VEOLIA

Green Corrosion & Scale Inhibitors for Cooling Systems

JCMEC Technical Conference

April 26th 2017

Dave Christophersen

WATER TECHNOLOGIES

Outline

VEOLIA

- *Corrosion & Scale Inhibitors in Cooling Systems*
- *What is “Green” for Industrial Chemicals*
- *Principles of Green Chemistry*
- *Green Molecules*
- *Green Polymers*
- *Case Studies*
- *Conclusion*

Overview

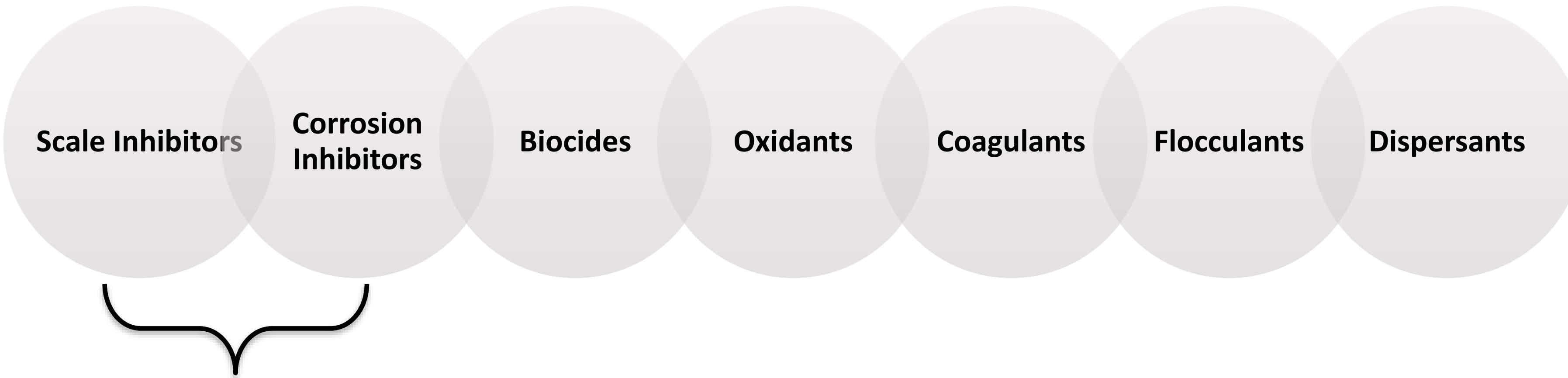
- Chemical treatment of cooling systems is a generally accepted need to minimize water related problems

- There has always been a balance between safe handling, application of chemicals, performance, reliability, and cost.

- This presentation will address:
  - ✓ What is meant by green in industrial cooling water treatment
  - ✓ What developments there have been in green treatment chemicals
  - ✓ Are there green attitudes that you may want to consider for your site

Water Treatment Chemicals

- Water treatment chemicals are used in water systems and processes including:

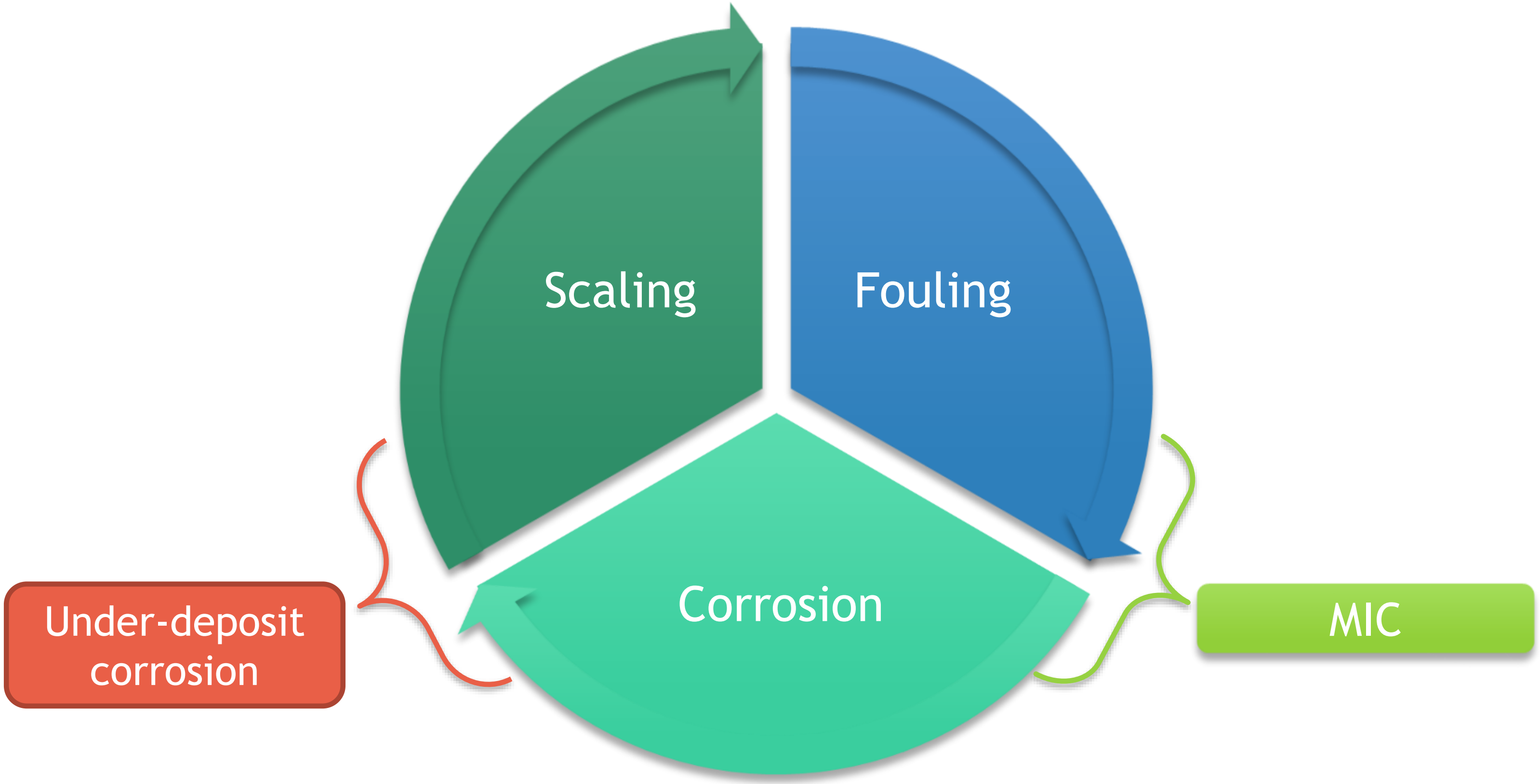


Most commonly used

- Each category has number of chemicals, and has green and toxic ones
- Each one works under specific conditions

Problems in Cooling Systems

- The main problems in cooling systems are:



Green Can Have Many Shades

- What does it mean to be green?
- How green am I?
- What more should I do?

What is the Big Picture?

- We need to take everything into account:
  - Carbon footprint
  - Life cycle assessment
  - Water Impact Index (WII)
  - Other impacts on environment and human health
  - Principles of green chemistry and green engineering
  - Quality of life

- We need to innovate with the basis being:
  - Safety
  - Sustainability
  - Energy & water conservation
  - Green principles

Principles of Green Chemistry

Common Measures of Green

- Organic and Biodegradable
- Aquatic Toxicity
- Non Phosphorous (causes Eutrophication)
- Minimal pollutants or By-products to Water, Solids, or Air
- Carbon Footprint
- Water Use Efficiency

- Common emphasis on green is the direct environmental affect and discharge limitations for corrosion inhibitors and scale control chemicals that readily biodegrade, have low mobility for minimum environmental impact, and are still cost-effective.

Heavy Industry Requirements

- Heavy industry generally has **higher stress** than C&I and middle industry.
- **High water temperatures** and high heat exchanger skin temperatures require stronger scale and corrosion inhibition. So selection of effective chemistry and dosages are critical.
- Biofilm and bacteria control extremely important. Common to include effective biocides and biopenetrants / biodispersants.
- Greater stress requires **high performance polymers**.
- Establish **Key Performance Indicators** (KPI's).
- Invest in good **monitoring and control equipment**.
- Set up proper service and maintenance program.

Types of Possible Cooling Water Conditions

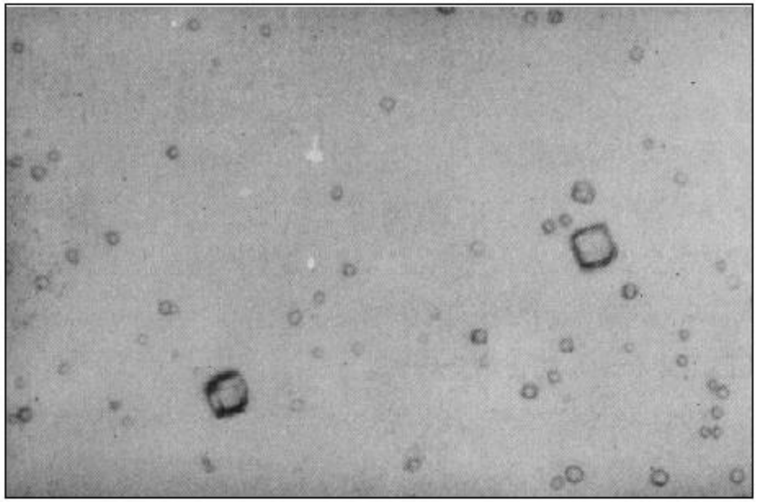
- Generally Corrosive Waters
- Pitting Corrosion Conditions
- Scaling Conditions
- Suspended Solids Concerns
- High Organic and/or Biological Concerns
- Low or Moderate Skin Temperatures
- High Skin Temperatures
- Low Stress
- High Stress
- Short, Medium, Long Retention Times (Holding Time Index, Half-life)
- Changing Water Sources or Quality

Some Considerations on Inhibitor Selection

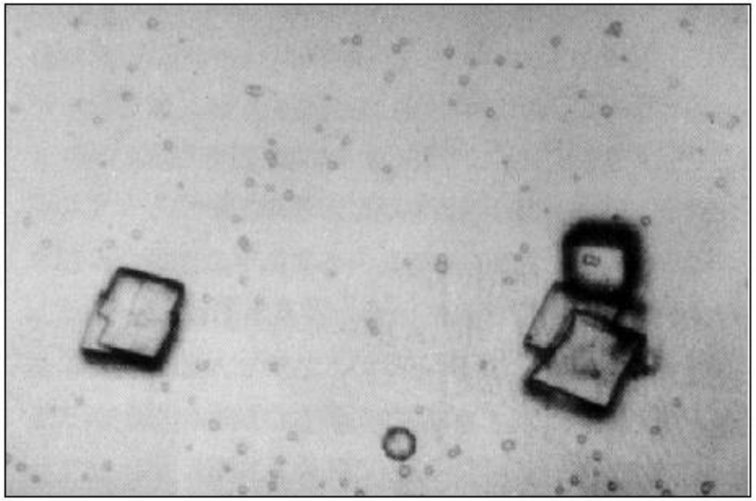
- Stability in the system
- Effectiveness at high cycles and long retention times
- Relative performance capabilities to established chemistries
- Metals protected (carbon steel, yellow metals, galvanized metals)
- Effectiveness on disposition inhibition (calcium carbonate, calcium sulfate, silica, iron, suspended solids, etc)
- Contribution to biological growth
- Compatibility with chlorine, other oxidants, biocides, and other chemicals
- Formulation compatibility
- Dosage requirements and effective dosage range
- Cost effectiveness
- pH range, LSI Range, Calcium Tolerance

Scale Inhibitors

- Scale inhibitors are surface-active negatively charged chemicals
- As minerals exceed their solubility's and begin to merge, the inhibitor become attached.
- Scale Inhibitors are: organic, inorganic, polymeric
- Each inhibitor inhibits specific scales @ specific saturation level



a) After 2 minutes from crystal deposition (x 400)



b) After 12 minutes from crystal deposition (x 400)

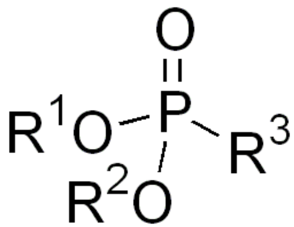
Scale Inhibitors

- The following groups of scale inhibitors are the most common ones used in cooling water treatment applications:

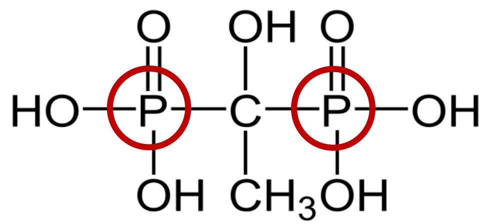
- Polyphosphates
- Phosphonates
- Polymers

Scale	Effective inhibitor
Calcium carbonate	Phosphonates Maleic anhydride homopolymers Acrylic acid homopolymers
Calcium phosphate Zinc phosphate	Acrylic acid copolymers and terpolymers Maleic anhydride copolymers
Magnesium silicate	Acrylic acid copolymers Acrylamide homopolymers Maleic anhydride copolymers
Calcium sulfate	Polyphosphates Phosphonates Acrylic acid homopolymers

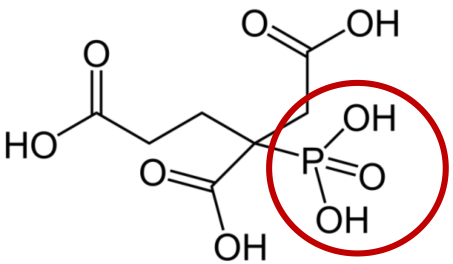
Current P-Based Inhibitors



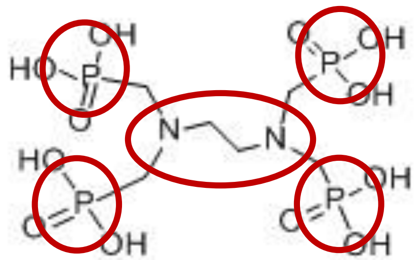
Phosphonate general formula



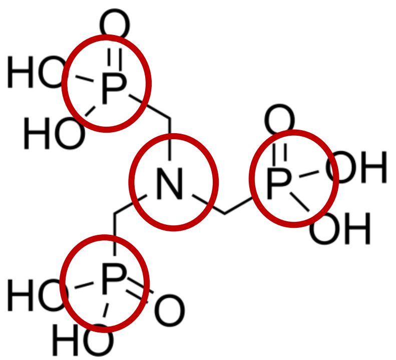
HEDP



PBTC



EDTMPA

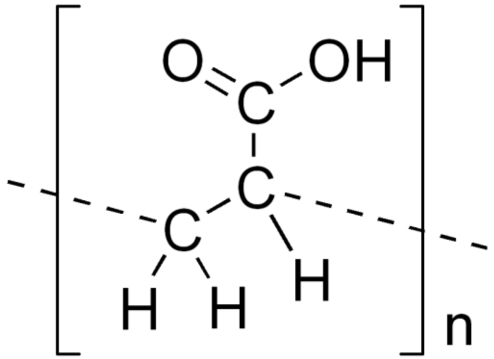


EDTNP

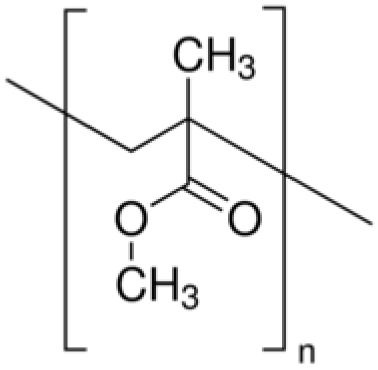
Eutrophication

Polymeric Inhibitors

- There are wide range of polymers can be used as below:
- Acrylic acid homopolymer (PAA)
- Acrylic acid copolymers and terpolymers
- Polyesters



PAA



Polyester

Low biodegradability

Corrosion Inhibitors in Cooling Systems

- Corrosion inhibitors can be classified as below:

Type of corrosion inhibitor		Example of inhibitor	Characteristics of protective film
Oxide film type (passivation film type)		Chromates, Nitrites, Molybdates	Fine and thin film (30-200Å), excellent corrosion protection
Precipitation film type	Forming insoluble salts with ions, etc., in water	Polyphosphates, o-PO_4 Phosphonates, Zinc salts	Porous and relatively thick film, slightly poor adherence to metal, fairly good corrosion protection
	Forming water insoluble salts with the protected metal ion	Azoles	Close and thin film, good corrosion protection
Adsorption film type		Amines, Surfactants	Formation of adsorption layer on metal surface

Most of them are restricted: CrO_4^{-2} , MoO_4^{-2}, NO_3^-, NO_2^-, Zn

New Chemistry - Green

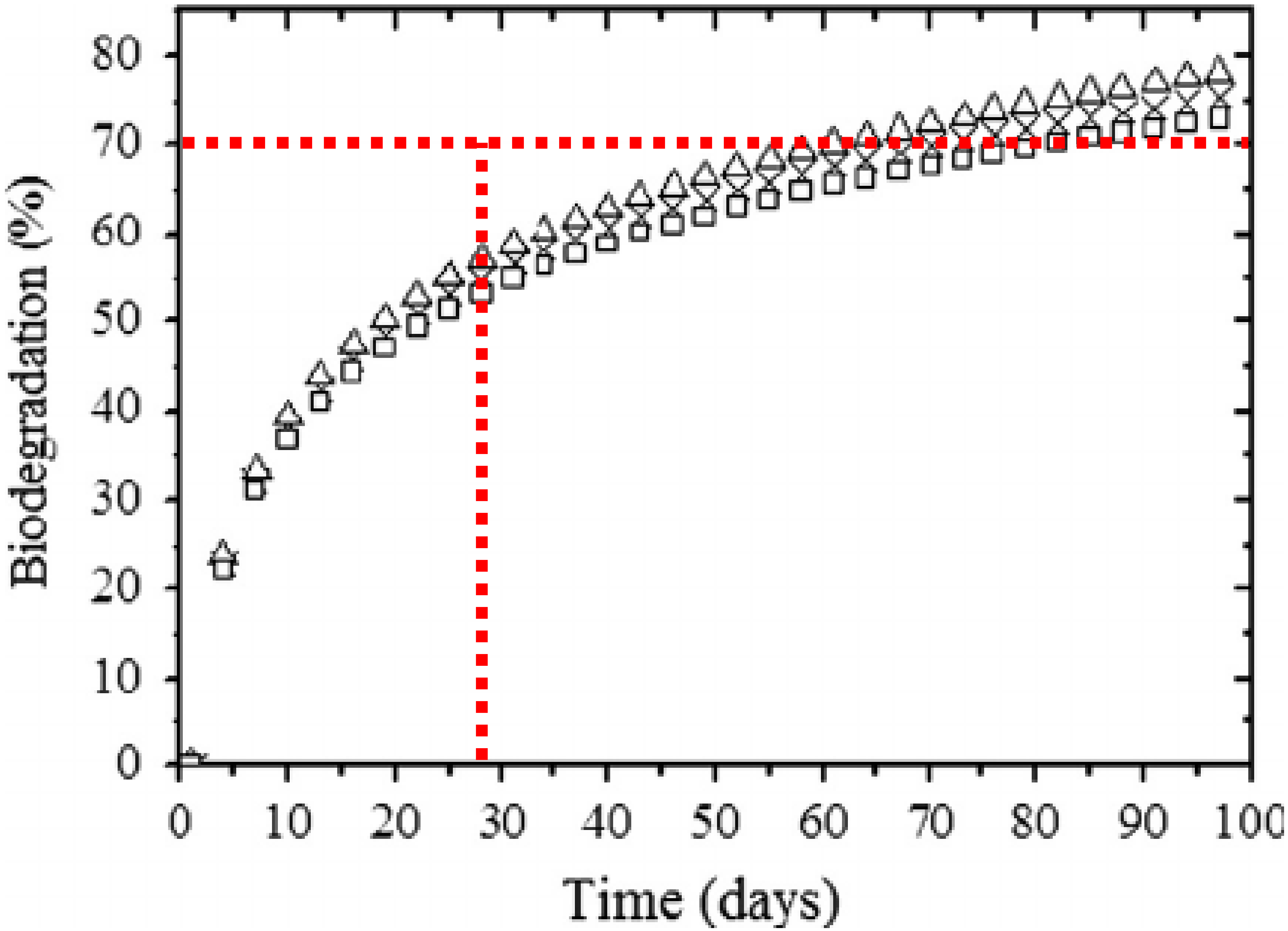
There is a need for new generation of corrosion & scale inhibitors matching the "Green Principles" to be used for the Industrial applications

Biodegradability Measurements

- Biodegradation testing of commercial chemicals is generally performed using test guidelines of the Organization for Economic Cooperation and Development (OECD).
- Information on the degradability of organic chemicals may be used for hazard assessment or for risk assessment.
- Hazard assessment or risk in general, and aquatic hazard classification in particular, are normally based on data obtained in standardized tests for ready biodegradability.
- Degradation rates, or half-lives, are preferably determined in simulation biodegradation tests conducted under conditions that are realistic for the particular environmental compartment.
- **Readily Degradable :** Six Test Methods in OECD Guidelines: Biodegradability: **70%** DOC reduction in 28 days.
- **Inherently Degradable: 20%** DOC Reduction in 28 days.

Achieving High Biodegradability

- OECD 306 Degradation Study

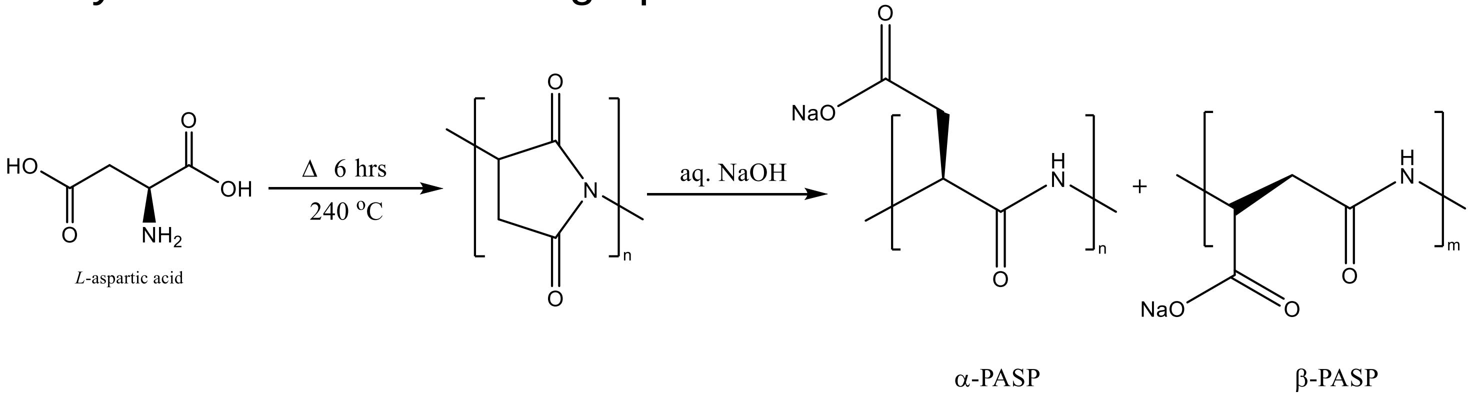


Some "Green Chemical" Considerations

- Inulin derivatives
- Thermal Polyaspartite (PASP)
- Starches
- Polyepoxysuccinate (PESA)
- Polymaleic acid
- Xylonic Acid
- Glyceric Acid
- Gluconic Acid
- Tartronic Acid
- Glucaric Acid
- Glucoheptaric Acid
- Other organic acids
- Low P phosphonates
- Carboxylic & Phoshinocarboxylics
- Mimosa tannin
- Guar Gum
- Carboxymethylcellulose (CMC)
- Other Misc. Organics

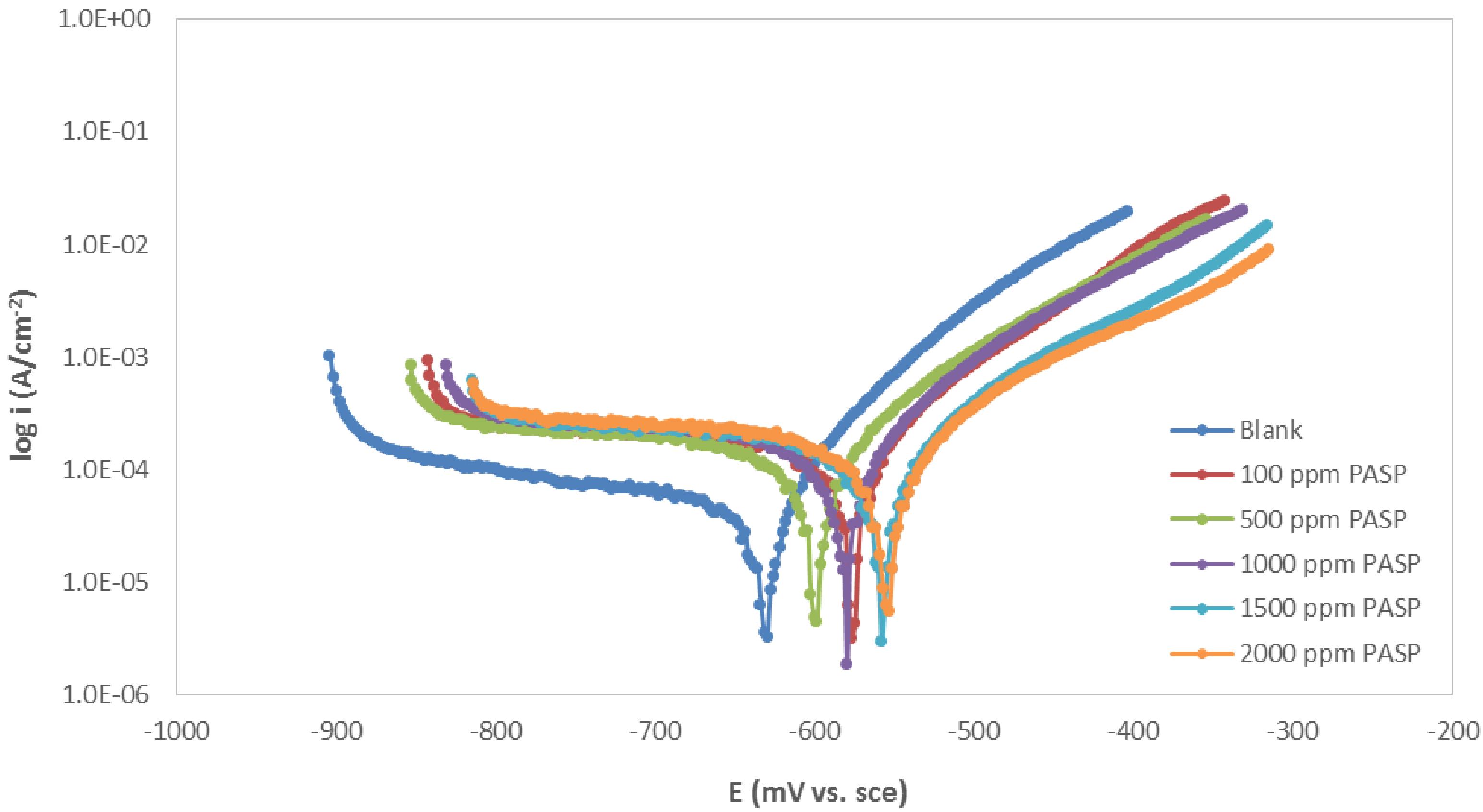
Green Chemical - Polyaspartate (PASP)

- Polyaspartate (PASP) can be produced in high yield and with little or no waste products.
- Polyaspartate is a biopolymer synthesized from L-aspartic acid, a natural amino acid.
- Polyaspartate has similar properties to the polyacrylates and so it can be used as a dispersant, or scale inhibitor with high effciency.
- Polyaspartate is readily biodegradable.
- PASP is excellent scale inhibitor for some conditions and good anodic mild steel corrosion inhibitor
- Potentiodynamic study shows its good efficiency in corrosion inhibition study and proofed by SEM and AFM micrographs



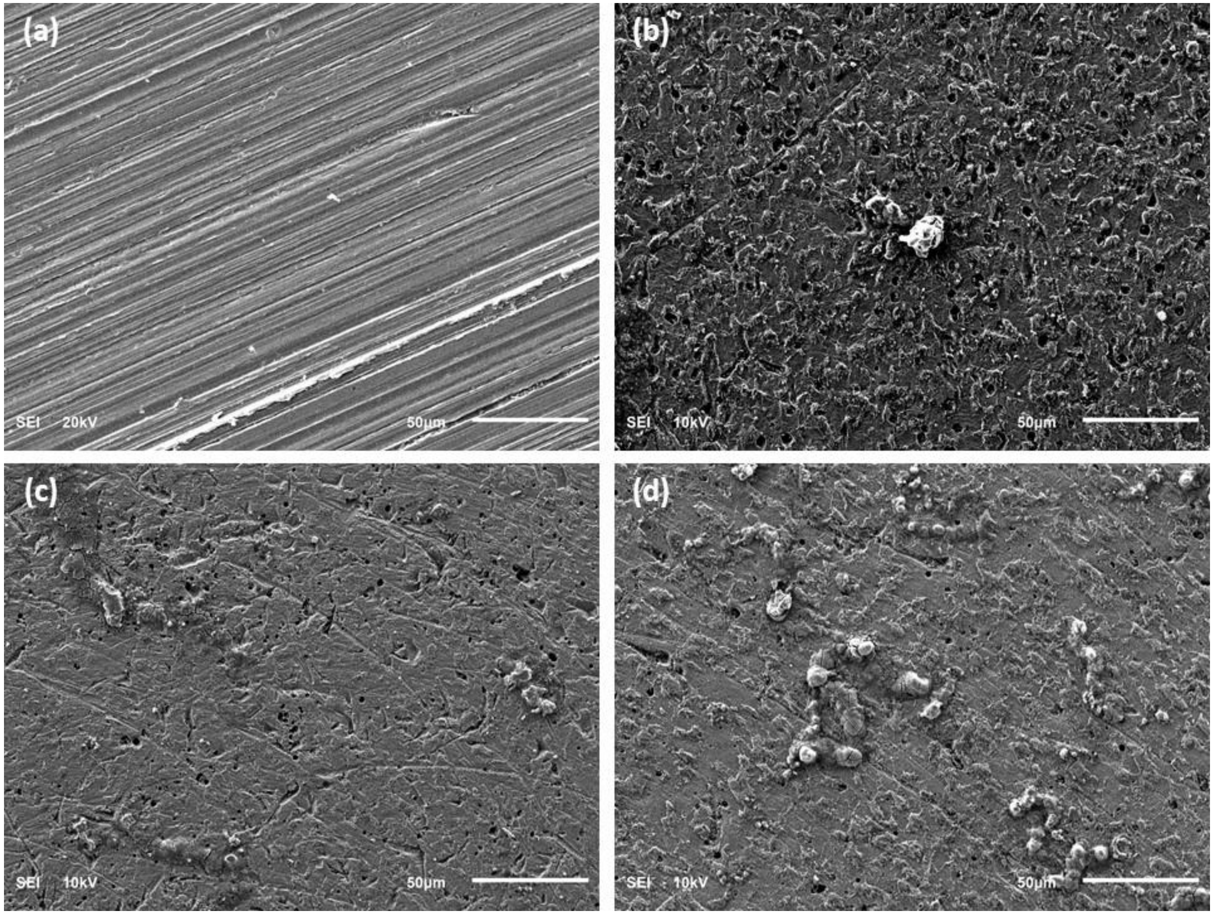
Green Chemical - Polyaspartate (PASP)

- Tafel graphs comparing to 3% NaCl as Blank under aeration conditions



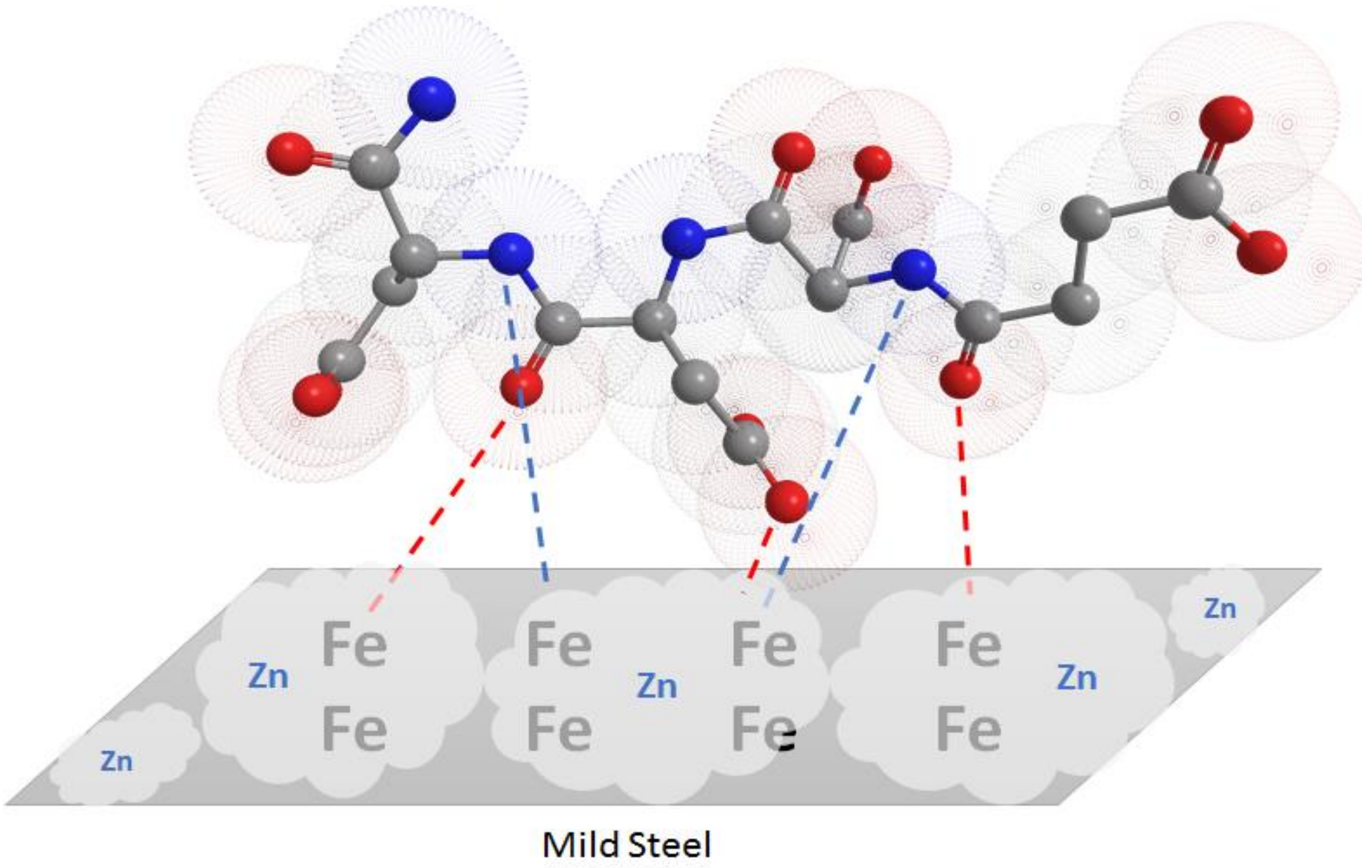
Green Chemical - Polyaspartate (PASP)

SEM micrographs of mild steel in 3% NaCl solution after 24 hrs immersion time at 25 (a) polished before immersion, (b) after immersion without inhibitor, (c) after immersion with 2000 ppm PASP (d) after immersion with 2000 ppm PASP and 10 ppm Zn.



Green Chemical - Polyaspartate (PASP)

- The suggested inhibition mechanism by Veolia team



Green Chemical - Carboxymethylinulines (CMI)

- Carboxymethylinulins (CMIs) are derivatives of inulin
- It is a natural polydisperse poly(saccharide) consisting of fructosyl fructose units and carboxylate groups are introduced into the poly(saccharide) by carboxymethylation.
- Renewable backbone chemistry that is functionalized
- Good inhibitory performance with regard to CaCO3 and CaSO4 scale formation
- High biodegradability
- Works at acceptable dosage
- Implemented commercially for bulk quantity

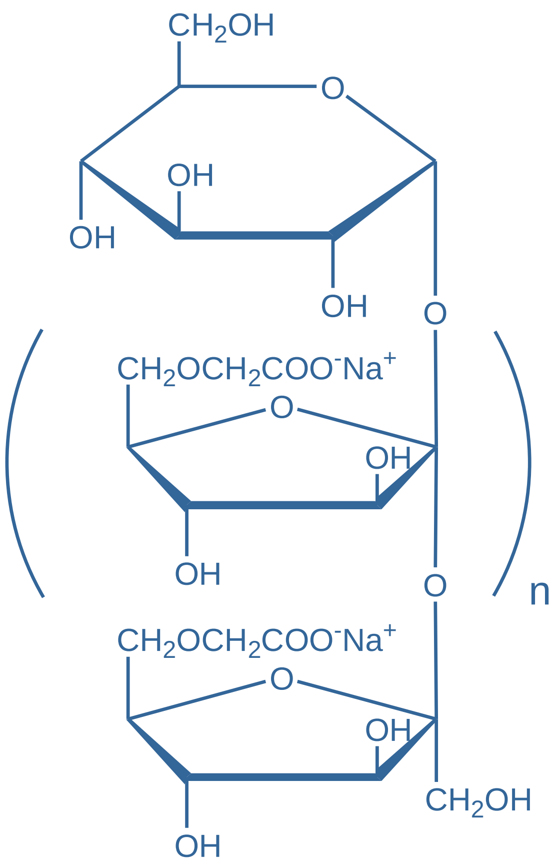
The source of Inulin: Cichorium Intybus

Chicory leaves → Salad

Chicory roots → Source of Inulin

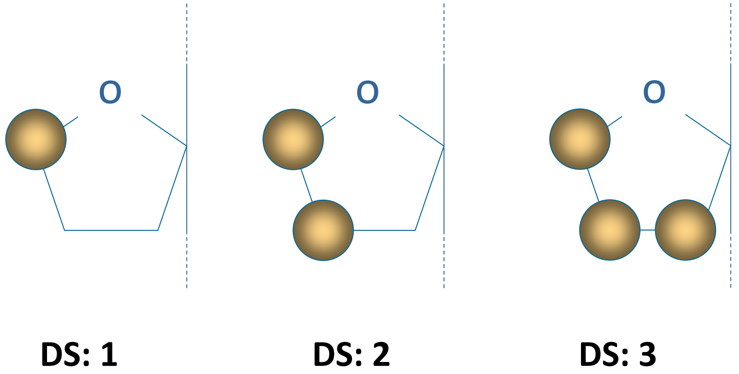
Roasted Chicory roots → Coffee substitute

Structure of Carboxymethyl Inulin (CMI)



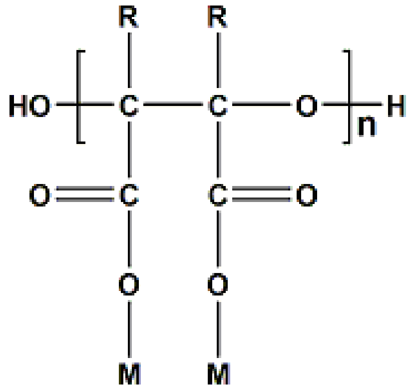
Average Molecular Weight = 2000

Degree of substitution (DS): average amount of carboxymethyl groups / monosaccharide unit.



Green Chemical - Polyepoxy succinate (PESA)

- PESA can be produced in high yield and with little or no waste products.
- PESA is produced commercially in bulk quantities
- PESA has outstanding scale inhibition on $CaCO_3$ and $CaSO_4$ and dispersion properties
- PESA is readily biodegradable.
- PESA is good anodic mild steel corrosion inhibitor and work synergistically with other organic inhibitors
- PESA has different chemical forms depending on the application

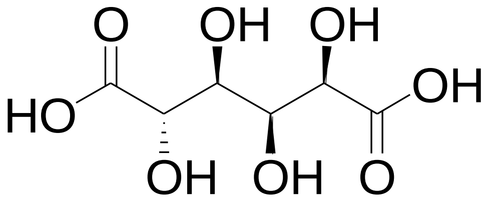


Notes: n=2-10

M--- Na^+ or H^+, K^+, NH_4^+

R---- H or C_{1-4} alkyl

Sodium Glucarate - Safe & Sustainable Chemistry



D-Glucaric acid

SAFER CHOICE
Meets U.S. EPA Safer Product Standards
epa.gov/saferchoice

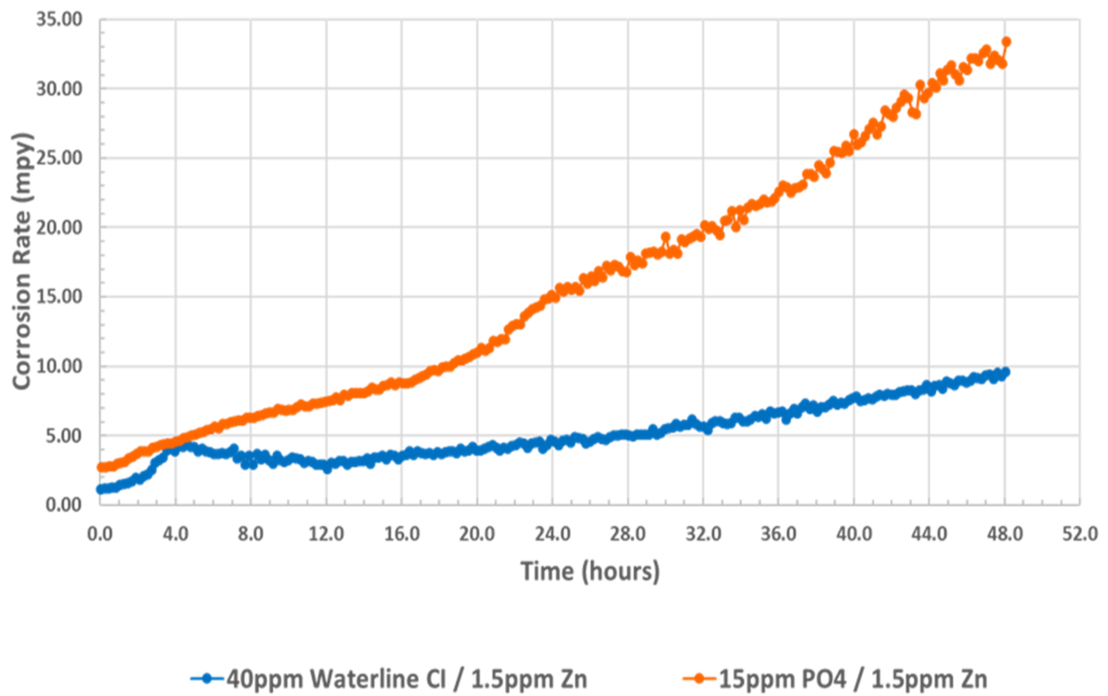
Sodium glucarate is listed with a full green circle on the U.S EPA Safer Chemical Ingredients List

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 97%
FP

Mild steel Test in simulated Heavy Industry water

- Glucaric vs. Stabilized Ortho-PO_4 Program – Corrosive Water Analysis and Test Results

Ion	Concentration (mg/L) 5 COC
Na^{+1}	40.9
Mg^{+2}	60.0
Ca^{+2} (as $CaCO_3$)	550
Cl^{-1}	564
SO_4^{-2}	450
HCO_3^{-2} (as $CaCO_3$)	61.0
Additional Parameters	
TDS (mg/L)	1414
Conductivity (µS/cm)	2210
Temperature (°C)	40.0
pH	7.90-8.00
LSI	0.98 ± 0.05

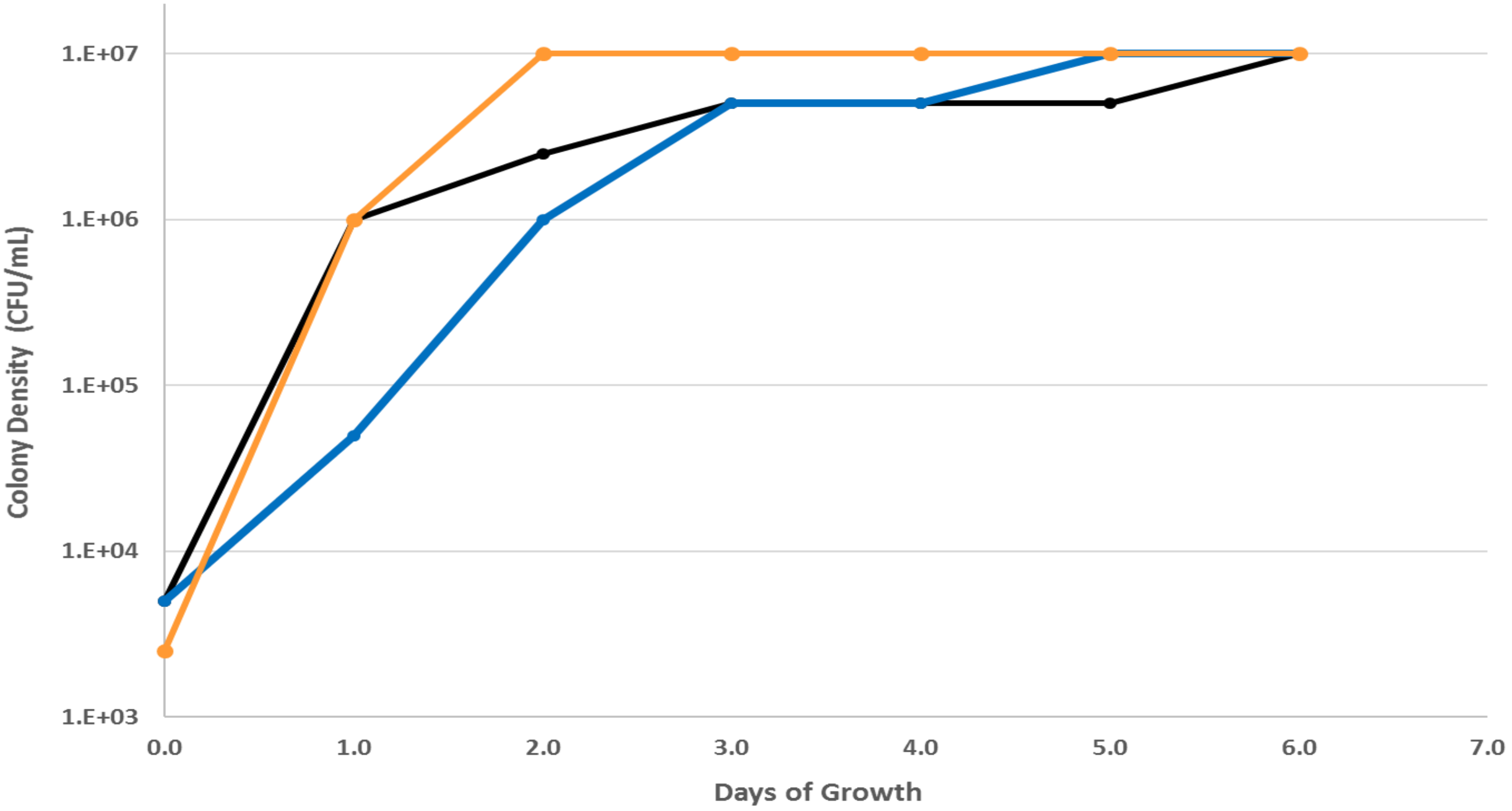


40.0mg/L *Glucaric product*
1.50mg/L Zn
41.5mg/L tot. act. product

15.0mg/L PO4
1.50mg/L Zn
18mg/L stabilizing copolymer
34.5mg/L total active product

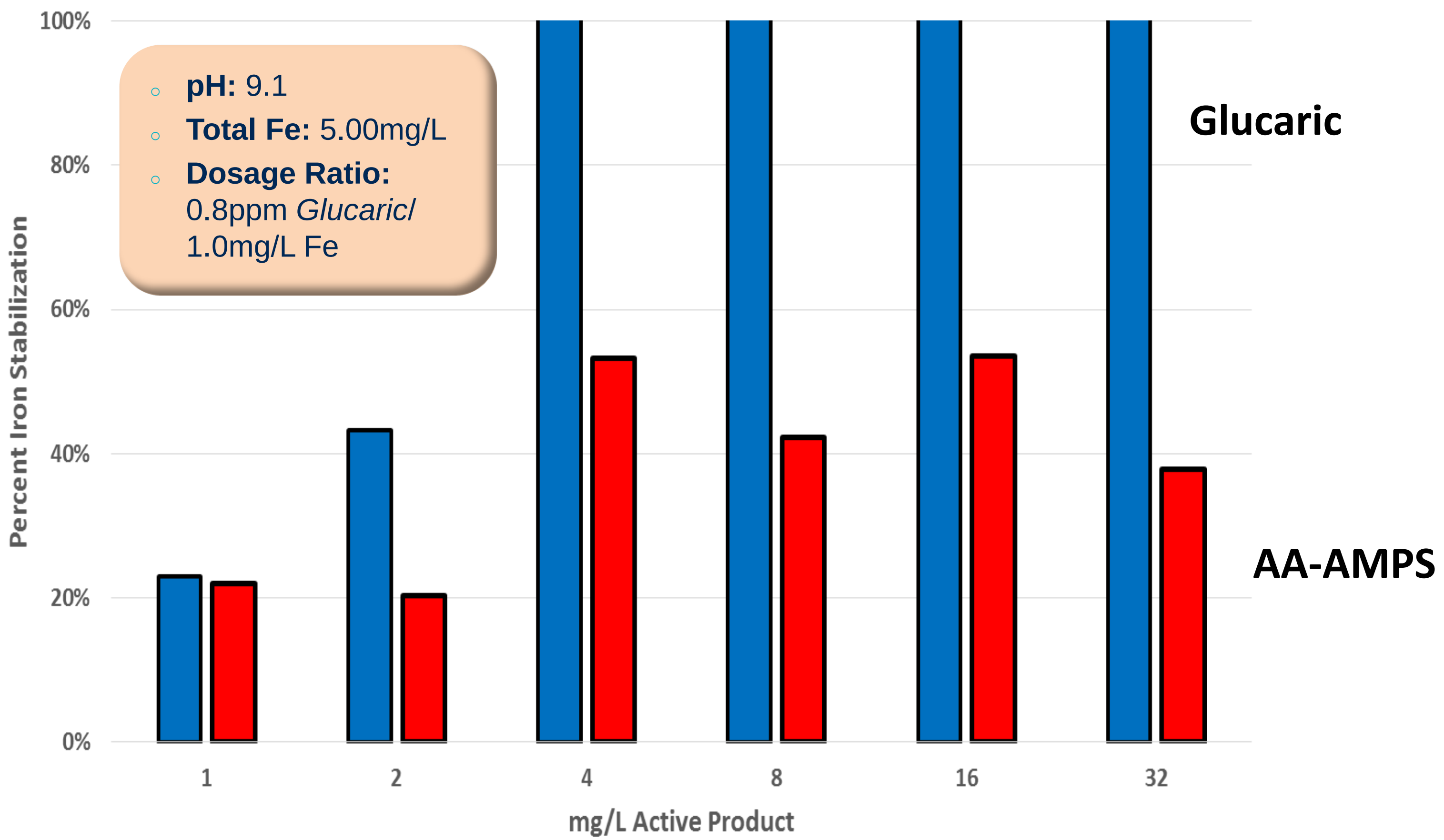
Sodium Glucarate - Biological Contributions

- Gluraric does not contribute to measurable biological growth in cooling tower water



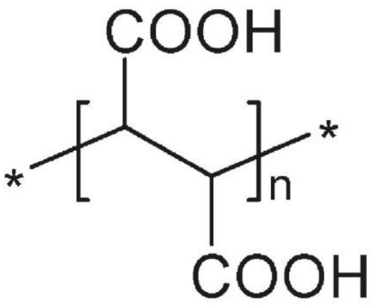
Sodium Glucarate - Iron Stabilization Performance

- Glucaric performed well versus AA:AMPS when compared at equal active dosages

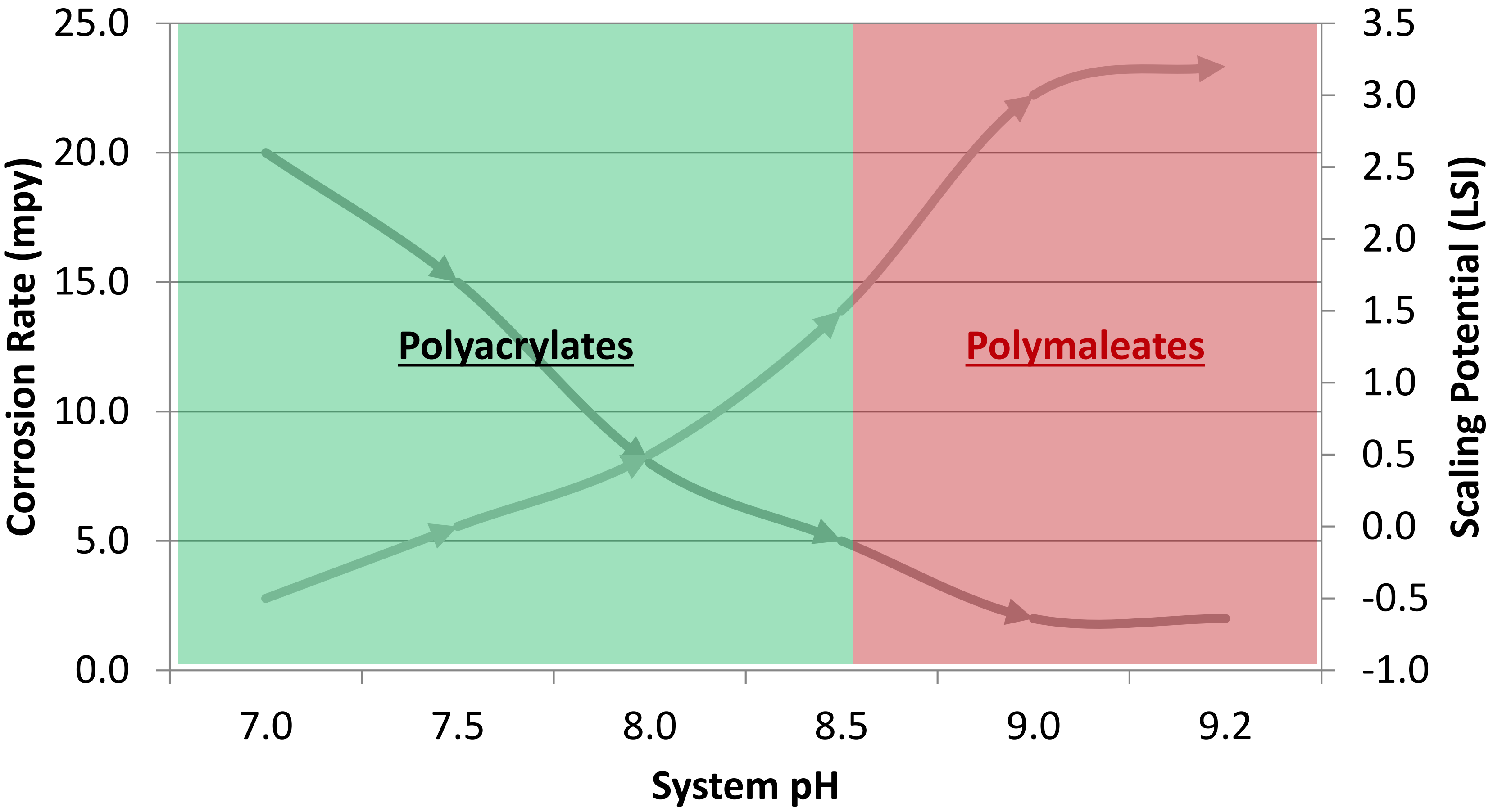


New Enhanced Polymaleic Acid

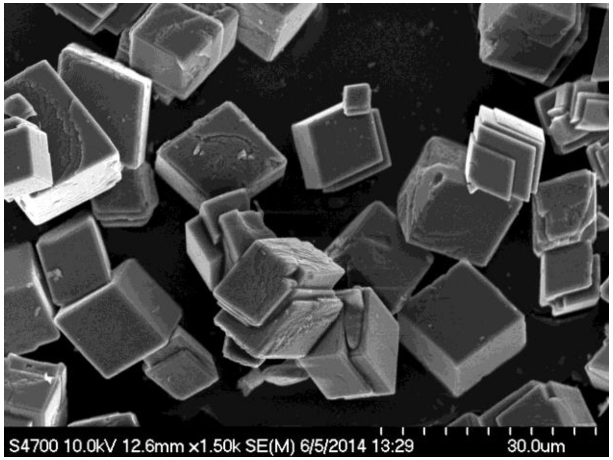
- Exceptional polymer stability in harsh water conditions
- Best-in-Class crystal habit modification for calcite ($CaCO_3$)
- Effective calcium carbonate threshold inhibitor
- Exceeds efficacy of common maleic:acrylic copolymers
- Used to replace or reduce phosphonates and P contribution
- Applied currently by Veolia as scale inhibitor in specific applications
- Highly effective at low dosages

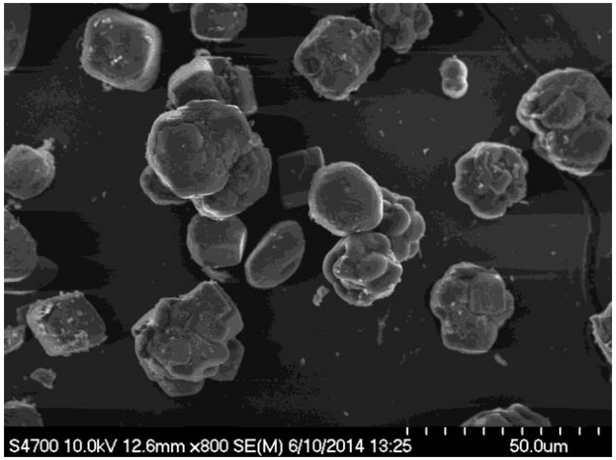


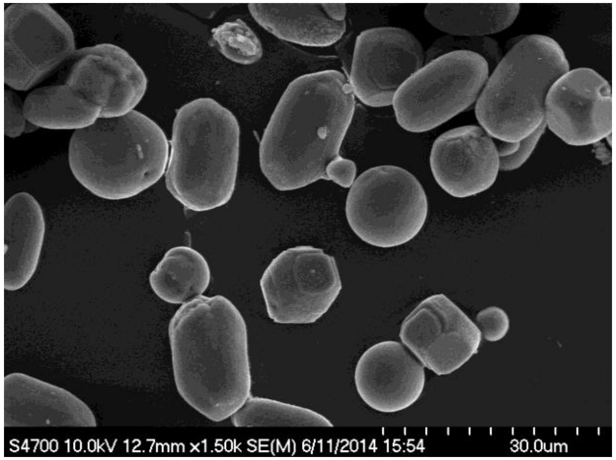
Typical Approaches for Calcium Carbonate Control



Calcium Carbonate Crystal Modification







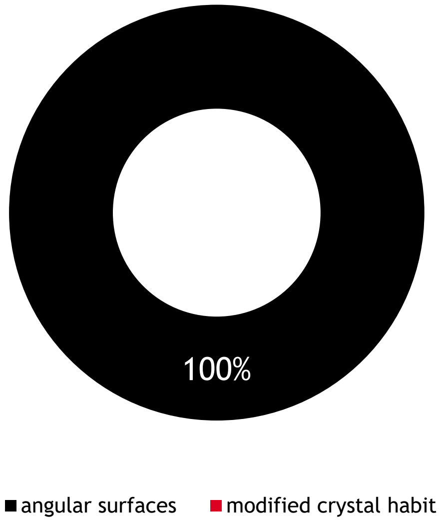
Blank

Standard Polymaleic

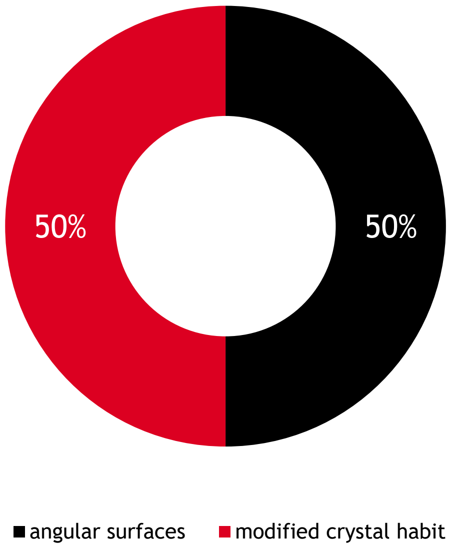
Enhance Polymaleic

600 ppm Ca^{2+}, 600 ppm CO_3^{2-}, pH 9.5-10.2, 18 hours, 70° C

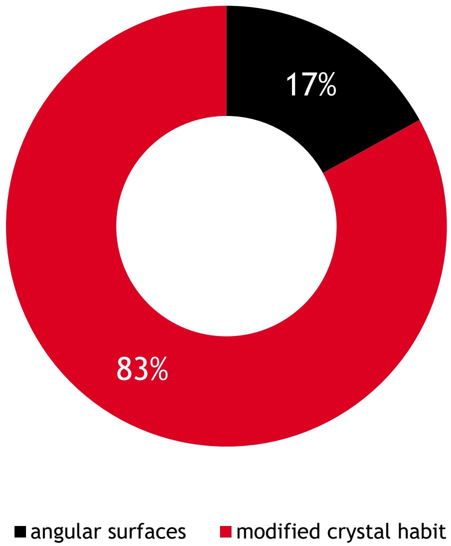
Degree of Distortion



Blank (no treatment)



Traditional PMA



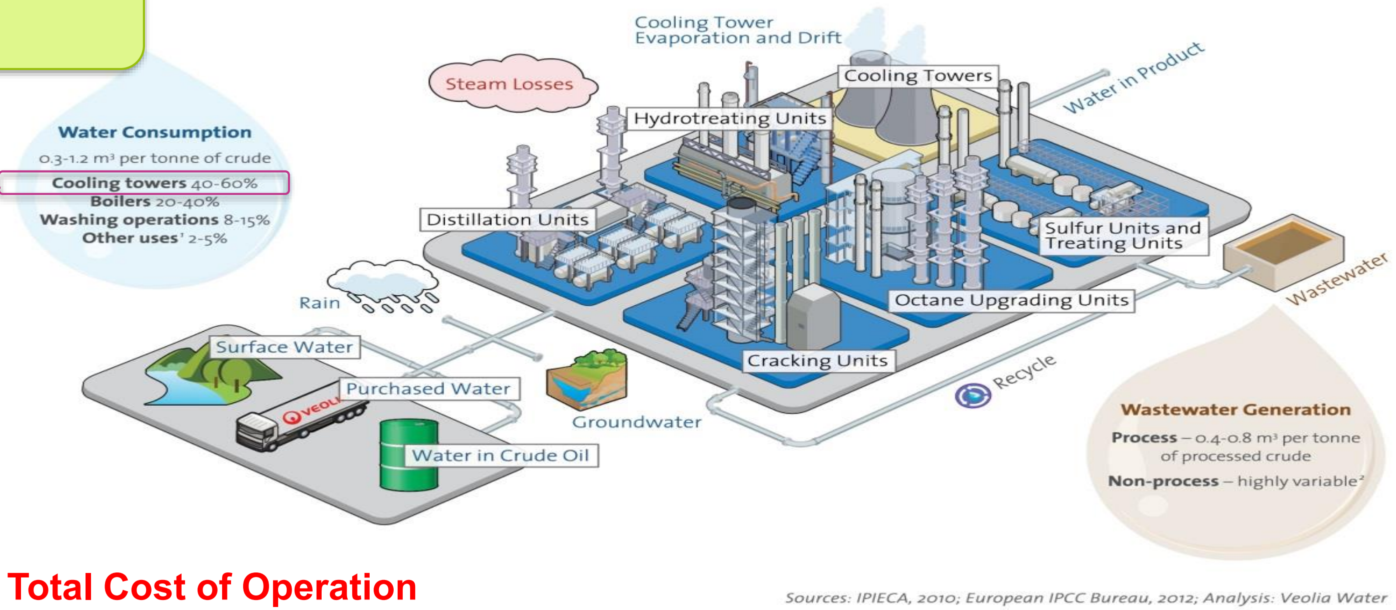
Enhanced PMA

What About My Cooling Water System?

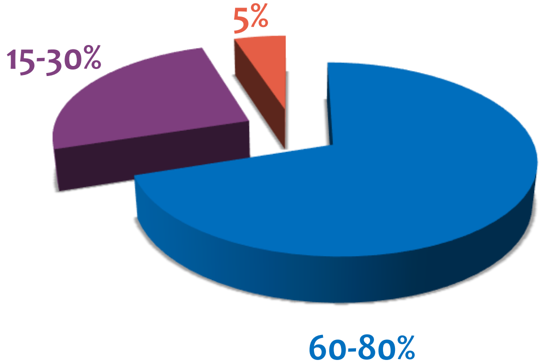
- What chemicals are in use now?
- Maybe you are already pretty green (remember there are many shades)
- Do you need a low or non phosphorous program?
  - Maybe, if blowdown goes directly to the environment.
- Does your blowdown go to a biological treatment plant?
  - Is so, phosphorous is needed for biological treatment
  - Will chemicals in the cooling system be degraded by the biological treatment plant and not harm the bacteria?
- Does your blowdown go to a recycle treatment?
  - Make sure chemicals are compatible with the process
- Does your blowdown go directly to the environment?
  - Look for low P or non P programs and products that are readily or inherently biodegradable
- Are there opportunities to improve on local social responsibilities?
  - What are corporate or local green initiatives and what chemicals might help?

Veolia Innovative Approach For Cooling Water Management

Cooling water is one of the most important elements in **Water Cycle Optimization**



Cooling Water's Total Cost of Operation



Cooling Tower's OPEX

1. **Optimize energy efficiencies: pumps, fans, heat exchangers**
2. **Optimize makeup water selection and cycles of concentration**
3. **Optimize chemical selection and control**

Conclusions

- Green is complicated, but should be implemented
- Understanding greener solutions takes a lot of work. It is not just what feels right
- Many greener solutions are in use in industry today
- Veolia innovates starting with green in mind: chemicals, energy, and water
- Good News: Many green solutions are already in use. We have many greener solutions integrated into our existing product line of chemicals

VEOLIA

Thank you

WATER TECHNOLOGIES