

*Desalination and Water Treatment* www.deswater.com

1944-3994 / 1944-3986 © 2011 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2011.2371

# Project for the development of innovative solutions for brines from desalination plants

# Domingo Zarzo Martinez\*, Elena Campos Pozuelo

Valoriza Agua. Molina de Segura, n. 8, 30007 Murcia, Spain Tel. +34 (96) 8354028; Fax +34 (96) 8213716; email: dzarzo@gruposyv.com

Received 11 June 2010; Accepted in revised form 1 April 2011

#### ABSTRACT

One of the most important aspects of the desalination projects is the environmental impact and particularly the brine discharges. For seawater projects it seems that the problem is solved or at least controlled, by means of the usual practices (previous environmental studies, previous discharge dilution, use of diffusers and other devices, location of the brine discharge and/or vigilance plans). In the case of brackish water and mainly inland, the brine discharge is a very important problem with a no clear solution. The main solutions used for these plants are: Discharge to the sewer nets (with the associated problems at the recipient WWTP); Deep well injection; Zero liquid discharge (ZLD) systems based mainly in evaporation-crystallization technologies; Blending with other discharges (e.g. wastewater); Sea discharge in coastal areas. Currently it seems that the main R&D projects in desalination are focussed about energy consumption as well as brine impact reduction. This paper will show a R&D project about innovative solutions for brine discharges. The project is focused on developing systems with less environmental impact and technologies about recovery and appreciation of salts from brines. The research is distributed in 5 different subprojects all related with brines from desalination plants: 1) Development at pilot scale of a novel system for recovery and valorization of salts from brines; 2) Study of technical and economical feasibility of zero liquid discharge systems based on evaporation-crystallization technologies for brine elimination; 3) Study about possible industrial applications of salts and other byproducts obtained from brines; 4) Study of technical and economical feasibility of deep-well injection; 5) Study of direct osmosis and other parameters over the dilution of brines in seawater and the modeling and comparison with current mathematical models. This paper will show the results obtained for each one of these sub-projects. This study involved 4 Spanish universities as well as other 3 companies lead by Sadyt-Valoriza Agua. The project includes a patent for the technology and important subsidies from the Spanish Ministries of Industry and Environment.

Keywords: Brine discharges; Zero liquid discharge; Salt recovery; Brine dilution

### 1. Introduction

#### 1.1. Background

The company SADYT (Valoriza Agua), together with

the companies Sacyr, Scrinser (all from the Spanish group Sacyr-Vallehermoso) and Ecoagua, agreed in 2007 to develop a research and development program under the name "Research project for the development of innovative solutions in the management of desalination brines". This ambitious project aimed to study the problems of brine discharge produced by desalination technologies

Presented at EuroMed 2010 — Desalination for Clean Water and Energy: Cooperation among Mediterranean Countries of Europe and MENA Region, 3–7 October 2010, David Intercontinental Hotel, Tel Aviv, Israel. Organized by the European Desalination Society.

31 (2011) 206–217 July

<sup>\*</sup> Corresponding author.

and innovative solutions to minimize the environmental impacts or even promoting brine reuse.

This project was designed for a period of three years and has received public funds of about  $\in$  2.5 million from the tourism and commerce, Spanish Ministry of Industry and Ministry of Environment.

The participation is remarkable from some public research centres.

Spanish universities:

- University of Alicante, Alicante, Spain.
- Universidad Politecnica de Catalunya, Tarrassa, Spain.
- Universidad Complutense de Madrid, Madrid, Spain.
- University of Alcala de Henares, Madrid, Spain.

Other public research centres:

- IMDEA Agua (Madrid Water Advanced Studies Institute).
- CETENMA (Technological Centre of Energy and Environment, Murcia, Spain).

#### 1.2. General objectives

This project aims to research and develop some alternatives technically and economically possible for the management and development of desalination brines by innovative solutions. It also includes the development and implementation of pilot plants and demonstration systems. These general objectives are developed through works undertaken to achieve specific objectives in the form of five lines of research:

- Research about a novel technology for recovery of divalent salts from brines at pilot scale.
- Study of technical and economic feasibility of the application of brines and by-products from desalination plants for different uses e.g. frost control, industrial applications, production of brine and salt, etc.
- Determination of technical and economical feasibility of zero liquid discharge systems by evaporationcrystallization technology.
- Study of deep well injection of brines and environmental implications.
- Research and modelling of the effect of different parameters in dilution of brines in seawater and comparison with mathematical models.

#### 2. Project description

#### 2.1. General data

The projects budget was spread over 3 years 2007–2009, although it was officially completed in March 2010 with extensions, was as follows:

2007	2.547.814€
2008	1.823.814€
2009	1.823.814€
Total	6.185.442€

Sadyt lead the project and assumed approximately a 60% of the budget.

- The main milestones of the project were as follows:
- 1) Bibliography collection, market research and definition of alternatives.
- 2) Development of pilot plant technologies.
- 3) Design and implementation of pilot plants.
- 4) Start-up of pilot plants.
- 5) Implementation testing in pilot plants and conclusions.

Below are the objectives for each subproject with descriptions.

2.2. Research on a novel technology for the recovery of divalent salts from brine. Characterization and possible uses for brines and byproducts

### 2.2.1. Objectives

The removal of salts from brines from desalination plants, to reduce the impact of the discharges and to obtaining salts or by-products able to be reused. The purpose being to separate the salts present in the brine with several objectives:

- Increase the performance of desalination process (increasing recovery).
- Recovery of dissolved salts in brine for further reuse.
- Elimination or reduction of discharges and/or landfill.
- As a result of the process chosen, the production of energy from fuel from sustainable agricultural crops (which can be considered renewable energy).

#### 2.2.2. Applied process

The technology used in this project is based on the salt precipitation from brines, mainly divalent salts such as sulphates, using an organic solvent extraction. The idea is to remove these salts from water to increase the recovery of the desalination system and secondly to obtain salts susceptible to marketing (sulphates, nitrates, etc.). Since divalent salts the process is logically only useful for water desalination systems for brackish water systems.

Different solvents have been tried for this purpose and the final choice was to use ethanol, which allowed the process costs to be recovered by means of energy production, although this is not the ultimate goal of the project it removes a part of the problem of brines discharge inland. Although none of the used processes are new, extraction with solvents, precipitation, evaporation, etc. the combination of method and application are new, so it has also been registered as a patent.

The outline of the process broadly speaking is as follows:

- 1. Blending of brine with bio ethanol.
- 2. Partial precipitation of the salts present in the brine, mainly sulphates and bicarbonates.

- 3. The removal of these salts allows the continuation of the process of osmosis to obtain a new fraction of desalinated water.
- 4. Separation of ethanol and salts present, mainly chlorides and nitrates, the remaining water through a distillation process, which would be obtained in three fractions: distilled water, salts and ethanol.
- 5. Combustion of ethanol to produce the necessary heat for distillation and electricity needed for reverse osmosis.

The process described requires in addition to bio ethanol, an injection of energy which is partially electrical and heat. To obtain the energy needed for this process it must surely go to the use of renewable energies and as we will need for the process heat and electricity, the best option would be undoubtedly the use of a cogeneration plant.

2.3. Study of technical and economic feasibility of the application of brines from desalination plants for different uses, e.g. frost control, industrial applications, production of brine and salts, etc. Brine recovery

# 2.3.1. Objectives

The objectives of this sub-project is to determine the technical and economic feasibility of the application of brine from desalination plants for different uses (frost control, industrial applications, production of brine and salt, etc.) proceeding in this way to its recovery. Some possible applications of these brines could be;

- a) The production of salt for food industry from seawater brine.
- b) Environmental restoration of wetlands.
- c) Industrial use e.g. regeneration of resins, electro chlorination etc.
- d) Frost control in roads, highways, streets etc,
- e) Obtaining different chemicals and salts.

#### 2.3.2. Applied process

A report was completed as a result of the works coordinated by the University of Alicante, an extensive document of 96 pages including a market study. The document analyzed the most interesting aspects of the possible uses of brines and by-products as the following:

- 1. Using brine as a source of minerals e.g. evaporation ponds.
- 2. Use of brines for aquaculture.
- 3. Use of brines to obtain energy e.g. solar ponds Annexes:
  - Solar evaporation ponds
  - Microalgae production
  - Salt for food industry
  - Limestone
  - Gypsum
  - Sodium sulphate

- Chlorine-alkali production
- Characterization of brines

Following these studies and waiting for the results on other research lines that it could open up market opportunities, the decision was made to open a new line of work based on the cultivation of micro algae and their ability for the reduction of nutrients and/or salts in brines.

#### 2.4. Development of zero discharge systems for desalination brines by evaporation-crystallization technology and determination of their technical and economic feasibility

Zero liquid discharge (ZLD) systems are based mainly on evaporation-crystallization technologies that combine both techniques to produce a solid residue from a liquid effluent. ZLD has been used for different applications such as the reduction of different effluents; brines from membrane technologies, refrigeration circuits purges, manufacturing process pickles e.g. olives, preserves or oil, waste gas cleaning in power stations, coal or steel industry, wastes from metallurgical processes, leachates or other difficult to treat effluents.

#### 2.4.1. Objectives

To study the technical and economic feasibility of the evaporation-crystallization technology as a solution to the discharges from desalination plants in areas where it is not possible to make the discharge, zero liquid discharge technologies are required. This is especially interesting for desalination in inland areas or with brines which may contain toxic or undesirable compounds.

#### 2.4.2. Applied process

In this case 2 pilot plants were installed:

- 1 pilot plant at laboratory scale at the University Complutense of Madrid
- 1 pilot plant installed at the Cuevas de Almanzora desalination plant (25,000 m<sup>3</sup>/d brackish RO plant) (Fig. 1).



Fig. 1. Cuevas de Almanzora desalination plant.

The aspects researched with the pilot plants were:

- Quality of salts obtained.
- Nature and size of crystals obtained.
- The quality of distilled product water.
- Potential problems of unwanted precipitation in the system
- Studying the possibility of seeding crystals to improve precipitation
- Optimization of energy consumption and gas
- Assessing the cost of operation

Logically we knew that it would be very difficult to estimate costs of operation and energy consumption based on pilot plant experiences, due that the scale economy and the limitations of the pilot plants but at least we tried to bring some conclusions from the research.

# 2.5. Development of deep well injection systems for brines with study of environmental implications

One of the possible solutions for brine discharges in inland plants is to be injected into isolated deep aquifers. This could be a viable solution in some cases, but ensuring that there are no pollution risks for other aquifers. This form of disposal has been used in other countries (for example in abandoned oil wells in the USA), but the few experiences conducted in Spain were not positive and there are even some resistance from the Spanish water authorities to allow such solution.

#### 2.5.1. Objectives

This research aims to assess the feasibility of the injection of brines in deep aquifers. In the first part of the project in 2007, was focused on a rigorous study for a particular case in the Abrera treatment plant (river water treated by EDR) currently in operation, but it was finally shifted to a more general study of the possibilities of this solution in the whole of Spain.

#### 2.5.2. Applied process

This project is divided into two distinct stages:

- 1) Experiences at Abrera drinking water treatment plant (DWTP)
  - Installation of EDR pilot plant in Abrera DWTP (Fig. 2) to evaluate the performance of the installation, production and quality of treated water and brine.
  - Hydrogeological studies to assess the feasibility injection of brine.
  - Conducting a study analyzing data and drawing conclusions from the Water Treatment Group of the Polytechnic University of Catalunya.
- 2) General studies about the situation of this technology in Spain.



Fig. 2. EDR pilot plant at Abrera DWTP.

Studies from the University of Alcala de Henares, with the following scope:

- 1. Bibliography
  - a. Legislation
  - b. Geological and hydro geological characterization, permeability of the hydro geological units in Spain and location of aquifers with brackish water, which it may be subject to application of desalination processes and generation of brines
  - c. Information available on deep drilling for geothermal, oil and gas made in Spain. Inventory of old wells from oil and gas in Spain
- 2. Geological characterization
  - a. Identification from existing maps of Spanish hydro geological units that could meet the criteria of permeability and porosity adequate to support the injection of brines from desalination rejection
  - b. Analysis of temperatures and pressures of these units
- 3. Hydro chemical characterization. A guide to define the methodology to be applied in the analysis of the interaction between water injections water-bearing formation water solid matrixes of the aquifer formation.
- 4. Control program deep injection. Guides to regulate the technical documentation that should be developed to justify the suitability of the application of deep injection for desalination reject brines.
- 5. Authorization procedure for deep injection. Review of the procedures used in different countries for the consent of deep injection of fluids (any type) and the operations of artificial recharge of aquifers (both to improve their quantitative and qualitative).

2.6. Development of advanced dilution of brines. Research and modeling of different parameters and comparison with mathematical models

#### 2.6.1. Objectives

This research line aims to evaluate the effect of some parameters about brine dilution in seawater, and among others, the phenomenon of direct osmosis between brine and seawater. Concentrated brine when it is discharged into the sea, this will result in an exchange of salts to balance the chemical potential by transporting salts between the two solutions, thus producing a direct osmosis. This is one of the phenomenon's that has been investigated and how it affects the mathematical models of brine dilution.

#### 2.6.2. Applied process

This part of the research has been conducted at different levels:

1) Laboratory scale

At laboratory scale has been studied the diffusion coefficient between brine and seawater by means of holographic interferometry

2) Pilot plant

To study the dilution models it has been designed and installed a 50 m<sup>3</sup> pilot plant consisting of a GRP tank with a series of conductivity sensors at different heights and lengths, in order to customize the way of dilution. The pilot plant results are compared with those obtained by means of mathematical software used to simulate this dilution.

3) Real plants

This is the 3rd part of the study but it has not been developed until now, this will be a later study.

#### 3. Results

#### 3.1. General data

The research results have been quite interesting. Logically there are lines of research that have led to disappointing or poor results, but this is the risk of every investigation. Overall conclusions have been drawn quite interesting and new lines of possible research have been opened. The following are the most important results of the project for each of the subprojects. Logically, it is also difficult to express in a few pages the results of more than three years of research, but we have tried to summarize these results. 3.2. Subproject 1. Research on a novel technology for the recovery of divalent salts from brine. Characterization and possible uses for brines and byproducts

#### 3.2.1. Works completed

During 2007 the following works were completed:

- Laboratory tests were carried out with the process with excellent results, with significant recovery of divalent salts
- Besides ethanol other solvents were tested as acetone, isopropanol and glycerol and mixtures thereof. Also tests were conducted in hyperbaric chamber.
- The energy part of the project (energy production from bio ethanol) was studied by Valoriza Energy (company from Sacyr-Vallehermoso group, parent company of Valoriza-Sadyt) and it was subject to the availability of fuel and a suitable turbine for this purpose.

During 2008 the following activities were done:

- Continuation of laboratory studies of solvent extraction from seawater
- Studies on the economic and legal feasibility of using ethanol as fuel for power generation, which is the limiting aspect from economic point of view of the project
- Studies on the application of technology to solve the problems caused by brines from water treatment plants removing arsenic.
- Study of the zero liquid discharge facilities of an industrial RO plant.

During 2009 the following activities have been undertaken:

- The University Complutense of Madrid focused the studies on the feasibility of the process of brine concentration for arsenic removal process.
- Study of the possibilities of water ethanol separation by pervaporation process (separation membrane in vapour phase), conducted by the University of Alcala de Henares
- Studies on the application of technologies to solve the problems caused by discharges from plants that remove arsenic.

#### 3.2.2. Key findings

The key findings of the project are:

- Extraction of divalent salts from brine using organic solvents is technically feasible
- To make the process economically feasible it is necessary the implementation of a solvent removal system that allows energy production
- It is necessary to optimize the process by way of reducing the degradation of the solvent, which can be achieved with the use of technologies such as reverse osmosis membranes and pervaporation

• Technologies for reject minimization become especially important when components are toxic brines containing components as arsenic. In this case the only viable solution for treating water is the mandatory reduction and treatment of reject generated, which can be done with the technologies proposed in this project.

3.3. Subproject 2. Study of technical and economic feasibility of the application of brines from desalination plants for different uses (frost control, industrial applications, production of brine and salts, etc.). Brine recovery

#### 3.3.1. Works completed

During 2007 a bibliography study of all the possible uses of brines with the objective of designing some experiences or recovery processes applied or used was completed. In 2008 a new study began, in this line of research by the University of Alicante on the use of micro algae for use/treatment of brines.

The main objectives of this research were:

- 1. Nitrate reduction in desalination brines by culturing micro algae.
- 2. Possible commercial use of micro algae produced (food supplements, cosmetics, cellulose, vitamins, antioxidants, etc.).

Completed in its development stages were:

- 1. Species selection.
- 2. Optimization of cultivation in the laboratory.
- 3. Scaling to 2 L volumes under controlled conditions.
- 4. Simulation of process reactors outdoors in intermediate volume (As shown in Fig. 3).
- 5. Development of pilot plant studies.

One species was found with the best results in nitrate removal (46.84%) and the amount of biomass obtained was quite important. It was the largest in size species studied, and although there are some problems of sedimentation it has many industrial applications and has been studied extensively.

Table 1			
Summary	of	some	results



Fig. 3. Microalgae production pilot plant.

In the experiments the main determinants of the mass production of micro algae, were also taken into account they are: lighting dissolved CO<sub>2</sub> concentration and pH, agitation and concentration of nitrogen and phosphorus. A summary of the main results is shown in Table 1

Finally some experiences were done to determine the sedimentation rate of these micro algae in order to choose the best technology available for the separation of micro algae from the treated effluent.

# 3.3.2. Key findings

The key findings of the project are:

- There are numerous applications for brines that could be profitable depending on required quality or degree of dryness or distance between producer and user
- The use of micro algae as biomass for the removal of certain salts (in general nutrients), opens a good possibility of treatment for some brines. The results obtained with reductions over 45% for nitrates are really encouraging. However, further work must be done on the research about the applications of this biomass once used in the removal of nutrients.

Species	Operation	DCM* (cells/ml)	Maximum micro- algae concentration (g/l)	Nitrate eliminated (mg/l)	Nitrates eliminated (%)
Species 1	Discontinuos and semi-discontinuous	5.06×10 <sup>6</sup>	0.405	136.65	42
Species 1	Discontinuous	820000	0.066	31.96	10
Species 1	Continuous	720000	0.058	28.06	8
Species II	Discontinuos	426000	0.085	41.53	12
Species II	Continuous	506000	0.101	49.32	14

\*DCM: Maximum cell density

3.4. Subproject 3. Development of zero discharge systems for desalination brines by evaporation-crystallization technology and determination of their technical and economic feasibility

#### 3.4.1. Works completed

Apart from the laboratory experiences, the most interesting research was done with the pilot plants.

#### 3.4.1.1. Pilot plant I trials

This pilot plant (Fig. 4) has an evaporation capacity of 7 l/h. It works in a continuous mode, and vacuum conditions, so that the evaporation temperature is in the range of 45–55°C. Working with the heat pump principle, with this team the recovery is possible and reuse of distillate, which conductivity level is less than 70  $\mu$ S/cm. The system is more energy efficient than conventional evaporation-crystallization (pilot plant II) because it uses the heat that transfers the vapor to condense to the evaporation process. It is a process used commercially for small plants where the energy cost is not the fundamental variable. The energy consumption was very high, about 0.9 kWh/kg, with an estimated final cost of 0.095 €/kg brine evaporated. The salt production in the early stages is about 10 g/l brine evaporated.

#### 3.4.1.2. Pilot plant II trials

This pilot (Fig. 5) is an evaporation-crystallization plant with simple effect and continuous feeding. Control of this plant is done by the feed flow and the pressure in the evaporator that are a function of temperature in the evaporator, and therefore the heat flow provided by the exchanger. The plant capacity is 100 l/h, although experiments have worked with a flow rate of approximately 70 l/h. The flash type evaporator, operated under vacuum conditions, allows evaporation in a temperature range of 40–60°C. The composition of brine feed was quite variable, up 7% compared to the conductivity and 40% over the calcium content, because the Cuevas desalination plant that is fed by different wells with different types of water.

The problem with this plant is that, due to its large size, it took a rather long time to come to steady state. Thus, the conductivity in the crystallizer increased during the experiment closer to an asymptotic value, about  $188 \,\mu$ S/cm, value that reaches from  $12 \,\text{m}^3$  of brine evaporated, which corresponds to about  $180 \,\text{h}$  of continuous operation. The temperature crystallizer is about  $5^{\circ}$ C below the evaporator, which favours the precipitation of salts. The conductivity in the evaporator was slightly higher (2–5  $\mu$ S/cm) than the crystallizer, which may reflect the effect of removing salts in solution to be precipitated.

We found a linear relationship between conductivity and density of the concentrated solution. The salt that was precipitated mainly along the experiments was CaSO<sub>4</sub>



Fig. 4. Evaporation pilot plant I.



Fig. 5. Evaporation pilot plant II.

 $x H_2O$  ( $x = \frac{1}{2}$  or 2), due to the low solubility product of this salt as well as the brine composition. It did not reach saturation of NaCl or at least this salt did not become the majority in any of the samples tested, although there was a small percentage of NaCl in precipitated salts (about 2–4% w) that was increased throughout the experiment. This may be due to increased concentration of sodium chloride in the solution bathing salts.

The prismatic crystals are composed of  $CaSO_4$ . Fig. 6 shows the scanning electron microscope images of different salt samples analyzed. The cost to evaporate the brine in the evaporator with steam boiler fuelled by propane is approximately 0.099  $\in$ /kg of brine evaporated.

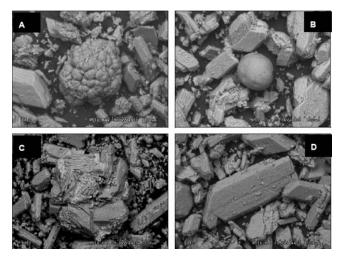


Fig. 6. Enlarged photos of the different types of structures found in different samples of salts. A: Agglomeration areas S2. B: Salt S3.C spherical shape: prism Agglomeration salts 'dissolved' by the surface in S4. D: Prism in S2.

### 3.4.2. Key findings

The key findings of the project are:

- The evaporation-crystallization technology a priori appears to be economically viable only if it is associated with a system to recover residual heat or steam as the process has a high energy consumption.
- It is necessary to optimize the process for lower fuel consumption. Several studies have been done in the pilot plant to determine the feasibility of this technology (evaporation-crystallization) for the disposal of brines. These studies have identified several variables that affect the process and the composition of the salts drawn on the basis of operating parameters. It is necessary to continue these studies and examine the economic aspects of the process (mainly energy consumption).

# 3.5. Subproject 4. Development of deep well injection systems for brines with study of environmental implications

#### 3.5.1. Works completed

In 2007 the following activities were conducted:

- Installing an EDR pilot plant in Abrera DWTP to evaluate the performance of the installation, production and quality of treated water and brine
- Making two hydrogeological studies to assess feasibility of the injection of brine
- Conducting a study analyzing data and drawing conclusions from the Water Treatment Group of the Polytechnic University of Catalunya

As mentioned, with the obtained results, it appeared that it was not a very adequate solution the brine injection in the deep aquifer in this case. Therefore, the conclusion was that it had no sense to continuing this research, at least in the case of Abrera, although the pilot plant tests were continued as well as the results from the industrial plant operation. For this reason, the decision was made to refocus the study since 2008 for the purpose of carrying out the study of the feasibility of applying deep injection techniques in Spain.

In order to evaluate the management of deep well injection of brines from desalination plants the weaknesses of the deep injection (pollution of water and seal the store) were studied. In order to avoid these weaknesses, the requirements for the selection of potential underground sites of rejection were studied in detail:

- Development of methods to calculate the volume of the site;
- Possible methods to model the chemical behaviour of fluids in the store and avoid the filling of this;
- Considering the use of Geographic Information Systems to assess the suitability of zone against a possible storage of brine.

Moreover cited operational requirements set by the program UIC (Underground injection control) from the EPA (Environmental Protection Agency of the USA). Finally, a SWOT analysis (strengths, weaknesses, opportunities and threats) was completed, about the situation of Spain in response to the possible brine injection and potential sites for this application in Spain were studied, having based their choice on criteria established in the research and in previous studies carried out underground for other purposes, such as CO<sub>2</sub> storage.

Finally, as a consequence of the works, a Best Practices Manual was done, for the deep well injection of brines.

#### 3.5.2. Key findings

The key findings of the project are:

- In Spain there have been no successful experiences of this type, although there are some facilities built.
- In the case of the DWTP Abrera, it was demonstrated that it was not feasible the brine injection of brines due to the hydrogeology of the area, but with a consequence which was to cancel the research line about this particular case.

The water authorities and water managers are challenged to find a balance between appropriate treatment technologies, disposal practices for safe waste generated the safety of workers and costs, while ensuring compliance with drinking water regulations for maximum public health protection. These challenges are causing them to consider the deep well injection of brine and other wastes sometimes as the only possible disposal option for the residues obtained from potable water.

The deep well injection of the concentrate by-product

from drinking water treatment is currently the most viable option for the management of desalination concentrates inland. In the USA this practice takes place in more than 100 infrastructures. The various legal aspects that may affect the deep injection of brines and concentrates in Spain are contained in various rules and laws, because there are no specific regulations for these actions.

3.6. Subproject 5. Development of advanced dilution of brines. Research and modeling of different parameters and comparison with mathematical models

#### 3.6.1. Works completed

During 2008 and 2009 the installation of pilot plant facilities at desalination plant of Cuevas de Almanzora

were completed, where the first tests about dilution were performed. These jobs have been outsourced to the University Institute of Water and Environmental Sciences at the University of Alicante.

Some tests (Fig. 7) were carried out on laboratory scale to set some parameters before performing the test at a pilot scale in the tank. Test tank dimensions were  $18 \times 31 \times 15$  cm<sup>3</sup> methacrylate.

Parallel development of a pilot scale plant was carried out located in Cuevas de Almanzora. Below are some pictures of the final state of the plant, auxiliary tank and control panel (Fig. 8).

The pilot plant consists on the dilution tank (50 m<sup>3</sup>, rectangular), brine feed tank with agitation, discharge pump and flow control system, diffuser nozzle system,



CuSO<sub>4</sub> (60 g/L)

Fig. 7. Images of some laboratory experiments.



CoCl<sub>2</sub> (60 g/L)



60 g/L NaCl and 20 ppm methylene blue



Fig. 8. Pilot plant details at Cuevas de Almanzora desalination plant.

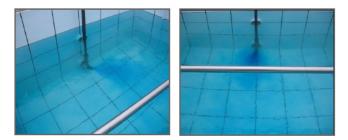


Fig. 9. Sights of the dilution plume.

a set of 23 conductivity probes, data logging, electromagnetic flow meters and control panel. The tank was painted white for better contrasts of colour, and painted with a 0.5 m scale, to provide a reference chart. The calibration and validation of equipment for measuring the conductivity, flow meters and data recording were also carried out. The first experiment with dye to determine a priori the best location of conductivity probes, was conducted using a synthetic solution using sodium chloride and methylene blue, simulating the increase in conductivity that it could be expected in brine discharge compared to the marine environment, using a flow of 128 l/h. The results are shown in Fig. 9.

#### 3.6.1.1. Holographic interferometry studies

To study the dilution of brine in seawater a technique using a holographic interferometry technique was used. It is an optical technique that combines holography and interferometry, allowing an observation of the changes of optical path as interference fringes.

This optical path is the product of the refractive index by the distance travelled by a laser beam. Therefore, if you use a physically stable and transparent container, you can display the refractive index changes that are taking place in a transparent medium in form of interference fringes. Since the refractive index is directly related to the con-



Fig. 10. Holographic interferometry assembly.

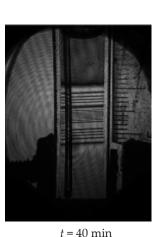
centration of the solution, it is possible to determine concentration profiles in mass transfer processes (osmosis, ultrafiltration, diffusion, etc.). The experimental device consists of assembling and holographic interferometry module where the process occurs under study (diffusion, dilution, dispersion) (Fig. 10).

Using the described procedure the diffusion coefficient of brine in seawater can be obtained. Prior to that, there have been experiments using sodium chloride at different concentrations, as is the majority salt in seawater. The value of the NaCl diffusion coefficient obtained in the experience was  $1.52 \times 10^{-5}$  cm<sup>2</sup>/s. If you compare this value with literature data ( $1.53 \times 10^{-5}$  cm<sup>2</sup>/s) it has an error of 0.7%, which is considered acceptable.

After obtaining the diffusion coefficient of sodium chloride, the next objective was the calculation of diffusion coefficient between seawater and brine undiluted, obtaining a value of the diffusion coefficient of  $1.27 \times 10^{-5}$  cm<sup>2</sup>/s. This value may be used in the subsequent analysis of the discharge of an emissary from a desalination plant. Fig. 11 shows some of the interferograms obtained:

An important step in this research is to design a





 $t = 30 \min$ 

Fig. 11. Interferograms of brine and seawater.



 $t = 50 \min$ 



 $t = 60 \min$ 

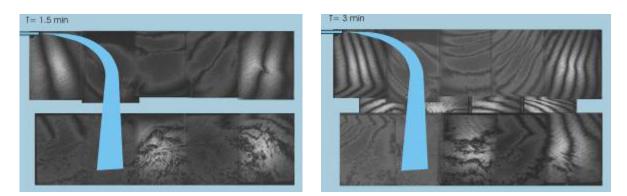


Fig. 12. Interferogram integration.

module that plays the best possible behaviour of the phenomenon being studied; in this case, the discharge of brine from desalination plants to the sea.

As a prelude to the design of the module, various tests to determine the module dimensions have been conducted. The experiment was to introduce a stream of brine, stained with a dye, at different speeds in a bath containing seawater. This is the extent of the plume of brine and dispersal in the seawater.

Finally there have been integrated the results of some interferograms with different times and using the mathematical software MATLAB program; a program that simulates what happens in the module has also been developed. To do this, from the data obtained we have started by measuring the interference fringes of different experiments and has been interpolated information module areas where no data are available. In Fig. 12 the integration of single interferograms in one combined representation is shown.

#### 3.6.2. Key findings

The key findings of the project are:

- The mathematical models used in Spain for the simulation of the dilution of brine discharges are normally from other different applications (not specific) and they have not considered all possible effects (such as direct osmosis) in the blending of brine in the sea. This means that disposal facilities are being designed with inaccurate information.
- Laboratory results prove the above statement as it requires a more rigorous analysis of these models through a pilot system with enough size to properly simulate the process.

Regarding the studies with holographic interferometry, basically at this stage the devices and technology have been optimized, and numerous tests to determine the diffusion coefficients of brine blending with seawater have been conducted. Finally, it has to be found the mathematical model that adequately could simulate discharges of brine into the sea. This works are going continued to use the current pilot facilities.

#### 4. New projects and ideas

As a consequence of the results and conclusions obtained during the development of this project there were opened new lines of research, as the following:

- Study of the causes of the degradation of ethanol in the separation process of water and brine
- Study of separation of mixtures ethanol/water or brine by evaporation and membrane technologies (pervaporation)
- Exploring the possibility of freezing technology combined with other processes for its optimization. This seems particularly interesting because freezing is thermodynamically more favourable than evaporation.
- Studying the possibility of using solar energy or other renewable energies combined with any of the processes described above

These new research lines will be included in one or more new projects as well as continuation of some of the main lines which should be investigated further.

## 5. Conclusions

The main conclusions obtained during this experience are indicated next.

- Brine discharges in desalination and mainly in inland installations still remains being a problem, with not many feasible alternatives
- Increasing the R&D efforts to reduce the environmental impact of the desalination technologies is needed
- Some solutions adopted for the management of brines as ZLD by evaporation require further development in order to reduce energy consumption

- Microalgae production for elimination of water pollutants or nutrients (even in brines) seems a very interesting way for future treatments, taking in account the possible further use of micro algae biomass for energy production or other applications.
- Deep well injection seems the only economically feasible way to solve brine discharges in many plants and it must be considered studying all the environmental implications
- The mathematical simulation of the dilution process of brine in seawater requires more research to represent more accurately the real phenomenon
- As a consequence of R&D project presented, some important objectives have been achieved as the increasing in knowledge on the state of the art brine management in inland areas, the developing of a best practices manual for the injection of brines in deep aquifers and training of the researchers in this important area of knowledge.