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ZERO BRINE

# D7.5: Report on selection of demonstrated technologies and possible verification

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[1] **R**=Document, report; **DEM**=Demonstrator, pilot, prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other

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

# Executive Summary

The Environmental Technology Verification (ETV) is an independent verification system developed by the EU. It aims to give new environmental technologies an easier route to the market. It should also help a purchaser or public procurement body to select technologies with credible performance claims despite a lack of demonstrated full-scale performance.

In the European Union (EU) funded project Zero Brine, several technologies are further developed and their Technology Readiness Level (TRL) advanced. A selection of these technologies was included in work package 7 ( Task 7.3) to investigate and prepare for the verification process. These are the MED-evaporator from NTUA, the MF-PFR from UNIPA and the EFC from TU Delft. The ETV procedure consists of several phases, which are closely described in the EU ETV General Verification Protocol. Depending on TRL, market readiness level and assessed performance (e.g. using Life Cycle Assessment (LCA)), the verification procedure can proceed into different phases. The most crucial step for a verification procedure is to select suitable environmental claims, which are later verified by a third party, called the verification body.

In this project, all technology developers defined their performance claims. However, due to the relatively low TRL level of all the selected technologies only the MF-PFR from UNIPA completed the initial step of completing a quick scan which was accepted by an external verification body as sufficient to move forward in the process. The MED-evaporator completed a quick scan which has been reviewed by a verification body. The third technology the EFC did not complete a quick scan but is well prepared for the next step in the verification process once the TRL has increased. The next step for the developers is to define and evaluate the market to evaluate whether the cost for a full verification process is justified.

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| | |
|---|---|
| CrIEM | Crystallization with Ion Exchange Membranes |
| EFC | Eutectic Freeze Crystallization |
| ETV | Environmental Technology Verification |
| FF-MED | Forward-feed evaporator |
| IEX | Ion Exchange |
| MD | Membrane distillation |
| MED | Multi-effect distillation |
| MF | Membrane Filtration |
| NF | Nanofiltration |
| QS | Quick scan |
| RO | Reverse Osmosis |
| SME | Small and Medium Enterprises |
| TRL | Technology Readiness Level |
| VB | Verification Body |
| ZB | Zero Brine |

# 1. Introduction

The Zero Brine project aims to minimise the flow of brine from industrial processes into natural waters by recovering minerals and producing clean water for reuse in other industrial processes. Several novel technologies were combined in suitable process configurations and tested at bench scale and at four pilot sites. The purpose of this report is to describe the process of investigating and preparing three selected technologies from Zero Brine for the process of Environmental Technology Verification (ETV) (Task 7.3 with the Zero Brine project).

The coordinator of the Task 7.3 is IVL Swedish Environmental Research Institute and participating partners involved are SEALEAU, NTUA, TU Delft and UNIPA.

## 1.1 Environmental Technology Verification

The Environmental Technology Verification (ETV) aims to provide an independent and credible process where a third party confirms the performance claims of the technology provider (European Commission, 2012). The aim is three folded; to help manufacturers, especially small and medium enterprises (SMEs) to reach the market; to provide technology vendors with credible information and to give investors and decisionmakers assurance on the performance of novel environmental technologies. To benefit from the verification the technology developer should have a technology that has the potential to improve the environmental performance of products, processes or organisations. The result of the EU ETV process is that the declaration and performance claims of the technology vendor are validated by experts in the relevant technology, backed by the EU.

The pilot programme for the EU ETV began in 2011 and at that time there were already similar verification systems in both North America as well as in Asia. In the EU it was employed together with the Eco-innovation Action Plan (EcoAP) to promote and support eco-innovation (Molenda & Ratman-Kłosińska, 2018). The verification is performed by an independent third party, accredited by the ETV program. In Europe there are today a total of 11 verification bodies, each belonging to one or several thematic three areas, which are water treatment and monitoring, materials, waste and resources, and energy technologies (European commission, 2021).

The EU scheme for the ETV process is well described and can be found in various sources (European Commission, 2012; European Union, 2018). The verification process is proceeded stepwise. In short, the Proposer presents a ‘quick scan’ (QS) to a verification body (VB). The quick scan is a document which contains various information about the technology, the verification claims and possibly data supporting the claims. The Proposer could be the technology developer, the manufacturer, or a representative. The verification body reviews the information provided in the QS together with existing performance data. If needed a suitable test body (TB) is contacted, which could be within the same organisation as the VB or a specialist from a relevant field. Thereafter, the VB suggests a test plan, implements the tests at a suitable site for the technology developer and produces a test report. A verification report is drafted by the assessment body. In the last step, which is the publication phase, a synthesis report is written, and the technology is awarded a verification certificate.

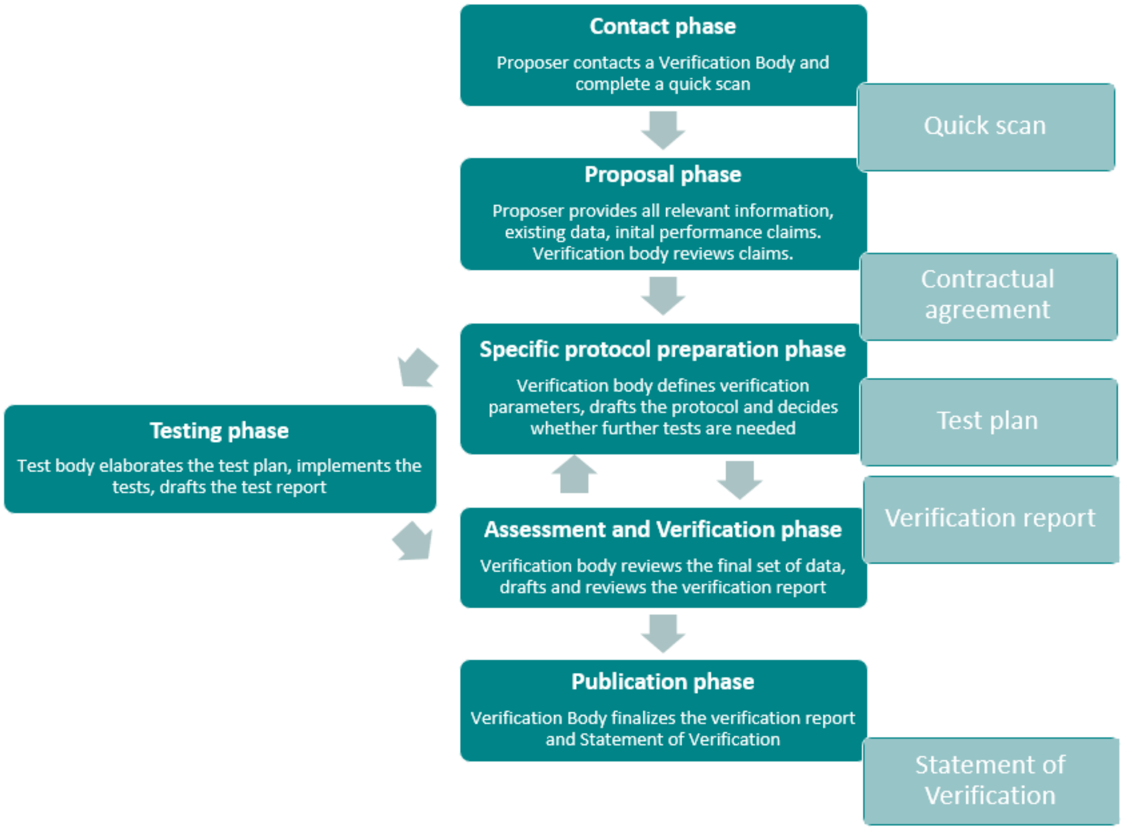



*Figure 1: Phases of the EU ETV pilot program verification procedure. Adapted from European Union (2018).*

By March 2016, 175 quick scan documents had been submitted to the ETV scheme. Sixty-two technologies had been contacted for verification and 12 technologies had verified (Molenda & Ratman-Kłosińska, 2018). In 2020, after nine years of being a pilot scheme, the verification program was made permanent. In 2021, 278 quick scan documents had been submitted, 123 verifications had been initiated and 45 technologies been verified.  The number of verification bodies in 2021 are lower than in 2016 (11 compared to 15) (European Commission, 2021).

## 2. Methodology

The selected technologies were reviewed, and separate meetings were held with the technology developers in order to initiate the ETV process.

## 2.1 Selection of technologies

The first selection of technologies in ZeroBrine was based on potential market benefit, market readiness, ETV criteria and expected target markets. In the grant agreement the following processes were presented to for consideration in the ETV process: the MED-(Multi Effect Distillation)-SEALEAU evaporator, the CrIEM (Crystallizer with Ion Exchange Membrane) from UNIPA and the EFC (Eutectic Freeze Crystallization) from TU Delft. However, the CrIEM from UNIPA process was still a very immature technology with a low Technology Readiness Level (TRL) of 5 and was not suitable for ETV. In addition, another technology from UNIPA the MF-PFR (Multiple Feed Plug Flow Reactor), which had a TRL of 7, was used in the pilot demonstration of one of the test sites. Therefore this was chosen instead for the ETV investigation.

## 2.2 Understanding the ETV process

The ETV process is well described in many easily accessible sources, such as web-material from the European Commission (European Commission, 2012) and in a few academic publications. These were utilised for this project to develop an educational presentation on the ETV process for the technology developers. Next, information meetings about the ETV process were held with each developer to define what type of information needed to be included in the process. This clarified which steps should be prepared by the Proposer or the Technology developer and which steps depended on a third-party, initiating certain costs for verification.

## 2.3 Reviewing the technologies and preparing a quick scan

In subsequent meetings the technologies were discussed from a technical and commercial perspective to match the ETV criteria and to find suitable performance claims. Once the performance claims are set, the quick scan document was filled in. The quick scan document is a tool to initiate the verification process. A template of this document is provided in Appendix 1. The quick scan contains questions like:

- General description of the technology
- Performance claims – which should be quantifiable and measurable together with conditions under which the above performance claims could be met as well as potential standards used
- Market readiness level and TRL
- Information about raw material, manufacturing phase, user phase, end-of-life phase
- Legal requirements
- Intellectual Property Rights (IPR)
- Existing operational data

This information should be documented and communicated with the chosen third-party selected for the verification process.

## 2.4 Initiating the verification process

Once the quick scans were filled out the documents were sent to a relevant verification body, usually one that was located in the same country. The verification bodies could then give an offer for the preliminary costs for a full verification. The costs for an actual verification were not included in this project and was therefore this step was not conducted.

# 3. The Technologies

Among the different technologies developed within the Zero Brine project three were selected as case studies for approaching the verification.

The selected water technologies, described in the next sections are:

1. Multiple Effect Distillation (MED), forward-feed evaporator from NTUA
2. Multi Flow Plug Feed Reactor Crystallization (MF-PFR) from UNIPA
3. Eutectic Freeze Crystallization (EFC) from TU DELFT

## 3.1 Multiple Effect Distillation, forward-feed evaporator

The MED evaporator aims to recover high quality water from brines and a concentrate brine. The evaporator has been demonstrated as the final part of a process train for the recovery of water and salts from a desalination brine pilot system in the Netherlands.

The MED evaporator operates below atmospheric pressure and is made up of two consecutive effects or steps (as shown in Figure 2). In each of the MED effects, brine is evaporated resulting in the production of two streams: (i) a water vapor stream which is condensed and recovered as fresh water and (ii) a concentrated brine stream. The vapor stream from the first effect heats the concentrated brine produced in the second effect, which improves the energy efficiency of the process. The brine is then sprayed on top of the tubes-bundle and runs down over each of the tubes by gravity. The vapor stream produced by the second effect is condensed through a plate heat exchanger, used for pre-heating purposes, thereby transferring its thermal energy to the brine stream of the inlet feed.

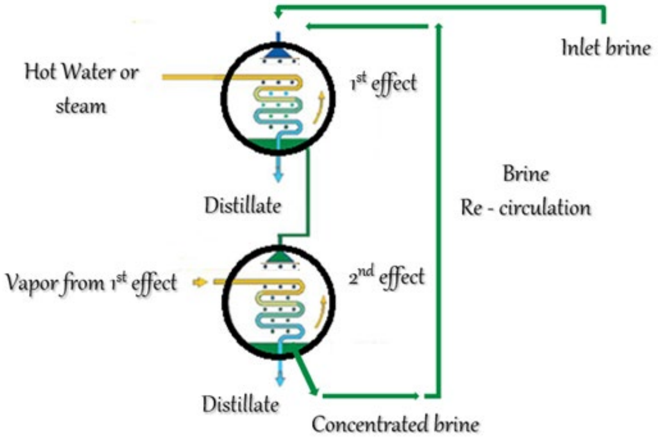



*Figure 2: MED evaporator working principle.*

The main heat supply for the system is steam, which flows into the first effect (heat exchanger) transferring heat to the brine. A steam trap is draining any remaining water or condensate in the system. A major benefit is that the evaporator unit can work with waste heat. But the system can also work with electricity through an installed boiler.

A mathematical model was developed for each component of the MED evaporator unit, based on mass and energy balances and on the equations used for sizing and designing purposes. The models were used for the development of a simulator that was built in Visual Basic Environment.

To minimize the formation of limescale or fouling by other deposits, at these conditions with high TDS concentration, advanced thermal analysis was used together with the correct boundary conditions on the heat exchangers and depending on the chemical characteristics of the system suitable materials are selected. By doing so, lower grade materials can be incorporated which reduce investment cost and provide a competitive advantage.

Throughout the design embodied carbon and operational carbon footprint is kept to a minimum. The evaporator technology has been piloted at the Evides Site I and Evides Site II with industrial brine water and at a textile industry (Zorlu) in different process configurations.

## 3.2 Multiple Feed Plug Flow Reactor (MF-PFR) crystallizer

An MF-PFR reactor can be used to precipitate dissolved ions in high concentrated industrial streams. This is done by using a reactant and shifting the pH.

The crystallizer is a cylindrical reactor in which both reactants, i.e. brine and sodium hydroxide-water solution, react in order to precipitate/remove magnesium (in a first step) and calcium (in a second step) in the form of hydroxides. The precipitation in two steps is controlled by careful adjustment of the pH level. The brine is fed into the MF-PFR along with NaOH-water solution for the precipitation of magnesium as hydroxide at pH around 10.4, as shown in Figure 3. Thereafter, the resulting slurry is collected in a vessel for settlement of the crystals. When magnesium hydroxide crystals are settled, the clarified brine is collected in a second feed tank (d). From this tank it is again sent in the crystallizer, along with NaOH-water solution, for the precipitation of calcium in the form of calcium hydroxide at pH above 13. Lastly, the produced slurry is collected in the last tank (c) for the settling of calcium hydroxide crystals.

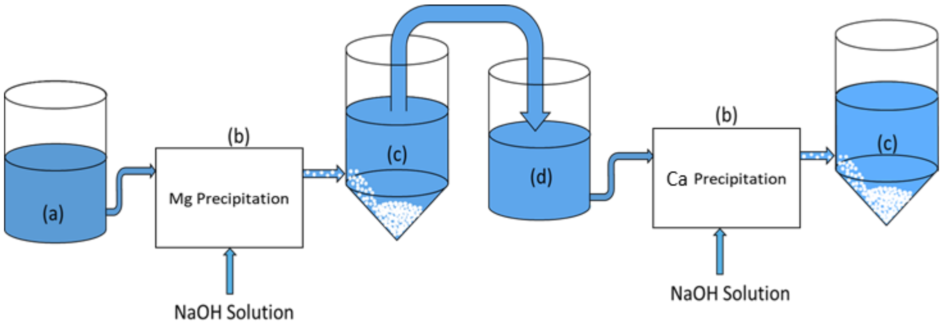



*Figure 3: Process scheme of fractionated removal of magnesium and calcium as hydroxide.*

The following environmental claims linked to the MF-PFR technology, are: (i) purity of the product, (ii) the control of the crystals size distribution and (iii) save electrical energy respect the conventional Continuously Stirred Tank Reactors (CSTR) crystallizers. Tests were performed in the laboratory and using a real industrial effluent. In the case study Magnesium and Calcium were recovered from the brine. This crystalliser technology has been operated at the Evides Site I with industrial brine water.

## 3.3 Eutectic Freeze Crystallization (EFC)

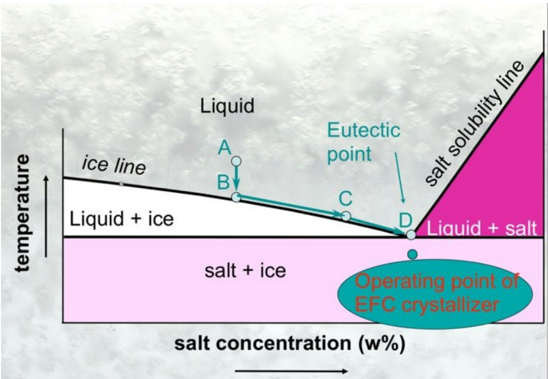
Eutectic freeze crystallization is a new technique for processing waste and process streams of aqueous electrolyte solutions. By separating them into pure water and pure solid salt products respectively. By cooling saturated solutions of various compounds, two solid phases – ice and inorganic crystals, will separate out of solution simultaneously (as illustrated in Figure 4). Ice will float and the inorganic crystals settle.

When a solution in the unsaturated area with a concentration lower than eutectic concentration (A) is cooled down below its freezing point, ice crystals start to form (B). Further cooling decreases the temperature and increases the concentration of salt in the solution with the formation of ice crystals along the ice line (B to C). At point C (eutectic point), the concentration of salt reaches saturation and further cooling will result into the simultaneous formation of ice and salt crystals. Similarly, starting with a solution having higher concentration than eutectic concentration will first result in the formation of salt and reach the eutectic point (C) by following the salt solubility line.

In a suitably designed device, this will capture an aqueous solution that is concentrated in ions associated with more-soluble inorganic compounds and has an increased concentration of any organic compounds present in the initial mixture (Figure 4).

The heat flux from the crystallizer will control the yields of ice and salt. The outlet of the crystallizer is connected to the solid/solid separator, where ice and salt are separated by gravity. The underflow of the separator is fed to a filter. Excess liquid is removed from the salt crystals and recycled to the crystallizer. The ice crystals will be on top of the separator, and flows into a wash column. The ice is washed by a reflux stream of molten ice crystals and pure water leaves the column at the top. At the bottom, wash liquor is leaving the column and is recycled to the crystallizer. The feed stream can thus be separated into pure water and salt, apart from the purge streams.

EFC could be used for treatment of relatively concentrated solutions, such as salty brines and the retentates from reverse osmosis membrane processes.



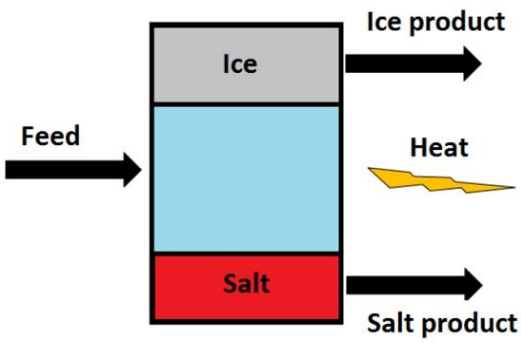




*Figure 4: a) Phase diagram of salt – liquid -ice system. At the eutectic point the phases may be separated. This is the operating point of the EFC. b) The basic working principle of the EFC technology.*

The EFC technology has been operated at the Evides Site II with industrial brine from RO, at a coal brine site (PGG) with waste brine and at a chemical industry (IQE) with high salinity wastewater from silica production in different process configurations.

# 4. Preparing for the ETV

After initial meetings it was clear that the selected technologies were relatively immature and their TRL was too low for ETV. A verification can be done when a new technology is 'market ready'. According to European Commission, (2012) a new technology is said to be market ready when:

- It has already been available on the market or ready for commercialisation, or
- Full-scale units are available, or

- It is at a minimum stage of development where no substantial change affecting its performance will be implemented before introducing the technology on the market, i.e. the next unit sold shall be similar to the unit tested and verified.

In Figure 5, the TRL in relation to the readiness for the ETV process is illustrated. At the end of the Zero Brine project, the EFC is at TRL 5 and is not mature enough to complete a quick scan. The MF-PRF and FF-MED are at TRL 7 which is the minimum level of TRL to start a quick scan. To complete a ETV the TRL should be 8 to 9, but the intention of this work package was only to prepare the technologies for the ETV.

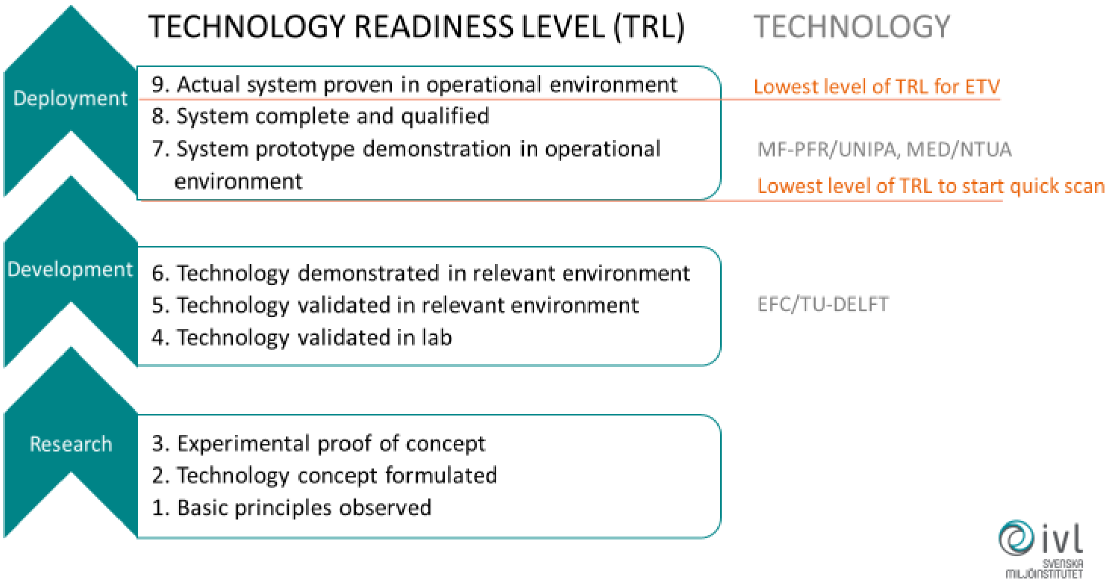



*Figure 5: Technology readiness level (TRL) in relation to readiness for ETV for the Zero Brine technologies*

The IVL Swedish Environmental Research Institute was to act as a moderator for the ETV process but the actual driver of the process should be the technology developer themselves, stating the environmental claims, which should relate to the planned market . But at low TRL development the market may not yet be defined, and other aspects such as manufacturing plants or marketing and sales actions, sufficiently developed.

A core task was to set the performance claims for the different technologies. This work is not only for the quick scan but could also be very useful for the technology developers themselves, to identify the benefits and advantages of the technologies and differentiate them from similar technologies.

The performance claims and their status are described and discussed in the next sections.

## 4.1 Multiple Effect Distillation, forward-feed design evaporator (FF-MED)

The forward-feed design evaporator is to recover high quality water from brines and a concentrate brine of high purity. The technology has chosen the following performance claims:

1. Concentration factor: Up to 16% TDS
2. Energy use: Gain-output-ratio (GOR) of 4

A full quick scan was completed for this technology and a preliminary verification body was contacted.

## 4.2 Multiple Feed Plug Flow Reactor (MF-PFR) crystallizer

The Multiple Feed Plug Flow Reactor can recover minerals that exist in ionic form from any industrial effluent by precipitation. The technology developer has chosen the performance claims based on the following three aspects:

1. Purity of the products: $Mg(OH)_2$ and $Ca(OH)_2$ .
2. The control of the crystals size distribution: based on market requirements.
3. Save electrical energy respect the conventional CSTR crystallizers: <1.5 $kWh/m^3$.

The first claim has been well explored and published results show a purity of 84-96% of the recovered $Mg(OH)_2$ in the first step and 92-99% of the recovered $Ca(OH)_2$ in the second step (Vassallo et al., 2021). The target for the second claim has not yet been stated but could be defined from a market analysis, if needed. Regarding the third claim operational data is only available from pilot operation. The expectation is that a full-scale plant would have a lower energy demand and a lower energy demand than conventional methods, based on for example a completely stirred reactor (CSTR) process, at the market.

A full quick scan was completed for this technology. The quick scan document (a template can be seen in Appendix 1) was sent to a verification body and preliminary costs were presented once the technology is ready to proceed with the verification.

## 4.3 Eutectic Freeze Crystallization (EFC)

Eutectic freeze crystallization can process waste and process streams of aqueous electrolyte solutions, by separating them into pure water and pure solid salt products respectively. Adequate performance claims were not formulated during the project due to the low TRL. However, future performance claims for a verification would most probably be formulated based on the large benefits of the technology, which include:

1. Low energy demand.

2. High purity of recovered products.

A full quick scan was initiated for this technology but due to the low TRL (5) for this technology the quick scan was not completed.

# 5. Discussion and conclusions

The ETV process is well described in many easily accessible sources, such as web-material from the European Commission and in a few academic publications, but if the methodology is applied to insufficiently mature technologies, the outcome is very limited. However, the first step of the ETV process by defining the technology performance claims is likely to be extremely useful for understanding the technologies potential in relation to the market and other similar technologies. Potentially, this could help facilitate the identification of markets niches and help target design improvements towards optimising the most appropriate performance variables.

In the process of the Zero Brine project the following lessons are highlighted in relation to the ETV:

- The performance claims should be selected in relation to the future market.
- The claims should preferably be based on input from an LCA or more simplified, similar assessment.
- Common meetings between the technology providers could have been helpful to support each other's formulation with the performance claims.
- It is not always evident that the costs of a full ETV are justified, and therefore careful market analysis and selection of timing (which stage of development) is required to help ensure that the benefits of performing a full ETV outweigh the cost.

In conclusion, the relatively low TRL level of all the selected technologies resulted in one complete quick scan which was reviewed and approved by a potential verification body. This was for the MF-PFR technology from UNIPA and means that this technology could proceed in the process of a full verification. In addition, the MED-evaporator completed a quick scan which has been reviewed. However, the EFC technology have initiated a quick scan and is well prepared for the next step in the verification process once the TRL has increased and the market is defined in order to motivate the costs for a full verification process.

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# 7. Appendix

- Appendix 1: EU-ETV Quick scan