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Save Energy In Water Systems, Part I

Plants often miss opportunities to more fully use hot water

By Ven V. Venkatesan, Energy Columnist

WATER IS a critical utility at process plants, often serving both as a heating and a cooling medium. In this first of two columns about opportunities to cut energy consumption in water systems, we'll focus on hot water. Many process plants rely on this water for processing and other applications. Providing the water, usually by heating via steam coils or direct steam injection nozzles, takes significant energy. So, here, we will cover five useful tips to cut energy use.

Tip 1: Recover waste heat, wherever available, to maintain the hot water system. Stack gases at high temperatures, chillers, and air compressor cooling are typical waste-heat sources that are applicable to the hot water system. In a few cases, deviating from conventional approaches like adding economizers to boilers also may make sense. For instance, a medium-sized chemical plant in Oklahoma, instead of installing an economizer to heat boiler feed water, as was initially recommended, uses the unit to heat the inlet line to the hot water tank. With a lower inlet-water temperature than the boiler feed water, the hot water system recovers more waste heat using the same economizer.

Tip 2: Insulate all bare and exposed hot water piping and tanks. Unfortunately, at too many chemical plants, sizable sections of hot water return lines are left un-insulated. The hot water and condensate return lines only get short lengths of personal-protection-type insulation. When one medium-sized chemical plant was designed 20 years ago with coal as the main fuel, insulation couldn't be justified for the hot water tank and the return lines. However, when the plant replaced the coal-fired boiler with natural-gas and diesel fired boilers, it still left the hot water lines bare.

Tip 3: If steam condensate can't serve as boiler feed water, use it as hot water. Some plants that fire liquid fuels and heavy oil in their boilers heat the liquid fuel and heavy oil with steam before sending them to the burners, to improve atomization. Usually the condensate from these heaters isn't returned to the boiler due to worries about contamination but instead is simply is drained to grade. Consider routing this off-specification condensate to the hot water tank catering to wash water demand. The same action applies to condensate drained at tank farms. In a lubrication oil plant in Illinois, we suggested sending the steam condensate to the firewater tank rather than draining it to grade. This firewater tank was heated with steam during the winter months every year.

Tip 4: Replace conventional gas-fired indirect-contact hot water boilers with direct-contact hot water generators. In conventional hot water boilers, the flame and flue gases travel through tubes inside a water drum and finally exit through the stack. These units typically are designed for 85% thermal efficiency. In contrast, the more recently developed hot water generators directly contact water and hot flue gas to transfer the heat, and are designed to achieve 95+% thermal efficiency. These hot water generators are most suitable when no hot water or only a small portion of it is re-circulated.

Tip 5: Match the hot and warm water needs in the plant with the hot and warm water drains in the plant. Most batch processing operations need hot or warm water for periodic cleaning of equipment and for the shop area. Plants generally heat city water with steam (directly or indirectly) for such washing or cleaning duties. However, hot or warm water drain streams such as blowdown water from boilers and seal water from vacuum pumps could handle such chores. Collecting and routing the hot/warm water drains to the hot water tank would save both heat energy and fresh water addition to the hot water tank. One medium-sized chemical plant used about 40,000 gallons of 170°F water every day for equipment washing and floor cleaning. That same facility drained about 8,000 gallons/day of clear, not turbid, 210°F blowdown water from the boiler to the grade. Because the washing process required only clear hot water, we suggested routing the blowdown water to the wash water tank. The plant implemented this suggestion and saved significant energy.

Hot water isn't inexpensive. So, consider ways to make fullest use of its heat, and thus cut energy consumption. Next month, we'll look at some energy-saving tips for cooling water. ●

VEN V. VENKATESAN is energy columnist for *Chemical Processing*. He can be reached at VVenkatesan@putman.net

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Save Energy In Water Systems, Part II

Recover cold cash from cooling water systems

By Ven V. Venkatesan, Energy Columnist

MANY PLANTS rely on water for cooling, e.g., to control reaction rates, recover light ends from a distillation column, maintain vacuum systems, and lower the temperatures of product streams. As with hot water (see Part I on page 5), opportunities often exist to cut energy consumption. Here, we'll look at five tips for achieving energy savings.

Tip 1: Maintain cooling water quality. Checking the water chemistry can give an idea of the required blowdown for the cooling water system. In one chemical plant the blowdown level was so low that most of its heat exchangers got fouled within a few weeks of cleaning. The well water being used to make up for evaporation losses was the culprit. Once the blowdown level was increased, the fouling rate in the heat exchangers dropped. This allowed the plant to reduce the number of operating pumps for cooling water circulation while achieving the same cooling targets.

Tip 2: Stop circulating cooling water when not needed. In a large chemical plant in Alabama, we found that 30% of its heat exchangers were circulating the tower water even when the process side of the heat exchanger was stopped. So, the plant engineers asked operators to shut off cooling water flow whenever an exchanger wasn't in service. Eliminating the unnecessary cooling water circulation enabled shutdown of at least one pump. At a pharmaceuticals and fine chemicals plant in Michigan, heat exchangers on the third floor of a process building sometimes suffered from inadequate cooling water pressure. Closing the cooling water supply lines of some heat exchangers on the lower floors not in cooling mode improved the supply pressure.

Tip 3: Consider staged cooling. At a pharmaceutical plant, we found that a newly added production building relied on chilled water to cool compressed air and for several other exchangers. The plant didn't install cooling water supply and return lines to avoid a cost over-run on the project. Management was surprised when we pointed out that operating the chiller for ambient level cooling is about three times more expensive than using cooling water. So, the plant made the necessary piping changes to send cooling tower water to the air compressor and other exchangers. This decreased the chiller load, which, in turn, led to a net reduction in cooling tower load. Overall energy use for process cooling also came down.

Tip 4: Don't reject heat to the cooling water system if a suitable process heating application is available nearby. Air compressors and chillers that are water-cooled and trim coolers handling substantially higher temperature process streams are good candidates.

Tip 5: Look for alternatives to rejecting heat to the circulating cooling tower water. The ground water in regions close to the Great Lakes is good quality and available throughout the year at temperatures of about 60°F. As many plants in states like Michigan have found, you can directly use this water as once-through cooling water and then send it for other process applications. It may suit modest process cooling loads like air compressors and smaller chillers.

Automatically controlling cooling water temperature can optimize fan power consumption in a cooling tower. When cooling demand decreases, less water flows through the partially loaded cooling tower. Such conditions also may require less airflow and, hence, lower fan speed. In one chemical plant that uses dual-speed cooling tower fans, when seasonal cycles permit and cooling water well temperature reaches the set point, the automatic control system changes to the lower fan speed. The same controller also may stop some fans in the multiple-cell cooling tower. These steps provide measurable energy savings. However, when cooling towers form part of a chiller train, lower fan speed may boost the load on the chiller compressor — sometimes resulting in a net increase in power consumption. So, carefully evaluate negative effects before stopping or reducing the speed of cooling tower fans.

A health-care-products manufacturer in Virginia was operating a large fountain in the middle of a pond in front of its main office building. It was a closed-loop system with a recirculation pump and a filtration system before the pump to remove any particulates brought in with rainwater collected in the pond. We recommended using that water as the cooling water for the condenser of the building's air conditioner whenever it is in service. Doing this allowed the site to reduce operation of a cooling tower installed exclusively to cater to the air conditioner. Process engineers may find similar alternative cooling opportunities in their plants, too. ●

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Consider Polymer Piping

Material offers numerous benefits over metallic systems and spans various applications

By Jorge Solorio, Lubrizol

EXPENSIVE REPAIR and replacement of processing infrastructures pose major headaches for operations across the chemical processing, mineral processing and power generation industries, and polymer piping solutions can help.

Corrosion and premature piping failure are two problems that plague chemical piping applications everywhere. Metallic systems are limited in their life spans by corrosion concerns, and operations managers always face the question of when their pipes will eventually need repair or replacement.

However, polymer piping systems have made great strides across multiple industries in the past few decades, and investigating the benefits that can be realized by making the switch from metallic systems can help to bring unexpected value to many applications.

Polymer materials, specifically chlorinated polyvinyl chloride (CPVC), can enable operational benefits that have previously gone undiscovered. Due to the chemical and physical properties of CPVC, the material is able to mitigate many of the concerns that continually hang over metal piping, and can be a solution that brings unexpected value to many industrial facilities.

CHEMICAL PROCESSING APPLICATIONS

With more demanding applications than most, chemical processing requires a piping infrastructure that can maintain efficiency and safety. Dependability is paramount, and as with other applications, corrosion and necessary expensive repair and replacement are a major concern.

The highly corrosive substances of the chemical processing industry plague metallic piping systems, with process leaks and premature failure being of top concern, jeopardizing plant operation, safety and environmental compliance. Lined carbon steel, as well as non-metallic options including HDPE and FRP, has demonstrated issues, with long-term reliability becoming problematic.

CPVC again displays the necessary mechanical strength

and chemical resistance to make it a solution for all types of chemical processing applications—production facilities, blending operations, reagent processes, air scrubbing, demineralization operations and more. CPVC compounds have displayed inherently superior resistance to corrosive chemicals, high temperatures and other harsh application conditions, making CPVC a logical choice to maintain operational efficiency and dependability far outstripping that of many metallic systems.

POWER GENERATION APPLICATIONS

Power generation facilities require dependability across all components while simultaneously adhering to the many and stringent regulations that can complicate system choices and solutions. Oftentimes, fewer choices are readily available.

Piping, however, is one area where choices aren't strictly limited to particular materials — opening the door for CPVC in its applicable uses. Here, an opportunity exists for increasing operational efficiencies, minimizing downtime, and improving bottom-line performance across all necessary piping systems in a given power generation facility.

CPVC displays the necessary mechanical strength to stand up to all of the caustic fluids that need to be transported throughout a power generation facility, with its excellent balance of properties to help improve overall reliability and user confidence. For instance, Lubrizol CPVC's Corzan HP Industrial Systems have helped power generation facilities reduce capital and lifecycle costs, avoid costly downtime and boost operational efficiencies.

All metallic piping systems, whether used to transport aggressive chemicals or simply potable water, are susceptible to corrosion — pricey alloys and lined carbon steel, common of chemical lines, will only go so far in keeping corrosion at bay before costly repair or replacement becomes inevitable. CPVC products like Corzan HP are inherently resistant to this problem, and Corzan specifically is the first and only Schedule 40/80 piping system made from

fully pressure-rated materials, allowing systems to work underground (cooling water loops, for instance) and within elevated structures (tower risers and headers) to reliably handle some of the common aggressive chemicals utilized in many power generation plants.

Other applications include demineralized systems for creating boiler feed water, condensate return water applications, flue gas desulfurization systems, environmental systems (common of coal-fired steam plants) and wastewater treatment. Corzan HP has proven reliable in moving all forms of corrosive material, including hypochlorite, caustic soda, sulfuric acid, and sodium sulfite, as well as seawater and high temperature fluids. The material is similarly inert to most acids, bases and salts, as well as aliphatic hydrocarbons.

Due to the corrosion-resistant properties of CPVC, the material can offer a cost-effective choice when deciding upon replacement of chemical processing infrastructure. CPVC has a track record of outperforming competitive non-metallic systems for similar applications, including PVC pipe, FRP, HDPE and polypropylene, and is able to operate continuously for many years without interruption caused by leaks or corrosion concerns. Often, operations managers will find that a CPVC solution like Corzan can pay for itself in as little as a few months, depending upon the scale of the project in question.

MINERAL PROCESSING APPLICATIONS

Mineral processing proves a demanding job of piping infrastructure, and the challenge of maintaining long-term reliability is significant. Indeed, that difficulty is only expected to increase, as existing pits and mine sites are now frequently extracting ores of lower concentration from deeper in the earth's crust, causing a shift in the chemistry of processed ores.

Whether leaching precious materials from the ground or processing raw materials after excavation, the highly corrosive chemicals typically utilized throughout various mining operations can cause ongoing maintenance challenges and costly, premature failures for metallic piping systems. CPVC has built a track record as a suitable and preferable alternative for this application.

The specialty, high-performance polymers that make up Corzan HP systems enable them to perform at higher levels, demonstrating the necessary mechanical strength for industrial-grade systems along with a host of benefits to offset constant maintenance and repair. Throughout mineral processing operations specifically, CPVC has demonstrated advantages in eliminating internal and external corrosion, as well as minimizing sedimentation-crystallization. CPVC has proven to handle extremely

aggressive chemicals, including:

- Copper sulfate
- Zinc sulfate
- Sodium sulfite
- Metabisulphite
- Sodium cyanide
- Sulfuric acid

By resisting corrosion, sedimentation and crystallization that compromise the integrity of metallic systems, CPVC can prove advantageous for a variety of mineral processing applications, including electrolysis operations, electrowinning, electrorefining, acid service lines, tailings lines, gas vent scrubbers, froth flotation operations, and wastewater treatment. This translates to lower life-cycle costs, as well as the reduction of maintenance time and corrosion monitoring. Coupled with the benefits that CPVC can offer through its simplified solvent-welding installation process and stable pricing, replacing a metallic system with CPVC can prove to be a preferable option.

COST BENEFITS

The cost of installation and the cost of maintenance — must be considered when weighing chemical piping options, no matter the specific industry. Replacement means downtime, and downtime can translate to major losses, often exceeding the cost of the installation itself. It is of utmost importance to limit the amount of downtime experienced when performing repair or replacement.

Metallic systems pose several challenges for installation — first, working with and welding large metallic pipes will often require the use of specialized, heavy-lifting machinery in order to place the pipes in the desired locations. Additionally, welding — the use of open flame — within chemical environments requires special care, sometimes necessitating additional downtime. In all, replacement and retrofitting using metallic piping are often slow and cumbersome processes — and the time can add up to meaningful losses for a given facility.

Polymer piping systems like CPVC often can help sidestep these issues. CPVC piping weighs far less than metallic counterparts, and doesn't require specialized heavy-lifting equipment. Additionally, the solvent welding process used to join CPVC pipes and fittings together doesn't necessitate the same safety precautions that must be taken when welding with open flame, and can be performed far more quickly than traditional welding with metallic pipes and fittings. ●

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Tackle TOC Analysis Challenges

Technique addresses barriers to standard online TOC measurement methods

By Ali Dogan Demir, Martin Horan and Seamus O'Mahony, BioTector Analytical Systems Ltd.

Editor's Note: This paper was presented at the 51st Analysis Division Symposium, April 2006, Anaheim, Calif.; Copyright 2006 by ISA - The Instrumentation, Systems and Automation Society, www.isa.org.

AN ONLINE total organic carbon (TOC) analyzer, which uses a revolutionary oxidation process, is proving to overcome many of the recognized barriers associated with online TOC measurement. The analyzer uses a patented two-stage advanced oxidation technique as an alternative to the standard oxidation methods of thermal and ultra-violet (UV) persulfate oxidation. The sample is oxidized by hydroxyl radicals, which are created by exposing high pH reagents to ozone. The analyzer is designed to eliminate current difficulties encountered when determining TOC online. It can oxidize a very wide range of samples and effluents without any need for filtration. Samples are therefore fully representative. The process itself is a self-cleaning technology and it does not require any cleaning of the reactor or other wetted parts.

The oxidation technique also is not affected by the presence of salts or calcium in the sample. It is possible to measure fatty and fibrous materials without any risk of clogging or contamination. The volume of the sample injected into the reactor of the analyzer is automatically adjusted for the optimum measuring range. The analyzer has three ranges, which can cover organic loads from 0 to 25,000 milligrams carbon per liter (mgC/l) with three different sample volumes. Prior to the oxidation process, total inorganic carbon (TIC) in the sample is removed by the addition of an acid reagent and is measured. The analyzer does not allow any TIC carryover to the TOC phase. Ozone is applied to a high pH reagent to produce hydroxyl radicals (a strong oxidizing agent), which are then used for the complete and effective oxidation of the sample. Acid is added to remove the total organic carbon content of the oxidized sample as carbon dioxide (CO₂) gas. The carbon

dioxide is then measured with an infrared detector. The analyzer does not require any calibration between services. The accuracy of the analyzer is ±3% of the reading or ±0.5 mgC/l. The analyzer helps to control and minimize the waste from treatment and process plants, to monitor plant performance and to measure the organic pollution in water. There are over 300 analyzers operating worldwide which use this technology. The service requirement for the analyzer is two times per year. The applications for the analyzer include: surface water monitoring, filter breakthrough, spill monitoring, effluent treatment loading, process control and other customized applications.

Industries, which have successfully applied this technology, include airport deicing, pulp and paper, municipal treatment plants, refineries, food, pharmaceutical and chemical industry.

ONLINE TOC MEASUREMENT CHALLENGES

There are recognized barriers associated with online TOC measurement. Some examples can be given as: low TOC recovery due to the inadequate oxidation, clogging of the analyzer and contamination problems, unrepresentative TOC results when filtration is required, salt and calcium interference, cleaning and high maintenance of the analyzers. The standard methods applied to measure online TOC do not overcome most of the barriers described above. Industries such as refineries, pulp and paper, food, chemical and pharmaceutical have looked for many years, for an online TOC Analyzer, which will defeat all of the above barriers and:

- i) Supply the user a representative TOC result without any filtration,
- ii) Give full TOC recovery regardless of the type and chemical content of the sample,
- iii) Will not be interfered by the presence of salt or calcium in the sample,
- iv) Require minimum maintenance due to contamination and cleaning problems.

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Today, two of the most common methods used to monitor TOC online are thermal and ultraviolet (UV) persulfate oxidation. Thermal oxidation is the process of oxidizing organic materials by raising the temperature of the material above its auto-ignition point in the presence of oxygen and maintaining it at high temperatures for sufficient time to complete combustion to carbon dioxide and water. The sample (typically 0.0225 micro liters per reaction) is fed into a furnace, where it is oxidized at temperatures of 600 to 1,300°C sometimes in the presence of a platinum catalyst. The advantage of this method is, when applied on clean streams, the efficiency of the oxidation is very good for most chemicals. The disadvantages of this method are, filtering for online applications prevents the measurements from being representative and the requirement for high maintenance due to clogging of the reactor with salts [1].

Organic carbon is oxidized to carbon dioxide by persulfate radicals in the presence of ultraviolet light in the UV persulfate oxidation technology. The advantage of this oxidation technique is the rapid oxidation of biological molecules such as proteins and monoclonal antibodies. The disadvantages are: large organic particles or complex organic molecules such as tannins, lignins and humic acid are oxidized slowly because persulfate oxidation is rate limited. Turbidity is a major interference factor where the intensity of the UV light reaching the sample is reduced and this affects the rate of oxidation significantly. UV light generates small quantities of ozone, but the quantities are very small. Thus the contribution of ozone to the oxidation process is minimal. The oxidation of the organic matter is inhibited by chloride concentrations above 0.05% or 500 parts per million (ppm) [2]. It has been recorded that when used in waste-

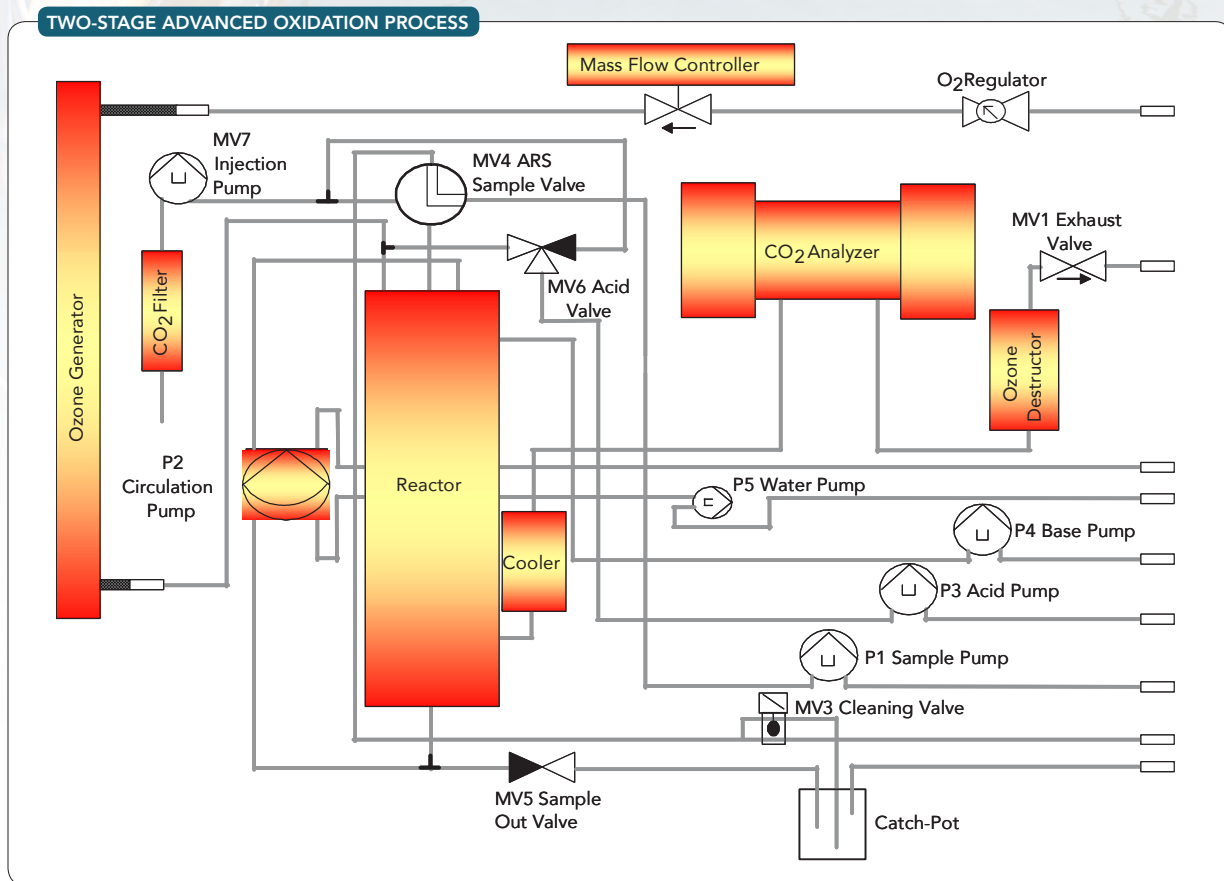


Figure 1: This flow diagram illustrates the analyzer and other components of the advanced oxidation system.

water and process applications, the analyzers using UV persulfate oxidation technique require intensive maintenance each year, which can be as high as the capital cost of the instrument.

The patented two-stage advanced oxidation process [3] has been outlined and discussed in this paper, as an alternative to the thermal and UV persulfate oxidation for TOC analysis. The objectives are:

- i) Introduce the two-stage advanced oxidation method and its strengths to the user,
- ii) Evaluate the oxidation levels achieved during the oxidation process,
- iii) Present the potential problems associated to TOC measurement and solutions found.

TWO-STAGE ADVANCED OXIDATION PROCESS

The two-stage advanced oxidation process has been developed as a true online method. Figure 1 shows the flow diagram of the analyzer (BioTector) and analyzer components of the advanced oxidation system.

The online operation of the analyzer can be summarized as follows:

1. A representative unfiltered sample containing particulates, suspended fibers and colloidal material is brought to the analyzer with a peristaltic sample pump from the process streams.
2. The analyzer automatically selects the optimum sample volume from the available three TOC ranges (from 0 to 25,000 mgC/l).
3. An accurate amount of sample for the corresponding range is injected into the reactor where the oxidation process takes place. Initially the inorganic carbon content of the sample is removed by the addition of an acid reagent. The acid solution used is typically 1.8N sulfuric acid. The CO₂ gas released during this phase is carried by oxygen and measured by an infrared CO₂ detector (CO₂ analyzer). This process is called the “Total Inorganic Carbon (TIC) Phase”.
4. Having removed all inorganic carbon content, a high pH reagent (typically 1.2N sodium hydroxide solution) is added and the ozone generator is switched on. The ozone is generated by the corona-discharge method where oxygen gas passes through an electrical field. The electrical current causes the oxygen molecules to split into atomic oxygen. The resulting oxygen atoms, which seek stability, attach to other oxygen molecules and form ozone [4]. Ozone promotes the production of hydroxyl radicals (a very

strong oxidizing agent) when applied to a high pH reagent such as sodium hydroxide [5]. In the presence of excess hydroxyl radicals, the effective and complete oxidation of the sample takes place. The first stage is named as the “Base Oxidation Phase” where all organic content of the sample is oxidized to carbonate and oxalate.

5. The acid reagent typically containing 40 mg/l manganese sulfate monohydrate catalyst (Mn) is then added to remove the total organic carbon content of the oxidized sample as carbon dioxide gas. The released CO₂ gas is sparged by the carrier gas and measured by the CO₂ detector. The second and final stage is called the “TOC Phase”. The duration of a typical two-stage advanced oxidation reaction is less than 7 minutes (including both TIC and TOC measurement).

OXIDATION CHEMISTRY

Table 1 shows the oxidation/reduction potential of some of the oxidizing agents [6, 7]. As can be seen in the table, the oxidizing agent hydroxyl radicals, which are used in the two-stage advanced oxidation process, have higher potential than sulfate radicals, hydrogen peroxide and chlorine dioxide.

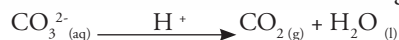
OXIDATION POTENTIAL OF OXIDIZING AGENTS

AGENT	POTENTIAL (VOLTS)
Fluorine (F)	3.06
Hydroxyl radical (OH)	2.80
Sulfate radical	2.60
Oxygen atom (O)	2.42
Ozone molecule (O ₃)	2.07
Hydrogen peroxide (H ₂ O ₂)	1.77
Chlorine (Cl)	1.36
Chlorine dioxide (ClO ₂)	1.27
Oxygen molecule (O ₂)	1.23

Table 1. Hydroxyl radicals have a higher oxidation potential than sulfate radicals, hydrogen peroxide and chlorine dioxide.

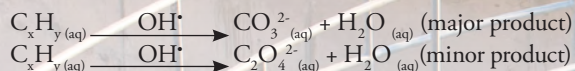
Some of the key reactions during the two-stage advanced oxidation process are outlined below:

In TIC phase, the reaction between sulfuric acid and carbonate forms water and carbon dioxide gas.

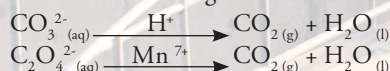


During the base oxidation phase, hydroxyl radicals are formed and the oxidation takes place as follows:

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Finally the reaction process is completed in the TOC phase with the following:



The characteristic pink (a mixture of red and brown) color of Mn VII is visible in the oxidized sample fluid. The function of the Mn catalyst is to take part in the oxidation process directly by oxidizing the minor compound (e.g. oxalate) formed. The manganese catalyst has the form of Mn II in acidic solution. During the oxidation process, in the presence of ozone, Mn II is converted to Mn VII (MnO_4^-) via a number of intermediate steps [8].

MATERIALS AND METHODS

The oxidation levels achieved in the two-stage advanced oxidation process has been verified using three different tests:

Test 1. Several compounds containing organic carbon were selected. Standard solutions containing 100 mgC/l were prepared for each compound applying the typical dilution techniques. 20 reactions were run for each compound. The base oxidation times have been increased from 0 to 360 seconds with 30 and 60 seconds increments. The percent

oxidation levels (percent TOC recoveries) were assessed at each base oxidation time from the average results. The point where the TOC recovery has become independent of time revealed the optimum base oxidation time and the maximum achievable oxidation level for the corresponding chemical. The oxidized fluids from selected chemicals are collected and marked.

Test 2. The fluids collected from the first test are oxidized for a second time with the thermal oxidation technique [1]. Each reaction in the first test produced 13.5 ml of oxidized fluid.

Therefore 270 ml fluids were collected from each compound. 10 thermal oxidation reactions were run using these fluids as the sample. The TOC results as obtained from the thermal oxidation method and the base oxidation times (applied in test 1) were recorded. The objective of the second test was to confirm that all organic carbon is oxidized. Thus the absence of organic carbon in the oxidized sample fluids measured with thermal oxidation technique would indicate complete oxidation in the two-stage advanced oxidation process.

Test 3. The oxidation levels were checked by integrating the calibrated CO_2 detector's readings over time. A computer program was written in Matlab and the CO_2 data was captured during the reactions. The objective was, as the CO_2

PERCENT OXIDATION LEVELS AT VARIOUS BASE OXIDATION TIMES

Organic Carbon Compounds	BASE OXIDATION TIME (SECONDS)								
	30	60	90	120	150	180	240	300	360
Acetic Acid	14	39	82	97	101	102	102	101	102
Acetonitrile	15	51	83	96	99	97	98	99	99
Butyric Acid	12	34	78	97	99	103	101	102	101
Dimethylformamide	57	95	102	103	101	100	102	101	100
Ethylene Diamine	6	22	67	93	98	100	99	98	100
Ethylene Glycol	68	93	95	99	101	99	100	100	99
Formic Acid	45	90	100	100	99	100	101	99	100
Glucose	26	63	98	97	98	98	98	99	98
Hexanoic Acid	11	33	78	98	99	99	99	98	99
Methanol	57	97	100	100	99	101	102	100	101
Phenol	47	71	92	98	100	101	99	98	100
Potassium Hydrogen Phthalate (KHP)	40	76	99	101	101	102	101	100	99
Propylene Glycol	7	29	80	96	100	102	102	100	100
Sodium Oxalate	88	98	101	101	100	101	102	100	100

Table 2: Each compound has different characteristics during oxidation.

detector is calibrated accurately with known concentrations of CO₂ gas, TOC results should match to the carbon concentration of the known standard solutions. This would also confirm the complete oxidation of the samples in the case where all organic carbon content of the solutions is removed as CO₂ gas and measured by the calibrated CO₂ detector. The TOC content is calculated from the CO₂ detectors readings using equation 1:

$$TOC \text{ mg/l} = k \left[\frac{M [CO_2] \rho t}{V} \right]$$

Where k = Constant (7.575×10^{-5}), M = Oxygen gas flow rate (l/h), $[CO_2]$ = Detector's CO₂ reading (ppm), ρ = CO₂ gas density (1.98 g/l), t = Time (seconds), V = Sample volume (ml).

Oxygen gas flow rate is measured by the mass flow controller during the TIC and TOC phases and recorded by the computer every second of the reaction. Similarly eight instantaneous CO readings are captured every second of the reaction and recorded by the computer. The CO₂ readings are integrated over time and the TOC results are calculated (equation 1).

The standard solutions containing both TIC and TOC were prepared. Sodium hydrogen carbonate was used as the TIC source and methanol was used as the TOC source. Two liters of standard solution containing 50 mg/l TIC and 50 mg/l TOC were prepared. 20 reactions were run. The TIC and TOC results were compared with the carbon concentrations of the standard solution.

Test 4. The effect of salt concentration on the oxidation process has been investigated. 100 mgC/l standard solutions were prepared from acetic acid and potassium hydrogen phthalate (KHP). They were mixed with quantities of sodium chloride to contain concentrations of 0, 2.5, 5, 10, 20 and 30% salt. 10 oxidation reactions were run with each standard solution. The oxidation levels were investigated with respect to salt concentration from the TOC results recorded.

RESULTS AND DISCUSSIONS

The oxidation results of the first test, described in the materials and methods section, is given in Table 2. Table 2 shows that each compound has different characteristics during oxidation.

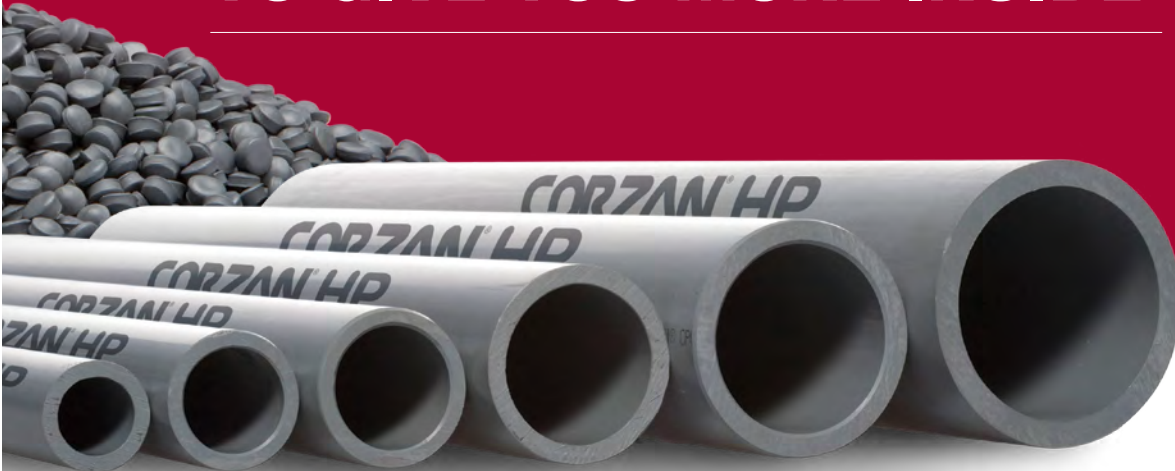
Some are easily oxidized within 60 seconds such as sodium oxalate and methanol. Ethylene diamine and hexa-

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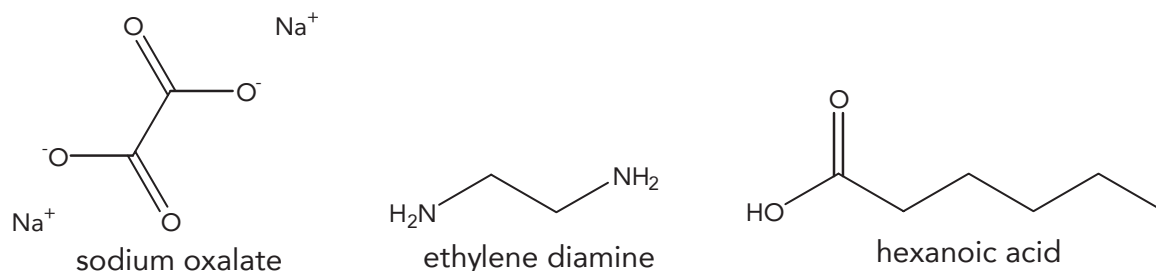


Figure 2. This illustrates the carbonyl bonds of sodium oxalate and the chemical structures of ethylene diamine and hexanoic acid.

noic acid requires more than 120 seconds of base oxidation time for their complete oxidation. Several explanations can be given for the diverse base oxidation times required for numerous carbon compounds. Methanol is a single carbon compound, thus there are no intermediate or secondary compounds formed during the oxidation/reduction reaction.

In sodium oxalate (C₂H₄Na₂O₄) case, ozone and manganese catalyst plays an important role to break down the carbonyl bonds [9, 10]. Therefore the oxidation of these compounds is relatively easy in the two-stage advanced oxidation process. Ethylene diamine (C₂H₈N₂) and hexanoic acid (C₆H₁₂O₂) contain more than one carbon, and secondary compounds are formed. The oxidation process of these compounds takes longer relative to the single carbon compounds and compounds containing carbonyl bonds only. Figure 2 shows the carbonyl bonds of sodium oxalate and the chemical structures of ethylene diamine and hexanoic acid.

Figure 3 shows the oxidation levels versus base oxidation time of some of the compounds presented in Table 2. The distinction between the oxidation levels achieved with various base oxidation times for different compounds is clearly visible in Figure 3. Figure 3 shows that sodium oxalate has the fastest response, whereas acetic acid has the slowest response in terms of reaching the highest oxidation level in time. The complete oxidation of all compounds, as can be seen in Table 2 and Figure 3, is achieved in less than 150 seconds base oxidation time. Further increase above 150 seconds does not have any affect on the oxidation process where the oxidation becomes independent of time. Table 2 illustrates when the base oxidation time is reduced (less than 150 seconds) the oxidation levels (the TOC recoveries) will drop significantly for certain compounds. Note that, the variation in the TOC results is ±3% or ±0.5 mg/l on the full scale. This variation is the combination of the dispersion coming from the mass flow controller, amount of sample injected with the peristaltic pump and the infrared CO₂ detector. Therefore, 150 seconds base oxidation time is regarded as the optimum base oxidation time and applied as standard in analyzers operating on sites. Table 3 gives the average TOC results

OXIDATION LEVELS

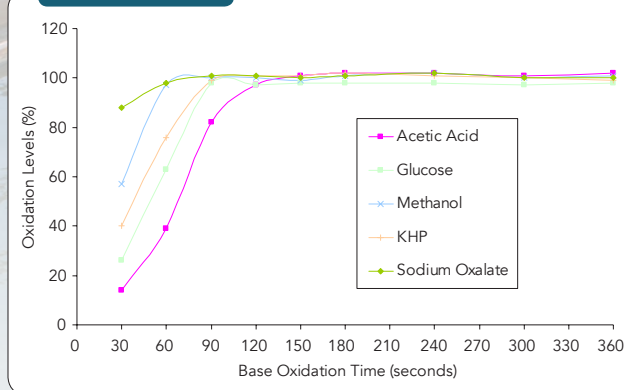


Figure 3. The distinction between the oxidation levels achieved with various base oxidation times for different compounds is clearly visible here.

as obtained from the thermal oxidation (Test 2).

TOC results given in Table 3 confirm the complete oxidation result obtained in 150 seconds base oxidation time in the first test. No trace of carbon is found in the oxidized sample fluids at 150 seconds of base oxidation time and above in the second test performed with thermal oxidation. Note that the dilution effect (approximately 51%) coming from the acid and base addition during the two-stage advanced oxidation process was accounted for in results shown in Table 3. The TOC results in Table 3 are also in good agreement with the percent oxidation levels at 30 to 120 seconds base oxidation times as given in Table 2.

Figure 4 shows the captured CO₂ curves during the two-stage advanced oxidation of mixed standard solution containing both inorganic and organic carbon as described in Test 3. The initial peaks in Figure 4 are the TIC and the second peaks are the TOC readings of the CO₂ detector. Note that there are 20 curves in the figure and each curve is formed of eight instantaneous CO₂ readings captured every second of the reaction. The flat line between the TIC and TOC peak represents the 150 seconds of base oxidation phase. As can be seen in the figure, because both TIC and TOC source compounds (sodium hydrogen carbonate and methanol) contain single carbon, their CO₂ peaks are almost identical as there are no secondary compounds forming in

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AVERAGE TOC RESULTS

Organic Carbon Compounds	BASE OXIDATION TIME (SECONDS)								
	30	60	90	120	150	180	240	300	360
Acetic Acid	85	59	19	1.5	0.3	0.2	0.0	0.2	0.3
Glucose	73	35	1.2	0.2	0.3	0.1	0.2	0.0	0.2
Methanol	42	1.1	1.0	0.3	0.2	0.3	0.2	0.2	0.0
Potassium Hydrogen Phthalate	59	22	0.0	0.2	0.1	0.2	0.1	0.3	0.1

Table 3. Sample fluids oxidized for the second time confirm the complete oxidation result obtained in 150 seconds base oxidation time in the first test.

the base oxidation stage. The CO₂ detector was calibrated previously with accurate concentrations of certified CO₂ gas (1,500, 3,000, 5,000, 7,500 and 10,000 ppm). A 99.995% purity oxygen gas was used as zero gas for the calibration of the CO₂ detector. The error introduced from the certified CO₂ gases was ±0.5%.

The average TIC and TOC results were calculated as 49.6 mg/l and 51.1 mg/l respectively from the 20 reactions using equation 1. TIC result confirms the accurate CO₂ readings of the CO₂ detector. Figure 4 and the TOC result verifies the complete oxidation achieved with the two-stage advanced oxidation process.

Figure 5 shows the effect of salt concentration on the oxidation levels as described in Test 4. The effect of salt concentrations from 2.5 to 10% is found to be less than 0.6%. The effect of 20 and 30% salt concentration is less than 1.6%. Therefore, the salt interference has shown to be negligible in the two-stage advanced oxidation process. The oxidation has proven itself with numerous successful operations in chemical plants where salt concentrations are up to 30%.

There are two main reasons for having no salt interference during the two-stage advanced oxidation process:

- i) The aggressive agents (which are hydroxyl radicals and ozone) are not interfered by the presence of any type of salt.
- ii) Oxidized sample fluid (where salts remain as a solution throughout the reaction) is purged completely from the reactor at end of every cycle.

Any salt built up inside the reactor (Figure 1) is prevented and the system is therefore self-cleaning.

RESOLVING TOC ANALYSIS PROBLEMS

One of the main problems in most online TOC analyzers is the requirement for filtration for their correct operation. A representative sample should be analyzed in order to make the TOC measurements valid. A truly representative sample contains particulates and colloidal materials. Filtration causes the sample to lose its particulates, suspended fibers and colloidal materials and thus the accuracy of the TOC results are affected considerably. Figure 6 represents the effect of filtration on the TOC analysis of a sample. The data was taken from an online TOC analysis made in a wastewater treatment plant.

TIC AND TOC DATA OF OXIDATION REACTIONS

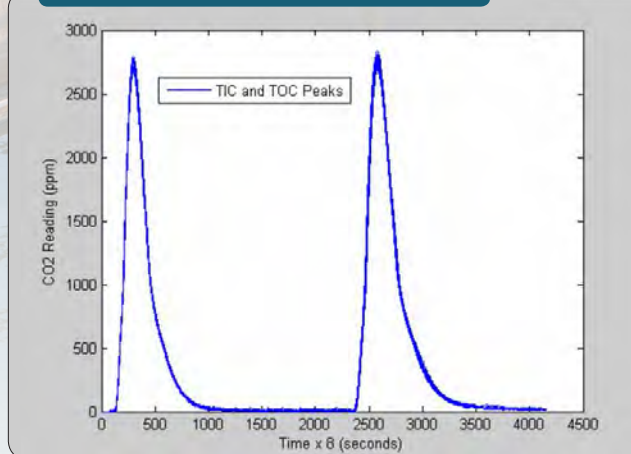


Figure 4: TOC result verifies the complete oxidation achieved with the two-stage advanced oxidation process.

EFFECT OF SALT CONCENTRATIONS ON OXIDATION LEVELS

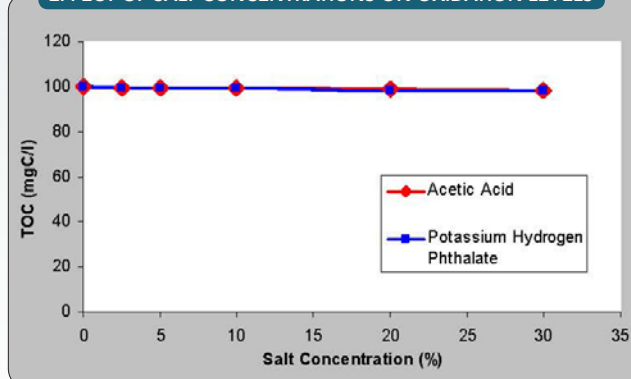


Figure 5. Results indicate salt interference is negligible in the two-stage advanced oxidation process.

Figure 6 shows that even though the TOC results obtained from filtered and unfiltered sample follow a pattern, the unpredictable percent value lost (shown in the secondary y axis) shows the inaccuracy of the analysis and the errors introduced due to filtration. Filtration is not required in the two-stage advanced oxidation process, and therefore the sample is truly representative and accurate.

Another problem is during the analysis of streams with high inorganic carbon content, where inadequate TIC purging

EFFECT OF FILTRATION ON TOC RESULTS

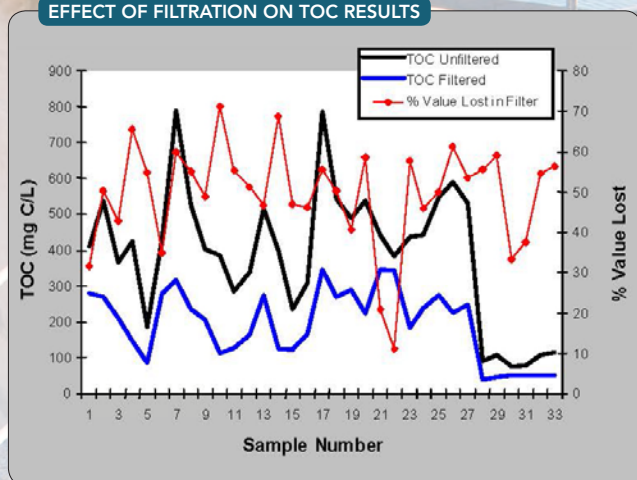


Figure 6. TOC results obtained from filtered and unfiltered sample follow a pattern, indicating filtration isn't required in the two-stage advanced oxidation process.

(typically done by adding acid to the sample and sparging with a gas) results in the TIC carryover to the TOC phase. Therefore the TOC results will be affected drastically causing inaccurate and unreliable results. The analyzer has been designed to overcome this problem and no TIC carryover to the TOC analysis phase is guaranteed. This is achieved by the complete removal of TIC, where the analyzer monitors the CO₂ detector's online readings and extends the TIC phase automatically until all the TIC content of the sample is removed.

The complete oxidation of the sample is not achieved in many online TOC analyzers because of several physical and chemical barriers such as turbidity, salts and calcium presence, pH, fatty and fibrous materials and rate limitation in the oxidation reactions. Two stage-advanced oxidation process assures complete and full oxidation of the sample and none of the physical and chemical barriers affects the oxidation levels.

The wearing of the components in an online analyzer such as pumps, tubing, CO₂ detector due to corrosive materials, vapors, moisture etc. (coming from the samples) is unavoidable.

This can reduce confidence in results, be expensive and require constant maintenance. The components of the two-stage advanced oxidation system is designed "for purpose" using robust materials (such as teflon and hastelloy) to withstand extremely corrosive environments (caused by ozone and hydroxyl radicals). Thus the system is more reliable surviving all corrosive materials coming from the samples and requires low maintenance. This gives rise to a dependable online analyzer where the measurement results can be accepted with confidence.

The analyzer with the two-stage advanced oxidation process has proven itself in the industry for more than 10 years. Examples of industries, which have successfully applied this technology, are:

- 1) Dairy processing plants where the effluents are high in fats, sugar and protein.
- 2) Chemical plants and applications where the process streams are high in salt content.
- 3) Refineries where wastewaters contain oil, calcium and salts.
- 4) Municipal treatment plants where the wastewaters have high turbidity and many particulates.
- 5) Airports where the surface water contains deicing chemicals, particulates and salts.
- 6) Pulp and paper industries where wastewater contain fibrous materials and particulates.
- 7) Pharmaceutical industries where the waste streams contains a wide variety of chemicals.

CONCLUSIONS

This paper described and introduced a two-stage advanced oxidation process to the user. The oxidation chemistry and the oxidation levels achieved have been analyzed and illustrated. Problems associated with online TOC analysis have been emphasized and the solutions found were explained.

Complete oxidation of various organic carbon compounds can be achieved in less than 150 seconds of base oxidation time. Increasing this time did not have any affect on the oxidation process whereas when it was reduced, the oxidation levels dropped for certain chemicals. The distinction between the oxidation rates achieved for different compounds has been demonstrated and the chemistry is clarified. The oxidation levels have been verified with alternative methods such as thermal oxidation and a precisely calibrated CO₂ detector. Both analyses showed that the two-stage advanced oxidation process results in the complete oxidation of the organic compounds. The effect of salt concentrations on the oxidation levels has been examined. The interference coming from salt concentration up to 30% has been found to be negligible on the oxidation process. Finally problems related to online TOC analysis have been outlined and the solutions found with the two-stage advanced oxidation technique have been described.

Today, the two-stage advanced oxidation process is proving to be a reliable online TOC analyses technique with its oxidation levels, accuracy, low maintenance requirements and its ability to overcome many barriers related to online TOC measurement. ●

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