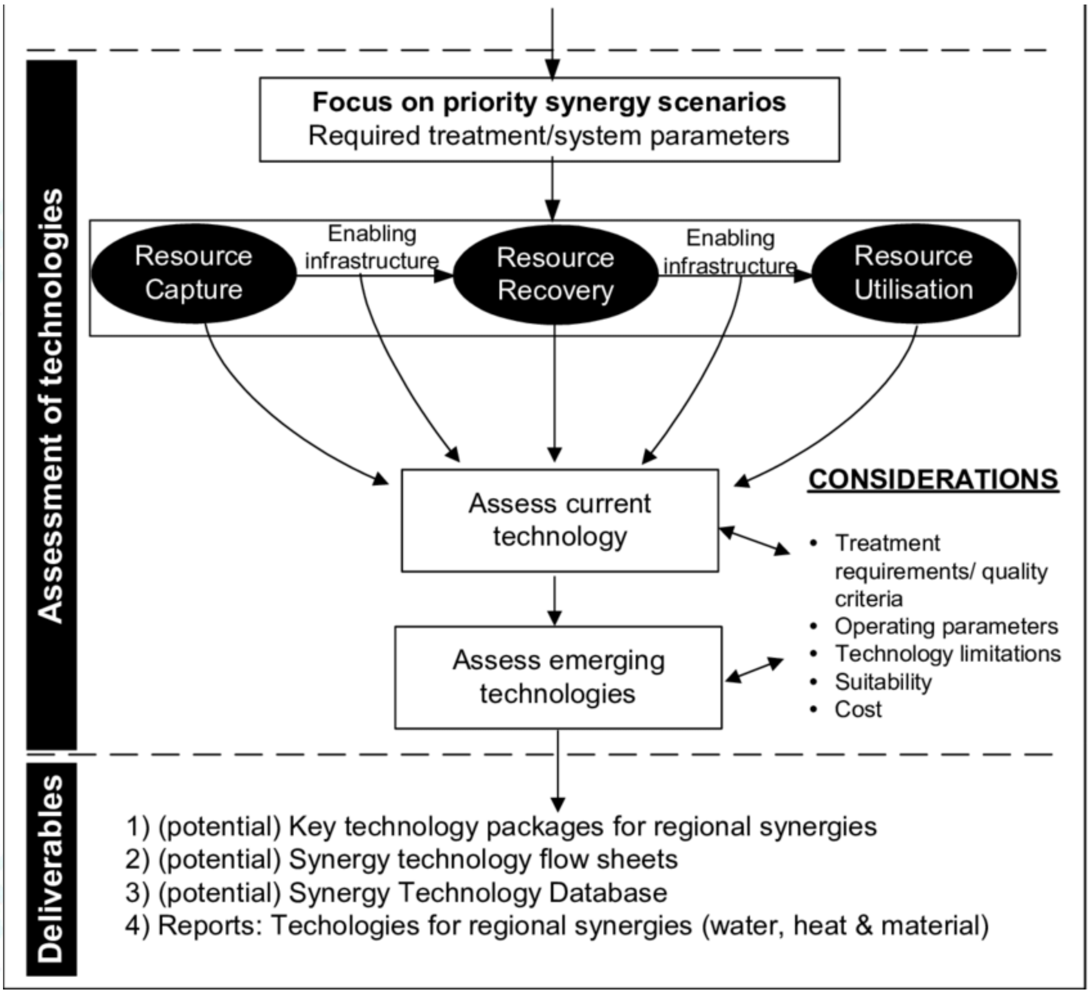

Figure 1 – Technology assessment criteria (Source: Harris et al. 2006)

According to this Figure 1, considerations to assess the existing and new technologies are:

1. Treatment requirements/quality criteria.
2. Operating parameters.
3. Technology limitations.
4. Suitability.
5. Cost.

In this ZERO BRINE Work Package 7 the environmental, social, and economic factors are taken into account. In the Work Packages 2, 3, and 4 all operating parameters are discussed in detail, as presented in the previous chapter.

We interpret that the ‘suitability’ in Figure 1 refers to both the social acceptance and the environmental performance, this means that this topic will be taken into account in other deliverables, as well as the ‘cost’. In the remainder of this report, the first and third consideration will be used to compare the technologies, by filling in the following table, Table 1 – Technology assessment table. In the column ‘Technology’, the treatment steps will be listed that are used in the process chains at the four demonstration locations. The ‘Treatment Requirements’ are seen as the water and minerals recovery that is obtained in the experiments. The ‘Quality Criteria’ give the various water reduction and CO2 reduction of the processes. When applicable, also ‘Technology Limitations’ will be provided. By completing Table 1, the considerations for current and future technologies are provided that are the basis for the technical evaluation of the demonstration locations.

This completion will be done throughout the report, and the final product is in Table 6. Since this is an assessment focussed on the outcomes of experimental work, we will look for treatment achievements (the outcome of the experiments) and quality requirements (the technology performance).

Table 1 – Technology assessment table

Location	Technology	Quality Achieved	Treatment Achievements	Technology Limitations
The Netherlands				
Poland				
Turkey				
Spain				

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3 Results of the demonstration locations

First a short description of the ZERO BRINE demonstration locations is given, again here is referred to the other Deliverable reports that provide the necessary details for understanding the technologies and the underlying choices.

3.1 Demonstration location The Netherlands

In The Netherlands, the demonstration is performed in two locations, called Site 01 and Site 02. Site 01 pilot treats the regeneration effluent (spent regenerant) of the softening ion exchange unit of the Evides Demineralization Water Plant located in Botlek industrial area, see Figure 1. Site 02 pilot treats the reverse osmosis concentrate stream of the Evides Demineralization Water Plant located in Botlek industrial area, see Figure 3.

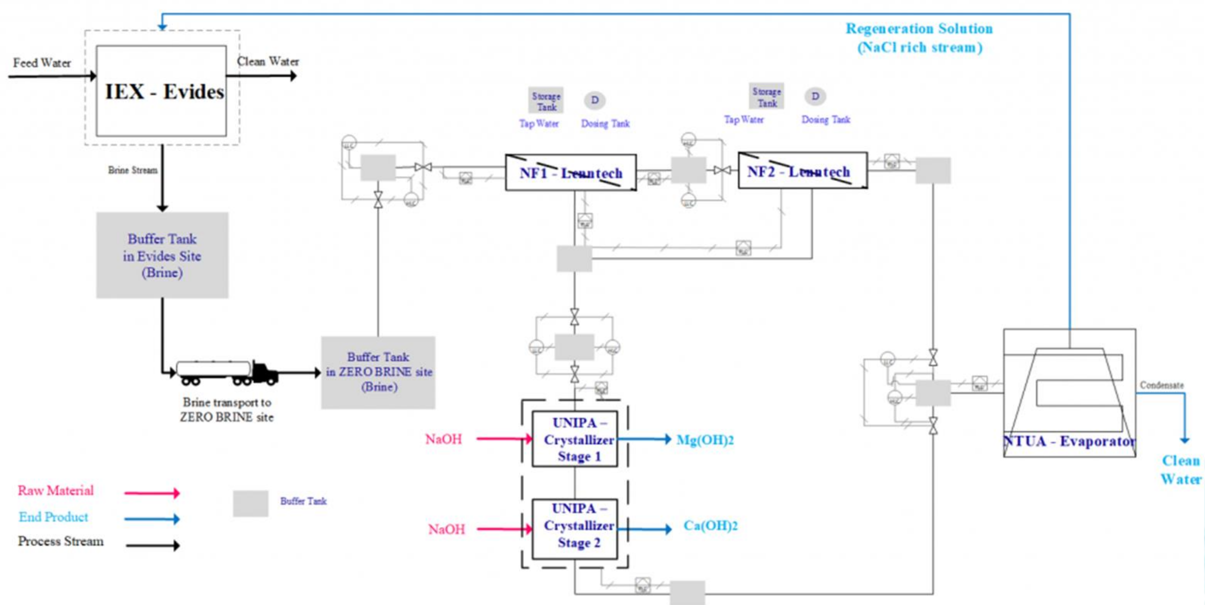

Figure 2 – Demonstration location The Netherlands – Site 01

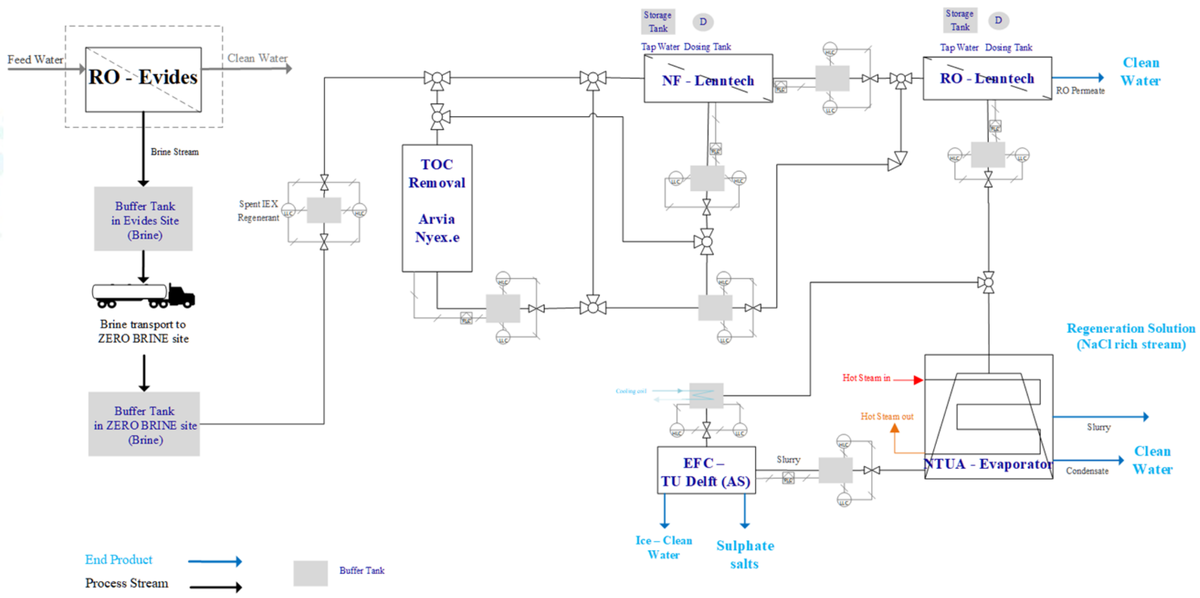

Figure 3 – Demonstration location The Netherlands – Site 02

In Table 2, the consolidated results are given for the ZERO BRINE system of the Demineralized Water Plant in Rotterdam.

Table 2 – Consolidated results of the demineralized water plant in The Netherlands

Reductions in			**Recovered resources:**
Water	**Emissions**	**Energy**	
15-20% reduction in water withdrawal	>98% reduction of brine discharged to the environment (>2.5 million m^3/year) 1,012 tons/year CO_2 emissions or 14% CO_2 reduction by recovering minerals, salts, and clean water	Thermal energy required for the evaporation process can be supplied by waste heat/residual heat of neighbouring industries 44% less energy used by MED evaporator when compared to conventional methods	92% water recovery for internal use (demineralized water) 6.2% IEX regeneration solution recovery for internal use (>3.1% purity) 94.7% Calcium Hydroxide recovery ($Ca(OH)_2$) for external valorisation (>95.6% purity) 87.8% Magnesium Hydroxide recovery ($Mg(OH)_2$) for external valorisation (>88.9% purity) 93% Sodium Sulphate recovery (Na_2SO_4) for external valorisation (unwashed: 94.6% purity)

3.2 Demonstration location Poland

In Poland a pilot plant in the "Bolesław Śmiały" coal mine in Łaziska Górne, has been operated. The tested system consisted of pretreatment, ultrafiltration, decarbonization, nanofiltration, reverse osmosis, and electrodialysis, see Figure 4. Recovery of magnesium hydroxide was tested in both conventional precipitation with slaked dolime suspension and crystallization with ion-exchange membrane. The recovery sodium chloride using eutectic freeze crystallization has also been tested. The proposed setup is as follows: the brine pretreated with ultrafiltration is subjected to the first pass of nanofiltration (NF1); the permeate is subjected to a second pass of nanofiltration (NF2). The NF2 permeate is fed to the hybrid reverse osmosis (RO), from which the RO permeate is recovered, the ED concentrate is fed to a modern evaporator (MED), the ED dilute is recycled back to RO.

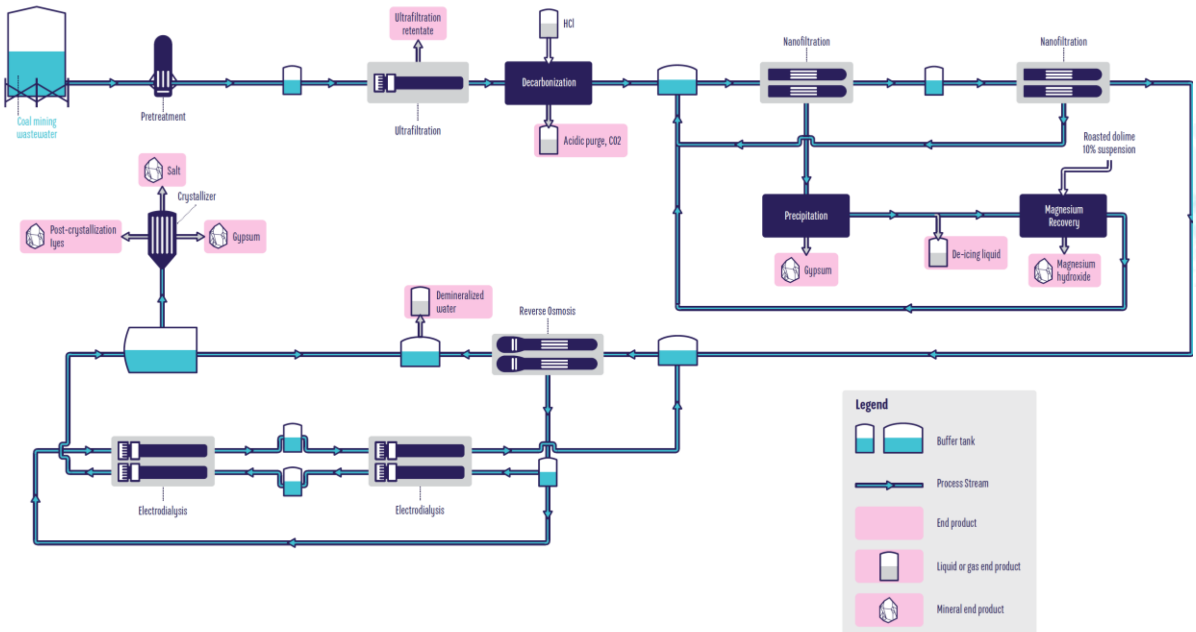

Figure 4 – Demonstration location Poland

In Table 3, the consolidated results are given for the coal mine demonstration location in Poland.

Table 3 – Consolidated results of the coal mine in Poland

Reductions in			**Recovered resources:**
Water	**Emissions**	**Energy**	
n.a.	92.8% reduction of Sodium Chloride (NaCl) discharged to freshwater resources 347 kg CO_2 /ton Sodium Chloride (NaCl) or 32.5% CO_2 reduction	33% energy reduction	90.6% water recovery (demineralized water) 92.8% Sodium Chloride (NaCl) recovery (99% purity) 94.9% Magnesium Hydroxide recovery $Mg(OH)_2$) for external valorisation (97% purity) 0.84 kg/m^3 Gypsum for external valorisation

3.3 Demonstration location Turkey

The developed ZERO BRINE system located at Zorlu Textile Industry (Luleburgaz/Tekirdag/Turkey) was operated in the field of manufacturing polyester yarn and cotton home textile products. The system was designed for the treatment of reverse osmosis (RO) retentate of Zorlu Textile to recover recyclable salt as well as reusable water streams. The TPS comprised of a primary pre-treatment as well as a secondary concentration and softening stages, see Figure 5. The pretreatment was designed to remove impurities in the RO retentate, whereas, in the following stage the pretreated RO retentate was concentrated and further softened to conform to the textile dye processes prerequisites. Along these lines two different configurations were tested: 1) IEX softening the NF permeate, which then was concentrated by RO, 2) RO concentrating the NF permeate, followed by IEX softening the RO retentate.

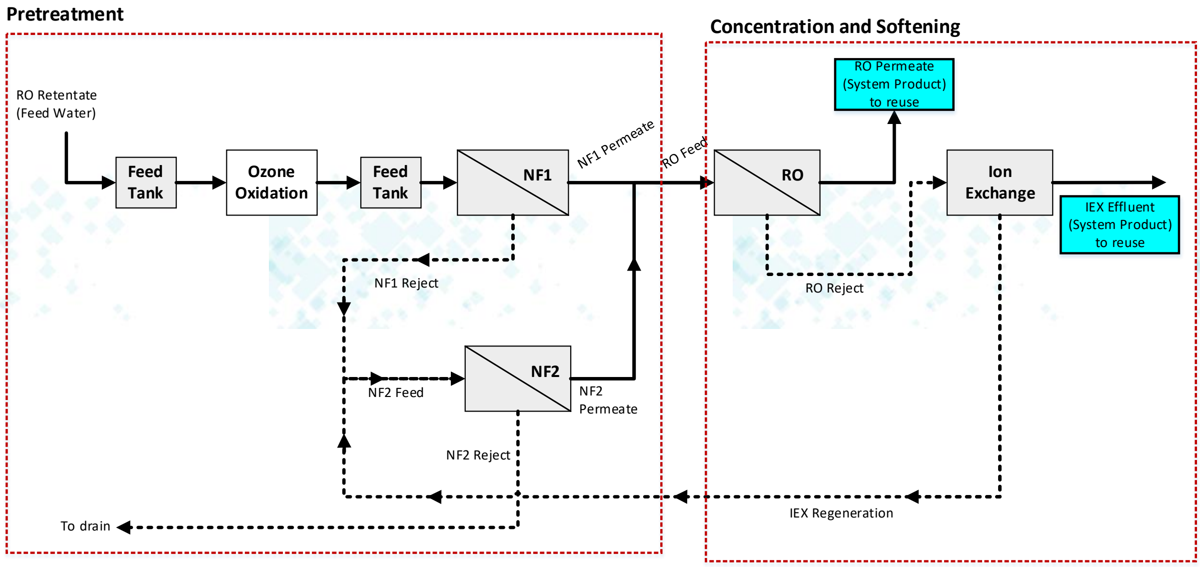

Figure 5 – Demonstration location Turkey

In Table 1 – Technology assessment tableTable 4, the consolidated results are given for the ZERO BRINE system at the textile plant in Turkey

Table 4 – Consolidated results of the textile plant in Turkey

Reductions in			Recovered resources:
Water	**Emissions**	**Energy**	
7% reduction in total freshwater consumption or freshwater abstraction by 123,000 tons/year	90-95% reduction of brine discharged to the environment 150-200 tons/year CO_2 reduction	n.a.	70-80% water recovery from brine treatment system for onsite use 600-700 tons/year of Sodium Chloride for onsite dyeing of textiles

3.4 Demonstration location Spain

Industrias Químicas del Ebro (IQE) in Spain is the demonstration sites of ZERO BRINE in relation to the precipitated silica industry. Waste effluents containing high concentration of salts (saline wastewater) are treated by a concentration step with regenerated membranes followed by a crystallization step in which sodium sulphate is recovered, see Figure 6. Permeate had an adequate quality to be reused in the production process as process water and the concentrate was the one submitted to the crystallization step for the recovery of sodium sulphate. After a pre-treatment to remove Aluminium and Iron, the concentration step consisted in the use of regenerated membranes to obtain water at a suitable quality to be reused and a brine with Na_2SO_4 as concentrated as possible.

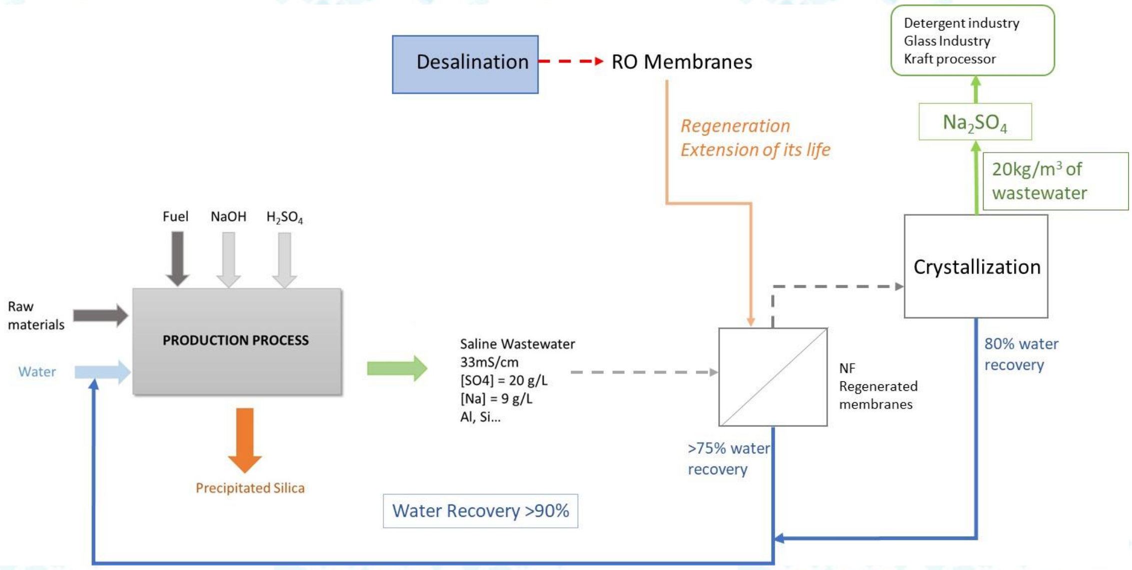

Figure 6 – Demonstration location Spain

In Table 5, the consolidated results are presented of the silica plant in Spain.

Table 5 – Consolidated results of silica plant in Spain

Reductions in			Recovered resources:
Water	**Emissions**	**Energy**	
30% reduction in overall annual water consumption at IQE	100% reduction of brine discharged to the environment 60% reduction of Sodium Sulphate (Na_2SO_4) releases into the Ebro River	72% reduction by waste heat (Eutectic Freeze Crystallization technology compared to direct evaporation)	75-90% water recovery suitable for internal use 90% recovery of Sodium Sulphate (Na_2SO_4) or 20,000 tons/year for external valorisation (>99% purity) Sodium Hydroxide (NaOH) (94% purity) and sulphuric acid (H_2SO_4)

	6,000 tons/year CO_2 reduction or 5 kg CO_2/m^3 of wastewater		(72% purity) for external valorisation

4 Technology assessment of the results

According to the reports on the experiments in the four demonstration locations, the following overview can be made in the overview table as presented in Chapter 2 ‘Methodology and approach’, Table 1. The results are given in Table 6 after which the assessment is discussed.

4.1 Overview Table

On the next pages, the overview Table 6 – Technology assessment table with results from four demonstration locations). In the table, the comments related to heat exchange are given in **bold** and will be discussed later. The reduction of brine water and salt are presented in **green** to highlight the reduction capacities of the several locations. Also the water recovery is presented in **green** to underline the importance of water recovery in the systems. In **red**, the technical limitations are given, which are also discussed afterwards.

Table 6 – Technology assessment table with results from four demonstration locations

Location	Technologies	Quality Achieved	Treatment Achievements	Technology Limitations
Demineralized Water Plant – The Netherlands	Nano filtration Crystallizer Eutectic Freeze Crystallizer Evaporator Multi effect distillation evaporator Reverse Osmosis	15-20% reduction in water withdrawal **>98% reduction of brine discharged to the environment (>2.5 million m^3/year)** 1,012 tons/year CO_2 emissions or 14% CO_2 reduction by recovering minerals, salts, and clean water **Thermal energy required for the evaporation process can be supplied by waste heat/residual heat of neighbouring industries** 44% less energy used by multi effect distillation evaporator when compared to conventional methods	**92% water recovery for internal use (demineralized water)** 6.2% Ionic exchange regeneration solution recovery for internal use (>3.1% purity) 94.7% Calcium Hydroxide recovery ($Ca(OH)_2$) for external valorisation (>95.6% purity) 87.8% Magnesium Hydroxide recovery ($Mg(OH)_2$) for external valorisation (>88.9% purity) 93% Sodium Sulphate recovery (Na_2SO_4) for external valorisation (unwashed: 94.6% purity)	**The target purity for Magnesium Hydroxide ($Mg(OH)_2$) crystals was not always achieved due to the co-precipitation of $CaCO_3$.** **Eutectic Freeze Crystallization was not always possible.**
Coal Mine – Poland	Nano filtration Reverse Osmosis Electro Dialysis	**92.8% reduction of Sodium Chloride (NaCl) discharged to freshwater resources** 347 kg CO_2 /ton Sodium Chloride (NaCl) or 32.5% CO_2 reduction overall 33% energy reduction Nano filtration can be safely operated at high permeate recovery (80%), without the observable scaling	**90.6% water recovery (demineralized water)** 92.8% Sodium Chloride (NaCl) recovery (99% purity) 94.9% Magnesium Hydroxide $Mg(OH)_2$) recovery for external valorisation (97% purity) 0.84 kg/m^3 Gypsum for external valorisation. The application of intermediate gypsum precipitation in the two-pass nano filtration is a necessary step in order to achieve salt recovery higher than the reference	**n.a.**

Location	Technologies	Quality Achieved	Treatment Achievements	Technology Limitations
Textile Factory – Turkey	Ozone oxidation Nano filtration Crystallizer Ion Exchange Reverse Osmosis	7% reduction in total freshwater consumption or freshwater withdrawal by 123,000 tons/year **90-95% reduction of brine discharged to the environment** 150-200 tons/year CO_2 reduction	**70-80% water recovery from brine treatment system for onsite use** 600-700 tons/year of Sodium Chloride (NaCl) for onsite dyeing of textiles	n.a.
Silica Factory – Spain	Nano filtration Crystallizer Reverse Osmosis Eutectic Freeze Crystallization Evaporator	30% reduction in overall annual water consumption **100% reduction of brine discharged to the environment** 60% reduction of Sodium Sulphate (Na_2SO_4) releases into the Ebro River 6,000 tons/year CO_2 reduction or 5 kg CO_2/m^3 of wastewater **72% reduction by waste heat (EFC technology compared to direct evaporation)**	**75-90% water recovery suitable for internal use** 90% recovery of Sodium Sulphate (Na_2SO_4) or 20,000 tons/year for external valorisation (>99% purity) Sodium Hydroxide (NaOH) (94% purity) and Sulphuric Acid (H_2SO_4) (72% purity) for external valorisation	n.a.

4.2 Discussion of the overview table

In Table 6, the overview is provided for the four demonstration locations. Based on this table, the following observations can be given:

1. The ZEROBRINE systems are designed for and adapted to the specific circumstances of the demonstration locations. This shows that the approach is flexible and can be optimized for the quality requirements that are needed per location. The main elements of the ZEROBRINE systems (nano filtration or reverse osmosis) are tested under several conditions and the experimental results are discussed extensively in the several work package reports. This information can be helpful to use the technology in new contexts as well.
2. In all cases, the brine or salt discharge to the environment has improved a lot. This differs per location, because of the specifications of the brine intake, but in all locations, the reduction of brine discharge is above 90% or in the Silica industry 100%. In three out of the four cases also the intake of clean water is substantially lower. Only in the coal mine case, we do not see this, but that is because no intake of fresh water happened here in the first place, all water intake is the salt mine water.
3. The recovery of water is above 70% in all cases, in the demineralized water plant even above 92%. This makes the project a great example of closing the loop and it also means that the water cycles can play an important role in the realization of industrial symbiosis.
4. In all cases, minerals are recovered with good quality and high purity, for more details on this, see the reports of Work packages 2, 3, and 4. And also the deliverables related to the business models, Work package 8. In Deliverable 9.3 it is discussed how the minerals meet the quality criteria for selling externally. The recovery of the minerals is an important element in the achievement of a local circular economy. With the comment above, it means that ZEROBRINE can both serve industrial symbiosis and circular economy, making it a very interesting tool for sustainable development of various kinds of industry.
5. The four locations also show a reduction in CO_2 emissions, which is also an indicator for the energy efficiencies of the process. Since all locations still can be optimized in terms of energy integration, like the several reports on the work packages illustrate, the CO_2 emissions can be reduced even further in full scale operation. In both the Dutch case and the Spanish case, the possibilities for heat exchange are studied. An integration of the ZEROBRINE system in an existing heat exchange network will have a positive impact on the CO_2 emissions. In Poland and Turkey, this heat exchange is not possible at the moment, but this could be a nice addition to operate the brine treatment systems in a more sustainable manner.
6. The experiments in the four locations also have shown limitations, as indicated in the table. Further experimentation is necessary to show under which conditions the Eutectic Freeze Crystallization can work and what hinders its applicability. The same can be said about the co-precipitation of Calcium that can hinder the production of ultra-pure Magnesium Hydroxide.

In conclusion, we want to state that the ZEROBRINE systems can contribute to closing the cycles in chemical industry, silica industry, coal mine, and textile industry. Its system performance is dependent on the composition of the intake water and whether recovery balances increased resource use of the ZEROBRINE systems.

5 Concluding remarks

The main objective of this report is to collect the outcomes of the four demonstration locations of ZEROBRINE, in order to do a technology assessment and to have a discussion about what the experiments have in common and how they contribute to circular economy. The main result to meet this objective is the assessment table in Chapter 4.

The technology assessment as presented in Chapter 4, shows overlaps and differences in the four demonstration locations. All locations show that a treatment configuration consisting of various technologies can deal with several types of brine water. This shows that ZEROBRINE systems have the potential to act as utility providers to different kinds of industry and also act as an intermediate between industries to make industrial symbiosis happen. The differences in outcomes also show that for each new waste water type, process designs need to be made and optimization is necessary to adapt ZEROBRINE systems to other industrial contexts.

In conclusion, we like to state that ZEROBRINE systems contribute to closing the cycles in chemical industry, silica industry, coal mine, and textile industry. Its system performance is dependent on the composition of the intake water and whether recovery balances increased resource use of the ZEROBRINE systems.

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Harris, S., Corder, G., Beers, D., & Berkel, R. (2006). *Technology Needs Review for Regional Synergies.* Centre for Sustainable Resource Processing.