Some of the first recorded history of water treatment goes back to about 2000 B.C., which states: “Impure water should be purified by being boiled over a fire, or being heated in the sun, or by dipping a heated iron into it, or it may be purified by filtration through sand and course gravel, and then allowed to cool.”

Industrial water treatment had its beginnings many centuries later during the industrial revolution in the 19th century. It began with the internal treatment of boiler water used to generate steam. One quoted reference to some of the first water treatment relates that, “In the early days of Watt’s Engine, it is said that once after cleaning a boiler and refilling it, the workmen hung a bag of potatoes in the boiler to cook, forgot them, closed the boiler, and put it back in operation. Then, when the boiler was shut down again in order to chip off the scale by hand, it was found that very much less scale had formed, much of it having come down as sludge, and that which had formed was much softer and easier to remove. Probably the tale is true because for many years, engineers made it a practice of throwing some potatoes in the boiler after every cleaning.”

Patents for internal water treatment for boilers go back to 1857. Most of them involved using natural organic tannins for boiler scale control.

In 1863, a patent was issued for the use of di-sodium phosphate, and in 1887, a tri-sodium phosphate patent was issued. During the late 1880s through 1920s, many boiler explosions occurred, probably related to caustic embrittlement of the boiler metals. A book was published in 1919 in England recommending external softening of boiler makeup water by a lime soda process.

1920s
During the 1920s, heat transfer rates were raised and boiler pressures were increasing, causing new problems. Foaming and carryover of solids into the
steam became more prevalent. Calcium sulfate scale was being prevented with phosphate and excess carbonate. Tannins were used for chemical deaeration through oxygen absorption. Carbon dioxide generation from bicarbonate degradation was identified as a major cause of condensate corrosion. In 1927, it was generally recognized that embrittlement was caused by a combination of metal stress and high concentration of sodium hydroxide.

1930s
During the 1930s, more investigation went into controlling boiler scale. The Navy began using a compound consisting of di-sodium phosphate, soda ash, and cornstarch. By the late 1930s, boiler pressures had increased to up to 1200 psig with units as high as 2400 in the design stages. Sodium sulfite was being used as an oxygen scavenger. Organic anti-foam agents were in use.

With increased interest in steam purity during the 1930s, specific conductance became accepted as the method to determine dissolved solids.

Cooling towers began to see efforts of water treatment during the 1930s. The primary treatment was pH adjustment with either acids or alkalis. The Langelier Saturation Index (LSI) was developed in 1936. Threshold treatment with sodium hexametaphosphate at a few parts per million was introduced.

Cooling towers began to see efforts of water treatment during the 1930s.

1940s
In the 1940s, companies began catalyzing the sodium sulfite for more rapid dissolved oxygen removal.

The first scientific study of neutralizing amines to control carbon dioxide corrosion in condensate lines was conducted. Also, filming amines were introduced. Sodium nitrate began being used to inhibit embrittlement in boilers, and the coordinated phosphate/pH control program was introduced.

Phenol derivatives were suggested for use of microbiological control in cooling systems.

1950s
Ryznar introduced his stability index for cooling water. In the 1950s, processed lignins were implemented to improve boiler scale control and the application of synthetic low molecular weight acrylic polymers to replace natural tannins and lignins in boiler water sludge conditioning began.
Hydrazine was introduced as an oxygen scavenger, especially for high pressure boilers, and continued improvements in neutralizing and filming amines occurred.

In raw water clarification and wastewater treatment, organic polymers were introduced as coagulants to replace or augment the use of inorganic coagulants.

Chromates were used as corrosion inhibitors in cooling systems at high concentrations and provided excellent corrosion inhibition and good microbiological control. pH adjustment downward with acid prevented scaling problems.

1960s
Internal chemical treatment programs for boiler systems continued to be refined in the 1960s through the use of synthetic dispersing agents such as polyacrylates, polymethacrylates, and carboxymethylcellulose. These synthetic dispersants became well established and showed significant improvement over the natural lignins and tannins or sulfonated lignins; however, the sulfonated lignins were used into the 1980s.

The use of chelants for internal treatment of high pressure boilers developed rapidly in the '60s. Chelants were initially misapplied, which caused some corrosion to metals, which gave chelants a bad reputation. Proper feed into the feedwater at low use concentrations where zero oxygen was present was recognized as an acceptable, usable program.

In water coagulation, the use of zeta potential was advocated. The use of synthetic organic flocculants of industrial wastewater was introduced.

Investigations of polyphosphates as corrosion inhibitors in cooling systems under varied temperature, pH, and heat transfer conditions were studied. Chromate levels were successfully reduced by supplementally adding polyphosphates and/or zinc.

Major advances in deposit control in cooling water systems were achieved in the 1960s. The introduction of phosphonates, acrylates, and various synthetic and natural organics became widespread.

Microbiological aspects of cooling water treatment also saw advancements. The effect of microbiological activity on corrosion was investigated, including the effect of sulfate reducing bacteria.

1970s
Chelants continued to be popular for scale control in boilers. Also, combinations of chelant, phosphate, and dispersant programs became popular.
Cooling water treatment became affected by environmental considerations. The use of polymers in cooling water treatment progressed along with a beginning trend to more alkaline cooling water treatment programs.

Two themes that began to dominate the industrial water treatment market were energy and environment. Clean boilers to maximize heat transfer and minimize fuel costs and reduction of boiler blowdown became very important.

The highly effective chromate-phosphate-zinc cooling water corrosion inhibitors were under attack for environmental and health concerns and, in many cases, had to be replaced with treatments of less proven effectiveness because of environmental considerations.

1980s
The use of chromate was initially banned in HVAC applications and then in all industrial cooling tower applications for environmental and health reasons. Also, the use of sulfuric acid came under attack because of safety problems. There was a definite trend toward highly alkaline, high pH programs. This required more effective scale control agents to work under stress conditions.

pH control programs for cooling waters were changed from chromate-based programs to orthophosphate-based programs with the introduction of more and more phosphate stabilizing polymers.

The use of bromine-based chemistry to replace chlorine-based chemistries became popular because of bromine’s improved effectiveness at higher pH compared to chlorine. In boiler water treatment, improved feedwater quality was stressed and an all polymer program for boiler water treatment became more popular.

Hydrazine, which was the oxygen scavenger of choice in high pressure boilers, was under attack because of its carcinogenic nature. Many new high pressure oxygen scavengers were introduced as substitutes.

Molybdate chemistry became a more popular replacement for chromate. Although molybdenum is in the same chemical family, it does not have the passivating or oxidation value of chromate, so it was used to supplement other corrosion inhibitors and was popular because of its ease in testing.

1980s: The use of chromate was initially banned in HVAC applications and then in all industrial cooling tower applications for environmental and health reasons.
Because of environmental concerns, “all organic” cooling water programs became popular, which essentially were based on phosphonate and polymer chemistry.

Beginning in the 1980s, consolidation of many of the national water treatment companies started to occur. There were six major companies known as the “Six Pack.” These included Nalco, Betz, Calgon, Dearborn, Drew, and Mogul. They dominated the U.S. water treatment market.

The Association of Water Technologies (AWT) was formed in 1985. It is a group of independent water treatment companies, which today provides high level technical training, networking opportunities, educational events, marketing assistance, legislative monitoring, regulatory compliance assistance, and a national reputation.

The large water treatment companies marketed many chemical products by program name and tried to differentiate themselves by trade names, chemical delivery systems, and technology.

1990s
There was much consolidation during the 1990s in the water treatment industry. Mogul was purchased by Diversey and then by Nalco. Betz purchased Dearborn in 1996. Then in 1998, Hercules purchased BetzDearborn, Inc.

During the 1990s, U.S. Filter became a major equipment supply corporation through hundreds of acquisitions.

In 1999, Suez Lyonnaise des Eaux Group purchased Nalco and Calgon Corporation. Suez is a French company who later changed their name to Ondeo with the water treatment division being called Ondeo-Nalco.

Also in 1999, another French-based company, Vivendi, purchased U.S. Filter.

Meanwhile, ChemTreat out of Virginia grew rapidly and became a major player in the industrial water treatment market.

The emphasis on water reuse intensified during the 1990s and membrane technologies including micro-filtration, ultra-filtration, and reverse osmosis became much more popular and affordable.

The use of molybdenum came under attack for environmental concerns in the sludge of municipal wastewater treatment plants. Regulation for land-applied sludge required molybdenum to be 75 milligrams per kilogram or less, so municipalities began limiting molybdate levels going to the POTWs.
Continued acquisitions occurred in the 2000s. GE purchased Hercules (BetzDearborn) and became the GE Water Technologies. GE Water also had purchased Glegg and Osmonics; both being manufacturers of water treatment equipment. Ondeo sold Nalco to a group of investors and the name Nalco was restored.

The major water treatment chemical companies are trying to maintain relatively high margins by limiting on-site field service and using automation and remote monitoring as much as possible.

AWT type companies are doing well, by being customer service focused and minimizing representative turnover at client accounts.

The cooling water chemical emphasis is on programs allowing high cycles of concentration to minimize water usage and application of wastewater into cooling systems. High performance polymeric dispersants are commonly required for these stressed conditions of high hardness, high silica, high alkalinity, and sometimes high iron.

The use of high purity feedwater for even lower pressure industrial boiler applications is becoming common to reduce boiler blowdown and minimize energy costs.

Raw water clarification and wastewater treatment are seeing more and more membrane processes and there is a heavy emphasis on wastewater recycle.

Vivendi separated off their water group, which became known as Veolia Environnement, a world leader in water applications with over $30 billion in revenue. US Filter was sold to Siemens. The end of 2006, Veolia Environnement expanded their water capabilities in North America with the purchase of Crown Solutions, an integrated water management company providing high quality water management services since 1984.

References
- *Ultrapure Water*, December 2003
- *Ultrapure Water*, January 2004