USE OF OZONE FOR COOLING TOWERS

Brendan van Wyk, Xylem
Alexis Métais, Xylem

Abstract
Treatment of cooling water is essential for sustainable operation of cooling towers. The water quality in cooling water circuits deteriorates due to evaporation, intake of make-up water and ambient air impurities. Therefore water treatment chemicals such as corrosion inhibitors, scaling inhibitors and biocides are used to treat the cooling water. The treatment of cooling water with ozone is an alternative method to conventional biocides and has been established over several decades. Ozone provides excellent disinfection rates, reduces algae formation, lowers COD and avoids AOX formation. Authors will introduce fundamentals of cooling water treatment and introduce impacts of ozone.

INTRODUCTION

Cooling Towers are an important means of ensuring efficient and reliable operation of all industrial plants, like pulp and paper mills. Water is the preferred medium for the extraction of heat from exothermic processes and the cooling of motors. Cooling water circulates in a loop where heat is taken up from the process and then discharged in the cooling tower. In the cooling tower the circulating water is brought into direct contact with air and cooling is achieved through evaporation. The draft caused by the cooling tower draws in dust and other organic material and creates an ideal growth environment for bacteria and algae. This growth leads to slime and scale, lowering the heat transfer efficiency and resulting in corrosion. Chemicals are added to the system to minimise the growth of bacteria and reduce the risk of scale formation. Normal cooling tower water treatment consists of the addition of about 6 different chemicals: biocide, anti-scale chemicals, corrosion inhibitors, defoaming agents, pH control and dispersants. The addition of all these chemicals and the removal of water through evaporation limits the amount of times the cooling water can be circulated before concentration of dissolved solids and chemicals becomes so high that scale can begin to form and become problematic. Therefore some cooling water must be discharged (blowdown) and the basin water diluted with fresh water (makeup water). This blowdown needs to be treated in an effluent treatment plant before it can be discharged to the environment because of all the chemicals it contains.

Ozone can fulfil the role of most of the treatment chemicals. It is a very strong oxidant and biocide. It does not add any organic material to the water, so no defoamers or dispersants are required. If the cooling water is run at high cycles of concentration, then corrosion inhibiters are not required since the water is already saturated with metal ions. The pH of the ozone treated tower water stabilizes out at around 8 to 8.5pH, above the corrosion pH, so no pH adjustment is required. Scale does not tend to form in ozone treated water because no colony forming bacteria are present (thanks to the biocide action of ozone), so there is no glue to start the scale process and as a consequence metals reaching their concentration of saturation precipitate into the water body as fine powder. This powder is easily removed in the system sand filters. The cooling water can safely be concentrated to high cycles of concentration, or even operate on a zero blowdown basis because of the good quality of the circulating water.

FUNDAMENTALS OF COOLING TOWER OPERATION

A cooling tower is used to remove unwanted heat from a process or equipment. Water is circulated through the equipment, where it is heated. This hot water is then allowed to flow down through the cooling tower, where evaporative cooling takes place. Rate of evaporation is roughly 1% of the circulation flow for each 5°C drop in the circulating flow. Why? Let's consider a 100 L flow at 30°C. Heat capacity of water at 30°C is 4.18 kJ/kg/K so a temperature drop of 5°C cooling water means 100 x 4.18 x 5 = 2,090 kJ shall be released. Heat of vaporization of water is 2430 kJ/kg at 30°C so theoretically a temperature drop of 5°C leads to evaporation of 0.86 L, in practice 1% is considered. During evaporation, only water is removed while the salts and chemicals are left behind in the

circulating water. This results in increase of the Total Dissolved Solids (TDS) (and the related conductivity) leading to the risk of scale. The limit of this increase is usually calculated with the Langelier Saturation Index (LSI) which predicts precipitation of calcium carbonate ($CaCO_3$). Numerous calculation tools allows for calculating the LSI which is defined by LSI = pH – pHs where pH is the measured water pH and pHs is the saturation pH depending on calcium ion concentration, alkalinity, TDS and the temperature. There is no risk of scale if the calculated LSI value is negative, but the water would be corrosive, while water with a positive LSI calculated value is saturated in $CaCO_3$ and scale may form. Acid is normally added to the cooling water flow to keep the pH below that of scale potential, but above that of corrosion.
Typical feed water and operating conditions usually limit the number of cycles of concentration to between 2 and 5 before scale becomes an issue even with the pH correction. The cycles are controlled by discharging, or blowing down, the basin water and making this water loss up by adding fresh water. This control is normally done based on the water conductivity, so a maximum conductivity is calculated When this conductivity is reached, the blow down valve is opened, and the water is discharged to waste until a lower conductivity value is reached.

TREATMENT OF COOLING TOWERS

Bacterial growth within a cooling tower is a constant problem. The warm water, along with the constant ingress of airborne contaminants, like dust and other organic material, results in an excellent breeding ground for microbial life. This growth, if left unchecked, will result in a thick biofilm growth and loss of cooling tower efficiency and corrosion. This biofilm can also harbour pathogens such as legionella, resulting in a toxic environment and public health risk. To control this microbial activity, conventional treatment methods include the dosing of biocidal chemicals. These need to be dosed in high enough concentrations to ensure a high log reduction of growth. Bacteria can build up immunity and tolerances to these chemicals, and so a routine change in chemicals and chemical dose is required.
So conventional chemical treatment programs, used to maintain a cooling tower in good operation, consist of the following:

- Biocides
- Anti-scale chemicals
- Corrosion inhibiters
- pH control
- Defoamers
- Dispersants

All of the above then end up being dumped into the treatment works during cooling tower blow down, and can cause problems in the environment. They also limit the degree of cycles of concentration that can be achieved in a well operated tower.

OZONE TREATMENT OF COOLING TOWERS

Ozone (O_3) is a gas with a strong oxidizing power produced from oxygen (O_2). Because it self-decomposes rapidly into oxygen, ozone is produced on-site. There is no delivery, storage or handling of chemicals and no remaining biocidal effect in the effluent discharge stream. Ozone is usually dosed through venturi injectors at 0.1-0.3 g/m^3 depending on the cooling water quality. As an oxidizing biocide, ozone kills all microbes, such as bacteria, viruses, spores and algae through cell lysis, rather than through poisoning like conventional biocides. This means that organisms cannot become immune to ozone, as so often happens with conventional biocides. While, contrary to chlorinated chemicals, ozone does not form AOX.
Ozone ensures that there is no microbial or bacterial growth within the water of the tower and removes any biofilm that may have been present before ozone was introduced, effectively cleaning up the full cooling water loop. Nalco [1] reported as far back as 1992 "numerous case histories of the use of ozone in "zero discharge" cooling tower applications" and operated a cooling system at a concentration of 100 cycles. Ferguson and Freedman [2] reported that in ozonated cooling waters of high calcium carbonate saturation ratios, when scale would be expected, calcium carbonate precipitates in the bulk water and not as scale. Indeed the high biocidal efficiency of ozone avoids slime formation that could give opportunity for scale to appear, so calcium carbonate precipitates as

crystals and then these crystals grow because of their own very high surface area. These precipitated crystals are easily removed in the system sand filters. Pryor and Fisher [3] also reported that "there have been numerous documented cases of ozonation systems operating for extended periods with zero intentional blowdown". Actually the use of ozone allows for increasing the cycles of concentration well beyond that predicted by the LSI, so Pryor and Fisher developed the Practical Ozone Scaling Index (POSI) for cooling tower operated with ozone [3]:

maximum conductivity in cooling tower = $10^{(1/(\log(CaxMg)/(Na+Cl)]x\log(Alk/10)}$ x conductivity of the make-up water.

So the strong biocidal effect of ozone results in water savings since less blow down and make-up water are required. Significant water savings were also reported more recently in other ozone treated cooling towers [4, 5, 6]. By increasing the cycles of concentration, there is a direct impact on the operating costs of the tower, through:

- Reduction in fresh water make-up
- Reduction in effluent discharge
- Lower need for equipment cleaning
- Higher efficiency of the heat transfer

A first consequence of scale not forming, through the use of ozone as a biocide, is that no anti-scale chemicals are required to be dosed into the tower. Since acid is normally dosed to maintain pH and avoid calcium carbonate precipitation, this is no longer required when using ozone because the calcium precipitates in a non-scaling manor.

As stated by Strittmatter et al [1] "the corrosion rate of mild steel is dominated by the saturation level of the water, and not by the presence or absence of ozone in the system". So cooling water loops operated at high cycle of concentration (and that is made possible thanks to the use of ozone) have minimal corrosion rates because of the high levels of dissolved metals and the subsequent reduction in the corrosion potential of the water. So no corrosion inhibitor needs to be dosed.

Finally, since no chemicals are being added to the system, there is no foaming in the tower, and there is no need for the addition of dispersants to increase the solubility of chemicals, so no defoamers or dispersants need to be added to the system.

CASE STUDY

Each tower needs to be evaluated separately because of differences in the chemical programme used, the cost of water and power, and the reasons for using ozone. Here is a case study of a cooling tower with a circulation flow of 11,000 m3/h reducing temperature from 37°C to 30°C with an evaporation flow of 133 m3/h. Conventional chemical treatment, supplied by a cooling tower treatment services company, operates very well with 5.5 cycles of concentration. The required ozone dose is 0.3 g/m3 and ozone production requires a total of 12.5 kW/kgO3 including all the power used for the VSA to generate the oxygen as well as the power for ozone generation. At the end both treatment solutions cost the same.

But, increasing the cycles of concentration to 15, thanks to ozone, allows for a reduction in the make-up water flowrate from 163 m3/h to 143 m3/h and significant savings.

Further benefits can be expected, related to the improved heat transfer efficiencies and energy savings that can be expected due to improved cooling of the process equipment, and would need to be calculated on a site specific basis. Other cost and environmental benefits that need to be considered are the lower, or zero AOX values in the effluent and the improved COD discharge to the effluent treatment plant.

CONCLUSIONS

Cooling Towers that are treated with ozone can expect the following benefits:

- Excellent cooling water quality, e.g. very good visibility depths
- Long term protection against microbiological growth (bio fouling) because of a reduction of colony forming units CFU by approx. 3 - 4 log steps
- Effective control of Legionella
- Improved heat transfer
- Reduced waste water costs since COD levels are low and AOX values will be reduced because there is no chlorine or bromine additions
- Corrosion rates decreased as cycles of concentration increase
- Improved industrial safety due to no storage, and handling of hazardous chemicals
- Operation at higher cycles of concentration

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1. Strittmatter, R.J., Yang, B. and Johnson, D.A., Application of Ozone in Cooling Water Systems, Corrosion'92, Nashville, TN, USA, (1992).
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3. Pryor, A. and Fisher, M., Practical Guidelines for Safe Operation of Cooling Tower Water Ozonation Systems, Ozone Science & Engineering, Vol. 16, pp. 505-536, (1994).
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Use of Ozone for Cooling Towers

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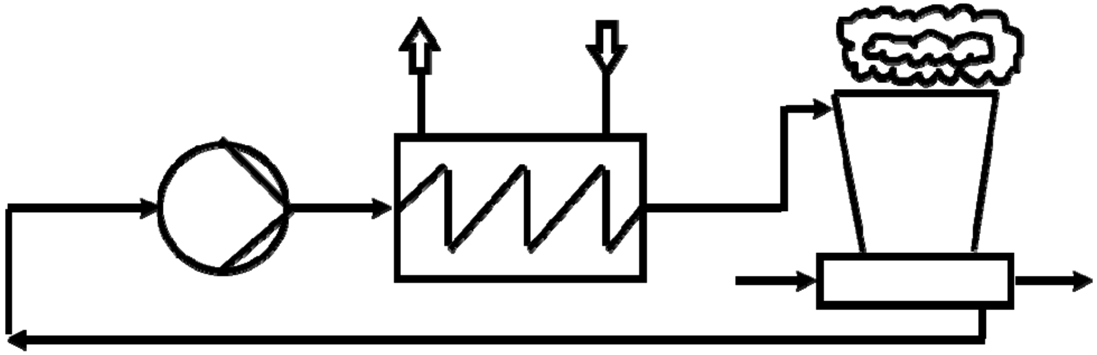
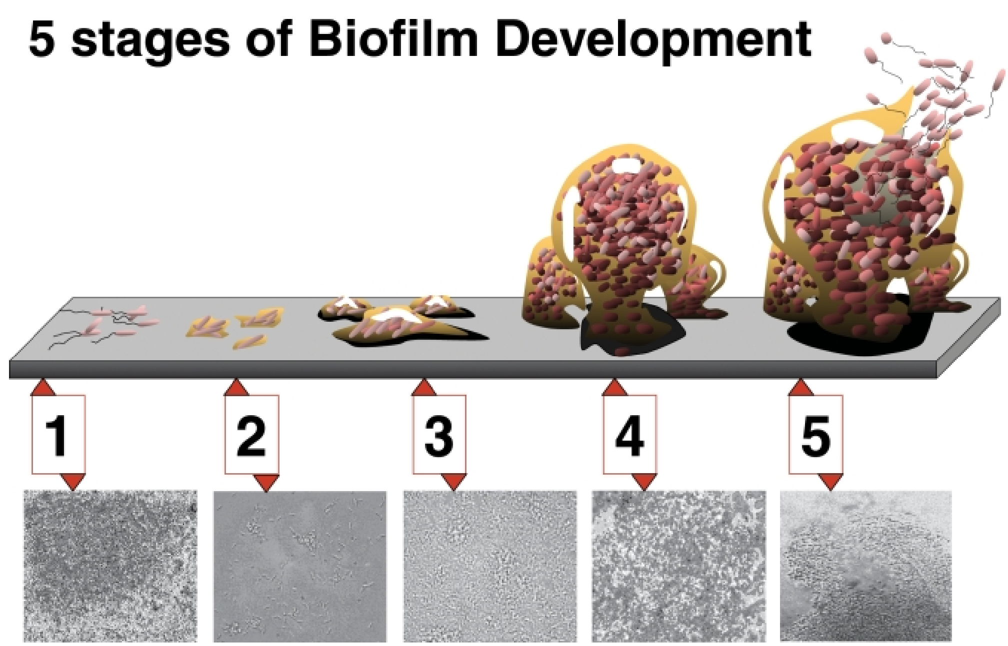
Principle Operation of a Cooling Tower



- Cooling water circulates in a loop where heat is taken up from the process.
- The circulating water is brought into direct contact with air so cooling is achieved through evaporation. Evaporation also results in a loss of circulating water and an increased concentration of dissolved solids.
- Some water is discharged and makeup water is added.

Why Treat Cooling Water

- The draft caused by the cooling tower draws in dust and other organic material.
- It creates an ideal environment for microbiological growth.
- Biofilm significantly reduces heat transfer and initiates corrosion.
- Biofilm provides ideal living conditions to bacteria such as legionella.



Stage 1, initial attachment; stage 2, irreversible attachment; stage 3, maturation I; stage 4, maturation II; stage 5, dispersion.
Source: Monroe, D., Looking for chinks in the armor of bacterial biofilms, PLoS Biol. 2007 Nov;5(11):e307.

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Conventional Treatment Protocols

- Chemicals are added to the system to minimise the growth of bacteria and reduce the risk of scale formation.
- Normal cooling tower water treatment consists of the addition of 6 different chemicals:
  - Biocide
  - Scaling inhibitors
  - Corrosion inhibitors
  - Defoaming agents
  - pH control
  - Dispersants

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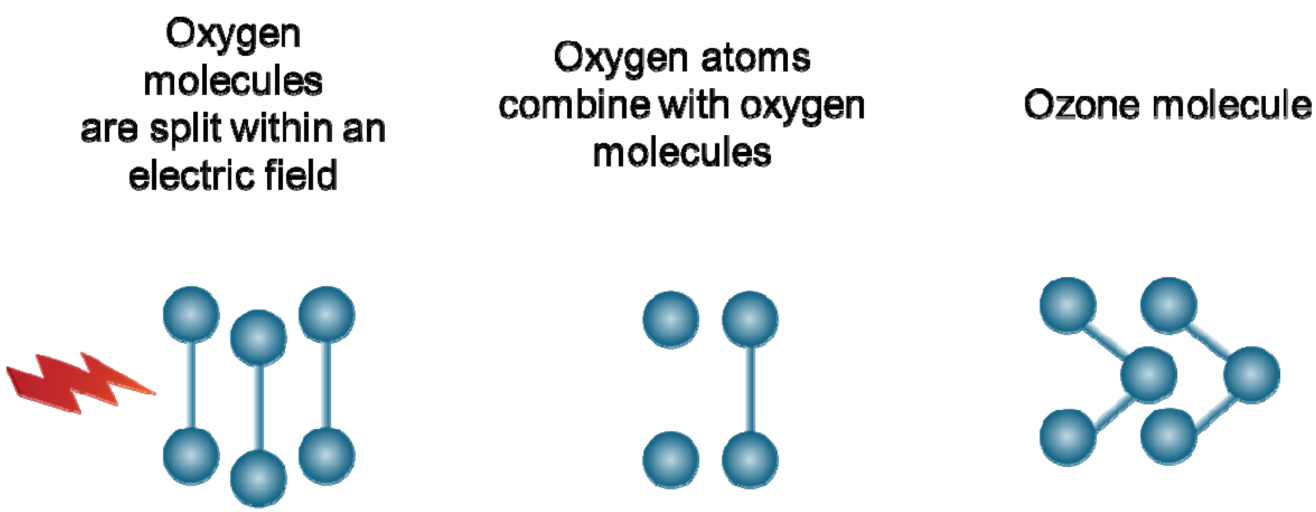
Cooling Tower Operational Issues

- Control of biological activity and biofouling
- Scale formation
- Corrosion
- Water consumption
- Blowdown water disposal
- Chemical Handling

Ozone

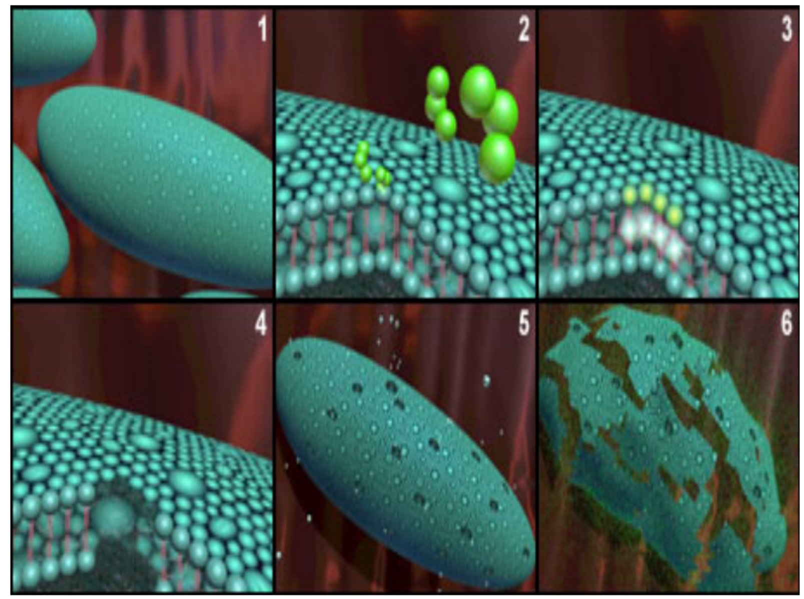
- Ozone (O_3) is a gas with a strong oxidizing power produced from oxygen (O_2).
- Ozone production requires only electricity, oxygen and cooling water.



Ozone

- Because it self-decomposes rapidly into oxygen, ozone is produced on-site. There is no delivery, storage or handling of chemicals and no remaining biocidal effect in the effluent discharge stream. Contrary to chlorinated chemicals, ozone does not form AOX.

- As an oxidizing biocide, ozone kills all microbes, such as bacteria, viruses, spores and algae through cell lysis, rather than through poisoning like conventional biocides. This means that organisms cannot become immune to ozone, as so often happens with conventional biocides.



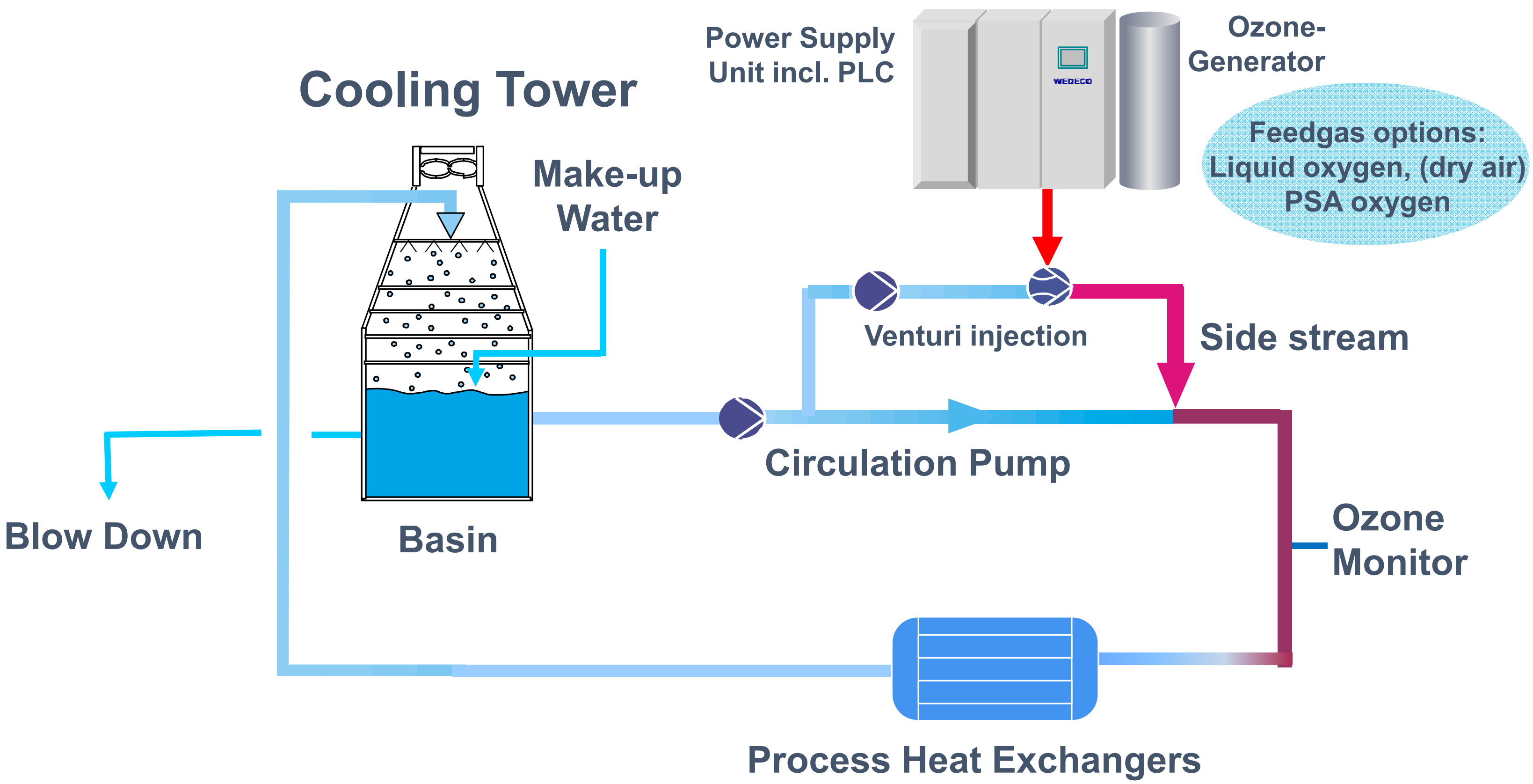
Comparison of Different Disinfection Means

CT-values for 2-log reduction @ 5 °C

Mikroorganismus	Cl_2 pH = 6-7	Chloramin pH = 8-9	ClO_2 pH = 6-7	Ozon pH= 6-7
E.coli	0,034- 0,05	95-180	0,4-0,75	**0,02**
Polio virus	1,1-2,5	768- 3740	0,2-6,7	**0,1- 0,2**
Rotavirus	0,01-0,05	3800- 6500	0,2-2,1	**0,006- 0,06**
Giardia lamblia cysts	47-150	2200	26	**0,5-0,6**
Giardia muris cysts	30-630	1400	7,2-18,5	**1,8-2,0**
Cryptosporidium parvum	7200	7200 (1-log)	78 (1-log)	**5-10**
Cryptosporidium parvum (1°C)	-	-	-	**10**
Cryptosporidium parvum (22°C)	-	-	120	**7 (3,5-log)**

Source: **von Gunten**, U. and **Laplanche**, A., Oxidation and Disinfection with Ozone, an Overview, Proc. International Specialized **Symposium IOA**, pp. 39–73, **Toulouse**, France, **2000**

Ozone Treatment Diagram



Ozone Treatment Impacts

- Ozone can fulfil the role of most of the treatment chemicals.
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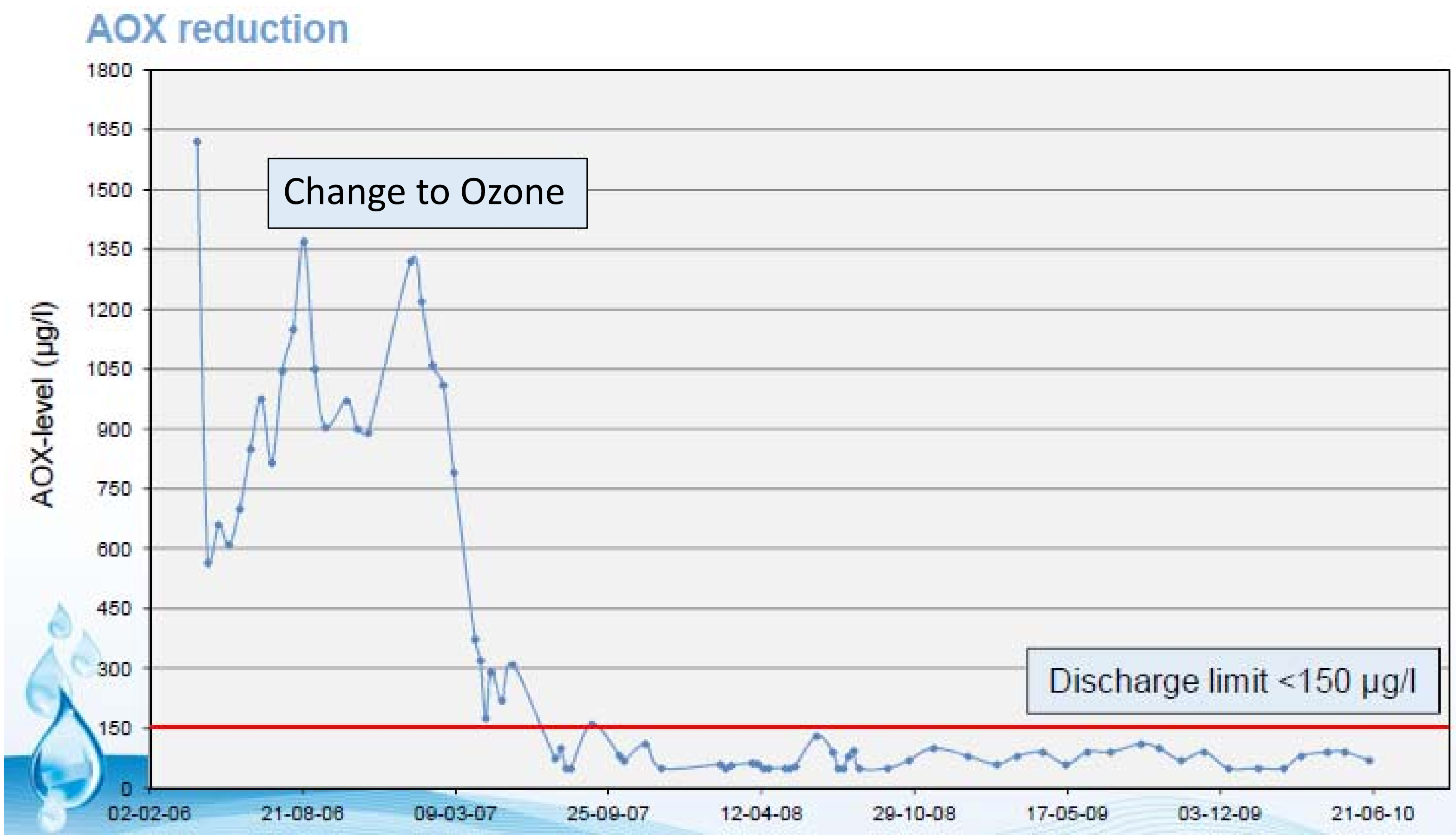
- It does not add any organic material to the water, so no defoamers or dispersants are required to increase solubility of other chemicals.
- If the cooling water is run at high cycles of concentration, then corrosion inhibiters are not required since the water is already saturated with metal ions.
- The pH of the ozone treated tower water stabilizes out at around 8 to 8.5pH, above the corrosion pH, so no pH adjustment is required.
- Scale does not tend to form in ozone treated water because no colony forming bacteria are present (thanks to the biocide action of ozone), so there is no glue to start the scale process and as a consequence metals reaching their concentration of saturation precipitate into the water body.

Industrial Results (Refinery)



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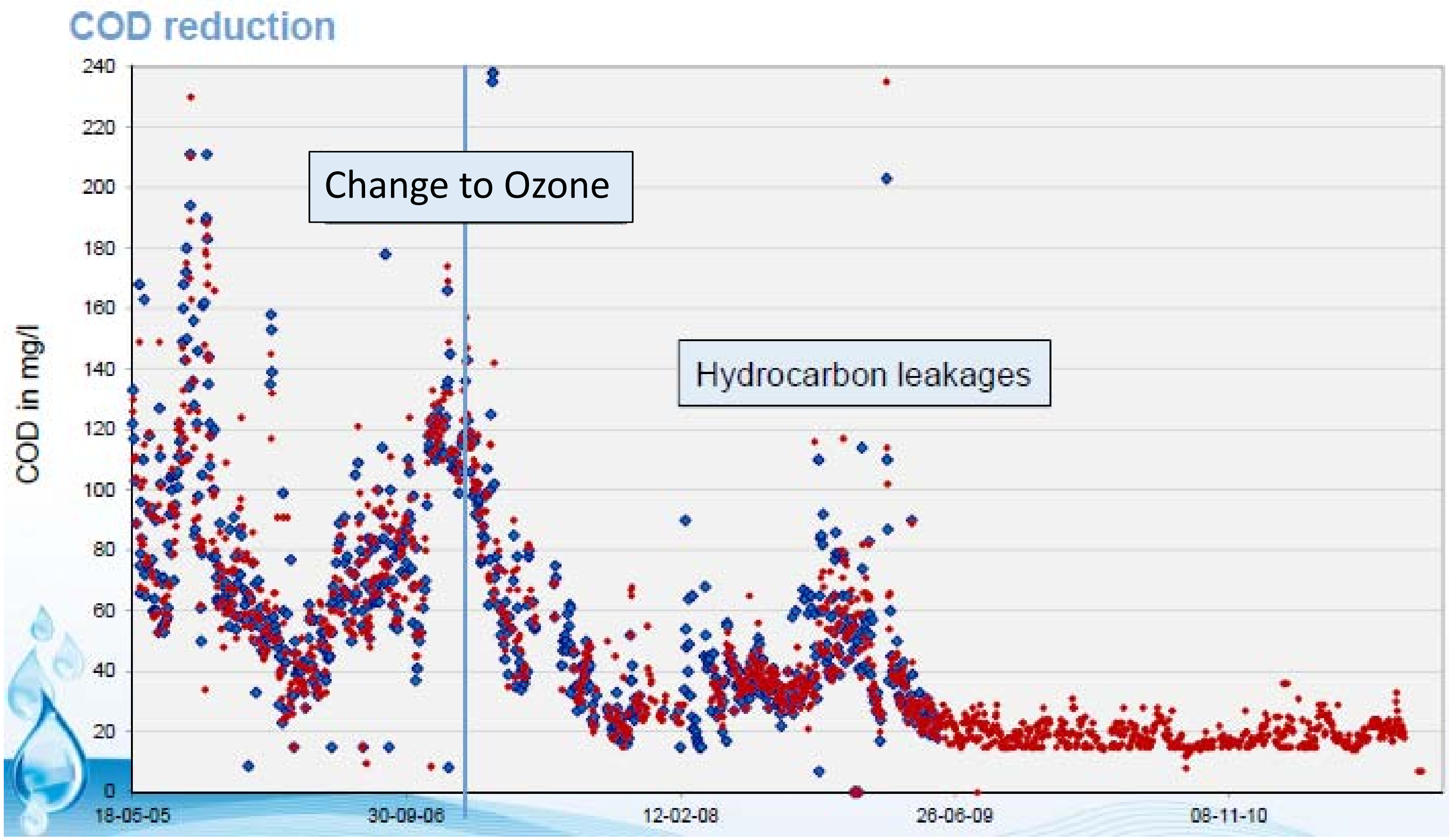

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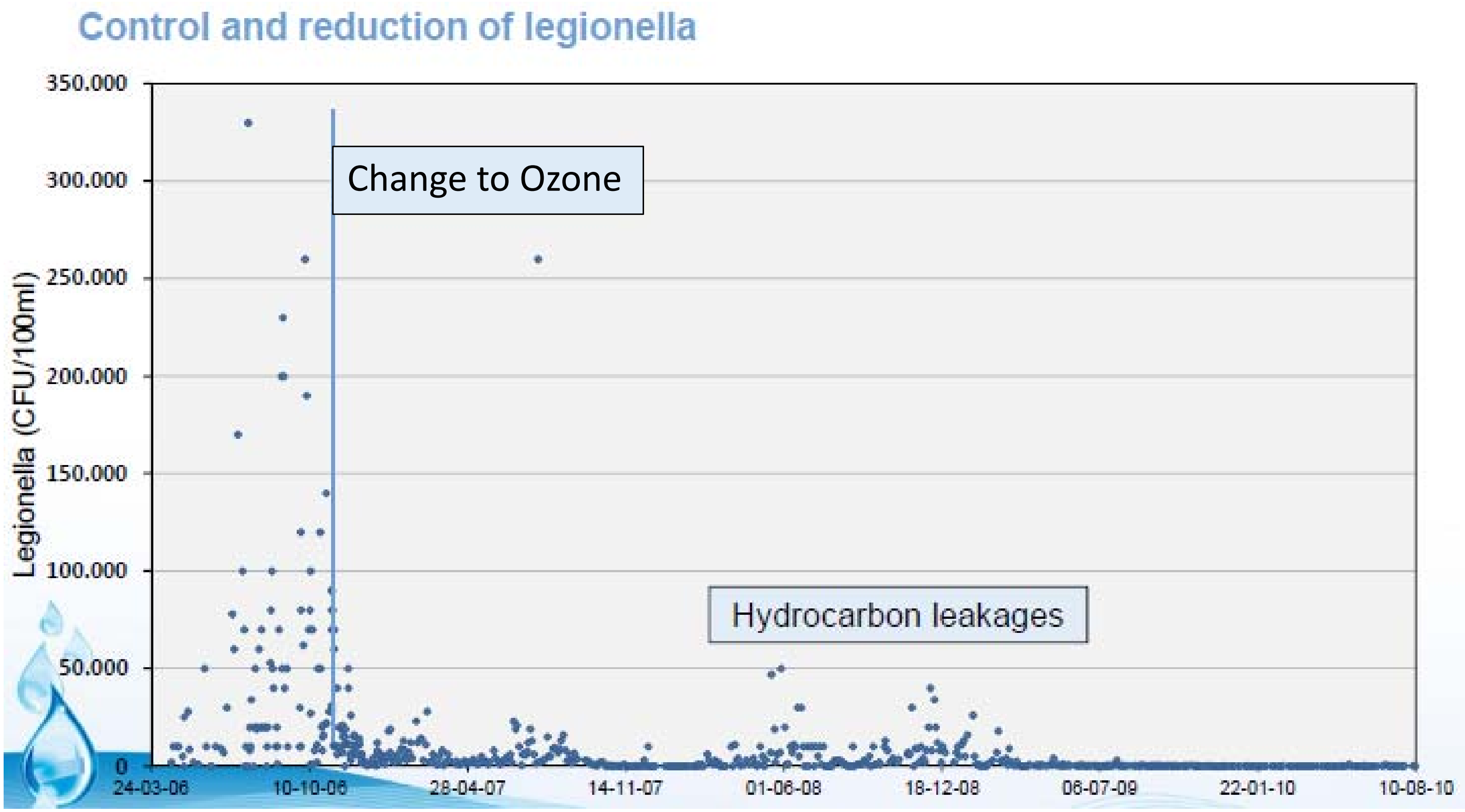

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Case Study

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Thank You!

alexis.metais@xyleminc.com