"Development of an advanced, innovative, energy autonomous system for the treatment of brine from seawater desalination plants"

SOL-BRINE

Deliverable 6.1	**Literature review on the potential alternative uses of the final products from similar brine treatment processes on a worldwide basis**

Action 6 **Alternative uses of the system's final products**

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Disclaimer

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List of Abbreviations

GCC	Gulf Cooperation Council (Bahrain, Kuwait, Oman, Qatar, Saudi Arabia and the UAE)
ZLD	Zero Liquid Discharge
FGD	Flue Gas Desulphurization
MF	Microfiltration
RO	Reverse Osmosis

1 Executive Summary

This report presents case studies with Zero Liquid Discharge systems, used in industrial applications producing brine effluents of similar chemistry with brine from desalination plants. It is structured upon seven chapters, the executive summary being the first of which.

In Chapter 2, an introduction to brine effluents and industrial activities is provided. Eight main industries are mentioned that employ reverse osmosis (or similar) (waste)water treatment plants that lead to the production of brine effluents.

Two of these industries, power and coal mine plants, are especially examined since they comprise industries with a lot of Zero Liquid Discharge plants in operation. A brief discussion of the process involved is provided in Chapter 3.

In Chapters 4 and 5, data about water and salt usage on a worldwide basis are provided. With reference to salt, technical specifications are given by salt and use, with the aim to shed light on the possibilities to exploit the salts recovered from ZLD plants. The same is provided in Chapter 5 for water.

In Chapter 6, specific case studies are examined. Six (6) plants are analyzed where alternative direct uses of brine effluents are provided in the end of the chapter. For each case study the following information is provided: (a) Location; (b) Stage of development (bench-scale, pilot system, application); (c) Use of water produced (potable; industry recycle; distillate water); (d) Use of salt produced (table salt; chemical industry; road salt); (e) Year of commissioning; (f) Ownership; (g) Technology and process involved and (h) Technical specifications and uses of end-products.

In Chapter 7, the conclusions of the report are provided.

Περίληψη στα Ελληνικά

Η μελέτη αυτή παρουσιάζει περιπτώσεις βιομηχανιών που έχουν εφαρμόσει τεχνικές Μηδενικών Υγρών Αποβλήτων. Οι τεχνικές αυτές έχουν συνήθως ως στόχο την αποφυγή περιβαλλοντικών επιπτώσεων από τα υγρά απόβλητα που παράγονται από τις διεργασίες της παραγωγικής διαδικασίας. Άλλοτε, οι τεχνικές αυτές χρησιμοποιούνται και για την παραγωγή χρήσιμων τελικών προϊόντων, τα οποία ανακτώνται κατά την επεξεργασία των υγρών αποβλήτων. Σε κάθε περίπτωση, οι βιομηχανίες που εφαρμόζουν τέτοιες τεχνικές, δεν απορρίπτουν υγρά απόβλητα στο περιβάλλον.

Στο Κεφάλαιο 2, το οποίο αποτελεί την εισαγωγή της μελέτης, αναφέρονται οκτώ βιομηχανίες που παράγουν υγρά απόβλητα παρόμοια με το υγρό απόβλητο που παράγεται από τη διαδικασία της αφαλάτωσης (άλμη). Τα απόβλητα αυτά, στις περισσότερες περιπτώσεις προκύπτουν μετά την εφαρμογή κάποιας τεχνικής επεξεργασίας με χρήση μεμβρανών.

Στο Κεφάλαιο 3, δύο από τις οκτώ βιομηχανίες αναλύονται περαιτέρω: η βιομηχανία παραγωγής ηλεκτρικής ενέργειας και η βιομηχανία εξόρυξης άνθρακα. Ο λόγος που επιλέχθηκαν οι εν λόγω βιομηχανίες είναι ότι αποτελούν τις βιομηχανίες με τις περισσότερες καταγεγραμμένες εφαρμογές συστημάτων Μηδενικών Υγρών Αποβλήτων. Η εφαρμογή των συστημάτων αυτών οδηγεί στην ανάκτηση σημαντικών ποσοτητων νερού και στερεών αλάτων.

Στα Κεφάλαιο 4 και 5, δίνονται στοιχεία σχετικά με τις ποσότητες και τις διαφορετικές προδιαγραφές αλατιού (Κεφάλαιο 4) και νερού (Κεφάλαιο 5) που καταναλώνονται σε παγκόσμιο επίπεδο. Τα στοιχεία αυτά, αποτελούν τις προδιαγραφές που πρέπει να καλύπτουν τα προϊόντα από τις τεχνικές Μηδενικών Υγρών Αποβλήτων, έτσι ώστε να καθίστανται εμπορεύσιμα αγαθά.

Στο Κεφάλαιο 6, παρουσιάζονται συγκεκριμένα παραδείγματα από βιομηχανίες που έχουν εφαρμόσει τεχνικές Μηδενικών Υγρών Αποβλήτων. Συγκεκριμένα, έξι παραδείγματα αναλύονται δίνοντας πληροφορίες σχετικά με: (α) την τοποθεσία, (β) το στάδιο της τεχνολογικής ωριμότητας της εφαρμογής (εργαστηριακή, πιλοτική κλίμακα ή εμπορικό προϊόν), (γ) Χρήση παραγόμενου νερού (πόσιμο, βιομηχανική, αποσταγμένο κ.λπ.) (δ) Χρήση παραγόμενων αλάτων (επιτραπέζια, βιομηχανική, εκχνιονιστική χρήση κ.λπ.) (ε) έτος λειτουργίας, (στ) περιγραφή της τεχνολογίας και (ζ) τεχνικές προδιαγραφές τελικών προϊόντων.

Στο Κεφάλαιο 7, παρουσιάζονται τα συμπεράσματα της μελέτης.

2 Introduction

2.1 Brine effluents & chemistry

Brine effluents are the by-product produced by water or/and wastewater treatment operations.

With reference to the brine chemistry, brine can be categorized into the following categories, according to the number/type of salts present in the effluent:

- Brines with single-salt present (e.g. chlorine, sulphate, nitrate, fluorine, ammonia, phosphate etc.);
- Brines with a mix of salts (e.g. calcium chloride, sodium chloride, sodium, sulphate, sodium phosphate);
- Brines that also contain organic matter (this kind of brines have Chemical Oxygen Demand for their proper treatment) and
- Brines that also contain heavy metals.

2.2 Industries

Reverse Osmosis (RO) is the predominant source of concentrated brine, especially when referring to wastewater treatment. It accounts for 79% of the total installed capacity for wastewater treatment on a worldwide basis, with the largest shares in United States of America and East Asia (see also Figure 2-1 and Figure 2-2). Some of the industries producing brine effluents include, but are not limited to, the following :

- Desalination facilities;
- Energy production (flue gas treatment and cooling water blowdown);
- Food industry;
- Leather industry and textile;
- Oil and gas industry;
- Chemical industry (including biotech and pharmaceutical);
- Mining industry;
- Pulp and paper.

The brine effluent generated by the above mentioned industries causes an ever growing management problem, both in terms of increasing volumes and pollutants load. Different waste water treatment techniques are currently applied so as to manage the brine effluent and the final discharge to the water recipient to be safe for the environment, according to local regulations.

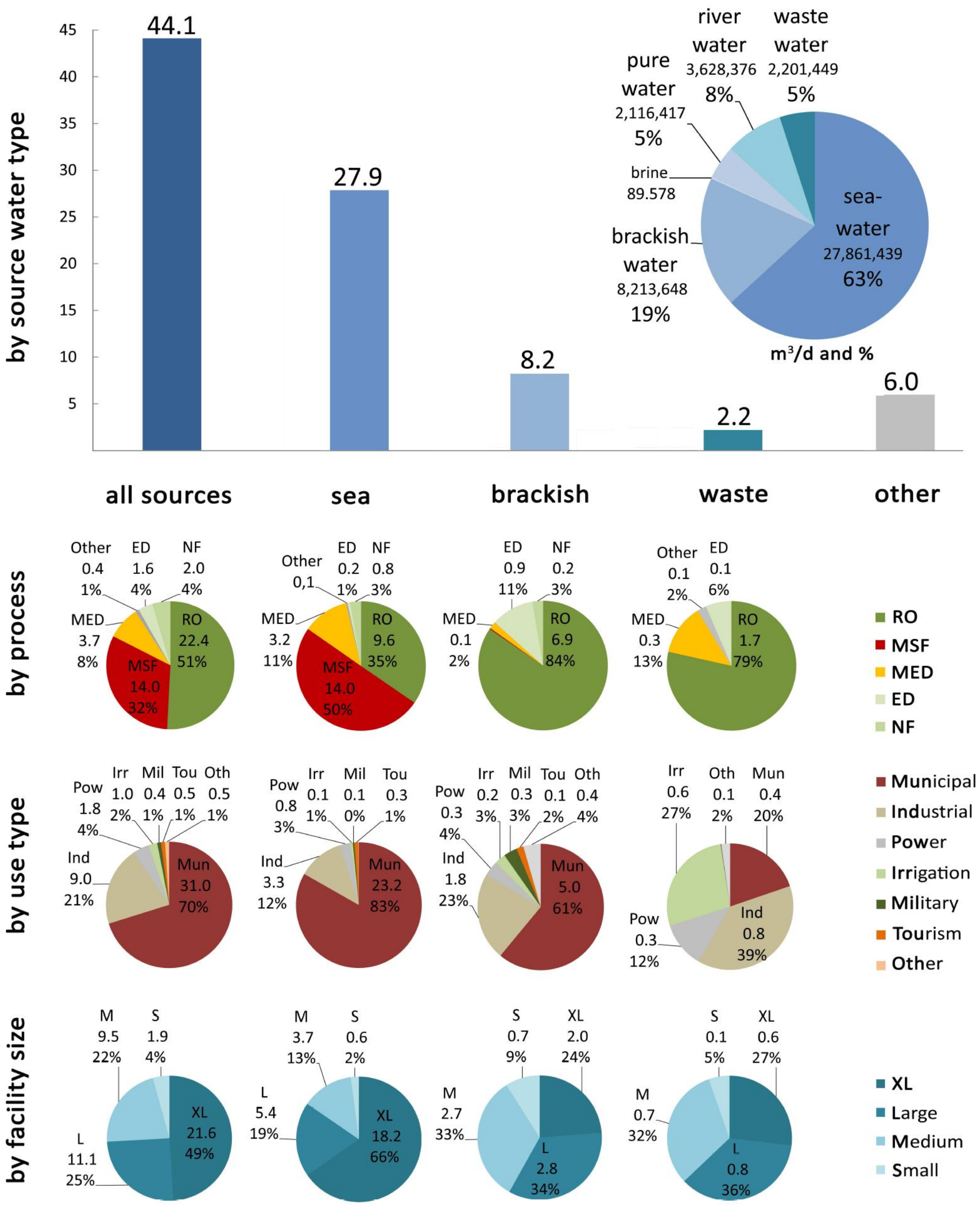


Figure 2-1: Global desalination capacity by source water type (1st row), by process and source water type (2nd row), by use type and source water type (3rd row) and by plant size and source water type (last raw) (Latteman, 2010)

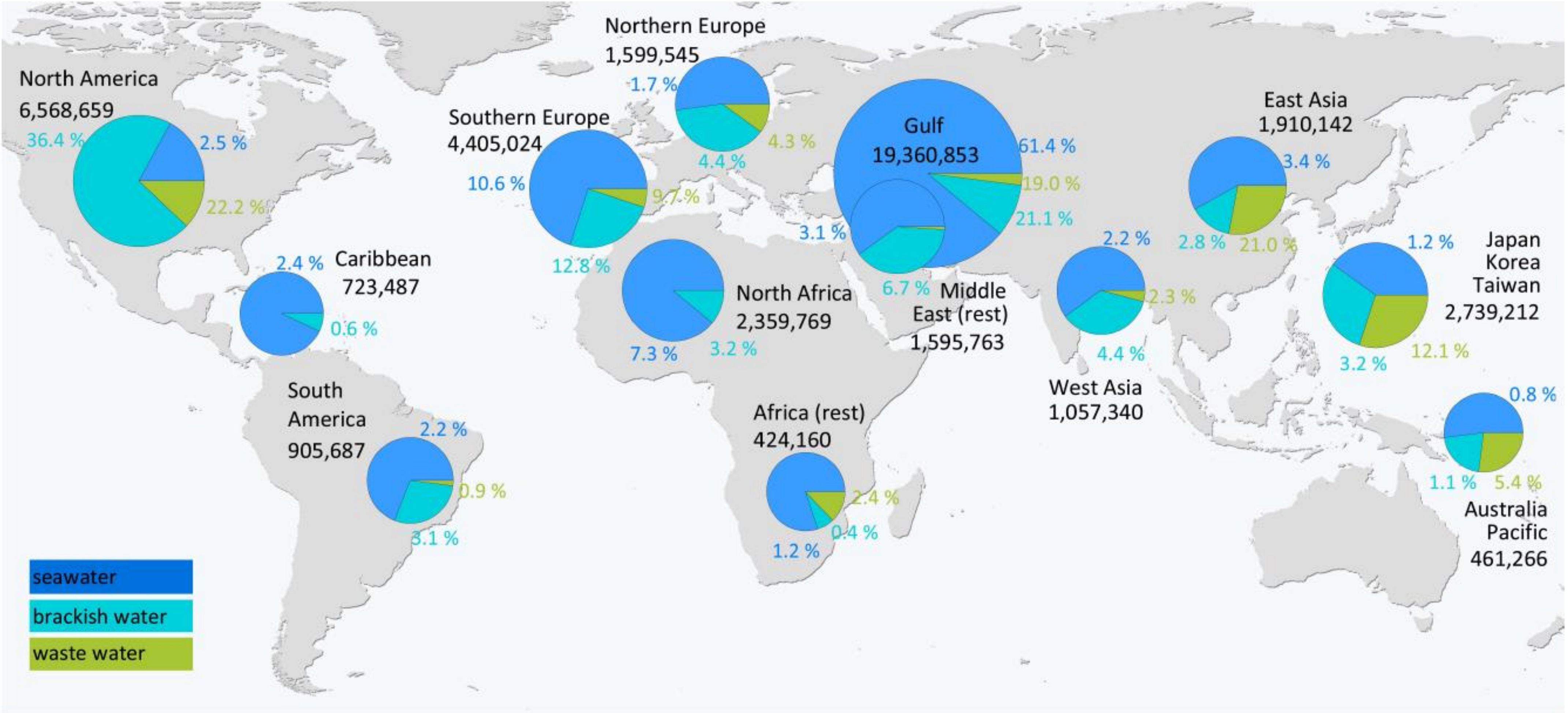


Figure 2-2: Global desalination capacity in cubic meters per day and as a percentage to global production (Latteman, 2010)

However, it is increasingly recognized the ultimate need for brine elimination, by applying zero liquid discharge technologies. Many research projects have been developed or are in progress for investigating the potential to apply new techniques for ZLD. However, the recording of the research activity is outside the scope of this study, as its main aim is to study how proven techniques have been applied in industrial applications and also how the products recovered have been exploited. In general it is noted that there is an identified need for water treatment innovation with the view to brine elimination and recovery.

2.3 Zero Liquid Discharge

Zero Liquid Discharge has been a focus for research since early '70s. The driving force for its development is the threat of scarcity both of water and raw materials, as well as the need for long-term sustainability, expressed through more stringent environmental legislation (WssTP, 2012). It was the US federal regulatory pressure that gave birth to the ZLD sector.

Even though, some technologies have been developed for achieving Zero Liquid Discharge, the three major ZLD providers are: Aquatec, GE Power and Water, and HPD, a subsidiary of Veolia Water Treatment & Technologies. United States is by far the largest ZLD customer with approximately 120 industrial (non municipal) wastewater Zero Liquid Discharge facilities (see also Figure 2-5 and Annex I). During the process a solid by-product is inevitably generated, that in most cases must be disposed of in a landfill. These technologies include mainly the following:

- Membrane separation;
- Evaporation ponds;
- Evaporators/Brine Concentrators;
- Crystallizers; and
- Spray Dryers.

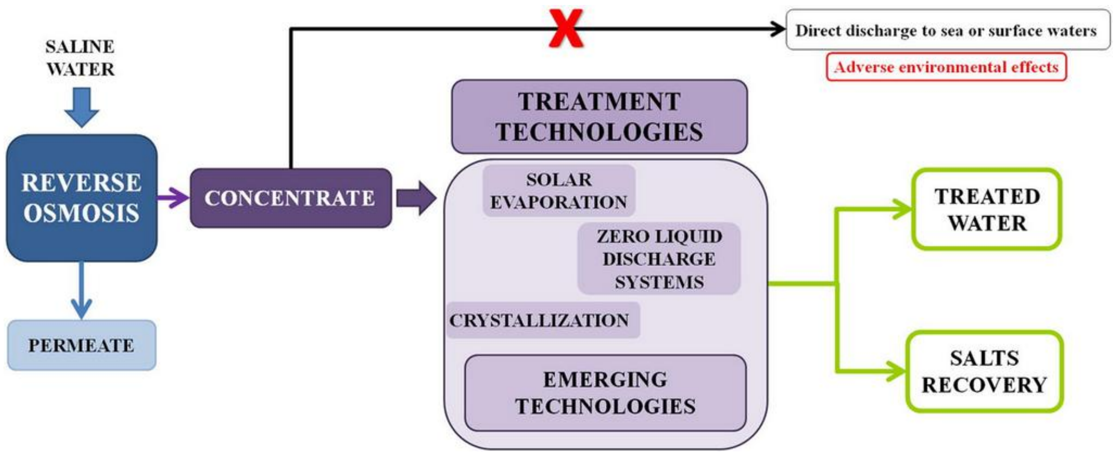


Figure 2-3: Zero Liquid Discharge schemes for saline water streams (Pérez-González, 2012)

GENERAL PROCESSING SCHEME 1

Conventional ZLD plants almost exclusively involve the use of thermal brine concentrators in one of the following three schemes:

A: concentrate → pretreatment (minimal) → thermal brine concentrator → evaporation pond (standard/enhanced)

B: concentrate → pretreatment (minimal) → thermal brine concentrator → crystallizer → solids (with possible very small blowdown stream)

GENERAL PROCESSING SCHEME 2

More recently, *high-recovery RO systems* have been used to reduce the volume of solution going to the thermal brine concentrators. The processing schemes include:

A: concentrate → treatment → second-stage RO → thermal brine concentrator → evaporation pond

B: concentrate → treatment → second-stage RO → thermal brine concentrator → crystallizer → solids

In general, the treatment used in this high-recovery RO scheme is significantly more intensive than in Processing Scheme 1.

GENERAL PROCESSING SCHEME 3

In some cases, the two-stage membrane system is used alone without any thermal processing:

concentrate → treatment → second-stage RO → evaporation pond

GENERAL PROCESSING SCHEME 4

Another more recent processing scheme (Geo-Processors, 2007), not yet used in the United States, entails selective or sequential recovery of individual salts from the effluent. The processing scheme used depends on the particular effluent being treated:

concentrate → salt removal → second-stage RO → salt removal → brine concentrator → mixed salts recovery

Figure 2-4: Frequently used ZLD schemes (Svensson, 2005)

However, it must be noted that these systems have been applied to other wastewater types and not brine effluent from desalination plants, including power generation and mining industry mainly. The production process of these industries is discussed in Section3, while case studies with Zero Liquid Discharge systems applied in these industries are presented in Section 6. Efforts have been made to describe the technologies involved as far as possible, but most of the described systems comprise proprietary technologies and as a result the suppliers avoid to provide plentiful information.

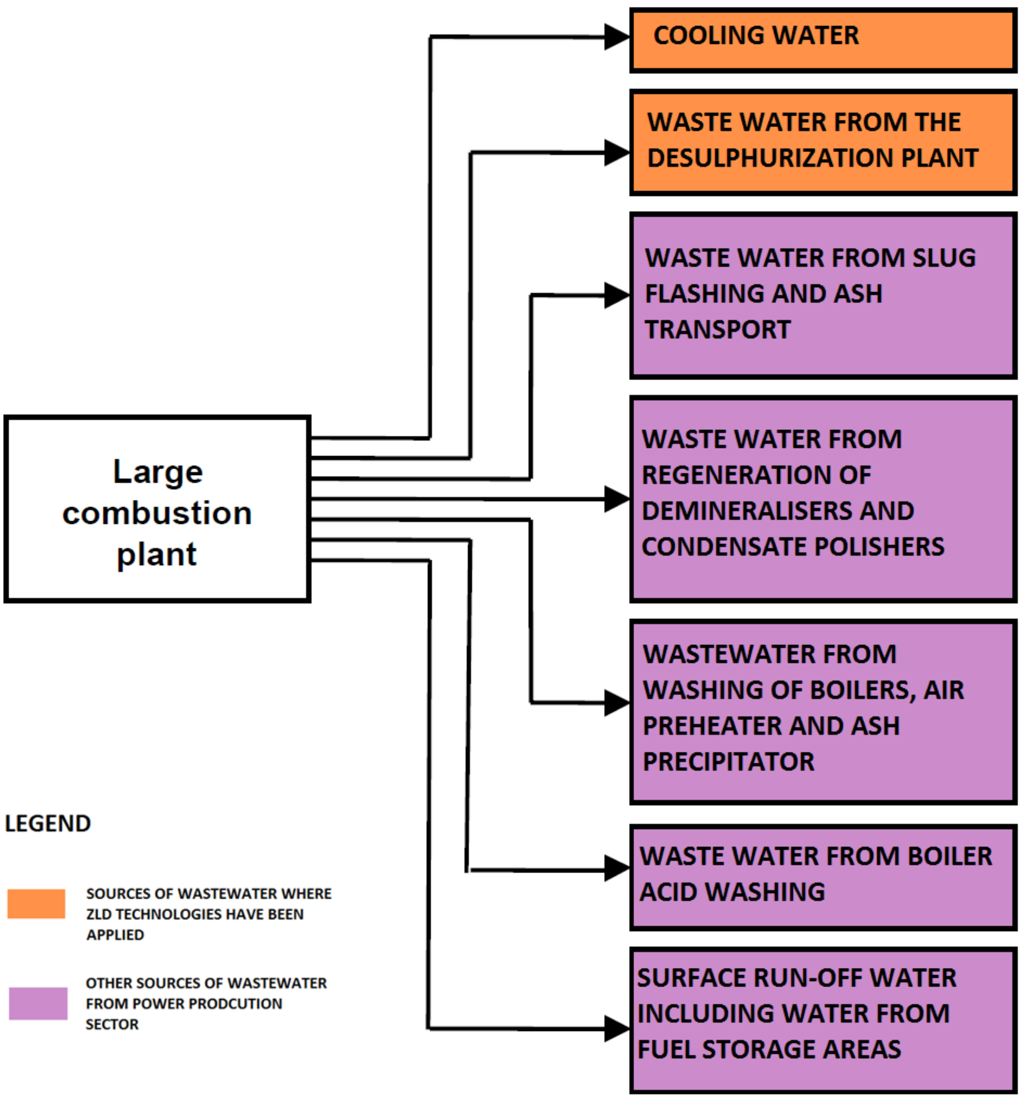
Figure 2-5: Zero Liquid Discharge systems executed by Veolia Water on a worldwide basis (Veolia Water, 2008)

3 Industries with ZLD needs and applications

3.1 Power Production

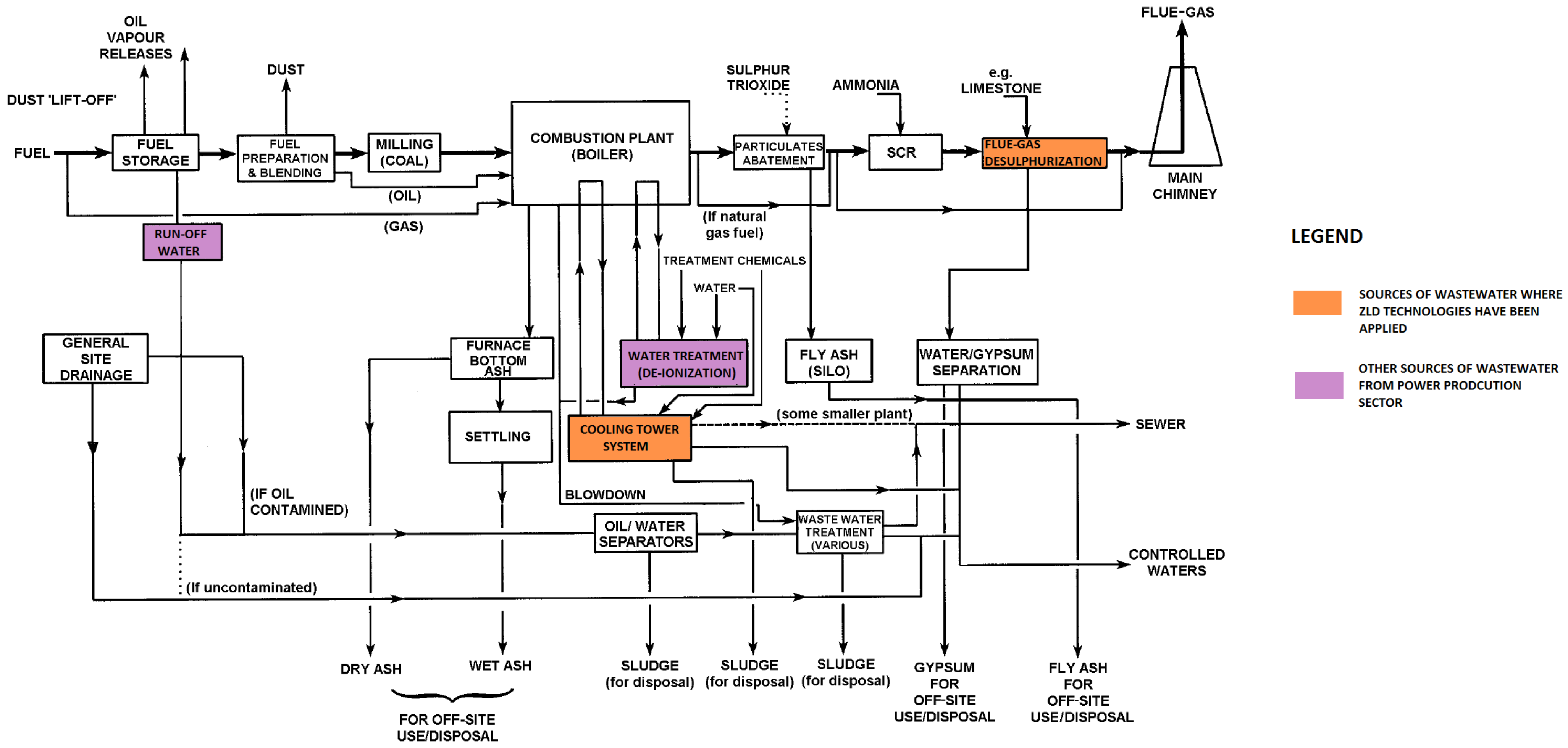
Power production units generate a great amount of wastewater effluents at different stages of their operations. Among these waste streams some are more challenging both in terms of volume and contaminant load. As illustrated in Figure 3-1 and Figure 3-2, Zero Liquid Discharge applications have only been developed for the following two wastewater effluents:

- Cooling water effluent; and
- Waste water from the desulphurization plant.



Adapted from (European Commission, 2006)

Figure 3-1: Wastewater effluents from fossil-fuel fired large combustion plants



Adapted from (European Commission, 2006)

Figure 3-2: Generalized flow diagram of a combustion plant and main sources of wastewater

Cooling Tower Blowdown

For the purposes of cooling, two systems have been developed and applied in the power production industry:

(a) Open or once-through systems; and

(b) Recirculating systems.

The latter systems result to relative small water usage, about one twentieth compared to once-through systems. However, the cooling tower employed must be periodically discharged to surface waters so as to control the build-up of solids. Cooling towers require approximately 90% of the power plant's total water needs, thus straining the importance of water treatment and recycling back into the process.

The cooling water blowdown is contaminated with: (a) Particulate Matter; (b) Organic Compounds; (c) Metals and their salts; (d) Chlorine (as hypochlorite) and (e) Mercury or/and Cadmium. The level of contamination depends on the frequency of the blowdown. This is usually referred to as Cycles Of Concentration (*COC*), with typical values varying from 4 to 7 COC, to minimize water requirements.

Flue-Gas Desulphurization

The fossil fuel-fired power plants use fuels that often contain varying amounts of sulphur. These fuels may be coal, peat and oil. To avoid high SOx emmissions large combustion plants treat the flue gas generated with special equipment, named Flue Gas Desulphurization (FGD) plants. The FGD techniques used as end-of pipe equipment, can be categorized into two broad categories:

- Regenerative processes; and
- Non-regenerative processes.

Both categories include many sub-categories (see also Figure 3-3), but all can be seen as either dry or wet processes. All wet-type flue gas cleaning systems produce a waste water effluent, with varying contaminants according to the treatment process followed. For instance, the brine effluent can be contaminated with limestone, sodium hydroxide or ammonia.

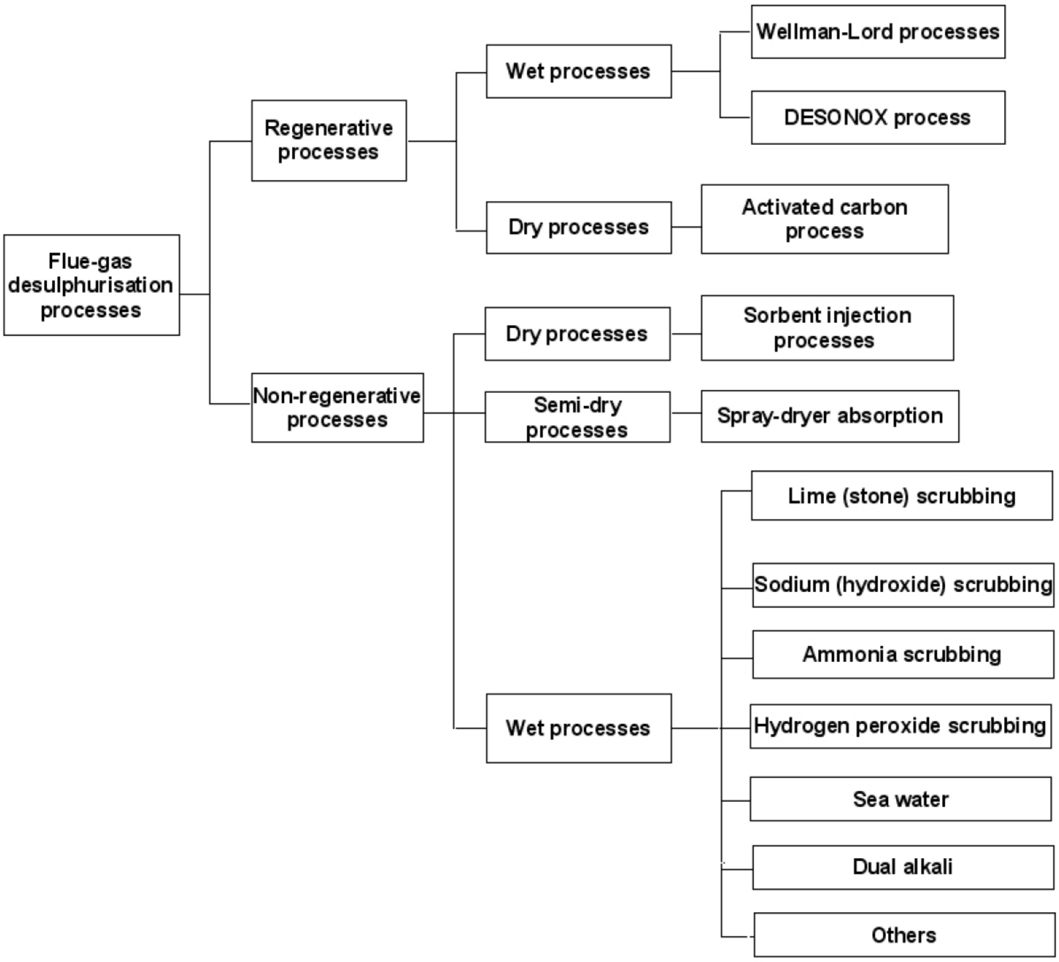


Figure 3-3: Overview of technologies used to reduce SOX emmissions (European Commission, 2006)

3.2 Mining and energy resource industries

The mining industry involves: Aluminium, base metals (this term usually refers to industrial non-ferrous, excluding precious metals, such as Cadmium, Copper, Lead, Nickel, Tin, Zinc), Chromium, Iron, Manganese, precious metals (gold and silver), Tungsten, potash mining while the energy resource industry involves crude oil, gas, coal and methane gas production. All these industries produce large volumes of highly saline wastewater effluent. Indicatively, the production process for the case of coal is provided in Figure 3-4.

The drainage water effluents from mines can be acidic or alkaline and may be contaminated with the following pollutant loads:

- dissolved metals
- soluble and entrained insoluble complex organic constituents from mineral processing,

- natural occurring organic substances such as humic and long-chain carboxylic acids from mining operations.

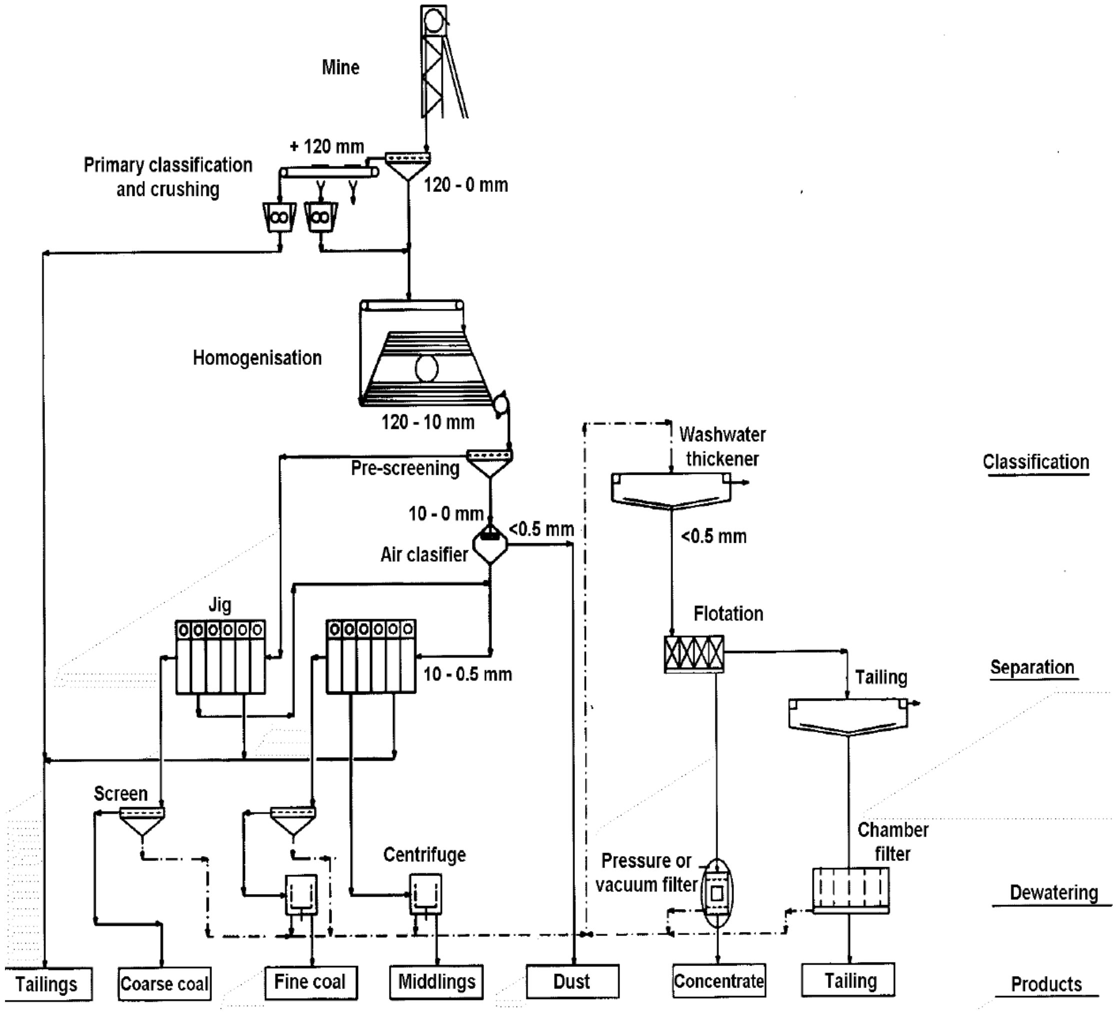


Figure 3-4: Typical flow sheet for coal mineral processing (European Commission, 2009)

4 Salt uses

4.1 Salt Production Worldwide

The annual production of salt was 290 million tons in 2011 (Serra Salt Engineers, 2005). In 2012 it dropped down by 4.2% compared to 2011 and recovered to 286 million tons in 2013 (Roskill, 2014), in response to a recovery in demand from the de-icing market.

More than one third (40%) of the total salt production, is produced by solar evaporation of sea water or inland brines. Mined rock salt deposits follow with a share of 34%, while the balance is obtained with brines, mainly by solution mining (see also Figure 4-3).

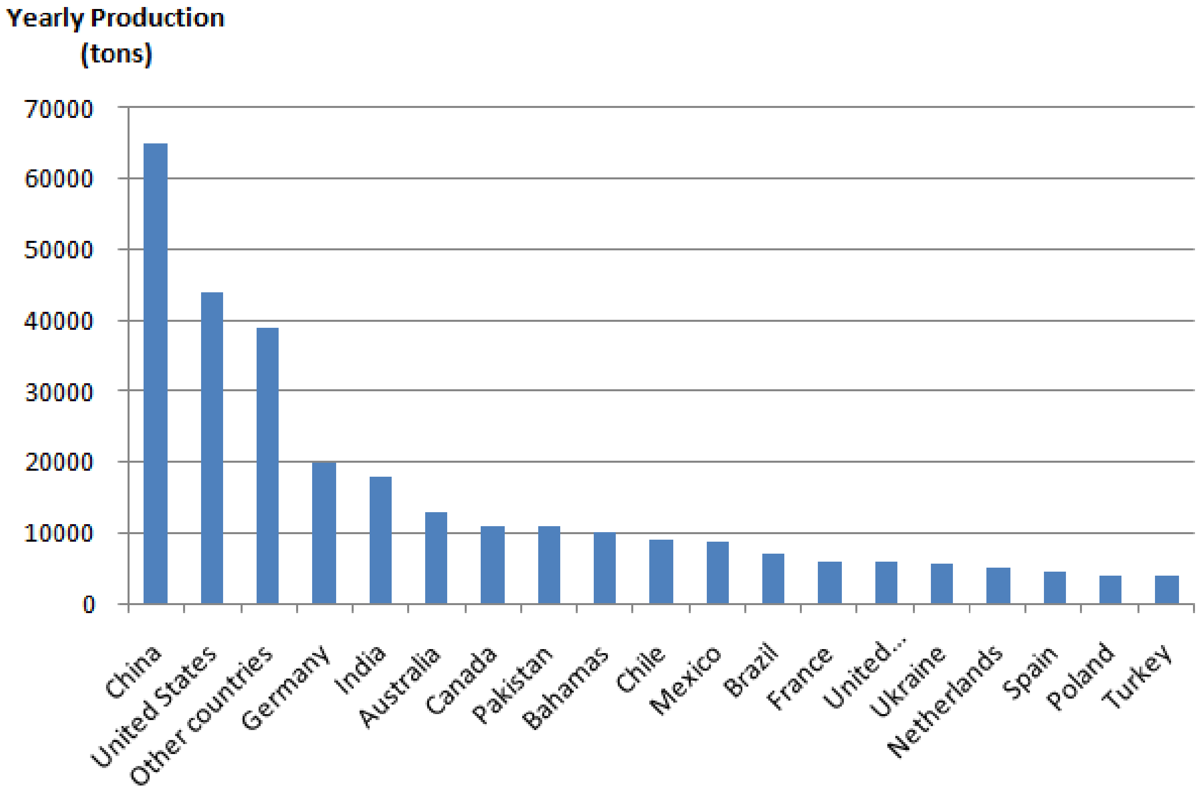


Figure 4-1: Production of salt by country in 2011

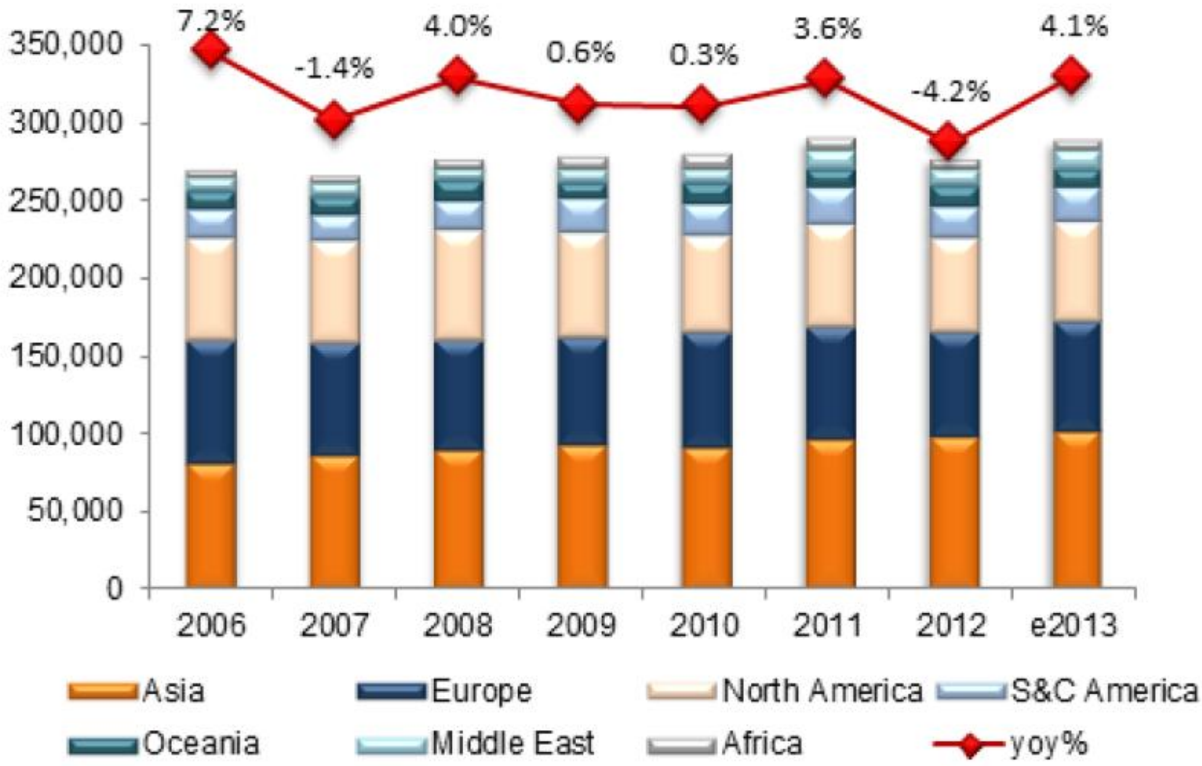


Figure 4-2: World: salt production by region, 2006-2013 (Roskill, 2014)

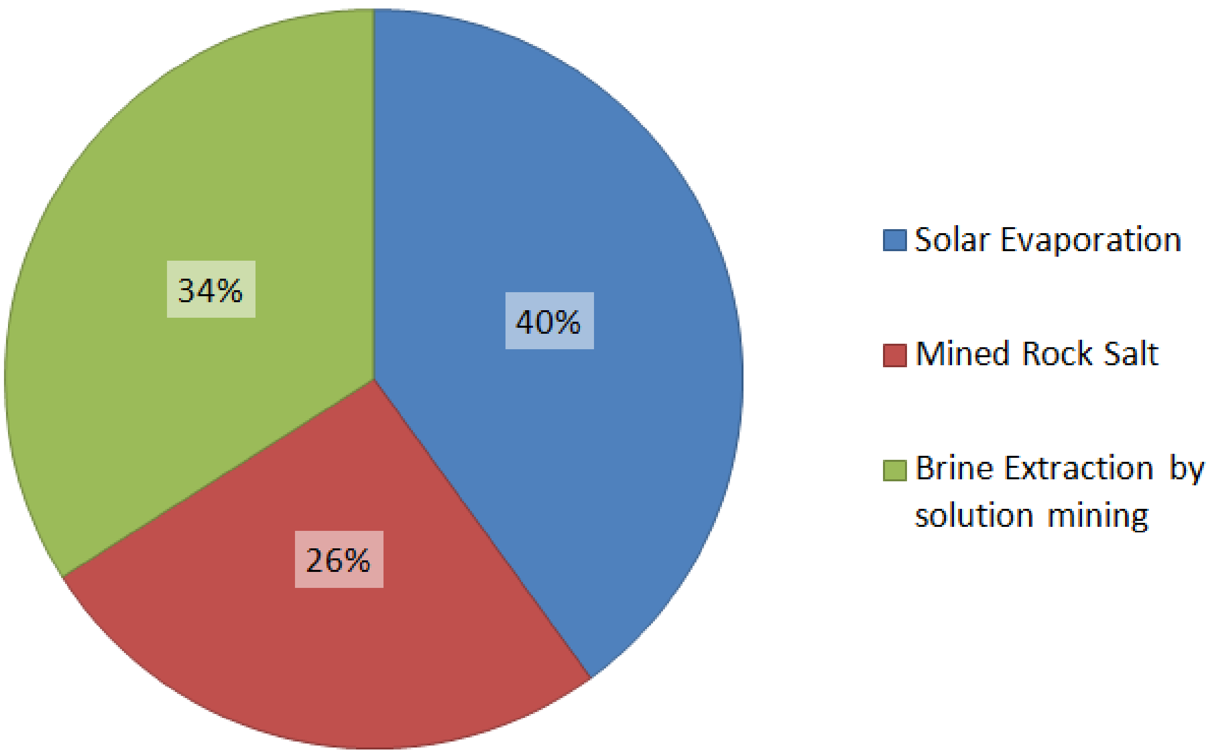


Figure 4-3: Production of salt by source, 2013 (Roskill, 2014)

4.2 Salt Uses & technical specifications

Salt is used mainly for the following three consumers:

- Chemical industry;
- Human consumption;
- Road de-icing.

The use of salt in the chemical industry accounts for 60% of the world market, while table salt accounts for about 30%. The rest 10% is needed for road de-icing, water treatment and other smaller applications (Serra Salt Engineers, 2005) (Roskill, 2014).

The technical specifications of the salt is dependent highly on its use. The following table presents typical salt quality requirements and unit prices for different salt consumers in Netherlads.

Table 4-1: Indicative market size, unit price and product quality requirements (Netherlands) (WssTP, 2012)

Type	Amount (ton/year)	Price (€/ton)	Composition
De-icing salt	200,000	25	> 97% sodium chloride
			Max. 4% moisture
			Heavy metals 15 ppm (total sum)
			Grain Size distribution demands
Industrial salt *	> 1,000,000	50-100	99.8 % sodium chloride
Industrial Broxo salt (water softening)	≈100,000	100-200	> 99.9% sodium chloride
			Max. 0.1% moisture
			Grain size distribution demands
Pharmaceutical salt	<100, 000	> 500	ultra-pure vacuum salt quality without additives

Following, a list of other salt commercial products is given that can be recovered from various types of brine effluents. It is noted that both the quantities and type of recovered products depend heavily on the quality characteristics of the feed raw water (Svensson, 2005).

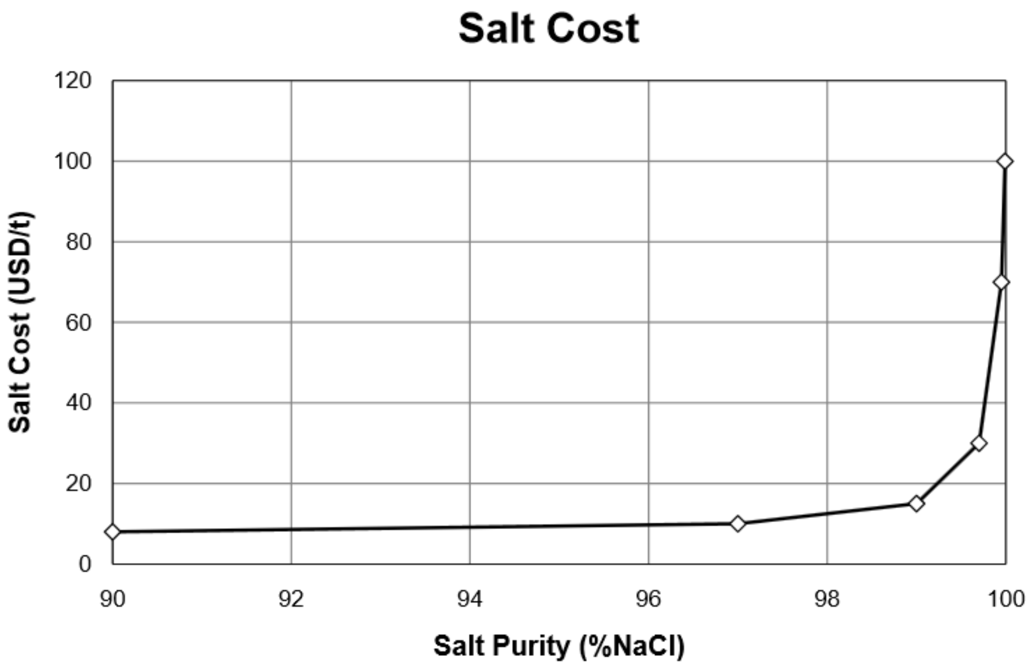
Table 4-2: Valorization options and market prices of salts relevant to beneficial use of brine

Type	Salt uses		Price ($/ton)	Reference
	Application areas	Composition		
$CaCO_3$ Calcium Carbonate (2 types: GCC and PCC)	❖ Paper coating pigment and pulp (GCC) ❖ Filler for paper manufacturing (GCC) ❖ Rubber (PCC) ❖ Paint ❖ Building Construction ❖ Water Treatment	❖ 96% as CaCO3 ❖ Less than 0.5% by weight of sulfate, chlorides and other constituents	60-350	(Mickley, 2009)
$CaCl_2$ Calcium chloride	❖ Dust suppresants ❖ Sodic soil remediation ❖ Cement, concrete stabilizer	❖ Construction industry ❖ Road stabilizers	132-354	(Mickley, 2009)
$CaSO_4$ Gypsum (Calcium Sulfate)	❖ Manufacturing of building products (wallboard and plaster) ❖ Cement production ❖ Sodic soil remediation ❖ Evaporation pond liners	❖ 99% pure by weight for use in powdered detergent	8-36	(Fowlie, 2011)

Type	Salt uses		Price ($/ton)	Reference
	Application areas	Composition		
$CaSO_4 \bullet 2H_2O + Mg(OH)_2$	❖ Wastewater treatment ❖ pH buffering	❖ Sodic soil remediation		
NaCl, Halite	Chlor-alkali production	❖ Brine used in chlor-alkali process must be free of sulfate, calcium and magnesium that will affect electrolytic process ❖ Rock Salt – 96% pure NaCl	50-200	(WssTP, 2012)
	Bulk salt supply for industries			
	Industrial purposes		8-35	(WssTP, 2012)
	Food			
	De-icing agent	>97%	25	(Fowlie, 2011)

Sources: (Mickley, 2008), (WssTP, 2012),(Mickley, 2009)

Note: GCC stands for Ground Calcium Carbonate and PCC for Precipitated Calcium Carbonate



Source: (Sedivy, 2008)

Figure 4-4: Sodium chloride sale price versus salt purity

5 Water uses

At most cases the water produced during the treatment of the generated brine effluent in the examined industries, is used as process water. The produced water is of high quality, reaching distilled water standards, due to the evaporation process involved at the ZLD flow diagram. As the wastewater is evaporated and then condensed, all salts are left behind, resulting to high qualities, in the order of 50 ppm (TDS).

Following, the quality standards for different water uses are provided:

- Potable water, According to Drinking Water Directive (see Table 5-1)
- Urban reuse (e.g. irrigation of public parks, school yards, highway medians, and residential landscapes, as well as for fire protection and toilet flushing in commercial and industrial buildings),

Agricultural reuse (restricted and unrestricted irrigation): According to Common Ministerial Decision 145116/8 March 2011 (see Table 5-2 and

- Table 5-3)

Industrial reuse (cooling waters, boilers and process water): According to Common Ministerial Decision 145116/8 March 2011 (see Table 5-2 and

- Table 5-3)

Groundwater aquifer recharge: According to Groundwater Directive and Common Ministerial Decision 145116/8 March 2011 (see Table 5-2 and

- Table 5-3.

Table 5-1: Parameters for drinking water

Parameter	WHO	EU	USA	Canada
Acrylamide	“	0.10 μg/l	“	“
Arsenic	10μg/l	10 μg/l	10μg/l	“
Antimony	ns	5.0 μg/l	6.0 μg/l	“
Barium	700μg/l	ns	2 mg/L	“
Benzene	10μg/l	1.0 μg/l	5 μg/l	“
Benzo(a)pyrene	“	0.010 μg/l	0.2 μg/l	“
Boron	2.4mg/l	1.0 mg/L	“	“
Bromate	“	10 μg/l	10 μg/l	“

Parameter	WHO	EU	USA	Canada
Cadmium	3 μg/l	5 μg/l	5 μg/l	"
Chromium	50μg/l	50 μg/l	0.1 mg/L	"
Copper	"	2.0 mg/l	TT	"
Cyanide	"	50 μg/l	0.2 mg/L	"
1,2-dichloroethane	"	3.0 μg/l	5 μg/l	"
Epichlorohydrin	"	0.10 μg/l	"	"
Fluoride	1.5 mg/l	1.5 mg/l	4 mg/l	"
Lead	"	10 μg/l	15 μg/l	"
Mercury	6 μg/l	1 μg/l	2 μg/l	"
Nickel	"	20 μg/l	"	"
Nitrate	50 mg/l	50 mg/l	10 mg/L (as N)	"
Nitrite	"	0.50 mg/l	1 mg/L (as N)	"
Pesticides (individual)	"	0.10 μg/ l	"	"
Pesticides — Total	"	0.50 μg/l	"	"
Polycyclic aromatic hydrocarbons l	"	0.10 μg/	"	"
Selenium	40 μg/l	10 μg/l	50 μg/l	"
Tetrachloroethene and Trichloroethene	40μg/l	10 μg/l	"	"

*Note: " indicates that no standard has been identified by editors of this article and **ns** indicates that no standard exists. μg/l -> Micro grams per litre or 0.001 ppm, mg/L -> 1 ppm or 1000 μg/l*

Table 5-2: Limits of different biological and conventional parameters for different water uses (Common Ministerial Decision 145116/8 March 2011)

Use	Escherichia coli (EC/100ml)	BOD5 (mg/l)	SS (mg/l)	Turbidity (NTU)
Agricultural – Limited [1]	≤ 200	According to Common Ministerial Decision 5673/400/1997		-
Agricultural – Unlimited [2]	≤ 5	≤ 10	≤ 10	≤ 2
Urban use [3]	≤ 2	≤ 10	≤ 2	≤ 2

Use	Escherichia coli (EC/100ml)	BOD5 (mg/l)	SS (mg/l)	Turbidity (NTU)
Industrial use [4]	≤ 5	≤ 10	≤ 10	≤ 2
Single pass cooling water	≤ 200	According to Common Ministerial Decision 5673/400/1997		-
Underground Aquifer Recharge	≤ 200	According to Common Decision 5673/400/1997		-

Note: [1] *Areas where no public access is anticipated, feed crops, industrial crops, meadows, trees, seed crops.*

[2] *All crops including fruit trees, vegetables, vineyards or crops whose products are consumed uncooked, greenhouses.*

[3] *Cemeteries, highways slopes, golf courses, public parks, leisure installations, putting out fires, soil compaction, cleaning streets and sidewalks, decorative fountains etc.*

[4] *Recirculated cooling water, feedwater for boilers, process water etc. (except for single pass cooling water)*

Table 5-3: Concentration Limits for metals and other elements (Common Ministerial Decision 145116/8 March 2011)

Metal	Concentration limit (mg/l)
Al (Aluminium)	5.0
As (Arsenic)	0.1
Be (Beryllium)	0.1
Cd (Cadmium)	0.01
Co (Cobalt)	0.05
Chromium (Cr)	0.1
Copper (Cu)	0.2
F (Fluorine)	1.0
Fe (Iron)	3.0
Li (Lithium)	2.5
Mn (Manganese)	0.2
Mo (Molybdenum)	0.01
Ni (Nickel)	0.2
Pb (Lead)	0.1
Se (Selenium)	0.02

V (Vanadium)	0.1
Zn (Zinc)	2.0

For the different water uses, the reader can check the examined case studies as follows:

- Potable Water: Case studies #2, #6 (**Sections** 6.2 and 6.6)
- Irrigation Water: Case study: #5 (**Section** 6.5)
- Industrial Reuse: Case studies: #3, #4, #5, #6 (**Sections** 6.3, 6.4, 6.5 and 6.6)
- Cooling Water: Case Studies: #5, #6 (**Sections** 6.5 and 6.6)

6 Case studies

6.1 Eilat project (Evaporation Pond)

Overview

<table>
<tr><td colspan="2">Case study: 1
Country: Israel
City: Eilat</td><td></td><td colspan="2">Bench-Scale system ☐ YES ☐ NO
Pilot System ☐ YES ☐ NO
Application ☑ YES ☐ NO</td></tr>
<tr><td colspan="2" rowspan="4">Treatment process
Zero Liquid Discharge with only salt recovery (the water is evaporated to the environment)</td><td rowspan="2">Salt
Quality</td><td>☑ Table Salt</td><td>☑ Chemical Industry</td></tr>
<tr><td>☑ Road Salt</td><td>☐ Other use</td></tr>
<tr><td rowspan="2">Water
Quality</td><td>☐ Potable water</td><td>☐ Industry recycle</td></tr>
<tr><td>☐ Distillate water</td><td>☐ Other use</td></tr>
<tr><td>Year

1997
(operated until now)</td><td colspan="4">Ownership

Merokot Water Company (National Water Supply Corporation of Israel) and a private corporation, Israel Salt Company.</td></tr>
<tr><td colspan="5">Description

Hybrid facility for water and salt production with increased salt recovery (by 30% compared to conventional salt lakes). The salt produced is claimed to be of very high quality, satisfying even the most severe standards. This project depicts how governmental and private sector collaborations may lead to substantial benefit of both parties. The two corporations have shared investment in initial capital expenditure and operating costs. The desalination unit of the dual purpose plant is the sole application in the world to treat a blend of seawater and brine rejected from adjacent brackish water desalination plants.</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td colspan="5">Reference
(Ravizky, 2007)</td></tr>
</table>

6.1.1 Process and Technology involved

This is, in essence, a practice rather than technology, which comprises a modified version of salt works. Common salt works use seawater for producing different salt products. This practice involves blending the feed seawater stream with brine effluent from brackish water desalination plants. This combined plant is a dual purpose plant that produces water (from the desalination plants) and salt (from the salt processing factory than involves salt lakes and purification units).

The combined plant has the following characteristics:

- Desalination plant capacity: 10,000m^3/day
- Increased salt production compared to current practice (salt production from seawater alone)
- High quality standards of produced salt
- Quality achieved: covering all the spectrum of produced salts (from refined table salt to industrially used salts)
- No water is recovered from the treatment of brine (it evaporates to the environment)
- Elimination of brine discharge needs

6.1.2 Uses of Salt produced

This plant produces different types of salts for various applications such as:

- Food
- Industrial applications
- Functional Salts
- Dish Washers Salts
- Base products
- Bath salts
- Licking lamps

Table 6-1: Uses of salt produced by the Eilat solar pond

<table>
<tr><th colspan="4">Table Salts</th></tr>
<tr>
<td>
</td>
<td>Assay as NaCl 99.8%
Calcium (Ca) 0.04%
Magnesium (Mg) 0.03%
Sulfate (SO_4) 0.1%
Insoluble 0.01%</td>
<td>
</td>
<td>Assay as NaCl 99.8%
Calcium (Ca) 0.04%
Magnesium (Mg) 0.03%
Sulfate (SO_4) 0.1%
Insoluble 0.01%
$H_2$0 0.1%</td>
</tr>
<tr><th colspan="2">Finest Table Salt</th><th colspan="2">Table Salt</th></tr>
<tr><td colspan="2">Best for food and meat koshering</td><td colspan="2">For reducing risks of blood pressure and other chronical disease</td></tr>
<tr>
<td>
</td>
<td>Assay as NaCl 98%
Calcium (Ca) 0.5%
Magnesium (Mg) 0.5%
Sulfate (SO_4) 1%
Insoluble 0.03%
$H_2$0 2-12%</td>
<td>
</td>
<td>Potassium chloride KCl 48+-2%
Sodium chloride NaCl 48+-2%</td>
</tr>
<tr><th colspan="4">Industrial Uses</th></tr>
<tr><th colspan="2">Water Industry</th><th colspan="2">Chemical Industry</th></tr>
<tr>
<td>
</td>
<td>Assay as NaCl 99.8%
Insoluble 0.01%</td>
<td>
</td>
<td>Assay as NaCl 99.5%
Calcium (Ca) 0.08%
Magnesium (Mg) 0.05%
Sulfate (SO_4) 0.25%
Insoluble 0.03%
$H_2$0 0.15%</td>
</tr>
</table>

<table>
<tr><th colspan="2">Water Softening</th><th colspan="2">Detergent</th></tr>
<tr><td>
</td><td>Assay as NaCl 99.5%
Insoluble 0.03%</td><td>
</td><td>Assay as NaCl 98%
Calcium (Ca) 0.55%
Magnesium (Mg) 0.45%
Sulfate (SO_4) 0.5%
Insoluble 0.25%</td></tr>
<tr><th colspan="4">Dish Washers</th></tr>
<tr><td colspan="2">
</td><td colspan="2">Assay as NaCl 99.5%
Insoluble 0.03%</td></tr>
</table>

Table 6-2: Impurities in raw salt precipitate in salt ponds before and after the integration of SWRO brine

Element	Salt produced before SWRO integration			Salt produced after integration	
	12/1995	11/1996	6/1997	11/1997	5/2000
SO_4 (%)	1.0	1.02	1.12	1.16	1.06
Ca (%)	0.25	0.24	0.21	0.30	0.23
Mg (%)	0.30	0.28	0.41	0.32	0.32
Fe (ppb)	<1.2	0.8	<1	0.8	1
Mn (ppb)	2.5	0.3	2.5	0.3	<2
Pb (ppb)	<20	0.3	0.1	0.3	0.3
Cu (ppb)	<0.25	0.3	<0.5	0.3	<0.4

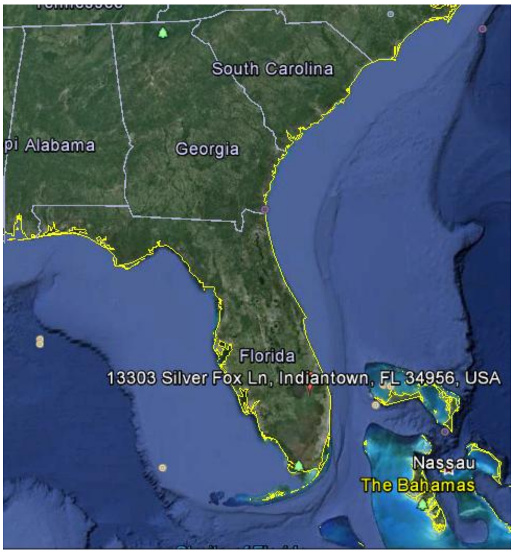
Source: (Ravizky, 2007)

6.1.3 Uses of water produced

The water is used for municipal purposes. No water is recovered from the brine treatment process.

6.2 Indiantown, USA (Power Station)

Overview

<table>
<tr><td colspan="2">Case study: 2
Country: Florida (USA)
City: Indiantown</td><td></td><td colspan="2">Bench-Scale system ☐ YES ☐ NO
Pilot System ☐ YES ☐ NO
Application ☑ YES ☐ NO</td></tr>
<tr><td colspan="2" rowspan="2">Treatment process
Zero Liquid Discharge with only water recovery (salt must be disposed)</td><td>Salt
Quality</td><td>☐ Table Salt
☐ Road Salt</td><td>☐ Chemical Industry
☐ Other use</td></tr>
<tr><td>Water
Quality</td><td>☐ Potable water
☐ Distillate water</td><td>☑ Industry recycle
☐ Other use</td></tr>
<tr><td colspan="2">Year
1994 (Original Version)
2011 (Modified Version)</td><td colspan="3">Ownership
Indiantown Cogeneration Company, LP</td></tr>
<tr><td colspan="5">Description
The Indiantown Cogeneration plant is a coal fired power plant with a total capacity of 360MW. Since 1992 it was equipped with a Zero Liquid Discharge system for treating the cooling water blowdown, based on a brine concentrator, crystallizer flow scheme. A modification was made in the system, replacing the brine concentrators with an integrated membrane system (MF/RO) due to extensive corrosion problems. The modified system was commissioned in 2011.</td></tr>
<tr><td colspan="5">

</td></tr>
<tr><td colspan="5">Reference
(Drake, 2012)</td></tr>
</table>

6.2.1 Process and technology involved

This Zero Liquid Discharge plant has been installed at a cogeneration coal-fired, 360 MW power plant. Its purpose is to treat the wastewater produced from the flue gas desulphurization

The Cooling Water is from three (3) different sources:

(a) Surface water from nearby river (primary source water, high in organics);

(b) Underground water (high saline, used only during drought periods); and

(c) Treated municipal water.

Table 6-3: Typical feedwater analyses

Parameter	Units	Blend of Well Waters	Waste Water	Surface Water from Taylor Creek
Turbidity	NTU	3-10	N.R	3-30
Conductivity	uS/cm	6200	960	590
Iron	mg/l	0.13	0.05	0.56
Total Organic Carbon	mg/l			31
Ca Hardness	mg/l	440	260	98
Mg Hardness	mg/l	540	14	48
Sodium	mg/l	850	76	55
Aluminum	mg/l	<0.1		0.21
Silica	mg/l	15.0	21.0	9.7
Sulfates	mg/l	300	31	58
Chlorides	mg/l	2000	97	110

The original design of the process units involved the following components (see also Figure 6-1):

(a) Two evaporators/brine concentrators; and

(b) One spray dryer absorber.

The water cooling blow down is mixed with other wastewater streams of the power plant and the combined waste stream is sent first to a lamella separator and filter to remove suspended solids. Then it is directed with a flowrate of about 300 gpm (1.1 m^3/h) to the vapor compression evaporator. The concentrated stream is then passed to a spray dryer with a flowrate of approximately 2 to 4 gpm.

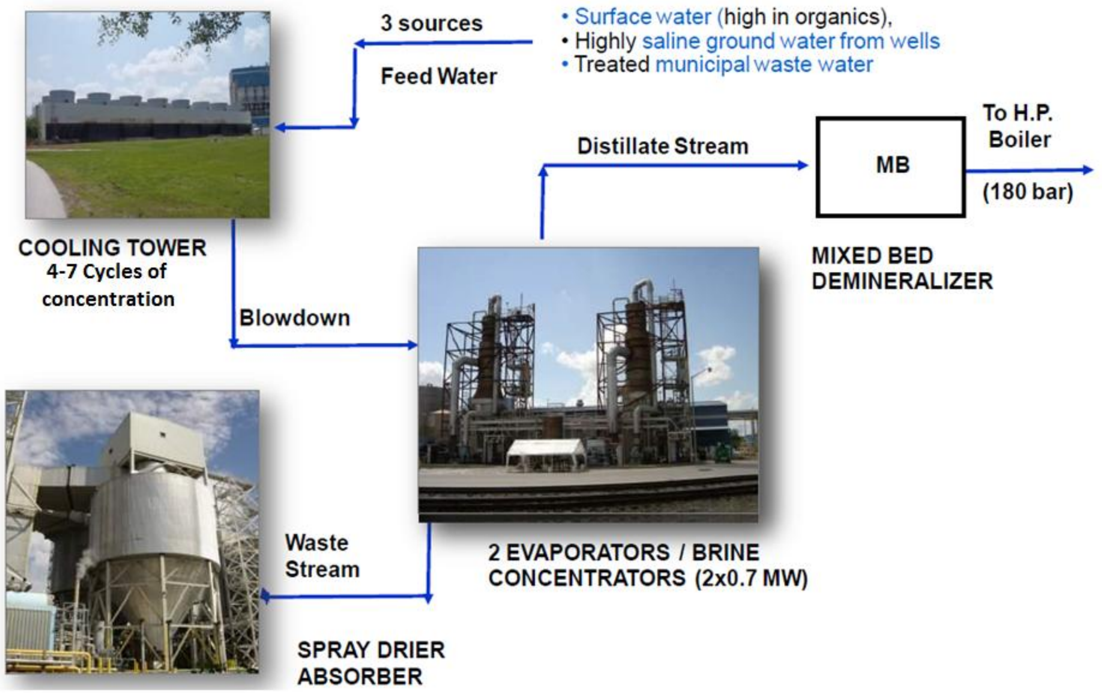


Figure 6-1: Original Flow Scheme for Zero Liquid Discharge, Indiantown, Florida

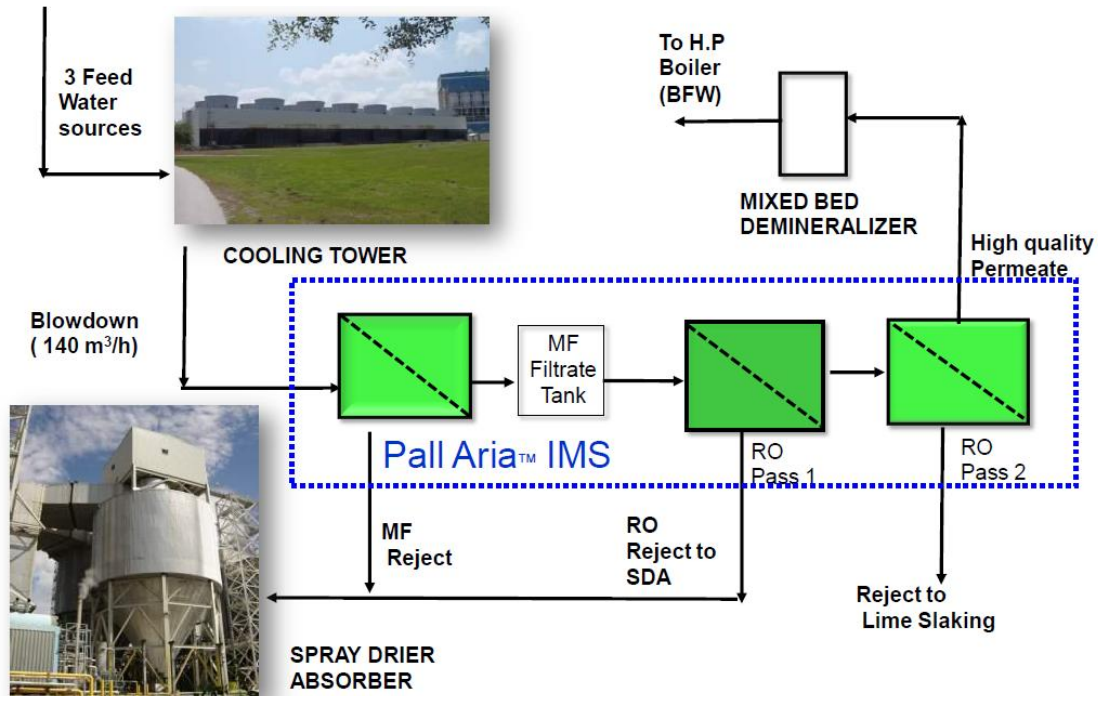


Figure 6-2: Replacement of evaporators with reverse osmosis units (May 2011)

The modified design involved the replacement of the evaporators with a microfiltration unit and two reverse osmosis units. The flow scheme is presented in Figure 6-2. The reason for this replacement (May 2011) was the fact that the two brine concentrators suffered from stainless steel skin corrosion problems, as well as required large amounts of energy (1.4 MW in total).

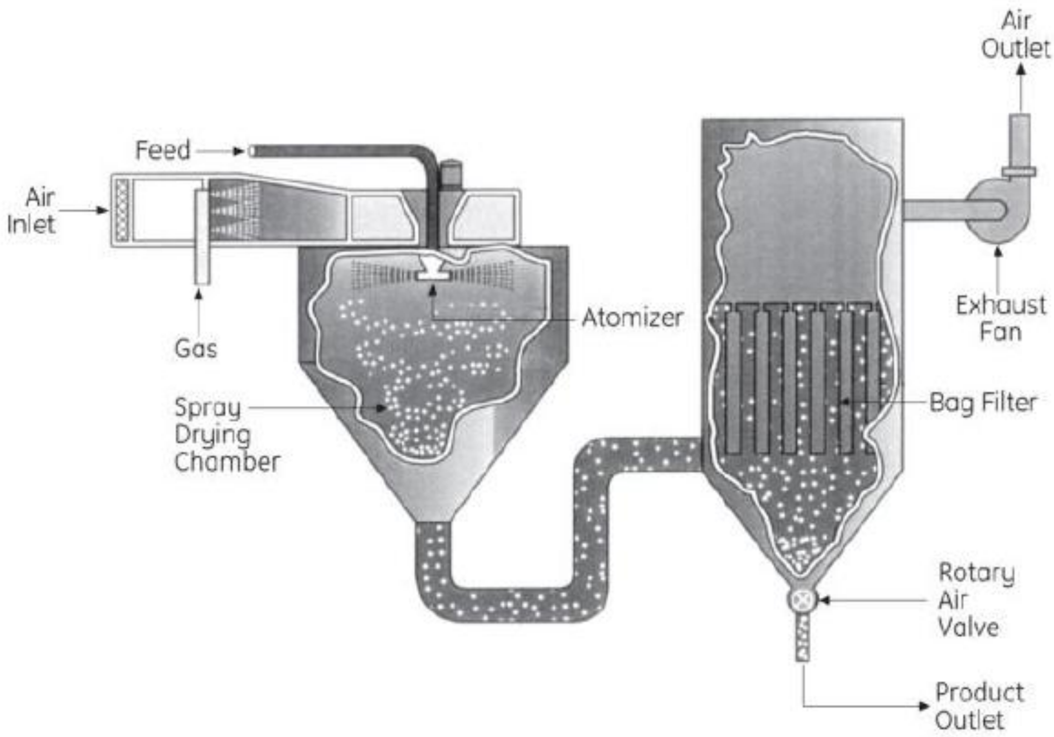


Figure 6-3: Schematic diagram for spray dryer, Indiantown power plant (Bostjancic, 2013)

The spray dryer consists of an atomizer which rotates at a 16,800 rpm speed, spraying the slurry into a gas-fired vessel. The solids are drawn into a bag filters and then collected for on-site disposal at a landfill (20 tons per week)

Technology involved: the technology (brine concentrators and spray dryer) was purchased by Resources Conservation Company.

6.2.2 Uses of salt produced

The salt is of very low quality, with no market value (20 tons per week). On the contrast, the power production facility must care for its disposal in landfills (Bostjancic, 2013).

6.2.3 Uses of water produced

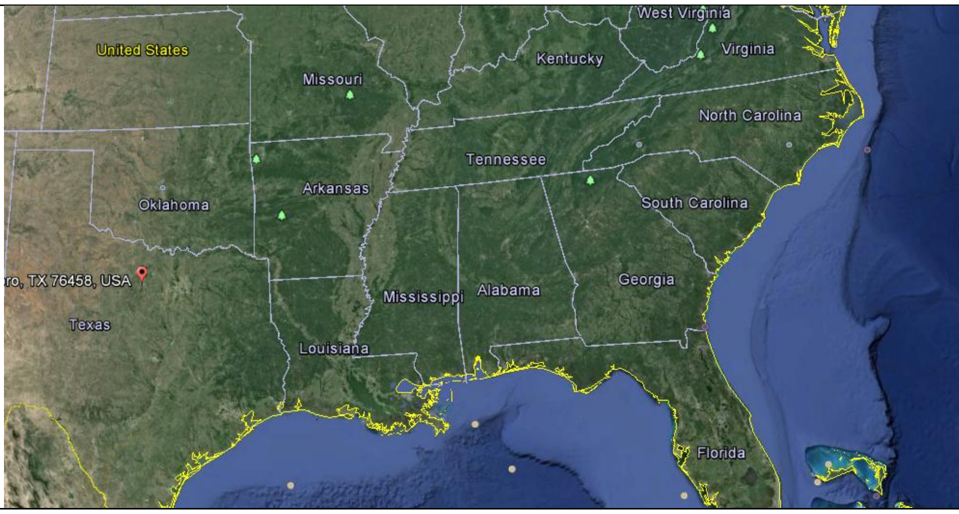
The water produced by the Zero Liquid Discharge unit (in its original and modified version) was used as process water. More particularly, the recovered water is used as boiler feed water after mixed bed demineralizer treatment.

The blowdown volume of wastewater was designed to be around 180 cubic meters per hour (650 gallons per minute), while the recovery of distillate water was around 115 cubic meters per hour (418 gallons per minute).

6.3 Brazos Electric Cooperation, Texas (Power Station: Cooling Water Effluent)

Overview

<table>
<tr><td colspan="2">Case study: 3
Country: TEXAS (USA)
City: Jacksboro</td><td></td><td colspan="2">Bench-Scale system ☐ YES ☐ NO
Pilot System ☐ YES ☐ NO
Application ☑ YES ☐ NO</td></tr>
<tr><td rowspan="2">Treatment process
Zero Liquid Discharge with only water recovery (salt must be disposed)</td><td colspan="2">Salt Quality</td><td>☐ Table Salt
☐ Road Salt</td><td>☐ Chemical Industry
☐ Other use</td></tr>
<tr><td colspan="2">Water Quality</td><td>☐ Potable water
☐ Distillate water</td><td>☑ Industry recycle
☐ Other use</td></tr>
<tr><td>Year
2006</td><td colspan="4">Ownership
Brazos Electric Cooperative</td></tr>
<tr><td colspan="5">Description

Brazos Electric Cooperation is the largest power company in Texas and is the responsible utility for producing and distributing wholesale electricity to its 16 cooperatives and two municipal systems. Jack County Generation Facility is a combined cycle power plants, consisted of four (4) gas turbine generators with a total capacity of 1,240 MW. Brazos decided to install two Zero-Liquid Discharge (ZLD) water treatment facilities for the treatment of the blowdown effluent from the water cooling system.</td></tr>
<tr><td colspan="5">
</td></tr>
<tr><td colspan="5">Reference
(Drake, 2012) (Aquatec, 2012) (Combined Cycle Journal, 2010)</td></tr>
</table>

6.3.1 Process and Technology involved

Process Involved:

A Zero Liquid Discharge system was installed for the treatment of the cooling water blowdown from the power plant. The ZLD process includes the following treatment steps:

- Zero Liquid Discharge clarifier;
- Gravity filters;
- Softeners (Weak Acid Cations);
- Mechanical Vapor Compression (Aquatech crystallizer technology);
- Coagulant, polymer, lime and acid feed systems;
- HERO RO Units;
- Anti-foam system;
- Crystallizer;
- Recovered Water and blowdown storage tanks; and
- Crystallizer solids dewatering system (Belt Filter Press).

Technology involved:

- HERO has been installed by US supplier AquaTech.

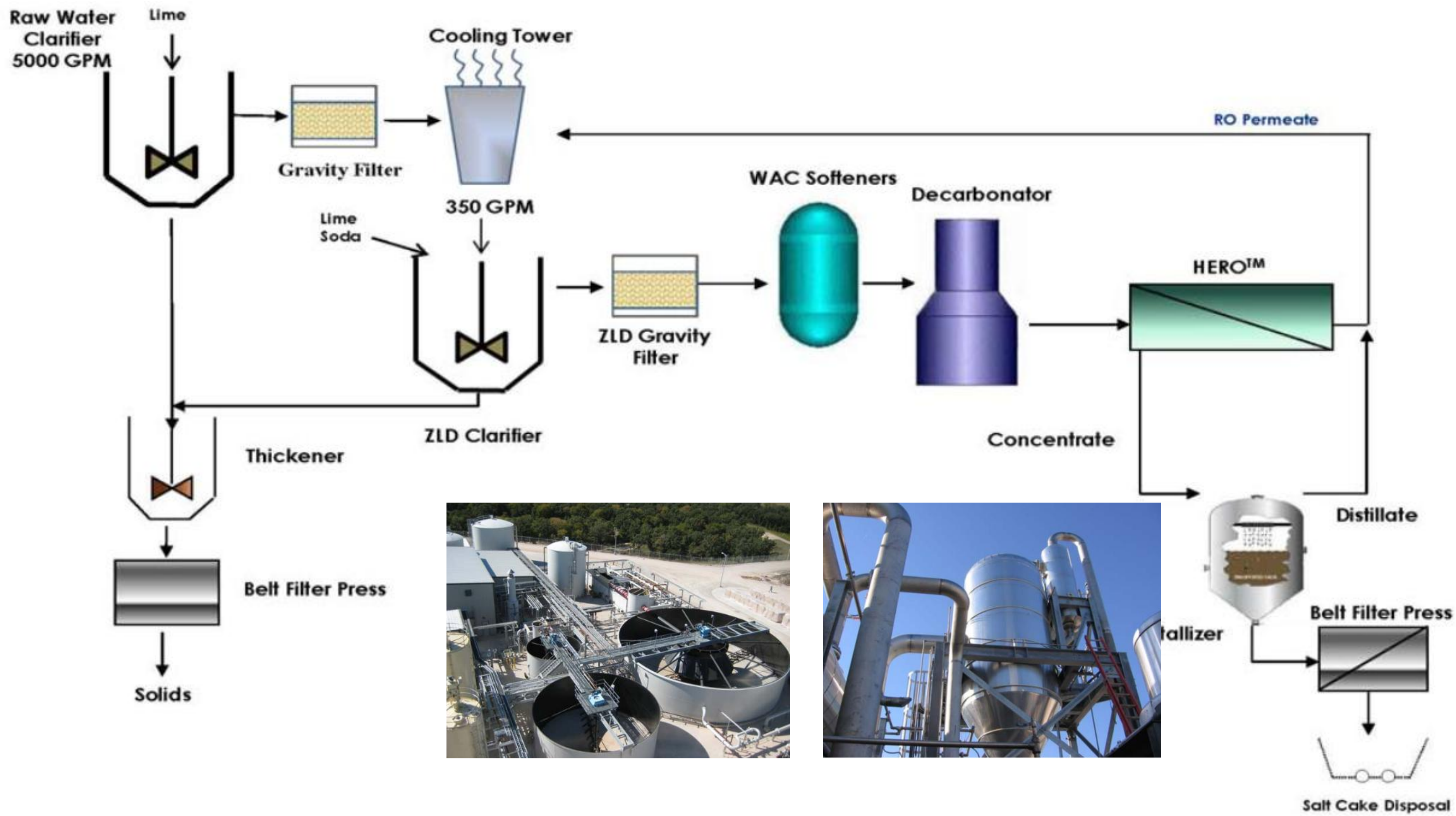


Figure 6-4: Simplified process Flow Diagram, TEXAS

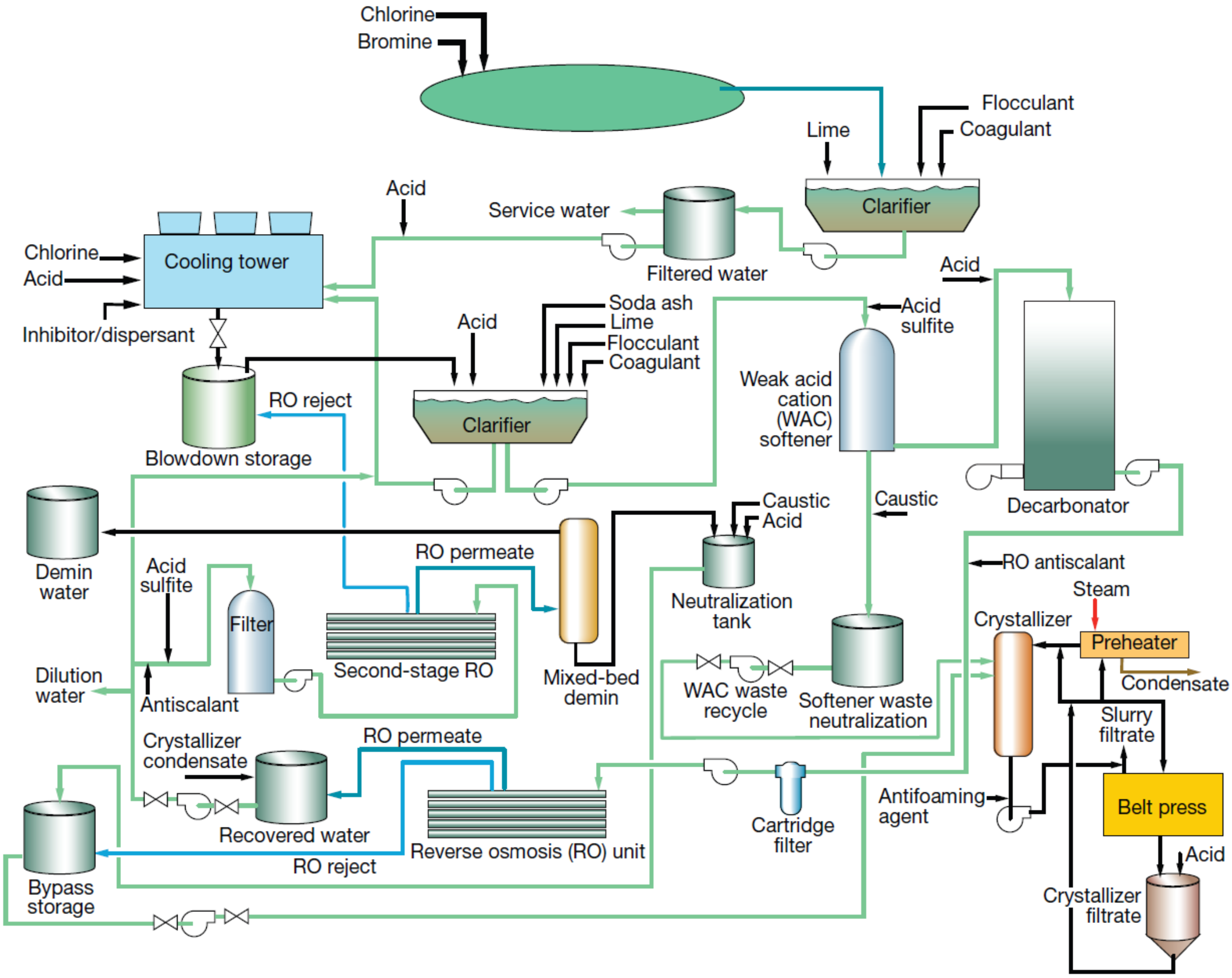


Figure 6-5: Detailed process flow diagram

6.3.2 Uses of salt produced

The salt produced after the filter press dewatering is directed for off-site disposal.

6.3.3 Uses of water produced

The water produced is recycled and used as process water.

6.4 ENEL, Italy (Power Production: Desulphurization Stage)

Overview

<table>
<tr><td colspan="2">Case study: 4
Country: Italy
City: Venice
</td><td colspan="2">Bench-Scale system ☐ YES ☐ NO
Pilot System ☐ YES ☐ NO
Application ☑ YES ☐ NO</td></tr>
<tr><td rowspan="4">Treatment process
Zero Liquid Discharge with only water recovery (salt must be disposed of)</td><td rowspan="2">Salt Quality</td><td>☐ Table Salt</td><td>☐ Chemical Industry</td></tr>
<tr><td>☐ Road Salt</td><td>☐ Other use</td></tr>
<tr><td rowspan="2">Water Quality</td><td>☐ Potable water</td><td>☑ Industry recycle</td></tr>
<tr><td>☐ Distillate water</td><td>☐ Other use</td></tr>
<tr><td>Year

2008</td><td colspan="3">Ownership

ENEL S.P.A.</td></tr>
<tr><td colspan="4">Description
The Fusina plant in Italy is owned by the largest power company of Italy, ENEL S.P.A.. It comprises four coal-fired power plants with a total capacity 975MW[2]. All units have DeSOX and DeNOx facilities for the protection of the air environment. The flue gas generated is treated in scrubbers with limestone, while the wastewater blow down are treated in the dealkalizer clarifier with lime. However, due to stringent Italian legislation applied to wastewaters and EU environmental regulations, the treated wastewater could no longer be discharged into the sea. As a result, ENEL decided to install zero liquid discharge systems for eliminating the brine effluent produced by the scrubber blow down of the Flue Gas Desulphurization unit.</td></tr>
<tr><td colspan="4"> </td></tr>
<tr><td colspan="4">Reference
(Aquatec, 2009)</td></tr>
</table>

[2] http://globalenergyobservatory.org/geoid/3079

6.4.1 Process and technology involved

The process included the following steps:

(a) **Softening**: the softening process comprises 2 x 50% Softener Clarifiers (reduction of calcium with soda ash)

(b) **Evaporation**: 2 x 50% Falling Film type Brine Concentrators with mist eliminators and are operated in seeded slurry mode and

(c) **Crystallization:** 1 x 100% crystallizer which is equipped with a Thermal Vapor Compression (TVC) for energy recovery and is operated in forced circulation method.

(d) **2 x 50% Belt Filter Presses**

The plant is also equipped with several chemical dosing systems, instrumentation control and other auxiliaries (pumps, storage tanks etc.).

Figure 6-6: Photograph from the installed ZLD system in the Fusina plant in Italy

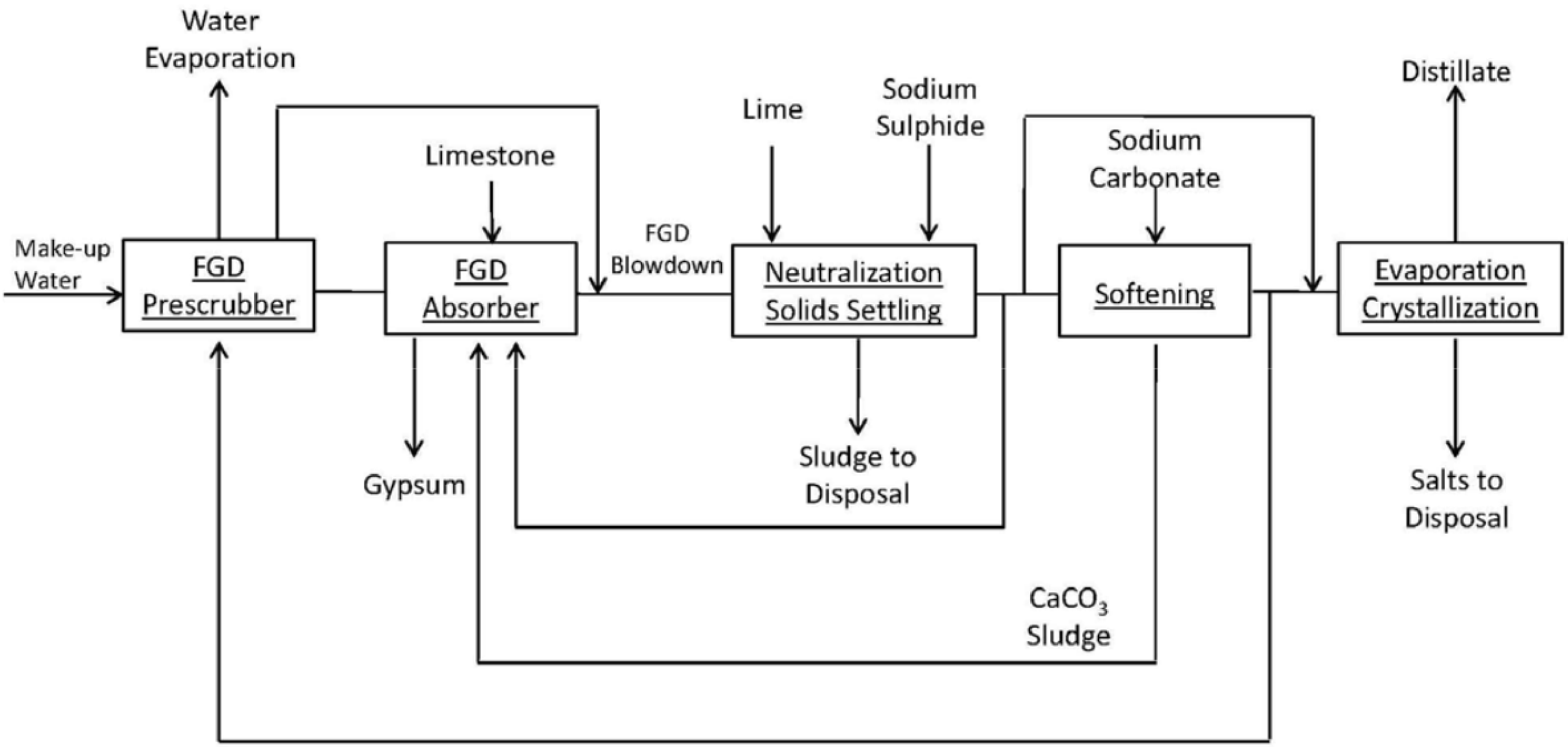


Figure 6-7: Process flow diagram, Fusina power plant, ENEL, Italy

Wastewater Analysis (input to ZLD system):

- Design flow: 70 m^3/h
- Calcium: 8,400ppm
- Magnesium: 1,700 ppm
- Sodium: Balance
- Chlorides: 25,000 ppm
- Nitrates: 300 ppm
- Sulfate: 1,200 ppm
- TSS: 80 ppm
- pH: 9.5 to 10

6.4.2 Uses of salt produced

The salts produced after the crystallization process are directed for off-site disposal.

6.4.3 Uses of water produced

The water produced is recycled internally and is of industrial grade. The evaporation - crystallization step of the Zero Liquid Discharge system produces high quality distillate water which is used in the main power plant.

Finally, it must be noted that the exact same process has been employed at four additional plants owned by ENEL S.P.A., as illustrated in the following Figure.

The Brindisi Sud Power Plant is equipped with four coal-fired units each of 660 Mwe capacities (Source: http://www.aquatech.com/wp-content/uploads/51-Brindis-ZLD.pdf)

The Torrevaldaliga Nord Power Plant is being converted (torn down and rebuilt) to three coal-fired units each of 660 Mwe capacity. (Source: http://www.aquatech.com/wp-content/uploads/55-Torrevaldaliga-FGD-ZLD.pdf)

The La Spezia Power Plant is equipped with 1 x 600 MW coal-fired power unit and 2 x 350 MWe gas-fired combined cycle power units for a total of 1300 MWe. (Source: http://www.aquatech.com/wp-content/uploads/53-La-Spezia-FGD-ZLD.pdf)

The Sulcis Power Plant is equipped with 1 x 345 MW fluidized bed boiler and 1 x 240 MW conventional boiler. This coal-fired power plant is located in Sardinia Island and has a total of 585 Mwe capacity. (Source: http://www.aquatech.com/wp-content/uploads/54-Sulcis-FGD-ZLD.pdf)

Figure 6-8: Other ZLD plants operated by ENEL S.P.A. in Italy

6.5 Pearl GTL, Qatar (Gas Production Facility)

Overview

<table>
<tr><td colspan="2" rowspan="3">Case study: 5 
Country: Qatar
City: Ras Laffan Industrial City</td><td>Bench-Scale system</td><td>☐ YES</td><td>☐ NO</td></tr>
<tr><td>Pilot System</td><td>☐ YES</td><td>☐ NO</td></tr>
<tr><td>Application</td><td>☑ YES</td><td>☐ NO</td></tr>
<tr><td rowspan="4">Treatment process
Zero Liquid Discharge with Resource Recovery (only water, salt residue is disposed in a landfill)</td><td rowspan="2">Salt Quality</td><td>☐ Table Salt</td><td colspan="2">☐ Chemical Industry</td></tr>
<tr><td>☐ Road Salt</td><td colspan="2">☐ Other use</td></tr>
<tr><td rowspan="2">Water Quality</td><td>☐ Potable water</td><td colspan="2">☑ Industry recycle</td></tr>
<tr><td>☑ Distillate water</td><td colspan="2">☑ Other use</td></tr>
<tr><td>Year
-</td><td colspan="4">Ownership
Qatar Shell GTL Limited, Government of the State of Qatar</td></tr>
</table>

Description

The Pearl's project is the largest Gas To Liquid (GTL) project in the world to produce GTL products, liquefied petroleum gas and ethane. It produces approximately 140,000 barrels of GTL products per day and around 120,000 barrels of condensate, liquefied petroleum gas and ethane per day.

Shell's gas production facilities in Qatar required a Zero Liquid Discharge system, capable of treating a combined waste effluent, involving 12 different waste streams with a total 45,000 m^3/day treatment capacity. The ZLD system has been designed in a way to provide 5 different water qualities for different uses such as industrial, agricultural and cooling water.

Reference

(Bostjancic, 2013), (Svensson, 2005), (Veolia Water, 2002)

6.5.1 Process and Technology involved

Process Involved:

The process involved the treatment of a combined wastewater effluent, including 12 different waste streams. The overall treatment comprised the following stages (see also Figure 6-9):

- Sweet and Sour CPI separators
- Oil tankage, water tankage
- Controlled Discharge Facility (8000m^3 basin with 3x 14m long Archimedan pumps)
- Heat exchangers
- Flocculation & Flotation Units
- Aerobic biological treatment (conventional) with circular settlers (conventional)
- Submerged Ultrafiltration
- 3 pass Reverse Osmosis
- Irrigation water treatment by UV
- Evaporation & Crystallisation of concentrated waste streams
- Cooling water blowdown treatment (Submerged Ultrafiltration & Reverse Osmosis)
- Mineral sludge dewatering with centrifuge
- Activated sludge dewatering with centrifuge

Technology Involved:

- HPD evaporator & Crystallizer combined system, provided by Veolia Water Solutions & Technology

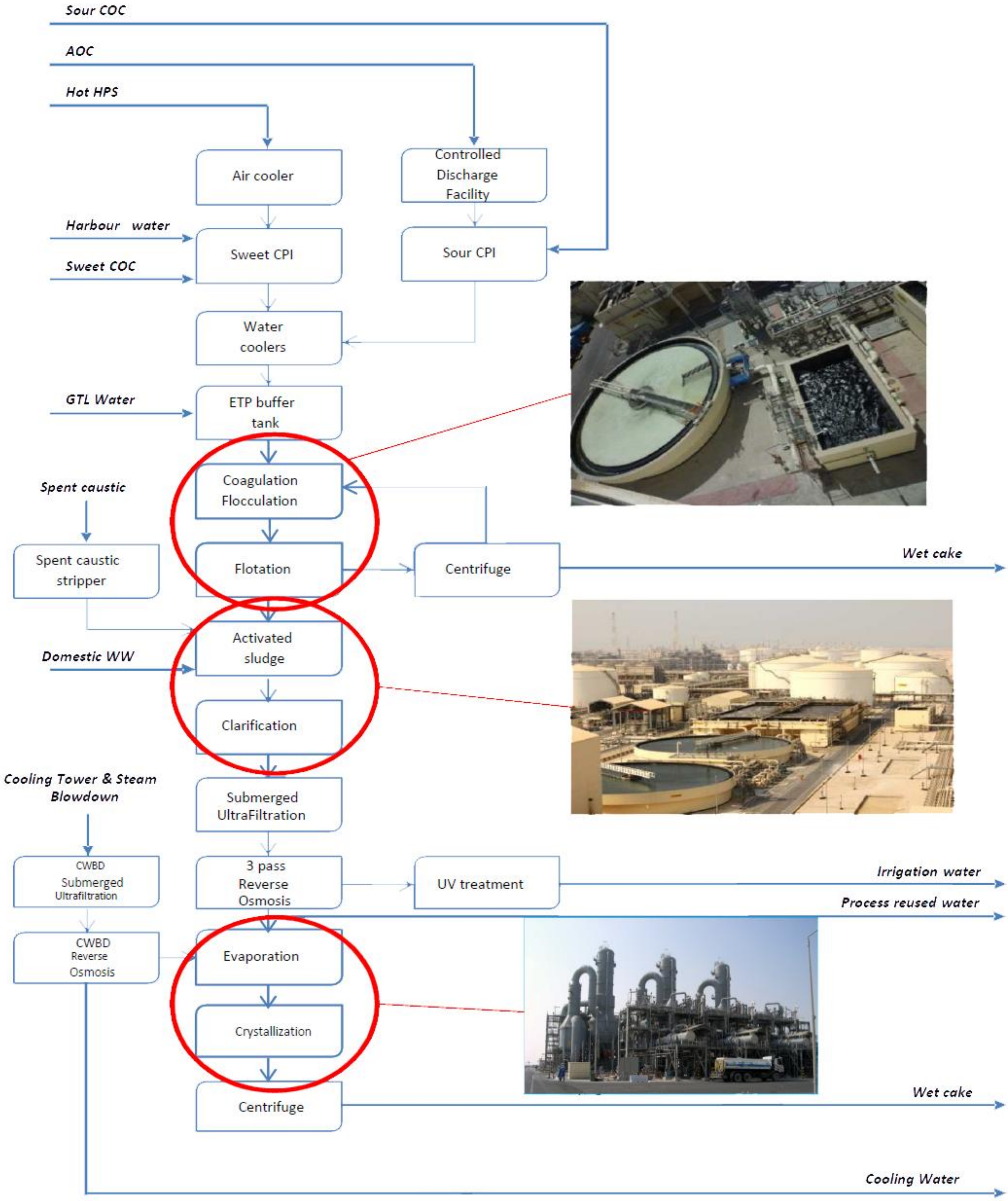


Figure 6-9: Process flow diagram, Pearl GTL, Qatar

6.5.2 Uses of salt produced

The crystallization residue produced is a mixed salt residue of very low quality that cannot be directed to any market. As a result, it is disposed in an offsite landfill.

6.5.3 Uses of water produced

During the process, five different water qualities were produced. Following the quality specifications are provided for three out of five available by the Pearl GTL company (Veolia Water, 2008).

Table 6-4: Recycled Water Specifications (cooling water)

Parameters	Units	Design Data
Flowrate	t/d	12,639
Conductivity	µS/cm	75
COD	mg/l	30
Total N	mgl/l	0.8
pH	pH u.	6-8

Table 6-5: Recycled Water Specifications ("Raw Water")

Parameters	Units	Design Data
Flowrate	t/d	16,000
Conductivity	µS/cm	3
COD	mg/l	3
pH	pH u.	6-8

Table 6-6: Recycled water specifications (Irrigation Water)

Parameters	Units	Design Data
Flowrate	t/d	1,200
Conductivity	µS/cm	75
COD	mg/l	30
SAR index	-	<6
pH	pH u.	6-8

6.6 Debiensko plant, Poland (Coal mine industry, water drainage)

Overview

<table>
<tr><td colspan="2">Case study: 6

Country: Poland
City: Katowice</td><td></td><td colspan="2">Bench-Scale system ☐ YES ☐ NO
Pilot System ☐ YES ☐ NO
Application ☑ YES ☐ NO</td></tr>
<tr><td colspan="2" rowspan="4">Treatment process
Zero Liquid Discharge with Resource Recovery</td><td rowspan="2">Salt Quality</td><td>☑ Table Salt</td><td>☑ Chemical Industry</td></tr>
<tr><td>☑ Road Salt</td><td>☑ Other use</td></tr>
<tr><td rowspan="2">Water Quality</td><td>☑ Potable water</td><td>☑ Industry recycle</td></tr>
<tr><td>☑ Distillate water</td><td>☐ Other use</td></tr>
<tr><td colspan="2">Year

1993</td><td colspan="3">Ownership

NWR CARBONIA S.A. (since 2008)</td></tr>
<tr><td colspan="5">Description

Polish mines discharge a large amount of wastewater effluent, estimated at approximately 3.6 million m³/day, with Total Dissolved Solids varying from 600mg/l to 120,000mg/L (mostly common salt, NaCl). About 60% of this quantity can be recovered while the rest is discharged uncontrolled into surface waters, causing environmental degradation.

Debiensko Coal Mines decided to install a Zero Liquid Discharge system so as to treat the saline effluent and recover also water and saleable salts. This unit comprises the first Zero Liquid Discharge coal mine application.</td></tr>
<tr><td colspan="3">
</td><td colspan="2"></td></tr>
<tr><td colspan="5">References:
(Ericsson, 1996) (Mortazavi, 2008) (General Electric, 2011) (Bostjancic, 2013)</td></tr>
</table>

6.6.1 Process and technology involved

Process Involved:

The water purification involved the following treatment operations (see also Figure 6-12):

1. Pretreatment;
2. Reverse Osmosis;
3. Brine Concentration;
4. Salt Crystallization; and
5. Purge treatment.

Water Pretreatment: The coal mine drainage was pretreated to prevent membrane fouling in the reverse osmosis unit. The pretreatment components accounted almost for 40% of the total cost.

The pretreatment involved the following components:

(a) Algaecide dosing;

(b) Polymer dosing (sedimentation);

(c) Sodium bisulphate usage (disinfection, chlorination & intermittent shock treatment);

(d) Alum and acid dosing (flocculation and pH control);

(e) Filtration in dual media sand, anthracite and granular activated carbon; and

(f) Sludge thickening.

The pretreatment system produces: (a) one liquid stream: this is the water treated stream that is directed next to the RO unit, and (b) one solid residue: this residue is produced after the sludge thickening process and is directed for off-site disposal in a landfill.

Reverse Osmosis: A desalination unit was employed for concentrating the brine effluent and for the production of freshwater. The RO unit has the following characteristics:

(a) A 2-stage microfiltration section;

(b) The RO unit consisted of more than 500 vessels and operated at 60-70 bar.

The RO unit produces two liquid streams: (a) The permeate, which was used for drinking purposes after de-carbonation, chlorination and lime treatment; and (b) The concentrated brine stream, with 80,000 to 90,000 mg/L total dissolved solids.

Brine Concentration:

The treatment system is equipped with a vertical, falling film evaporator for further concentrating the brine effluent. The brine concentration involved the following treatment processes:

(a) pH adjustment, sulfuric acid is added to the reject stream from the RO unit;

(b) Pre-heatment to near boiling temperature: the steam produced in the brine concentrator is used in a plate heat exchanger for the pre-heatment of brine;

(c) Deaerator: steam stripping of CO_2 and air

(d) Dosing of antifoam and caustic soda.

The concentration of the brine effluent is designed to reach the crystallization point of the sodium chloride. The chemistry of the feed brine stream to the brine concentrator is given in Table 6-7.

Table 6-7: Feed to brine concentrator, mg/L

Ca	1,063
Mg	981
Na	26,451
K	382
Sr	36
Fe	0.5
Si	3
Cl	42,698
NH_4	16
HCO_3	1,145
SO_4	3,420
F	5
TDS	76,400
pH	7.3

Given that the brine effluent contains also less soluble salts than sodium chloride which would normally precipitate within the evaporator, calcium sulphate crystals were added as seeds to the input feed solution at the start up. This allowed the precipitating salt a place to attach and thus prevented precipitation (the crystals remained in suspension). The seeds are continuously recycled in a series of hydrocyclones.

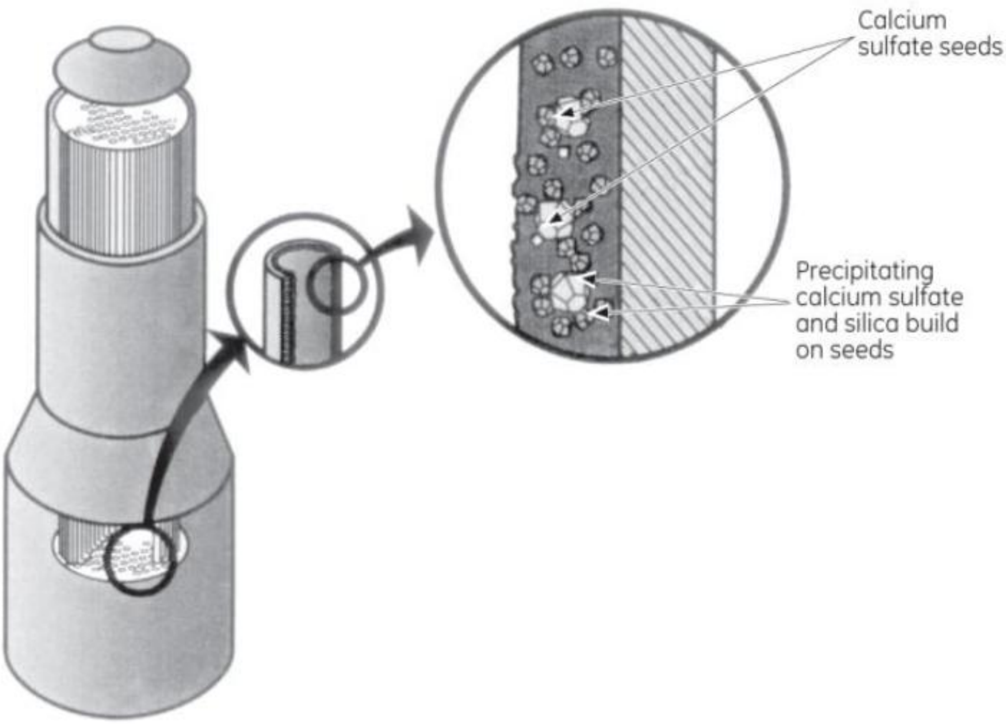


Figure 6-10: Seeded slurry process

The vapor produced inside the brine concentrator is passed through mist eliminators to get rid of brine droplets and then compressed through a vapor compressor system. It is then condensed in a plate heat exchanger and recovered as distillate water. The distillate is used in the power and heat generation system or other industrial use at the coal mine.

Crystallizer:

The feed stream to the concentrator has approximately 258,000 ppm total dissolved solids and 3,000 ppm total suspended solids. Prior to the crystallization step, the exit stream from the brine concentrator is passed through a lamella clarifier for separation of the suspended calcium sulfate. Then, the brine splits into two streams (see also Figure 6-11):

- 60% of the prepared brine is pre-heated into two submerged heat exchangers. The brine is kept under pressure to avoid boiling and thus prevent scale formation in the heat exchangers. After pre-heatment, the brine is directed at an angle into the crystallization vessel. The brine flashes into vapor, which is then compressed through the use of a vapor compressor and subsequently condensed in the exterior surface of the heat exchanger;
- 40% of the prepared brine is sent to the bottom of the elutriation leg to trap the small crystals which return to the crystallization sump and then released with the crystallization purge.

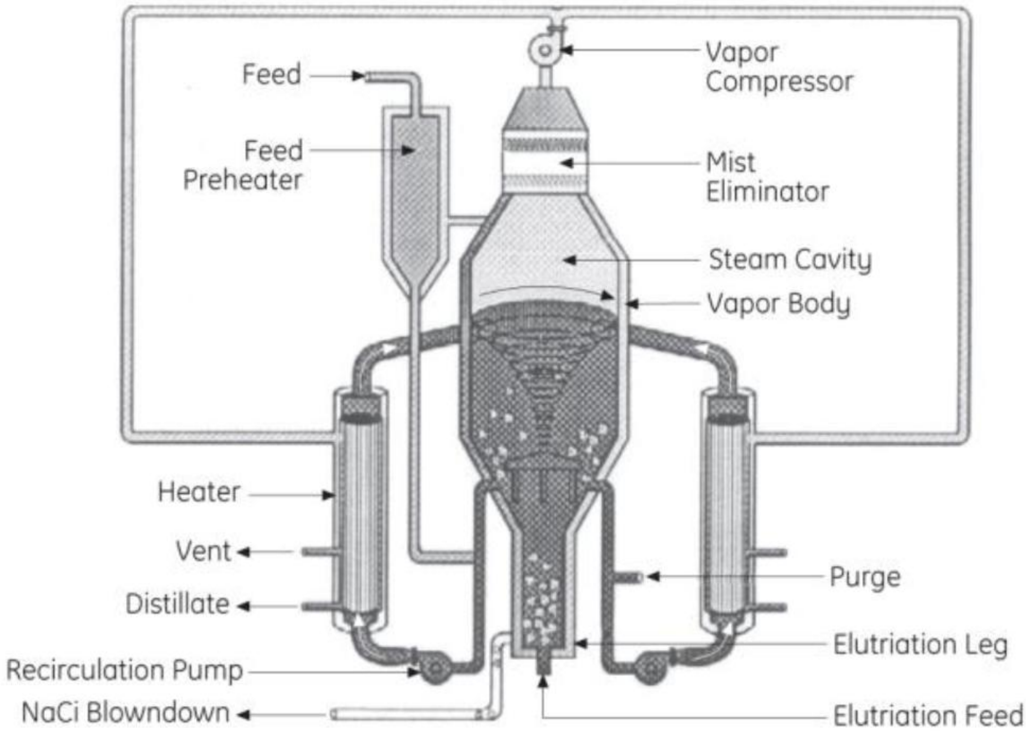


Figure 6-11: Brine concentration unit

Technology involved (Mortazavi, 2008):

- **Water Treatment Technology** from U.S.A. and Sweeden. More particularly, the brine concentrator and the crystallizer were purchased by Resources Conservation Company (U.S.A.) while the vessels (brine concentration and crystallizer) were manufactured in Sweeden.

- **Total cost**: $60 million USD;

- **Pretreatment system cost**: about 40% of the total cost.

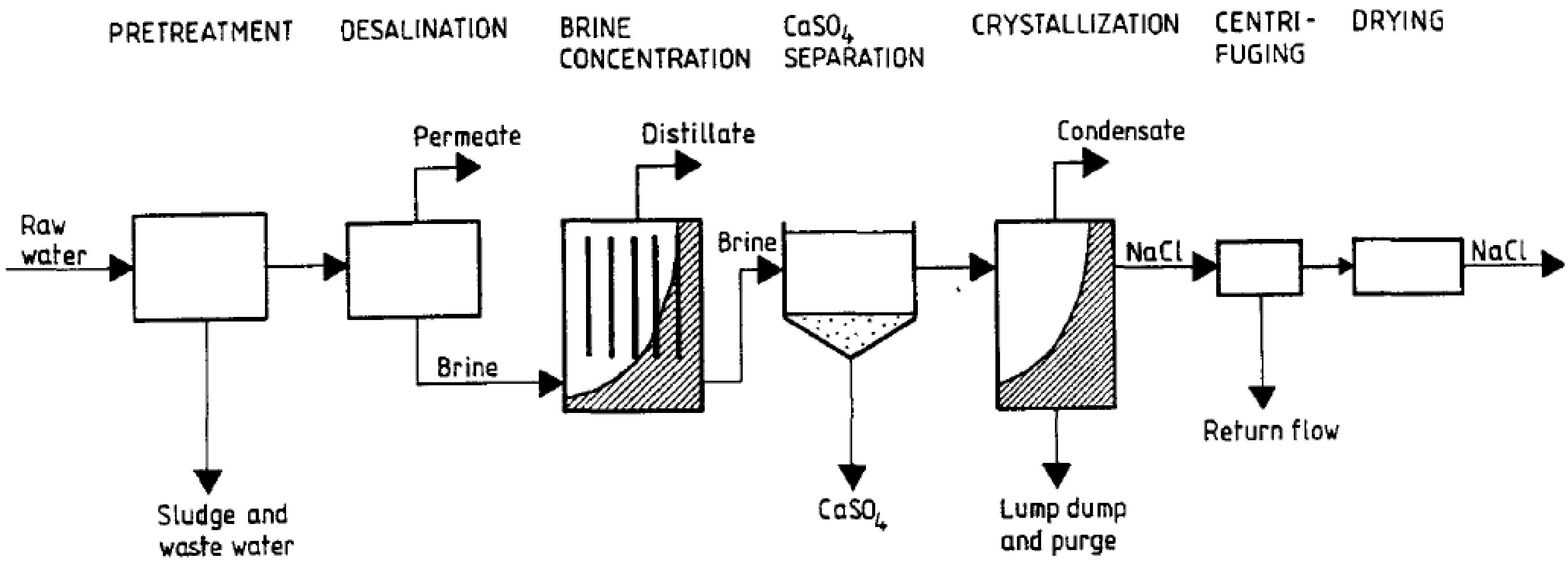


Figure 6-12: Process flow scheme, Debiensko plant, Poland (Ericsson, 1996)

6.6.2 Uses of salt produced

Debiensko plant has applied suitable technology (as presented in the previous section) for the separate production of salts for different markets as presented in the following table.

Figure 6-13: Salt produced in the Debiensko plant, Poland

Table 6-8: Salts produced from mine drainage, Debiensko plant

Product	Quantity per day	Price
Salt tablets for water softening	150 metric tons	$40/metric ton
Bag and bulk salt	250 metric tons	$40/metric ton
Calcium suphate	25 tons	
Products from crystallizer purge:		
Lower quality salt (animal feed)	30 metric tons	$15/metric ton
Iodine to chemical industry	54 kg	$4,000/metric ton
Bromine to chemical industry	280 kg	$300/metric ton
Carnallite for fertilizer	12.5 metric tons	$90/metric ton
Magnesium chloride for bricks	13 metric tons	$60/metric ton

6.6.3 Uses of water produced

Through the use of the Zero Liquid Discharge system at the Debiensko coal mine the following quantities and qualities of water were recovered:

Table 6-9: Water recovered from mine drainage, Debiensko plant

Product	Quantity per day	Price
Drinking water	10,500 m^3/day	\$0.2 per m^3
Distilled water	~ 4,500 m^3/day	\$0.8 per m^3

It is estimated that through the recovery of these valuable products, the returning period of investments is approximately 10 years.

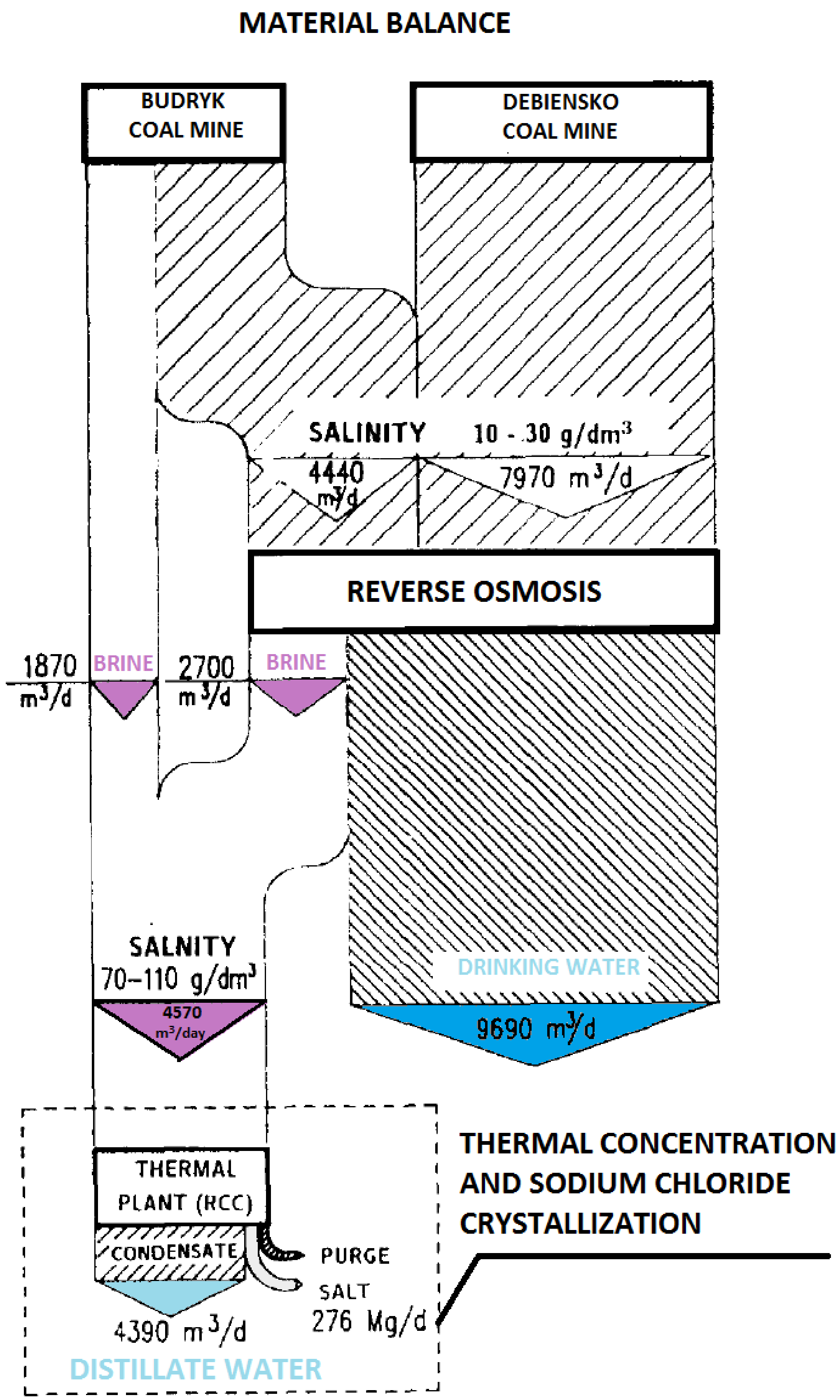


Figure 6-14: Material Balance for Debiensko ZLD plant.

6.7 Alternative uses of brine effluent from desalination plants

Some of the alternative uses of the brine effluent include the following:

- Fish culture (Fish like Barramundi, Red Snapper, Black Bream, Milk fish, Mullet and Tilapia can grow and prosper in high salinity water);
- Algae production;
- Brine shrimp production;
- Irrigation (salt tolerant species); and
- Electricity generation.

Most of the above mentioned techniques can be coupled with evaporation ponds, so as to reduce total cost through synergies. With reference to the electricity generation, the following two techniques can be used:

- Salinity gradient solar ponds combine collection of solar energy with long-term storage providing therefore opportunities for thermal energy storage or even power production; and
- Salinity Gradient Power (SGP) represents a viable renewable energy source associated with the mixing of two solutions of different salinities. Reverse Electrodialysis (SGP-RE) is, in turn, a promising technology to exploit this energy source and directly generate electricity. However, although the principle of this technology is well known since several years, further R&D efforts are still necessary in order to explore the real potential of the SGP-RE process. Within the REAPower project (www.reapower.eu) an innovative system for power production by SGP-RE process, will be developed using seawater as dilute solution and brine as concentrate.

Samarina farm

Brine Outlet into furrow irrigation

The brine is used for furrow irrigation in the rows of trees in the background

Figure 6-15: Alternative use of brine for irrigation of halophytic trees

7 Conclusions

This report provides an insight on treatment processes that are used in industrial applications producing brine effluents of similar chemistry with brine from desalination plants. Even though the SOL-BRINE project is focused on the wastewater effluent generated by desalination plants, one of the main findings of this report was the identification of other brines that have similar characteristics and originate from different processes. More particularly, the following eight sectors have been identified as being the largest chloride releases in Europe:

- Chemical Industry
- Waste treatment;
- Steel industry;
- Energy;
- Oil and gas;
- Pulp and paper;
- Agro-food; and
- Leather and tannery.

The industrial brines generated by the aforementioned industries are similar to the desalination brine on the one hand, but with specificities for each of these industries according to the production process and treatment technologies applied by case. These concentrates are very complex wastewaters and represent today a big challenge for the companies both in terms of management and costs. There is a knowledge gap about the issues of brine management and a lack of development of economic treatment solutions for brines. There is also a lack of understanding the scale of the challenges surrounding brines both in terms of quantities and composition due to limited information publically available from across industrial sectors and individual companies, tending to focus on specific issues which hampers insight in the overall schemes and effects. Progress needs to be made by industries in closing the water cycle to enable reuse of all resources including water, energy and other components, implying re-focus to integrated views and solutions.

In this report, 6 cases were studied for industries that belong to the aforementioned list. These applications involve mainly the mine industry and the power production sector. No Zero Liquid Discharge system has been applied on the desalination sector so far (at industrial level).

More particularly, the following cases were studied:

- 1 coal mine facility: Debiensko plant in Poland
- 3 power stations: (a) Indiantown (USA); (b) Brazos Electric Cooperation (Texas); (c) ENEL (Italy);
- 1 gas production facility: Pearl GTL (Qatar); and
- 1 desalination brine facility: Eilat (Israel)

Technology employed:
In most cases, in order to achieve zero liquid discharge, evaporators (or brine concentrators) were employed. This implies that even if membrane processes were used, this usually only served as a pre-concentration step. A subsequent evaporation technique is necessary for achieving zero liquid discharge.

Products recovered:
By applying these processes, the products that can be recovered are: (a) water; and (b) salts. The water in all cases was of high purity, demineralized water. The only case study that does not recover water is the Eilat case study, since this does not involve evaporators/crystallizers but evaporation ponds, which evaporate the water to the environment. What is of particular value, was the finding about the salts recovered. In most cases these salts are mixed and thus cannot be exploited by a particular market. A distinction between Zero Liquid Discharge and Zero Waste Discharge systems is of particular value. This review revealed that the Zero Liquid Discharge systems applied on a worldwide basis, produce a solid residue that in most cases must be inevitably disposed of in a landfill. This is relevant to the following case studies:

- All (3) case studies for the power stations; and
- The case study for the oil & gas industry.

In the cases of Eilat project (Case study #1) and Debiensko plant (Case study #6) the salts recovered have market value. Between these two case studies, Debiensko is of particular value since it applies different processes to achieve this result. It is demonstrated that combination of different processes must be applied such as pH adjustment, precipitation, membrane processes and evaporation/crystallization processes.

Overall, it can be said that most Zero Liquid Discharge systems succeed to recover water of good quality and for different water uses but this is not the case for the salt recovered also (see also Table 7-1). The separation and further exploitation of salts recovered could contribute significantly to capital recovery, as well as to minimizing environmental pressures, as no discharge is caused to the environment (neither in a liquid nor in a solid form). However, further research is required in the field to achieve better valorization and exploitation of brine effluent salts.

Table 7-1: Summary table of end-products produced from the case studies of similar treatment processes examined

Case Study	#1	#2	#3	#4	#5	#6
Distillate Water					☑	☑
Drinking Water		☑				☑
Process Water			☑	☑	☑	☑
Irrigation Water					☑	
Cooling Water					☑	☑
Aquifer recharge						
Table Salt	☑					☑
Lower quality salt (animal feed)						☑
Chemical industry	☑					☑
Salt for fertilizer						☑
Other						☑

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Client	Plant	Location	Startup	Vol. gpm	Industry	Provider
Asarco	Hayden	AZ	1984	200	Copper smelt	RCC
IBM	Tucson	AZ	1985	100	Electronics	RCC
Salt River Project	Phoenix	AZ	1986		Power	HPD
Apache Nitrogen	Benson	AZ	1994	90	Fertilizer	RCC
Calpine	South Point	AZ	2000	400	Power	RCC
Intel	Fab 22	AZ	2001	155	Manufacturing	RCC
Pinnacle West Energy	West Phoenix	AZ	2001	100	Power	RCC
Pinnacle West Energy	Phoenix	AZ	2001		Power	HPD
Pinnacle West Energy	Tonopah	AZ	2001		Power	HPD
NEPCO	Gila River	AZ	2003	900	Power	RCC
Salt River Project	Navajo	AZ	1974-1980	1400	Power	RCC
Los Angeles County	Pitchess	CA	1988	150	Power	RCC
Thermo Electron Corp.	Mendota	CA	1988	38	Power	RCC
National Energy Constructors	Hanford	CA	1989	75	Power	RCC
Aerojet	Sacramento	CA	1990	15	Chemical	RCC
Harbert International	Tracy	CA	1990	50	Power	RCC
Walsh Construction	Mecca	CA	1991	50	Power	RCC
Simpson Paper	Ripon	CA	1993	11	Paper	HPD
La Paloma Generating	La Palmoa	CA	2001	600	Power	RCC
Constellation Energy	Victorville	CA	2001		Power	HPD
FP&L	Blythe	CA	2003	420	Power	RCC
SMUD	Cosumnes	CA	2004	280	Power	RCC
Con Agra	King City	CA	2005	50	Food	RCC
Public Service of CO	Hayden	CO	1976	250	Power	RCC
Tri-State Generation & Trans.	Craig	CO	1978	700	Power	RCC
Public Service of CO	Pawnee	CO	1980	450	Power	RCC
City of Colorado Springs	RD Nixon	CO	1980	350	Power	RCC
Calpine	Rocky Mountain	CO	2003		Power	HPD
City of Gainesville	Deerhaven	FL	1981	300	Power	RCC
Orlando Utilities Commission	Orlando	FL	1986			
Orlando Utilities Commission	Stanton	FL	1993	600	Power	RCC
Northern Canadian Power	Lake	FL	1993	3	Power	RCC
Pasco Cogen/Zurn/Nepco	Pasco	FL	1993	3	Power	RCC
Misson Energy	Auburndale	FL	1993	130	Power	RCC
Bechtel/US Generating	Cedar Bay	FL	1993	300	Power	RCC
Bechtel/US Generating	Indiantown	FL	1994	580	Power	RCC
Pasco County	N Port Richey	FL	1997	30	Ash landfill	RCC
U.S. Navy	Jacksonville	FL	1997	3.5	Mfg cleanup	RCC
Tallahassee Electric	St. Marks	FL	2000	230	Power	RCC
Orlando Utilities Commission	Stanton CC	FL	2004	500	Power	RCC
Cogentrix Rathdrum	Rathdrum	ID	2001	2	Power	RCC
Global Energy	Wabash River	IN	2002	100	Power	RCC
Brown & Root	Shreveport	LA	1990			HPD
CRS Sirrine	Stratton	ME	1988	20	Power	RCC
Westinghouse	Bellingham	MA	1991	30	Power	RCC
Harquahala Generating	Foxboro	MA	2001		Power	HPD
Tractabel/Parsons	Choctaw	Missouri	2005	106	Power	RCC
Resources Technology Group	Weldon Springs	MO	1995	50	Pit cleanup	RCC
Aquila Utilicorp	Aries Power	MO	2000	280	Power	RCC
Pennsylvania Power & Light	Colstrip	MT	1977	350	Power	RCC
Nevada Power	Clark	NV	1982	600	Power	RCC
Southern California Edison	Mojave	NV	1985	600	Power	RCC
Kerr-McGee Chemical Corp.	Henderson	NV	1989	100	Chemical	RCC
Stone & Webster	Apex	NV	2002	82	Power	RCC
Arizona Public Service	Four Corners	NM	1979	400	Power	RCC
Phelps Dodge	Hidalgo	NM	1991	200	Copper smelt	RCC
Public Service of NM	San Juan	NM	1974-1984	3300	Power	RCC
New York State Gas & Elec	Milliken	NY	1993	30	Power	RCC
Panda	Rosemary	NC	2002	50	Power	RCC
NC Power	E-Town	NC	2003	23	Power	RCC
East Penn	Lyon Station	PA	1995	100	Battery mfg	RCC
AES Ironwood	Ironwood	PA	2001	200	Power	RCC
Ocean State Power	Harrisville	RI	1990		Power	HPD
Ocean State Power	Harrisville	RI	1997	150	Power	RCC
EMI/Stone & Webster	Tiverton	RI	1998	20	Power	RCC
Otter Tail Power	Big Stone	SD	1980	600	Power	RCC
Texas Utilities	Monticello	TX	1982	250	Power	RCC
Texas Utilities	Martin Lake	TX	1983	500	Power	RCC
Texas New Mexico Power	Bremond	TX	1989	322	Power	RCC
Asarco	El Paso	TX	1991	150	Copper smelt	RCC
EI Dupont	Orange	TX	1992			HPD
Texas Independent Energy	Guadalupe	TX	2000	400	Power	RCC
Hays Energy	San Marcos	TX	2001	1,000	Power	RCC
Parsons/Tractebel	Wise County	TX	2002	60	Power	RCC
Utah Power & Light	Huntington	UT	1974	200	Power	RCC
US Army	Tooule	UT	1990			HPD
PacifiCorp	Huntington	UT	2002	200	Power	RCC
Fluor Daniel/Doswell	Doswell	VA	1991	90	Power	RCC
Northwest Alloys	Addy	WA	1981	80	Magnesium	RCC
Japanese Gas Corp	Hanford	WA	1994	20	Nuclear power	RCC
USKDK Corporation	Moses Lake	WA	1997			HPD
Coastal Chemical	Cheyenne	WY	1991	150	Chemical	RCC

Note: RCC stands for Resources Conservation Company
HPD evaporation and crystallization system of Veolia Water Treatment Technologies

Sol – Brine

LIFE+-Environment project: LIFE 09 ENV/GR/000299