Management and treatment of brines in food industry

Xavier Martínez, 14th May 2015
• Salt is used for food conservation
• Agro-food sectors requiring the highest amount of salt:
  - Meat canning
  - Pickled vegetables
  - Dairy products
  - Fish processing
• Generation of saline effluents during food processing: saline wastewater, brines, osmotic solutions
• Saline effluents polluted with suspended solids, salts and organic matter
Brines represents a high proportion of the total contaminating discharge of wastewater.

Brines can’t be discharged into the main sewer system without treatment.

Saline effluents are difficult to be treated by means of conventional biological treatments.

Brine disposal has become an increasingly costly and environmentally challenging issue.

Administrative constrains
Union Directive 2000/60/EC: prevention of saline pollution

Process modification to minimize brine volume generated
Implementation of processes for brine treatment
How to handle industrial brines?

- Internal valorisation, meaning re-use (after treatment if needed) of the brines in the production site.
- External valorisation, meaning a fit-for-use product which can be re-used in another industrial site/sector.
- Final brine disposal. This is the least preferable pathway but it is unavoidable for some brines which are too difficult to handle or for the by-products coming from the treatments applied to produce brines which are “fit-for-use”.

Brines (Cl, SO4, NO3, F, NH4, mix of salts, organic matter, salts & heavy metals)

- Internal Reuse
- External Valorisation
- Final Disposal

Definition of Required Quality

Volume of waste stabilisation
Nature of salt and “impurities” present with the salt (organic matter, heavy metals, other salts, suspended solids) are drivers for strategy definition and technology selection.

The most important points regarding salts valorization are:

- Produce salt product “fit-for-use” (food, textiles regeneration, chemical)
- Removal of impurities
- Internal re-use often easier than external valorisation
- Quality/purity has a big influence on price

In disposal, the focus of brine treatment maybe on volume reduction and/or complete liquid elimination.
Existing technologies for brines treatment

• Separative technologies - Membranes technologies (conventional, membrane distillation, forward osmosis, electro-membranes technologies such as electrodialysis)

• Selective removal - Selective precipitation/crystallisation processes, ion exchange and development of selective materials (e.g. for valuable compounds recovery)

• Treatment processes:
  - a final treatment of brines before disposal (evapococoncentration, stabilization, thermal treatment)
  - removal of some polluting compounds regarding re-use of salts (e.g. organic compounds in brines, nitrates)

**ZERO LIQUID DISCHARGE (ZLD)**
Process that fully remove water from brine stream, so the end product is a solid residue of precipitate salt.
## Existing technologies for brines treatment

<table>
<thead>
<tr>
<th>Technology</th>
<th>Principle</th>
<th>Concentration</th>
<th>Energy</th>
<th>Attention points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse osmosis</td>
<td>Membrane filtration under high pressure</td>
<td>Limited due to osmotic pressure ~ 100 g/l</td>
<td>3-7 kWh/m³, electric</td>
<td>Fouling, scaling</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>Application ion-selective membrane influx by electrical field</td>
<td>Concentrate to 100 g/l</td>
<td>5-20 kWh/m³, electric</td>
<td>Fouling, scaling</td>
</tr>
<tr>
<td>EDBM</td>
<td>Electrodialysis with bipolar membranes</td>
<td>Recovery of acids and lye</td>
<td>5-20 kWh/m³, electric</td>
<td>Pre-treatment, costs of BP membrane</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Water evaporation under the influence of temperature</td>
<td>Max. about 500 g/l</td>
<td>20 to 500 kWh/m³ heating (+ 2 kWh/m³ elect.)</td>
<td>Corrosion / scaling</td>
</tr>
<tr>
<td>Precipitation / Crystallization</td>
<td>Supersaturation, crystallization</td>
<td>100 %</td>
<td>See evaporation for crystallization</td>
<td>Solids processing</td>
</tr>
<tr>
<td>Lyophilization</td>
<td>Water removal through freezing</td>
<td>100 %</td>
<td>approx. 12 kWh/m³, electric or cold</td>
<td>Investments; Recover pure water and salts</td>
</tr>
</tbody>
</table>


Evaporation can take place in different ways and with different types of evaporators, such as Multi-effect Distillation (MED), Vapour Compression Distillation (VCD) and Multi-Stage Flash (MSF).

**Advantages**
- Can produce zero liquid discharge
- Can commercially exploit concentrate
- Recovery of salt and minerals

**Disadvantages**
- Expensive
- High energy consumption
- Production of dry solid waste – precipitates
- Scaling and corrosion
Membrane Technology

Advantages
• Water recovery
• Very large number of separation needs
• Most economical process for salinity reduction associated with secondary effluent (or other wastewater source) TDS levels

Disadvantages
• High cost technology
• Pre-treatment needed for some technologies, solids removal
• Fouling problems
• Concentrate and waste stream disposal issues
Saline wastewater from food industry: global treatment chain

Biological treatment recommended before physico-chemical treatment
• Brine represents 70% of the pollutant load and 20% of volume
• Elimination systems: evaporation in shallow ponds

• Other options for brine management:
  • Elimination using:
    ✓ Evaporation with cogeneration
    ✓ Membrane filtration
  • Reuse in the final product: fermentation brine has similar composition to final packing solution
    ✓ Treatment with active carbon
    ✓ Membrane filtration

• Production of useful substances
La Española experiences

- Brines reuse
- Reduction of wastewater treatment cost
- Reduction of water consume

Brine

Evaporation combined to advanced oxidation technologies

- 900L Destilled Water
- 88kg salt

Reuse in the process

Salt for animal feed

http://www.cleanwatertech.com/
Tri Valley Growers (TVG) Inc. (California)

Treatment of 264m³ per day

http://www.cleanwatertech.com/
Table olive production: ZLD process for water reuse

<table>
<thead>
<tr>
<th>Sample</th>
<th>FOG mg/L</th>
<th>TSS mg/L</th>
<th>COD mg/L</th>
<th>APC ch/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Effluent</td>
<td>450</td>
<td>900</td>
<td>8,000</td>
<td>3,000,000</td>
</tr>
<tr>
<td>After Screening</td>
<td>400</td>
<td>500</td>
<td>7,600</td>
<td>3,000,000</td>
</tr>
<tr>
<td>After BAF 1</td>
<td>15</td>
<td>20</td>
<td>3,800</td>
<td>800,000</td>
</tr>
<tr>
<td>After BAF 2</td>
<td>3</td>
<td>4</td>
<td>3,200</td>
<td>200,000</td>
</tr>
<tr>
<td>After UF</td>
<td>2</td>
<td>1</td>
<td>2,900</td>
<td>4,000</td>
</tr>
<tr>
<td>After RO</td>
<td>0</td>
<td>0</td>
<td>45</td>
<td>50</td>
</tr>
</tbody>
</table>

Evaporator

Membrane Filtration

http://www.niroinc.com/
http://www.cleanwatertech.com/
http://www.gea-wiegand.com/
• Process evaluation at pilot scale.
• Reduction of the brine management cost (40%).
• Valorization of wastes obtained: salts and extracted proteins can be sold or used as fertilizers and food for pets.
• Distilled water obtained can be reused.

http://www.uvic.es/sart
WO2004049828A1: Salt whey product and method of making
Recovery and reuse of salt whey from cheesemaking as a salt substitute and whey protein source in food processing

Fat removal
Also skimming, or microfiltration

Concentration
Also RO

To obtain powder product
Also roller or drum drying

<table>
<thead>
<tr>
<th>Table 3. Composition of salt whey products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Product</td>
</tr>
<tr>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Salt Whey</td>
</tr>
<tr>
<td>Separated Salt Whey</td>
</tr>
<tr>
<td>Condensed Salt Whey</td>
</tr>
<tr>
<td>Dried Salt Whey (Salt Whey Product)</td>
</tr>
<tr>
<td>Salt Whey Cream</td>
</tr>
</tbody>
</table>
Salty Cheese Whey treatment in dairy industry

Solids content: 4-6%
BOD 45.000 mg/L

Mixed with normal whey

Divalent salts (i.e. CaCl2), sugars, proteins, and other higher molecular weight components.

NF system retains whey proteins and lactose whilst allowing salts to pass through to the permeate stream. Whey concentration up to 25% TS, allowing for its re-use.

http://www.mmsx.com/
Salty Cheese Whey treatment in dairy industry

http://www.kochmembrane.com/
Brines treatment from fish processing

### Pollutants and Concentrations

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Units</th>
<th>Concentration, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Waste brine</td>
</tr>
<tr>
<td>pH</td>
<td>pH</td>
<td>6-8</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>mg/l</td>
<td>500</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>mg/l</td>
<td>120-50000</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>mg/l</td>
<td>400</td>
</tr>
<tr>
<td>Sulphates, SO₄²⁻</td>
<td>mg/l</td>
<td>200</td>
</tr>
<tr>
<td>COD</td>
<td>mgO₂/l</td>
<td>1000-60000</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>mg/l</td>
<td>500</td>
</tr>
<tr>
<td>Chlorides, Cl⁻</td>
<td>g/l</td>
<td>120-160</td>
</tr>
</tbody>
</table>

http://www.hydropark.ru/projects.en.htm
New Zero Liquid Discharge technology for brine treatment: brine treatment based on a combination of electro-separation processes and valuable compound recovery.
Electrodialysis Metathesis stage

- Separation of the multivalent anions and cations in two different waste streams
- Highly concentrated waste streams can be obtained without precipitation

<table>
<thead>
<tr>
<th>Treatment capacity: 1m³/h</th>
<th>Value:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (RO brine streams)</td>
<td>5 – 20 g/L TDS</td>
</tr>
<tr>
<td>Feed (NaCl feed)</td>
<td>20 – 30 g/L</td>
</tr>
<tr>
<td>Output (diluate) streams</td>
<td>0.02 – 3 g/L TDS</td>
</tr>
<tr>
<td>Output (concentrate)</td>
<td>30 – 120 g/L TDS</td>
</tr>
</tbody>
</table>
ZLD stage

Step 1. Calcium sulphate precipitation

CaCl₂·2H₂O → Calcium sulphate

EDM C1

EDM C2

Step 2. Calcite precipitation

Na₂CO₃, NaOH → Calcite

Step 3. Brucite precipitation

NaOH → Brucite

NaCl stream

This stage must be evaluated and adapted according different brine composition
ZLD stage: treatment of NaCl stream by solar evaporation

**Technology description**

- Evaporative technology based on:
  - Minimal air volume contained within the greenhouse
  - Brine depth control
  - Inner temperature and humidity control
  - Thermal isolation of the pond
  - Air flow speed over the evaporation film
- Based on solar energy
  - Electrical consumption only due to humidity removal fans
- Advanced control strategy
  - Model based control
  - Model predictive control
  - Seeking the optimal evaporation for every single weather condition
ZLD stage: treatment of NaCl stream by solar evaporation

Pilot plant description

- Brine evaporation to obtain dry salt
- 2 ponds for comparison between natural evaporation and advanced evaporation
- Located in Almería, (bests solar irradiation of Spain)
- Brine treated near saturation (30%)

Specifications

- Advanced evaporation estimated performance: 2 m$^3$/m$^2$.year
- Natural evaporation estimated performance: 1,2 m$^3$/m$^2$.year
- Pond surface: 25 m$^2$
- Total evaporation surface: 50 m$^2$
- Total plant capacity: 80 m$^3$.year