Modern Developments in Water Treatment Technologies

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with special thanks to John Lindeman
(water treatment consultant)

Dr Alan Pomfret of GE Infrastructures
DJMs background in water treatment (academic/industry jobs)

• 1) preventing corrosion of radiators in central heating systems using standard inhibitors (benzoate, nitrite etc)

• 2) Similarly with car radiator systems (mixed metal systems etc).

• 3) Minimizing corrosion in boilers in power stations (hydrazine, ammonia treatments-keeping pH high, keeping $O_2$ levels low (but problems can arise if $O_2$ kept TOO low))
DJMs background in water treatment (BNF period et seq )

• seawater was dosed with ferrous sulphate to reduce the effect of chlorine on corrosion of condenser tubes.
• I tested various "magic gadgets" to prevent scale build up.

More up to date
• knowledge about the academic research that goes on into corrosion inhibitors (very big in the oil and gas industry). I annually review the inhibitors section of the European Federation of Corrosion's Eurocorr conference.
• Interest in cheap environmentally friendly inhibitors which could be added to water for high pressure water blasting so that the flash rusting problem that plagues that technology could be all but eliminated.
John Lindeman’s ideas-recent developments

• Innovation in cooling system water treatment technology has continued to be in terms of:
  1) reducing calcium carbonate scale by adding polymers products
  2) improving calcium phosphate inhibitors - don’t want calcium phosphate scale on surfaces or blocking pipes
  3) the introduction of halogen resistant actives.
Phosphate

• Drinking water systems
• Phosphate added - because of Lead in Drinking Water regulations, : 1 to 6 ppm phosphate produces lead phosphate film on the lead pipes and prevents the lead leaching.

Cooling systems
INHIBITION OF CORROSION phosphate effective inhibitor for the mild steel inhibitor, used at 10 - 20 mg/l at neutral pH (anodic inhibition), or 4 – 8 mg/l in alkaline waters (cathodic inhibition)
• in some cases sodium molybdate or zinc sulphate are also added.
Phosphate : possible problems

• Cooling systems
  Phosphate addition – can get calcium phosphate fouling on heat transfer surfaces - To avoid
  i) suppress pH by acid addition;
  ii) by bring to market various co and ter polymers latter has better ability to control calcium phosphate deposition in alkaline waters.

• Domestic systems
  Phillip Munn has observed attack on Copper tubes. There is strong evidence that this is phosphate related
Phosphate induced attack?

**FIGURE 5.3** Type I pitting in a water with high phosphate. (Photograph courtesy of P. Munn.)
Inhibitor and biocide developments (Lindemann)

- Cooling systems – development of P free calcium carbonate inhibitors, - Phosphinosuccinic oligomer (PSO) and AEC polymers as examples. These are halogen stable, which the phosphonates in common use are not (although some are better than others)

- Cooling systems - biocide control driven by Legionella legislation – as opposed to non-oxidising biocide
  - continuous application of chlorine or bromine,
  - shock dosages (40ppm) typically 2 x per week.
  - This leads to on-going presence of free halogen, and raised chloride ions as a result,
  - Increased corrosion rates in mild steel, stainless steel and yellow metals.
Inhibitor developments (continued)

• Traditional yellow metal inhibitors (Tolyl Triazole, Benzotriazole) are not halogen stable. New azoles with ‘halogen resistant’ chemistries have been developed.

• Also novel volatile corrosion inhibitors - provide film inhibition after a plant or piece of equipment has been drained down (chemistry tends to be a close secret as patents are applied for !) One of the latter might solve the water jetting flash rusting problem?
Main drivers for change (P Munn)

• ENVIRONMENTAL
• Human Toxicity
• Thus move away from traditional inorganic substances used for pH control and as metal inhibitors for example Borates which are now considered possible carcinogens
• To Organic treatments (more expensive) – see later in talk for examples
Boiler Water Treatment in the 21st Century (A Pomfret)

- Why is effective boiler water treatment necessary?
- Requirement to minimise
- Corrosion of the boiler feedwater, boiler and condensate system
- Deposition of hardness salts and metal oxides on heat transfer surfaces
- Carryover of boiler water to maintain steam purity requirements
What do we need to know before we decide on a “chemical” boiler water treatment programme?

- The boiler system to be treated
- Raw water source    Water chemistry    Pre-treatment    plant type
- Hot well or deaerator–  Feedwater dissolved oxygen–
- Type of boiler(s)
- Boiler operating pressure
- Cycles of concentration–
- Economiser, superheaters  Spray water  Steam flow rate  Steam usages  Space Drying heating  –Power generation–Process heating–Sterilisation Humidification
- Condensate treatment
- **Regulatory requirements**
Power Industry

• Steam turbine manufacturers - steam purity specifications include sodium and or potassium, silica, iron, copper and after cation conductivity (ACC)
• Basic inorganic chemicals
• Hydrazine (N₂H₄) – Toxic, suspected carcinogen
• Ammonia (NH₃)
• Trisodium phosphate (TSP – Na₃PO₄)
Types of pre-treatment plant

- Precipitation softening – 19/20th century
- Ion exchange
- Base exchange softener
- Dealkalisation
- Demineralisation
- Membrane systems – 21st century
- Reverse Osmosis (RO)
- Electrodeionisation (EDI)
Mechanical deaeration

- Hot well  Oxygen level related to temperature
- Semi-deaerator
- Deaerating head
- Vacuum Deaerator Reduces $O_2$ to $<100$ ppb
- Pressure Deaerator Reduces $O_2$ to $<7$ ppb
Types of Boilers

- Fire tube – very standard type of boiler) (Bottom left picture)
- Water tube (Top left picture)
- Waste heat boilers
- HRSG (heat recovery steam generator) (Right hand picture)
- Steam generators - not so commonly used)
Types of Boilers
Fire tube boilers

• Low pressure systems
• Also referred to as smoke tube boilers, shell boilers, package boilers
• Multiple gas paths - 2, 3 and 4 pass
• Internal furnace or fire box as the 1st pass
• Dry back or wet back design
• Single fuel or dual fuel design
• Little or no steam separation equipment
Water tube boilers

• Medium to high pressure systems
• Steam separation equipment - drum furniture
  – Cyclone separators
  – Demister pads
  – Chevrons
  – Baffle plates
• Have economisers and superheaters
• Large water tube boilers are field erected and may be unique design
Waste heat boilers

- Various types and designs
- Shell and tube exchangers
- Heat recovery steam generators (HRSG)
- Water tube boilers
- Multiple drum, pressure systems
  - low pressure (LP)
  - medium pressure (MP)
  - high pressure (HP)
Steam generators

- Low pressure systems
- Coil design vertical or horizontal
- Bucket types
- Steam water separator
- Boiler water returned to feed tank
- May include economiser and superheater
Typical boiler water treatment programme can include:

1) Oxygen Scavenger
   - Inorganic (Non volatile) Low to medium pressure boilers
   - Organic (Volatile) High pressure boilers
2) Internal Treatment
   - Precipitating  Low to medium pressure boilers
   - Solubilising
3) Corrosion control  High pressure boilers
   - Condensate Treatment
   - Neutralising or filming technology
Inorganic Oxygen scavengers

- Sodium metabisulphite (Na$_2$S$_2$O$_5$) - powder
- Sodium bisulphite (NaHSO$_3$) - liquid
- Sodium sulphite (Na$_2$SO$_3$) – powder or liquid
- To improve oxygen scavenger reaction rates, products are typically catalysed with transition metal salt such as cobalt chloride or cobalt sulphate
- Cobalt chloride has been classed as a substance of very high concern (SVHC) under REACH
- TANNINS
Organic Oxygen scavengers

- Ascorbic acid
- Carbohydrazide
- Hydroxylamines
- Diethylhydroxylamine (DEHA)
- Hydroxypropylhydroxylamine (HPHA)
- N-Isopropylhydroxylamine (NIPHA)
- Hydrazine
- Hydroquinone
- Methylethylketoxime (MEKO)
Internal boiler water treatments

- All Polymers - Low to medium pressure boilers
- Phosphate/Polymer
- Chelant/Polymer
- Phosphate/Chelant/ Polymer
- Polyamines        High pressure boilers
- Coordinated pH/Phosphate
- All Volatile Treatment (AVT)
Phosphates etc

- Sodium hexametaphosphate (SHMP –$\text{NaPO}_3$)
- Sodium tripolyphosphate (STPP -$\text{Na}_5\text{P}_3\text{O}_{10}$)
- Tetrasodiumpyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$)
- Disodiumhydrogenphosphate(DSP-$\text{Na}_2\text{HPO}_4$)
- Trisodiumphosphate (TSP –$\text{Na}_3\text{PO}_4$)
- Chelant -EDTA
- Sodium hydroxide
- Polyamines eg Helamine
Boiler water polymers

- crucial to the success of internal boiler water treatment programmes
- Typical polymer structures
- Polymethacrylate $\text{CHO-CH}_2\text{C} = \text{O}$
- Polyacrylate $\text{OXCH}_2\text{OHCH CH}_2\text{NH}_2\text{CHXC} = \text{OC}$
- Acrylate-Acrylamide Copolymer $\text{CH}_3\text{O-XCCH}_2$
- Sulfonated Styrene-Maleic Anhydride Copolymer $\text{OCH}_2\text{SO}_3\text{-CH CHCHCXYC}=\text{OOO}=\$
- Phosphonate
- HEDP
- Polyethylene glycol allyl ether (PEGAE)
- Poly (isopropenyl phosphonic acid) PIPPA !!
Condensate treatments

- Neutralising amines
- Filming amines
- Film formers – non nitrogen containing
- Neutralising/filming mixtures
- Oxygen scavengers/metal passivators
Neutralising amines

- Aminomethylpropanol (AMP)
- Cyclohexylamine
- Diethylaminoethanol (DEAE)
- Methoxypropylamine (MOPA)
- Morpholine
- Monoethanolamine (MEA)
- Cyclohexylamine

EU Directive 67/548/EEC Dangerous Chemical Substances

- The 31st Adaptation to Technical Progress stipulates that all preparations containing \( \geq 5 \% \) w/w of cyclohexylamine will get revised handling and labelling definitions.
- Preparations containing \( \geq 5 \% \) of cyclohexylamine require risk phrase R62.
- R62 indicates: “Possible risk of impaired fertility” while mention of “Repr. Cat 3” must be made.
- “Category 3 reproductive toxin”, Chemicals that produce or increase the incidence of non-heritable effects in progeny and/or impairment in reproductive functions or capacity.
Filming amines and film formers

- Filming amines
- Octadecylamine
- Film formers
- Sorbitolanhydride esters
- Polyethylene glycol (400) monooleate
Future

What do we want for the future of boiler water treatment?

• An environmentally friendly cheap inhibitor that is highly effective at all temperatures typically used in boilers against corrosion of all metals!

• Fully approved by all boiler manufacturers, Govt and safety authorities!
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Thanks for your attention!

Any questions?