Polysaccharide based scale inhibitors for cooling water systems

Circular Biobased Products Symposium 2023

June 22th 2023, Lambertus (Ben) van den Broek

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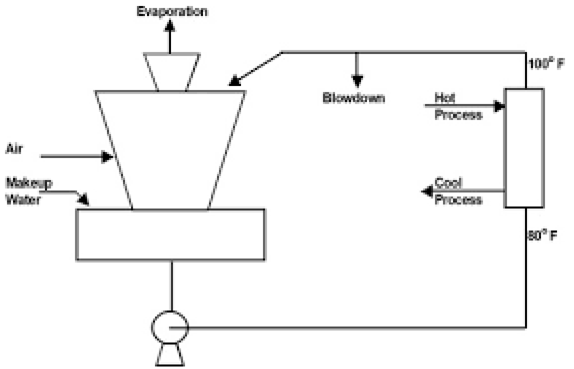

Scale deposition

- In cooling water systems, the water constituents become concentrated due to water evaporation
- Scaling ions such as Ca^{2+} and carbonate alkalinity gradually concentrate to exceed solubility and form scale deposition

$$Ca^{2+} + 2\ HCO_3^- \leftrightarrows CaCO_3\ (s) + CO_2\ (g) + H_2O$$

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Scale deposition

- In general a crystallizing procedure involves four stages

    - Oversaturation
    - Nucleation
    - Crystal growth around nucleus
    - Continuous growth of microcrystals resulting in scale layer thickening

Scale deposition

- Scale deposition can results in
    - Reduced heat transfer efficiency of heat exchange equipment
    - Obstructing pipelines
    - Economic loss due to inefficient cooling

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Scale inhibition

- Scale inhibitors can delay or prevent scale formation when added in small concentrations in water that would normally create scale deposits

- Different scale inhibition mechanisms are known
  - Complexation of scale inhibitors with free scaling ions in order to prevent them from being precipitated via strong chelation and dispersion effect (suspended in aqueous solution)

Scale inhibition

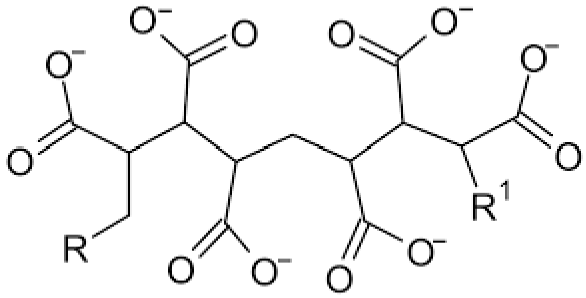
- Threshold inhibition. These inhibitors effectively inhibit scale formation at very low dosages (e.g., 1,000 times less than stochiometric ratio of scaling cations)

- Functional groups of the scale inhibitors can adsorb active sites of the scale crystal's particular growth location, hereby modifying crystal morphology and distorting the crystal lattice

Scale inhibition

- Phosphorus scale inhibitors include phosphates and phosphonates
  - Increase in phosphate content (eutrophication)
  - Formation of persistent compounds (aminomethylphosphonic acid (AMPA))

- Polycarboxilic, polysulfonic acids, and their derivatives
  - Non-degradable

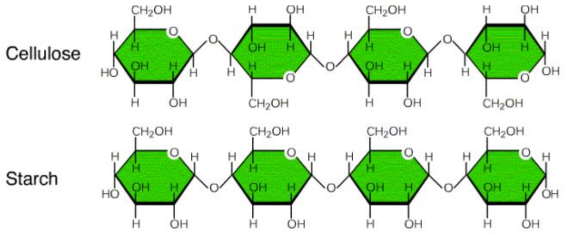


Scale inhibition

- Environmental protection pressure and government legislation lead to research towards ‘green’ scale inhibitors
    - Excellent anti-scaling capacity
    - Non-toxic
    - High biodegradability after discharged
    - Non-corrosiveness
    - Thermostability
    - Free of phosphorus, nitrogen and heavy metals
    - Use of biobased/renewable sources (side streams) to lower carbon footprint

Polysaccharide based scale inhibitors

- Examples of promising bio-materials
  - Polysaccharides
  - Proteins
  - Plant extracts
  - Natural microbiological products



Polysaccharide based scale inhibitors

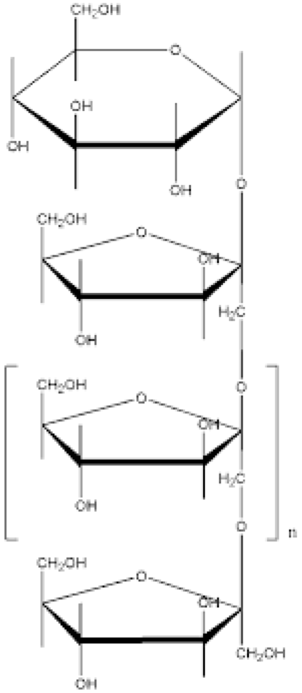
- The advantages of polysaccharides is their wides source, biodegradable, non-toxic and low price

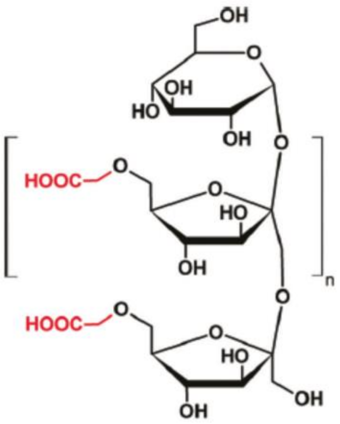
- The disadvantages of polysaccharides is their poor water solubility, easy decomposition and large doses needed

Polysaccharide based scale inhibitors

- Most common polysaccharides based scale inhibitors are modified by introducing functional groups
  - Starch (carboxyl, sulfonate)
  - Inulin (carboxymethyl)

- Introduction of copolymers
  - Starch
  - Chitosan
  - Cellulose





Polysaccharide based scale inhibitors

- Anionic polysaccharides such as alginates from seaweed and pectin from fruits can be used to bind calcium ions in their native form
- Ca^{2+} ions form a bridge between two uronic acid units

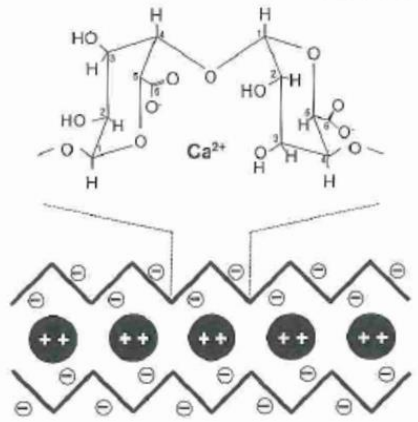
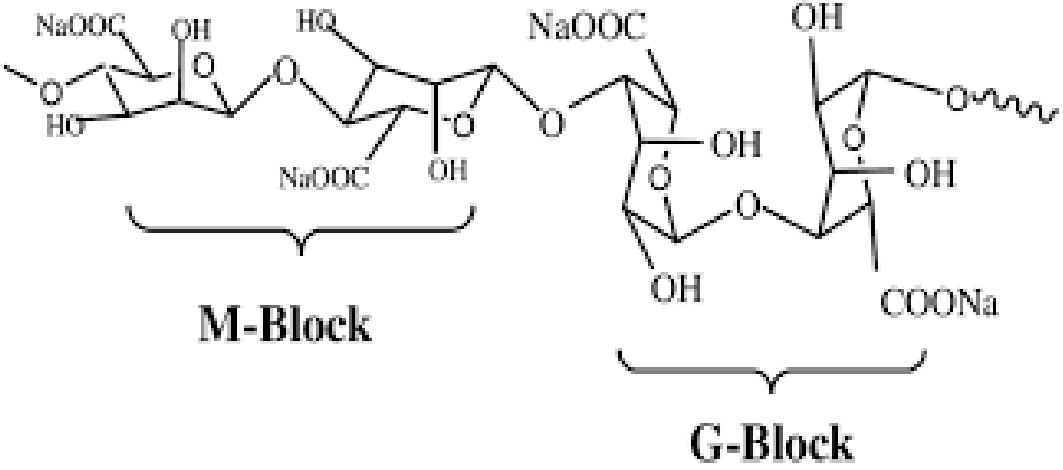


Fig. 1. Schematic representation of the "egg-box" model for junction zone formation in pectin–calcium gels. Polygalacturonic acid chains are represented by black lines, calcium ions and carboxyl groups by circles.

Polysaccharide based scale inhibitors

- Alginate consists of mannuronic acid (M) and guluronic acid (G) moieties
- Alginate can bind Ca^{2+} ions, however, guluronic acid moieties bind Ca^{2+} ions more tightly



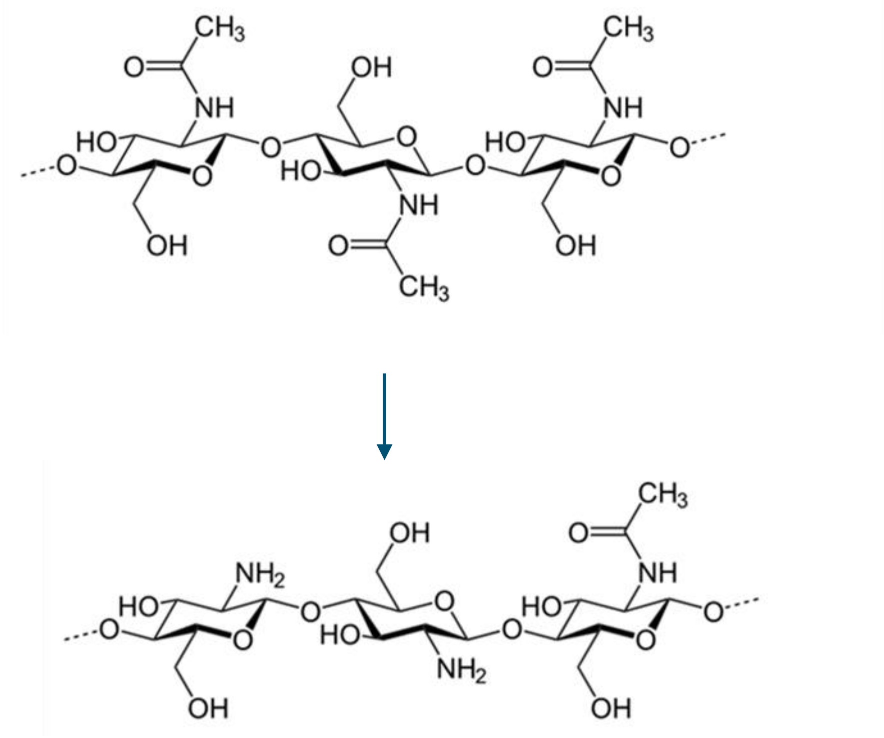
Polysaccharide based scale inhibitors

- Higher concentrations of alginates are very viscous
  - To improve solubility the alginate chain can be hydrolysed by enzymes or acid to lower the viscosity

- Methods to influence the calcium binding of alginates
  - Playing around with the M-G ratio and pattern (depending on the source) will also influence the calcium binding of the alginate

Polysaccharide based scale inhibitors

- Chitin (insoluble)
- Chitosan (soluble at low pH)



Polysaccharide based scale inhibitors

- To increase the solubility of chitosan can be modified by quaternary ammonium salinization and grafted with copolymerization for anti-scaling purposes

- Without modification chitosan can be mixed with alginate
  - Chitosan inhibits calcium carbonate scales formation
  - Sodium alginate showed the highest inhibition of calcium sulfate
  - However, the addition of sodium alginate to chitosan, as a package, has a dual control effect on carbonate and sulfate scale formation

Polysaccharide based scale inhibitors

- Furthermore, chitosan can be further fine-tuned by de degree of acetylation and the pattern of acetylation

- The increase in solubility can be achieved by producing chitosan oligosaccharides by acid or enzymes

Conclusions

- Modified polysaccharides are used to prevent scale formation in cooling water systems

- The antiscalent properties of these modified polysaccharides is good, although the biodegradation could be improved in some cases

Conclusions

- The use of native polysaccharides such as alginate, pectin and chitosan can be improved for antiscalent purposes without introducing new functional groups

- Enzymes and/or acids can be applied to increase the antiscalent properties and to improve the biodegradability. This will results in ‘greener’ scale inhibitors

Thank you for your attention

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