thermPhos

Successful antiscalant field trial – Optimization at higher pH & Sea water Temperature

Larnaca Desalination Plant, Cyprus

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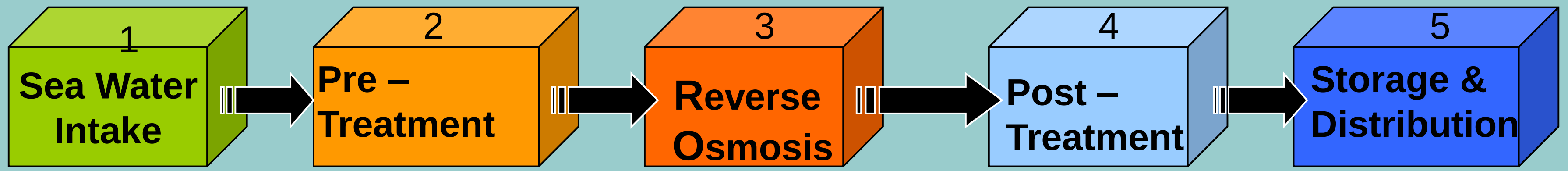
Sea Water
Desalination process

<u>Objectives</u>

- Produce drinking water using R.O. process to remove salts and impurities from sea water
- Use Energy efficient systems
- Water Quality complying with WHO guidelines (Boron < 1 ppm at Larnaca Desalination Plant)
- Achieve contractual water Quantity requirements
- Operate R.O. plant cost efficiently

Larnaca Desalination Plant Process



The Boron issue

<u>Boron Removal necessary due to</u>:

- Health effects
  - on mankind / infertility

- Plants / vegetation
  - fruit yield
  - leaf damage
  - ripening process

Boron membrane rejection

Function of *:*

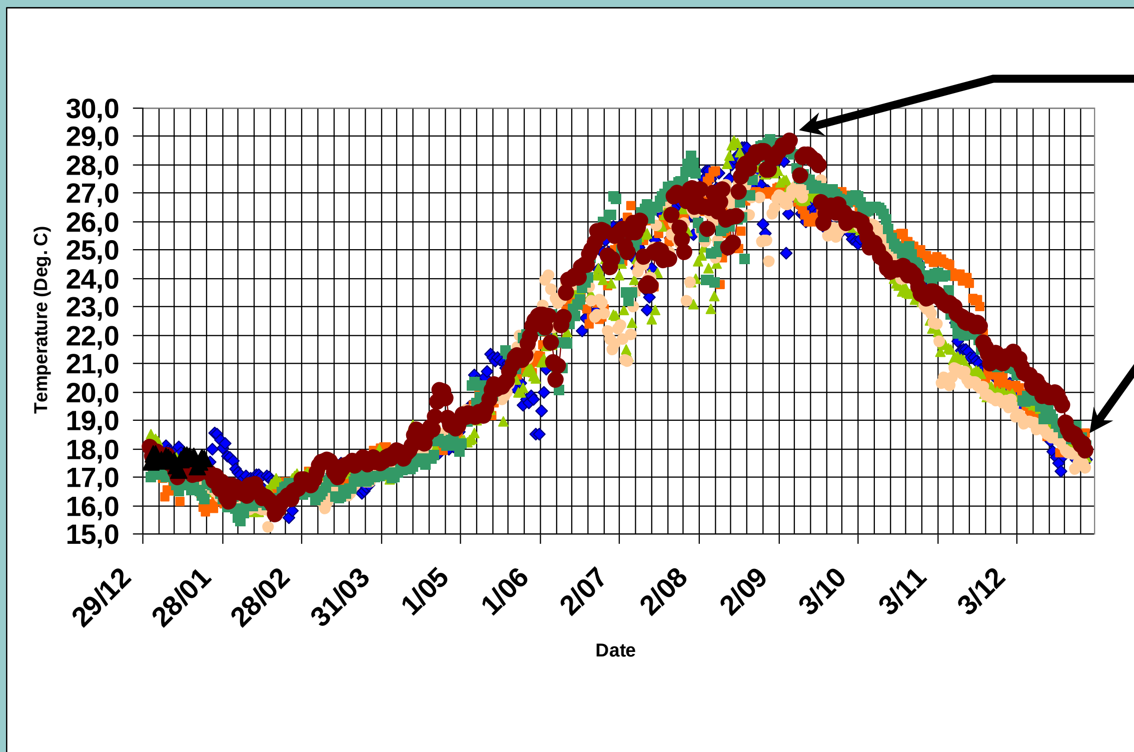
- Boron sea water concentration
- Sea Water Temperature
- Feed Water pH

Boron membrane rejection-Larnaca Desalination Plant

- Mediterranean Sea Water typical value for boron: 5 ppm
- Larnaca Desalination Plant - drinking water contractual value is < 1 ppm

Boron membrane rejection

Larnaca sea water temperature (5 year data)



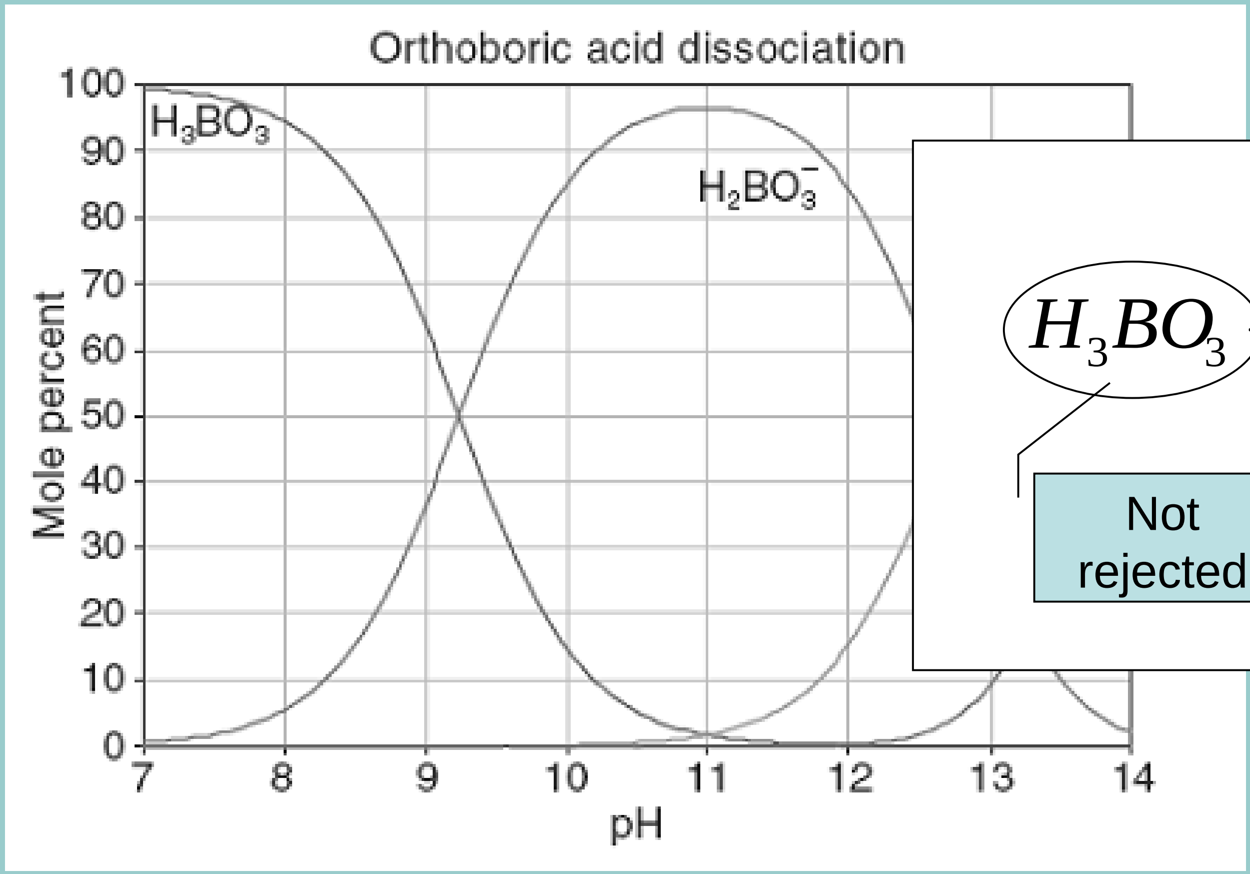
29°C

15°C

Boron rejection is decreasing when temperature increases

Boron membrane rejection

Boron species in seawater versus pH



$$H_3BO_3 \Leftrightarrow H^+ + H_2BO_3^-$$

Not rejected

Well rejected

Improve the Boron removal at Larnaca Desalination Plant

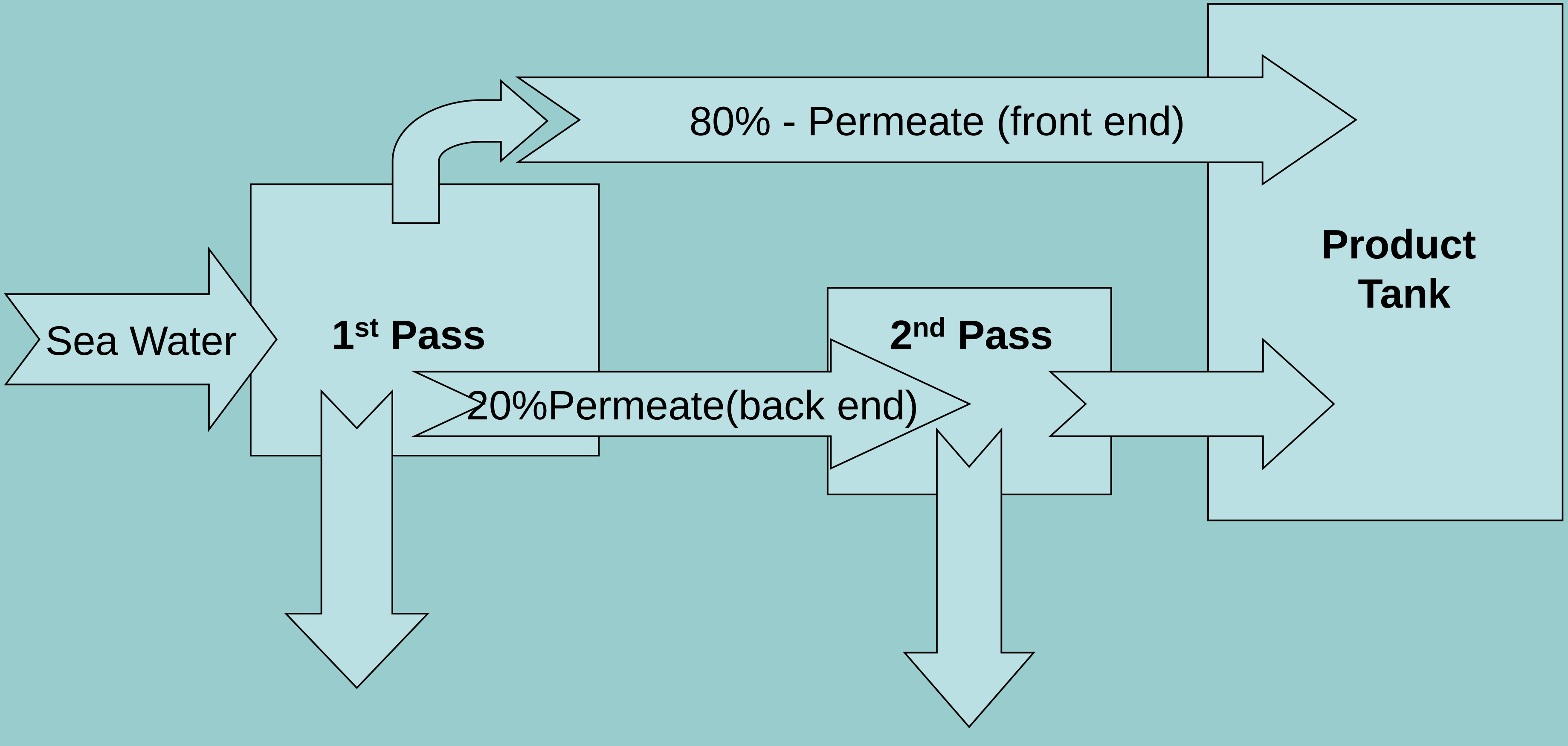
- Monitor uncontrollable parameters such as Sea water temperature & Boron feed concentration

- Innovative designs of Membrane Boron Removal

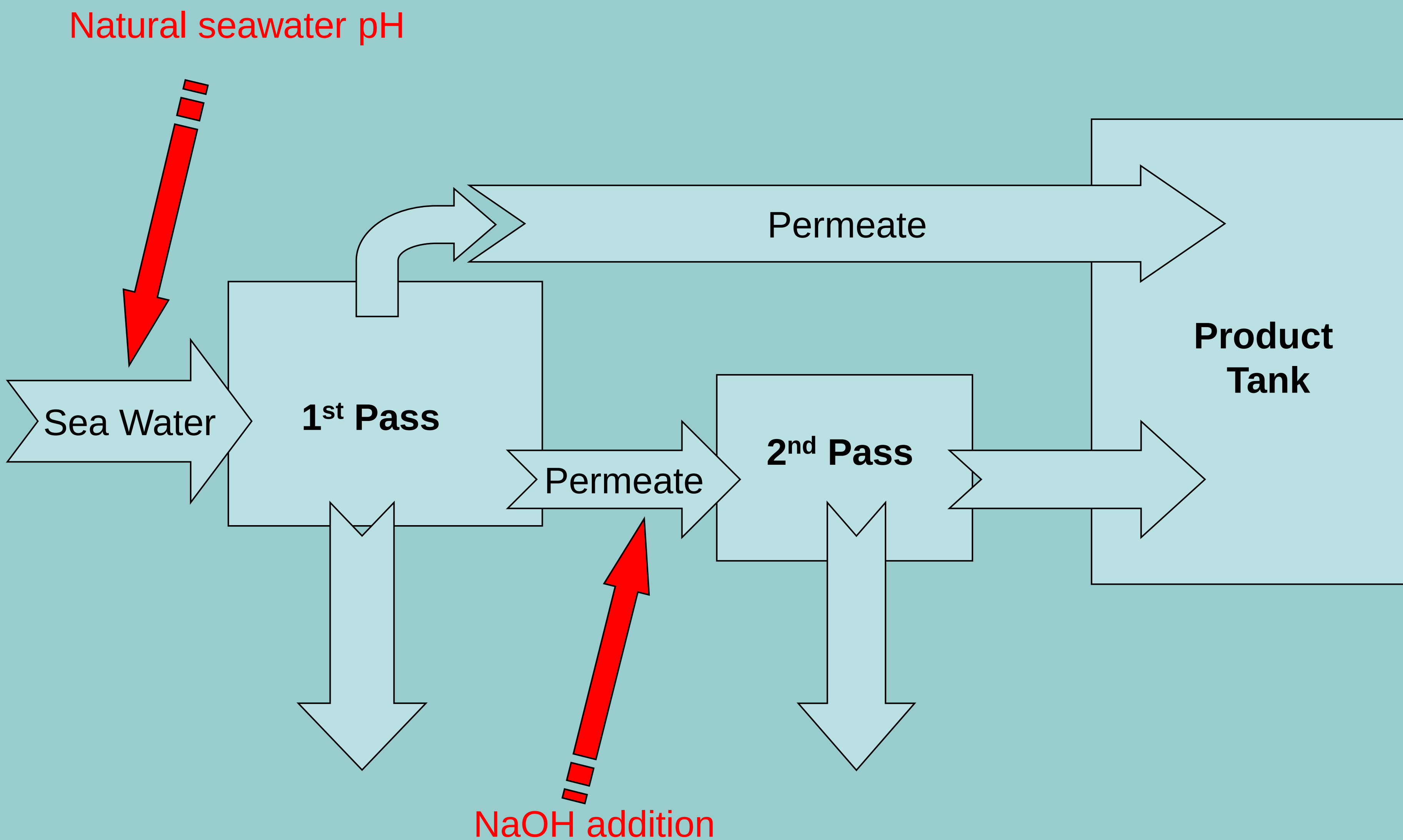
- Increase Boron removal of membranes by increasing pH

Larnaca innovative RO design

- Two pass design - LWP (Cyprus)

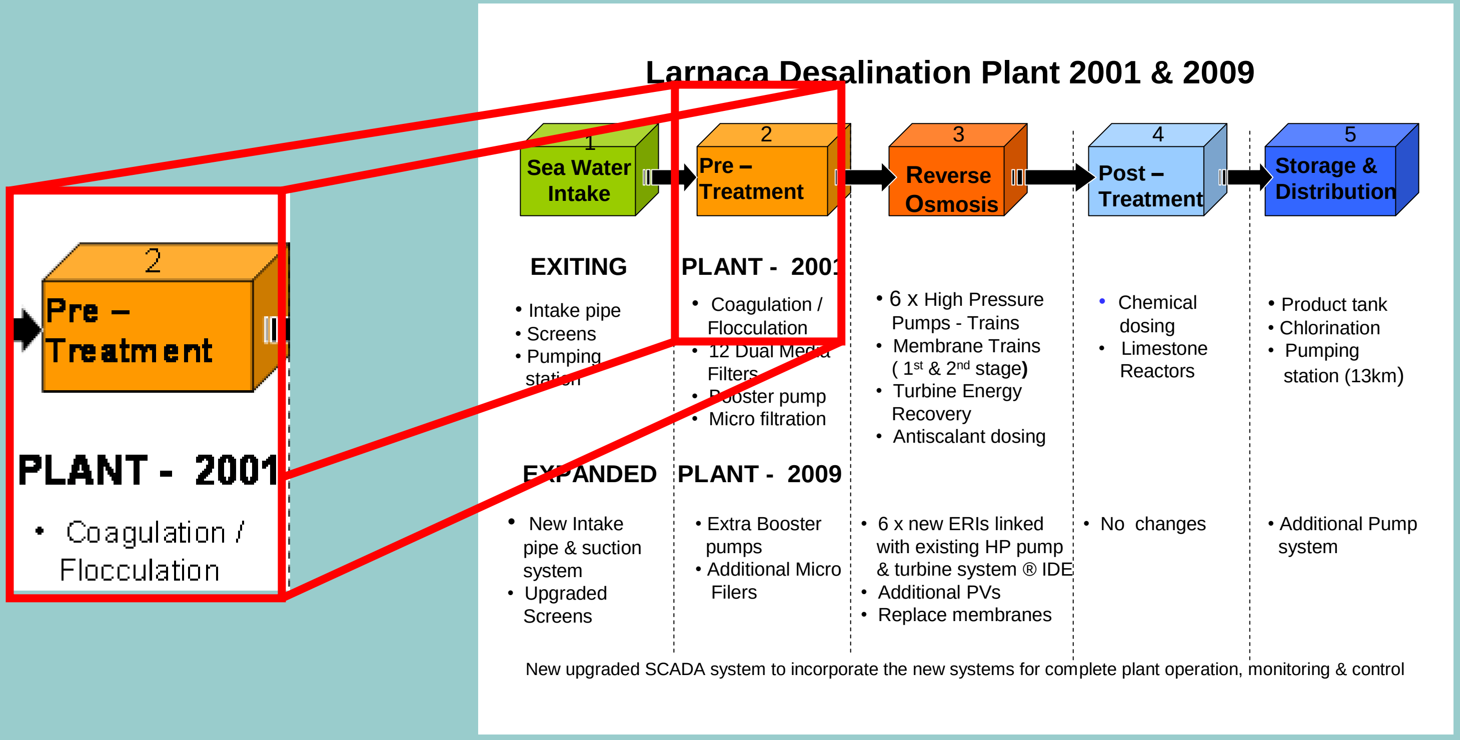


Increasing water pH



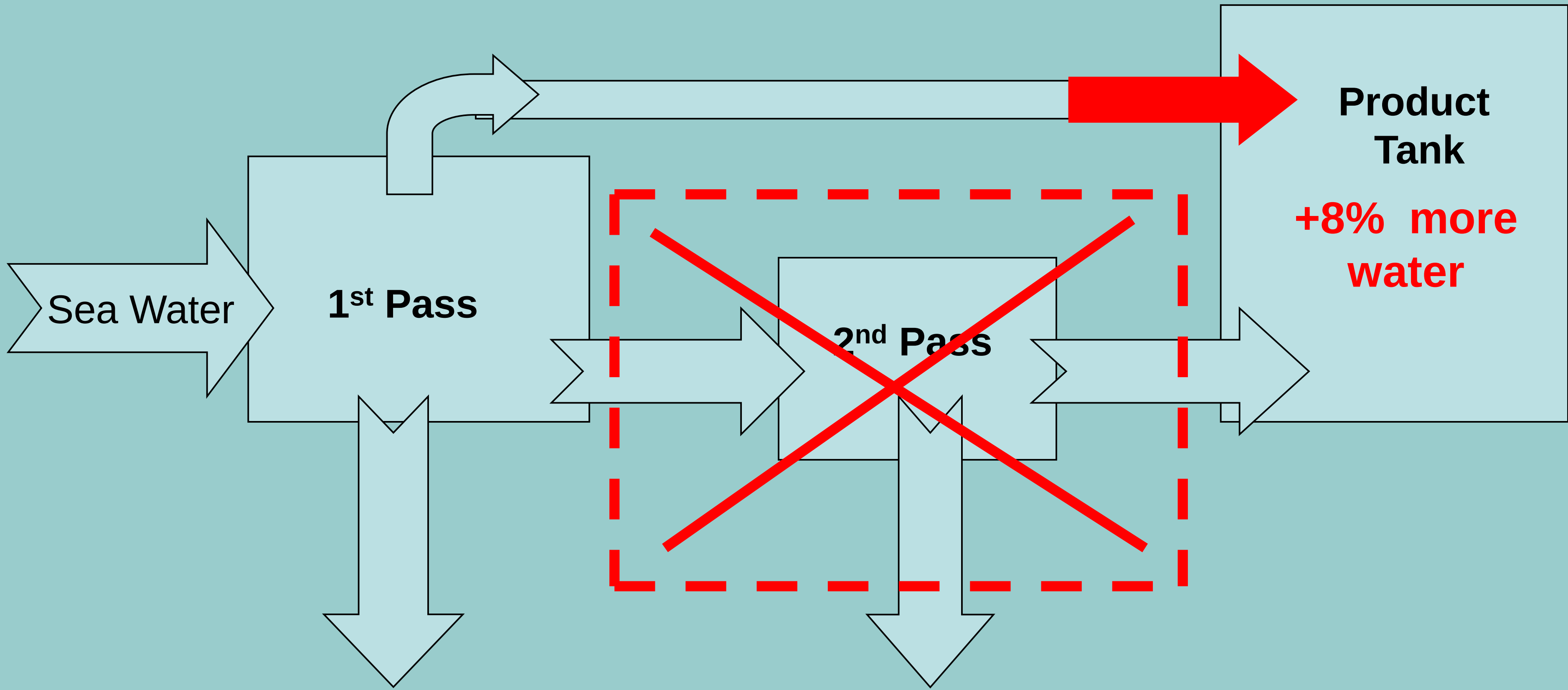
First pass high pH

Necessary steps - LWP global improvement processes



Innovative Operation

higher 1st RO stage pH ⟶ no 2nd pass for 6 months/ year



No 2nd pass → Less Energy → More Water

Problems induced by increased pH

- **<u>First pass</u>** (natural Sea Water pH=8.2)
  - $CaCO_3$ precipitation

- **<u>Second pass</u>** (pH > 9.0)
  - $CaCO_3$ precipitation
  - $Mg(OH)_2$ precipitation

Problems induced by increased pH

General parameters affecting plant operation

- Seasonal temperature variability (15°c to 30°c)
- LDP operational plant conditions versus time of the year
- LDP seawater composition and pH

Problems induced by increased pH

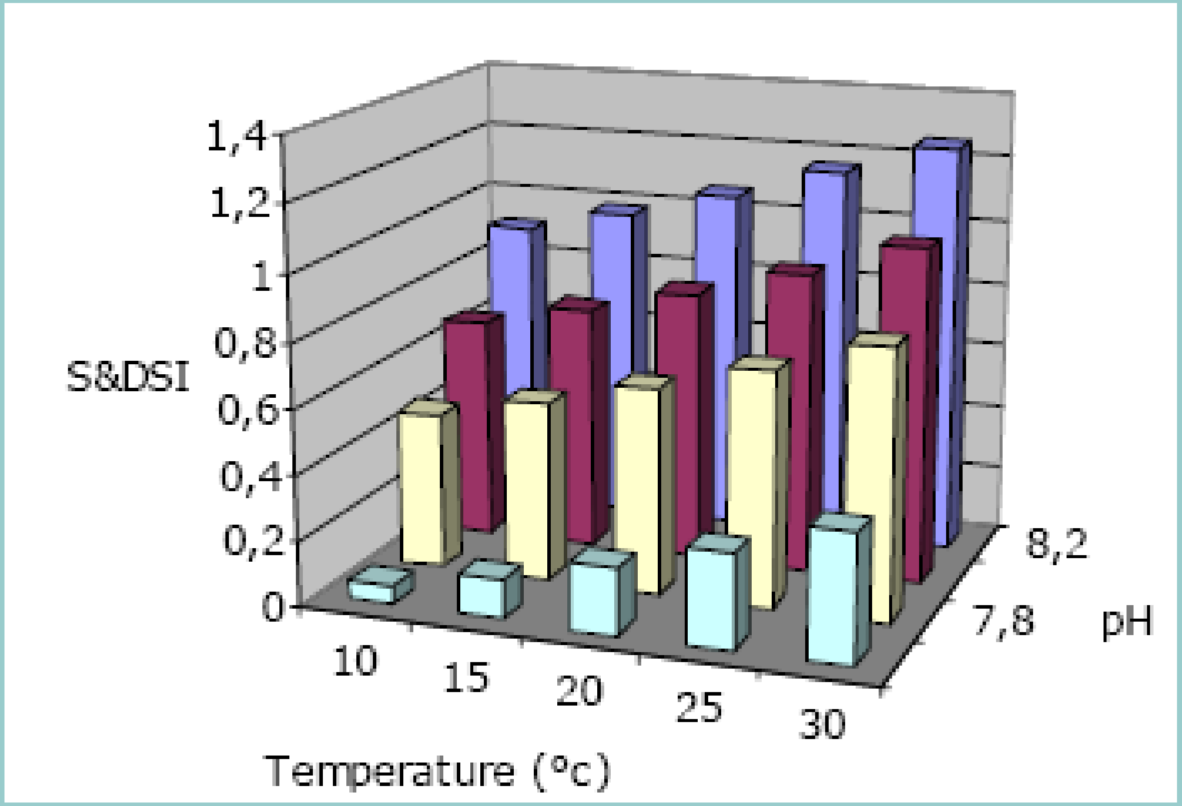
Saturation index estimation

- <u>First pass (pH=8.2)</u>
  - Issue: CaCO3 precipitation
  - classical S&DSI calculation approach
- <u>Second pass (pH > 9.0)</u>
  - Issue: CaCO3 precipitation
    - classical LSI calculation approach
  - Issue: $Mg(OH)_2$ precipitation – brucite (highly insoluble)
    - laboratory scaling simulation approach

Problems induced by increased pH

Saturation index calculation

First pass: S&DSI

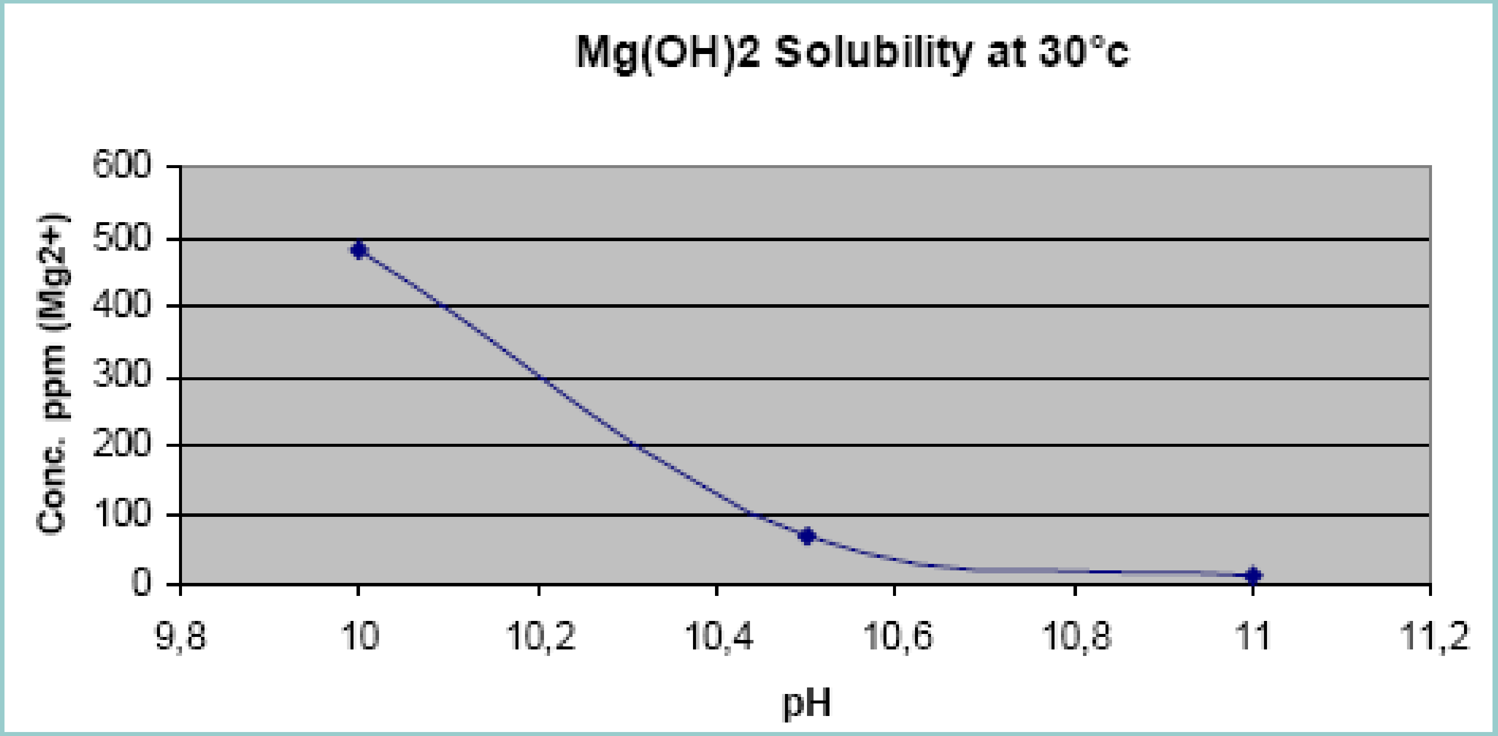


Problems induced by increased pH

Saturation index investigation

Second pass:

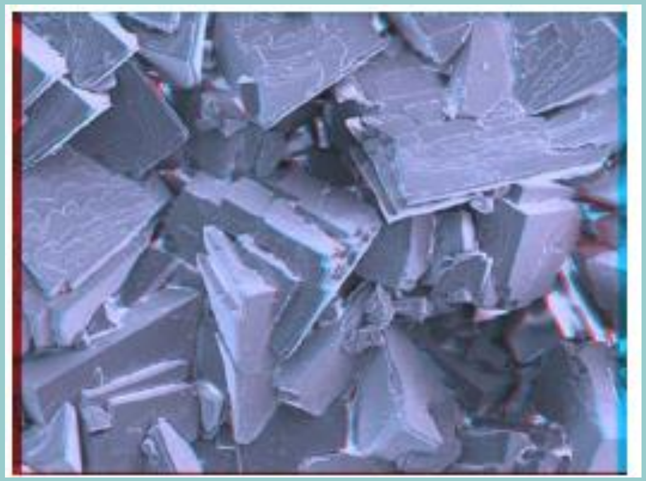
- Laboratory investigation under typical LWP conditions



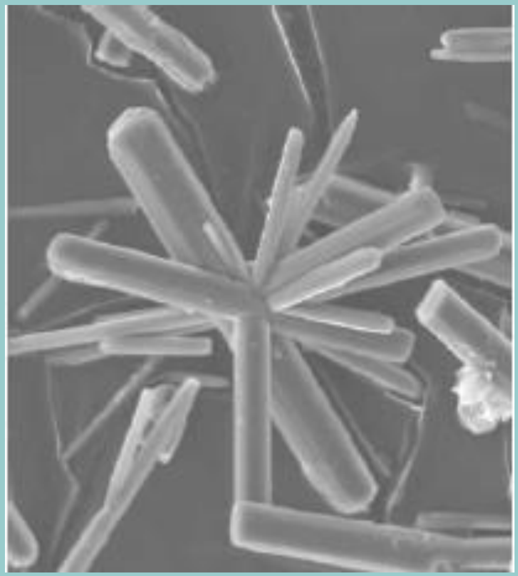
How to avoid problems induced by increased pH

Scaling potential statement

Both species are crystalline (SEM pictures)



$CaCO_3$



$Mg(OH)_2$

How to avoid problems induced by increased pH

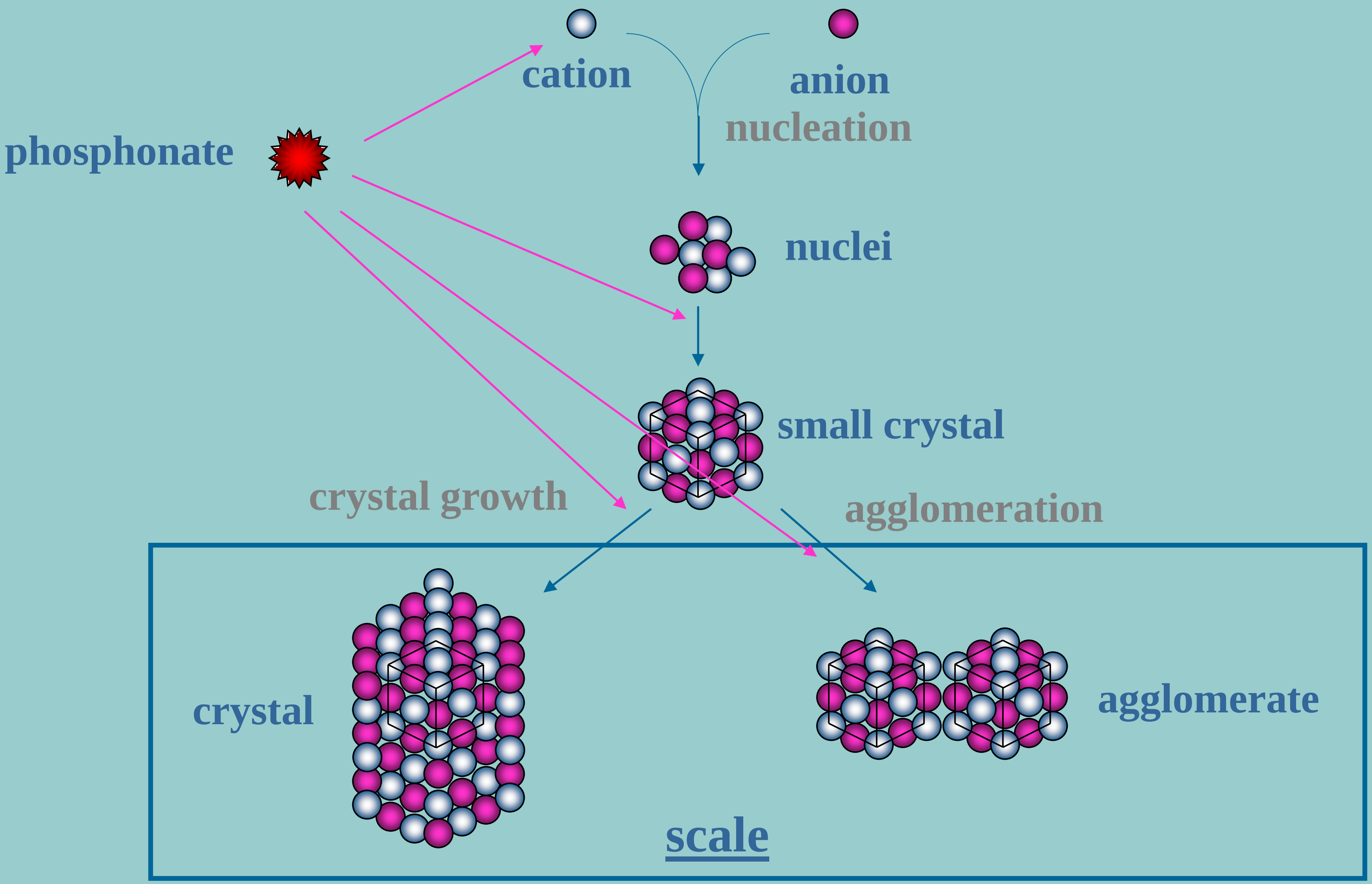
Scaling inhibition

⇒Dose specific anti-scalants with their specific capabilities/limitations

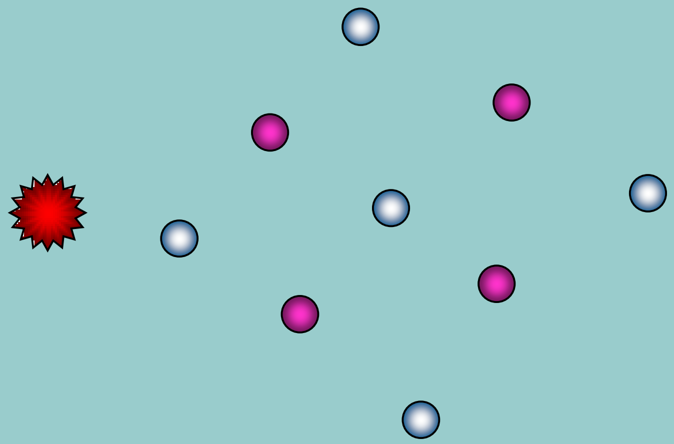
⇒Phosphonate based technology

- ⇒How does antiscalant work ?

Scale formation

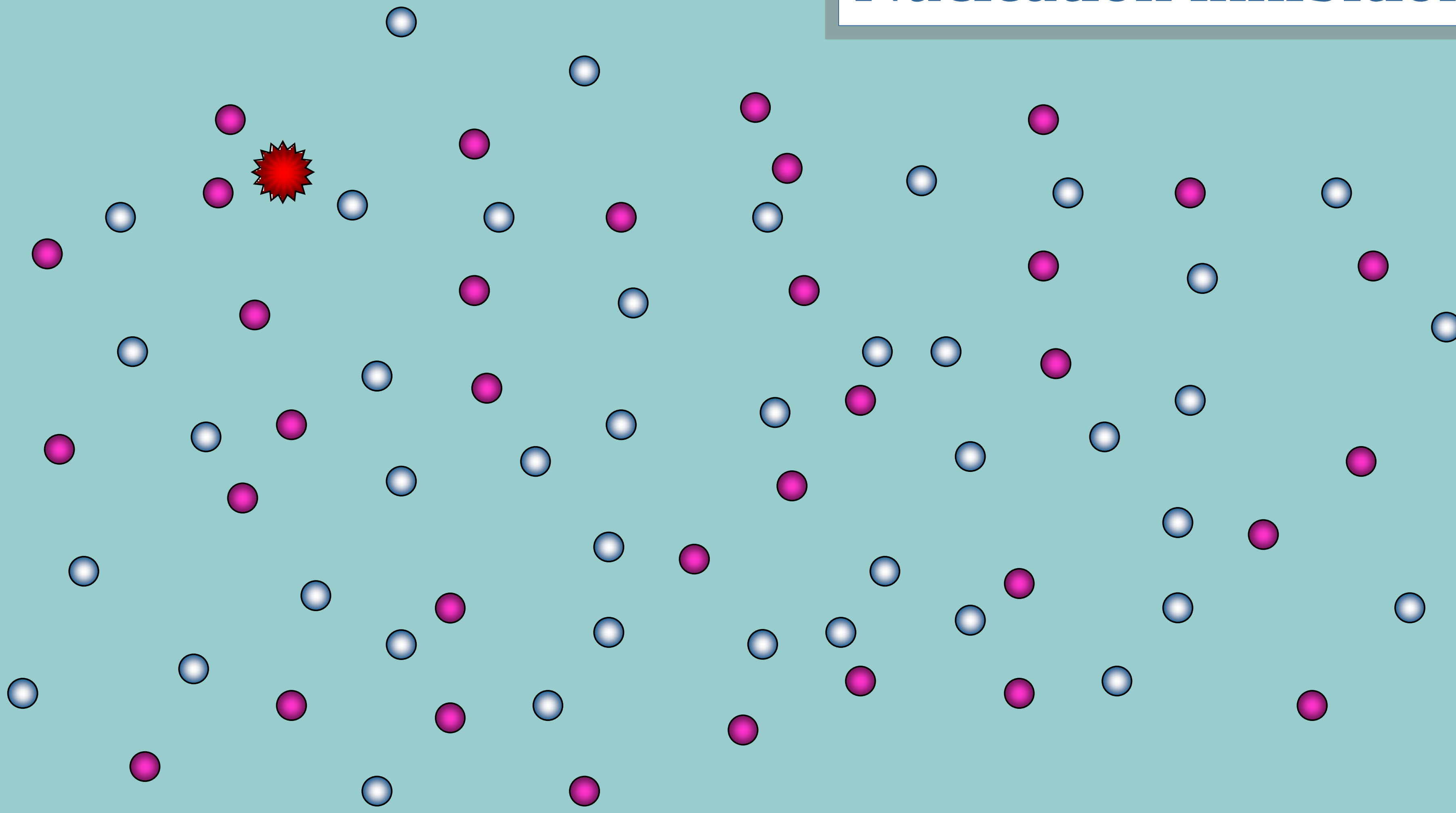


Chelation



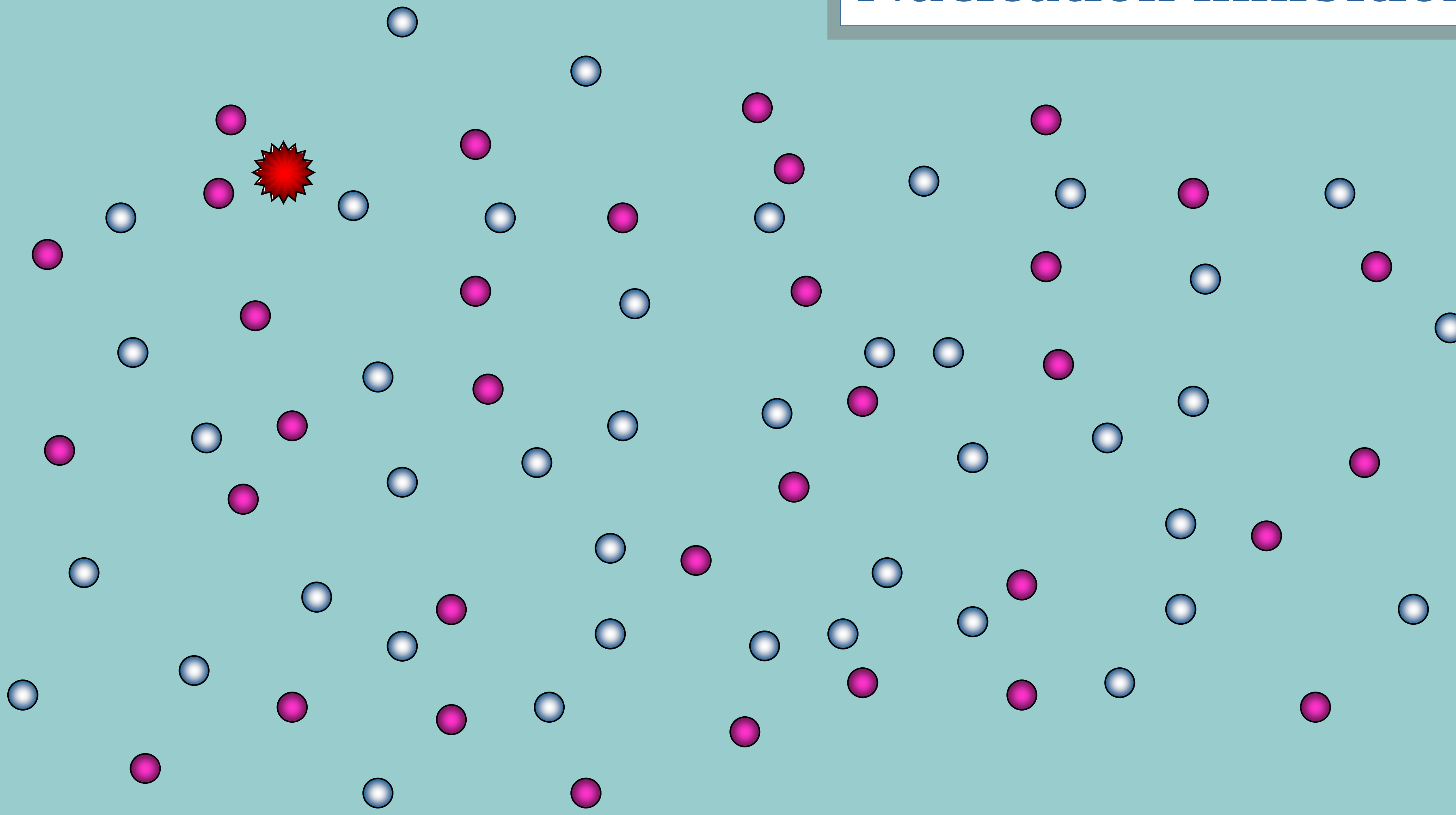
Multivalent positive ions are made unavailable

Nucleation inhibition



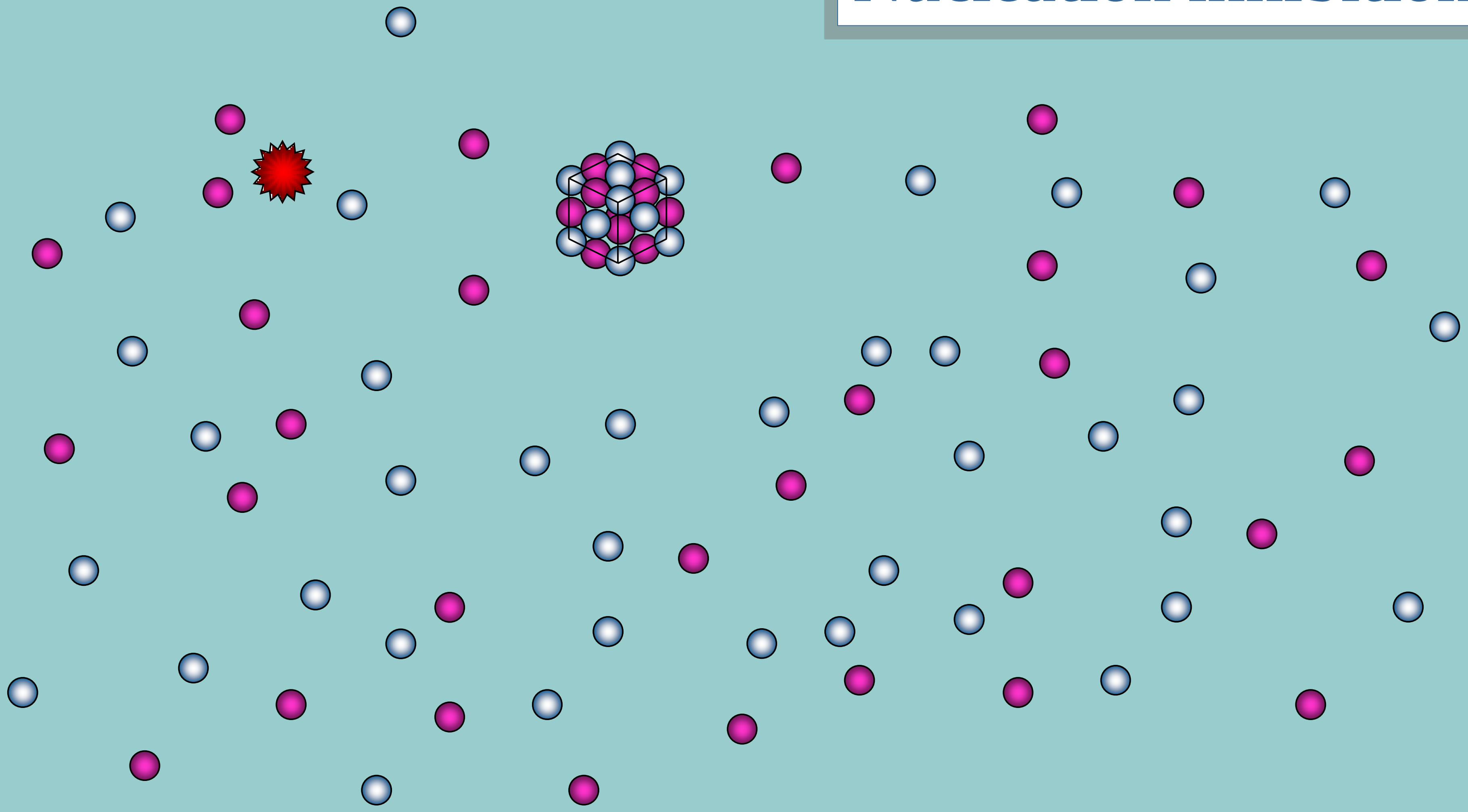
Competition between formation (K_f) and destabilization of (K_d) of nuclei

Nucleation inhibition



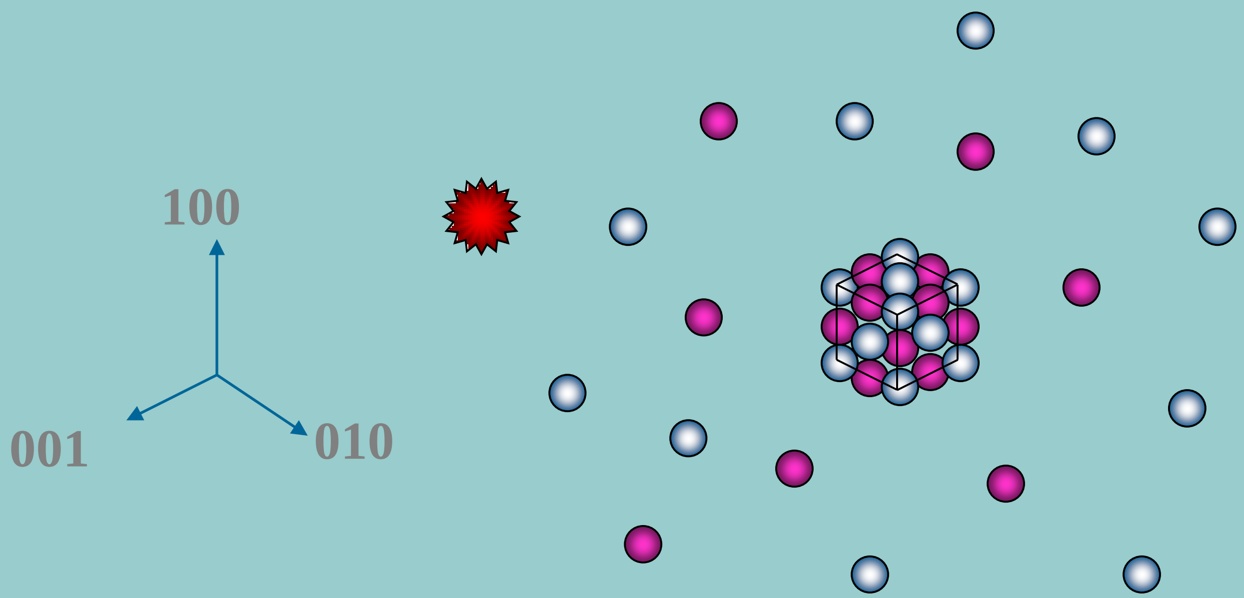
Induction time *f* of K_f, K_d, $[\text{cation}]^{n+}$, $[\text{anion}]^{n-}$ and [PhPh]

Nucleation inhibition



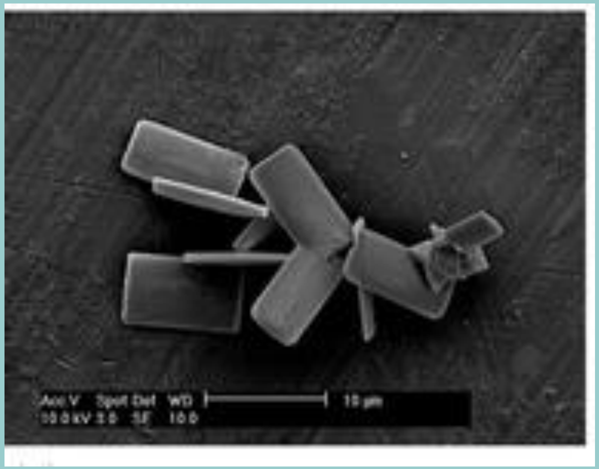
Crystal growth

Crystal growth modification

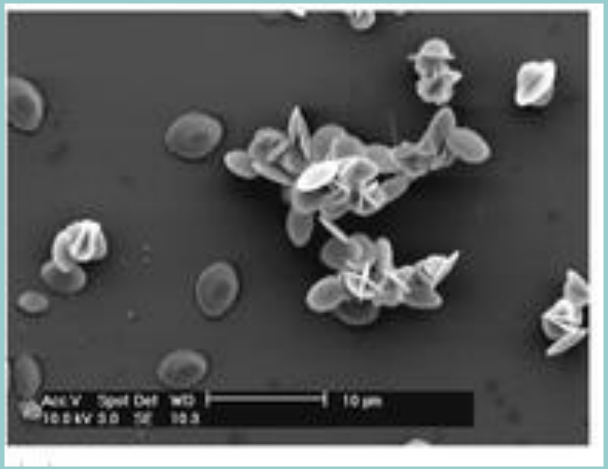


Adsorption on crystalite: small size distorted crystalite

Crystal growth modification



No inhibitor



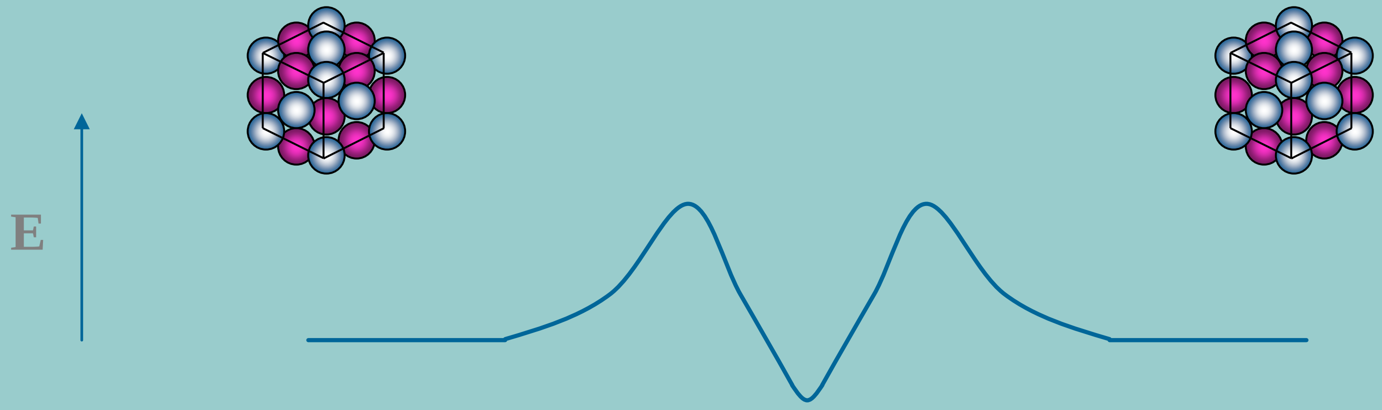
ATMP (5 ppm)

25 °C, pH 5.6 (0.25 mM BaSO4 – super-saturation ratio 25)

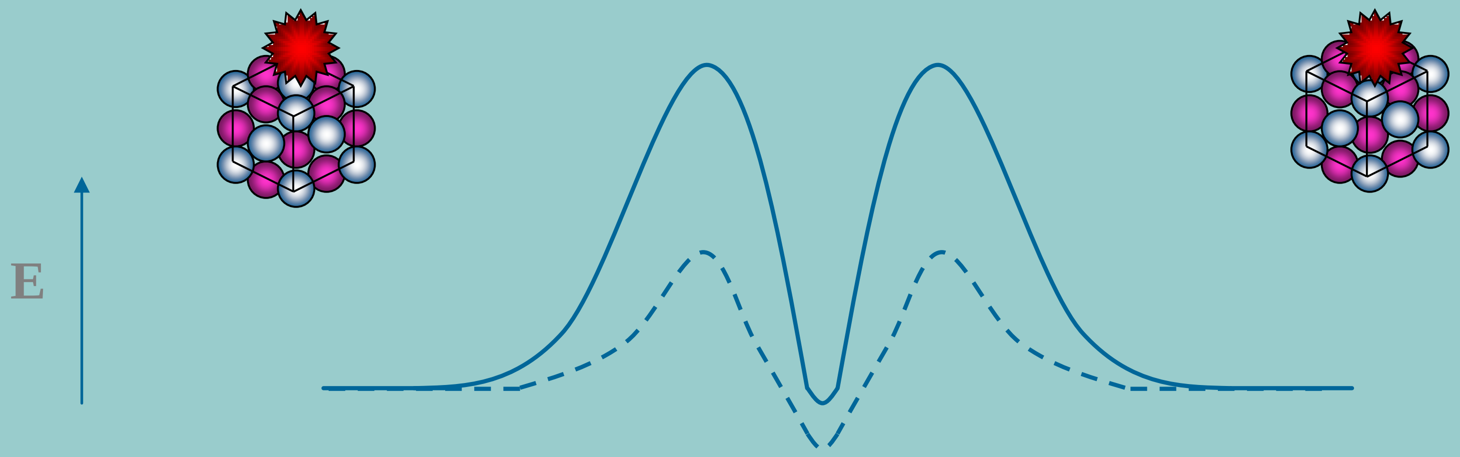
Jones et al. *CrystEngComm*, 2001, 3, 165-167

Dispersion

Without phosphonate

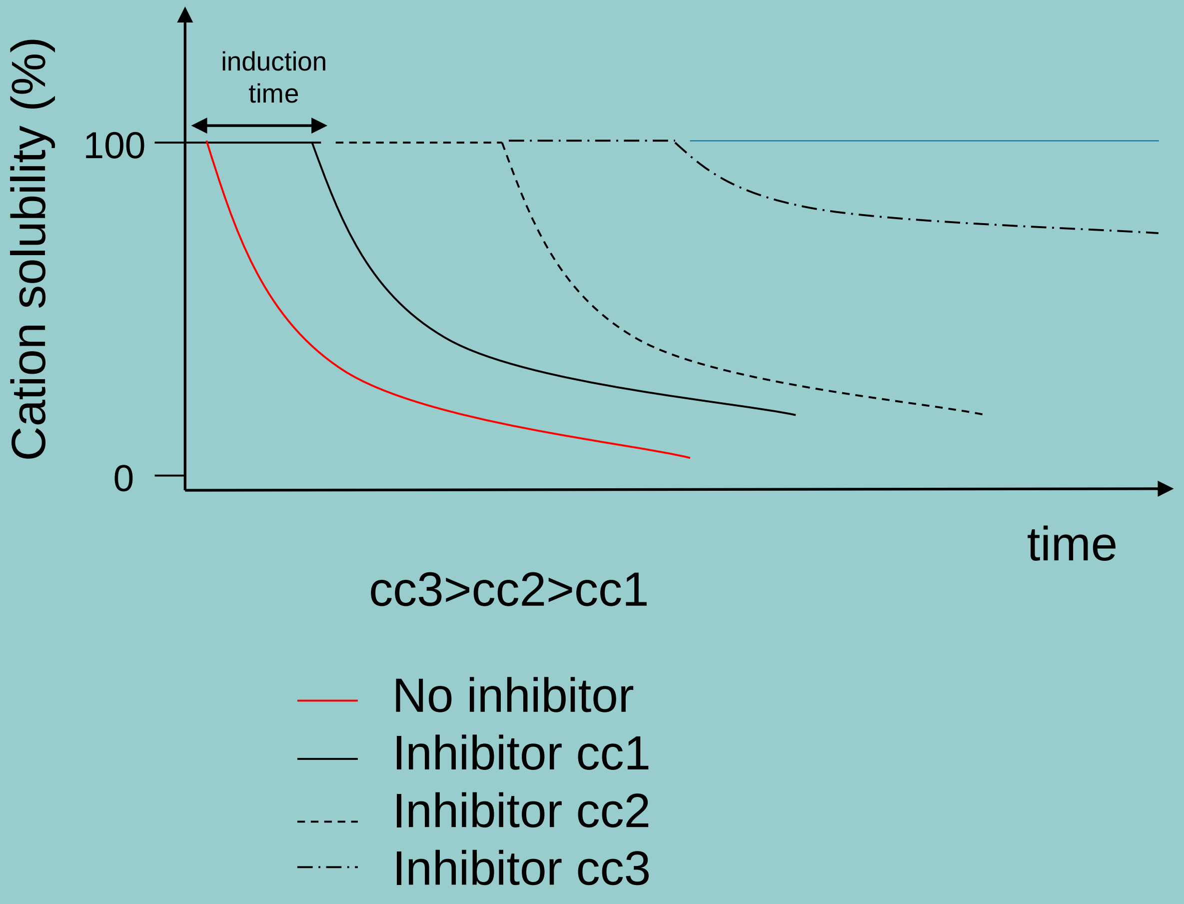


With phosphonate



Adsorption on particle: electrostatic repulsion

Inhibitor concentration effect



How to avoid problems induced by increase of pH

Antiscalant selection

- *SPE0111 selected from in-house phosphonate antiscalant solution*

- Improved performance to a level of

  -$CaCO_3$: S&DSI to 2,6 without scaling formation

  -$Mg(OH)_2$: increasing solubility by a factor of two

Antiscalant SPE0111 implementation

Trial data

- Dose rate based on the high temperature and the most critical operational conditions
- Monitoring
  - Plant operation follow up (DP, flows, …)
  - Historical data comparison
  - Product analysis (feed/brine) for loss detection
  - Membrane autopsies

Results:

No evidence of scaling during one year

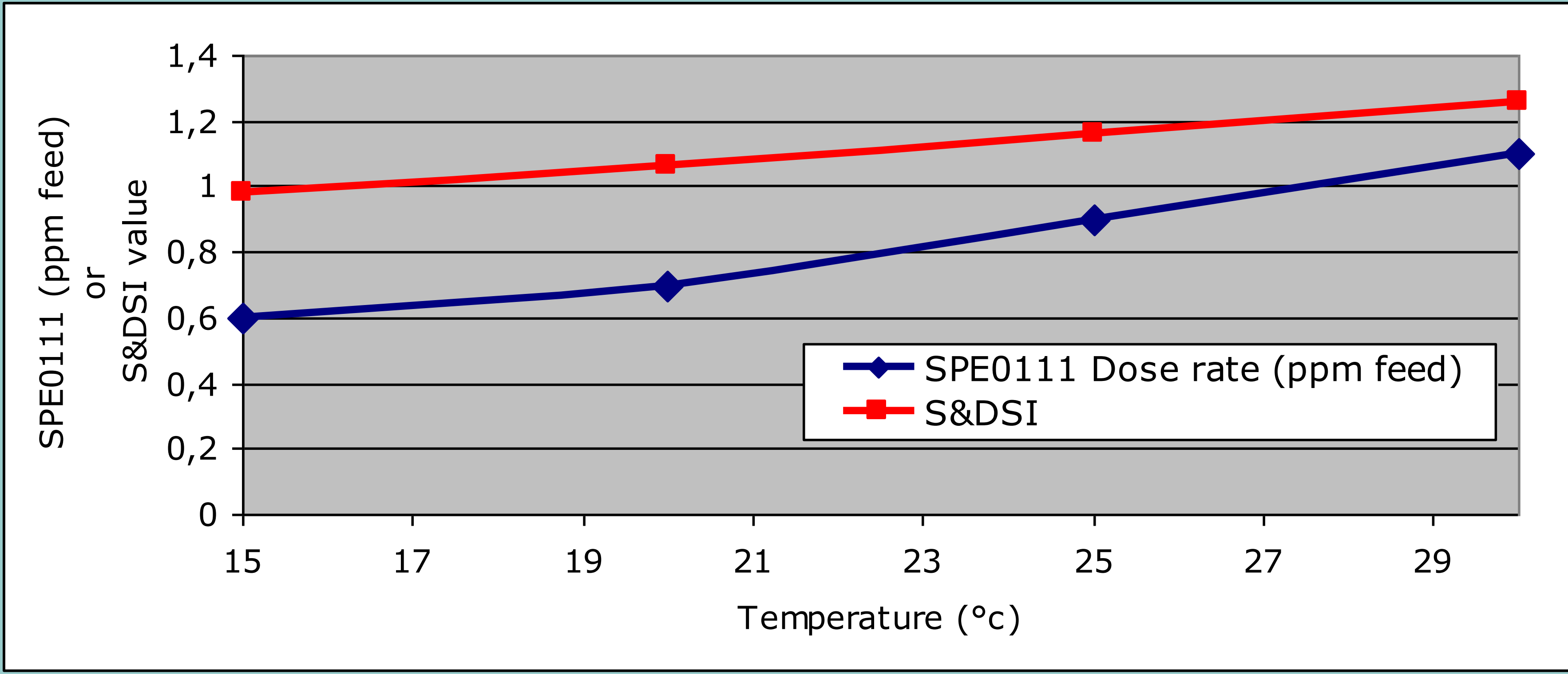
Antiscalant SPE0111 optimization

Next steps

- Completion of 2nd plant expansion (20% increase in production capacity)
- First stage SPE0111 dose rate optimization - rate calculation versus Modes and period of operation

Antiscalant SPE0111 optimization

Dose rate calculation versus mode of operation and period of the year



Conclusions

- LDP meets all its contractual objectives operating at higher feed water pH – no evidence of membrane scaling.

- Required boron levels achieved using appropriate antiscalant in combination with correct membrane changes and adequate chemical cleaning

- thermPhos is supporting successfully LDP in optimizing the dosing rate of the chosen antiscalant

- Recent LDP +20% plant expansion makes boron rejection more critical - further work required for finer antiscalant dosing adjustments

Thank you