



# **Modeling of temperature governed saturation states and metal speciation's in the Marine waters of Kuwait Bay- concern to the desalination process.**

Dr. Chidambaram Sabarathinam  
Research Scientist, WRC,  
Kuwait Institute for Scientific Research  
Kuwait

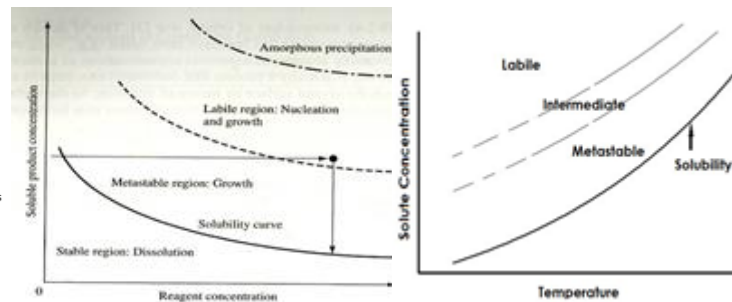
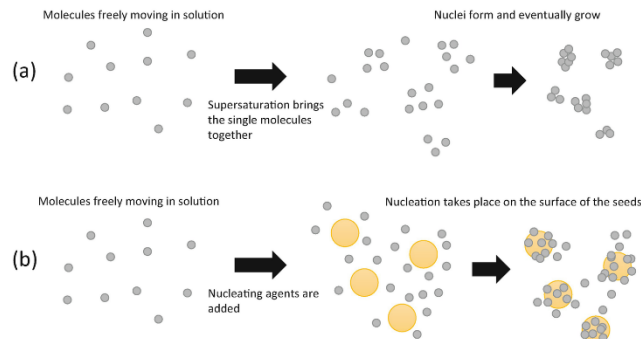


# Overview

- Introduction
- Methodology
  - Saturation index
  - Minerals in database
- Results
  - **SI variation with respect to Temperature in**
    - Carbonates
    - Sulfates
    - Oxides
    - Hydroxides
    - Alumino silicates
    - Silicates
    - Fluorides
- Conclusion

# Introduction

- The formation of salts is dependent on several factors like feed water composition, temperature, pH, operating pressure, flow velocity, permeation rate, etc.
- the saturation state is higher at the surface of the membrane though the solution may be under saturated or near saturated (Antony et al 2011). Apart from the surface precipitation the deposition of salts along the membrane pores were also subsequently studied by various researchers (Oh et al 2009).
- Involvement of minor quantities of a different precipitating salt will affect the salt structure, its precipitation and thermodynamic properties. As the salts may act as a seed or absorbent or may dissolve or may contribute to the growth of salts (Sheikholeslami et al 2003a, 2003b).
- Hence the study of co-precipitation of several salts simultaneously from a feed solution is complex



**Supersaturated solution:**  
thermodynamically unstable

**Metastable region:**  
solute will deposit on existing crystals but no new crystal nuclei formed

**Intermediate zone:**  
both growth of the existing crystals and the formation of new nuclei occur simultaneously

**Labile zone:**  
nuclei are formed

- Source: Hickey A.J., Giovagnoli S. (2018) Crystallization. In: Pharmaceutical Powder and Particles. AAPS Introductions in the Pharmaceutical Sciences. Springer, Cham

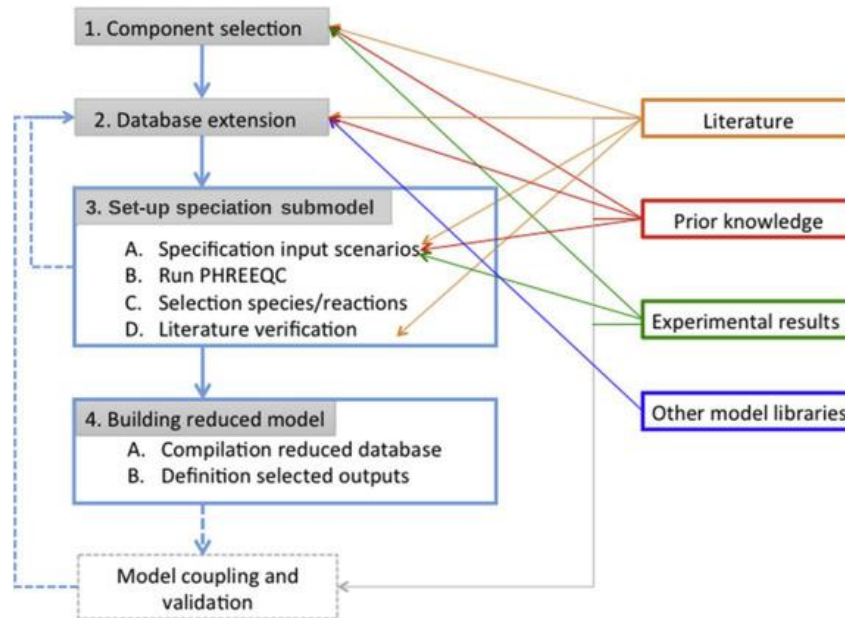
## Objectives:

- To understand the co-precipitation behavior of different salts from the feed water the feed water by varying temperature of the feed solution.
- To classify the state of saturation of minerals or salts with respect to different salts.
- To obtain an insight on the saturation states with respect to season.

# Methodology

**Table 1.** Average values of samples the observed chemical constituents of the Kuwait Bay (all values in mg/L except for Temperature in deg C)

Al	0.0703	Li	0.2863
HCO <sub>3</sub>	137.75	Mg	1711.3
As	0.003	Mn	0.0003
B	4.8738	NO <sub>3</sub>	0.6612
Ba	0.0117	Na	14555
Br	85.482	Ni	0.0006
Ca	588.12	P	0.0526
Cl	26449	pH	8.123
Cu	0.0097	SO <sub>4</sub>	3694.4
F	3.2737	Si	0.2882
Fe	0.0042	Sr	7.2475
K	524.79	Temp	24



$$(SI) = \log (IAP/KT)$$

**IAP** – Ionic Activity Product (derived from the composition of the solution).

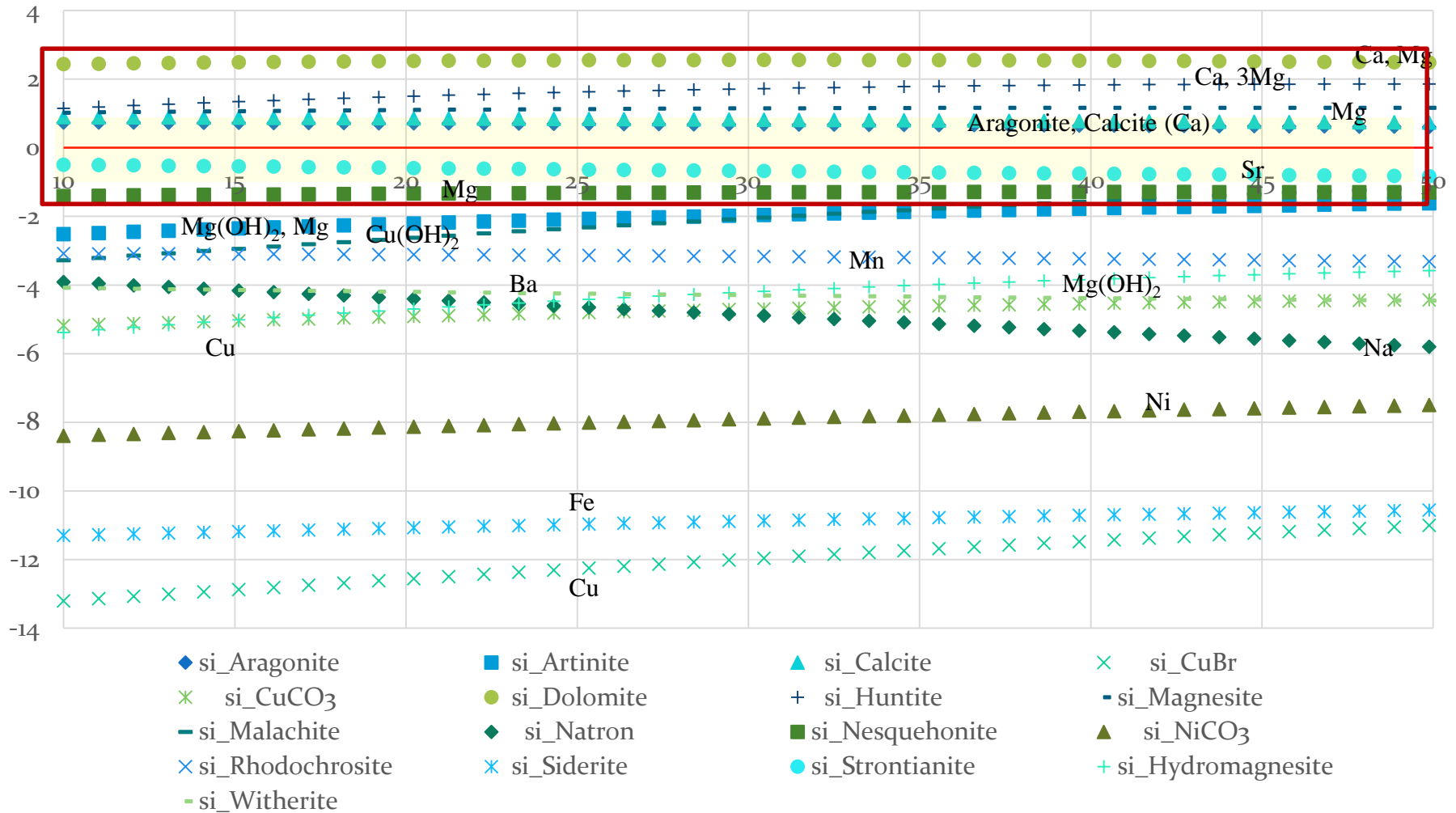
**KT** – Solubility Product of the specific compound (From data base).

**SI =0, SI>0 and SI<0** (equilibrium, saturated and under saturated)

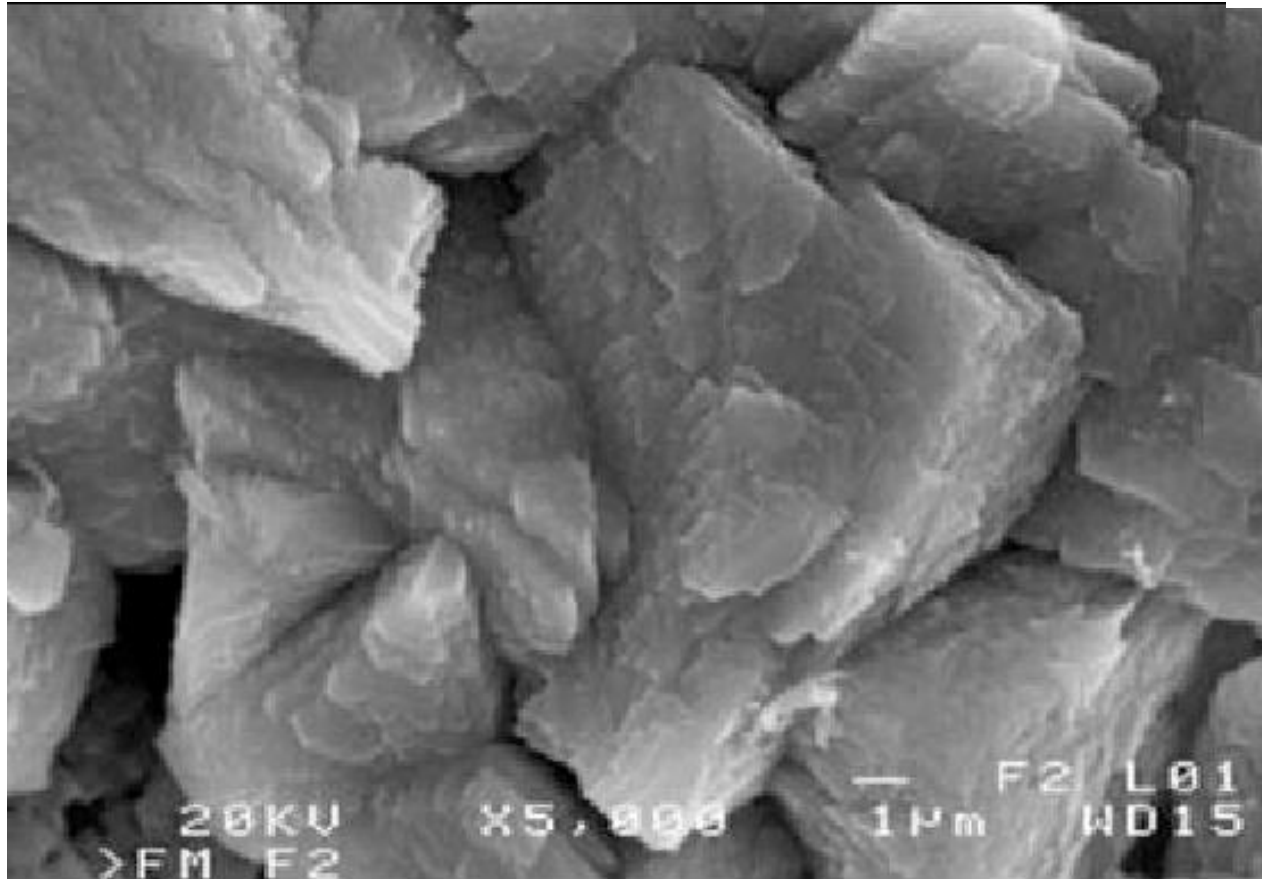
**Table 2.** The saturation indexes considered for study with their chemical formulae

Carbonates and its composition		Oxides and its composition	
Aragonite	CaCO <sub>3</sub>	Birnessite	MnO <sub>2</sub>
Artinite	MgCO <sub>3</sub> .Mg(OH) <sub>2</sub> .3H <sub>2</sub> O	Bixbyte	Mn <sub>2</sub> O <sub>3</sub>
Calcite	CaCO <sub>3</sub>	Bunsenite	NiO
	CuCO <sub>3</sub>	Hausmanite	Mn <sub>3</sub> O <sub>4</sub>
Dolomite	Ca Mg (CO <sub>3</sub> ) <sub>2</sub>	Haematite	Fe <sub>2</sub> O <sub>3</sub>
Huntite	Ca Mg <sub>3</sub> (CO <sub>3</sub> ) <sub>4</sub>	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
Magnesite	Mg CO <sub>3</sub>	Nsutite	MnO <sub>2</sub>
Malachite	Cu <sub>2</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>	Pyrolusite	MnO <sub>2</sub>
Natron	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Alumino-silicates and silicates and its composition	
Nesquehonite	Mg CO <sub>3</sub> .10H <sub>2</sub> O	Adularia	KAl Si <sub>3</sub> O <sub>8</sub>
	NiCO <sub>3</sub>	Albite	NaAl Si <sub>3</sub> O <sub>8</sub>
Rhodochrosite	MnCO <sub>3</sub>	Analcime	NaAl Si <sub>2</sub> O <sub>6</sub> .H <sub>2</sub> O
Siderite	FeCO <sub>3</sub>	Chlorite	Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>
Strontianite	SrCO <sub>3</sub>	Chrysolite	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Witherite	BaCO <sub>3</sub>	Clinoenstatite	MgSiO <sub>3</sub>
Hydromagnesite	Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> .4H <sub>2</sub> O	Halloysite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Sulfates and its composition		Illite	K Mg Al Si O <sub>10</sub> (OH) <sub>2</sub>
Anhydrite	CaSO <sub>4</sub>	Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Antlerite	Cu <sub>3</sub> (OH) <sub>4</sub> SO <sub>4</sub>	K. Mica	KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>
	Ba <sub>3</sub> (ASO <sub>4</sub> )	Laumontite	Ca Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> .4H <sub>2</sub> O
Barite	BaSO <sub>4</sub>	Leonhardtite	Ca <sub>2</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> .7H <sub>2</sub> O
Basaluminitite	Al <sub>4</sub> (OH) <sub>10</sub> SO <sub>4</sub>	Montmorellonite	(Na,Ca) <sub>0,3</sub> (Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> .n(H <sub>2</sub> O)
Celestite	SrSO <sub>4</sub>	Phyllipsite	Na <sub>0,5</sub> K <sub>0,3</sub> Al Si <sub>3</sub> O <sub>8</sub> .H <sub>2</sub> O
Chalcanthite	CuSO <sub>4</sub> .5H <sub>2</sub> O	Phloghopite	K Mg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>
Epsamite	MgSO <sub>4</sub> .7H <sub>2</sub> O	Prehnite	Ca <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>
Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	Pyrophyllite	Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Jurbanite	Al OH SO <sub>4</sub>	Chalcedony	SiO <sub>2</sub>
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	Quartz	SiO <sub>2</sub>
	MnSO <sub>4</sub>	Sepiolite	Mg <sub>2</sub> Si <sub>3</sub> O <sub>7,5</sub> .OH.3H
Thenardite	Na <sub>2</sub> SO <sub>4</sub>	Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Tremolite	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>
Jarosite	K - KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> : Na- NaFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Cristobalite	SiO <sub>2</sub>
Hydroxides and its composition		Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>
Al(OH) <sub>3</sub>		Phosphates and Fluorides and its composition	
Bohemite	AlOOH	FCO <sub>3</sub> Apatite -	Ca <sub>10</sub> NaMg(PO <sub>4</sub> ) <sub>5</sub> (CO <sub>3</sub> )F
Cu(OH) <sub>2</sub>		Fluorapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F
Brucite	Mg(OH) <sub>2</sub>	Fluorite	CaF <sub>2</sub>
Diaspore	AlOOH	Hydroxyapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH
	Fe(OH) <sub>3</sub>		Mn HPO <sub>4</sub>
Gibbsite	Al(OH) <sub>3</sub>		Sr F <sub>2</sub>
Goethite	FeOOH	Strengite	Fe PO <sub>4</sub> .2H <sub>2</sub> O
Manganite	MnOOH		
	Ni(OH) <sub>2</sub>	Halite	NaCl
Portlandite	Ca(OH) <sub>2</sub>		
Pyrochrosite	Mn(OH) <sub>2</sub>		

# Results



Variation of the saturation states of carbonate minerals with respect to temperature (°c)



**SEM image of CaCO<sub>3</sub> deposit formed on the membrane surface during the MD process of ground water.**

Source: Gryta, Marek. (2009). Calcium sulphate scaling in membrane distillation process.

Chemical Papers. 63. 146-151. 10.2478/s11696-008-0095-y.

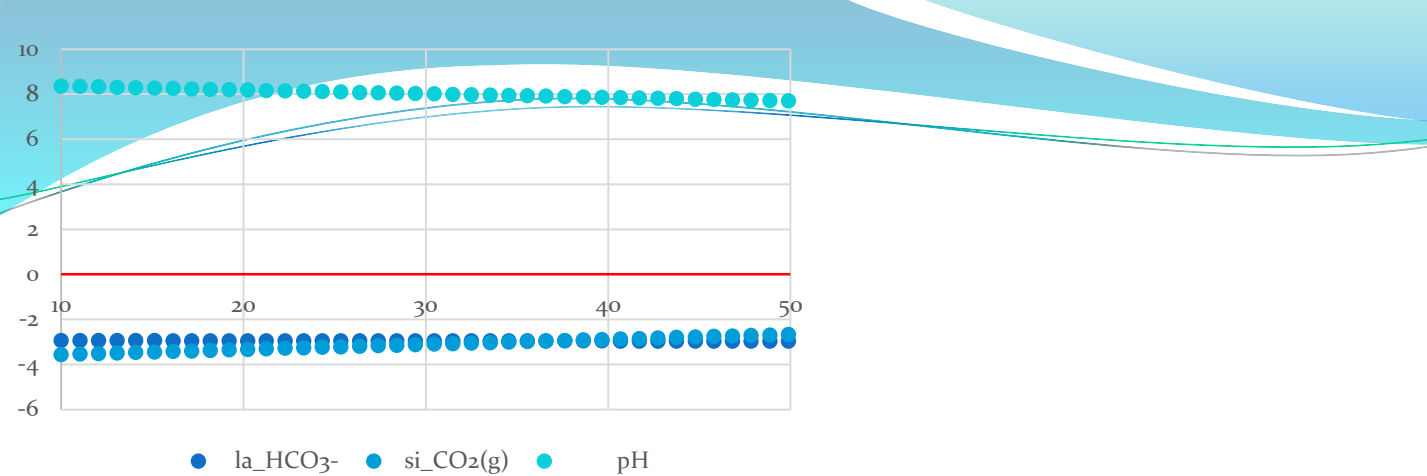


Fig 2. Variation pH,  $\text{HCO}_3^-$  and  $\text{pCO}_2$  with respect to temperature ( $^{\circ}\text{C}$ ).

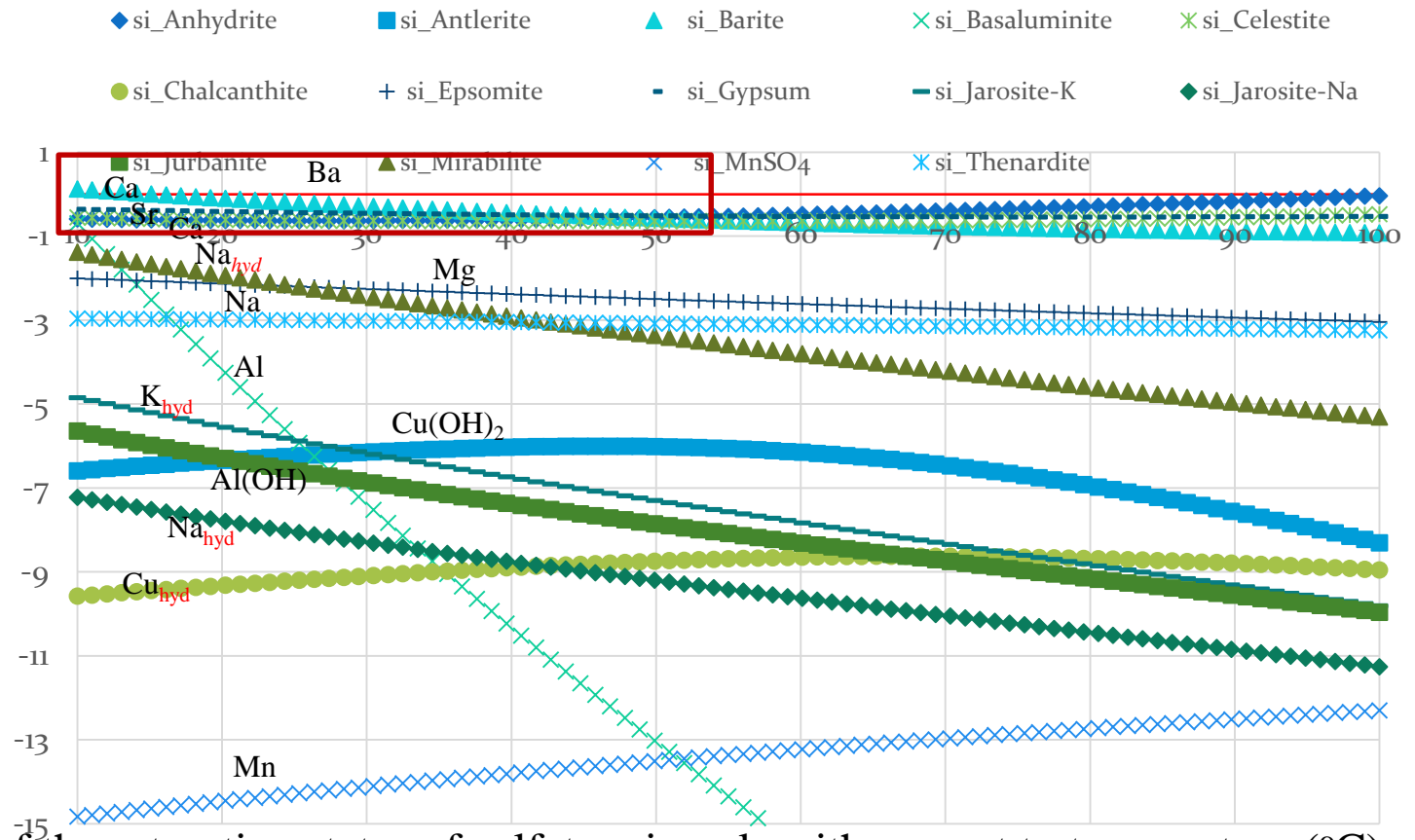


Fig 3. Variation of the saturation states of sulfate minerals with respect to temperature ( $^{\circ}\text{C}$ ).





**SEM image of calcium sulfate deposit on the membrane surface during the MD process.**

Source: Gryta, Marek. (2009). Calcium sulphate scaling in membrane distillation process.

Chemical Papers. 63. 146-151. 10.2478/s11696-008-0095-y.

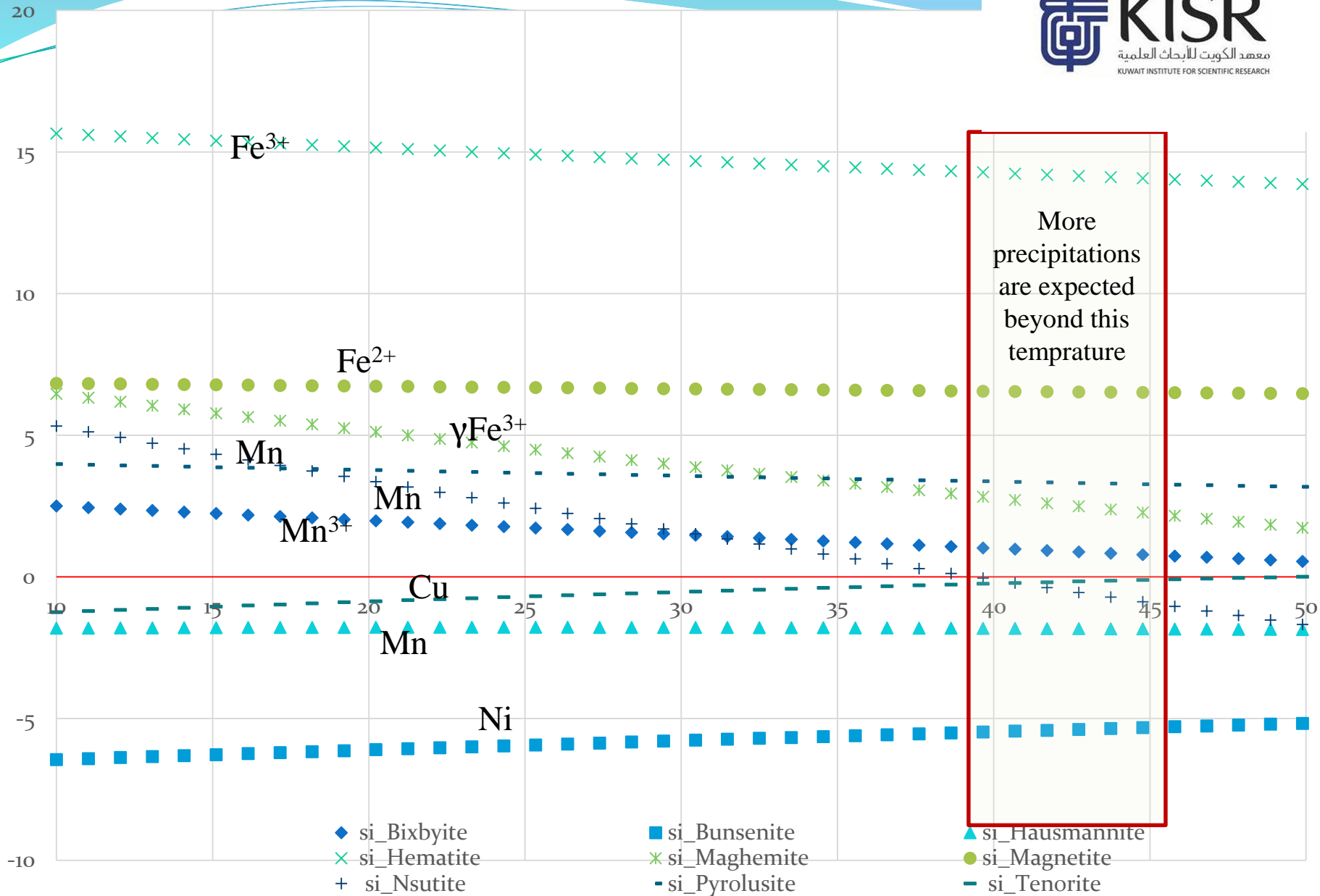


Fig 5. Variation of the saturation states of oxide minerals with respect to temperature (°C).

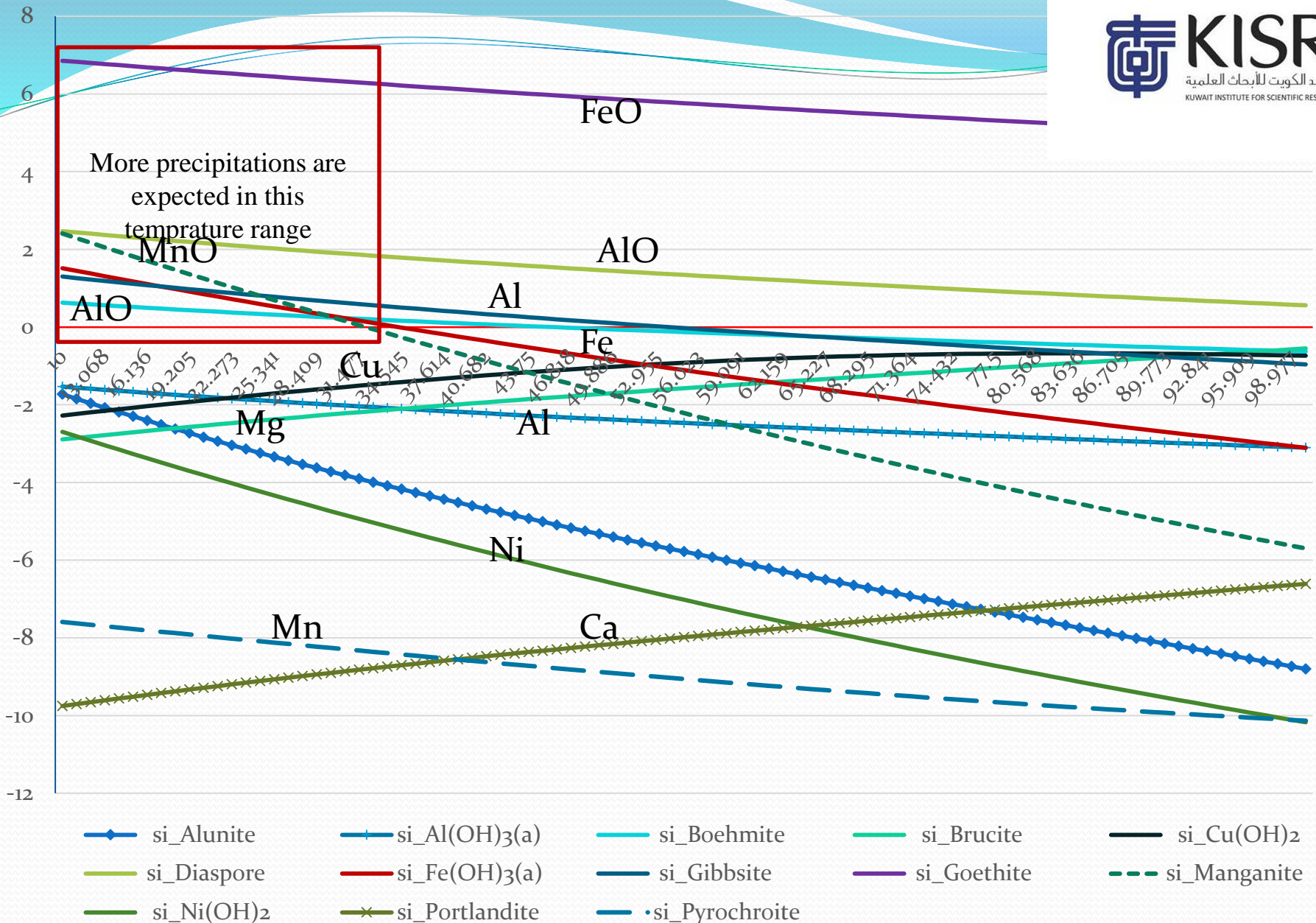


Fig 4. Variation of the saturation states of hydroxide minerals with respect to temperature (°C).

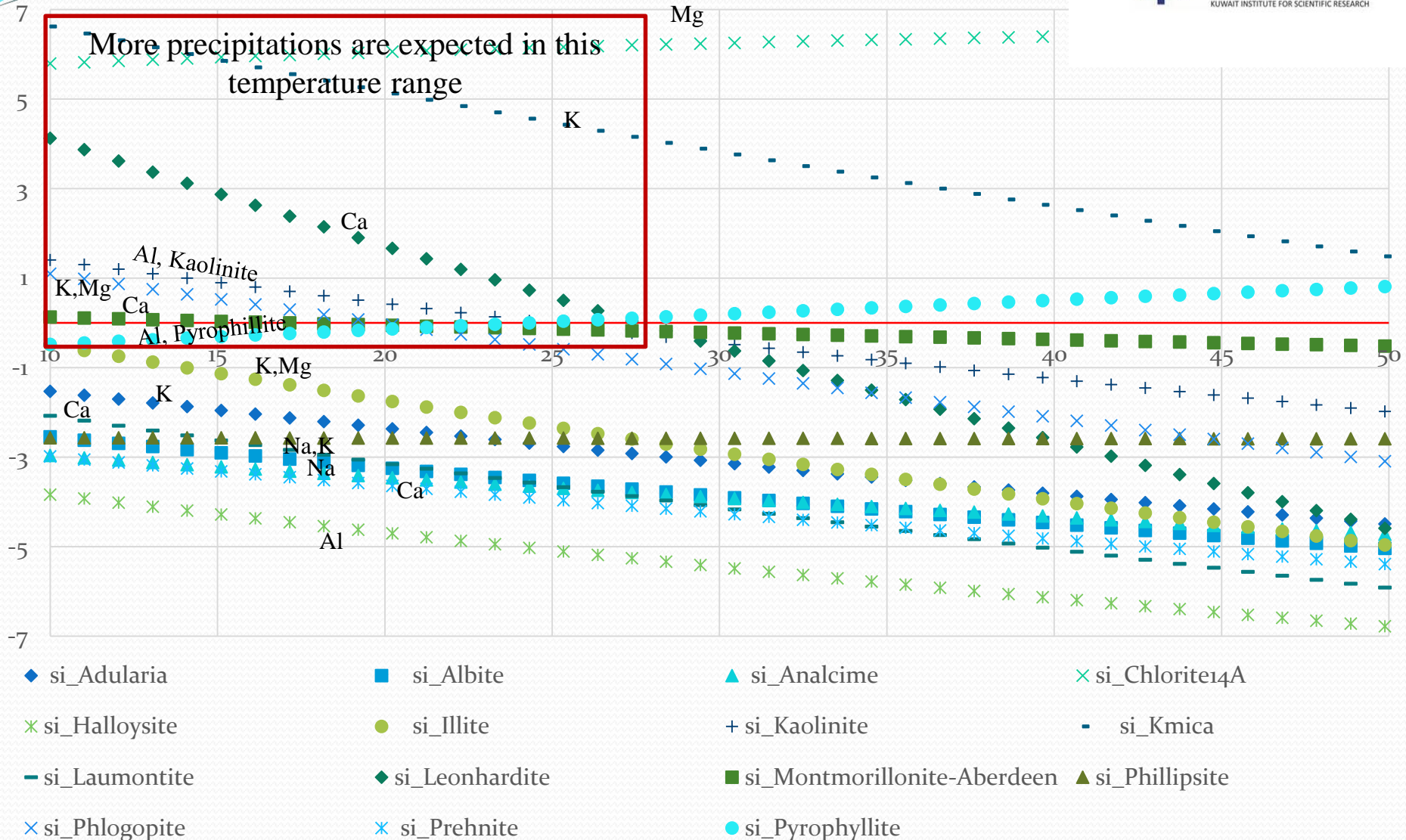
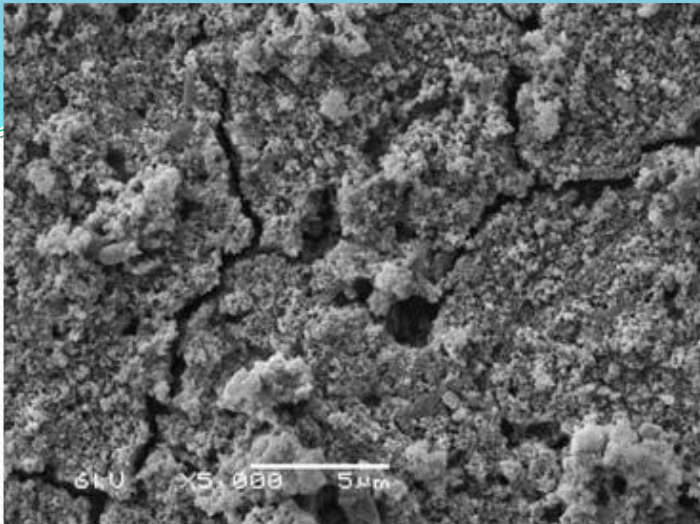


Fig 6. Variation of the saturation states of Aluminosilicate mineral minerals with respect to temperature (°C).

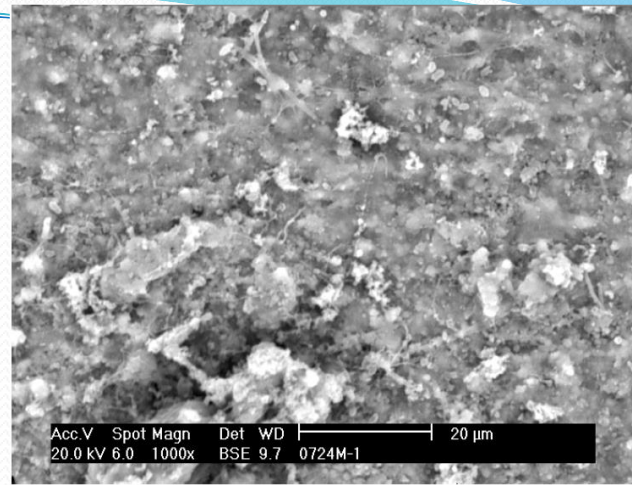
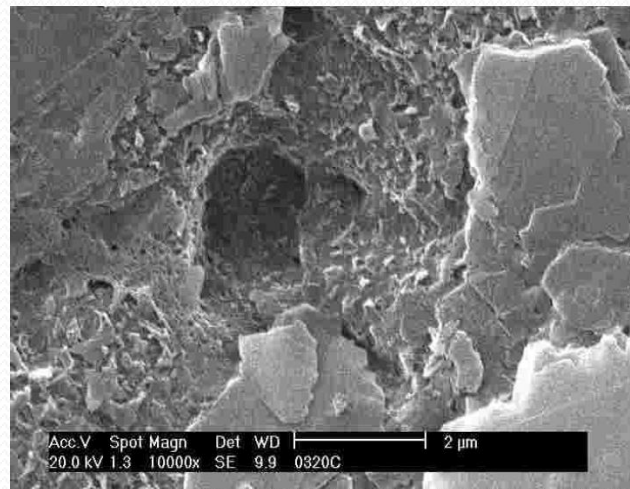




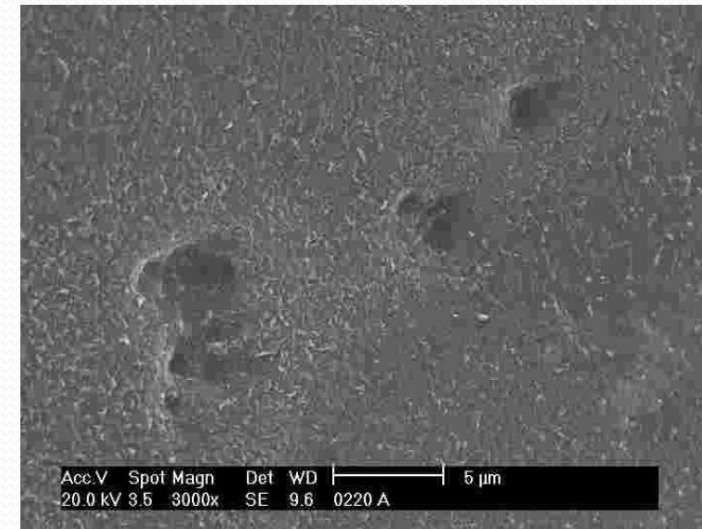
Scaling of amorphous silica

**Source:** Salvador Cob, Sara & a Beupin, C & Hofs, Bas & M a Nederlof, M & Harmsen, Danny & Cornelissen, Emile & Zwijnenburg, Arie & Genceli Guner, Fatma Elif & Witkamp, Geert-Jan. (2013). Amorphous aluminosilicate scaling characterization in a reverse osmosis membrane. Desalination and Water Treatment. 51. 936-943. 10.1080/19443994.2012.694202.

SEM Micrograph.  
Membrane partially covered by a silica deposit

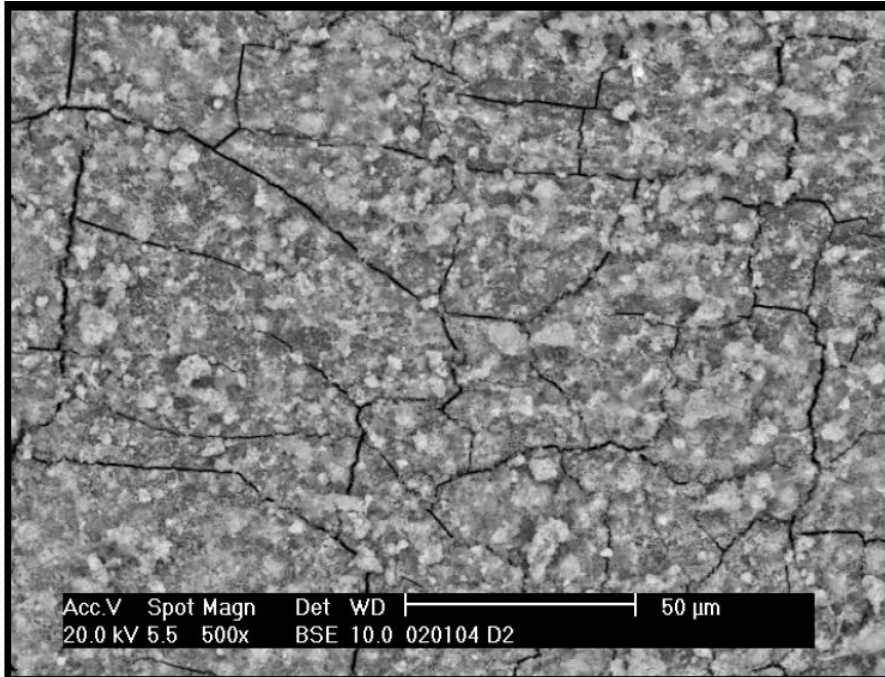


SEM Micrograph. Silica deposit on membrane

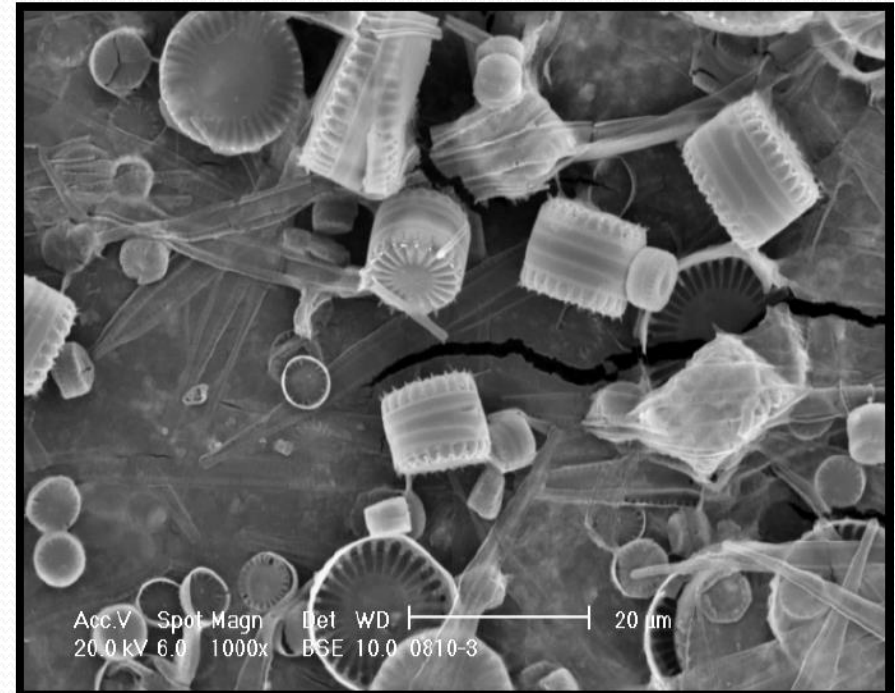


SEM Micrograph. Damaged membrane after chemical cleaning

**Source:** Silvia Gallego, Fernando del Vigo and Steve Chesters (2008). PRACTICAL EXPERIENCE WITH HIGH SILICA CONCENTRATION IN RO WATERS. WIM 2008 International Congress on water management in the mining industry. Santiago Chile July 9-11th 2008 REF:WIM08-53.



SEM-EDX Micrograph. Aluminosilicates on membrane surface



Diatoms on a membrane surface. SEM-EDX Micrograph.

**Source:** Silvia Gallego, Fernando del Vigo and Steve Chesters (2008). PRACTICAL EXPERIENCE WITH HIGH SILICA CONCENTRATION IN RO WATERS. WIM 2008 International Congress on water management in the mining industry. Santiago Chile July 9-11th 2008 REF:WIMo8-53.

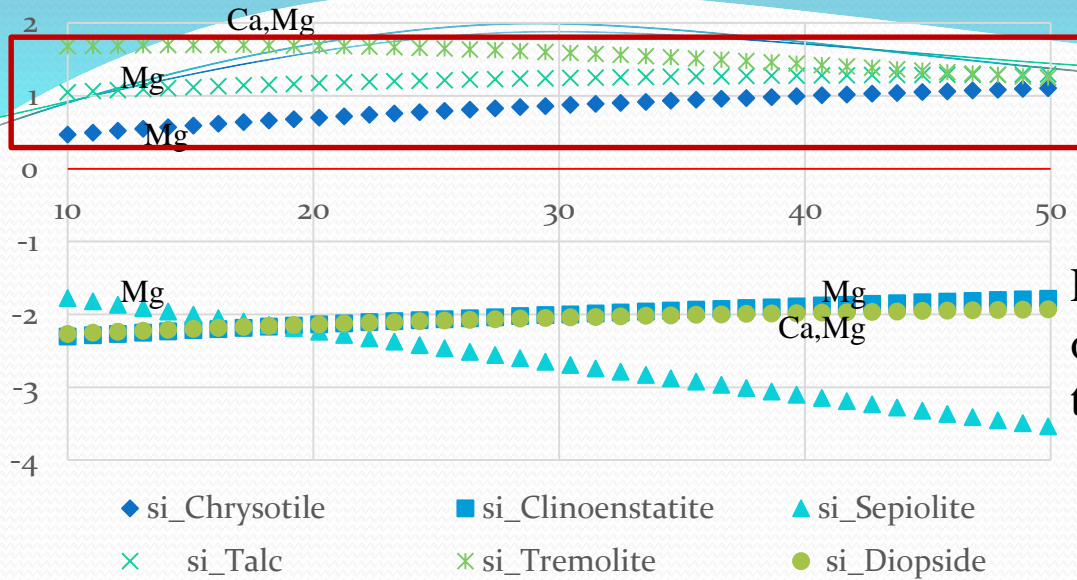


Fig 7. Variation of the saturation states of Silicate mineral minerals with respect to temperature (°C).

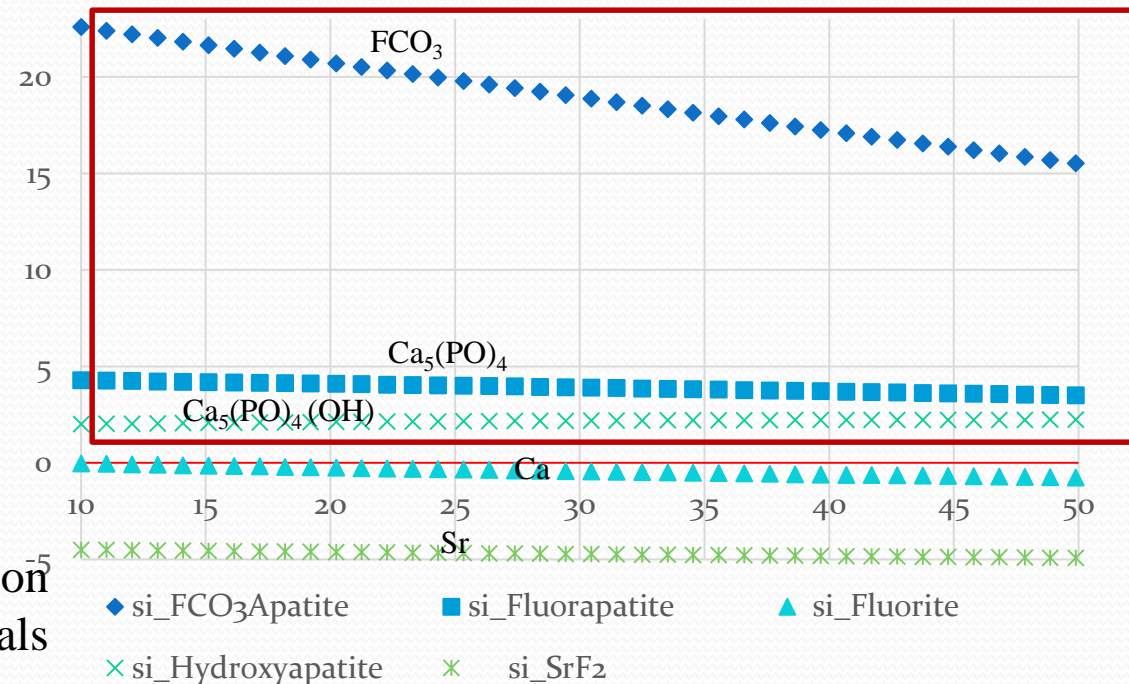
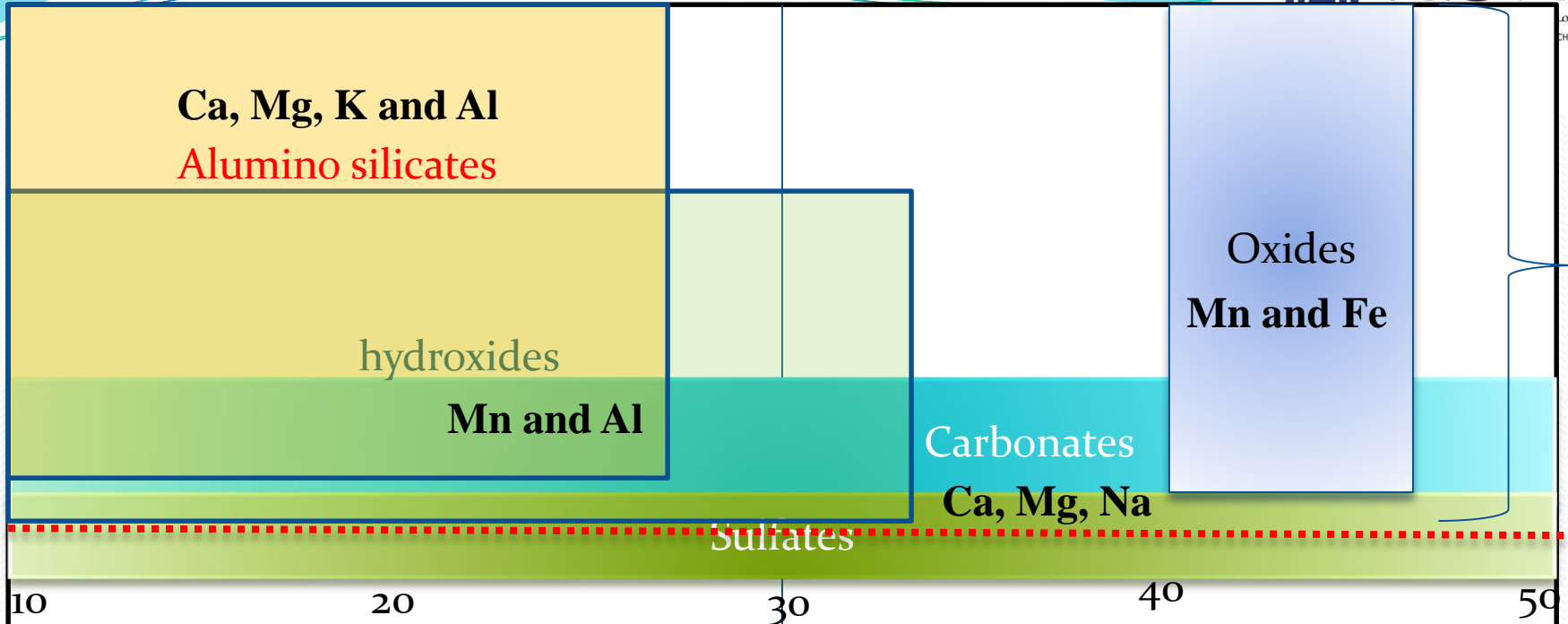


Fig 8. Variation of the saturation states of Fluoride mineral minerals with respect to temperature (°C).



Saturation Index of minerals



- SI index of certain compounds are not affected by the change in temperature.
- Decrease of an element in one compound with temperature may increase the formation of a different compound of the same mineral.
- Same composition may prefer different crystallisation systems (Calcite -Aragonite) with variation in temperatures.

Temperature -----> (in deg C)



# Conclusion & Recommendations

- The SI of carbonate minerals and oxides are higher **during summer**.
- The SI of sulfates, hydroxides and most of the alumino silicates are noted to be higher **during winter**.
- The **saturation states of silicate and fluorite** minerals **do not vary** with respect to temperature.
- **Sr** compounds play a critical role as they **do not show** significant variation in saturation states with temperature.
- **The major ions** play a significant role in saturation states of **sulfates and carbonates**. **Mn and Fe** in **oxides** ; **Mn and Al** in **hydroxides**. **Ca, Mg, K and Al** play an important role in saturation states of **alumino silicates**.
- **SI of all the compounds of Mn** are noted to decrease with temperature and **reverse** is noted for its sulfate compounds.
- **SI of Ca alumino silicates** decrease with temperature but the **SI of Ca increase in carbonates, sulfates and oxides**.
- The saturation states reveal that most of the minerals are **more saturated during winter**, with higher probability of hard incrustations.
- The study reveals the fact that predominantly the dissolution capacities of the feed water have increased **during summer resulting in reduced pH and lesser ionic strength** under ideal conditions.

# Limitations

- Inferences are based on average results and theoretical modeling.
- The study has to be calibrated with the field observations.
- Analytical result of the salts in the membranes have to be compared with the present results and decide on preprocessing.

# Acknowledgement

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Thank you...