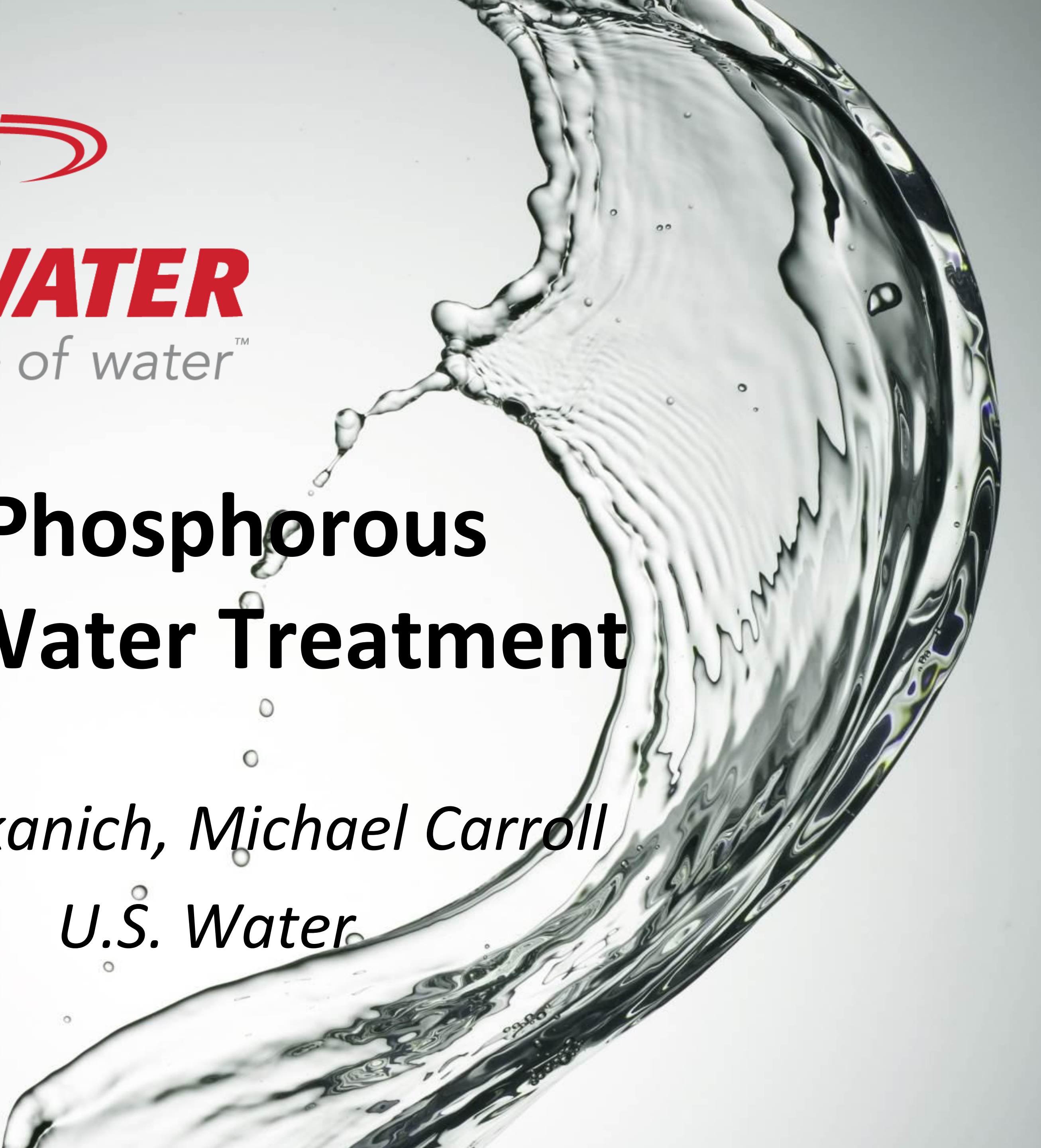

Zero Phosphorous Cooling Water Treatment

Jim Lukanich, Michael Carroll

U.S. Water

Phosphorous and the Environment

- Phosphorous is a common constituent of fertilizers, detergents, and water treatment chemicals.
- Phosphates are used as corrosion and scale/deposit inhibitors in cooling, boiler, and domestic water systems.
- Phosphorous compounds used in water treatment are discharged either to a POTW or directly into the aquatic environment under NPDES permitting.
- Phosphorous is a nutrient which stimulates the growth of phytoplankton and aquatic plants.
- Excessive levels of phosphorous can lead to eutrophication of water resources.

Phosphorous and the Environment

- **Eutrophication**: *The process by which excess nutrients accumulate in water causing accelerated growth and decay of algae or plants resulting in deoxygenation and death of other life forms.*

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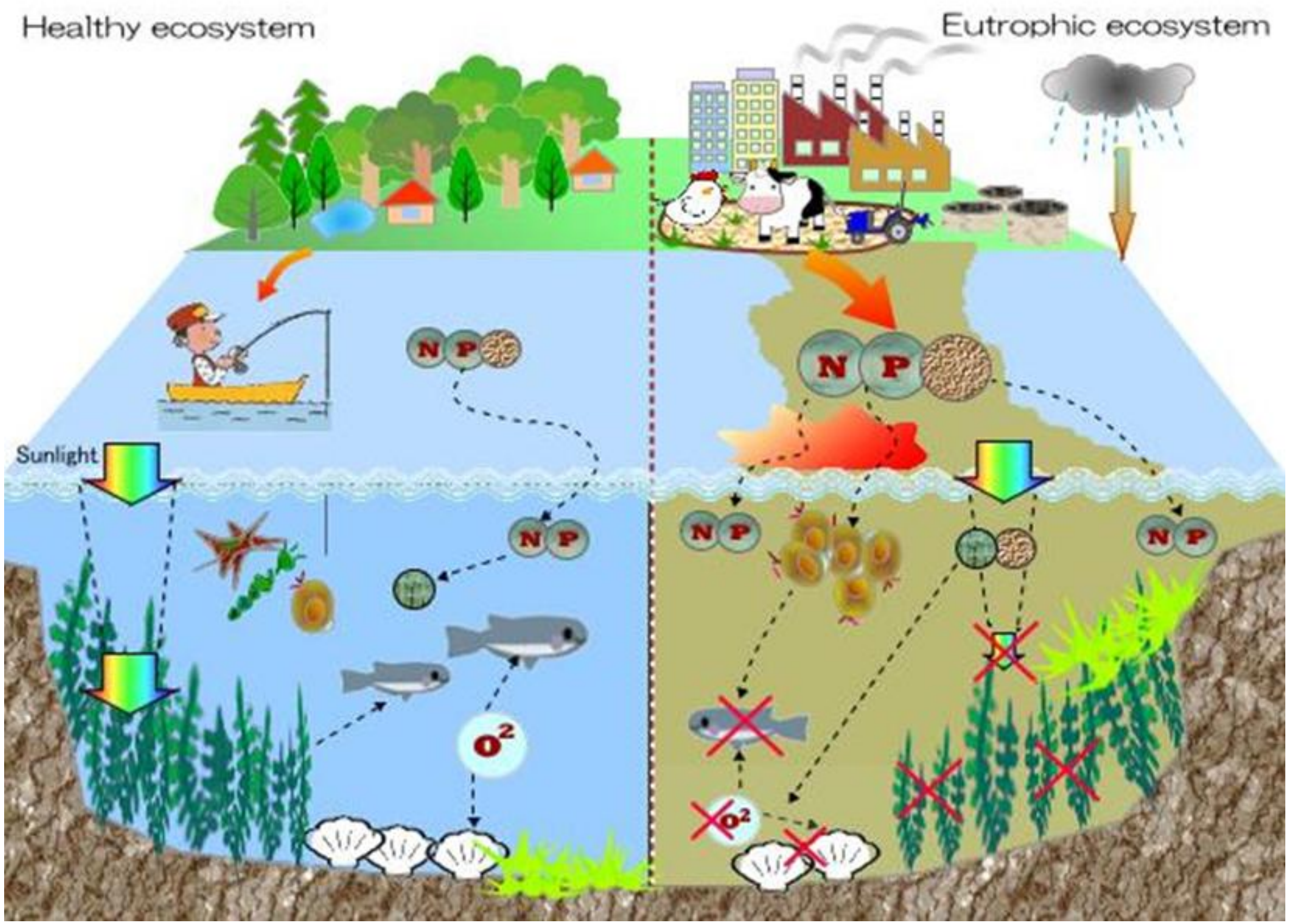
Healthy vs Eutrophic Ecosystem



Phosphorous and the Environment

Just another day at the beach!

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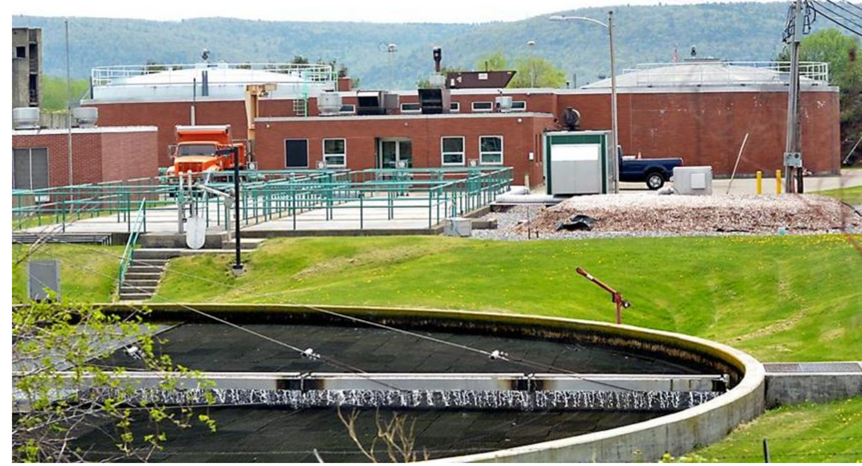
Zero Phosphorus – Why?

- **For facilities where discharge is to a POTW, the municipality may limit phosphorus contribution or increase surcharges to meet their discharge limits.**
- **Many states are now, or soon will, impose more stringent discharge limits for phosphorous.**
  - Wisconsin: 88% of plants have "P" limits
  - Michigan: 70% of plants have "P" Limits
  - Minnesota: 43% of plants have "P" limits
  - Ohio, Pennsylvania, New York, New Jersey
  - Chesapeake Bay States – DE,MD,VA
  - New England States



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Zero Phosphorus – Why?

- Updating treatment facilities to reduce phosphorous levels to limits being proposed is costly. A State of Wisconsin economic impact study projected the cost to be nearly 1.6 billion dollars for just POTW's.

Table ES-1: Summary of Estimated Cost by Category (in Millions, 2014 Dollars)

Category	Number of Permitted Facilities in each Category	Capital Cost Estimate	O&M Cost Estimate
Municipal WWTP: Mechanical	334	$1,382	$65.3
Municipal WWTP: Lagoon	91	$185.1	$4.1
Municipal Subtotal	425	$1,567.1	$69.4
Cheese/Dairy	27	$72.5	$3.0
Aquaculture	10	$51.7	$3.2
Food Processing	14	$43.9	$1.6
NCCW/COW	59	$215.0	$20.1
Paper Mills (300 mg/l dose)	17	$325.8	$96.2
Paper Mills (1000 mg/l dose)	17	$414.4	$255.8
Paper Mills (1800 mg/l dose)	17	$448.5	$488.4
Power Plants	15	$991.3	$47.5
Other	25	$93.8	$4.9
TOTAL (with 1000 mg/l dose for Paper)	**592**	**$3,450**	**$405**
TOTAL (with 300 mg/l dose for Paper)	**592**	**$3,361**	**$246**

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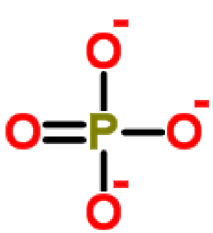
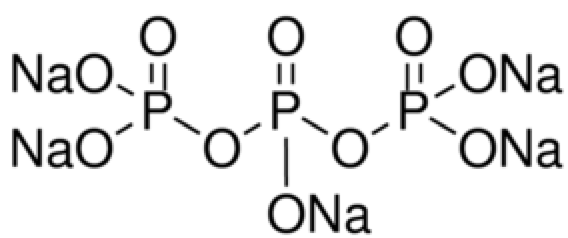
Zero Phosphorus – Why?

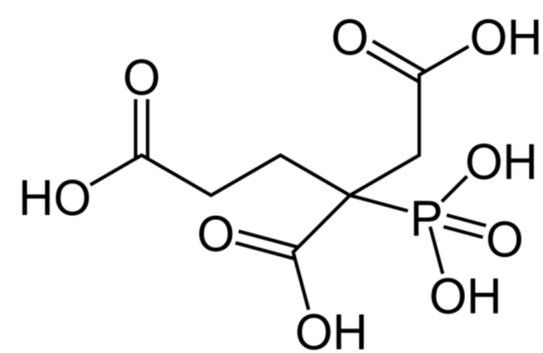
- Many corporations and universities are seeking out "green" or low environmental impact solutions to meet their energy and water sustainability goals.
- Decreasing phosphorous discharge can be a part of a comprehensive program to reduce a facility's environmental impact even when regulations do not require it.

Zero Phosphorous Technology

- Traditional water treatment effectively uses phosphorus for many purposes:
  - Inorganic phosphates minimize deposits and corrosion in many applications.
  - Widely used in municipal water.
  - Organic phosphonates for scale control in cooling water.







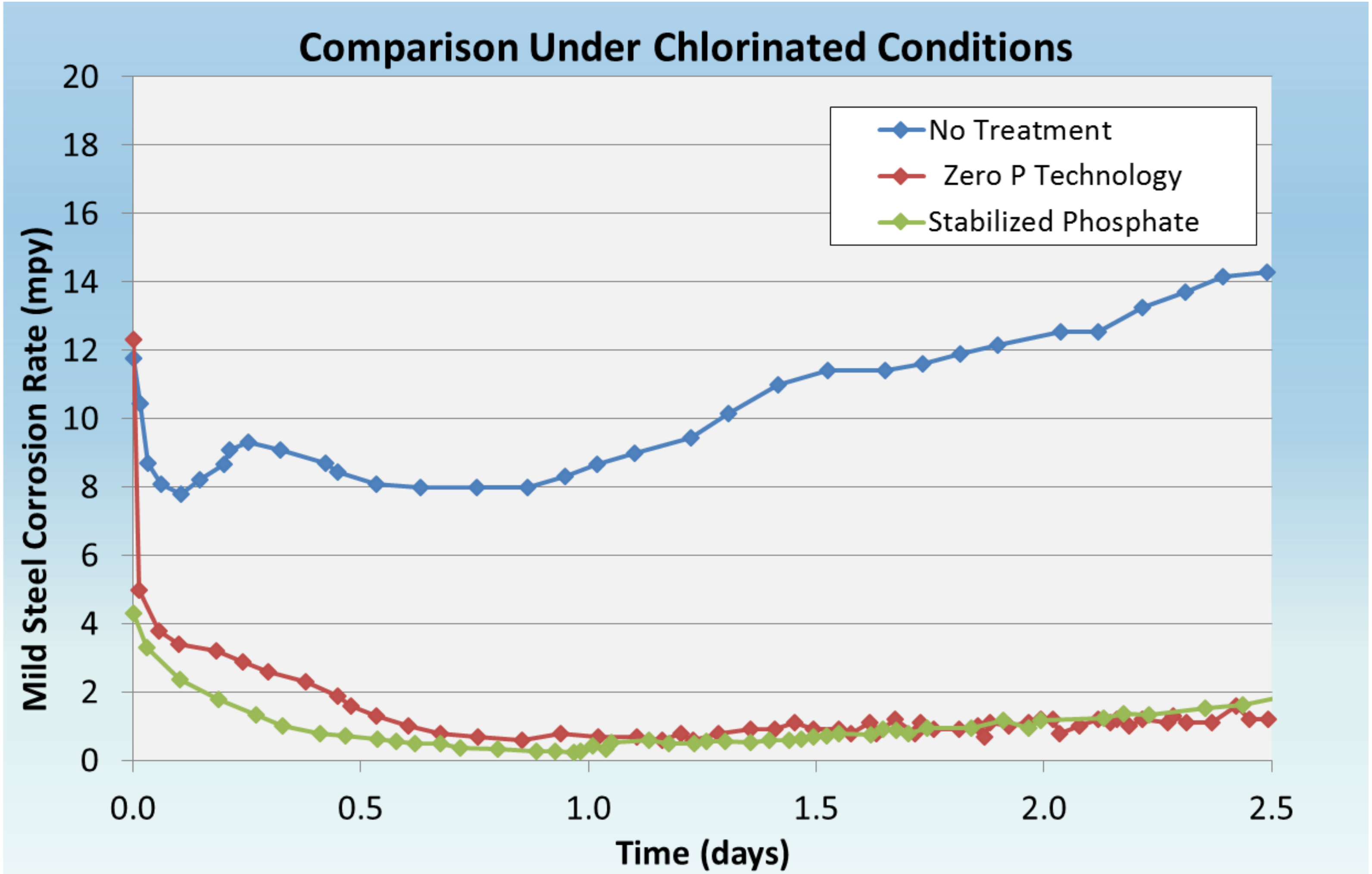
Zero Phosphorous Technology

- Developing an effective scale and corrosion inhibition program without phosphorus is not easy.
- This zero phosphorous technology provides scale and corrosion inhibition equivalent to traditional phosphorous based treatments, without the environmental concerns.
- It contains no molybdate or zinc and has a favorable aquatic toxicity profile.

Zero Phosphorous Technology

- Laboratory pilot work indicated equivalent corrosion results compared to industry standard “stabilized phosphate” cooling water treatment.

Laboratory Results



Phosphate-free technology comparable to stabilized PO_4 treatment.

Field Trial Result No. 1

Commercial cooling tower with low hardness water

Tower 1: Zero P

Tower 2: HEDP,Poly,TTA

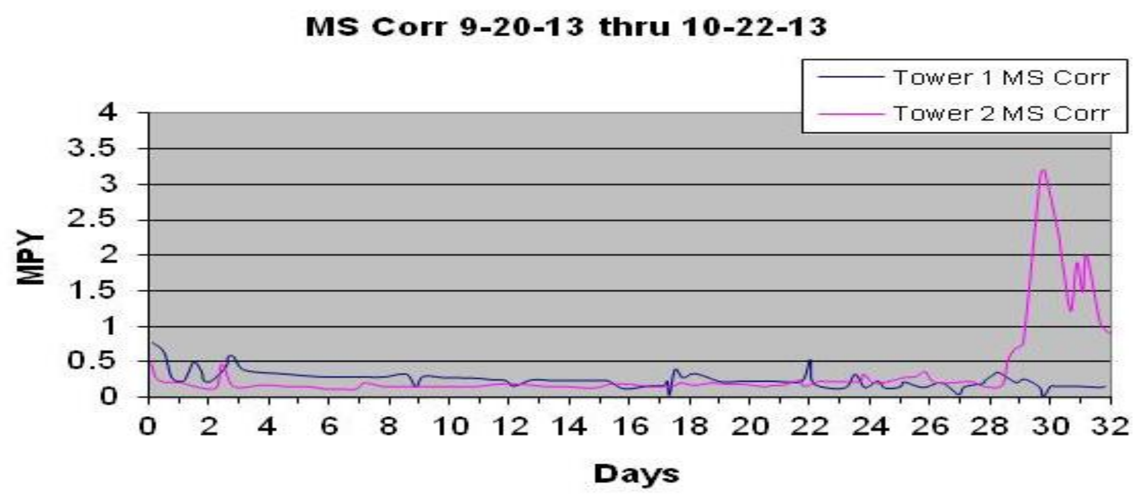
Coupon Results, Twr 1:

Mild Steel: 1.014 mpy

Copper: 0.054 mpy

No indication of microbiological or mineral deposition.

Parameter	TOWER #1	TOWER #2
Conductivity	3000-3200 uhmos	3000-3200 uhmos
pH	8.5-9.5	8.5 - 9.5
Total Hardness	50 ppm $CaCO_3$ Maximum	50 ppm $CaCO_3$ Maximum
Total Alkalinity	1500 ppm $CaCO_3$ Maximum	1500 ppm $CaCO_3$ Maximum
Total Bromine	2.5 ppm Maximum	2.5 ppm Maximum

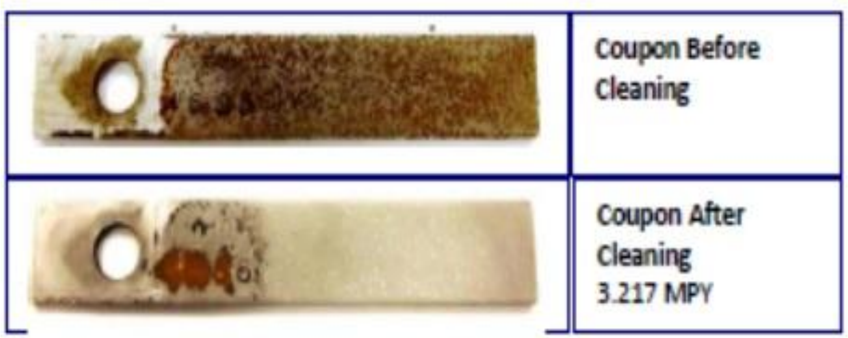


Field Trial Result No.2

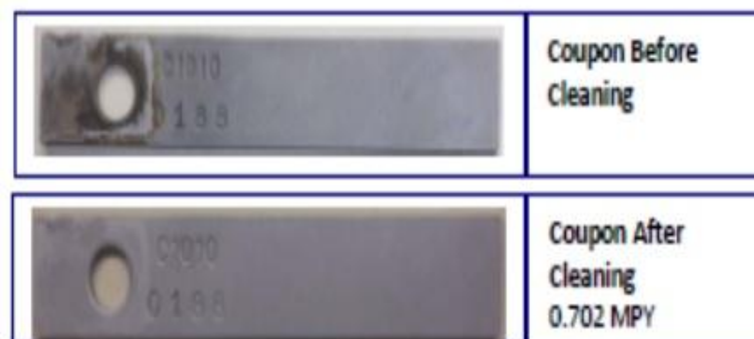
Ethanol Tower with high scale and moderate Corrosion potential.

TH = 1300 ppm Ca = 718 ppm M Alk = 400 ppm
Cl = 127 ppm SO4 = 664 ppm pH = 8.3 Avg

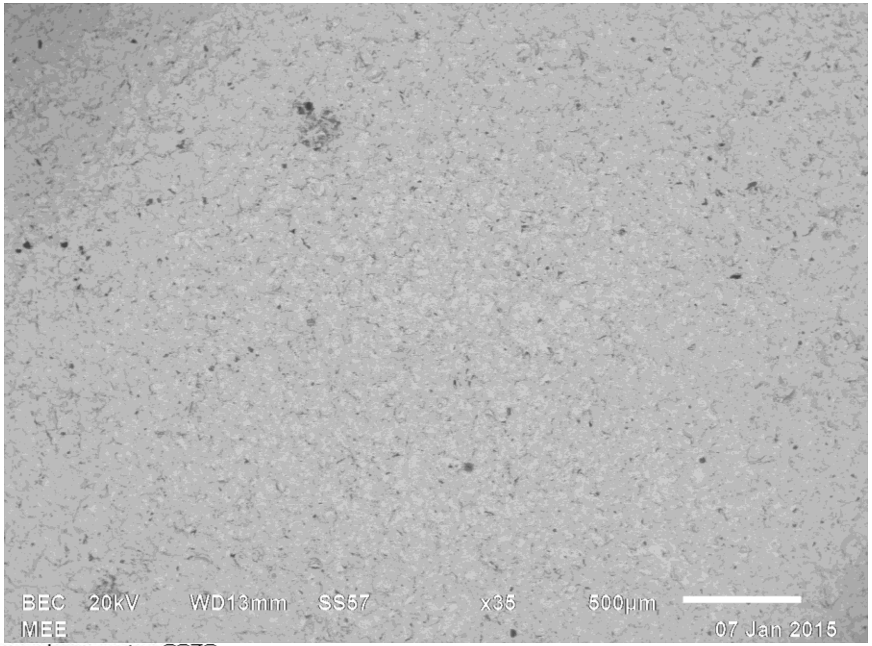
Program	MS	Cu
Alkaline PO_4	3.22	0.35
Zero P	0.70	0.43



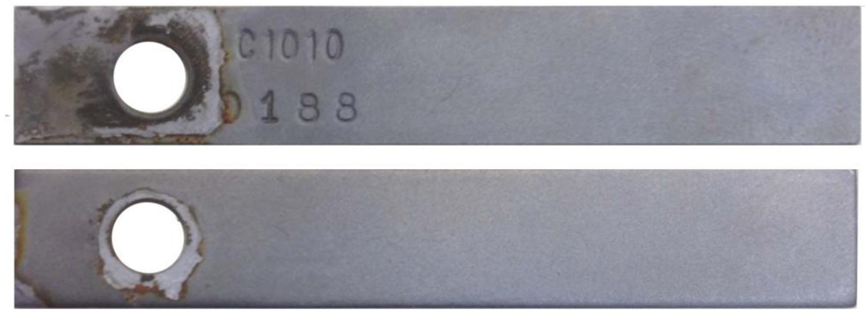
Alkaline PO_4 Coupons

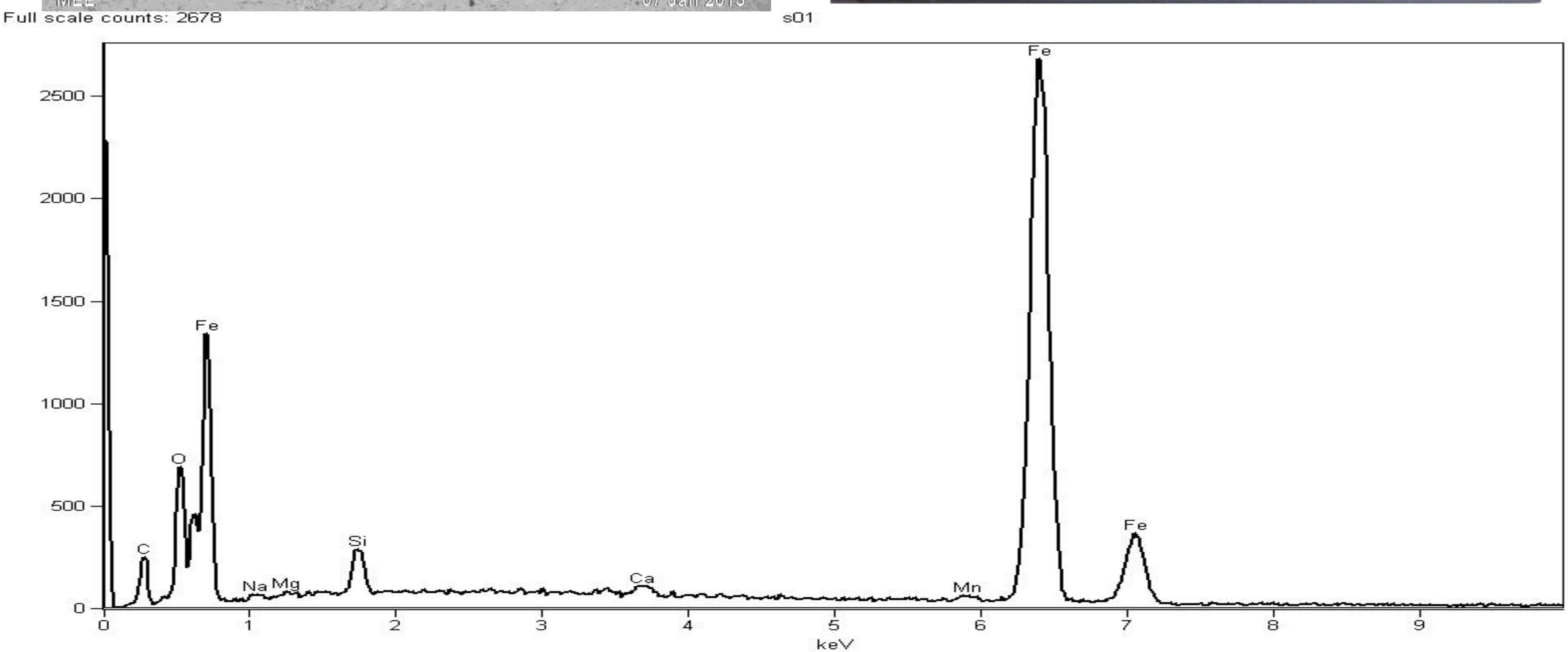


Zero P Coupons



Scanning Electron Microscopy (SEM) analysis of mild steel coupon (0188) surfaces (prior to cleaning) shows the very uniform iron oxide passivation layer formed.





Zero Phosphorous Case Study

Midwestern University Distributive Power Station
Softened Water Make Up

- Cooling tower discharges to a lake with severe pollution issues and undergoing remediation.   Part of the effort involved eliminating all phosphorous and chloride discharge, which required a change to the cooling water corrosion inhibitor and biocide program.

Saint John's
UNIVERSITY

Midwestern University Case Study

- Zero phosphorous program proposed along with alternative oxidant.
- State EPA approved the program for discharge.
- Results:
  - Iron levels dropped from 2.0 ppm to 0.2 ppm.
  - Corrosion rates consistently <1.0 mpy on carbon steel.
  - Phosphorous discharge requirements being met.
  - University contributing to improving water quality.

Additional Benefits

Aquatic Toxicity

The zero phosphorous treatment technology exhibits a more favorable aquatic toxicity profile when compared to a standard stabilized phosphate program.

Zero Phosphorous treatment	Species	Acute LC50 mg/l	Chronic IC25 mg/l
1	Water Flea - Daphnia Magna	3300	1750
2	Water Flea - Ceriodaphna dubia	3540	830
3	Fat Head Minnow - Pimephales promelas	2100	1430
4	Rainbow Trout - Oncorhynchus mykiss	1260	
5	Sheepshead Minnow - Cypinodon varigatus	2830	
6	Midge Fly Larvae - Chironomus dilutes	5550	
7	Amphipod Crustacean - Hyalella azteca	1770	
8	Black Worm - lumbriculus variegatus	13200	

Stabilized Phosphate, polymer, and azole	Species	Acute LC50 mg/l	Chronic IC25 mg/l
1	Water Flea - Daphnia Magna	2290	
2	Water Flea - Ceriodaphna dubia	1890	105
3	Fat Head Minnow - Pimephales promelas	1075	
4	Rainbow Trout - Oncorhynchus mykiss	825	

Summary

- Excess phosphorous in the aquatic environment can have a significant detrimental effect on water quality from both an environmental and economic perspective.
- Regulations and discharge limitations of total phosphorous are becoming more prevelant.
- Improving phosphorous removal at POTWs will require significant infrastructure investment and increases in operational cost.
- Point-source dischargers will have to restrict phosphorous discharge or add removal capabilities.

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Summary

- A new development in chemical technology can provide a **zero phosphorous** cooling water treatment program which can:
  - help facilities meet discharge requirements.
  - eliminate potential waste discharge surcharges.
  - provide exceptional corrosion control protecting operating assets.
  - maintain clean heat transfer surfaces and operational efficiencies.
  - help meet sustainability and green initiative goals.

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Questions?

Padarn Lake in Llanberis, Wales, United Kingdom. (Credit: Flickr User Hefin Owen via Creative Commons 2.0