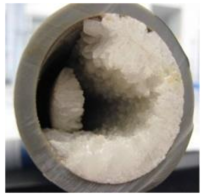
Characterization and Identification of Organic Molecules in Thermal Desalination Plant Scale



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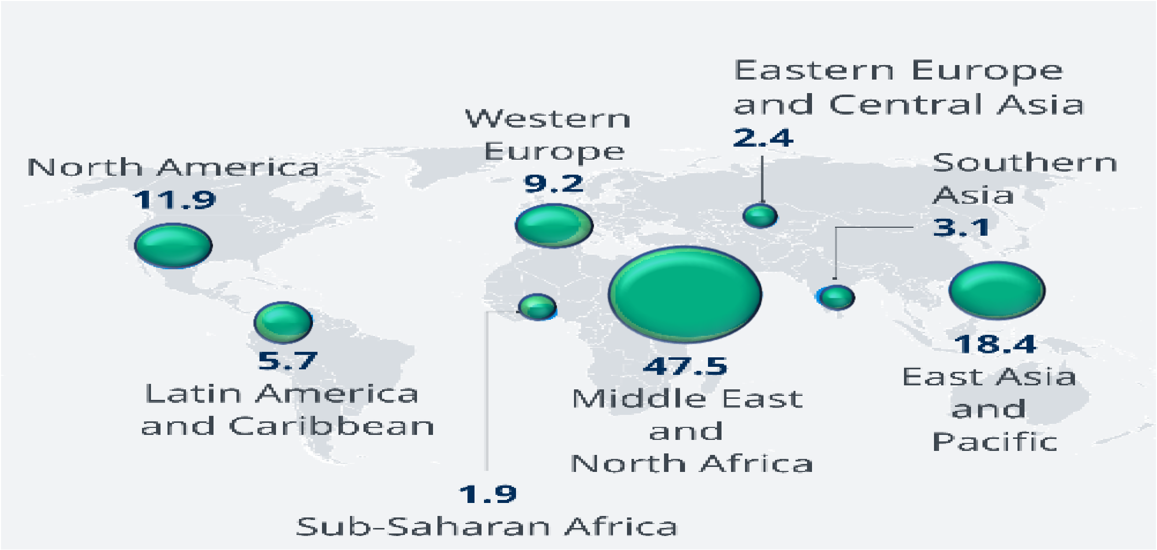
Overview of Desalination Technologies and Operational Costs

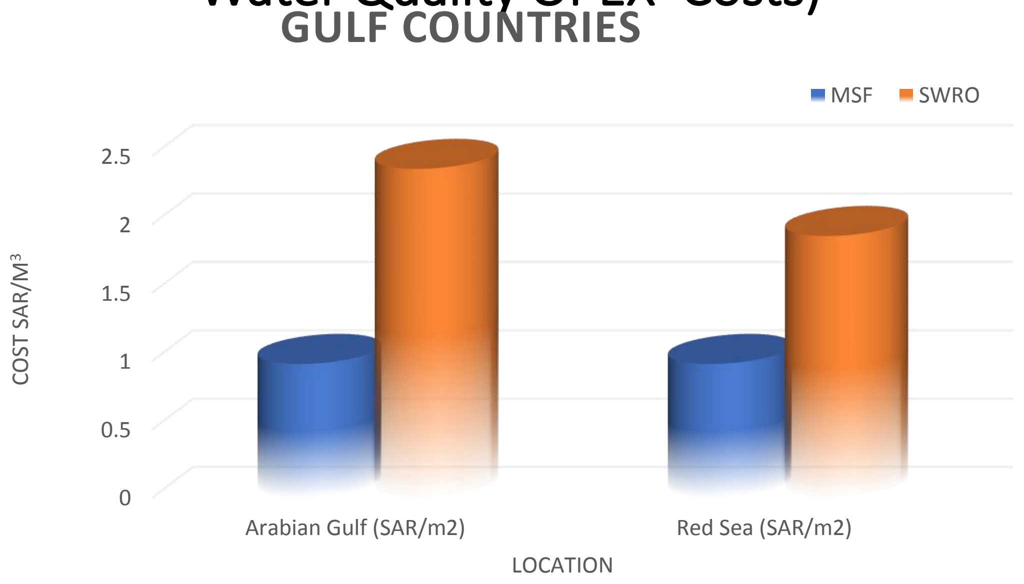
Global Desalination Assets



- The Middle East and North African (MENA) region has the highest production percentage of desalinated water.
- Of the MENA region, Saudi Arabia has the largest daily production capacity (nearly 5.6 million m^3/day).
- Capital Expenditures (CAPEX) of membrane mediated desalination technologies are similar, and those of thermal mediated technologies are similar because process methods are nearly the same from location to location.

- Operational Expenditures (OPEX) for membrane technologies vary from location to location depending on water quality conditions.
- However, thermal technologies are not as dependent on water quality conditions and have a lower OPEX profile per m^3 than SWRO (in the Arabian Gulf and Red Sea).
- Fouling and corrosion are the two main problems associated with OPEX costs which can affect energy consumption and production.

Water Quality OPEX Costs)



Overview of Desalination Technologies and OPEX Costs

	MENA O&M Costs		
	Parameters	Thermal Processes	Membrane Processes
O&M-Varaible Cost (%)	Energy Consumption	49.5-55.5%	37.0-45.0%
	Chemicals	5.0-7.5%	16.5-23.0%
	Membranes		
	Waste Disposal		

- Yearly replacement for membrane mediated processes are between 15-20%. This problem in SWRO systems is due to fouling. Fouling is a problem in both membrane and thermal systems.
- Fouling may have process impacts that increase energy consumption and reduce product quality.
- Fouling can result in cumulative process declines that increase losses over time.
- Repairing problems from fouling reduces production and may involve equipment replacement.
- Strategies to deal with fouling problems focus on root causes and solutions to problems that extend Plant operation time and Plant longevity.

Industrial Fouling

There are basically **6 categories of foulants** in Industrial Systems

- **Particulate Fouling**

  Fouling that occurs on surfaces and heat exchangers due *to gravitational sedimentation*

  - Sludge
  - Sand
  - Microbes
  - Ex Situ Corrosion Products
  - Minerals
  - Detrius
  - Diatomaceous Material (from diatoms)

- **Chemical reaction fouling**

  Deposits from chemical reaction in fluid

Industrial Fouling

- **Corrosion Fouling**

  Attachments from corrosion products on surfaces and heat exchangers that are:

  - **In situ**

    Coming from the corrosion surface reaction

  - **Ex situ**

    Coming from corrosion products from a different location which settle on surfaces

- **Solidification Fouling**

  Solid attachment to surface from freezing/ cooling (oil and gas Industry)

  - Paraffin
  - Hydrocarbons
  - Ice (cryogenic plants)

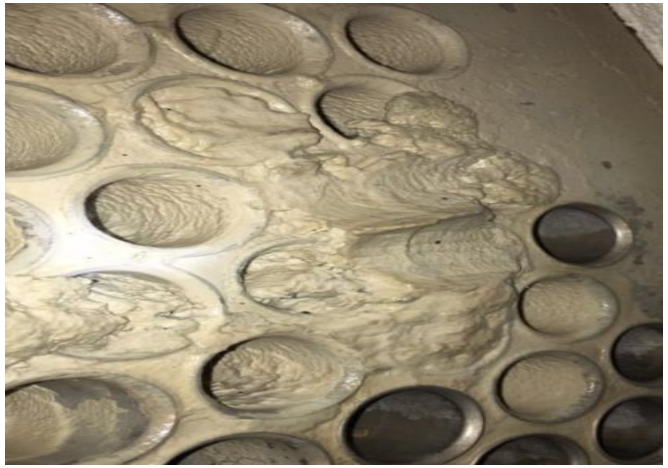
Industrial Fouling

- **Biological Fouling**

  Deposition of surfactant matter on surfaces that leads to the growth of Exopolymeric Substances (EPS- Known as biofilm) from microbial metabolism and growth.

  As biofilm growth advances, deposition of the organic film can provide nutrients and adhesive properties for attachment and growth of macro-foulants that include:

    - Barnacles
    - Muscles
    - Bivalves
    - Gastropods



Industrial Fouling

Precipitation Fouling

- Precipitation fouling is the crystallization of dissolved species from solution onto a surface (or in thermal desalination- a heat-transfer surface).
- In thermal systems, salts when heated gain kinetic energy and super-saturate upon evaporation of water. Evaporation can cause dissolved salts to go beyond their solubility limits precipitating out of solution and crystalizing on surfaces forming scale.
- It is commonly understood that when fluids heats up salts saturate more. In general this is true, but exothermic salts tend to exhibit inverse solubility when temperature increases causing precipitation and scale formation ($CaCO_3$, $Mg(OH)_2$, $CaSO_4$, $LiSO_4$, $LiCO_3$).
- In thermal systems, scale formation is a major problem with profound energy consumption costs and process impacts.

Impacts of Foulants on Desalination Plants

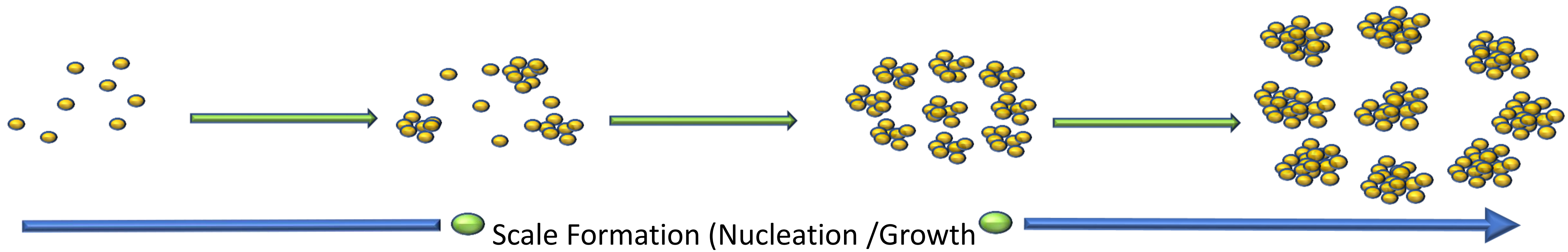
<table>
<tr><th>Systems</th><th>Impacts</th></tr>
<tr><td>Thermal Systems</td><td rowspan="2">• Heat Exchangers
• Pumps
• Sensors
• Large and Small Valves
• Storage Tanks
• Fuel Lines- Reduced Flow/blockage
• Concrete Foundations- Delamination
• Transmission Lines- Delamination, blockage, reduced flow and transmission
• Membranes-Change in differential pressure, damage.</td></tr>
<tr><td>Membrane Systems
-SWRO</td></tr>
<tr><td>Cooling Water Systems</td><td>Cooling towers, Process lines, water storage tanks</td></tr>
<tr><td>Power Generation Systems</td><td>Condensers, Heat Exchangers, Fuel lines</td></tr>
<tr><td>Fuel supply and Storage Systems</td><td>Tanks, pumps, valves, transmission lines</td></tr>
</table>

How Does Scale Form?

Scale is formed by a process of Nucleation and Growth of Crystals

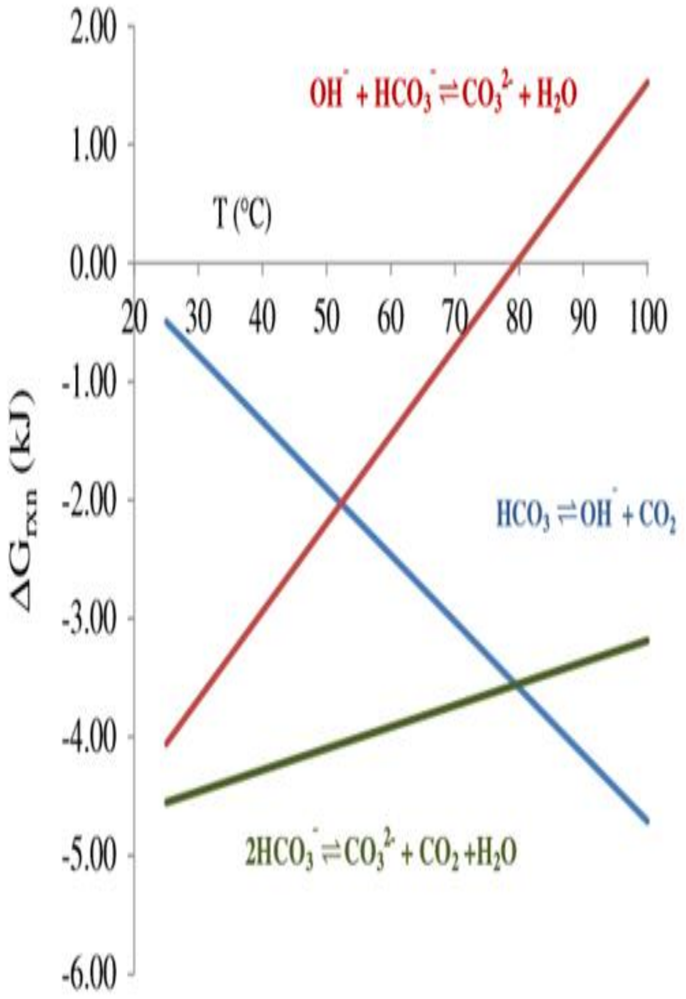
- Scale is derived from salt crystals and a crystal is a phase transition of matter in a solvated (liquid) state from a high free energy state to a lower free energy crystal lattice state.
- Crystallization or scale formation happens when the free energy of the initial solution is greater than the sum of the free energies of the crystalline phase plus the final solution phase (Gibbs 1876, 1878)

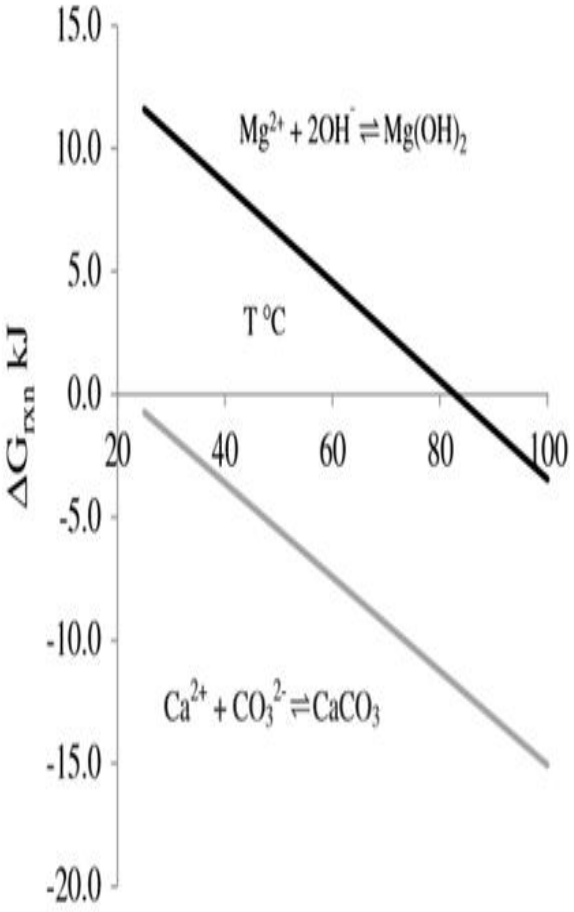
INITIAL SOLUTION ENERGY > energy of crystal + final energy of solution



Nucleation → Nucleation Stops (No new sites) → Growth

Thermodynamics: Scale Formation Gibbs Free Energy





- It is common for chemists to view scale nucleation and growth from the aspect of Gibbs Free Energy or Energy (Enthalpy) and Disorder (Entropy).

  ΔG= ΔEnthalpy– TΔEntropy

- When ΔG is negative (spontaneous) scale formation may occur as with the formation of magnesium hydroxide above 80°C.

- It should be noted that calcium carbonate formation occurs at lower temperatures but due to a positive ΔG in the formation of carbonate the reaction is limited and at high temperatures Magnesium hydroxide is thermodynamically preferred in seawater thermal processes.

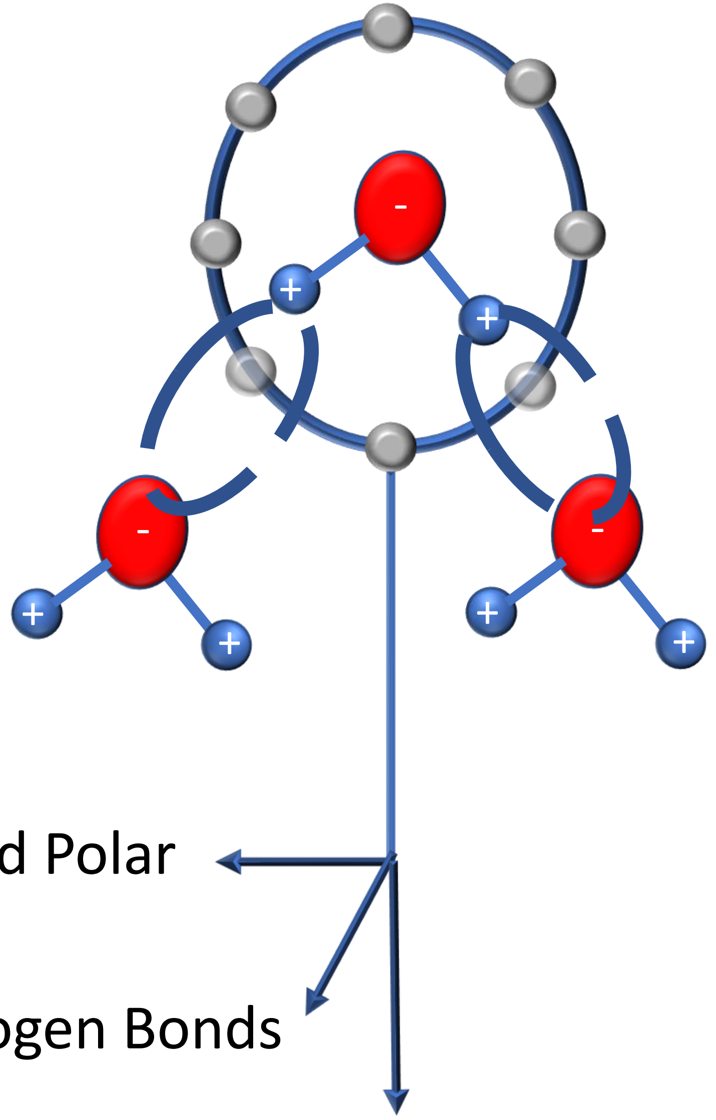
Project: Aim and Objectives

Scale Growth is a major problem occurring in thermal desalination plants.

As explained, problems with fouling have serious economic and process implications.

Based on the diversity and complexity of industrial fouling, it was hypothesized that scale (a major issue in thermal desalination plants) may consists of organic compounds that may possibly play a role in scale nucleation and growth.

- The objective of this project was to extract organic scale and analyze it for organic compounds and bio-active molecules (ATP).
- Inorganic characterization of scale was also performed.



Experimental Methodology

Sites (2):

-**Deaerator**

(Site of removal of Non-condensable gas removal)

-**Flash Chamber**

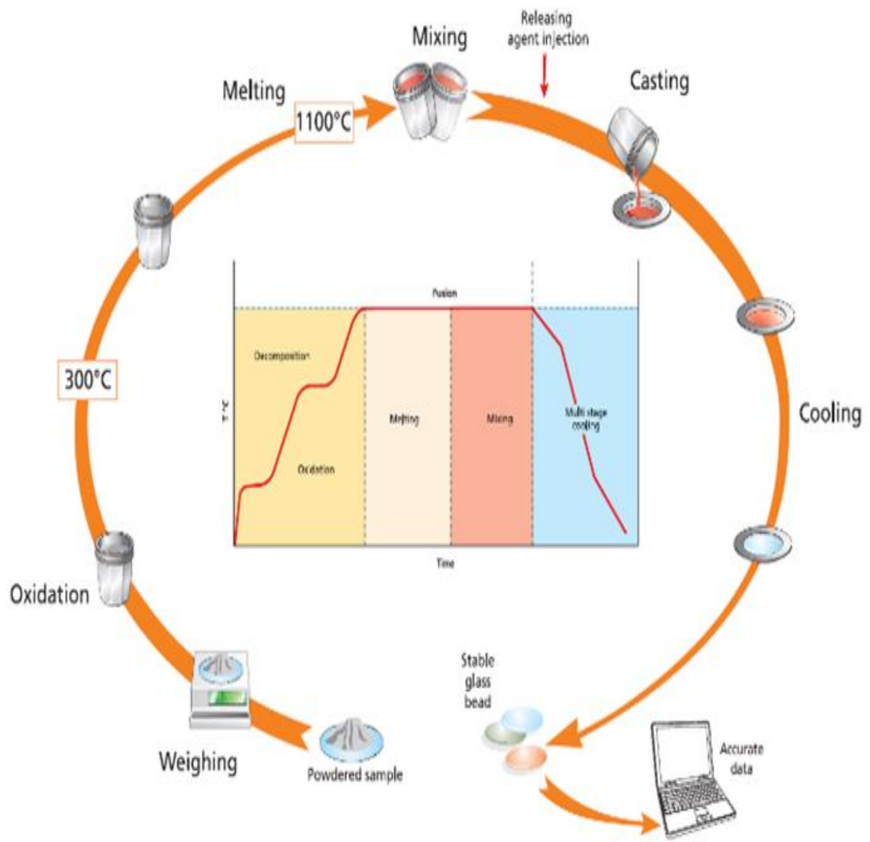
(Site of water vaporization and condensation)

Inorganic Analysis

- Sample Extraction
- SEM/EDX
- Light Microscopy

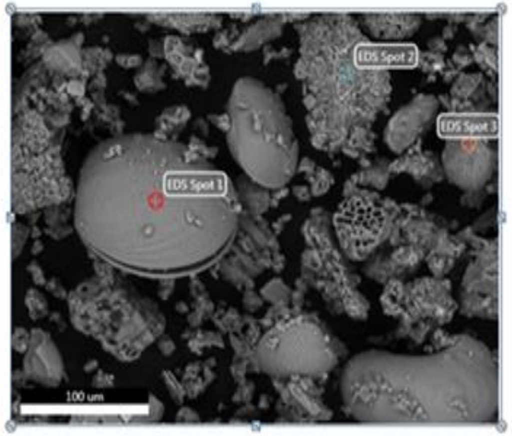
Organic Analysis

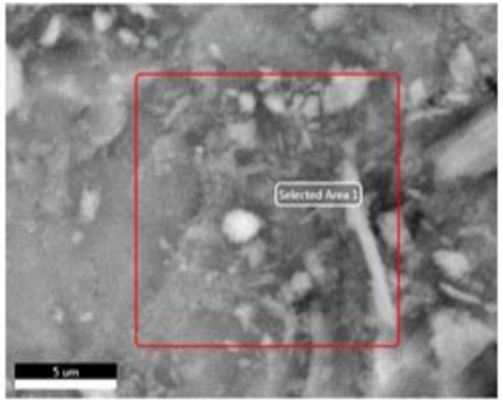
- Sample Extraction
- SEM
- XRD
- ATP
- GC/MS
- Light Microscopy

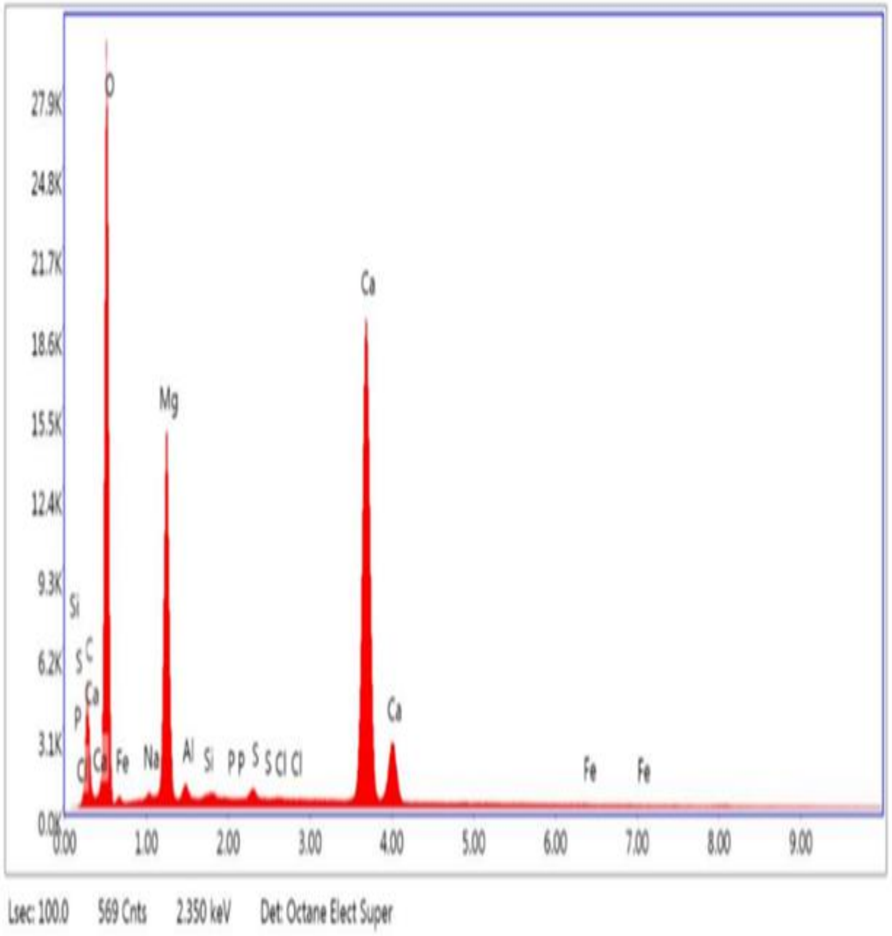


Results: Inorganic

- Deaerator



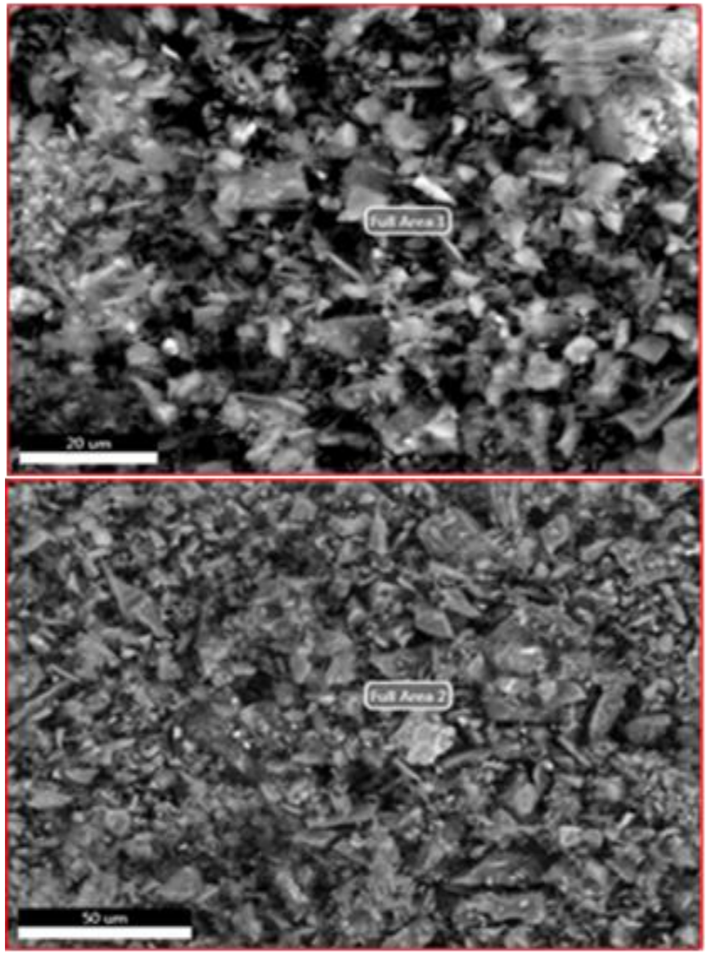


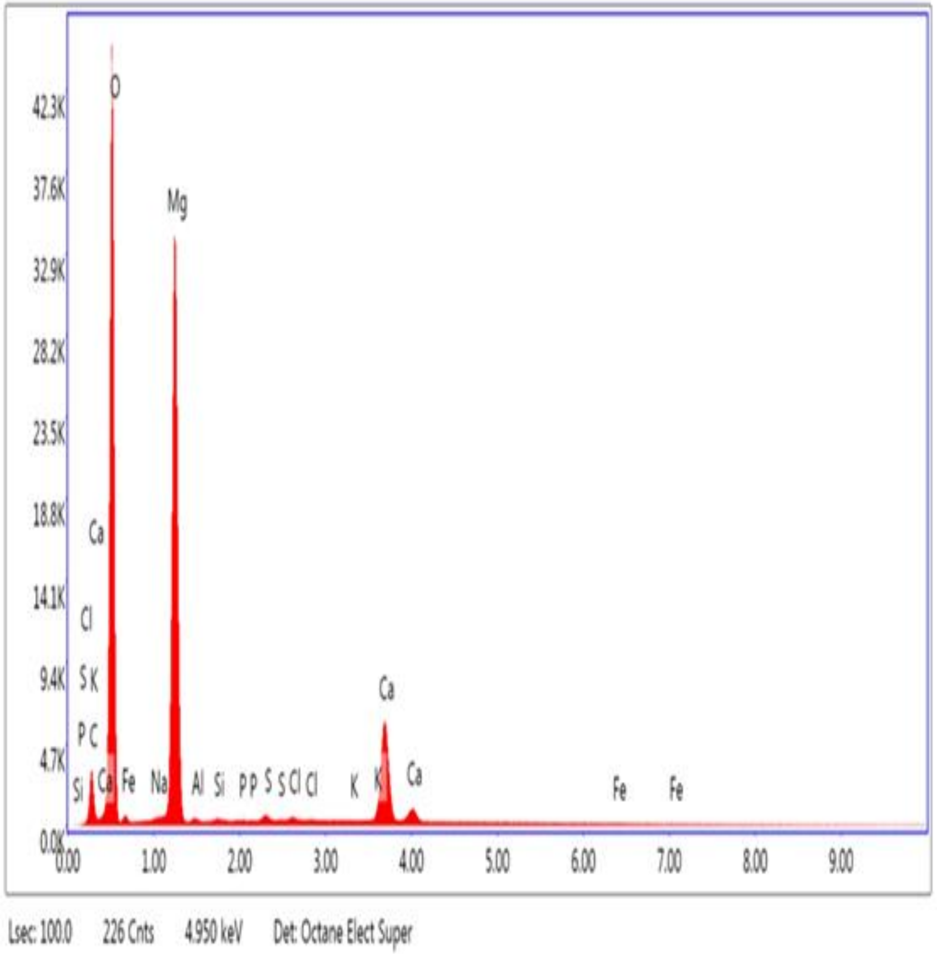


- Calcium carbonate and magnesium hydroxide exists as the major constituents of scale.
- Calcium carbonate is the dominant component.
- Bivalves larvae (which are comprised of calcium carbonate are observed in the matrix. Presence of bivalve larvae is significant in the discussion of scale nucleation.
- Presence of magnesium hydroxide due to NCG purge of CO_2

Results: Inorganic

Flash Chamber

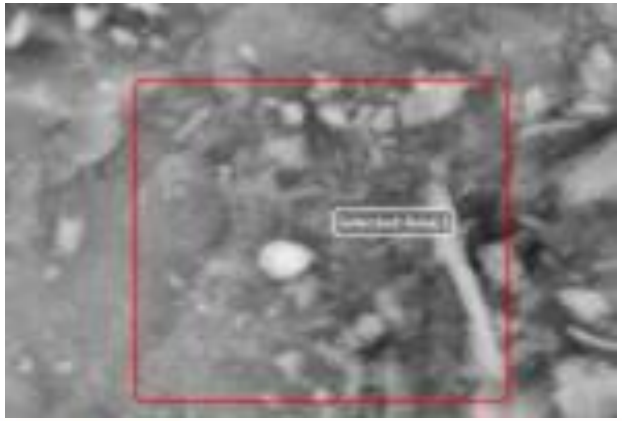


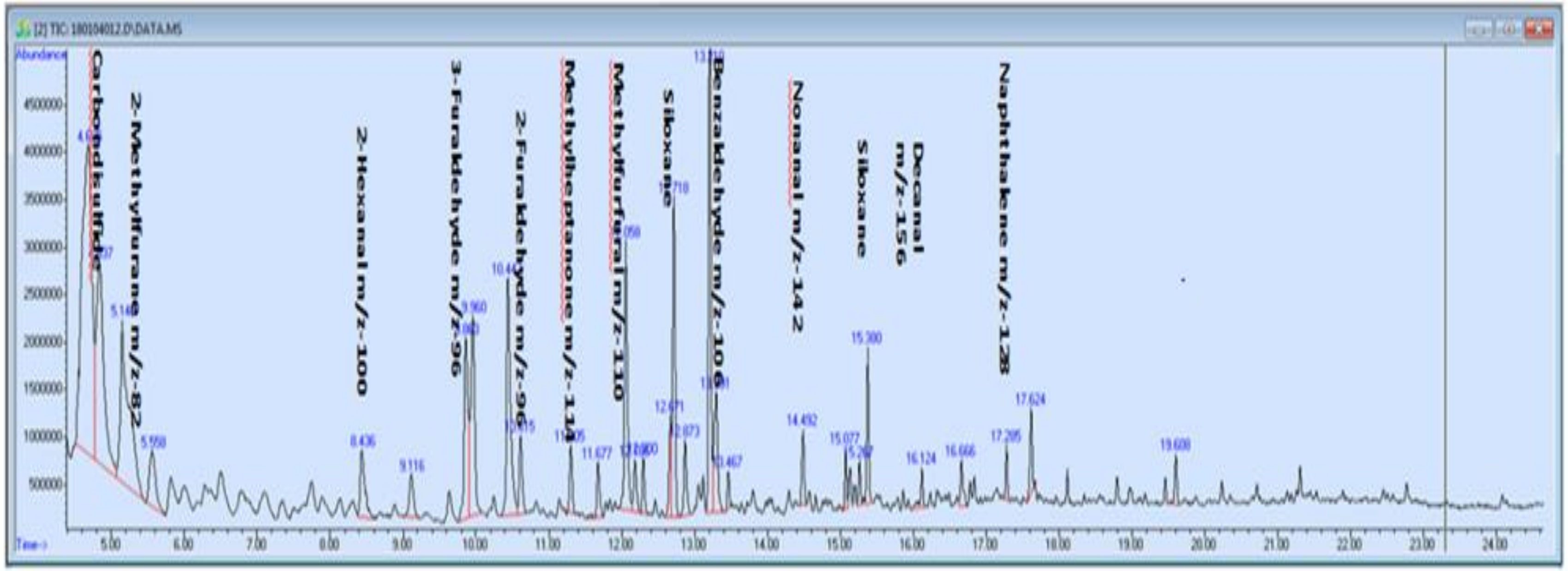


- Magnesium hydroxide is the main constituent of scale.
- No intact cellular structures are observed from macrofoulants such as bivalves and gastropods (due to high temperature (above 90^o C).

Results: Organic

- **Deaerator**

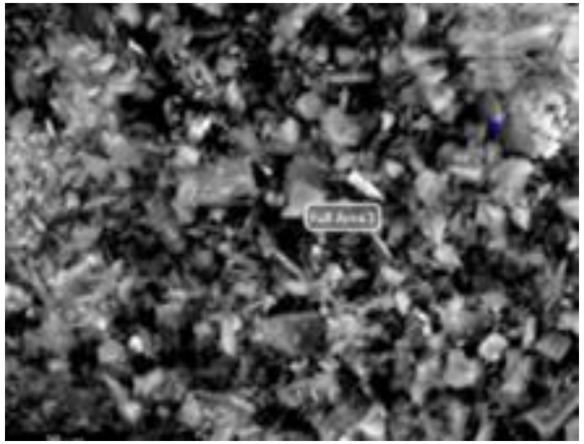


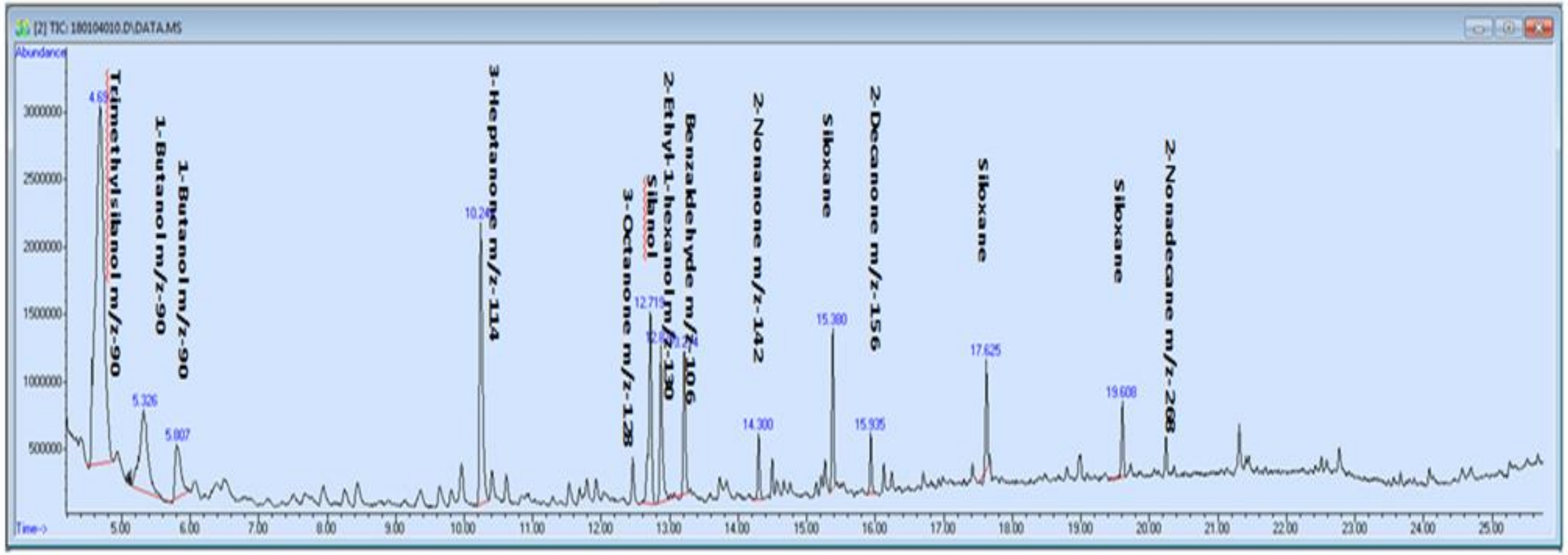


- SEM and EDX indicate the presence of biofilm (CH_2O).
- Microscopic examination and gram stain indicate the presence of gram negative locomotive bacteria.
- ATP analysis confirms the presence metabolic activity within scale.
- GC-MS reveal the presence of low molecular weigh organic compounds (ranging up to 200) that are ketones and aldehydes of a lipid and carbohydrate nature.

Results: Organic

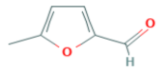
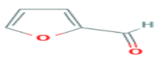
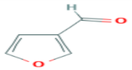
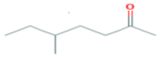
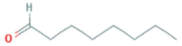
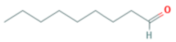
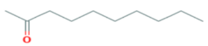
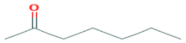
Flash Chamber





- Result reveals the presence of ATP activity though in low concentrations.
- Microscopic examination showed bacterial presence but microbes were not locomotive. Movement only by cytoplasmic streaming.
- No presence of macrofouling species.
- GC-MS results reveal the presence of aldehydes and ketones that were lipid based.

Organics Identified in Scale

		Structure	Compound	Boiling Point (°C)	Solubility in Water (g/L)	Density (g/cm³)
Carbohydrate-Based Organics	Aldehydes		5-Methylfurfural	187.0	29.100	1.107
			2-Furaldehyde (Furfural)	161.7	83.000	1.160
			3- Furaldehyde	145.3	44.000	1.110
			Nonanal (Nonyl aldehyde)	191.0	0.060	0.830
			Decanal	83.0	0.008	0.830
	Ketones		2-Heptanone	126.0	4.210	0.800
			Methy-Heptanone	151.0	2.260	1.480
Lipid-Based Organics	Aldehyde		Hexanal	131.0	4.800	0.815
			Octanal	171.0	0.560	0.821
			Nonanal	191.0	0.132	0.827
	Ketones		Decanone	208.5	0.008	0.83
			2-Heptanone	151.0	4.210	0.800
			6-Methyl-2-Heptanone	167.0	1.370	0.816

- Organic compounds were related to aquatic organics in the sea (Diatoms, blue green algae, seaweed, fungi, shell fish, fish, etc.).
- Organics are low molecular weigh slightly over 200 Daltons (D).
- Commercial Anti-Scalants used to control scale growth by distorting crystal lattice formations have molecular weights in the 2500 D range.
- Researchers at DTRI have produced an Anti-Scalant with molecular weights above 1200 D.
- Low molecular weight organic intercalants indicate that organics may play a role in scale development (nucleation/growth).
- Organics have partial negative charges and may act to regulate scale nucleation and growth.

Implications of Our Findings

- The implication of our findings alters the discussion on scale nucleation and growth in thermal processes.
- Scale nucleation and growth can not solely be understood from the thermodynamic aspect of Gibbs free energy.
- Introduction of organics and its effect on scale growth and nucleation necessitates that scale nucleation and growth be understood from
    - **Thermodynamic**
    - **Kinetic**
    - **Surface Interaction aspects**
- Our findings makes it possible to consider an alternative approach for arresting scale formation in industrial processes. This approach is to control scale formation **not** from the **growth stage** but from the point of **scale nucleation**.

Project Implications

- This work was conducted from scale of a commercial desalination facility. It is hypothesized that organics in scale and its effects on scale formation may also be extended to other industrials processes.

- Work on the kinetic aspect of scale formation exploring rates of reaction and scale formation are being explored.

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Thank You……