



ZERO BRINE

D9.2 Report on Policy Review and Assessment / Suggestions for BREF Updates

May 2021

FINAL



The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Deliverable D9.2	Report on Policy Review
Related Work Package	WP9 – Framework Conditions for Innovation
Deliverable lead	NTUA
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Reviewer	Gijsbert Korevaar (TU DELFT)
Grant Agreement Number	730390
Instrument	Horizon 2020 Framework Programme
Start date	1.6.2017
Duration	48 months
Type of Delivery (R, DEM, DEC, Other)¹	Report
Dissemination Level (PU, CO, CI)²	PU
Date last update	28/05/2021
Website	www.zerobrine.eu

Revision no	Date	Description	Author(s)
0.1	28 May. 21	First draft	Maria Kyriazi (NTUA), Eva Skourtanioti (NTUA), Maria Avramidi (NTUA), Jelica Novakovic (NTUA), Maria Loizidou (NTUA)
0.2	26 Nov.20	Reviewing	Gijsbert Korevaar (TU DELFT)
1.0	30 Nov.20	Second Draft	Maria Kyriazi
1.1	10 May 21	Third Draft	Maria Kyriazi (NTUA), Maria Avramidi (NTUA), Jelica Novakovic (NTUA), Maria Loizidou (NTUA)
1.2	27 May 21	Reviewing	Gijsbert Korevaar (TU DELFT)
2.0	28 May 21	Final	Maria Kyriazi (NTUA), Jelica Novakovic (NTUA)



The ZERO BRINE project has received funding from the European Commission under the Horizon 2020 programme, Grant Agreement no. 730390. The opinions expressed in this document reflect only the author's view and do not reflect the European Commission's opinions. The European Commission is not responsible for any use that may be made of the information it contains.

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

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Abbreviation List

BREF:	Best Available Techniques Reference Document
CAPEX:	Capital Expenditures
DAFF:	Dissolved Air Flotation Filtration
EC:	European Commission
ECHA:	European Chemicals Agency
ED:	Electro dialysis
EFC:	Eutectic Freeze Crystallization
EoW:	End-of-Waste Criteria
EPR:	Extended producer responsibility
EQW:	Ecological Quality of Surface Waters
IED:	Industrial Emissions Directive
IPPC:	Integrated Pollution Prevention and Control
MF-PFR:	Multiple Feed – Plug Flow Reactor
MSW:	Municipal Solid Wastes
NF:	Nanofiltration
OPEX:	Operational Expenditures
PAYT:	Pay-as-you-throw scheme
PRO:	Producers Responsibility Organization
REACH:	Registration, Evaluation, Authorization and Restriction of Chemicals
RO:	Reverse Osmosis
SDS:	Safety Data Sheet
TDS:	Technical Data Sheet
TDS:	Total Dissolved Solids
TOC:	Total Organic Carbon
UF:	Ultrafiltration
WFD:	Water Framework Directive
WWTP:	Wastewater Treatment Plant
ZB:	ZeroBrine

Executive Summary

The present deliverable comprises the report on policy review and assessment. Results from optimized pilot systems operation are used to complete the report and to suggest BREFs updates.

The Zero Brine project proposes combination of various technologies to treat effluent brines from four different industrial sectors, aiming to shift from the linear model to a circular economy model. Therefore, brine treatment systems focus on the recovery of resources from brines and not on the removal of salts as pollutants before the disposal of treated water to WWTPs or receiving water bodies.

Initially, the relevant legislative framework is reviewed, namely:

- Registration, Evaluation, Authorization and restriction of Chemicals (REACH),
- Waste Framework Directive and End-of-Waste Criteria,
- Water Framework Directive,
- Industrial Emissions Directive, and
- Best Available Techniques Reference Documents for waste management from extractive industries, large volume inorganic chemicals-solids and other industries, textiles industry, wastewater, and waste gas treatment/management systems in chemical sector

This section also investigates potential legislative barriers that could hinder the exploitation of salts and treated water.

Next, principles and economic instruments used in waste management policies are examined for possible incorporation in the wastewater management plans. Finally, the conclusions of this review are presented.

The deliverable includes tables with description of pilot systems and technologies, their efficiency, operational and capital costs, and physical and chemical properties of salts and water recovered. Data in these tables are compared with the respective tables of BREFs and, where applicable, the ZB consortium suggests the BREFs update.

1. Introduction

1.1 Scope of the deliverable

This deliverable includes the results of sub-task 9.1.1 “Policy Review-Transfer of experience from waste management to wastewater management sector”. The sub-task 9.1.1. is led by NTUA and involved partners are TU DELFT, Water Europe and Sealeau.

ZeroBrine (ZB) suggests five systems for brine treatment produced by four different industrial sectors (textile industry, silica industry, water industry and extractive industry). Inorganic salts and clean water are recovered from the treatment of brines produced by these industries. During the ZB proposal preparation it was found out that the commercialization of salts and clean water goes through the relevant European and National Legislation.

As there is no specific legislation for the products of wastewater treatment, ZB partners have decided to review legislation for waste management in order to address potential barriers and suggest enablers, transferring the experience from waste management to wastewater management.

1.2 Legislation Framework

The policy review and assessment has been based on five pillars, namely REACH (Registration, Evaluation, Authorization and Restriction of Chemicals); WFD (Water Framework Directive); BREFs (Best Available Techniques Reference Documents); WFD (Waste Framework Directive) and EoW (End-of-Waste Criteria); and IED (Industrial Emissions Directive). Furthermore, the existing legal and policy framework regulating salts and clean water produced by brine treatment systems, has been reviewed and assessed for the countries where demonstration activities are implemented (Netherlands, Spain, Poland, Turkey, and Greece).

1.3 Financial Instruments

ZB project and suggested systems are based on circular economy. Moreover, financial instruments such as:

- Extended producer responsibility (EPR)
- Landfill tax, incineration tax (TAX)
- Pay-as-you-throw scheme (PAYT)

have been studied, to help transfer know-how from waste management to the wastewater management section, and to encourage industries adopt brine treatment systems.

2. REACH

2.1 Introduction

ZeroBrine (ZB) proposes industrial brine treatment for inorganic salts and clean water recovering. Valorisation of the produced salts, NaCl, CaSO₄, Mg(OH)₂, Ca(OH)₂, NaHCO₃, and Na₂SO₄ is strongly taken into consideration by the ZB consortium. The market of chemicals in Europe is subjected to legislation to ensure their safe transportation, use and disposal. REACH is the main regulation for improving of human health and environmental protection from risks caused by chemicals. Therefore, the first pillar of this policy review is REACH.

2.2 REACH

On July 1st, 2007 European Parliament entered into force Regulation 1907/2006 concerning Registration, Evaluation, Authorization and Restriction of Chemicals. European Chemicals Agency (ECHA) proposed this regulation to improve protection of human health and environment from risks which can be caused by chemicals. The second REACH goal was to enhance competitiveness of the European Union chemicals industry.

In principle, every industry producing chemicals in a scale larger than 1 tonne per year (excluding food ingredients, animal feed, and medicinal products) need to comply with this regulation. Industries are obliged to apply a report on the risks of produced chemicals and on their safe use. Manufacturers (even if they use chemicals themselves), importers and downstream users have responsibilities under REACH [1].

In summary, manufacturers should apply to ECHA a report containing information on[1]:

- | | |
|--|---|
| • Identification of the substance or preparation | • Exposure controls/Personal protection |
| • Use of the substance or preparation | • Physical and chemical properties |
| • Company/undertaking identification | • Stability and reactivity |
| • Composition/Information on ingredients | • Toxicological information |
| • First aid measures | • Ecological information |
| • Fire-Fighting measures | • Disposal considerations |
| • Accidental release measures | • Transport information |
| • Handling and storage | • Regulatory information |

The above information is categorized in the next tables according to the produced quantity of chemical:

Table 1: Information requirements for tonnage band 1-10 tonnes per year (Annex VII of REACH) [1]

<i>Non-vertebrate animal endpoints</i>	<i>Vertebrate animal endpoints</i>
Description of the state of the substance at 20°C / 101.3 kPa	Acute toxicity: oral
Melting/freezing point	
Boiling point (if applicable)	
Relative density	
Vapour pressure (if applicable)	
Surface tension (if applicable)	
Water solubility	
Partition coefficient	
Flash-point	
Flammability	
Explosive properties	
Self-ignition temperature	
Oxidising properties	
Granulometry (if applicable)	
<i>In vitro</i> skin irritation/corrosion	
<i>In vitro</i> eye irritation	
Skin sensitisation	
<i>In vitro</i> gene mutation in bacteria	
Short-term toxicity on invertebrates	
Growth inhibition study aquatic plants	
Ready biodegradability (if applicable)	

Table 2: Information requirements for tonnage band 10-100 tonnes per year (Annex VIII of REACH) (in addition to information of table 1.)

<i>Non-vertebrate animal endpoints</i>	<i>Vertebrate animal endpoints</i>
In vitro mutagenicity study in mammalian cells or In vitro micronucleus study	In vivo skin irritation
In vitro gene mutation in mammalian cells	In vivo eye irritation
Activated sludge respiration inhibition test	Testing proposal for in vivo geno toxicity (if one of the in vitro tests is positive)
Degradation	Acute toxicity: inhalation
Hydrolysis	Short-term repeated dose toxicity (28-day)
Adsorption/desorption screening	Screening for reproductive/developmental toxicity
	Short-term toxicity on fish or Testing proposal for long-term toxicity on fish (if the substance is poorly water soluble)

Table 3: Information requirements for tonnage band >100 tonnes per year (Annex IX of REACH) (in addition to information of tables 1 and 2)

<i>Non-vertebrate animal endpoints</i>	<i>Vertebrate animal endpoints</i>
Stability in organic solvents	Sub-chronic toxicity (90 days)
Dissociation constant	Pre-natal developmental toxicity in one species
Viscosity	Extended One-Generation Reproductive Toxicity (if triggered)
Long-term aquatic toxicity on invertebrates	Long-term aquatic toxicity on fish
Degradation	Bioaccumulation in aquatic species

Importers and downstream users must follow all the precautions deriving from the above information to ensure safe transportation, use and disposal of chemicals.

Summarizing, a chemical industry needs to register in ECHA platform before introducing its product in the market. This means that the industry should compile a folder including all the appropriate safety and toxicological data and submit it to ECHA. Upon completion of folder inspection, the manufacturer of chemical can be granted permission for chemical substance commercialization. If this procedure has been already performed by another manufacturer and ECHA platform contains all the appropriate for tonnage band data, manufacturer should send an access letter to ECHA asking for these data. ECHA will help the new manufacturer of chemical substance to get in contact with manufacturer or manufacturers who have first uploaded the folder. The new manufacturer will pay a fee and get the data of the folder which they should keep in their facilities and use them for compiling the Safety Data Sheet (SDS) of the chemical substance.

Reviewing the ECHA registration procedure, a question arose if the same procedure should be followed for the commercialization of chemical substances recovered from wastewater.

A material existing in waste ceases to be waste after undergoing recovery operation and when it fulfils the 4 criteria below:

1. the substance or object is commonly used for specific purposes;
2. a market or demand exists for such a substance or object;
3. the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products;
4. the use of the substance or object will not lead to overall adverse environmental or human health impacts.

In that case, recovery operators for such substances or materials should comply with REACH regulation in order to use or commercialize them.

According to the “ECHA Guidance on waste recovered substances” (ECHA-10-G-07) and the use of article 2(7)(d) of REACH:

“The following shall be exempted from Titles II, V and VI: [...] (d) Substances, on their own, in mixtures or in articles, which have been registered in accordance with Title II and which are recovered in the Community if:

- (i) the substance that results from the recovery process is the same as the substance that has been registered in accordance with Title II; and*
- (ii) the information required by Articles 31 or 32 relating to the substance that has been registered in accordance with Title II is available to the establishment undertaking the recovery.”*

The recovery operator does not need to register a substance (recovered from waste) that has already been registered from other manufacturers. However, he has to submit some additional information in case of a tonnage band increase. However, recovery operator must collect and keep in his site information requirements of tables 1-3 and the aforementioned list.

All substances produced from ZeroBrine proposed waste recovery are inorganic salts already registered to ECHA. Four different trains of waste recovery are proposed in ZeroBrine for four different streams of waste. Thus, the products of each recovery procedure constitute a different case for ECHA. For this reason, each recovery operator needs to contact his national helpdesk (table 4) and give information on stream analysis, recovered salts analysis, tonnage, and recovery trains. Their national helpdesks will respond on the need to send inquiry to ECHA or not.

Table 4: National Helpdesks information [2]

Country	National Helpdesks
Spain	Portal de Información REACH y CLP C/ Julián Camarillo 6B, 4ª Planta, 28037 Madrid Email: info@reach-pir.es
Poland	Bureau for Chemical Substances ul. Dowborczykow 30/34 90-019 Lodz Telephone: +48 42 2538 424; +48 42 2538 427 Fax: +48 42 2538 444
The Netherlands	CtGB - College voor de toelating van gewasbeschermingsmiddelen en biociden Bennekomseweg 41, 6717 LL Ede Telephone: +31 0 317 47 18 10 Email: servicedesk@ctgb.nl
Turkey	Ministry of Health Üniversiteler Mah. Dumlupınar Bulv. 6001. Cad. No:9 06800 Bilkent - Çankaya / Ankara-TURKEY Telephone: +90 312 565 5212 / 5218 / 5222 E-mail: thsk.cevre@saglik.gov.tr

In the first case, recovery operators will be guided by their national helpdesks to fill and send the inquiry to ECHA. ECHA will get them in touch with the producer, who first registered the salt, and has the folder with all

environmental and toxicological studies for the salt. The first registrant will ask a fee in order to share the folder data with the recovery operator.

If the national helpdesk responds that there is no need to send inquiry to ECHA, a letter explaining the reasons of REACH exclusion will be sent to the operator. The national helpdesk will also inform the operator on the contents of their product folder.

3. Water Framework Directive

3.1 Introduction

Since 1970, several European countries e.g. United Kingdom and Sweden have expressed willingness to deal with water quality issues [1]. During the 1990s many countries worldwide saw the necessity of holistic environmental management for tackling pollution and ecosystems degradation. Thus, environmental sustainability was discussed and agreed to be pursued, in the Earth Summits in Rio de Janeiro (1992), New York (1995), Johannesburg (2002) and the 1992 Convention of Biological Diversity [3].

The Ecological Quality of Surface Waters (EQW), a European Directive proposal which was never adopted, was the precursor of WFD. The adaptation failure of this Directive was mainly due to inadequate consideration of socio-economic impacts. However, this non-adopted Directive comprised the draft on which WFD was written. After working on EQW the governments of United Kingdom, France and the Netherlands managed to convince the European Commission, in 1995, to adopt an integrated strategy for the environment which gives the EU members more flexibility in setting standards and enacting laws to achieve the common environmental European goals [4]. Clear parallels are also between WFD and Clean Water Act (CWA) which was published in the US in 1972 and amended during 1980s.

3.2 Quality and quantity of Europe's water

Water is not only the core of natural ecosystems and one of the main factors of climate regulation, but is also the main resource for humanity which generates and sustains economic and social prosperity. The main economic activities of European countries, such as farming, commercial fishing, manufacturing, energy production, tourism, and transport, rely on water. Therefore, water demand is growing, putting available supplies in pressure.

Scientists have been warning for droughts and water scarcity in Europe for the past 20 years. It is estimated that water scarcity and droughts are increasing, affecting 11% of European population and 17% of European territory [4]. It has been calculated that the last 30 years, water scarcity has costed European Community more than € 100 billion.

Apart from water quantity, its quality is also threatened by pollution, agriculture, industry and urban development, energy production, transport. The WFD is the corner stone of European Union water policy. WFD and its complementary Directives compile the European Commission interest on protecting and enhancing the status of aquatic ecosystems as well as on promoting sustainable water use.

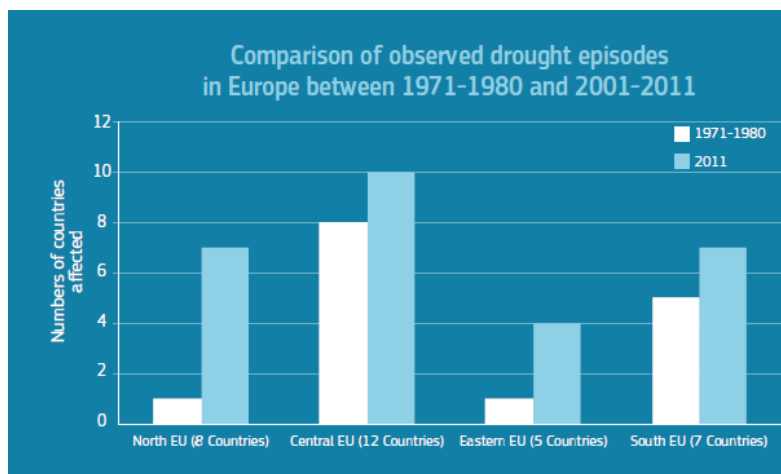


Figure 1: Drought episodes in Europe [4]

Table 5: WFD Complementary Directives [4]

WFD complementary Directives
The Environmental Quality Standards Directive (2008)
The Marine Strategy Framework Directive (2007)
The Floods Directive (2007)
The Groundwater Directive (2006)
The Bathing Water Directive (2006)
The Drinking Water Directive (1998)
The Urban Wastewater directive (1991)
The Nitrates Directive (1991)

3.3 Water Framework Directive objectives

The purpose of the WFD is to assure water quality and quantity in European Countries. Main goals of the WFD are:

- To protect aquatic ecosystems and consequently all ecosystems depending on them, such as terrestrial and wetland ecosystems.
- Water sustainability (based on availability of water resources).
- To minimize water pollution through reduction of discharges and emissions in water and environment in general.
- To mitigate floods and droughts effects. [5]

More than 100.000 surface water bodies have been recorded in EU following the distribution bellow.

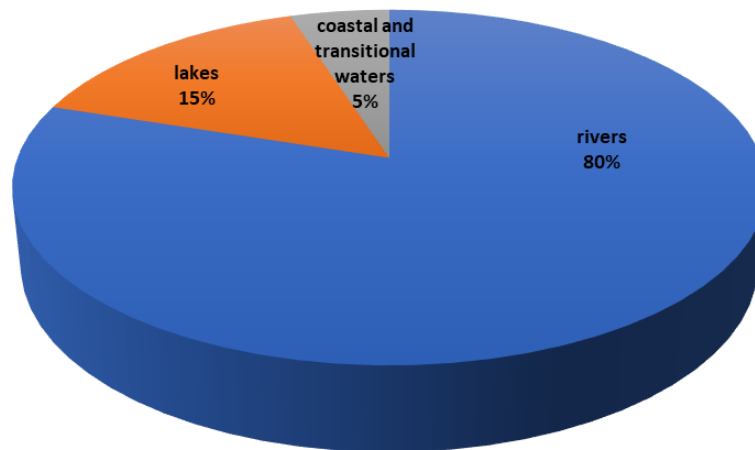


Figure 2: Distribution of water bodies in EU

Furthermore, all EU members share river systems with the countries they have common borders with. The only exceptions to this are the two islands Cyprus and Malta. Therefore, the approach of this directive is based on the rivers management. Management of water sources through river basins management covers the whole river system, from tributaries sources to the points that the river meets sea (estuary), including groundwater. Thus, water management in the European Union countries is finally based on the management of 110 river basins [3,4].

According to this approach, the characteristics of the river basin reflect its status and the impact of human activity on it. According to the WFD, each EU member-country must record regularly (every six years) the status of river basin district or the portion of the basin district falling within its territory, in case of an international river basin [5]. WFD classifies the chemical and ecological status of river basins in 5 categories, namely high, good, moderate, poor, and bad. For the classification of overall status, chemical and biological status, and morphological elements of the river basin should be considered. All EU members must work to reach at least a good status, which means that only a slight deviation from natural conditions is allowed (3).

3.4 Reuse of treated wastewater and WFD

Reuse of treated wastewater has been highlighted within EU water policy as one possible alternative water source in water-scarce regions, which may be appropriate to consider within water-scarcity planning. Wastewater treatment does not only contribute to and improve the index of water quantity but also the index of water quality, as less wastewater is rejected in urban sewage systems or, even worse, in surface water bodies. The “producers of wastewater” are strongly encouraged to collect and treat their wastewater in order for it to be reused by the same or another final user. In the recent years, many stakeholders have focused on the collection and treatment of mainly urban wastewater and the reuse of it for irrigation after proper treatment.

This reality has led the European Community to develop and publish a document with guidelines on water reuse “Guidelines on Integrating Water Reuse into Water Planning and Management in the context of the WFD, 2016”. These guidelines focused more on the reuse of urban wastewater. However, in this document some paragraphs refer also to industrial wastewater.

The reuse of industrial water contributes to greenhouse gas emissions reduction, as less energy is used for its treatment, compared to importing water, pumping deep groundwater, or desalination of seawater. Furthermore, treated water closes a loop in the circular economy.

“Guidelines on Integrating Water Reuse into Water Planning and Management in the context of the WFD, 2016” do not recommend a particular standard for the safe reuse of treated wastewater. However, this document provides information on the nature of standards, references to standards that have already been developed, and how they may be applied, including in the wider context of risk management.

Many European members have established the minimum standards that urban treated wastewater should comply with, in order to be used for irrigation or in industry, emphasizing on human health and on microbiological parameters. The example of Greek legislation is presented in the tables below.

Table 6: Standards for treated urban wastewater reuse as cooling water or for limited irrigation [6]

Type of reuse	Escherichia coli (EC/100mL)	BOD5 (mg/L)	SS (mg/L)	Turbidity (NTU)	Minimum required treatment	Minimum Sampling and Analysis Frequency
Limited irrigation	Average ≤200	CMD 5673/400/199	CMD 5673/400/199	-	biological treatment, disinfection	BOD5, SS, N, P according to CMD 5673/400/199
Industrial use (cooling water)						EC: once per week Cl (if used): continuously

Table 7: Standards for treated urban wastewater reuse in industry or for unlimited irrigation

Type of reuse	Escherichia coli (EC/100mL)	BOD5 (mg/L)	SS (mg/L)	Turbidity (NTU)	Minimum required treatment	Minimum Sampling and Analysis Frequency
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Unlimited irrigation	≤5 for 80% of samples	≤10 for 80% of samples	≤10 for 80% of samples	Average ≤2	secondary biological treatment, followed by tertiary biological treatment	BOD5, SS, N, P according to CMD 5673/400/5.3.97
Industrial use (except cooling water)	and ≤50 for 95% of samples					Turbidity and EC: 2 times per week and 4 times per week for treatment plants to population of 50000 Cl (if used): continuously

Table 8: Maximum concentration of heavy metals in treated wastewater [6]

Chemical element	Maximum concentration (mg/L)	Chemical element	Maximum concentration (mg/L)
Al	5	Mn	0,2
AS	0,1	Mo	0,01
Be	0,1	Ni	0,2
Cd	0,01	Pb	0,1
Co	0,05	Se	0,02
Cr	0,1	V	0,1
Cu	0,2	Zn	2,0
F	1,0	Hg	0,002
Fe	3,0	B	2
Li	2,5		

Sampling Frequency:

- 12 times per year for treatment plants equivalent to population of 200.000
- 4 times per year for treatment plants equivalent to population of 50.000-200.000

- 2 times per year for treatment plants equivalent to population of 10.000-50.000
- Once per year for treatment plants equivalent to population of 2.000-10.000
- No control is required for treatment plants equivalent to population of <2.000

In industrial practice, wastewater from specific procedure/procedures is collected and treated separately and then it is recycled back to the process it was produced from, used as cooling water, or it is discharged to the urban sewage system. This is one of the reasons that no specific legislation for the industrial treated wastewater exists in national level in all EU Members.

3.5 Conclusions

In conclusion, the WFD aims to good qualitative and quantitative status of water bodies and their dependent wildlife/habitats. Water recovery and reuse are encouraged and shown as alternative water source. This philosophy is mainly adopted for urban wastewater but not for industrial. The WFD and National water legislation are mainly oriented to the use of recovered water in agriculture and not in industrial sector. This use of water is not the most appropriate in an industrial zone as the water should be transferred far away, something that rarely happens and finally it is rejected to the closer water body losing a significant part of its value.

No specific standards are proposed in the WFD for recovered water used in industrial sector and many gaps appear in this issue in both European and National Legislation. Two options can be proposed to address this problem. The first is to incorporate these standards for industrial water reuse into the WFD and the second is to add these standards in a specific paragraph in BREFs. The second option seems to be more preferable, manageable, and less chaotic, as it will provide specific quality standards for water reuse in each industrial sector.

4. Waste Framework Directive

4.1 Main principles

Waste Framework Directive scope is to protect human health and the environment, minimizing the negative effects of waste generation and management. Although wastewaters are excluded from the WFD, this directive is reviewed to examine if its philosophy and main principles on handling waste could be transferred to wastewaters.

The WFD firstly focuses on successful resources management, aiming to waste prevention, secondly on reuse and finally on recycling and recovery (Figure 3). Based on this scheme, EU Members should take measures to achieve

the best overall environmental outcome. Members' governments should adopt a new waste legislation, built on existing legislation, and developed through a process including citizens and stakeholders. During the development of this new legislation, other factors besides environmental protection should be taken into consideration, such as sustainability, economic viability, technical feasibility, socioeconomic impacts, and human health.

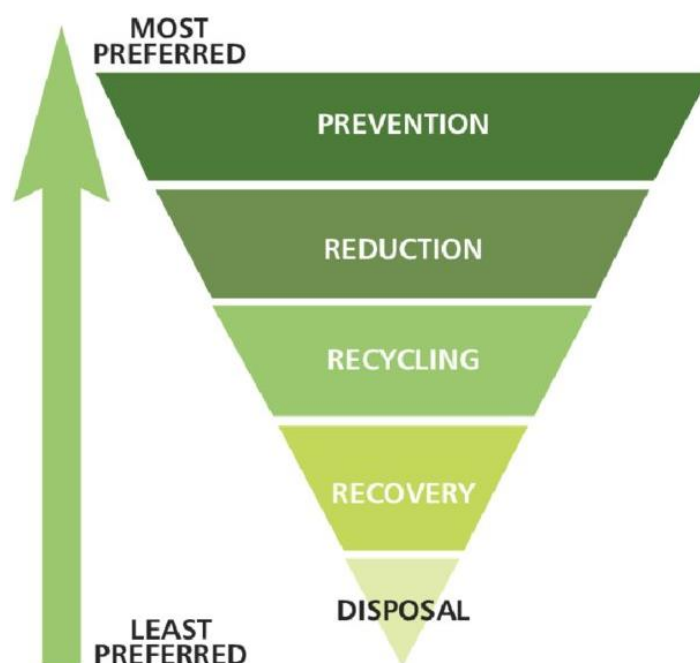


Figure 3: The waste hierarchy as described in WFD [7]

Through WFD, European Commission asks from EU Members to change the way new products are designed, inserting eco-designing processes which will reduce waste volume, minimize the presence of hazardous substances in waste, and aim to durable, reusable or recyclable products. However, this change could not be successful if it is not accompanied by a new consumption pattern.

According to WFD, EU members should also improve recovery operations. It is reported that division of waste in different streams with similar characteristics, and separate collection of these streams, when technically, economically and environmentally feasible, improves quantity and quality of recovered materials. Consequently, WFD asks Members States to use every available economic instrument to enhance start-up of enterprises for these waste streams processing. Apart from meeting higher quality and quantity standards for the recovered materials, European Commission promotes the idea of reuse and repair networks creation.

A part of the WFD, suggests that environmental management principles should be considered during production planning, so that the various waste streams produced are treated properly. The Directive also stresses the need for some secondary streams in the production, which could include valuable substances, to be characterized as

by-products and not waste. This way, a significant quantity of waste could be reused. A substance or object can be characterized as a by-product when certain requirements are met: the substance of object must be usable without any further processing than this adopted in normal industrial practice. Furthermore, the use of this substance or object must be consistent with the EU and National legislation and must not have any risk for human health or the environment.

Another crucial point in the Directive is the responsibility for waste management. In agreement with the polluter-pays principle, the producer of waste is also considered responsible for the waste treatment and the respective cost, entirely or in part. However, public or private waste collectors can undertake the waste treatment. Such private or public establishments can only operate by permission from the Member States Authorities. Member States Authorities are responsible to examine the application of an establishment for the collection and treatment of waste, and the level that this establishment fulfils the criteria of types and quantities of waste to be collected or treated, the site of installations, methodology and techniques used, and safety issues.

Member States are responsible to create an adequate network for collection, separation, and disposal of waste, following the Best Available Techniques. The design of this network must provide States with self-sufficiency. Installations for waste disposal or recovery of substances and/or materials from it, should be as near as possible to the source of waste. New or readily available technologies used in these installations should ensure the highest feasible level of human health and environment protection.

Hazardous waste should follow different paths of collection and treatment to ensure that it will not be mixed with non-hazardous waste, or waste of other hazardous categories. When hazardous waste must be transferred through EU countries, it must be properly packed and labelled. In addition, identification documents providing all the essential and required by the European legislation data must accompany the waste during transportation [8].

4.2 Waste prevention programmes and management plans

Through WFD, the EU asks from Member States to design and implement waste prevention programmes. In order to design such a programme, the existing situation should be recorded and realistic goals should be set. Furthermore, the existing programmes outcomes, if any, must be taken into consideration. For the new programmes evaluation new indicators should be set. The connection of these indicators with the decrease in waste production must be clearly defined. The objectives of these programmes must be based on breaking the link between waste generation and economic growth. Economic growth should not conflict with environmental and human health protection. Waste prevention programmes could be integrated into waste management plans or be part of a more general environmental policy programme.

Another obligation of Member States which arises from the WFD is the establishment of at least one management plan. The first step to be taken in the designing of such plans is the detailed analysis of the current situation in the geographical entity. The second is the decision on the measures that should be taken for the re-use, recovery, and

recycling of waste, and the motivations that will be offered to stakeholders in order to change the existing situation and minimize the waste production.

A waste management plan should contain a detailed description of:

- Waste streams characteristics
- Quantity of each stream in each geographical region and possible seasonal changes
- Prediction of possible changes of waste quantity in near future
- Recording of existing collection schemes
- Recording of transportation schemes and their environmental footprint
- Recording of recovery schemes
- Information and justification about the possible location where new infrastructure for recovery or incineration should be installed
- Existing waste National Policy
- Changes on existing or new National waste legislation
- Organizational aspects between public and or private sectors participating in the waste management
- Awareness campaigns to inform the public or specific group of consumers
- Recording and measures for the rehabilitation of sites that are or were contaminated in the past from waste disposal

Periodic inspections and recording of taken steps should be submitted to the EU. Finally, every Member State should submit a report on the results of plans and programmes [8].

4.3 End of Waste criteria

Legislation exists on the reuse of secondary recovery materials. This legislation aims to protect human health and the environment during different life cycle stages such as recovery, collection, transportation, and final use. However, when the risk of using these materials is very low, the legislation might impose restrictions on the recovery and exploitation of these materials. If the waste status changes, the material legislative framework will also change. Relaxation of a very strict legislative framework, where the level of risk allows it, will remove administrative burden and encourage recovery of materials from waste.

Article 6 of the WFD, mentions four requirements a material should meet, so as not to be characterized as waste [8]:

- *“The substance or object is commonly used for specific purposes;”*
- *“A market or demand exists for such a substance or object;”*
- *“The substance or object fulfils the technical requirements for the specific purposes and meets existing legislation requirements and standards applicable to products;”*

- *“The use of the substance or object will not lead to overall adverse environmental or human health impacts.”*

The first two requirements ensure that the recovered materials can find their way to the market. The third requirement ensures lawful use of material, while the fourth ensures material quality, and that both recovery process and use of recovered materials do not harm the environment or human health. To establish these criteria, a well described methodology has been applied on two scenarios, “the EoW scenario” and the “no action scenario”, the qualifying scenario assessing the following [9]:

- Environmental and health impact
- Economic impact
- Market impact
- Legislative impact
- Socioeconomic impact

Use of EoW criteria for the classification of a secondary material promotes quality and quantity of secondary products, improves alleviation of user prejudice against secondary materials, protects the environment, allows entrance of new players in the market and contributes to sustainable development.

4.4 Transferred experience from WFD to wastewater policy

The zero point for every waste management plan seems to be the detailed recording of type and quantity of waste produced by every sector. Respectively, the first step to be taken for a wastewater management plan should be the recording of wastewater sources, quantity, and characteristics, and the location of the wastewater sources. Separate stream collection is another, particularly good practice of the WFD and waste management that wastewater management could benefit from. It has been proven that the nearer to the source separation of waste streams the better the treatment results.

The decision on the best practice for wastewater treatment will depend on the geographical point of the wastewater source and on what exist around it. This means that the management plan should take into consideration the possible users of treated water and recovered materials from wastewater. For example, treated water or recovered materials could be used by the same or another nearly located industry (reinforcing industrial symbiosis) or for irrigation. Thus, the cost and the environmental footprint of water and recovered materials will be minimized, improving the economic feasibility of wastewater treatment plan.

The responsibility for wastewater treatment mainly falls on the producer, according to the polluter-pays principle. The Member States shall establish new legislation and motives for the industry to start new wastewater management plans. The new perspective which sees wastewater as a resource and not as a waste should be communicated by the local Authorities. New or existing economic tools shall be proposed and used for supporting industries with the capital expenditures (CAPEX). Finally, new techniques should be included in the BREF of each



industrial sector for the wastewater management with more details about operational expenditures (OPEX) and CAPEX and perspectives of this attempt.

5. Industrial Emissions Directive

5.1 Introduction

The Industrial Emissions Directive (IED) came into force in 2010. Its precursor, Integrated Pollution Prevention and Control (IPPC) directive 96/61/EC came into force in 1996, was withdrawn and included in IED in 2010. IPPC initiated the principle of integrated assessment of pollution, total pollution in the air, water and soil, and the concept of controlling industry pollution, giving them operation permission only in case that their emissions were under the limit values. Furthermore, IPPC initiated the BREFs as the tool for the organization of relevant information from each industrial sector [10]. Although a significant decrease of air emissions could be attributed to this directive, the administrative burden that IPPC with three other relevant directives (Large Combustion Plants Directive, Waste Incineration Directive, and Solvents Directive) imposed on the Member States makes its replacement necessary [11]. IED covers the operation of more than 50.000 industrial installations, including energy production, production and processing of metals, minerals, and chemicals, waste management, pulp and paper production, textile, food, intensive poultry, and pigs rearing.

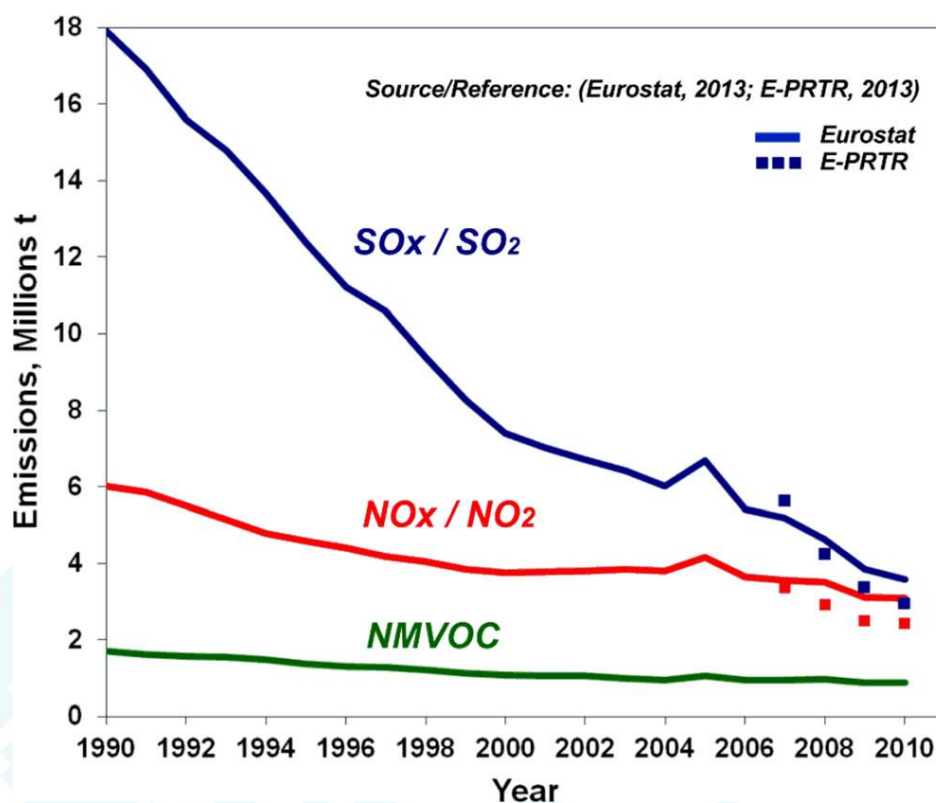


Figure 4: EU 27 air pollutants emission trend [12]

5.2 Industrial Emissions Directive main principles

IED aims to ensure human health and environmental protection through prevention, reduction, and elimination of industrial pollution. Furthermore, IED refers also to the best possible management of resources.

According to IED, the problem of emissions release should be solved as closely to the source as possible. IED encourages integrated control of emissions into the three environmental media, air, water, soil. It is mentioned that separate control of emissions to each environmental medium will probably shift the pollution problem from one medium to another. The integrated approach of emissions proposed in the IED is based on:

- emissions into the three environmental media
- produced waste
- accidents prevention
- energy efficiency.

Through the IED, EC asks Member States to make appropriate corrections, additions or extensions to the National legislation concerning industrial emissions. Member states should include in their National legislation the principles and communications results of Thematic Strategies on Air Pollution, Soil Protection and Prevention and Recycling of Waste.

BREFs are the main tool of IED implementation for National Authorities because they include the BATs description, emissions limit values, principles, and environmental management general directions for each industrial sector. EC is responsible to organize committees and communications with stakeholders and public for information collection and exchange. EC specific committees must update BREFs every eight year.

IED reinforces the role of the permission to operate, based on the achievement of the afore mentioned objectives. More precisely, an industry is allowed to operate only by permission from National Authorities. The permission should mention the measures for a high-level environmental media and human health protection as well as limit values for emissions. Permission conditions should be based on the BATs.

A relative flexibility is given by EC in setting limit values and techniques. Thus, in cases that environmental benefit is disproportionately lower than the capital and operational costs of BATs, higher emissions limits could be allowed. Additionally, in case that a technique which is not mentioned as BAT results in emissions lower than limit values, it could be included in the BREFs and allowed by National legislation.

When there is a need for changes or conversions on an industrial installation that will lead to higher emissions, a report mentioning changes reasoning and new emissions levels should be submitted to the National Authorities. In case of accidentally increase of emissions levels the National Authorities should be immediately informed. The operator/operators is/are responsible for the repairs that will ensure conformity with the IED and National

legislation. The operator/operators is/are responsible for rehabilitation of the environment and industrial installations. To avoid such cases, effective and dissuasive penalties should be established by Member States.

5.3 Industrial Emissions Directive and wastewater management

IED and IPPC directive writing has been affected by environmental problems arising from the operation of large combustion plants, waste incinerators and industries using organic solvents [11]. As a result, great emphasis is given to air pollutants produced by these industries, such as sulphur dioxide and other sulphur compounds, oxides of nitrogen and other nitrogen compounds, carbon monoxide, volatile organic compounds, heavy metals, dioxins and furans. The figure presenting the trend of air pollutants during the last 27 years shows that a significant release of air pollutants has been achieved.

Emissions of air pollutants, EU-28, 1990-2017
(Index 1990=100)

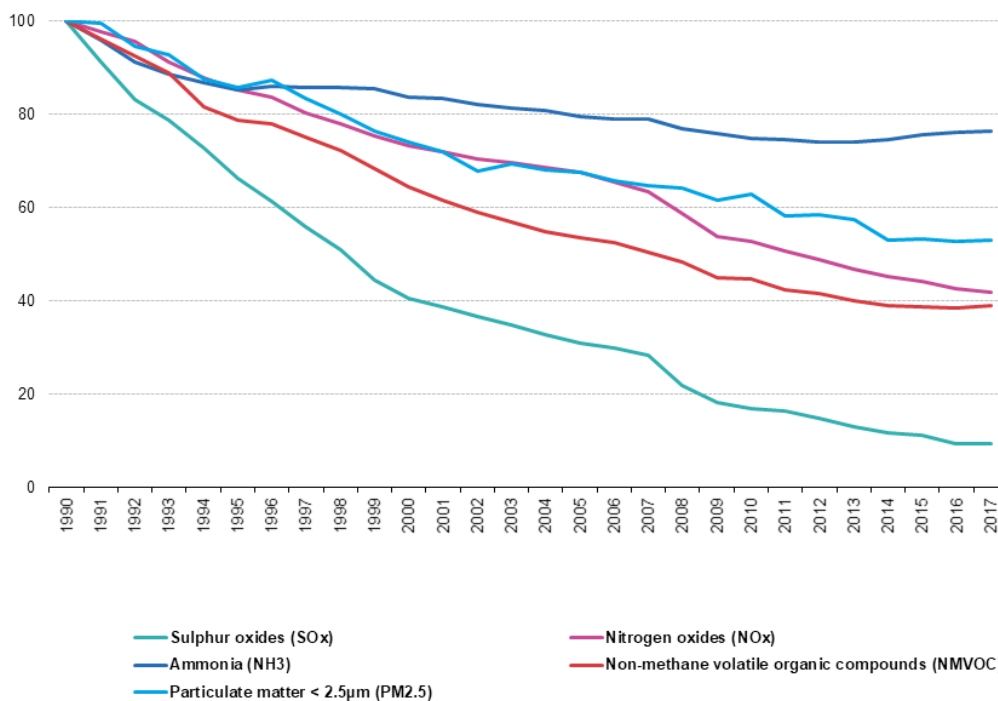


Figure 5: Emissions of air pollutants EU-28, 1990-2017 [14]

Although, the IED could be considered successful in driving down emissions to air and soil, its contribution to water quality and quantity is less extensive. Even though the IED is based on Thematic Strategy on Prevention and Recycling of Waste, it is not strongly combined with circular economy. Thus, wastewater is only seen under the perspective of pollutants removal and the safe discharge of treated wastewater to the receiving water bodies. Wastewater is not considered as a possible resource containing valuable substances, either for the industry which produced it or for another public or industrial market player. That means that the wastewater treatment is seen only as a burden for the industry without any economic profit.

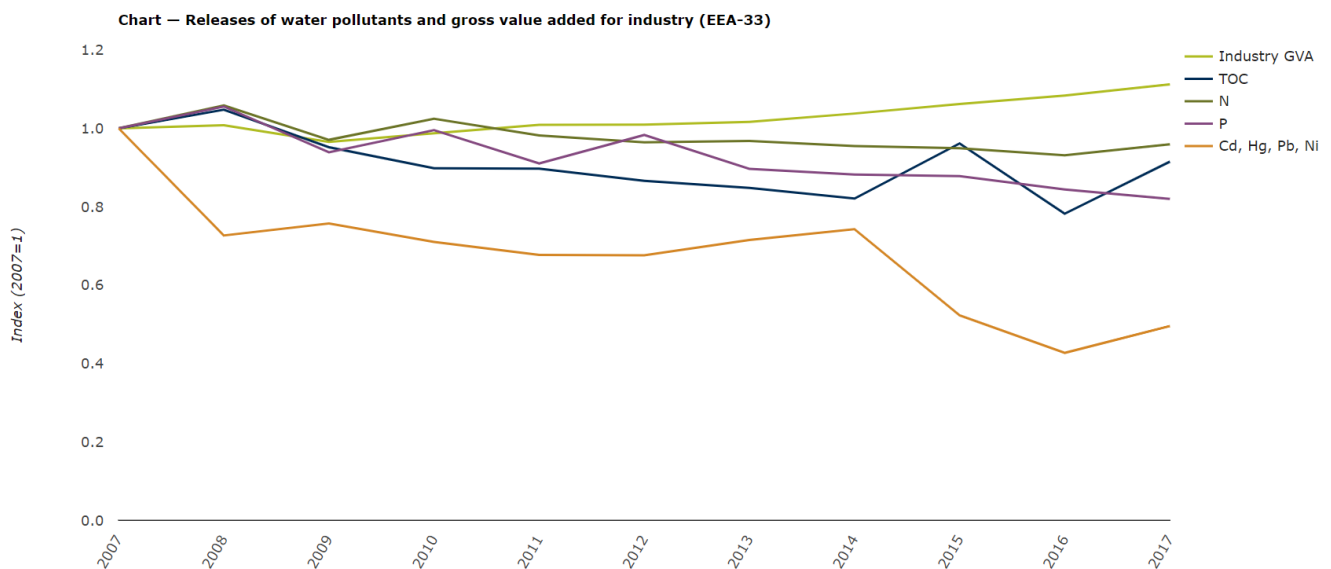


Figure 6: Release of water pollutants and gross value added for industry (EEA-33) [15]

No specific limits for emissions in water or quality characteristics for discharged water are mentioned in this directive. The IED uses and recommends BREFs for this reason. However, neither BREFs are written under this perspective. So, the principles of Circular Economy Strategy, Industrial Symbiosis, Zero Pollution Ambition and Green Deal should be considered for IED and BREFs update. Older or new techniques should be employed for the recovery of substances and clean water from wastewater with the minimum environmental footprint. Working on this direction, a new environmental management plan will arise for each industrial sector which will contribute to the sustainable development.

6. Best Available Techniques Reference Documents

6.1 General Information

A BREF is a publication resulting from a series of information exchange between stakeholders. These are regulators, industry, final users, and environmental non-governmental organisations. BREFs use operators' experiences of BAT to provide regulators with reference information for determining permit conditions. These documents describe applied techniques, emissions and consumption levels, methods used for the determination of the best available techniques, any new/innovative technique available, and conclusions on the above. The principles of integrated environmental management of a specific industrial sector are also presented into a BREF. BATs are described in BREFs according to the structure mentioned in the table 9.

Table 9: Standard 10-heading description structure of BAT [16]

Heading within the sections	Type of information included
1.Description	A brief technical description of the technique with a view to being used in the BAT Conclusions.
2.Technical description	A more detailed and concise technical description (using chemical or other equations, pictures, diagrams and flow charts if necessary).
3.Achieved environmental benefits	The main potential environmental benefits to be gained through implementing the technique (including reduced emissions to water, air and land; reduced consumption of energy, water, reagents and auxiliary materials; as well as production yield increases, reduced waste, etc.).
4.Environmental performance and operational data	<p>Actual and site-specific performance data (including emission levels, consumption levels - of energy, water, reagents and auxiliary materials - and amounts of residues/wastes generated) from well performing sites (with respect to the environment as a whole) applying the technique accompanied by the relevant contextual information.</p> <p>Any other useful information on the following items: how to design, operate, maintain, control and decommission the technique; emission monitoring issues related to the use of the technique; sensitivity and durability of the technique; issues regarding accident prevention.</p> <p>Links between inputs (e.g. nature and quantity of fuel, energy, water, reagents and auxiliary materials) and outputs (emissions, residues/wastes, products) are highlighted, in particular where relevant to enhancing an understanding of different environmental impacts and their interaction, for example where trade-offs have been made between different outputs such that certain environmental performance levels cannot be achieved at the same time.</p>

	<p>Emission and consumption data are qualified as far as possible with details of relevant operating conditions (e.g. percentage of full capacity, fuel composition, bypassing of the (abatement) technique, inclusion or exclusion of other than normal operating conditions, reference conditions), sampling and analytical methods, and statistical presentation (e.g. short and long-term averages, maxima, ranges and distributions).</p> <p>Information on conditions/circumstances hampering the use of the (abatement) technique at full capacity and/or necessitating full or partial bypassing of the (abatement) technique and measures taken to restore full (abatement) capacity.</p>
5. Cross-media effects	<p>Relevant negative effects on the environment due to implementing the technique, allowing a comparison between techniques, in order to assess the impact on the environment as a whole. Any side effects and disadvantages caused by the implementation of the technique.</p> <p>The Reference Document on Economics and Cross-media Effects (ECM) should be taken into account.</p>
6. Technical considerations relevant to applicability	<p>It is indicated whether the technique can be applied throughout the sector. Otherwise, the main general technical restrictions on the use of the technique within the sector are indicated. These may be:</p> <ul style="list-style-type: none"> • an indication of the type of sites or processes within the sector to which the technique cannot be applied; • constraints to implementation in certain generic cases, considering, e.g.: <ul style="list-style-type: none"> ○ whether it concerns a new or an existing site, taking into account factors involved in retrofitting (e.g. space availability) and interactions with techniques already installed; ○ site size, capacity or load factor; ○ quantity, type or quality of product manufactured; ○ type of fuel or reagents and auxiliary materials used; ○ animal welfare; ○ climatic conditions. <p>These restrictions are indicated together with the reasons for them. These restrictions are not meant to be a list of the possible local conditions that could affect the applicability of the technique for an individual site.</p>
7. Economics	<p>Information on the costs of techniques (capital/investment, operating and maintenance) and any possible savings (e.g. reduced consumption of energy, water, reagents and auxiliary materials, waste charges, reduced payback time compared to other techniques), revenues or other benefits including details on how these costs/savings or revenues have been calculated/estimated.</p>

	<p>Cost data are preferably given in euro (EUR). If a conversion is made from another currency, the data in the original currency and the year when the data were collected is indicated. The price/cost of the equipment or service is accompanied by the year it was purchased.</p> <p>Information on the market for the sector in order to put costs of techniques into context.</p> <p>Information relevant to both new and existing sites. This should allow assessment, where possible, of the economic viability of the technique for the sector concerned and possible economic limitations to its applicability.</p> <p>Information on the cost-effectiveness of the technique (e.g. in EUR per mass of pollutant abated) and related assumptions for their calculation may be reported.</p> <p>The Reference Document on Economics and Cross-media Effects (ECM) and the Reference Document on the General Principles of Monitoring (MON) are taken into account with regard to economic aspects and monitoring costs, respectively.</p>
8. Driving force for implementation	Where applicable, specific local conditions, requirements (e.g. legislation, safety measures) or non-environmental triggers (e.g. increased yield, improved product quality, economic incentives such as subsidies, tax breaks) which have driven or stimulated the implementation of the technique to date).
9. Example sites	Reference to (a) site(s) where the technique has been implemented and from which information has been collected and used in writing the section. An indication of the degree to which the technique is in use in the EU or worldwide.
10. Reference literature	Literature or other reference material (e.g. books, reports, studies) that was used in writing the section and that contains more detailed information on the technique. When the reference material consists of a large number of pages, reference will be made to the relevant page(s) or section(s).
<p>Source: Best Available Techniques (BAT) Reference Document for the Management of Waste from Extractive Industries in accordance with Directive 2006/21/EC, JOINT RESEARCH CENTRE, 2018</p>	

Conclusions are the final evaluations of BATs and one of the most important part of BREFs. They include:

- a description of each conclusion,
- an assessment of its appropriate application,
- emission levels associated with the best available techniques,
- associated monitoring,
- associated consumption levels,
- relevant site remediation measures, where appropriate.

As science and technology develop, new methods and techniques are introduced into the industries. These changes must be included into BREFs. As a result, BREFs are periodically reviewed and updated.

Any new installations must achieve the required standards mentioned in BAT conclusions before the operation start-up. Operators of existing installations are responsible for reconsidering everything in the production procedure to meet the BREF's required standards. In case of BAT conclusions absence, operators should continue to ensure that their installations meet the highest standards of environmental control.

Within the framework of ZB project, emission and consumption levels for each site are compared with those referred to in BREFs conclusions. Tables with streams concentrations, products, emissions, and efficiency of procedures in comparison with BREFs will be presented. Corrective actions and/or recommendations will be proposed.

6.2 Best Available Techniques Reference Document of the Textiles Industry

6.2.1 General Information

Global textile market size is estimated to \$ 1,041.8 billion in 2020, and an annual growth of 4.4 % is expected for the period 2021-2028 [17].

Textile is one of the most complicated types of industry that has one of the longest chains. At this sector, most Enterprises are of Small and Medium scale. The main three end-uses of this highly fragmented and heterogeneous sector are clothing, home furnishing, and industrial use.

This part of the industry in Europe represents:

- 3.4 % of manufacturing
- 3.8 % of the added value and
- 6.9 % of industrial employment [18].

This BREF covers the main environmental issues arising from the textile industry activities. These are primarily emissions to air and water, and energy consumption. As the textile industry uses water to almost all of its activities, the amount of water discharged, and its chemical load are the main concerns. The main environmental loads from textile industry in Europe are given in the next table.

Table 10: Main environmental loads from textile industry in Europe [17]

Substances	Environmental load (t/yr)
Salts	200 000 – 250 000
Natural fibres impurities (including biocides) and associated material (e.g. lignin, sericine, wax, etc.)	50 000 – 100 000
Sizing agents (mainly starch, starch derivatives, but also polyacrylates, polyvinylalcohol, carboxymethylcellulose and galactomannans)	80 000 – 100 000
Preparation agents (mainly mineral oils, but also ester oils)	25 000 – 30 000
Surfactants (dispersing agents, emulsifiers, detergents and wetting agents)	20 000 – 25 000
Carboxylic acids (mainly acetic acid)	15 000 – 20 000
Thickeners	10 000 – 15 000
Urea	5 000 – 10 000
Complexing agents	<5 000
Organic solvents n.d. Special auxiliaries with more or less ecotoxicological properties	<5 000
Source: Best Available Techniques (BAT) Reference Document for the Textiles Industry JOINT RESEARCH CENTRE Directorate B – Growth and Innovation Circular Economy and Industrial Leadership Unit European IPPC Bureau, Draft 1 (December 2019)	

The list of environmental issues relevant to water emissions which the Technical Working Group of this BREF has decided to investigate are presented in the table below:

Table 11: Key Environmental Issues (KEI) for emission to water

Group of Substances	Remarks
Total suspended solids (TSS)	KEI for direct discharges only
Chemical oxygen demand (COD)	KEI for direct discharges only
Total organic carbon (TOC)	KEI for direct discharges only
Total nitrogen (Total N)	KEI for direct discharges only
Total phosphorus (Total P)	
Hydrocarbon oil index (HOI)	
Sulphide (S ²⁻)	KEI for the installations using sulphur dye
AOX (adsorbable organically bound halogens)	
Alkylphenols and alkylphenol ethoxylates	
Brominated flame retardants	
Pesticides	KEI for wool scouring
Toxicity	
Antimony (Sb) and its compounds, expressed as Sb	
Chromium (Cr) and its compounds, expressed as Cr	

Copper (Cu) and its compounds, expressed as Cu	
Nickel (Ni) and its compounds, expressed as Ni	
Zinc (Zn) and its compounds, expressed as Zn	
Source: Best Available Techniques (BAT) Reference Document for the Textiles Industry JOINT RESEARCH CENTRE Directorate B – Growth and Innovation Circular Economy and Industrial Leadership Unit European IPPC Bureau, Draft 1 (December 2019)	

The main process activities referred to in this BREF and produce the main load of waste are listed below:

- coating
- dry cleaning
- fabric production
- finishing
- lamination
- printing
- singeing
- wool carbonizing
- wool fulling
- yarn production

Textile industry applies BAT to all these activities, in order to achieve minimum environmental disturbance. However, a waste with heavy pollutant load is produced at the end of the process. The treatment of this waste stream is covered by this BREF and it is not included in the directive 91/271/EEC.

6.2.2 Main BAT Conclusions for wastewater generated by textile industry

The main directions for wastewater management given in this BREF are listed below.

BAT Conclusion 9. Reuse and recycling techniques

According to this, Textile industry must reuse and/or recycle water streams produced by process activities. The degree of water reuse/recycling is limited by the content of impurities in the water streams. Thus, textile industry must adopt appropriate techniques for wastewater treatment, and/or reuse process liquor, extracted mainly from textile materials by mechanical dewatering.

BAT Conclusions 5 and 6

Operators and environmental managers of the unit should record the annual:

- consumption of water;

- energy and materials consumption;
- amount of wastewater generated;
- amount of materials recovered;
- amount of waste generated;
- amount of waste sent for disposal.

Monitoring includes direct measurements, calculations or recording. Monitoring is broken down to process level and records any significant changes in the processes.

Information about the quantity and characteristics of the waste water streams, such as: (a) average values and variability of flow, pH, temperature, and conductivity; (b) average concentration and load values of relevant substances/parameters and their variability (e.g. COD/TOC, nitrogen species, phosphorus, metals, priority substances, micro plastics); (c) data on bio eliminability (e.g. BOD, BOD to COD ratio, Zahn-Wellens test, biological inhibition potential, such as inhibition of activated sludge) should be recorded.

6.2.3 Optimised wastewater recycling and reuse

Effluents could be treated with a combination of filtration techniques (e.g. micro-, ultra-, nanofiltration, reverse osmosis) and/or evaporation. After wastewater treatment, the permeate is recycled in one of the process activities while the concentrate is either reused or further treated in order to recover auxiliary chemicals (e.g. sizing agents, dispersants, acids, salts) which can also be reused.

The efficiency parameters shown below, have been achieved in Life and Horizon projects on recycling and reusing of textile wastewater [18].

Table 12: Efficiency parameters on recycling and reusing of textile wastewater in Life and Horizon projects

Parameter reduction	Percentage
Fresh water consumption	40%, 70-100% for dyeing process (reuse up to 90% of treated water)
COD	80%
TSS	80%
Conductivity	70-80%
Turbidity	99%
Surfactants	62%
Colour	90-98%
NaCl	15% (60% for dyeing process)

6.2.4 Wastewater produced from Zorlu Textile Industry

Zorlu textile industry operates in the field of integrated polyester yarn and cotton home textile. Zorlu textile industry is located in Luleburgaz/Kirklareli/Turkey. Textile industrial wastewater of Zorlu Textile was treated with physicochemical, biological methods and membrane processes to obtain reusable stream. The water recovered from this advanced treatment system is used in the cooling system of the industry. This system is presented in Figure 7. However, a significant portion of the initial wastewater, namely RO concentrate, cannot be used.

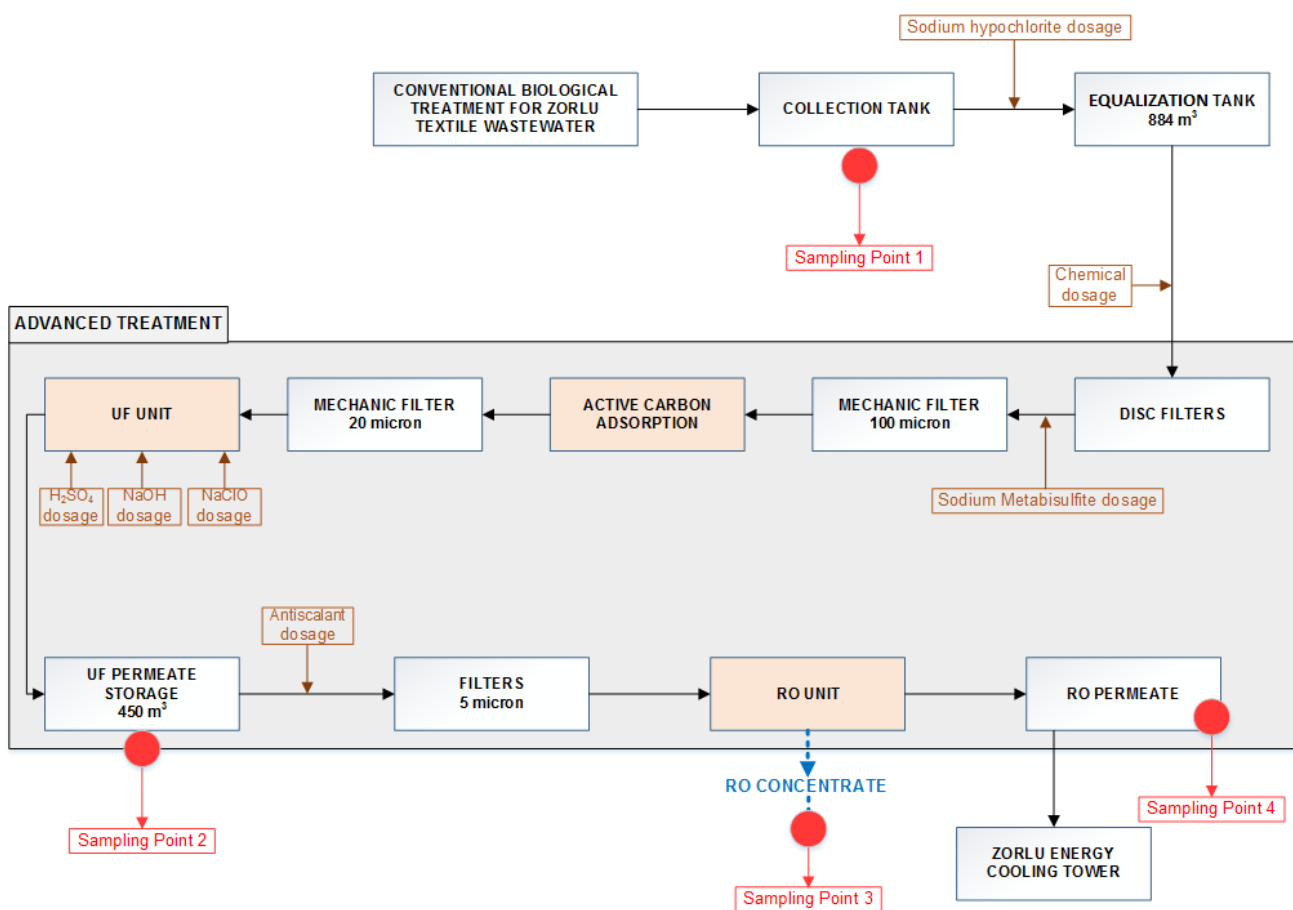


Figure 7: Process flow diagram of the advanced wastewater treatment system of Zorlu Textile industry

The goal of the system proposed in ZeroBrine is to treat this remaining wastewater in a manner that the recovered water can be used in the dyeing baths and the recovered salt in this or another industry procedure. It must be noted that hardness, colour, organic content, and sulphate content are fundamental parameters for the dyeing procedure.

The first step for the system design was the RO concentrate characterization. For this reason, regular sampling, and analyses of four streams were performed for a period of two months. The results of these analyses are shown in the table below.

Table 13: Analyses results of the four streams of Zorlu Textile advanced wastewater treatment system

Parameter	Unit	Biological WWTP Effluent	RO Feed Effluent	RO Retentate	RO Permeate Effluent
		Average \pm Standard Deviation	Average \pm Standard Deviation	Average \pm Standard Deviation	Average \pm Standard Deviation
Color Pt-Co	Pt-Co	236 \pm 54	30 \pm 2	72 \pm 5	0.9 \pm 0
Color SAC 436 nm	m-1	11 \pm 2	2 \pm 0.1	3 \pm 0.2	0.05 \pm 0.01
Color SAC 525 nm	m-1	17.1 \pm 30	0.4 \pm 0.03	0.73 \pm 0.1	0.02 \pm 0.01
Color SAC 620 nm	m-1	5.3 \pm 3	0.2 \pm 0.02	0.29 \pm 0.02	<0.01
Turbidity	NTU	15.4 \pm 9	1.6 \pm 0.3	1.88 \pm 0.2	<1
COD	mg/L	179 \pm 30	117 \pm 13	291 \pm 18	<10
TOC	mg/L	26 \pm 3	41 \pm 4	105 \pm 7	2 \pm 0.7
pH	-	7.96 \pm 0.2	8.2 \pm 0.1	8.2 \pm 0.1	6.5 \pm 0.2
Conductivity	μ s/cm	3384 \pm 794	4614 \pm 149	10630 \pm 253	62.7 \pm 13
TDS	mg/L	1781 \pm 438	2474 \pm 85	5980 \pm 152	30 \pm 6
Salinity, NaCl	%O	1.8 \pm 0.5	2.5 \pm 0.1	6.22 \pm 0.2	0 \pm 0
Total Hardness	mg CaCO ₃ /L	67 \pm 8	72 \pm 2	203 \pm 16	0.32 \pm 0.1
Total Alkanity	mg/L	895 \pm 158	918 \pm 10	2334 \pm 28	16.5 \pm 3
CO ₃	mg/L	8.5 \pm 5	11.1 \pm 1	34.87 \pm 10	0.01 \pm 0.004
HCO ₃	mg/L	887 \pm 154	907 \pm 11	2299 \pm 30	16.5 \pm 3
Cl	mg/L	336 \pm 42	590 \pm 28	1599 \pm 190	6.8 \pm 2
SO ₄	mg/L	480 \pm 367	779 \pm 45	1988 \pm 127	1.7 \pm 0.9
SiO ₂	mg/L	26 \pm 6	19 \pm 1	50 \pm 2	0.11 \pm 0.03
NH ₄ -N	mg/L	1.8 \pm 2	18.4 \pm 2	48.8 \pm 6	2.58 \pm 0.2
Total Nitrogen	mg/L	9.9 \pm 10	23 \pm 3	59.83 \pm 7	2.77 \pm 0.2
Total Phosphorus	mg/L	2.1 \pm 0.2	10.4 \pm 1	18.55 \pm 1	<1
Ag	(ppb)	0.1 \pm 0.03	0.1 \pm 0.1	0.09 \pm 0.03	0.18 \pm 0.1
Al	(ppb)	1644 \pm 210	123 \pm 19	283 \pm 73	15.13 \pm 4
As	(ppb)	0.9 \pm 0.1	1.4 \pm 0.1	3.42 \pm 0.3	0.04 \pm 0.02
B	(ppb)	172 \pm 37	189 \pm 28	372 \pm 21	44.2 \pm 6.9
Ba	(ppb)	9.05 \pm 2	10.1 \pm 0.4	25.79 \pm 2	0.65 \pm 0.2
Be	(ppb)	0.04 \pm 0.01	0.1 \pm 0.004	0.03 \pm 0.01	0 \pm 0.002
Ca	(ppb)	21007 \pm 2448	21890 \pm 716	61478 \pm 3736	105.7 \pm 26.2
Cd	(ppb)	0.1 \pm 0.02	0.1 \pm 0.005	0.04 \pm 0.01	0.01 \pm 0.003
Co	(ppb)	0.4 \pm 0.06	0.3 \pm 0.02	0.51 \pm 0.04	0.01 \pm 0.01
Cr	(ppb)	9.2 \pm 1.9	4 \pm 1	7.31 \pm 1	0.37 \pm 0.6
Cu	(ppb)	34.4 \pm 7.5	15.1 \pm 3	16.73 \pm 2	12.4 \pm 2.72
Fe	(ppb)	48.4 \pm 9	268 \pm 66	731.64 \pm 167	25.2 \pm 5
K	(ppb)	45810 \pm 8140	46538 \pm 1192	127759 \pm 6938	458.9 \pm 109
Li	(ppb)	50.5 \pm 12	65.22 \pm 3	173.57 \pm 13	0.38 \pm 0.1
Mg	(ppb)	3499 \pm 585	4074 \pm 101	11833 \pm 2876	13.8 \pm 4
Mn	(ppb)	4.5 \pm 2	21.68 \pm 1	57.48 \pm 6	0.23 \pm 0.1
Mo	(ppb)	2.2 \pm 0.5	1.6 \pm 1	2.38 \pm 0.2	0.22 \pm 0.1
Na	(ppb)	743231 \pm 240238	944316 \pm 32546	2392000 \pm 124778	8005 \pm 2217
Ni	(ppb)	1.96 \pm 0.4	3.8 \pm 3	4.73 \pm 1	0.38 \pm 1
Pb	(ppb)	1.57 \pm 0.3	1.3 \pm 1	1.38 \pm 0.4	0.62 \pm 0.1
Rb	(ppb)	19.33 \pm 4	23.9 \pm 1	60.92 \pm 4	0.32 \pm 0.06
Sb	(ppb)	3.98 \pm 1	2 \pm 0.1	5.53 \pm 0.5	0.08 \pm 0.03
Se	(ppb)	<0.05	0.3 \pm 1	1.32 \pm 0.3	<0.05
Sn	(ppb)	0.97 \pm 0.1	1.2 \pm 0.3	0.52 \pm 0.2	1.1 \pm 0.2
Sr	(ppb)	166 \pm 26	177 \pm 9	462 \pm 40	0.64 \pm 0.2
Tl	(ppb)	0.12 \pm 0.1	0.14 \pm 0.4	0.06 \pm 0.1	0.02 \pm 0.03
U	(ppb)	0.1 \pm 0.03	0.07 \pm 0.01	0.08 \pm 0.01	0.05 \pm 0.01
V	(ppb)	1.08 \pm 0.09	0.6 \pm 0.05	1.38 \pm 0.2	0.04 \pm 0.01
Zn	(ppb)	44.17 \pm 13	9.4 \pm 2	40.15 \pm 32	2.79 \pm 1

6.2.5 ZeroBrine proposed system for the textile wastewater treatment

The flow diagram of the pilot system for the retentate of reverse osmosis treatment is shown in Figure 8:

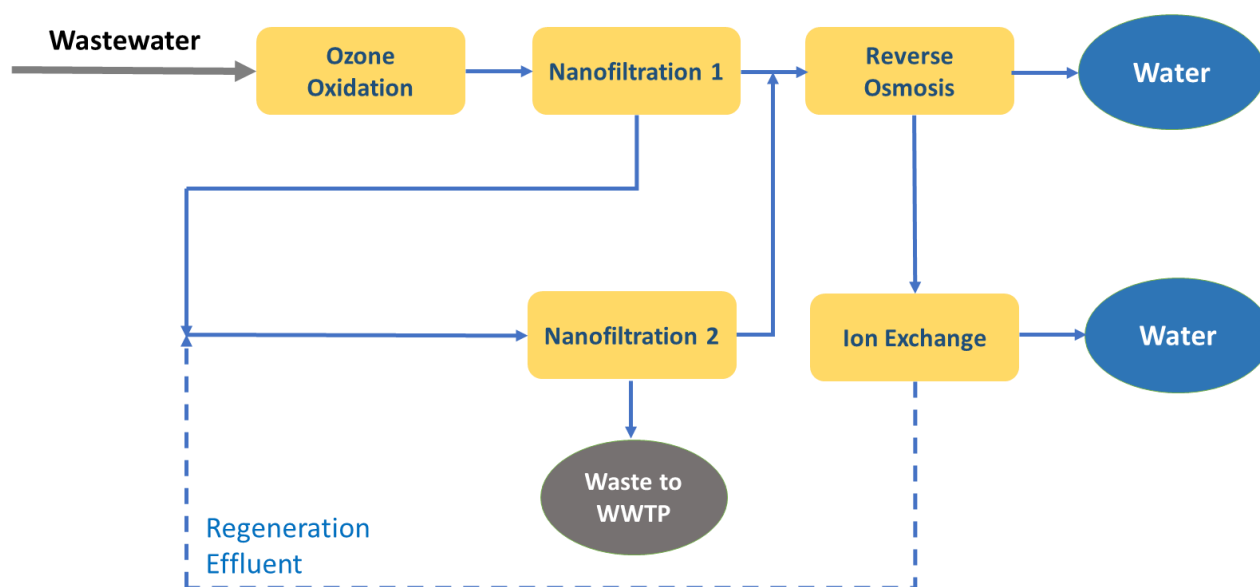


Figure 8: Process flow diagram of ZeroBrine proposed system for the textile wastewater treatment

The pre-treatment step consists of ozone oxidation and nanofiltration procedures. During ozone oxidation, the colour content and COD are removed. The effluent from ozone oxidation passes then through the first NF system. The concentrate stream of the first NF system is driven to the second NF system. The permeate streams of the two NF systems are mixed and feed to the reverse osmosis system. The concentrate of the second NF system is recycled back to the WWTP.. The divalent ions are removed by the nanofiltration procedure.

The second step is the concentration step, reverse osmosis. The reverse osmosis system effluents are divided in two streams, i.e., the permeate stream which has the appropriate characteristics to be used in the dyeing baths, and the concentrate stream which passes through an ion exchange system to be softened. The effluent/brine of the ion exchange unit can be also used in the textiles production. To achieve the goal of zero liquid discharge even the ion exchange regeneration effluents are mixed with NF1 concentrate stream and are driven to the second NF system.

The significant parameters of the effluents from ZeroBrine proposed wastewater treatment system, namely RO permeate and IEX system are presented in table 14. As it can be concluded all the efficiency parameters of table 12 are met by this ZeroBrine proposed system.

Table 14: Significant parameters of the effluents from ZeroBrine proposed wastewater treatment system

Parameter	Unit	Wastewater	RO permeate (recovered water)	IEX effluent (recovered salt solution)
Color Pt-Co		40	<1	24
Ca	mg/L	80	4	0.206
Mg	mg/L	28	2	0.251
Cl	mg/L	601	103	2,584
SO ₄	mg/L	1,350	<10	2,200
CaCO ₃	mg/L	340	22	1.64
COD	mg/L	220	<10	58
TDS	g/L	4.57	0.5	12.6

6.2.6 Zerobrine proposed system and BREF for Textiles Industry

The example of the ZeroBrine proposed system could be used as a prototype for the revision of the paragraph regarding prevention and reduction of emissions to water.

Some of the advantages of the system are:

- zero liquid discharge, as only a portion of about 6% (NF2 concentrate) are driven to WWTP.
- all the streams produced by the system are used in the production (high quality water, brine).
- 400 tons/year of NaCl, and 50,000 tons/year of high purity water recovered.
- saving of 20,000 €/year from NaCl recovery, 50,000 €/year from water recovery.

Following the Standard 10-heading description structure of BAT, characteristics and results from the ZB proposed system implementation for the treatment of wastewater produced by textile industry could be summarized in the next paragraphs.

Description: The proposed system is based on the combination of existing techniques, such as ozone oxidation, nanofiltration, reverse osmosis and ion exchange. Using these techniques, ions are separated from water. High purity water and a brine that can be used in textile production are recovered.

Technical description: The proposed treatment could be divided in three stages. At the first stage, pre-treatment, ozone oxidation and nanofiltration remove organics, colour, and a significant part of the divalent ions to prevent RO membranes operational problems.

At the second stage, concentration, RO membranes are used to separate the remaining ions from the wastewater. At this stage, the stream of permeate, high purity water, is the 80% of the inflow stream. The concentrate stream

is then softened, using ion exchange column. The product of this final step, softening step, is a brine with appropriate properties to be used in the textile production procedure.

Achieved environmental benefits: The environmental problems from the wastewater discharge are avoided, as about 94% of water is recycled and reused in the textile production line. Furthermore, the remain brine has the appropriate characteristics to be reused in the production procedure.

Environmental performance and operational data: Environmental assessment of ZB technology will be presented in the D7.7. In D7.3, preliminary LCA concluded that the highest environmental burden is caused by the operation step and mainly due to electrical power consumption from ozone oxidation and RO procedures. More recent data analysis, presented in Figure 9, shows that these two procedures account for ca. 75 % of the total environmental impact.

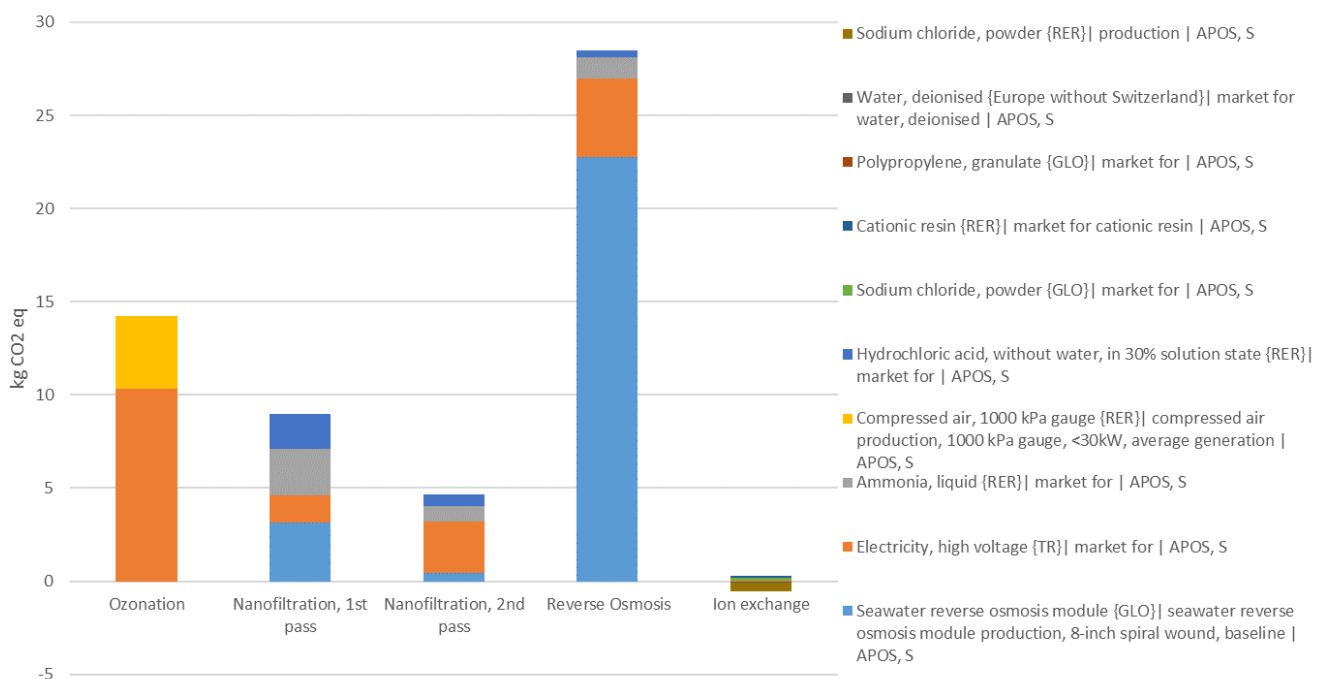


Figure 9: LCA results, Kg CO₂ per stage

Cross-media effects: The main cross effect of the system is CO₂ emissions corresponding to the electrical power used for system operation.

Technical considerations relevant to applicability: Generally, there are no technical restrictions to the applicability of this system.

Economics: The system can be fully automated, thus the operational cost, is due to the electrical power. It is estimated that the cost of electrical power is 2,7 €/m³ of wastewater, while the cost of used chemicals is three to four times lower. This low operational cost in combination with savings from recycled water and brine and the

wastewater discharge fees, make this techniques combination attractive. The final LCA and LCC analyses will be presented in WP7, deliverable 7.7 (M52).

Driving force for implementation: Apart from environmental legislation, and compliance with environmental standards for emissions to water, the driving force for system implementation are also the low cost of the treatment/m³ of wastewater and circularity adoption.

6.3 Best Available Techniques Reference Document for the Management of Waste from Extractive Industries

6.3.1 General Information

The extractive industry plays a crucial role in the socioeconomic status and the autonomy of European Union countries. In the last decade, demand for raw materials is continuously increasing and the European Community tries to rely on its own sources as much as possible, in order to minimize imports and increase its competitiveness. Extractive industry offers socioeconomic growth in the area it is established in, as many jobs are created.

Table 15: Major mineral commodity production in the EU-28 [19]

Country	Major mineral commodity production in the EU
Austria	Magnesite
Denmark	Diatomite
Germany	Aggregates, barytes, coal and lignite, kaolin, potash and salt
Greece	Bauxite, bentonite, nickel and perlite
Hungary	Manganese
Finland	Chromium, gold and platinum group metals (PGMs)
France	Mica and talc
Ireland	Alumina and zinc
Italy	Feldspar
Poland	Lead, copper and zinc
Portugal	Lithium and tungsten
Spain	Fluorspar, fuller's earth, gypsum, strontium minerals and tin
Sweden	Iron
U.K.	Oil and gas

Source: *Best Available Techniques (BAT) Reference Document for the Management of Waste from Extractive Industries in accordance with Directive 2006/21/EC, JOINT RESEARCH CENTRE, 2018*

However, extraction procedures generate great amounts of extractive waste that require appropriate management. The most preferable way to manage extractive waste during the last decades was to deposit it in Extractive Waste Facilities such as heaps, ponds etc. Nevertheless, the extractive waste facilities have increased the local concern due to their negative impact on the local environment and human health.

For this reason, one of EU priorities is to prevent, minimize and reuse waste from extractive industry with processes and techniques that will yield positive returns to the industry. The minimization of negative environmental and human health impact of waste generated from the extractive industry will also help local communities accept existing and new extraction projects.

Various techniques have been proposed in this BREF to minimize the environmental footprint of the extractive industry. The technique or the combination of techniques that will be chosen for the waste treatment depend on the pollutants, and the physical and chemical characteristics of waste. Regardless of the type of waste treatment, the whole process should follow BAT conclusions.

6.3.2 BAT conclusions for water waste produced from the extractive industry

When BAT is seen as a guidance of stakeholders, BAT Conclusions should be used as a reference:

- providing up-to-date information on the waste management
- providing techniques aiming to minimize adverse effects that the extractive process has to human health and the environment.

BAT conclusions referred to in management of water waste produced during extractive process are:

BAT Conclusion 1

In order to improve the overall environmental performance of the extractive waste management, operators must adopt:

- Organisational and Corporate Management system (O&CMS)
- Environmental Management System (EMS)

BAT Conclusion 2

In order to support the identification of potential environmental risks and impacts associated with the extractive waste characteristics, an initial extractive waste characterisation should be made.

BAT Conclusion 3

The extractive waste characteristics should be reviewed and verified.

BAT Conclusion 4

In order to support the identification of potential environmental risks and impacts associated with the extractive waste site and extractive waste management options, BAT is to use all of the following techniques:

- Identification of extractive waste site options
- Identification of extractive waste handling/ transport, treatment, and deposition options

BAT Conclusion 5

In order to determine the potential environmental risks and impacts brought about as a result of the management of extractive waste, BAT is to use all of the following techniques:

- Hazards and risk elements identification
- Environmental Risk and Impact Evaluation

BAT Conclusion 7

In order to reduce the generation of non-inert extractive waste and hazardous extractive waste, BAT is to use the following techniques:

- Management of extractive waste accumulated during exploration /prospecting
- Sorting and selective handling of extractive waste

6.3.3 Waste treatment efficiency parameters

The techniques or combination of techniques proposed in this BREF result to the below mentioned abatement of pollutants. Operators could compare the efficiency parameters of their system with those presented in the next table to evaluate the effectiveness of their treatment system. This evaluation could be used either for well referred techniques or for some new/innovative techniques, not mentioned in this BREF.

Table 16: Efficiency parameters proposed in extractive industry BREF

Efficiency parameter	Removal or reported levels at the end of waste processing
pH	6-9
Total Dissolved Substances (TDS)	<1g/L
Total Suspended Solids (TSS)	up to 90 %
Sulphates (SO_4^{2-})	80-99%
Nitrites (NO_2^-)	40%
Nitrates (NO_3^-)	60-90%
Ammonia/Ammonium ($\text{NH}_3/\text{NH}_4^+$)	70-90%
Total Nitrogen	50-95%
Phosphates (PO_4^{3-})	70%
Chloride (Cl^-)	<0,4 g/L
Chemical Oxygen Demand (COD)	<15mg/L-100 mg/L
Arsenic (As)	50-98%

Cadmium (Cd)	50-95%
Chromium (Cr)	60-70%
Copper (Cu)	80-99%
Iron (Fe)	94-99%
Lead (Pb)	60-99%
Manganese (Mn)	40%
Mercury (Hg)	<0,3-2µg/L
Nickel (Ni)	50-80%
Zinc (Zn)	80-99%
Cyanides	<0,1 mg/L

6.3.4 Wastewater from coal mine industry

It is estimated that the total hard coal production in the EU in 2019 was 65 million tons. Hard coal as well as brown coal are used in plants for production of electrical power or heat.

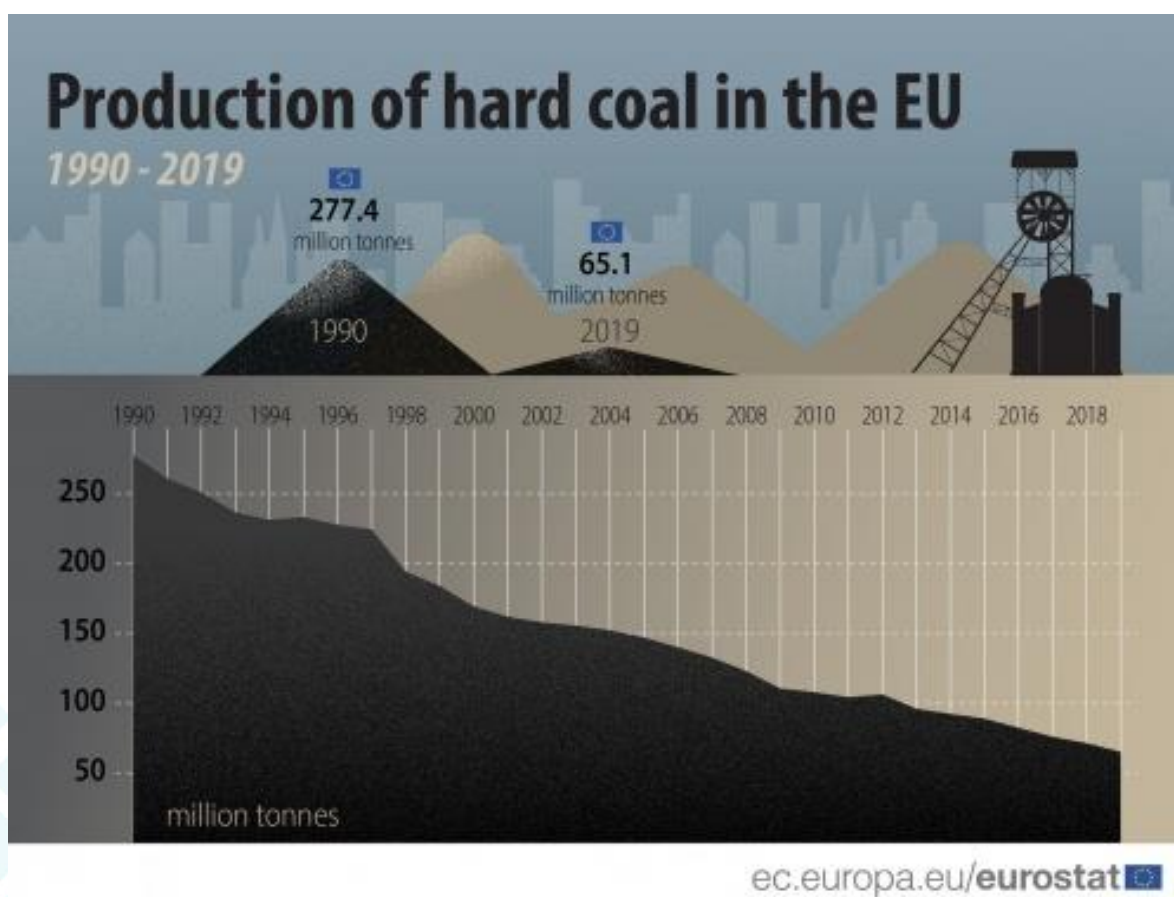


Figure 10: Hard coal production in the EU

Poland produces 95% of the hard coal produced in the EU. Coal mine extraction generates huge amounts of brine. Thus, Poland which is the dominant producer of hard coal in the EU needs to manage millions of tons of brine from coal extraction.

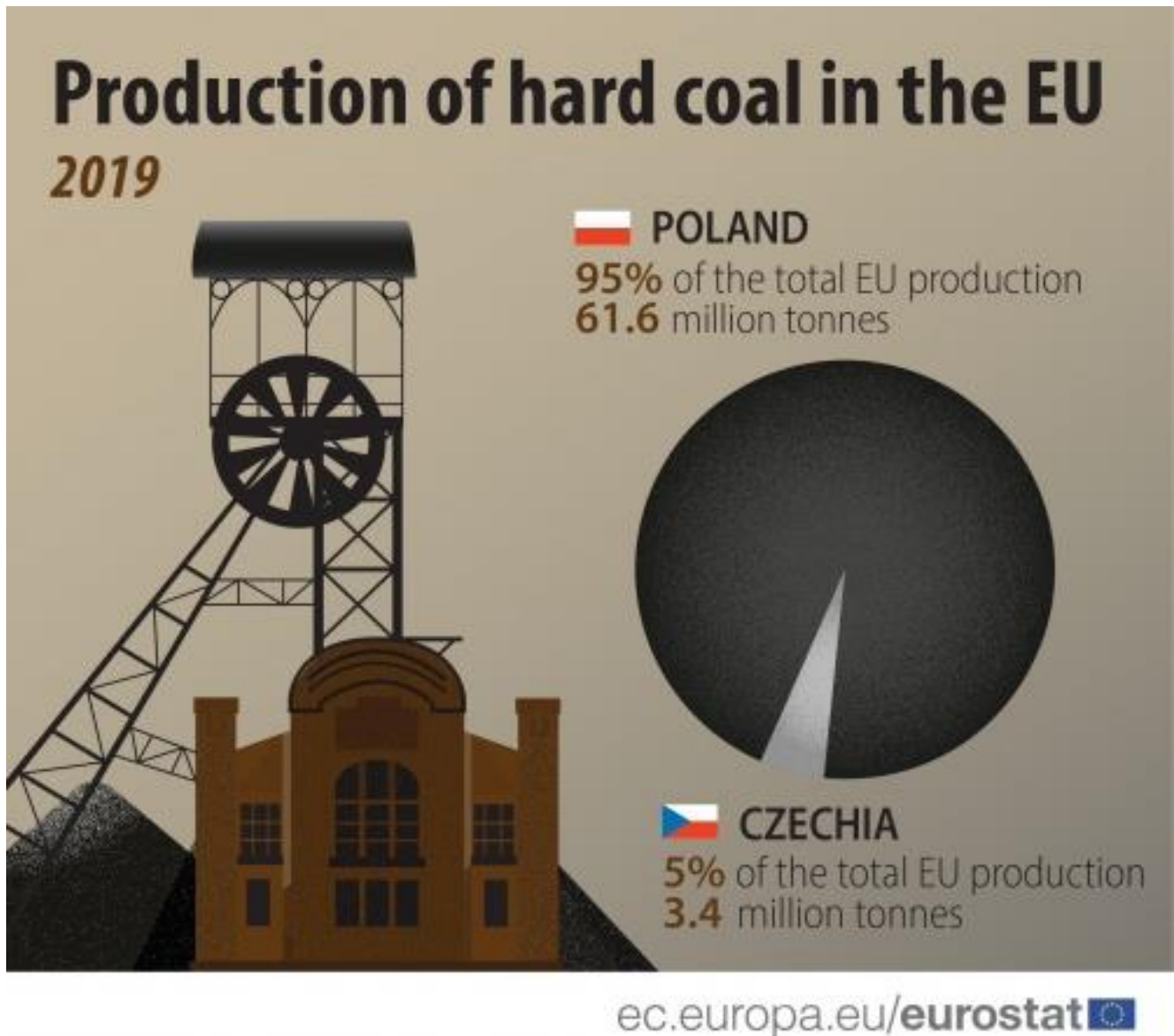


Figure 11: Countries with the largest production of hard coal in the EU

The main management strategy for most coal mines is the deposition of extractive brine into pond-type deposition areas. There, the wastewater is left to separate from salts and coal through gravity. Although this technique is the most used, direct or indirect drainage of this wastewater to water bodies results in significant degradation of Polish rivers' ecological status. According to the reports demanded by WFD the ecological status of Polish rivers is characterized as moderate. Vistula, which provides 55% of fresh water in Poland received high pressure from the Polish coal mines. It is estimated that Vistula salination has a cost of 150-200 million \$ per year (losses in industry, agriculture and from water transport).

In the BREF of extractive industry, many techniques for the management of this brine are mentioned. All these techniques are used to purify the water and produce a more concentrated brine. However, they do not recover salts in a form and purity that allow for market exploitation. Thus, the problem of the salts or concentrated brine remains. The Zero Brine proposed system was designed under the perspectives of zero liquid discharge and circularity.

PGG is the EU's largest black coal mining company, producing annually ca. 30 Mt of black coal. The Zero Brine proposed system operated in the PGG "Bolesław Śmiały" coal mine. "Bolesław Śmiały" wastewater has a TDS of ca. 23-24 g/dm³ and is saturated with calcium carbonate. The most significant brine characteristics are shown in Table 17:

Table 17: The most significant ingredients and characteristics of "Bolesław Śmiały" coal mine wastewater

Parameter	Unit	Wastewater
Cl	mg/L	13,500
Na	mg/L	8,200
Mg	mg/L	248
Ca	mg/L	263
SO ₄	mg/L	621
Si	mg/L	0.0014
Sr	mg/L	0.0016
Solid particles		high concentration
Carbonate ions		saturated
TDS	g/L	22.9

6.3.5 ZeroBrine proposed system for the treatment of coal mine wastewater

The proposed system for the treatment of the wastewater produced by coal mine industry, is based on the combination of existing innovative technologies such as ultrafiltration, nano filtration, reverse osmosis, electrodialysis, electro dialysis and evaporation. The wastewater treatment stages are shown in Figure 12.

The wastewater has a high concentration of suspended solids-particles, that could damage or cause operational problems to the NF and RO membranes. To remove all these materials, wastewater is initially treated by four different filters. Then, it is driven through an ion exchange column to be decarbonized. After ion exchange and ultrafiltration, the wastewater is treated following two nano filtration stages. The ratio of permeate/concentrate is equal to 75% in each stage. The concentrate from the first NF stage is the inflow for the two precipitation stages from which Ca and Mg are recovered in the form of gypsum and Mg(OH)₂. The effluent from the second precipitation stage is mixed with the concentrate of the second NF stream, in the inflow stream of the first NF stage. The RO inflow is the permeate of the second NF stage. The permeate/concentrate ratio of RO is equal to

56%. The RO concentrate passes through an electro dialysis unit, an evaporator and finally a crystallizer, to recover NaCl.

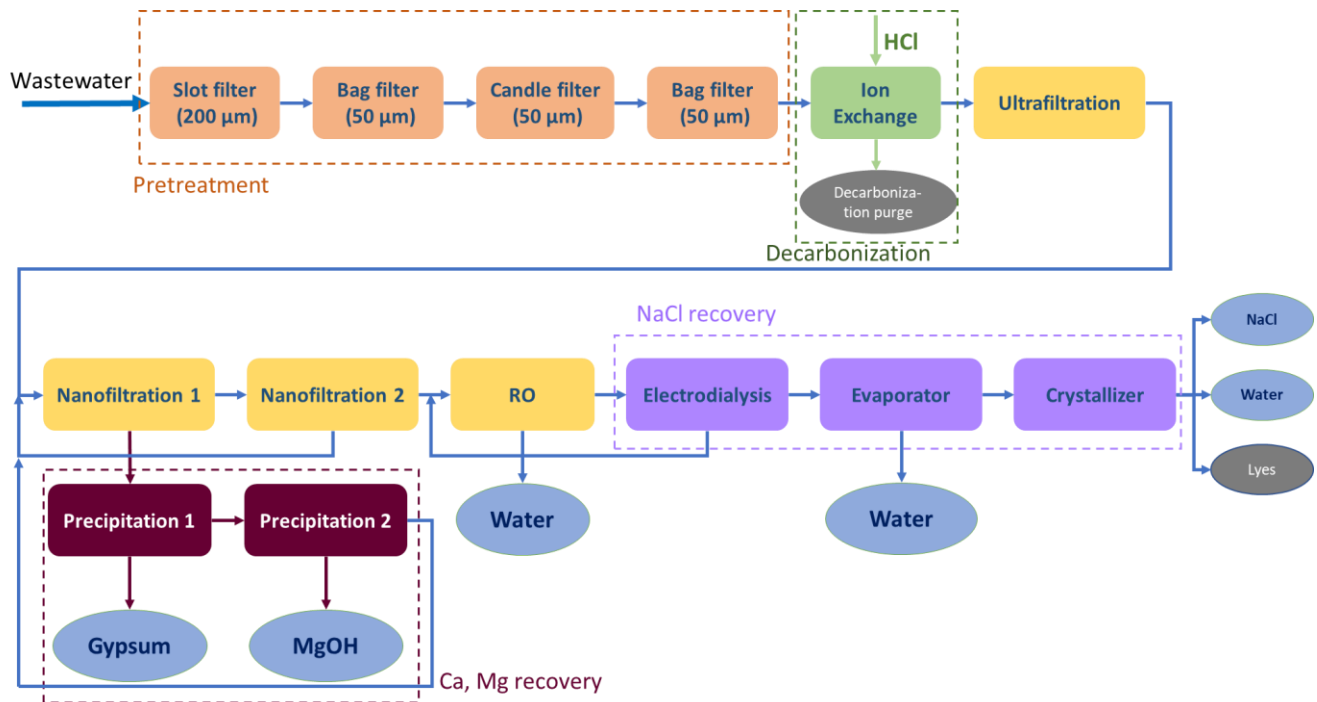


Figure 12: Process flow diagram of ZeroBrine proposed system for the coal mine wastewater treatment

6.3.6 ZeroBrine proposed wastewater treatment system and BREF for the Management of Waste from Extractive Industries

The example of the proposed system by ZeroBrine could be used as a prototype for the revision of the paragraph regarding techniques to prevent or minimize the visual impact and footprint from the management of extractive waste. In this paragraph, some of the techniques used, such as ion exchange, nanofiltration, reverse osmosis and filtration are suggested for the reduction of the wastewater to a brine. However, even though the total volume of wastewater is reduced, the management of a concentrated brine remains as a cross effect of these methods.

Some of the advantages of the system are:

- About 91% of the initial volume of wastewater is recovered as high-quality water, which could be used in industry, for irrigation, or for municipal purposes.
- 95.5% of NaCl recovery.
- 95% recovery of Magnesium as magnesium hydroxide with 98% purity. It must be highlighted that magnesium is one of the critical raw materials for Europe. The cost of magnesium hydroxide is estimated to \$ 1000/ton.
- 75.5% recovery of Calcium as gypsum.

- The total energy consumption of the system is 23-33% lower than this of the conventional system for salt recovery from coal mine brines.
- Electricity cost is estimated to 1.08 €/m³ of treated wastewater and the cost of added chemicals to 0.5 €/m³.
- It is concluded that the ZB proposed system meets all the efficiency requirements mentioned in Table 16.

Following the Standard 10-heading description structure of BAT the characteristics and results from the implementation of the ZB proposed system for the treatment of wastewater produced from coal mine industry could be summarized in the next paragraphs.

Description: The proposed system is based on the combination of existing techniques such as nanofiltration, ultrafiltration, reverse osmosis, electro dialysis, evaporation, crystallization. Using these techniques, dissolved salts are separated from water. High purity water, magnesium hydroxide, and sodium chloride are the end products of this treatment.

Technical description: The proposed treatment could be divided in four stages. At the first stage, pre-treatment, particles and suspended solids are removed from the wastewater to prevent membranes and systems operational problems. At the second stage the wastewater is treated by ion exchange to be decarbonized. At the third stage divalent ions such as Mg, Ca and SO₄ are removed with nanofiltration, and monovalent ions are removed with reverse osmosis. At the fourth stage, these ions precipitate/crystallize to give valuable market products.

Achieved environmental benefits: The most significant environmental problem solved by the proposed system is the rivers degradation, caused by the extracted wastewater salts. The environmental problems from the wastewater discharge are avoided, as 91% of water is purified and could be exploited as water of high quality and purity, and the sodium chloride is recovered. Furthermore, ions existing in the brine such as Mg and Ca are also recovered as commercially exploitable products.

Environmental performance and operational data: Preliminary environmental assessment of ZB technology is presented in the D7.3. In this deliverable it is shown that reverse osmosis and crystallization with ion exchange membranes (used for the magnesium recovery) are the stages with the highest environmental burden. All the other stages have very low environmental impacts. The main environmental impact of the system is due to electricity consumption. Chemicals used for the precipitation of Ca and Mg, and chemicals used for maintenance or cleaning purposes have a very low environmental impact. More recent data analysis, presented in Figure 13, indicates that decarbonisation and electro dialysis produce the highest amount of CO₂. Final LCA results of the system as well as comparison of them with the environmental impacts of the conventional system for coal mine brine treatment used in Poland will be presented in D 7.7 (M52).

Cross-media effects: The main cross effect of the system is CO₂ emissions corresponding to the electrical power used for system operation.

Technical considerations relevant to applicability: Generally, there are no technical restrictions to the applicability of this system.

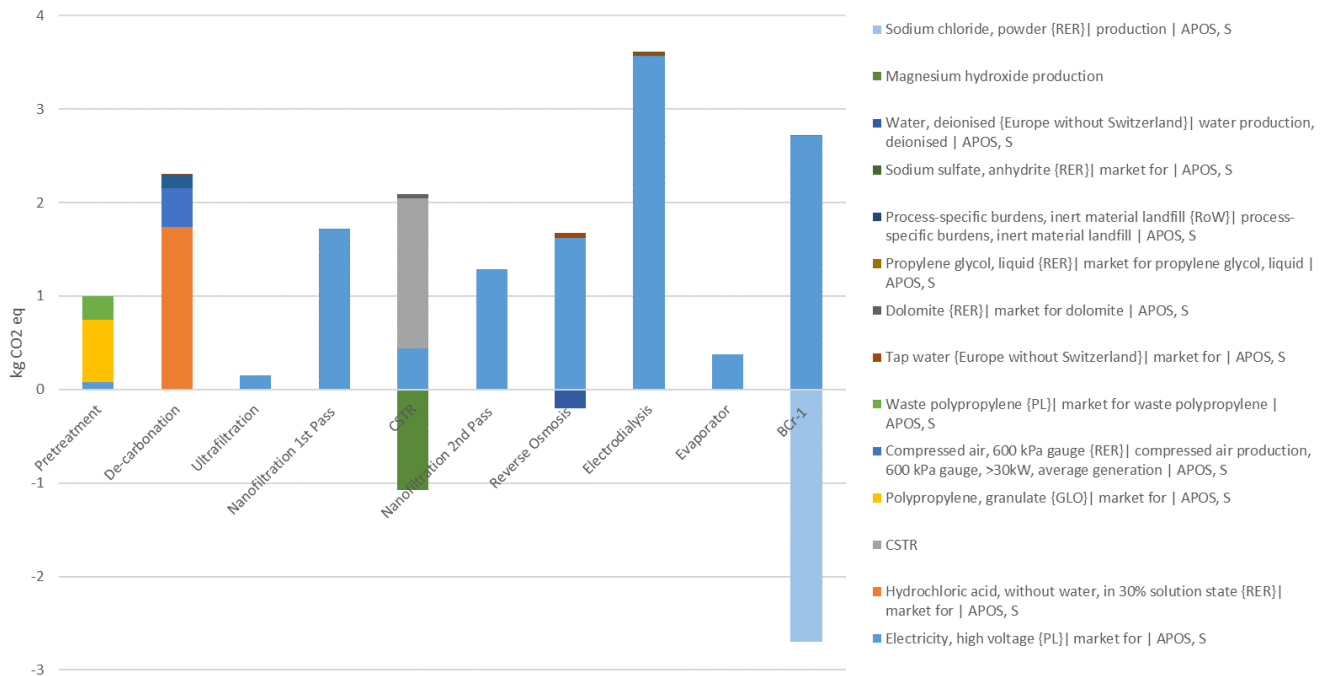


Figure 13: LCA results, Kg CO₂ per stage

Economics: Electricity cost is estimated to 1.08 €/m³ of treated wastewater and the cost of added chemicals to 0.5 €/m³. Income from magnesium hydroxide (very high price \$ 1000/ton), from the water, NaCl and gypsum, as well as savings from the environmental fees for the brine disposal, should be added to the system's business plan. The CAPEX of the system will be estimated and reported in the D7.7 (M52).

Driving force for implementation: Except of environmental legislation, driving force for system implementation are also the low cost of the treatment/m³ of wastewater, the high income from the produced salts and water, and the savings from the fees charged for the brine discharge.

6.4 Best Available Techniques Reference Document for the Manufacture of Large Volume Inorganic Chemicals - Solids and Others Industry

6.4.1 The significance of precipitated silica market

The global silica market size was estimated at USD 5.61 billion two years ago. It is expected to expand at a Compound Annual Growth Rate of 9.4% over the next five years.

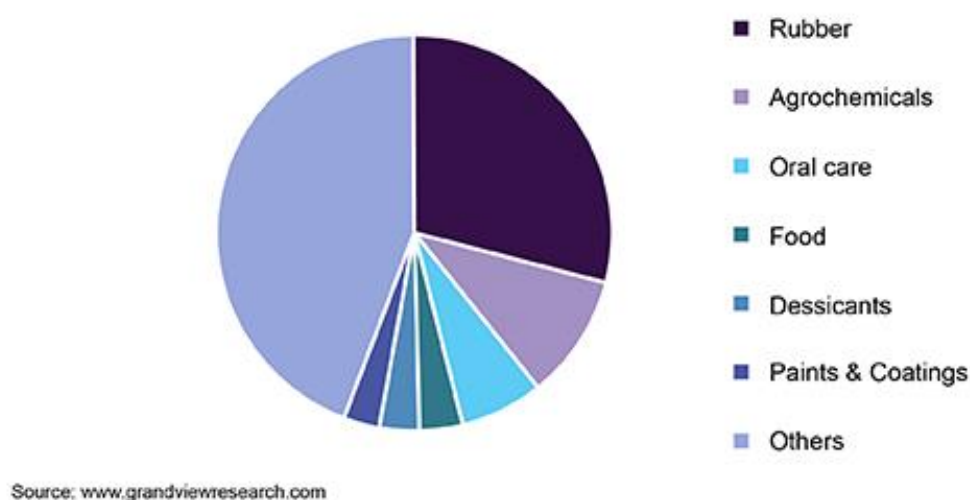


Figure 14: Global specialty silica market revenue share, by application, 2018 (%)

Precipitated silica led the silica market with a share of 35.7% in 2018. It is used in Tire and non-Tire Rubber, Personal Care & Cosmetics, Plastics, Chemicals, Agriculture & Animal Feed, Food & Beverages, Paints, Coatings & Inks, Paper & Textiles, Adhesives & Sealants Industry [21].

Precipitated silica industry growth is driven mainly by the rising demand from the rubber and coatings industry. Rubber products, especially automotive tires, and new coatings are the most significant applications of precipitated silica.

Recently, tire manufacturers are focusing on green tire production (tires containing almost the double quantity of silica). Green tires are considered to contribute to fuel economy and reduce emissions. A characteristic example of this increasing need for precipitated silica led is this of Evonik (in October 2018). Evonik Industries invested about USD 120 million for a new precipitated silica plant [22].

6.4.2 Wastewater from precipitated silica production process

During silica production, high amounts of water, NaOH, H₂SO₄, and sand are used. However, high amounts of high Na₂SO₄ concentration waste streams also produced from the silica production process. The main environmental concern is that these streams are normally discharged to natural watercourses (rivers, sea) directly or after passing through wastewater treatment plants, with a high cost and environmental impact associated.

Sodium sulphate is a commodity chemical, used in many industrial sectors such as paper, ceramic, textile, and pharmaceuticals. High doses of sulphates have short-term but acute effects on human and animal health. Additionally, sodium sulphate is one of the most damaging salts for the environment, as it is not biodegradable and when it accumulates in stone pores it can create high pressure and rock cracking. These are some of the reasons that regulatory agencies are insisting on reducing sulphates concentration in water [23].

In the Spanish Case study of the ZeroBrine project, waste effluents of IQE productive activity were treated by the proposed system described in the next paragraph. The purpose of this Case Study is to demonstrate an innovative treatment process for wastewater produced during precipitated silica filtration and washing procedures. This system aims to recover reagents and water to further valorise them, either in the production process at IQE or in other industries. Implementation of the new treatment process will allow a reduction of costs derived from water consumption and wastewater management.

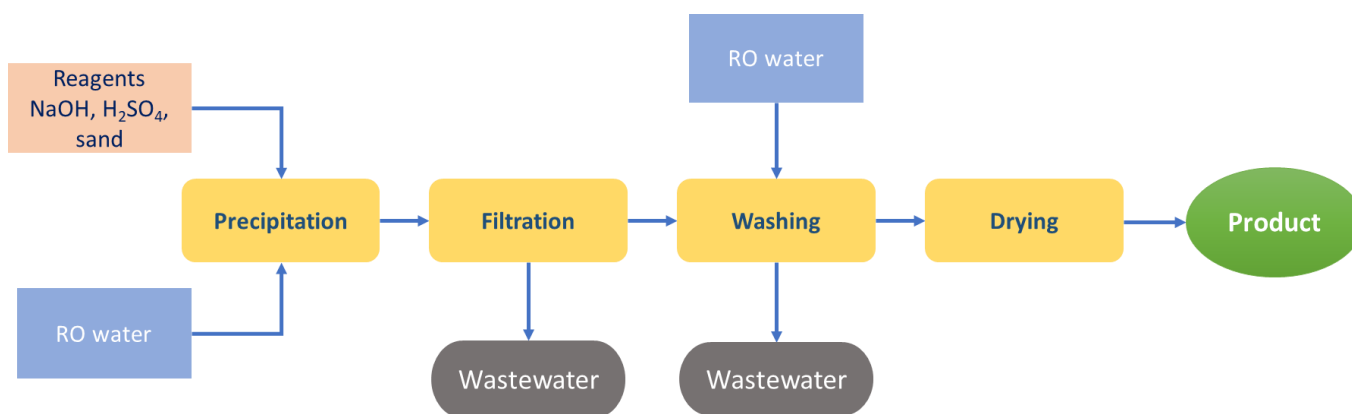


Figure 15: Production process of precipitated silica in IQE

As shown in Figure 15, at the first stage of the precipitated silica production, reagents are mixed with the well water, which has previously passed through a reverse osmosis system, to form the raw product. This mixture is heated at a set temperature and then filtered. The filtered product is washed with water from RO and dried. It has been calculated that the first (precipitation) and the third stage (washing) use about 920 to 1500 m³/day of RO water, respectively. The total amount of wastewater produced from the second and third stage is about 2350 m³/day (ZeroBrine, D4.1).

The composition and the main physicochemical characteristics of the final wastewater (after the mixing of the two streams) is shown in the table below.

Table 18: Precipitated silica wastewater analysis (ZB D4.2)

Parameter	Units	Value	SD
pH	upH	4.8	1.3
EC	mS/cm	27.3	5.9
Turbidity	NTU	67.4	133
Cl	mg/L	1,760	498
NO ₃	mg/L	11.8	0.61
SO ₄	mg/L	16,470	4,450
K	mg/L	434	11
Na	mg/L	7,320	2,060
Ca	mg/L	38.5	35.3
Mg	mg/L	213	235
TIC	mg/L	<5	n/a
Al	µg/L	2,270	2,880
Si total	mg/L	80.5	22.8
Si reactive	mg/L	77.1	23.0
Mn	µg/L	278	182
Fe	µg/L	855	712
Sr	µg/L	495	431
Ba	µg/L	49.2	16.4

6.4.3 ZeroBrine proposed wastewater treatment system

The ZB proposed system for the treatment of the wastewater produced by precipitated silica industry, is based on the combination of existing innovative technologies. The wastewater treatment stages are shown in Figure 16. Wastewater, apart from sodium and sulphate ions, contains metals such as Al and Fe, which could lead to membrane scaling, and operating problems. Thus, these metals should be removed from the wastewater before passing it through the RO regenerated membranes. For Al and Fe removal, the pH value of the wastewater is adjusted to 7. At this pH level Al and Fe precipitate and are removed by ultrafiltration. The pH of the ultrafiltration permeate is then adjusted to 9.0, to solubilize SiO₂. Finally, an antiscalant is added to the wastewater to prevent SiO₂, BaSO₄, SrSO₄ and CaSO₄ to precipitate to the RO membranes (ZeroBrine, D4.3).

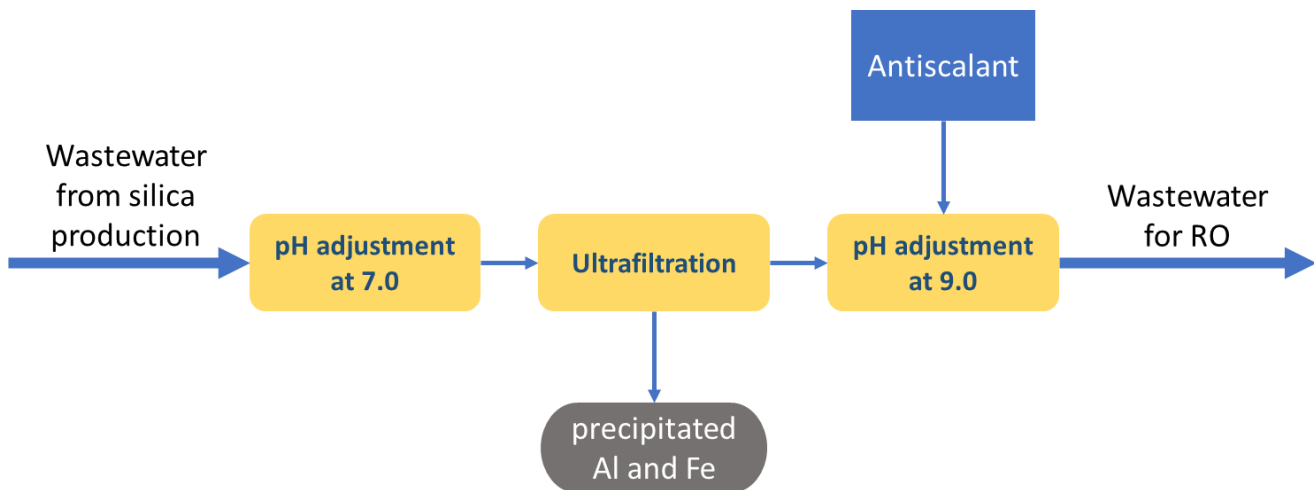


Figure 16: Process flow diagram of pretreatment stage

At the second stage, wastewater passes through the regenerated membranes for ions separation from the water. Water recovery at this stage is >80% and the electric conductivity of the water is about 13 mS/cm. This water stream is recycled and mixed with the well water and reused in the silica production process after passing through RO system.

The concentrate of high-pressure filtration stage is driven to the crystallization step. In this step, Na_2SO_4 is crystallized and removed from the water. In this stage, two techniques were engaged. Both give water of high purity which can be used directly (without passing through RO system) in the silica production line. In addition, at this stage Na_2SO_4 of high purity is also produced (ZeroBrine, D4.5).

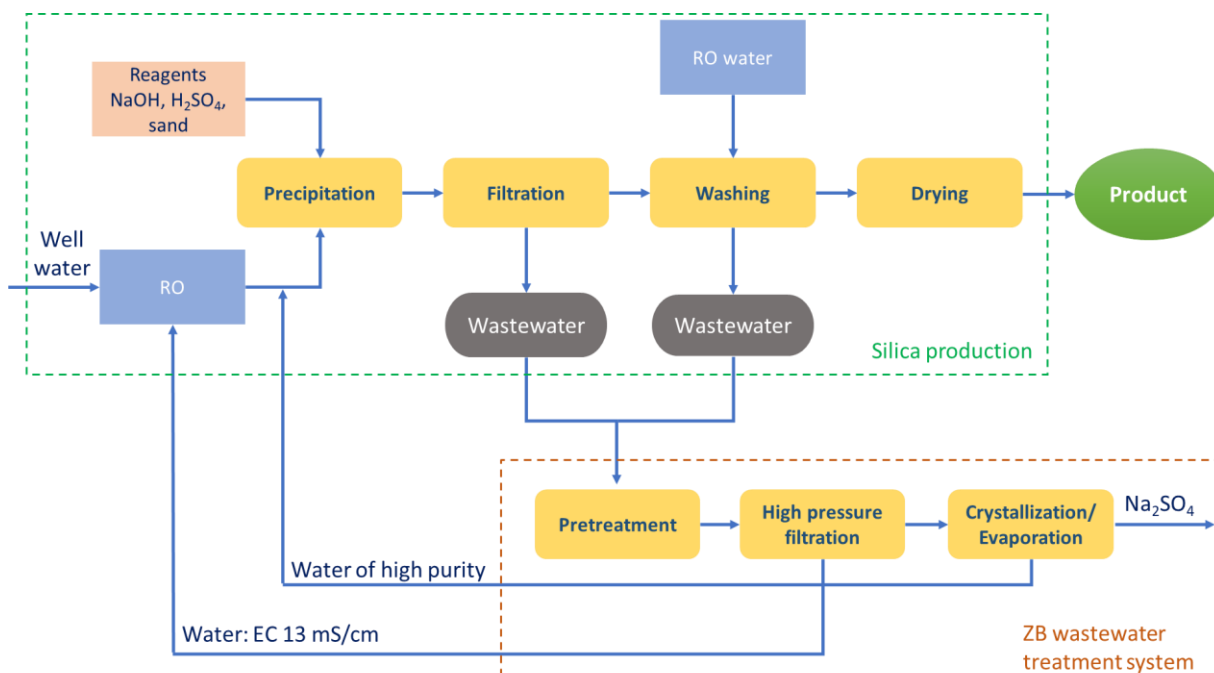


Figure 17: Process flow diagram of silica production and ZB wastewater treatment system

6.4.4 ZeroBrine proposed wastewater treatment system and BREF of Large Inorganic Chemicals-Solids and other Industry

The BATs for the industry of precipitated silica are described in the BREF of Large Volume Inorganic Chemicals-Solids and other Industry which is published in 2007 [24]. This edition as many other BREFs is under revision today. According to BAT Conclusions, operators should:

- Optimize the design and operation of their processing train to achieve waste, energy consumption, and dust emissions reduction.
- Try to keep energy consumption for the production of one tonne of silica between 15 and 24 GJ, or less. In this energy consumption, the waste treatment energy consumption is not included.

The example of the proposed ZeroBrine system could be used as a prototype for the revision of the paragraph regarding the emissions in water and mainly the sodium sulphate removal from the wastewater.

Some of the advantages of the system are:

- 92% of wastewater is recovered and reused in the precipitated silica production line.
- 80% of wastewater is recovered in the stage of high-pressure filtration. The total cost of this stage is very low due to low electrical power consumption, and low cost of membranes (regenerated membranes are used).
- Sodium sulphate produced at the final stage of the proposed system is of high purity. Thus, after a drying procedure it could be used by another industry giving some income to the depreciation of CAPEX and OPEX.

- As the largest part of the wastewater is recovered and reused, expenses for wastewater discharge are minimized.
- Waste heat could be used as energy source, minimizing energy consumption during the evaporation stage.
- IQE would be enabled to recover 20,000 t/y of sodium sulphate and 1,000,000 m³/y of water.
- Recovery of sodium sulphate and water are translated to 460,000 €/y from water supply services and a turnover of 1,800,000 €/y from sodium sulphate.

Following the Standard 10-heading description structure of BAT, the characteristics and results from the implementation of the ZB proposed system for the treatment of wastewater produced by precipitated silica industry could be summarized in the next paragraphs.

Description: The proposed system is based on the combination of existing techniques such as high-pressure filtration using regenerated membranes, and crystallization/evaporation. Using these techniques ions are separated from water. High purity sodium sulphate is also produced.

Technical description: The proposed treatment could be divided in three stages. At the first stage, pre-treatment, Al and Fe ions are removed from the wastewater to prevent membranes operational problems such as scaling and fouling. This is achieved through pH adjustment to precipitate Al and Fe, and ultrafiltration for their removal.

At the second stage, high-pressure filtration, regenerated membranes are used to separate the remaining ions from the wastewater. 80% of the water is recovered at this stage. The concentrate stream is then treated using crystallization/evaporation techniques. The products of this final step are sodium sulphate and high-purity water.

Achieved environmental benefits: The environmental problems from the wastewater discharge are avoided as 92% of water is recycled and reused in the silica production line. Furthermore, the recovered sodium sulphate can be used in industry, since it has the appropriate purity. So, the environmental effects from sodium sulphate discharge are also avoided.

Environmental performance and operational data: Environmental assessment of ZB technology is presented in the D7.3. In this deliverable it is concluded that reverse osmosis is the stage with the highest environmental burden, ca. 80%. Next to that, physicochemical treatment is responsible for ca. 20% of the impact, and UF for 15%. These contributions are mainly caused by the operation step. Energy consumption is the main contributor to the environmental impact.

ZERO BRINE Filtration plant

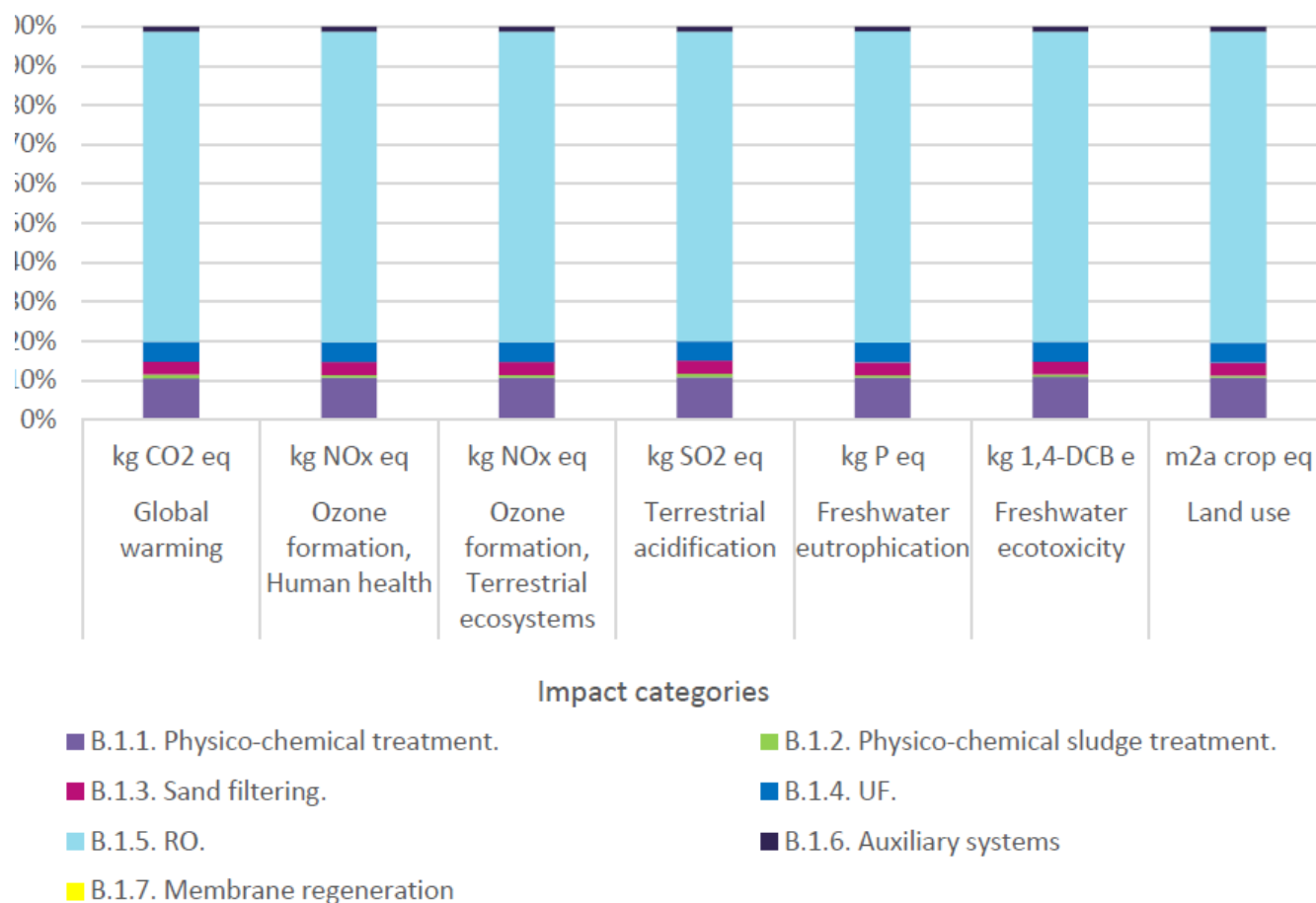


Figure 18: Results for Technology assessment of the ZeroBrine proposed system for IQE Brine Management

Concerning the impact of regenerated membranes, it is worth mentioning that membrane regeneration has negligible impacts in relation to the overall system impact. The regeneration process decreases the environmental impact of membrane production by ca. 90% for all environmental impact categories assessed.

Conventional RO production vs membrane regeneration

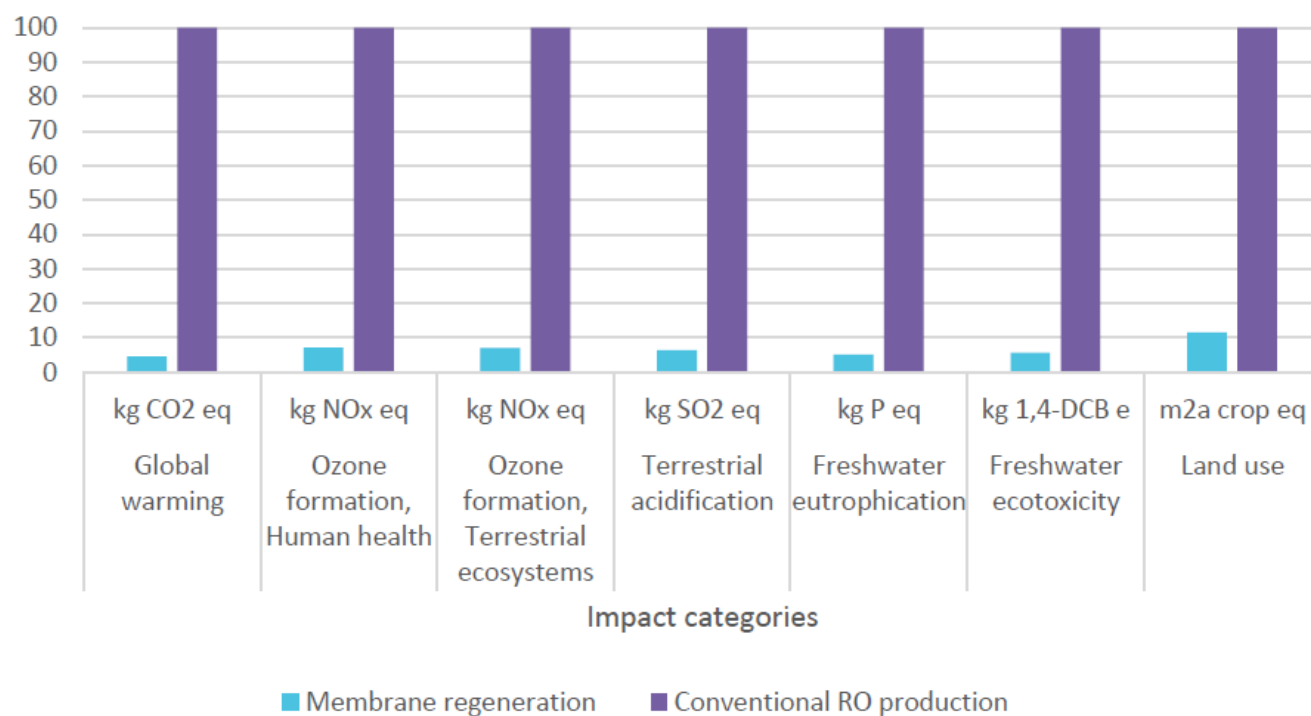


Figure 19: Comparison of Environmental Impact of RO and Membrane Regeneration Process

Finally, when considering ZB impact in the whole production system, results show that less than 1% of the impacts are related to ZB plant. The rest of the impacts are allocated to Silica production. Hence, it suggests that the ZB system will have a negligible impact when implemented in the whole system. Final LCA results will be presented in D 7.7 (M52).

Cross-media effects: The main cross effect of the system is CO₂ emissions corresponding to the electrical power used for system operation.

Technical considerations relevant too applicability: Generally, there are no technical restrictions to the applicability of this system.

Economics: The OPEX of regenerated membranes step is negative due to the economic benefits it provides to IQE. The operational cost of current techniques (referred in the BREF of Inorganic Industry) is almost 10 times higher than this of ZeroBrine proposed system. The OPEX for the proposed system with capacity of 120 m³/h and use of waste heat, has been estimated by IQE internally (Deliverable 4.5), 9.2 €/t of silica or 0.14 €/m³ of waste. The CAPEX for a system of 480 m³/day has been estimated 0.53 €/m³ (Deliverable 7.3).

Table 19: Operation cost analysis of ZeroBrine proposed system four steps

Regenerated membranes step (€/t Na ₂ SO ₄ recovered)	Evaporation (€/t Na ₂ SO ₄ recovered)	Crystallization (€/t Na ₂ SO ₄ recovered)	TOTAL (€/t Na ₂ SO ₄ recovered)
-10.2	8.1	8.1	6.8

Driving force for implementation: Apart from the environmental legislation, the driving forces for system implementation are also the low cost of the treatment/m³ of wastewater, and meeting of customer expectations for “green products”.

6.5 Best Available Techniques (BAT) Reference Document for Common Wastewater and Waste Gas Treatment / Management Systems in the Chemical Sector

6.5.1 General Information

This BREF describes the Best Available techniques and results for the independent treatment of wastewater which:

- is not discharged and mixed with public waste, and
- is generated from Chemical Industry activities covered by Directive 2010/75/EU

This document proposed techniques on:

- environmental management systems
- water saving
- wastewater collection, treatment, and management
- treatment of sludge generated from waste treatment excluding incineration
- gas collection, treatment, and management
- odour and noise emissions

6.5.2 Main BAT Conclusions for wastewater generated by the Chemical Sector

According to BAT conclusions operators should [25]:

- improve the overall environmental performance. BAT is to implement and adhere to an environmental management system (BAT Conclusion 1)
- facilitate the reduction of emissions to water and air and the reduction of water usage. BAT is to establish and to maintain an inventory of wastewater and waste gas streams, as part of the environmental management system (BAT Conclusion 2)
- monitor key process parameters (including continuous monitoring of wastewater flow, pH and temperature) at key locations (e.g. influent to pre-treatment and influent to final treatment). For relevant emissions to water as identified by the inventory of wastewater streams (BAT Conclusion 3)
- monitor emissions to water in accordance with EN standards with at least the minimum frequency given below. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality (BAT Conclusion 4).
- reduce the volume and/or pollutant load of wastewater streams, enhance the reuse of wastewater within the production process and recover and reuse raw materials (BAT Conclusion 7).
- prevent the contamination of uncontaminated water and reduce emissions to water, by segregation of uncontaminated wastewater streams from wastewater streams that require treatment (BAT Conclusion 8).
- prevent uncontrolled emissions to water, BAT by providing an appropriate buffer storage capacity for wastewater incurred during other than normal operating conditions based on a risk assessment (taking into account e.g. the nature of the pollutant, the effects on further treatment, and the receiving environment), and by taking appropriate further measures (e.g. control, treat, reuse) (BAT Conclusion 9).

Table 20: Monitoring frequency of emissions to water in accordance with EN

Substance/parameter		Standard(s)	Minimum monitoring frequency (1) (2)
Total organic carbon (TOC) (3)		EN 1484	Daily
Chemical oxygen demand (COD) (3)		No EN standard available	
Total suspended solids (TSS)		EN 872	
Total nitrogen (TN) (4)		EN 12260	
Total inorganic nitrogen (Ninorg) (4)		Various EN standards available	
Total phosphorus (TP)		Various EN standards available	
Adsorbable organically bound halogens (AOX)		EN ISO 9562	
	Cr	Various EN standards available	Monthly
	Cu		
	Ni		
	Pb		
	Zn		
	Other metals, if relevant		

Toxicity	Fish eggs (<i>Danio rerio</i>)	EN ISO 15088	To be decided based on a risk assessment, after an initial characterisation
	Daphnia (<i>Daphnia magna Straus</i>)	EN ISO 6341	
	Luminescent bacteria (<i>Vibrio fischeri</i>)	EN ISO 11348–1, EN ISO 11348–2 or EN ISO 11348–3	
	Duckweed (<i>Lemna minor</i>)	EN ISO 20079	
	Algae	EN ISO 8692, EN ISO 10253 or EN ISO 10710	
<p>(1) Monitoring frequencies may be adapted if the data series clearly demonstrate a sufficient stability.</p> <p>(2) The sampling point is located where the emission leaves the installation.</p> <p>(3) TOC monitoring and COD monitoring are alternatives. TOC monitoring is the preferred option because it does not rely on the use of very toxic compounds.</p> <p>(4) TN and Ninorg monitoring are alternatives.</p> <p>(5) An appropriate combination of these methods can be used.</p>			
Source: Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2016			

6.5.3 BAT-associated emission levels for emissions to water

The BAT-AELs are the pollutant load of the waste at the point where the waste leaves the installation.

Table 21: BAT-AELs for direct emissions of TOC, COD, and TSS to a receiving water body

Parameter	BAT-AEL (yearly average)	Conditions
Total organic carbon (TOC) (1) (2)	10–33 mg/l (3) (4) (5) (6)	The BAT-AEL applies if the emission exceeds 3.3 t/yr.
Chemical oxygen demand (COD) (1) (2)	30–100 mg/l (3) (4) (5) (6)	The BAT-AEL applies if the emission exceeds 10 t/yr.
Total suspended solids (TSS)	5.0–35 mg/l (7) (8)	The BAT-AEL applies if the emission exceeds 3.5 t/yr.
<p>(1) No BAT-AEL applies for biochemical oxygen demand (BOD). As an indication, the yearly average BOD₅ level in the effluent from a biological wastewater treatment plant will generally be ≤ 20 mg/l.</p> <p>(2) Either the BAT-AEL for TOC or the BAT-AEL for COD applies. TOC is the preferred option because its monitoring does not rely on the use of very toxic compounds.</p> <p>(3) The lower end of the range is typically achieved when few tributary waste water streams contain organic compounds and/or the waste water mostly contains easily biodegradable organic compounds.</p> <p>(4) The upper end of the range may be up to 100 mg/l for TOC or up to 300 mg/l for COD, both as yearly averages, if both of the following conditions are fulfilled:</p> <ul style="list-style-type: none"> • Condition A: Abatement efficiency ≥ 90 % as a yearly average (including both pre-treatment and final treatment). • Condition B: If a biological treatment is used, at least one of the following criteria is met: 		

- A low-loaded biological treatment step is used (i.e. ≤ 0.25 kg COD/kg of organic dry matter of sludge). This implies that the BOD₅ level in the effluent is ≤ 20 mg/l.

- Nitrification is used.

(5) The upper end of the range may not apply if all of the following conditions are fulfilled:

- Condition A: Abatement efficiency ≥ 95 % as a yearly average (including both pre-treatment and final treatment).
- Condition B: same as Condition B in footnote (4).
- Condition C: The influent to the final waste water treatment shows the following characteristics: TOC > 2 g/l (or COD > 6 g/l) as a yearly average and a high proportion of refractory organic compounds.

(6) The upper end of the range may not apply when the main pollutant load originates from the production of methylcellulose.

(7) The lower end of the range is typically achieved when using filtration (e.g. sand filtration, microfiltration, ultrafiltration, membrane bioreactor), while the upper end of the range is typically achieved when using sedimentation only.

(8) This BAT-AEL may not apply when the main pollutant load originates from the production of soda ash via the Solvay process or from the production of titanium dioxide.

Source: Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2016

Table 22: BAT-AELs for direct emissions of nutrients to a receiving water body

Parameter	BAT-AEL (yearly average)	Conditions
Total nitrogen (TN) (1)	5.0–25 mg/l (2) (3)	The BAT-AEL applies if the emission exceeds 2.5 t/yr.
Total inorganic nitrogen (Ninorg) (1)	5.0–20 mg/l (2) (3)	The BAT-AEL applies if the emission exceeds 2.0 t/yr.
Total phosphorus (TP)	0.50–3.0 mg/l (4)	The BAT-AEL applies if the emission exceeds 300 kg/yr.

(1) Either the BAT-AEL for total nitrogen or the BAT-AEL for total inorganic nitrogen applies.

(2) The BAT-AELs for TN and Ninorg do not apply to installations without biological wastewater treatment. The lower end of the range is typically achieved when the influent to the biological wastewater treatment plant contains low levels of nitrogen and/or when nitrification/denitrification can be operated under optimum conditions.

(3) The upper end of the range may be higher and up to 40 mg/l for TN or 35 mg/l for Ninorg, both as yearly averages, if the abatement efficiency is ≥ 70 % as a yearly average (including both pre-treatment and final treatment).

(4) The lower end of the range is typically achieved when phosphorus is added for the proper operation of the biological wastewater treatment plant or when phosphorus mainly originates from heating or cooling systems. The upper end of the range is typically achieved when phosphorus-containing compounds are produced by the installation.

Source: Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2016

Table 23: BAT-AELs for direct emissions of AOX and metals to a receiving water body

Parameter	BAT-AEL (yearly average)	Conditions
Adsorbable organically bound halogens (AOX)	0.20–1.0 mg/l (1) (2)	The BAT-AEL applies if the emission exceeds 100 kg/yr
Chromium (expressed as Cr)	5.0–25 µg/l (3) (4) (5) (6)	The BAT-AEL applies if the emission exceeds 2.5 kg/yr
Copper (expressed as Cu)	5.0–50 µg/l (3) (4) (5) (7)	The BAT-AEL applies if the emission exceeds 5.0 kg/yr
Nickel (expressed as Ni)	5.0–50 µg/l (3) (4) (5)	The BAT-AEL applies if the emission exceeds 5.0 kg/yr
Zinc (expressed as Zn)	20–300 µg/l (3) (4) (5) (8)	The BAT-AEL applies if the emission exceeds 30 kg/yr

(1) The lower end of the range is typically achieved when few halogenated organic compounds are used or produced by the installation.

(2) This BAT-AEL may not apply when the main pollutant load originates from the production of iodinated X-ray contrast agents due to the high refractory loads. This BAT-AEL may also not apply when the main pollutant load originates from the production of propylene oxide or epichlorohydrin via the chlorohydrin process due to the high loads.

(3) The lower end of the range is typically achieved when few of the corresponding metal (compounds) are used or produced by the installation.

(4) This BAT-AEL may not apply to inorganic effluents when the main pollutant load originates from the production of inorganic heavy metal compounds.

(5) This BAT-AEL may not apply when the main pollutant load originates from the processing of large volumes of solid inorganic raw materials that are contaminated with metals (e.g. soda ash from the Solvay process, titanium dioxide).

(6) This BAT-AEL may not apply when the main pollutant load originates from the production of chromium-organic compounds.

(7) This BAT-AEL may not apply when the main pollutant load originates from the production of copper-organic compounds or the production of vinyl chloride monomer/ethylene dichloride via the oxychlorination process.

(8) This BAT-AEL may not apply when the main pollutant load originates from the production of viscose fibres.

Source: Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2016

6.5.4 Brine produced from desalination plants

According to the 2019 Global Risks Report 2 of the World Economic Forum (WEF), water crisis is listed - for 8 consecutive years - among the top 5 risks that could undermine economic growth, impacting several countries within the next 10 years. The significance of water scarcity as well as the increasing need for fresh water has been discussed in previous paragraphs. This need has driven the global market of desalination equipment to the size of \$12.8 billion in 2019 and an annual growth rate at 9% from 2020 to 2027.

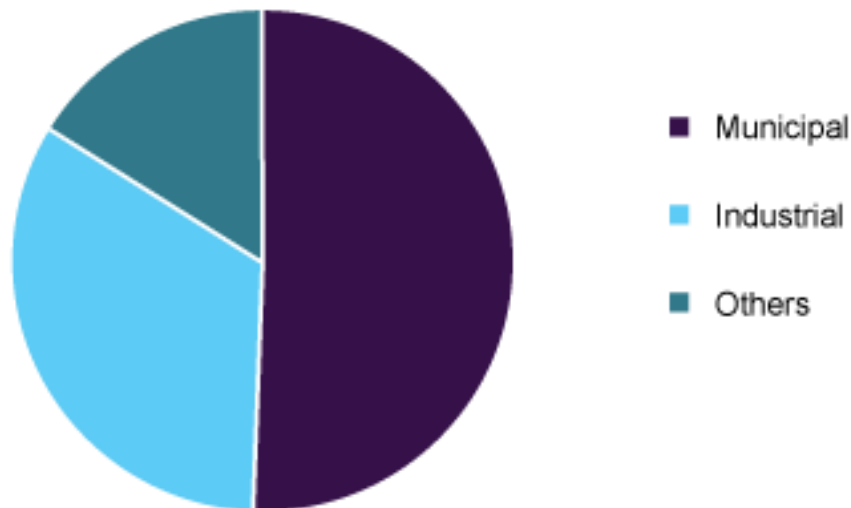


Figure 20: Global water desalination equipment market share, by application, 2019 (%) [26]

Some of the environmental impacts of the development of the desalination of sea and brackish water sector are listed below.

- Tones of brine discharged to the sea
- High accumulation of chlorides in the discharging points areas
- Higher alkalinity than usual (e.g. higher concentrations of calcium carbonate, calcium sulphate)
- Higher temperature
- Changes in flora and fauna of the discharging points areas
- Ecosystem degradation

Demi Water Plant (DWP) of Evides Industry Water in the Botlek industrial area (Rotterdam, The Netherlands) produces high-quality water by using several purification techniques. This high-quality water is supplied to a large number of companies in the Botlek area. The DWP is fed with water from Lake Den Briel (Brielse Meer), which is one of the branches of the river Meuse (Maas). In this plant EVIDES uses dissolved air flotation filtration (DAFF), cationic ion exchange, reverse osmosis and mixed bed ion exchange columns to remove impurities and ions from the brackish water.

During this procedure of water desalination-purification two streams of brines are produced. The first is the effluents from the regeneration procedure of IEX and the second is the concentrate stream from RO. The analyses of these two brine streams are presented in the following tables.

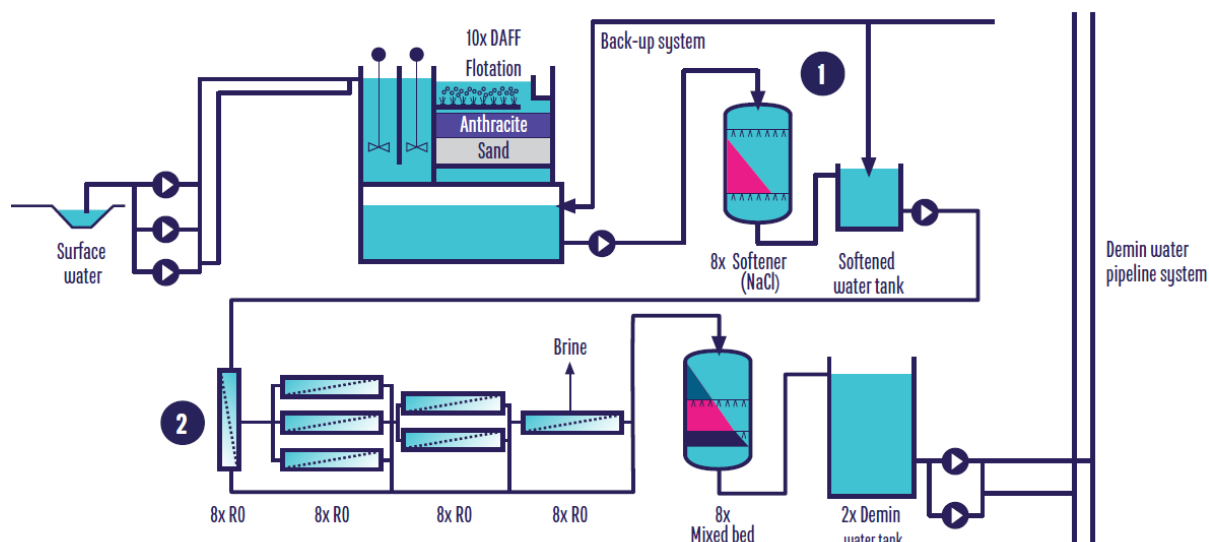


Figure 21: Process flow diagram of Demi water plant of EVIDES in Botlek area. The goals of ZB project are to treat the effluent from the regeneration of IEX (in the diagram 1) and the concentrate from RO (in the diagram 2). [Source: Demineralized Water Plant Pilot]

Table 24: Ions present in the spent regenerant of cationic Ion exchange [source: D2.3]

Element	Symbol	MW	Unit	IEX_EXP_Dec	IEX_EXP_Mar	IEX_EXP_Apr	IEX_EXP_Jul
Sodium	Na	23	mg/L	1703	7974	8145	6307
Magnesium	Mg	24	mg/L	1248	1337	1069	1414
Potassium	K	39	mg/L	236	228	321	257
Calcium	Ca	40	mg/L	6523	8538	7211	7038
Silica	SiO ₂	60	mg/L	1.97	0	0	0
Iron	Fe	56	mg/L	0	4.13	0.49	0.25
Strontium	Sr	88	mg/L	25	42	35	40
Titanium	Ti	48	µg/L	0.00	17.04	31.99	41.60
Vanadium	V	51	µg/L	84.57	274	0.58	0.00
Chromium	Cr	52	µg/L	13.77	154	40.0	6.14
Arsenic	As	75	µg/L	15.31	0	1.76	2.38
Selenium	Se	79	µg/L	3.63	0.66	43.7	28.23
Lithium	Li	7	µg/L	119	363	64.3	114
Boron	B	11	µg/L	20	67	1807	2223
Aluminum	Al	27	µg/L	0.14	1020	4.32	2447
Manganese	Mn	55	µg/L	10.21	226.81	0	0
Cobalt	Co	59	µg/L	0	88.98	4.86	2.35
Nickel	Ni	59	µg/L	205	2858	82.4	3.63
Copper	Cu	64	µg/L	34.16	59.52	0	60.45
Zinc	Zn	66	µg/L	103	156	173	44.6
Molybdenum	Mo	95	µg/L	1.27	13.81	7.61	0.37
Silver	Ag	107	µg/L	0.04	11.12	17.98	18.21
Cadmium	Cd	112	µg/L	0.35	0	14.19	12.22
Antimony	Sb	122	µg/L	0.59	22.8	0	0
Barium	Ba	137	µg/L	3554	4919	4436	5279
Thallium	Tl	205	µg/L	0.52	0	0	0

Lead	Pb	207	µg/L	0.03	220	502	424
Chloride	Cl	35	mg/L	17821	31305	28569	26440
Nitrate	NO3	62	mg/L	43.7	22.9	51.9	30.2
Phosphate	PO4	95	mg/L	1.78	0.29	0.02	0.72
Bicarbonate	HCO3	61	mg/L	143	140	115	109
Sulphate	SO4	96	mg/L	149	212	124	77
Total dissolved solids	TDS	-	mg/L	27874	49772	45614	41683
Electric. conductivity	EC	-	mS/cm	43.4	80.25	76.4	69.6
Averaged pH	pH	-	-	7.26	7.08	6.86	6.66

Table 25: Ions present in the RO concentrate [source: D2.3]

Element	Symbol	MW	Unit	RO_EXP_Dec	RO_EXP_Mar	RO_EXP_Apr	RO_EXP_Jul
Sodium	Na	23	mg/L	845	1202	959	1056
Magnesium	Mg	24	mg/L	0.17	2.17	0.07	0.06
Potassium	K	39	mg/L	13.4	14.3	0	18.3
Calcium	Ca	40	mg/L	0.52	3.34	2.16	2.30
Silica	SiO2	60	mg/L	42	38	28	16
Iron	Fe	56	mg/L	0	0.30	0.02	0.02
Strontium	Sr	88	mg/L	2.85	0	8.15	8.18
Titanium	Ti	48	µg/L	1.19	0	0	0
Vanadium	V	51	µg/L	5.38	4.72	0.05	0.16
Chromium	Cr	52	µg/L	1.81	4.09	11.3	5.10
Arsenic	As	75	µg/L	1.01	0	0.99	2.01
Selenium	Se	79	µg/L	0.69	1.75	8.27	7.35
Lithium	Li	7	µg/L	45.8	83.3	49.9	93.5
Boron	B	11	µg/L	122	123	183	98
Aluminum	Al	27	µg/L	0.70	2.70	0.06	0.06
Manganese	Mn	55	µg/L	0	0	0	0.45
Cobalt	Co	59	µg/L	0	2.92	1.61	1.81
Nickel	Ni	60	µg/L	9.02	13.6	20.1	22.1
Copper	Cu	65	µg/L	12.9	0	51.2	7.54
Zinc	Zn	66	µg/L	18.0	0	71.6	36.3
Molybdenum	Mo	95	µg/L	9.31	10.7	7.63	12.7
Silver	Ag	107	µg/L	0.15	0	0.83	0.99
Cadmium	Cd	112	µg/L	0.01	0	0.04	0.03
Antimony	Sb	122	µg/L	1.56	1.77	1.26	1.87
Barium	Ba	137	µg/L	0.60	0	4.62	3.10
Lead	Pb	207	µg/L	0.16	7.10	3.63	4.25
Chloride	Cl	35	mg/L	514	1122	704	846
Nitrate	NO3	62	mg/L	39.4	7.32	53.4	22.4
Phosphate	PO4	95	mg/L	0	2.93	0.03	0.05
Bicarbonate	HCO3	61	mg/L	871	863	947	955
Sulphate	SO4	96	mg/L	371	335	271	320
Total dissolved solids	TDS	-	mg/L	2696	3591	2966	3237
Electrical conductivity	EC	-	mS/cm	3.22	4.03	3.30	4.09
Averaged pH	pH	-	-	9.8	8.81	8.87	8.79

Table 26: Organics present in the RO concentrate [source: D2.3]

Sample name	biopolymers (µg/L C)	Humic Substances (µg/L C)	Building Blocks (µg/L C)	LMW Neutrals (µg/L C)	LMW Acids (µg/L C)	HOC (µg/L C)	POC (µg/L C)	CDOC (µg/L C)	DOC (µg/L C)	TOC (µg/L C)
EXP_Dec	239	5215	1975	1708	<200	325	38	9133	9460	9498
EXP_Mar	630	6911	2432	2841	<200	957	18	12800	13750	13800
EXP_Apr	492	6583	2068	2413	<200	722	60	11550	12275	12325
EXP_Jul	262	5528	2073	8935	<200	901	-82	10600	11500	11425

As it can be seen from the tables the effluent from the regeneration of IEX is a brine with high concentration in sodium, calcium, magnesium, and chloride ions. It is worth to pay attention to the high values of TDS and conductivity of this brine. The RO concentrate has high concentration in sodium, chloride, and sulphate ions. In addition, this stream contains also organics. For the treatment of these brines, two pilots have been designed.

6.5.5 ZeroBrine proposed brine treatment systems

The goals of the proposed system for the treatment of the effluent from the regeneration of IEX are to recover high purity water and solution rich in sodium chloride which could be used for the regeneration of the IEX columns. Thus, zero liquid discharge is achieved as well as recovery of sodium chloride, which is needed for the regeneration process. Moreover, the Ca and Mg ions of the initial brine are removed from the water and recovered in the form of Ca(OH)_2 and Mg(OH)_2 . It is worth to notice that Mg is one of the critical raw materials for the EU and Mg(OH)_2 price is about \$1000/ton.

To this aim, IEX regeneration effluents are initially treated by NF for the removal of Mg divalent ions (Ca, Mg) which are recovered in the form of Ca(OH)_2 and Mg(OH)_2 in MF-PFR stage. The permeate of MF-PFR and NF2 are mixed and driven to the evaporator. There the brine concentrates and water of high purity and quality is recovered. The concentrated brine returns to the Demi water plant for the IEX columns regeneration. The process flow diagram of the site 1 pilot is presented in Figure 22.

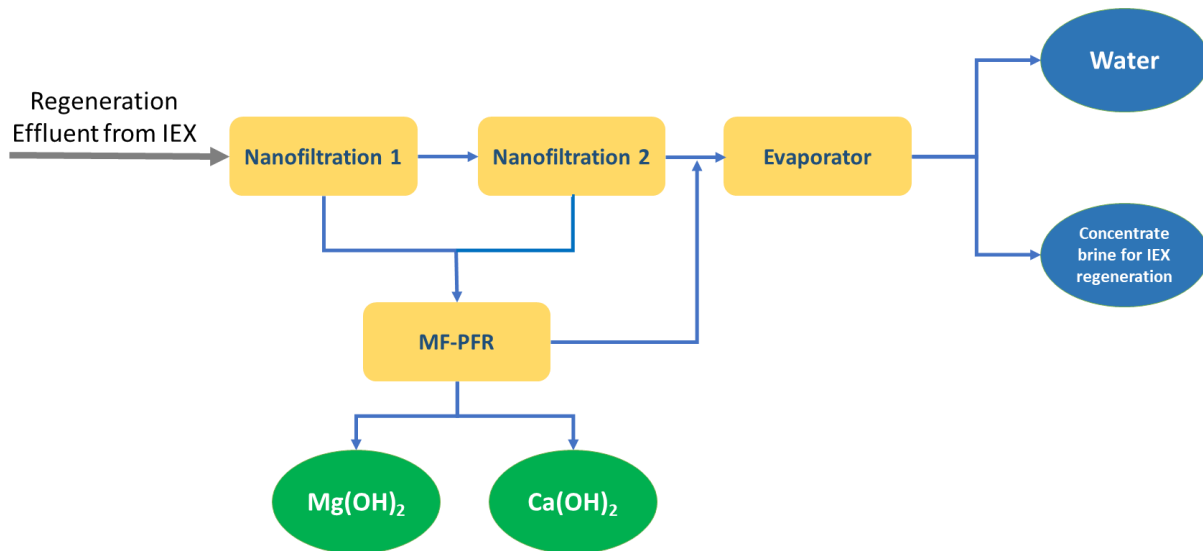


Figure 22: Process flow diagram of site 1 pilot

The goals of pilot 2 are to remove the organic content and sulphates from the RO concentrate of the Demi water plant, and recover high-purity water, a high-purity sodium chloride solution and sodium sulphate. This is achieved using the pilot of Figure 23.

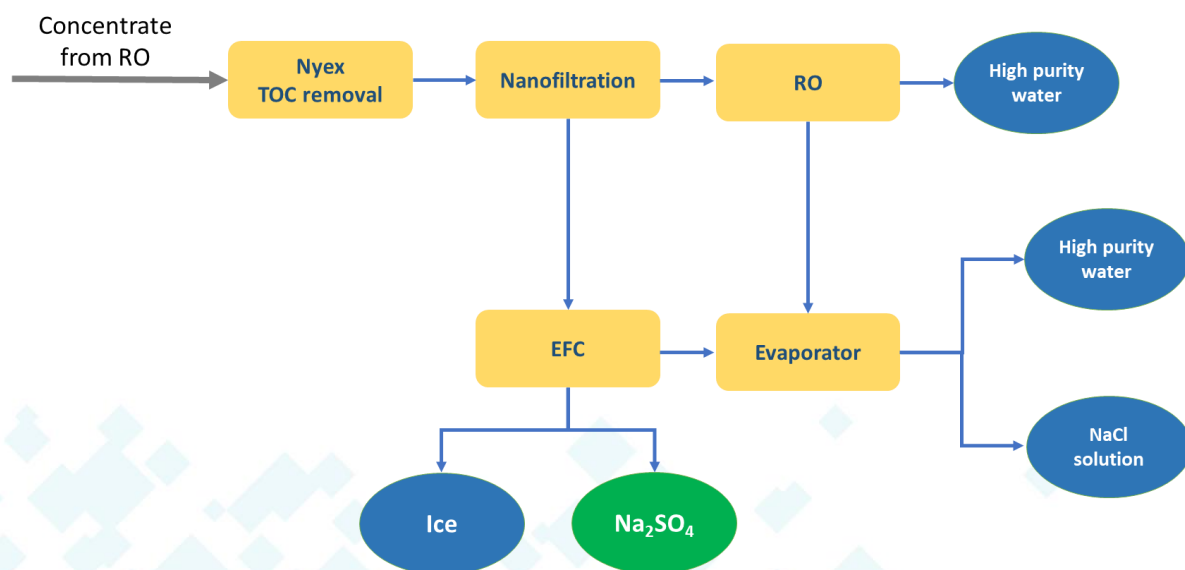


Figure 23: Process flow diagram of site 2 pilot

Firstly, the RO concentrate pass through the Nyex system for TOC removal. Then, it is treated by a nanofiltration system to remove sulphates from the brine. The stream of NF concentrate is treated by EFC. EFC produces ice and high purity sodium sulphate, which can be used in other industrial sectors and a slurry which is mixed with evaporator influents. The permeate of NF pass through an RO stage for high-purity water production. The RO condensate is further concentrated by an evaporator. A second set-up of the above systems has been also tested. To this second stage positions of Nyex and NF systems are changed.

6.5.6 ZeroBrine proposed wastewater treatment systems and BREF of Common Wastewater and Waste Gas Treatment/Management Systems in the Chemical Sector

As it can be concluded ZB pilots met the requirements of Tables 21-23. However, the BREF of Common Wastewater and Waste Gas Treatment/Management Systems in the Chemical Sector does not include the desalination plants and techniques to avoid the problems caused by brine disposal. Actually, desalination plants, “borrow” water discharge requirements from chemical industry and urban wastewater treatment plants which treat wastewater with very different composition. So, the addition of a special paragraph referring to the brines from the desalination plants or even better a special BREF for desalination plants could be suggested.

The example of the proposed system by the ZeroBrine system could be used as prototype for the brine treatment in a paragraph or even more a new BREF dedicated to the desalination plants and the management of produced brine.

Some of the advantages of the system are:

- Up to 90% of high-purity fresh water is recovered from brines.
- A concentrated brine rich in high-purity NaCl is recovered. This brine can be used during the regeneration of IEX units in the Demi water plant or by another industry.
- 80% magnesium recovery as magnesium hydroxide, purity 80-95%.
- 95% calcium recovery as calcium hydroxide, purity 92-98%.
- Sodium sulphate production.
- Waste heat could be used as energy source, minimizing energy consumption during the evaporation stage.

Following the Standard 10-heading description structure of BAT the characteristics and results from the implementation of the ZB proposed system for the treatment of wastewater produced by desalination/water industry could be summarized in the next paragraphs.

Description: The proposed system is based on the combination of existing techniques such as nanofiltration, reverse osmosis, TOC removal and crystallization/evaporation. Using these techniques ions are separated from water. High purity magnesium hydroxide, calcium hydroxide, sodium sulphate and NaCl brine are also produced.

Technical description: The treatment of pilot 1 could be divided in two stages. During the first, nanofiltration is used for the removal of divalent ions from the brine. At the second stage, MF-PFR is used for the recovery of magnesium and calcium in a market exploitable form, and evaporation is used for the concentration of NaCl brine.

The treatment of pilot 2 could be divided in three stages. At the first stage electrochemical oxidation technology is used for organics removal. Filtration systems are used for the removal of divalent (nanofiltration) and monovalent ions (reverse osmosis) from the water. Crystallization techniques are used for the recovery of sodium sulphate and sodium chloride in market exploitable forms.

Achieved environmental benefits: As almost zero liquid discharge is achieved, the environmental problems of brine discharge to the sea are avoided.

Environmental performance and operational data: Preliminary environmental assessment of ZB technology is presented in the D7.3, where it is shown that system impacts to the environment are mainly caused by the operation step. Energy consumption is the main contributor to the environmental impact followed by the NaOH which is used in the stage of $Mg(OH)_2$ and $Ca(OH)_2$ crystallization.

Many papers of previous decades suggest that brine disposal results in environmental burden when disposed in surface water sources or in the sea. However, the environmental impact of the brine discharge is not modelled in SimaPro software which is used for the LCA of the pilots. Thus, no effects were identified in toxicity impact indicators. Therefore, it is expected that the aquatic toxicity indicator will be underestimated in the Demi water plant (without the ZB plant) system. Final LCA results will be presented in D 7.7 (M52).

Cross-media effects: The main cross effect of the system is CO_2 emissions corresponding to the electrical power used for system operation.

Technical considerations relevant to applicability: Generally, there are no technical restrictions to the applicability of this system.

Economics: Although, the final data of OPEX, CAPEX, LCA and LCC data will be available on M52, preliminary results of LCC analysis and the CAPEX of pilots in comparison with the CAPEX of Demi Water Plant are presented in the charts below.

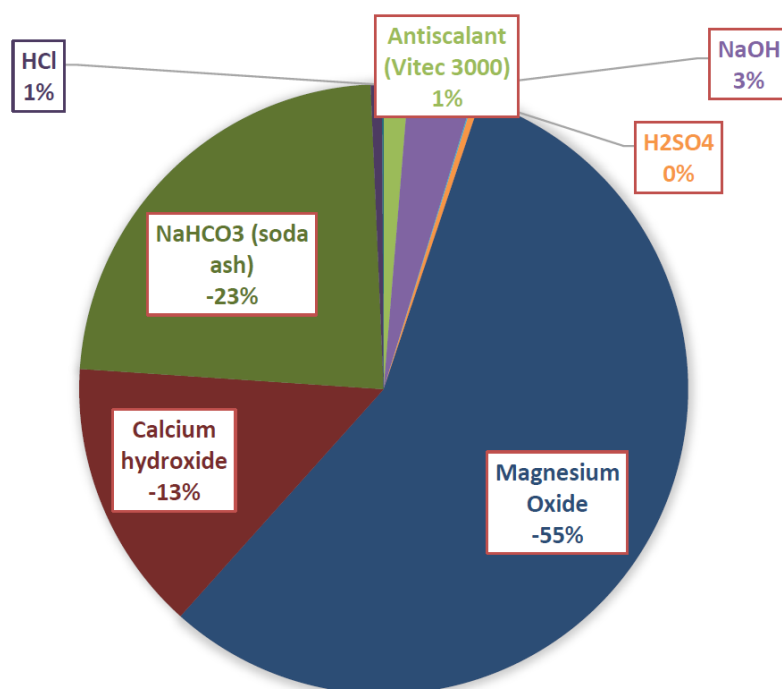


Figure 24: Contributions of consumables and recovered materials

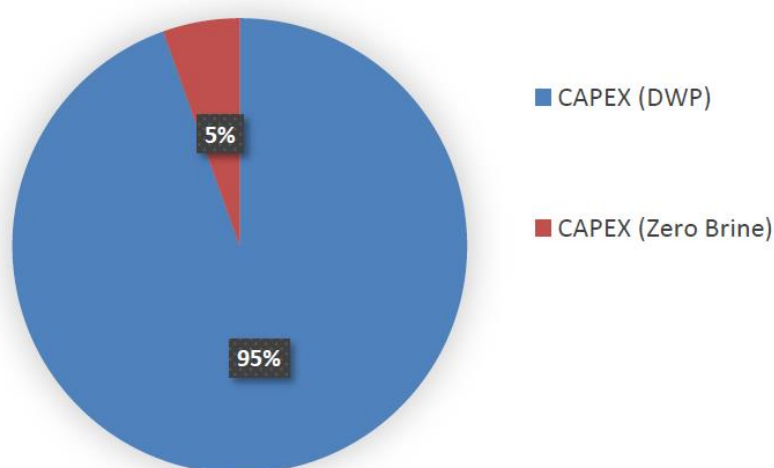


Figure 25: ZB pilots CAPEX in comparison with the CAPEX of Demi water plant

Driving force for implementation: Apart from environmental legislation, driving forces for system implementation are the income from the magnesium hydroxide and other produced salts, and meeting of customer expectations for “green products”.

7. Economic Tools in Waste Management

The sustainability of solid waste management systems is, from a financial perspective, one of the biggest challenges that low- and middle-income countries are facing around the world. The taxes used to finance solid waste management (SWM) costs, do not always exist, and if they do, the total cost of SWM (capital and operating costs) is rarely covered.

In most low- and middle-income countries economic instruments, except taxes and waste charging, are not adequately known. It is generally considered that applying them in these countries/regions is complicated or costly. Waste taxes, such as incineration and landfill taxes, have become a common choice in developed countries to promote the 3R's (reduce, reuse and recycle) principle. These taxes are used to finance a sufficient waste treatment plan and recycling.

Regarding the industrial waste management, few studies have been conducted, mainly due to the lack of data needed to assess the possible tax impact. The paragraphs below aim to review waste management tools already used to extract good practices and conclusions that could be transferred to the wastewater management in general, and particularly to industrial brine management.

7.1 Pay-as-you-throw schemes

As already mentioned, WFD suggests measures for the prevention of waste generation. Recovery of usable materials from waste can help conserve natural resources and increase the economic value of waste. It also strengthens a trend towards a waste management practice, eliminating the negative impact on the environment and human health. According to the "the polluter pays" principle, costs of waste disposal must be charged to the waste owner, to previous owner/s or to the operators of the process from which the waste derived [8].

Extended producer responsibility has been introduced in the framework of this Directive aiming to bring out consideration and facilitation on efficient use of resources. Economic instruments can play a key role in the prevention of waste generation and achievement of waste management objectives. Application of economic instruments can maximize environmental benefits by promoting waste valorisation as a source of material extraction. Also, waste deriving from a specific (industrial or not) process could be a valuable resource for another sector, thus promoting circular economy and industrial symbiosis.

PAYT schemes are strongly recommended for municipal waste management. Generally, they are implemented in local level and they cover a significant part of the overall waste collection and processing service. Taxes for these schemes can be estimated through waste volume, weight, and collection frequency. These taxes can be decreased through practices such as household waste prevention and recovery activities. However, infrastructure and services should be developed to stimulate taxes decrease for households and municipalities [27].

The Water Framework Directive does not allow profit from water charges. However, in the same directive the “polluter pays” principle asks Member States to impose charges for water used from households, agriculture, farms, and industries. An additional charge, usually covering the cost of water used, was calculated for management of waste produced in households, premises, plants, or farms.

The “polluter pays” principle can also be applied in cases of industrial saline wastewaters. Saline wastewater producers can be charged for the volume and the pollutant content of the discharged wastewater to be motivated towards treatment and recovery methods. This can be combined with an increase on the price of water for industrial use. Through combination of these measures, water recovery would be an appealing solution for industries to avoid charges and at the same time to ensure availability of resources. Valuable salts source recovery is also possible, shifting industrial process towards the circular economy principle.

7.2 Landfill taxes

7.2.1 Introduction

Disposal is the least favoured option in the waste hierarchy. Consequently, waste landfilling is the last procedure to be implemented in a waste management plan. The Landfill Directive 1993/31/EC aims to environmental and human health protection through minimization of waste quantity ending up in landfills. Additionally, this directive proposes directions for landfills operation, and measures minimizing the negative effects that improper or extended landfilling has on surface water, soil, and air [28]. Towards this direction, landfill taxes are implemented as a tool to ensure compliance with this directive.

Some Member States of the EU have adopted this economic instrument in different ways. For example, some Member States have incorporated these taxes to more general taxes which cover both incineration and landfilling (e.g. Denmark and Norway) [29].

7.2.2 The case of Austria

Implementation of landfill taxes in Austria is of high interest, as it is the only Member State that used the revenues of landfill tax (about 1.2 billion EUR in total up to 2014) exclusively to fund cleaning up of the contaminated sites. In 1989, Austria introduced the landfill tax known as ‘contaminated site contribution’ “(Altlastensanierungsbeitrag (‘ALSAG’))” and levied from 1990 to provide funding for the clean-up and identification of landfill sites.[30]

Initially, waste was divided in two charge categories:

- 1) hazardous waste, 14,53 EUR per tonne (ATS 200)
- 2) all other waste, 2.91 EUR per tonne (ATS 40)

The tax is paid by landfill operators. Tax rates are calculated on the basis of the tonnages disposed and landfill type. In 2016, the rate was 29.8 EUR per tonne of waste. It is particularly important to be mentioned that, since

2004, Austria banned waste with more than 5% Total Organic Carbon (TOC) content. This ban, led to adoption of either mechanical-biological pre-treatment, or incineration of the municipal solid waste (MSW).

On the other hand, there was no tax applied for mechanical-biological treatment and the tax for Incineration was 8 EUR per tonne. These two measures (the ban and the landfill tax), combined with other waste management regulations and policies also applied, played a very important role to ensure that the residual waste management shifted towards other treatment methods instead of landfilling. The implementation of Landfill Ordinance and the higher landfill taxes imposed on waste disposal in landfills of lower standards compared to state-of-the art landfills, played a very important role in ensuring that the operation of the current landfills result in lower environmental impact [30].

More specifically, landfills of lower technology standards, had to pay tax based on waste type and additionally surcharges. On the other hand, the landfill sites meeting the requirements in terms of both the Landfill Ordinance and technology were taxed only on the basis of waste type [27].

7.2.2.1 Drivers and barriers of the instrument in Austria

The main motivation and consequently the legal basis for the landfill tax enforcement in 1989 was to clean up the contaminated landfill sites. Specific problems due to the contamination of high-profile landfills triggered the Clean Up of Contamination Act. This Act recognized the need for funding to clean up these sites, a fact that led to landfill tax introduction. Amendments after 1996, aimed to prevent future problems caused by landfill sites and had as a target to reduce greenhouse gas emissions (GHGs), and to encourage waste pre-treatment [31]. However, the main role of landfill tax was to provide a revenue raising mechanism. The landfill tax did not encounter significant opposition, as it was introduced at such a low rate.

7.2.2.2 The effect of landfill tax and bans in Austria

More than 60% of waste produced in Austria was disposed in landfills before 1989, when the landfill tax was introduced. On 2009, five years after full implementation of the ban for waste containing more than 5% TOC, this percentage was decreased to 10%. The decrease of waste disposed in landfills, took place simultaneously with the significant increase of the proportion incinerated. Landfill tax increased quantities of waste used for composting/digestion, recycling, and incineration. However, it is difficult to estimate the contribution of each implemented measure to the decrease of waste disposed in landfills. This problem seems to become more complicated if the large number of different policies and regulations which influence the Austrian waste management are considered. Nevertheless, the final result was that source separation of different streams, and separate collection and processing of them, significantly decrease the fraction of waste ending up in landfills [32].

7.2.2.3 Transferability of the Austrian experience to saline wastewater management

The Austrian case is an interesting example on how the combination of economic instruments such as landfill tax and strict limits such as landfill ban could lead to great results in the effort of environmental and human health protection. This principle could be also transferred to wastewater. A tax on wastewater disposal in surface water

bodies or wastewater treatment plants (WWTP) could prevent industry operators from this type of wastewater management. The income from this tax could be used to fund new wastewater treatment installations (initial capital cost) in industries. Perhaps, this tax will become more effective if it is combined with a set of limits on the quantity and the quality of wastewater, and characteristics of disposal areas. The perspective of clean water and material recovery should be also taken into consideration as an additional revenue for industries and must be presented as an additional motive. Exploitation of recovered materials could cover the operational cost of such installations.

7.2.3 Landfill tax in EU

The impact of landfill taxes application in the EU was investigated in terms of reducing waste landfilling, also taking into consideration other parameters such as restrictions. In the report, a distinction between taxes and gate fees is made, more specifically:

“Taxes are defined as a levy charged by public authorities (in most cases at national level, although in some cases (e.g. Italy, Spain) for the disposal of waste in a landfill site, usually with an environmental purpose in mind, and where the revenue is accruing to the body responsible for the levy”

“Gate fees are defined as charges set by the operators of the landfills for the provision of the service (i.e. waste disposal) and which are designed to cover their costs and profit. This type of fee is subject to variation according to the landfill site used, and to other factors such as available landfill capacity and market variations. Gate fees do not always cover an operators’ cost due to the market situation at a given time. In this report, the term ‘gate fees’ refers to the costs before the application of landfill taxes”

“The term charge is referred to the sum of gate fees and taxes. This sum represents the total cost of landfilling. The level of taxation ranges very widely, and some countries do not levy any taxes.” [29]

The general conclusion is that the landfill taxes seem to have a strong impact on the amount of municipal solid waste (MSW) ending up in landfills, up to a certain point. Further improvements in landfilling decrease after that point can be achieved from a combination of landfill restrictions and adapted tariff policies.

Another conclusion, is that a clear correlation exists between the percentage of MSW composted and recycled in the Member States, and the cost (in total) of landfilling. For higher cost of landfilling, more MSW were led up to the waste hierarchy, towards treatment options such as recycling and composting.

It is estimated that Member States could achieve the 50% recycling target once the taxes of the cheapest disposal options approach the amount of 100 €/tonne. Such large taxes will lead the waste management to waste processing such as recycling and composting.

For Austria, Sweden, and the UK, it was observed that there is a strong correlation between increasing landfill tax rates and decreasing rates of landfill for MSW. However, this fact is not only due to the taxes alone. On the other

hand, for other Member States, there is a weak or no distinguishable correlation between landfill tax rates and the percentage of MSW landfilled. At this point, it must be stressed out that other factors that must be also taken into consideration, including the use of other EIs, the economic situation over time, broader waste policy, changes in gate fees charged by landfill sites, and the available capacity of landfills [29].

The examples of different countries show that there are different routes leading to the reduction of waste landfilling. It seems difficult to ‘eliminate landfilling’ through a tax alone. Taxes seem to have an effect towards material recovery, but there is no certainty that tax alone enables a complete switch from landfilling. Bans seem also to play an important role in the reduction of the waste quantities ending-up in landfills (close to zero in the case of bans which are effectively implemented and enforced) and of waste quantities incinerated.

According to the above, an economic instrument as the one of landfill tax could be also applied in cases of industrial saline wastewaters. The most important is that landfill taxes seem to lead to recycling options. This means that in case of industrial saline wastewaters, a possible tax in saline wastewater discharge could enable materials recovery (minerals and water). Finally, addition of other economic instruments such as bans could also lead to saline wastewater discharge reduction.

7.3 Extended Producer Responsibility

Reviewing environmental policies for management of continuously increasing amounts of waste, many governments concluded that a new option could be the extension of producer responsibility to the post-consumer phase. That means that producers are given responsibility for the collection and treatment of waste produced after the use of their products. The Extended Producer Responsibility (EPR) principle is nowadays applied in many products categories such as batteries, packaging, electrical appliances, electronics, used oils, graphic paper, end-of-life vehicles [33].

EPR is introduced as a policy approach in three European Directives: End of Life Vehicles (ELV) Directive 2000/53/EC, Waste Electrical and Electronic Equipment (WEEE) Directive 2012/19/EU and Batteries Directive 2006/66/EC. EPR principle also supports the implementation of Packaging and Packaging Waste Directive 94/62/EC. EPR is considered as the main tool to support the European Waste Hierarchy. Used in combination with other economic tools, EPR aims to change the way producers, retailers, authorities, and consumers buy, use, and dispose goods. EPR is also linked with the source-efficient Europe initiative.

Although theoretically the obligation of each producer is individual, many Producers Responsibility Organisations (PRO) have been established to implement the EPR on behalf of all the companies which are members of the PRO. PROs are financed by producers and their main functions are the collection and treatment of products at the end of their lives, fees collection, redistribution of funds, collection, management, and presentation of data to the EU [34].



EPR is a scheme that could be also transferred to industrial brine management. Producers of brine would be responsible for brine treatment, and management of recovered materials and water. In case of industrial clusters, a PRO could be established to undertake collection, treatment, exploitation of recovered materials and water, as well as the administrative burden and the redistribution of funds.

8. Conclusion

The scope of the present review was to explore legislative barriers to the market uptake of the ZB systems and to examine if changes or updates of the existing legislation and BREFs shall be suggested to the EC. Initially, REACH legislation was reviewed, aiming to define potential limitations and requirements on the commercialisation of salts produced by the pilot systems of ZB.

All inorganic salts produced in ZB are already registered to ECHA. To commercialise them, operators need to prepare material Safety Data Sheets (SDS) and Technical Data Sheets (TDS). Information for TDS and SDS are produced from the chemical analyses (exact composition) of the salts, and from data uploaded in the ECHA platform. To get access to this data, operators need to send an inquiry (access letter) to ECHA and pay a fee to the first registrant of data. This is a very well described procedure in ECHA site. National REACH Helpdesks, which are very easily accessible, can also provide information on how this letter shall be prepared, as well as on the cost of access to these data. However, if the recovered materials will be used in the same industry, no such data are needed.

The second step was to review the Water Framework Directive, regarding the use of the recovered water. No barriers were detected during this review. However, it is found that there are gaps in National and European legislation, on specific standards of recovered water for industrial use. For this reason, in the final version of this deliverable, the ZB consortium will propose tables with the main physicochemical properties and characteristics of recovered water used in four types of industries (desalination, textiles, coal mine, and silica).

ZB perspective is in fully agreement with the WFD in terms of:

- Achieving to recover water of high quality with an acceptable environmental footprint
- Implementing water reuse, mainly in industrial sector
- Designing and Building pilot systems for industrial wastewater treatment, based on European strategies for the environment
- Providing treated water to industry and this way decreasing the use of drinking, surface, or underground water
- Proposing, through BREFs, specific quality standards for recovered water which will be used in industry.

The Waste Framework Directive was reviewed to ensure that the produced salts meet the EoW criteria, and that these criteria will not hinder their commercialization. Waste management principles that could possibly be incorporated into wastewater management were also investigated. Based on the experience gained from the Waste Framework Directive implementation, ZB will suggest a new industrial brine-wastewater management plan. The initial step for such an integrated plan shall be the detailed recording of industries producing brine-wastewater, the qualitative and quantitative characteristics of it, and the geographical location of those industrial installations. The latter will help to establish synergies among closely installed industries, and to construct a map of recovered materials possible end users, in case that the installation recovering water and materials is not able to use them.

IED is the next European Directive studied, as it covers all industrial emissions. The main tools of the IED are the BREFs. EC workgroups make continuous efforts to keep BREFs updated. However, as the science and technology progress there is always place for suggestions and further updates to BREFs. ZB, trying to embed Circular Economy, Industrial Symbiosis, Zero Pollution Ambition, and the Green Deal, does not propose systems for pollutants removal from the wastewaters in order to be disposed in the nearer receiving water body. ZB sees wastewater as a resource and proposes systems that treat industrial wastewaters to extract clean water and salts that could be reused by the same or another industry. Another innovative characteristic of these systems compared to the most systems mentioned in the BREFs is that these systems are based on a combination of existing and new technologies. Thus, upon system optimization and processing of operation data, special paragraphs were prepared on the description of systems and technologies, their efficiency, operational and capital costs, physical and chemical properties of salts and water, to be suggested as BREFs updates. Information presented in this text, though generated from the final operational data of the pilots, does not include the final economic and environmental assessment, which will be presented in Deliverable 7.7 (M52).

Exploitation or reuse of recovered water and materials could provide a significant income for the industry and cover all or a part of the operational cost of systems. However, new or existing tools must be used as motives to fund the capital cost and the first steps. Economic tools which are used in waste management policies were reviewed to examine possible incorporation in the wastewater management plans. It seems that taxes for the direct disposal of wastewater to receiving bodies or WWTPs, in combination with bans on the quality and quantity characteristics of rejected wastewater could be used to finance installation of such systems. Creation of PROs in case of industrial clusters could also help to exploit recovered materials and water, to lift the administrative burden, and to redistribute funding.

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