# Crystallization Modeling in WaterTAP

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## Crystallization for Water Treatment

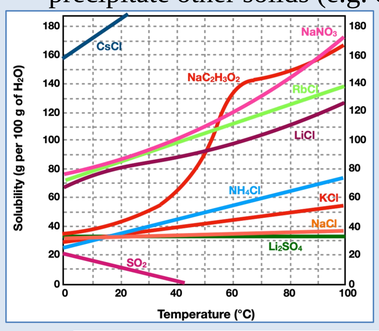
- Crystallization is the precipitation and extraction of the crystals from a mother liquor based on solute supersaturation.
- Potential solution to desalination's environmental brine management problem: brine crystallization systems shown to achieve ZLD and salt recovery.
- WaterTAP contains single- and multi-component crystallizer models that can be operated sequentially to achieve multi-stage crystallization.

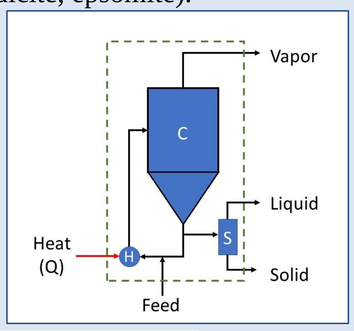
## Approach: Single, Multi-component & Multi-Stage Crystallization

- Traditional approach for industrial crystallizer design, based on material and energy balances + solubility constraints.
- Crystal production rate and degree of supersaturation largest determinant of crystallizer dimensions.
- Crystallizers for Na, Ca/Mg

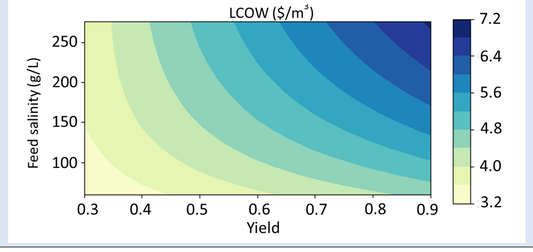
### NaCl (Halite) 0-D Crystallizer: Evaporative Crystallization

- Evaporative crystallization for $H_2O$-NaCl system: solid phase formed by water evaporation from boiling solution at fixed T
- Forced circulation (FC) crystallizer : most suitable type for substances with flat solubility curves, e.g., NaCl [1].
- Generic M&E balance equations –easily modifiable to precipitate other solids (e.g. calcite, epsomite).




*LCOW at varying yields and feed salinities for operation at 80°C*



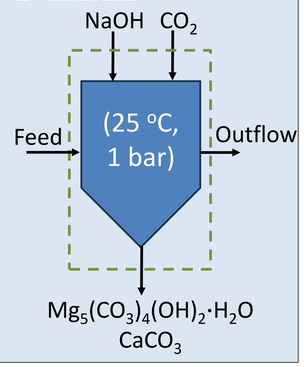

## Mg/Ca Crystallizer: Crystallization via Precipitation

- Hydromagnesite and calcite precipitation via NaOH & $CO_2$ addition

$$5\,Mg^{2+} + 4\,CO_2 + 10\,HO^- \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$$

$$Ca^{2+} + CO_2 + 2\,HO^- \rightarrow CaCO_3 + H_2O$$

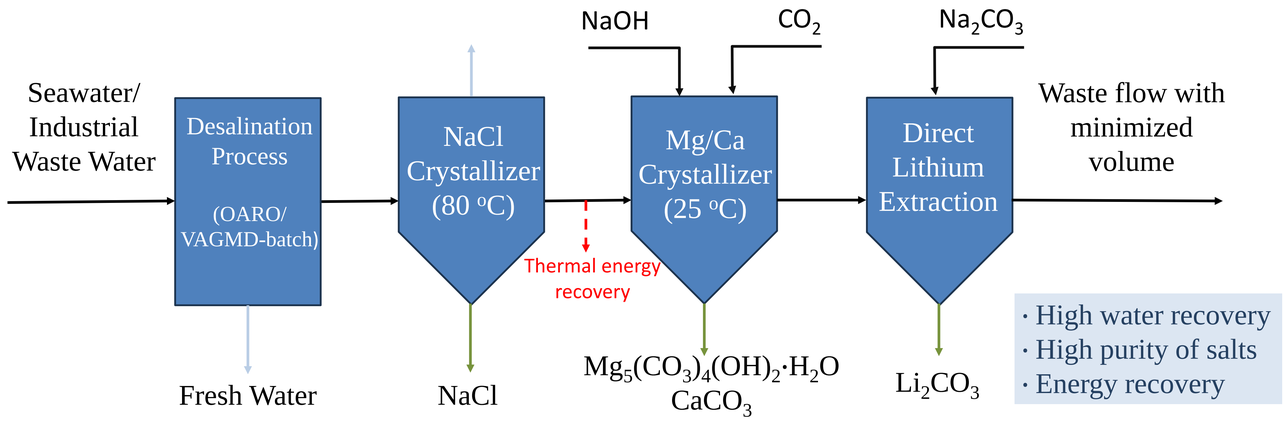
- Higher extraction rate of Mg compared to conventional crystallization of epsomite
- PhreeqC for determining saturation status, crystallization kinetics
- Given fully defined feed (FTPx), conversion rate and chemical kinetics information, WT model crystallizer estimates liquid and solid outlet flows, thermal and chemical requirements, salt production, LCOW




## Case Study: Multi-Stage Crystallization for Zero Liquid Discharge

- **Goal***: Technoeconomic assessment of brine treatment to zero liquid discharge (ZLD) via multi-crystallization separations*
- Sequential crystallization of NaCl, $MgCO_3$, $CaSO_4$ and $CaCO_3$ [2]
- Precious metal recovery: Lithium recovery with soda ash
- Pitzer activity model via PhreeqC for thermodynamic properties and ion activities.
- VAGMD-batch (85%), 90% NaCl yield, 90% Ca/Mg recovery

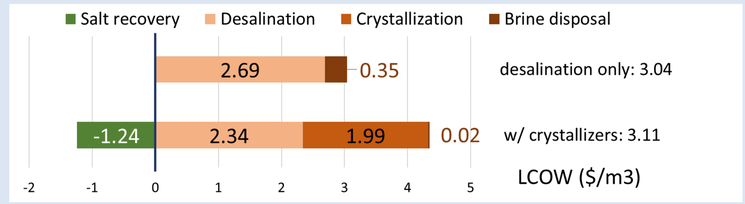
### Multi-stage Crystallization for Sequential Salt Extraction from Desalination Brine




## Results

| Seawater Feed | |
|---|---|
| Flow rate | 500 m³/day |
| NaCl | 35 g/L |
| Mg | 1.25 g/L |
| Ca | 0.4 g/L |

| Product | |
|---|---|
| Fresh Water | 425.63 m³/day |
| NaCl | 15785 kg/day |
| $CaCO_3$ | 494 kg/day |
| $Mg_5(CO_3)_4(OH)_2 \cdot H_2O$ | 2145 kg/day |
| Waste flow | 5.7 m³/day |




- Sequential crystallization post-desalination has similar LCOW (+2.3%) with conventional desalination in the base case, and can be further brought down with high Li concentration.
- Only 1.1% waste stream by volume – addresses brine disposal problem and lowers brine disposal costs.

## Future Work

- Incorporate Li recovery stage and costs for revenue computation.
- Extend Ca/Mg crystallizer model to enable variable operating temperatures and pressures.
- Improve PhreeqC integration for ion activity incorporation.

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## References

[1] Lewis, A.; Seckler, M. & Kramer, H. Industrial Crystallization: Fundamentals and Applications, **2015.**

[2] Techno-Economic Analysis of Brine Treatment by Multi-Crystallization Separation Process for Zero Liquid Discharge. *Separations, MDPI AG*, **2022**.

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