

A. Description of the model

For each process unit of the scenarios' treatment trains, a process model has been developed in Python. The models have been validated with experimental data (pilot scale). Table A.1. shows the feed seawater composition used in the present study.

Table A. 1 Feed seawater composition.

	Na ⁺	Cl ⁻	K ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	HCO ₃ ⁻
ConA. (mg/l)	11900	21800	400	1400	400	3200	-

For all units, the necessary electricity for pumping is determined by taking into account the volumetric flows of inputs (including chemicals and cooling water), outputs, and in-between streams. This calculation considers factors such as viscosity, pressure drop, and pump efficiency (assumed to be 0.8). Equation A.68 provides an illustrative example of this calculation.

A.1. Nanofiltration (NF) and Reverse Osmosis (RO) models

NF is a pressure-driven membrane process that is used to concentrate and separate solutes. In this work, NF aims to separate monovalent and multivalent ions from seawater or brine feed solutions. A process model was developed to simulate the NF process. The process model is built based on the Xevgenos *et al.* (2023) report (see Section 3.2.1), as described in Table A.2. The model calculates the flow rates and ion concentrations of the permeate and concentrate streams. Mass balances are employed to evaluate the concentration and flow rate on the concentrate and permeate sides. Additionally, the required energy is calculated based on the osmotic pressure.

Assumptions on NF model:

1. Rejection factors (from experimental data)
2. Water recovery ratio (from experimental data)
3. Pressure drop

Note that the same model is used for RO units with different assumptions for rejection factors and water recovery ratio.

Table A. 2. Equations for NF process unit (Xevgenos et al., 2023)

Equations		
$C_{permeate,i} = (1 - R_i) \cdot C_{feed,i}$		A. 1
$Q_{permeate} = WR \cdot Q_{feed}$		A. 2
$Q_{concentrate} = Q_{feed} - Q_{permeate}$		A. 3
$C_{concentrate,i} = \frac{Q_{feed} \cdot C_{feed,i} - Q_{permeate} \cdot C_{permeate,i}}{Q_{concentrate}}$		A. 4
$Q_{feed_pass\ I} = Q_{sea\ water} + Q_{concentrate_pass\ II}$		A. 5
$C_{feed,i_pass\ I} = \frac{Q_{sea\ water} \cdot C_{sea\ water,i} + Q_{concentrate_pass\ II} \cdot C_{concentrate,i_pass\ II}}{Q_{feed_pass\ I}}$		A. 6
$Q_{feed_pass\ II} = Q_{permeate_pass\ I}$		A. 7
$C_{feed,i_pass\ II} = C_{permeate,i_pass\ I}$		A. 8
$\pi = \sum C_i \cdot R \cdot T$		A. 9
$P_{applied} = \frac{\pi_{concentrate} + \pi_{feed}}{2} - \pi_{permeate} + dP$		A. 10
$P_{pump} = P_{applied} \cdot Q_{permeate}$		A. 11
$E = \frac{P_{pump}}{Q_{sea\ water}}$		A. 12

A.2. Multi-effect distillation (MED) model

MED is a thermal based process that is used to desalinate water. In this work, MED aims to recover high quality water and concentrate further the brine stream. The model is build based on Xevgenos *et al.* (2023) report (see Section 3.2.2.), as it is described in Table A.3. The model calculates the distillate and brine flow rates, brine stream ion concentration and the energy requirements (electrical and thermal).

Assumptions on MED model:

1. The product is salt free
2. Concentration factor
3. Cooling water temperature
4. Final effect temperature
5. Number of effects
6. Pressure drop

Table A. 3. Equations for MED process unit (Xevgenos et al., 2023)

Equations	
$B_n = \frac{X_f}{X_n - X_f} M_d,$	A. 13
$M_f = M_d + B_n,$	A. 14
$\Delta T_1 = \frac{\Delta T_t}{U_1 \cdot \sum_{i=1}^n \frac{1}{U_i}},$	A. 15
$\Delta T_t = T_s - T_n,$	A. 16
$U_{i+1} = 0.95 \cdot U_i,$	A. 17
$\Delta T_i = \Delta T_1 \frac{U_1}{U_i}, \quad i = 1, 2, 3, \dots, n-1, n$	A. 18
$T_1 = T_s - \Delta T_1,$	A. 19
$T_i = T_{i-1} - \Delta T_i, \quad i = 2, 3, \dots, n-1, n$	A. 20
$\lambda_{v_i} = 2499.5698 - 2.204864 \cdot (T_i - \Delta T_{loss}) - 2.304 \cdot (T_i - \Delta T_{loss})^2,$	A. 21
$i = 1, 2, \dots, n-1, n$	
$D_1 = \frac{M_d}{\sum_{i=1}^n \frac{\lambda_{v_1}}{\lambda_{v_i}}},$	A. 22
$D_i = D_1 \frac{\lambda_{v_1}}{\lambda_{v_i}}, \quad i = 2, 3, \dots, n-1, n$	A. 23
$B_1 = M_f - D_1,$	A. 24
$X_1 = X_f \frac{M_f}{B_1},$	A. 25
$X_i = X_{i-1} \frac{B_{i-1}}{B_i}, i = 2, 3, \dots, n-1, n$	A. 26
$A_1 = \frac{D_1 \cdot \lambda_{v_1}}{U_1 \cdot (T_s - T_1)},$	A. 27
$A_i = \frac{D_i \cdot \lambda_{v_i}}{U_i \cdot (\Delta T_i - \Delta T_{loss})}, \quad i = 2, 3, \dots, n-1, n$	A. 28
$\Delta T_i^{new} = \Delta T_i^{old} \frac{A_i}{A_m},$	A. 29
$M_s = D_1 \frac{\lambda_{v_1}}{\lambda_s},$	A. 30
$Q_c = D_n \cdot \lambda_{v_n},$	A. 31
$Q_1 = M_s \cdot \lambda_s,$	A. 32
$A_c = \frac{Q_c}{U_c \cdot (LMTD)_c},$	A. 33

$$(LMTD)_c = \frac{T_f - T_{cw}}{\ln \frac{T_n - \Delta T_{loss} - T_{cw}}{T_n - \Delta T_{loss} - T_f}} \quad A. 34$$

$$SA = \frac{\sum_{i=1}^n A_i + A_c}{M_d} \quad A. 35$$

$$M_{cw} = \frac{D_n \cdot \lambda_{v_n}}{C_p \cdot (T_f - T_{cw})} - M_f \quad A. 36$$

A.3. Thermal crystallizer (TCr) model

Thermal crystallizer is thermal based process that is used to crystallize salts. In this work, thermal crystallizer is simulated as an evaporative crystallizer enables to complete salt concentration up to saturation and promote NaCl crystallization. The model is build based on Xevgenos *et al.* (2023) report (see Section 3.2.6.) as it is described in Table A. 4. The model calculates the distillate and salt flow rates, the ion concentration and the energy requirements (electrical and thermal).

Assumptions on TCr model:

- Salt moisture
- Latent heat of vaporization
- Cooling water temperature
- Power consumption for filtration unit
- Pressure drop

Table A. 4. Equations for TCr process unit (Xevgenos et al., 2023).

Equations	
$M_{NaCl} = \frac{M_i \cdot C_{i,Na}}{d_i \cdot 1000} \cdot \frac{MW_{NaCl}}{MW_{Na}}$	A. 37
$M_{salt} = \frac{\frac{M_i \cdot C_{i,t}}{d_i \cdot 1000}}{(1 - \frac{SaltMoisture}{100})}$	A. 38
$M_d = M_i - M_{salt}$	A. 39
$Q = LHV_v \cdot M_d + M_i \cdot Cp_i \cdot (T_{op} - T_{in})$	A. 40
$T_{st} = \frac{Q}{UA} + T_{op}$	A. 41
$M_{st} = Q / LHV_s$	A. 42
$M_{cw} = \frac{M_{st} \cdot LHV_v}{Cp_{cw} \cdot (T_{cw,o} - T_{cw,i})}$	A. 43

A.4. Multiple Feed Plug Flow Reactor (MF-PFR) model

MF-PFR is an innovative a plug flow reactor that is used to precipitate salts. In this work, MF-PFR aims to precipitate Mg and Ca with the addition of chemicals. The model is build based on Xevgenos *et al.* (2023) report (see Section 3.2.3.) and Carmelo Morgante *et al.* (2022) as it is described in Table A. 5. The model calculates the effluent and salt flow rates, the quantity of alkaline reactant, the ion concentration of the effluent, and the electricity requirements of the unit.

Assumptions on MF-PFR:

- Concentration of alkaline reactant
- Concentration of acid solution
- Power consumption for filtration unit
- 1st and 2nd step conversion factors
- Pressure drop

Table A. 5. Equations for MF-PFR process unit (Xevgenos et al., 2023)

Equations	
$Q_{Mg^{2+}}^{feed} = Q_{brine}^{feed} \cdot C_{Mg^{2+}}^{IN}$	A. 44
$Q_{NaOH}^{1^{st} step} = \frac{Q_{brine}^{feed} \cdot C_{Mg^{2+}}^{IN} \cdot \left(\frac{Conversion_{1^{st} step}}{100} \right) \cdot 2}{C_{NaOH}^{1^{st} step}}$	A. 45
$Q_{tot}^{OUT, 1^{st} step} = Q_{brine}^{feed} + Q_{NaOH}^{1^{st} step}$	A. 46
$\dot{M}_{Mg(OH)_2}^{OUT, 1^{st} step} = \frac{Q_{tot}^{feed} \cdot C_{Mg^{2+}}^{IN} \cdot \left(\frac{Conversion_{1^{st} step}}{100} \right) \cdot MW_{Mg(OH)_2}}{1000}$	A. 47
$magma\ density_{Mg(OH)_2} = \frac{\dot{M}_{Mg(OH)_2}^{OUT, 1^{st} step} \cdot 1000}{Q_{tot}^{OUT}}$	A. 48
$pH_{1^{st} step} = 14 + \log_{10} \left(2 \cdot \sqrt[3]{\frac{K_{psMg(OH)_2}}{4}} \right)$	A. 49
$C_{Mg^{2+}}^{OUT, 1^{st} step} = \frac{Q_{Mg^{2+}}^{feed} \cdot \left(1 - \frac{Conversion_{1^{st} step}}{100} \right)}{Q_{tot}^{OUT}}$	A. 50
$C_{Na^+}^{OUT, 1^{st} step} = \frac{Q_{brine}^{feed} \cdot C_{Na^+}^{IN} + Q_{NaOH}^{1^{st} step} \cdot C_{NaOH}^{1^{st} step}}{Q_{tot}^{OUT}}$	A. 51
$C_i^{OUT, 1^{st} step} = \frac{Q_{brine}^{feed} \cdot C_i^{IN}}{Q_{tot}^{OUT}}$	A. 52
$Q_{Ca^{2+}}^{feed, 2^{nd} step} = Q_{tot}^{OUT, 1^{st} step} \cdot C_{Ca^{2+}}^{OUT, 1^{st} step}$	A. 53
$Q_{NaOH_{stoich.}}^{2^{nd} step} = \frac{Q_{tot}^{OUT, 1^{st} step} \cdot C_{Ca^{2+}}^{OUT, 1^{st} step} \cdot \left(1 - \frac{Conversion_{2^{nd} step}}{100} \right) \cdot 2}{C_{NaOH}^{2^{nd} step}}$	A. 54

$$Q_{NaOH_{added}}^{2^{o} \text{ step}} = \frac{(C_{OH}^{stoich.} - C_{OH}^{pH=13}) \cdot (Q_{tot}^{OUT, 1^{o} \text{ step}} + Q_{NaOH_{stoich.}}^{2^{o} \text{ step}})}{C_{OH}^{pH=13} - C_{NaOH}^{2^{o} \text{ step}}} \quad A. 55$$

$$Q_{tot}^{OUT, 2^{o} \text{ step}} = Q_{tot}^{OUT, 1^{o} \text{ step}} + Q_{NaOH_{stoich.}}^{2^{o} \text{ step}} + Q_{NaOH_{added}}^{2^{o} \text{ step}} \quad A. 56$$

$$\dot{M}_{Ca(OH)_2}^{2^{o} \text{ step}} = \frac{Q_{tot}^{OUT, 1^{o} \text{ step}} \cdot C_{Ca^{2+}}^{OUT, 1^{o} \text{ step}} \cdot \left(\frac{Conversion_{2^{o} \text{ step}}}{100} \right) \cdot MW_{Ca(OH)_2}}{1000} \quad A. 57$$

$$\dot{M}_{Mg(OH)_2}^{2^{o} \text{ step}} = \frac{Q_{tot}^{OUT, 1^{o} \text{ step}} \cdot C_{Mg^{2+}}^{OUT, 1^{o} \text{ step}} \cdot PM_{Mg(OH)_2}}{1000} \quad A. 58$$

$$C_{Na^+}^{OUT, 2^{o} \text{ step}} = \frac{Q_{tot}^{OUT, 1^{o} \text{ step}} \cdot C_{Na^+}^{OUT, 1^{o} \text{ step}} + (Q_{NaOH_{stoich.}}^{2^{o} \text{ step}} + Q_{NaOH_{added}}^{2^{o} \text{ step}}) \cdot C_{NaOH}^{2^{o} \text{ step}}}{Q_{tot}^{OUT, 2^{o} \text{ step}}} \quad A. 59$$

$$C_{Ca^{2+}}^{OUT, 2^{o} \text{ step}} = \frac{Q_{Ca^{2+}}^{feed, 2^{o} \text{ step}} \cdot \left(1 - \frac{Conversion_{2^{o} \text{ step}}}{100} \right)}{Q_{tot}^{OUT, 2^{o} \text{ step}}} \quad A. 60$$

$$C_i^{OUT, 2^{o} \text{ step}} = \frac{Q_{tot}^{OUT, 1^{o} \text{ step}} \cdot C_i^{OUT, 1^{o} \text{ step}}}{Q_{tot}^{OUT, 2^{o} \text{ step}}} \quad A. 61$$

$$magma \text{ density}_{2^{o} \text{ step}} = \frac{(\dot{M}_{Mg(OH)_2}^{OUT, 2^{o} \text{ step}} + \dot{M}_{Ca(OH)_2}^{OUT, 2^{o} \text{ step}}) \cdot 1000}{Q_{tot}^{OUT, 2^{o} \text{ step}}} \quad A. 62$$

$$pH_{2^{o} \text{ step}} = 14 + \log_{10}(0.1) \quad A. 63$$

$$C_{OH, i}^{OUT, 2^{o} \text{ step}} = 10^{-pH} / 10^{-pH_{2o \text{ step}}} \quad A. 64$$

$$C_{OH, o}^{OUT, 2^{o} \text{ step}} = 10^{-14} / 10^{-7} \quad A. 65$$

$$Q_{HCl_{added}}^{2^{o} \text{ step}} = \frac{Q_{tot}^{OUT, 2^{o} \text{ step}} \cdot C_{OH, i}^{OUT, 2^{o} \text{ step}} - Q_{tot}^{OUT, 2^{o} \text{ step}} \cdot C_{OH, o}^{OUT, 2^{o} \text{ step}}}{C_{OH, o}^{OUT, 2^{o} \text{ step}} + C_{HCl}} \quad A. 66$$

$$Q_{tot}^{OUT, 2^{o} \text{ step}} = Q_{tot}^{OUT, 2^{o} \text{ step}} + Q_{HCl_{added}}^{2^{o} \text{ step}} \quad A. 67$$

$$Energy_{pumping}^{1^{o} \text{ step}} \quad A. 68$$

$$= \frac{Q_{total}^{feed, 1^{o} \text{ step}} \cdot \Delta P^{feed, 1^{o} \text{ step}} + Q_{total}^{NaOH, 1^{o} \text{ step}} \cdot \Delta P^{NaOH, 1^{o} \text{ step}}}{\eta_{pump}} \cdot 10^{-3}$$

$$Energy_{pumping}^{2^{o} \text{ step}} \quad A. 69$$

$$= \frac{Q_{total}^{OUT, 1^{o} \text{ step}} \cdot \Delta P^{feed, 2^{o} \text{ step}} + Q_{total}^{NaOH, 2^{o} \text{ step}} \cdot \Delta P^{NaOH, 2^{o} \text{ step}}}{\eta_{pump}} \cdot 10^{-3}$$

A.5. Eutectic freeze crystallization (EFC) model

EFC is an alternative thermal based technology that is capable of separating aqueous solutions into pure water and pure solidified solutes, by cooling down the brine solution. In this work, EFC aims to recover sulphates, recover water in ice form and concentrate further the brine solution. The model is build based on Xevgenos *et al.* (2023) report (see Section 3.2.4.), as it is described in Table A. 6. The crystal distribution, growth and nucleation were not considered in this work. Still, the detailed mathematical

description can be found in Xevgenos *et al.* (2023). The model calculates the effluent and salt flow rates, the ion concentration of the effluent, and the electricity requirements of the unit.

Assumptions on EFC:

- Eutectic conditions based on the ternary system (Na, Cl, SO₄), impurities (K, Ca) were neglected
- Cooling rate
- Power consumption for filtration unit
- Pressure drop

Table A. 6. Equations for EFC process unit (Xevgenos et al., 2023)

Equation	
$V_{liq,total} = 0.7 \cdot V_{reactor}$	A. 70
$V_{mother\ liq} = V_{liq,total}$	A. 71
$V_{water} = \frac{V_{mother\ liq}}{(1 + \frac{C_{C1} \cdot MW_{C1} \cdot d_{water}}{(1000 \cdot d_{C1})}) + \dots + \frac{C_{Ci} \cdot MW_{Ci} \cdot d_{water}}{(1000 \cdot d_{Ci})})}$	A. 72
$V_{ci} = \frac{C_{C1} \cdot MW_{C1} \cdot V_{water} \cdot d_{water}}{1000 \cdot d_{Ci}}$	A. 73
$M_{water} = V_{water} \cdot d_{water}$	A. 74
$M_{ci} = V_{ci} \times d_{ci}$	A. 75
$M_{mother\ liq} = M_{water} + M_{c1} + \dots + M_{ci}$	A. 76
$M_{liq,total} = M_{mother\ liq}$	A. 77
$V_{total} = V_{liq,total} + V_{solids,total}$	A. 78
$M_{total} = M_{liq,total} + M_{solids,total}$	A. 79
$V_{ice} = V_{ice} + V_{ice,diff},$	A. 80
$V_{ci,cr} = V_{ci,cr} + V_{ci,cr,diff},$	A. 81
$V_{solids,total} = V_{ice} + V_{ci,cr},$	A. 82
$V_{water} = \frac{M_{water}}{d_{water}},$	A. 83
$V_{ci} = \frac{M_{ci}}{d_{ci}},$	A. 84
$V_{mother\ liquor} = V_{water} + \sum_{i=1}^N V_{ci},$	A. 85
$V_{liq,tot} = V_{mother\ liquor},$	A. 86
$V_{tot} = V_{solids,total} + V_{liq,tot},$	A. 87
$C_{ci} = \frac{M_{ci} \cdot 1000}{MW_{ci} \cdot M_{water}}$	A. 88

$$Q_{cryst_{ice}} = \frac{M_{ice, reactions} \times \Delta H_{fus, ice}}{\Delta t} \quad A. 89$$

$$Q_{cryst_{i, cr}} = \frac{M_{ci, cr, r} \times \Delta H_{fusion, ci}}{\Delta t} \quad A. 90$$

$$Q_{total} = Q_{cryst_{ice}} + Q_{cryst_{i, cr}} - r_{cooling} \quad A. 91$$

$$\%Na_2SO_4 = \frac{M_{ci, cr}}{M_{liq, total}} \times 100 \quad A. 92$$

$$\%Water = \frac{M_{water}}{M_{liq, total}} \times 100 \quad A. 93$$

$$\%Ci = \frac{M_{ci}}{M_{liq, total}} \times 100 \quad A. 94$$

$$\%Ice = \frac{M_{ice}}{M_{liq, total}} \times 100 \quad A. 95$$

$$Cp_{solution} = (0.9988 - 0.006494 \times \%Na_2SO_4 + 0.00003025 \times \%Na_2SO_4^2 - 0.0000001286 \times \%Na_2SO_4^3) \times 4.184 \times 1000 \quad A. 96$$

$$T_{reactor} = \frac{Q_{total} \times \Delta t}{M_{liq, total} \times Cp_{solution} + M_{ci, cr} \times Cp_{ci} + M_{ice} \times Cp_{ice}} + T_{reactor} \quad A. 97$$

A.6. Electrodialysis with Bipolar membranes (EDBM) model

EDBM is a membrane-based technology that allows the production of acidic and alkaline solutions by applying an electric potential to the electrodes. In this work, EDBM aims to convert NaCl molecules of a brine solution to NaOH and HCl solutions. The model is built based on Xevgenos *et al.* (2023) report (see Section 3.2.5.) and described in Table A.7. The process is simulated as feed and bleed configuration as it is described in (Cassaro *et al.*, 2023). The model calculates the flow rate of the acid, base and salt solutions, their ion concentration, and the electricity requirements of the unit.

Assumptions on EDBM:

- Active area of the membrane across which ion permeation occurs
- Number of triplets
- Membrane characteristics (from experimental data)
- Ideal transport phenomena
- Recycling rate
- Pressure drop

Table A. 7. Equations for EDBM process unit (Xevgenos et al., 2023)

Equation	
$I_{ext} = A \cdot I_d$	A. 98
$JA = \frac{3.6 \cdot I_{ext}}{F}$	A. 99

$$V_{ext} = EMF + \left(\frac{I_{ext} * R_{int}}{A * 10000} \right) N_{trip} \quad A. 100$$

$$EMF = \left(\frac{R * T}{z * F} \left(\ln \left(\frac{C_{H^+}^{m,acid}}{C_{H^+}^{m,bp}} \right) + \ln \left(\frac{C_{OH^-}^{m,bp}}{C_{OH^-}^{m,base}} \right) + \ln \left(\frac{C_{Cl^-}^{m,salt}}{C_{Cl^-}^{m,acid}} \right) + \ln \left(\frac{C_{Na^+}^{m,base}}{C_{Na^+}^{m,salt}} \right) \right) \right) N_{trip} \quad A. 101$$

$$P = V_{ext} * I_{ext} \quad A. 102$$

$$Q_{1 \text{ triplet}}^{IN,salt} = \frac{Q_{tot}^{salt}}{N_{trip}} \quad A. 103$$

$$Q_{1 \text{ triplet}}^{IN,acid} = \frac{Q_{tot}^{acid}}{N_{trip}} \quad A. 104$$

$$Q_{1 \text{ triplet}}^{IN,base} = \frac{Q_{tot}^{base}}{N_{trip}} \quad A. 105$$

$$M_i^{IN,j} = Q_{1 \text{ triplet}}^{IN,j} * C_i^{IN,j} * PM_i * 10^{-3} \quad A. 106$$

$$M_{Cl^-}^{INN,salt} = Q_{1 \text{ triplet}}^{IN,salt} * C_{Cl^-}^{IN,salt} * PM_{Cl^-} * 10^{-3} + \left(\frac{M_{H^+}^{IN,salt}}{PM_{H^+}} - \frac{M_{OH^-}^{IN,salt}}{PM_{OH^-}} \right) * PM_{Cl^-} \quad \text{if } pH_{salt} < 7 \quad A. 107$$

$$M_{Cl^-}^{INN,salt} = Q_{1 \text{ triplet}}^{IN,salt} * C_{Cl^-}^{IN,salt} * PM_{Cl^-} * 10^{-3} + \left(\frac{M_{OH^-}^{IN,salt}}{PM_{OH^-}} - \frac{M_{H^+}^{IN,salt}}{PM_{H^+}} \right) * PM_{Cl^-} \quad \text{if } pH_{salt} > 7 \quad A. 108$$

$$M_{1 \text{ triplet}}^{IN,j} = Q_{1 \text{ triplet}}^{IN,j} * density_{j \text{ sol.}} * 10^{-3} \quad A. 109$$

$$M_{H_2O}^{IN,j} = M_{1 \text{ triplet}}^{IN,j} - \sum_{i=1}^n M_i^{IN,j} \quad A. 110$$

$$K_w^{IN,j} = C_{H^+}^{IN,j} * C_{OH^-}^{IN,j} \quad A. 111$$

$$M_{H^+}^{OUT,acid} = M_{H^+}^{IN,acid} + JA * PM_{H^+} \quad A. 112$$

$$M_{Cl^-}^{OUT,acid} = M_{Cl^-}^{IN,acid} + JA * PM_{Cl^-} \quad A. 113$$

$$M_{OH^-}^{OUT,acid} = M_{OH^-}^{IN,acid} \quad A. 114$$

$$M_{Na^+}^{OUT,acid} = M_{Na^+}^{IN,acid} \quad A. 115$$

$$M_{H_2O}^{OUT,acid} = M_{H_2O}^{IN,acid} - 0.5 * JA * PM_{H_2O} \quad A. 116$$

$$M_{1 \text{ triplet}}^{OUT,acid} = \sum_{i=1}^n M_i^{IN,acid} \quad A. 117$$

$$Q_{1 \text{ triplet}}^{OUT,acid} = \frac{Q_{1 \text{ triplet}}^{OUT,acid} * 1000}{density_{acid}^{out}} \quad A. 118$$

$$C_i^{OUT,acid} = \frac{M_i^{OUT,acid}}{Q_{1 \text{ triplet}}^{OUT,acid} * PM_i * 10^{-3}} \quad A. 119$$

$$M_{Na^+}^{OUT,base} = M_{Na^+}^{IN,base} + JA * PM_{Na^+} \quad A. 120$$

$$M_{OH^-}^{OUT,base} = M_{OH^-}^{IN,base} + JA * PM_{OH^-} \quad A. 121$$

$$M_{Cl^-}^{OUT,base} = M_{Cl^-}^{IN,base} \quad A. 122$$

$$M_{H^+}^{OUT,base} = M_{H^+}^{IN,base} \quad A. 123$$

$$M_{H_2O}^{OUT,base} = M_{H_2O}^{IN,base} + 0.5 * JA * PM_{H_2O} \quad A. 124$$

$$M_{1 \text{ triplet}}^{OUT,base} = \sum_{i=1}^n M_i^{IN,base} \quad A. 125$$

$$Q_{1 \text{ triplet}}^{OUT,base} = \frac{M_{1 \text{ triplet}}^{OUT,base} * 1000}{density_{base}^{out}} \quad A. 126$$

$$C_i^{OUT,base} = \frac{M_i^{OUT,base}}{Q_{1 \text{ triplet}}^{OUT,base} * PM_i * 10^{-3}} \quad A. 127$$

$$M_{Na^+}^{OUT,salt} = M_{Na^+}^{IN,salt} - (M_{Na^+}^{OUT,base} - M_{Na^+}^{IN,base}) \quad A. 128$$

$$M_{Cl^-}^{OUT,salt} = M_{Cl^-}^{IN,salt} - (M_{Cl^-}^{OUT,acid} - M_{Cl^-}^{IN,acid}) \quad A. 129$$

$$M_{OH^-}^{OUT,salt} = M_{OH^-}^{IN,salt} \quad A. 130$$

$$M_{H^+}^{OUT,salt} = M_{H^+}^{IN,salt} \quad A. 131$$

$$M_{H_2O}^{OUT,salt} = M_{H_2O}^{IN,salt} \quad A. 132$$

$$M_{1 \text{ triplet}}^{OUT,salt} = \sum_{i=1}^n M_i^{IN,salt} \quad A. 133$$

$$Q_{1 \text{ triplet}}^{OUT,salt} = \frac{M_{1 \text{ triplet}}^{OUT,salt} * 1000}{density_{salt}^{out}} \quad A. 134$$

$$C_i^{OUT,salt} = \frac{M_i^{OUT,salt}}{Q_{1 \text{ triplet}}^{OUT,salt} * PM_i * 10^{-3}} \quad A. 135$$

$$PP = \frac{(\sum_{j=1}^3 Q_{1 \text{ triplet}}^{IN,j} * \Delta P_j) * N_{trip}}{eff_{pump}} * 10^{-3} \quad A. 136$$

A.8. Electrodialysis (ED) model

ED is a membrane-based technology that allows the transport of salt ions from one solution another solution by applying an electric potential. In this work, ED aims to concentrate further saline solution. The model is build based on (Nayar, Fernandes, McGovern, Dominguez, et al., 2019) as it is described in Table A.2. The model calculates the flow rates of dilute and concentrate streams, their ion concentration, and the electricity requirements of the unit.

Assumptions:

- Salinity at outlets ($S_{c,o}$)

- Number of identical parallel cell-pairs (N_{cp})
- Number of computational cells (N)
- Voltage applied across an ED cell-pair (V_{cp})
- Voltage across the electrodes (V_{el})
- Membrane efficiency (Mem_{eff})
- Pressure drop

Table A.2. Equations for ED process unit (Nayar, Fernandes, McGovern, Al-Anzi, et al., 2019).

Equation	
$S_{c,k+1} = S_{c,k} + \frac{S_{c,o} - S_{c,i}}{N - 1}$	A. 137
$S_{c,k+1} = \frac{N_{s,d,j} MW_s}{\frac{N_{w,d} MW_w}{1000}}$	A. 138
$N_{s,c,j} = \frac{m_{c,j} \cdot S_{c,j}}{1000 \cdot MW_s}$	A. 139
$N_{s,c,j+1} - N_{s,c,j} = A_{cp,tot,j} \cdot J_{s,j}$	A. 140
$N_{w,c,j+1} - N_{w,c,j} = A_{cp,tot,j} \cdot J_{w,j}$	A. 141
$N_{cp} = \frac{\sum_{j=1}^N A_{cp,tot,j}}{A_{cp}}$	A. 142
$J_{s,j} = T_{s,j} \cdot \frac{i_j}{F} - L_{s,j} \cdot (C_{c,m,j} - C_{d,m,j})$	A. 143
$J_{w,j} = T_{w,j} \cdot \frac{i_j}{F} + L_{w,j} \cdot (\pi_{c,m,j} - \pi_{d,m,j})$	A. 144
$T_s^{cp} = -4 \cdot 10^{-6} S_d^2 + 4 \cdot 10^{-5} S_d + 0.96 \pm 0.04$	A. 145
$T_w^{cp} = -4 \cdot 10^{-5} S_d^2 - 1.9 \cdot 10^{-2} S_d + 11.2 \pm 0.6$	A. 146
$L_s^{cp} = \min (2 \cdot 10^{-12} S_d^2 - 3 \cdot 10^{-10} S_d + 6 \cdot 10^{-8},$ $2 \cdot 10^{-12} S_c^2 - 3 \cdot 10^{-10} S_d + 6 \cdot 10^{-8}) \pm 6 \cdot 10^{-9}$	A. 147
$L_w^{cp} = 5 S_c^{-0.416} \pm 2 \cdot 10^{-5}$	A. 148
$N_{s,d,j+1} - N_{s,d,j} = -A_{cp,tot,j} \cdot J_{s,j}$	A. 149
$N_{w,d,j+1} - N_{w,d,j} = -A_{cp,tot,j} \cdot J_{w,j}$	A. 150
$Q_{d,j} = \frac{N_{w,d,j} MW_w}{\frac{d_w(1 - S_{d,j})}{1000}}$	A. 151
$Q_{c,j} = \frac{N_{w,c,j} MW_w}{\frac{d_w(1 - S_{c,j})}{1000}}$	A. 152

$A_{cp,tot,j} = N_{cp} \sum_{j=1}^N A_{cp,j}$	A. 153
$A_{mem,total} = 2 \frac{A_{cp,total}}{Mem_{eff}}$	A. 154
$W_{ED,stack} = \sum_{j=1}^N i_j A_{cp,j} (N_{cp} V_{cp} + V_{el})$	A. 155
$W_{ED,stack} = \frac{\Delta P_{dil} Q_{dil,in}}{n_{p,ED}} + \frac{\Delta P_{con} Q_{con,in}}{n_{p,ED}}$	A. 156
$W_{ED} = W_{ED,stack} + W_{ED,pump}$	A. 157

B. Economic models

The major costs of a desalination plant are composed of capital expenditure (CAPEX) and operating expenditure (OPEX).

B.1. Capital costs

The CAPEX consists of fixed-capital investment and working capital, and the former one includes hardware costs, costs of buildings, process, and auxiliary, land, working capital and other indirect costs (Peters, Timmerhaus and West, 2003).

For the economic analysis of a full-scale desalination plant, the equipment costs of pilot-scale units are scaled-up to a capacity of 30000 m³/d. The equipment (material) costs of the full-scale plant are derived from the cost of the same equipment in the pilot plant with known capacity using equation B.1, known as six-tenths factor rule (m=0.6) (Peters, Timmerhaus and West, 2003). For desalination plants the exponent m is usually closer to 0.8 (Wittholz *et al.*, 2008; Zhang *et al.*, 2021), which is used in this work:

$$\frac{\text{Cost of purchased equipment(Plant A)}}{\text{Cost of purchased equipment(Plant B)}} = \left(\frac{\text{capacity of plant A}}{\text{capacity of plant B}} \right)^m \quad \text{B. 1}$$

For the calculation of the annualized CAPEX, the amortization factor (α) is used (see equation B.2, B.3) (Abraham and Luthra, 2011; Bilton *et al.*, 2011; Kesieme *et al.*, 2013; Choi *et al.*, 2015).

$$\text{Annualized CAPEX} = \text{CAPEX} * \alpha \quad \text{B. 2}$$

The amortization factor (α) is defined by:

$$\text{amortization factor } \alpha = \frac{i(1+i)^n}{(1+i)^n - 1} \quad \text{B. 3}$$

where i is discount rate, n is plant lifetime (year).

B.2. Operating costs

The OPEX refers to expenditure directly generated by manufacturing operation or connected to the equipment of a technical unit. Table B. 1 gives an overview of the costs that constitute OPEX (Peters, Timmerhaus and West, 2003). In this study, the utilities in this system are mainly energy, chemicals, and water costs. The calculation of yearly electrical (C_{el}) and thermal (C_{th}) energy costs follows equations B.4 – B.6:

$$C_{el} = E_{tot_{el}} \cdot t_{operation} \cdot P_{el} \quad \text{B. 4}$$

$$C_{th} = E_{tot_{th}} \cdot t_{operation} \cdot P_{steam} \quad \text{B. 5}$$

$$C_e = C_{el} + C_{th} \quad \text{B. 6}$$

Where:

E_{el} and E_{th} are the total energy consumption per operating hour (in kWh/hr),

$t_{operation}$ is the total operation time in one year (in hr),

P_{el} and P_{steam} are the prices of electricity and steam, respectively (in €/kWh).

The calculation of chemicals and water costs is similar to the energy cost, multiplying the amount of consumption every year by their price.

Table B. 1. Assumptions on CAPEX & OPEX (Peters, Timmerhaus and West, 2003; Papapetrou et al., 2017).

CAPEX		Annual OPEX	
Installation	25% of purchased equipment cost	Maintenance	3% of the fixed-capital investment
Buildings, process, and auxiliary	20% of purchased equipment cost	Operating Supplies	5% of maintenance
Land	6% of purchased equipment cost	Operating Labor	15% of annual OPEX
Indirect costs	15% of direct cost	Direct supervisory and clerical labor	15% of operating labor
Working capital	20% of total investment cost	Laboratory charges	15% of operating labor

Patents and royalties 3% of annual OPEX

Fixed charges 5% of annual OPEX

Plant overhead costs 5% of annual OPEX

Nanofiltration & Reverse Osmosis

C Concentration, mol/kg
dP Net driving force (Pressure drop), bar
Q Flow rate, m³/h
P Pressure, bar
P Power, W
R Rejection rate
T Temperature, K
WR Water Recovery, -

Subscripts

i Sea water ion, mg/L

Greek letters

π Osmotic pressure, bar

Multi-Effect Distillation

A Heat transfer area, m²
B Brine flow rate, m³/h
C_p Specific heat capacity
D Distillate flow, m³/h
M Flow rate, m³/h
Q Thermal load, KW
SA Specific heat transfer area, m²/m³
T Temperature, K
U Heat transfer coefficient
X Salt concentration, mg/L

Subscripts

c Condenser
cw Cooling water

d	Distillate
f	Feed
i	Sea water ion
n	Number of effect
s	Steam

Greek letters

Δ	Difference
λ	Latent heat

Thermal Crystallizer

A	Heat transfer area, m ²
C	Concentration, g/L
C _p	Specific heat capacity
d	density
LHV	Latent heat
M	Flow rate, m ³ /h
Q	Thermal load, KW
T	Temperature, K
U	Heat transfer coefficient

Subscripts

cw	Cooling water
d	Distillate
i	Initial
o	Outlet
op	operating
st	Steam
v	Vapor

Multiple Feed Plug Flow Reactor

C	Concentration, g/L
M	Mass flow rate, kg/h
P	Pressure, bar
MW	Molecular weight, g/mol
Q	Flow rate, m ³ /h

Greek letters

Δ Difference

Eutectic freeze crystallizer

C Concentration, g/L
d density, kg/m³
H Enthalpy, kJ/kg
M Mass flow rate, kg/h
MW Molecular Weight, g/mol
Q Heat flux, J/s
r cooling rate, J/s
V Volume, m³

Subscripts

c component
cr crystal
i number of component
in inflow
liq liquid

Greek letters

Δ Difference

Electrodialysis with Bipolar membranes

A Active area, m²
C Concentration, mol/L
EMF Electromotive force, V
F Faraday constant, C mol⁻¹
Id Current density, A m²
I_{ext} Applied electrical current, A
JA Transmembrane flow rate of ions, kmol/h
M Mass flow rate, kg/h
N Number of triplets
P Power, W
MW Molecular weight, g/mol
Q Flow rate, m³/h

V	Voltage needed, V
z	chemical valence of ion

Subscripts

bp	bipolar membrane
i	ion
j	channel
w	water

Electrodialysis

A	Area, m ²
C	Concentration, mol/m ³
J	Molar flux, mol/m ² s
L	Permeability
N	Molar flow rate, mol/s
Q	Flow rate, m ³ /h
S	Salinity, g salt/kg solution
T	Membrane transport number, -
W	Power, W

Subscripts

c	Concentrate
cp	Cell-pairs
d	Diluate
el	Electrodes
eff	Efficiency
i	Inlet
o	Outlet
p	Product
s	Salt
w	Water

Greek letters

Δ	Difference
π	Osmotic pressure, bar

Economic

a	Amortization factor, -
C	Cost
i	Discount rate, -
m	Six-tenths factor rule, -
n	Plant lifetime, year
P	Price, €/kWh or €/Ton
t	Time, h

Subscripts

e	Energy
el	Electricity
th	Thermal energy

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