## Northern California Plant Engineering Conference Santa Clara, CA September 21, 1995

Sponsored By The American Institute of Plant Engineers

# RECYCLING TREATED WASTEWATER THROUGH COOLING TOWER OR PROCESS SYSTEMS

Eugene Wei Timothy Keister

ProChemTech International, Inc. Brockway, PA

### Background

The reuse of treated industrial wastewater as makeup for cooling towers, or reuse in a process, is being considered more often today as fresh waters become increasingly limited and costly, and discharge regulations become more stringent. Economic benefits include reduction and/or elimination of costs for fresh makeup water, sewerage fees, effluent monitoring, and permitting. A sometimes pleasant surprise is that treated wastewaters are often chemically superior to the fresh water source being replaced, allowing increased cycles and decreased chemical treatment costs to be realized in a cooling tower, or providing a decrease in chemical usage or water pretreatment requirements in process uses.

Unlike many "reuse" schemes, in which treated wastewaters are reused for low quality uses like landscape irrigation or dust control, reuse of treated wastewater as cooling tower makeup, or process water, are true "high value" replacements. The replacement of potable water used for cooling tower and process makeup with treated wastewater frees up the potable water for other high value uses. In many cases, the reuse of a treated wastewater as cooling tower makeup, and subsequent zero discharge of the cooling tower, as well as process water reuse, will totally eliminate the discharge of process wastewater from a facility. We do not have to expound in 1995 upon the value of running a facility "zero discharge".

Many items, which are not typically considered in design of a cooling water management program based on use of fresh makeup water, become quite important when treated industrial wastewater is used as makeup. A major consideration is that the wastewater generating process, and subsequent treatment process, must be included in the design of the program. The program designer must take full account of both the wastewater and the wastewater treatment chemistries, and the potential for upsets causing major problems in downstream cooling tower or process use. It is our goal to today present a basic outline of some specific items which must be considered when the use of treated industrial wastewater is being explored for replacement of fresh water as cooling tower makeup. If your plant presently has a source of treated wastewater, we would encourage you to evaluate it as a source of high quality makeup water for process and HVAC cooling towers. Reuse as process water is a world of its own, and we will today only briefly touch on the subject via two short case histories.

## Plant Survey

- A. SUPPLY: The first item of business in any consideration of industrial wastewater reuse for cooling tower makeup is to determine what wastewaters are available for reuse and their present quality. Plant water flow diagrams and wastewater discharge permits should be consulted to locate likely sources. Once likely sources are located, the following data should be obtained on each one:
  - 1. Where does the wastewater originate, what process produces it and how is it disposed of now.
  - 2. At what rate is the wastewater treated, how does the treated wastewater flow rate and amount vary with time. Both short and long term changes should be considered.
  - 3. What is the present raw and treated wastewater quality, all relevant parameters such as pH, dissolved solids, hardness, alkalinity, chlorides, metals, organic content, suspended solids, phosphate, and sulfates should be determined. Any parameters specific to the generating process, such as fluoride content in semiconductor manufacturing, should be included in the evaluation. The range of variation for each parameter should be ascertained and the reason for the variation noted, if possible.
  - 4. What is the specific wastewater treatment chemistry in use and what are the target parameters. If possible, alternative chemistries should be evaluated and the reason ascertained for selection of the particular chemistry in use.
  - How is the wastewater treatment process controlled. Are chemical reagents added proportional to set flow rates, or are wastewater parameters measured, such as pH or ORP, and reagents added to obtain specific set points.

- 6. A wastewater treatment system block flow diagram showing each wastewater source, the unit processes in the treatment system, and the various chemical additions should be prepared.
- 7. Any existing problems with the wastewater treatment process should be evaluated. What is causing them and what is the effect on the treated wastewater parameters.
- B. USE: Once a potential supply of treated wastewater has been located and evaluated, the potential uses for the supply must also be evaluated. A complete survey of the target cooling tower system(s) must be made. During this survey, answers must be obtained to the following questions.
  - 1. What is the present makeup water use rate and amount with time.
  - 2. How does the makeup water use vary with time, both short and long term changes should be considered.
  - What is the present makeup water quality, all relevant parameters such as pH, dissolved solids, hardness, alkalinity, chlorides, and sulfates should be determined.
  - 4. How many cycles are presently being obtained in the system and what is the specific treatment chemistry in use. If possible, the specific parameter limiting maximum cycles should be ascertained.
  - 5. What chemistry control systems are presently in use, how is blowdown, chemical inhibitor addition, and biocide feed controlled.
  - 6. The various cooling tower system parameters must be determined, in particular the following data is always of use to a water program designer:
    - a) bulk and maximum water temperatures
    - b) residence time of water in the system
    - c) minimum and maximum flow rates
    - d) metallurgy of the system with special emphasis placed on potential galvanic couples

- Are the cooling towers equipped with any form of by pass filtration.
- 8. Last, but of very great importance, any existing problems must be ascertained. Corrosion coupon results, microbiological test data, plant downtime reports, and equipment inspection reports can be consulted to determine the results obtained with the use of fresh water and the present management program.
- C. ECONOMICS: Now that we have located a source of treated wastewater in the plant and found a potential use for it, the next big question is, will it pay for itself. To answer this question, you should obtain the following data:
  - 1. Cost of fresh water for makeup.
  - 2. Cost of sewerage for wastewater.
  - 3. Cost of present cooling water management program.

Once we have these costs, it is a simple matter to calculate the potential cost savings from elimination of fresh water purchases and disposal of "one pass" treated wastewater. Against this cost savings has to be balanced the costs, capital and operating, of any equipment, such as filters, tanks, and pumps, needed to reuse the wastewater, as well as any specific additional chemistry or equipment that may be needed in the cooling water management program.

If you are one of those lucky people who find that reuse of treated wastewater allows higher cycles in your cooling towers, be sure to calculate your cost savings from reduced water treatment chemical usage.

### Water Chemistry Considerations

All cooling water treatment programs are implemented to prevent operating problems from cooling system outages, to reduce system energy usage, and protect capital assets from deterioration. To successfully meet these objectives, a cooling water management program must control scaling, corrosion, deposition and biological fouling in the system being treated. Use of treated wastewater in place of fresh water can introduce several parameters which are not normally considered in design of such programs, as well as put some unusual "twists" on the standard parameters considered. Given that the reuse of treated wastewaters as cooling tower makeup is still a "new" technology, the following discussion should be considered as only a guide. A. Calcium: This well known scale former must always be considered in design of a cooling water program. In the majority of cases, the calcium content of the makeup water is the controlling parameter determining the maximum cycles that can be obtained. Once the level of calcium in the wastewater is determined, the proper type and amount of scale inhibitor needed can be calculated to obtain the desired, or allowed by the calcium content, cycles.

We have found, however, that calcium may be totally absent in many treated wastewaters, dependent of course on the generating process and the wastewater treatment train, thus permitting increased cycles to be obtained with use of treated wastewater. In particular, wastewaters from plating and semiconductor processes are often found to have a very low calcium content.

Even if a large amount of calcium is found in the wastewater, its economical reuse is not ruled out. First, check your wastewater treatment process, many of the older systems are designed to use calcium hydroxide to adjust pH. A simple replacement of the calcium hydroxide with sodium hydroxide, or magnesium hydroxide, may reduce the calcium content of the wastewater to very low levels.

In the event that the high calcium is inherent in the wastewater producing process, recent developments in polymer chemistry allow use of water with calcium hardness values of 2000 mg/l, or higher, to be used in cooling water systems with no fear of scale formation.

Other changes in the wastewater treatment train should also be considered. For instance, on a recent zero discharge project our firm replaced the use of sulfuric acid in a pH reduction step with phosphoric acid. We thus obtained two benefits with one chemical addition, reduction of pH and precipitation of excess calcium from the wastewater.

B. Magnesium: This divalent cation is lumped in with calcium in the determination of total hardness and thus is often thought to be a major scale former. Our experience has been that magnesium base scales are really quite rare, problems only occur when high levels of magnesium and silicate are present. The chemical combination of magnesium and silicate can produce a very hard scale which is difficult to remove chemically. As with calcium, recent advances in water treatment polymer chemistry permit much higher levels of magnesium and silicate to be tolerated in cooling tower water than in the past.

C. Phosphate: In the interest of fairness, this anion has been responsible for almost as much scale formation as calcium. In combination with calcium, magnesium, or iron; it readily forms very insoluble scales. Watch out for the phosphate content of many wastewaters due to the use of phosphoric acid and phosphates in various cleaning and metal treatment processes.

If the treated wastewater is high in phosphate content and the content of scale forming cations is likely to be significant in the cooling water, you may wish to review the wastewater treatment process and add an aluminum based coagulant, such as polyaluminum chloride, to the train. Aluminum phosphate is extremely insoluble and a substantial reduction in phosphate content can often be easily achieved while improving the overall treatment process.

Several advanced polymers are available which substantially increase the amount of phosphate compounds which can be tolerated without scale formation in a cooling tower. Based upon some rather impressive scaling events by the major water treatment companies using phosphates as corrosion inhibitors, we would urge some caution in their application.

D. Silicate: This anion has a very bad reputation as to causing problems in cooling water systems, which we believe remains from the historic days of low pH, high chromate, cooling water treatments. In such acidic cooling waters, silicic acid would routinely precipitate when the level of silicate exceeded about 150 mg/l.

Today, when almost everyone is operating with high alkalinity treatment programs and it is the exception to find a cooling water with a pH below 8.0, silicate is much less of a problem. The higher pH values are directly responsible for elimination of the silicate precipitation problem, silicate anion actually increases in solubility as the pH value of the water goes up. Levels of silicate approaching 300 mg/l have been reported with no silicate scale formation noted. As noted under magnesium, advanced polymer chemistry can control silicate scale formation to some degree.

E. Fluoride: While uncommon in natural waters, fluoride is common in semi-conductor, glass, and metal finishing industry wastewaters. It can form a very nasty scale in combination with calcium and is also toxic at quite low doses.

The best way to address fluoride in a wastewater stream is to add an aluminum based coagulant to the existing treatment train to precipitate aluminum fluoride, a very insoluble compound. Aluminum is recommended in place of the commonly used calcium hydroxide so as to avoid retention of excess calcium in the treated wastewater. It is very easy to reduce the residual aluminum content to less than 1 mg/l using simple pH adjustment, while the residual calcium content can easily be over 1000 mg/l.

F. Chloride/Sulfate: We are considering these two anions here together as they are quite common in most treated wastewaters due to the universal use of hydrochloric and sulfuric acids.

Chloride ion is not scale forming, higher levels do increase the corrosivity of the water and care should be taken to provide an excellent corrosion control chemistry if levels higher than 500 mg/l are expected in the cycled cooling tower water. Please note that high levels of chloride are not limiting in any way, our firm has maintained 1 mil/yr mild steel corrosion rates in saturated sodium chloride brines.

Sulfate ion is a potential scaling ion if the solubility product of calcium sulfate is exceeded. Corrective measures include use of excellent dispersant polymers in the cooling water treatment program, removal of the offending cation (usually calcium) in the wastewater treatment process, and substitution of another acid, such as hydrochloric or nitric, in the process. Note should be made that sulfate ion contributes substantially less to corrosivity than chloride ion, while nitrate ion is a weak corrosion inhibitor. G. Chemical Oxygen Demand: This is a bit of a catch all parameter, basically consisting of all organic compounds, and some inorganics, that can be oxidized by a strong oxidizer. It is an excellent indicator of the amount of organics in a wastewater, which can be used for food by microbes in the cooling tower system and thus contribute to biological fouling. Anytime a higher COD wastewater is used in a cooling tower, great attention must be focused on the biological control portion of the cooling water treatment program to prevent biological fouling. We have found chlorine to be the most economical means to obtain acceptable control, with chlorine dioxide our second choice. Ozone, bromine donors, and UV/peroxide should also be evaluated for specific applications.

High chemical oxygen demand (COD) values in treated wastewater should be minimized as it will increase the amount of oxidizing biocides needed for proper control and will, in some cases, cause inactivation of non-oxidizing biocides.

Changes in the treatment train, such as adding adsorption and absorption type coagulants, or addition of an anaerobic reactor or ultrafilter, at the end of the train, should be considered to decrease the chemical oxygen demand of the treated wastewater. Use of strong oxidants, such as ozone, chlorine dioxide, and hydrogen peroxide, in the treatment train have also been used to some benefit.

You should also note here a major problem that is common with reuse of treated wastewater in cooling towers when the treatment process uses an organic flocculant in the train. In most cases, the dosage of the flocculant is not controlled very well and excess material is often present in the treated wastewater. While this flocculant presents no problem if discharged to the sewer, in a cooling tower it acts to precipitate any suspended solids within the system, resulting in severe deposition problems.

Our experience is that an inexpensive anaerobic reactor, placed at the end of the treatment train, totally controls this potential problem.

H. Oil/grease: While oil/grease is a component of COD, oil/grease as a separate parameter presents some really unique problems if it enters a cooling water system. Oil/grease in cooling water will "cement" any suspended solids present, forming stubborn hydrophobic deposits that encourage biological growth and severe underdeposit corrosion. We have seen steel corrosion rates jump by a factor of 20, or more, when oil/grease was introduced into a cooling water system.

Our best advice is to ensure that the treatment train can cope with any possible content of oil/grease in the wastewater. The technologies available include such things as adsorption and absorption via coagulation, carbon absorption, and ultrafiltration.

I. pH: Extremes in treated wastewater pH can cause severe corrosion and scaling problems in cooling towers. For example, zinc (galvanize) dissolves at both low and high pH values, while calcium solubility decreases as the pH value increases. A recently recognized problem is the phenomenon of "white rust", an accelerated corrosion of the galvanized metal in cooling towers of recent vintage. The problem has been directly linked to the alkaline cooling water treatments now in use, any time the cooling water pH exceeds 8.2 su, zinc will corrode to the carbonate, which forms the white deposit from where the descriptive term "white rust" comes.

White rust corrosion can be controlled via three techniques: operating at lower cycles to prevent development of high pH values in the cooling water, pH control via addition of acid to the cooling water to maintain a cooling water pH below 8.2, or use of a specific white rust inhibitor chemistry, such as our patent pending ZincGard.

In general, wastewater treatment trains should be adjusted, or modified, to produce treated wastewaters with pH values between 6.5 and 8.5 su so as to prevent any pH related problems in downstream reuse applications. We have found that all common heavy metals can be effectively precipitated within this pH range using various organic and co-precipitation technologies. J. Dissolved Solids: This parameter is again a sort of catch-all, measuring all the various materials in the wastewater that are in true solution. Our major concern with dissolved solids in cooling water is that they contribute to increased corrosivity as the level increases.

In order to minimize the amount of dissolved solids in a treated wastewater, the treatment process should be carefully reviewed for opportunities to reduce, or eliminate, input of reagents that increase the dissolved solids in the effluent. One example of such a change would be replacement of a coagulant, like ferric chloride, with polyaluminum chloride. For equivalent performing dosages, the polyaluminum chloride adds substantially less chloride ion that the ferric chloride. Decreased levels, and sometimes total replacement, of inorganic coagulants can be obtained with use of the newer organic coagulants, either alone or as components of blends with inorganic coagulants. Such replacement can substantially reduce the dissolved solids remaining in the treated wastewater.

When treated wastewaters are used as cooling tower makeups, or cooling towers are operated in zero discharge mode, the water treatment program designer faces a **paradigm shift** in thinking concerning acceptable levels of dissolved solids in cooling water. In general, many designers hesitate to allow the dissolved solids in any cooling tower system to exceed 5000 mg/l, with much lower limits in common use. We have found that operation of cooling towers at dissolved solids levels of 50,000+ mg/l to present no problems that cannot be addressed by proper selection of corrosion, scale, and deposition inhibitors.

K. Suspended Solids: Introduction of suspended solids into any cooling tower, operating with fresh or reuse makeup, will increase the potential for deposition. The best solution to this problem is to simply stop the suspended solids before they enter the cooling tower system. Both fresh and reuse makeup waters should be filtered, if needed, to remove as much suspended solids from the water as possible. A good guideline for installation of makeup filtration is to consider it any time the suspended solids level in the makeup exceeds 5 mg/l. The wastewater treatment process can usually be profitably reviewed as to reducing the suspended solids content of the effluent. Particular attention should be given to the coagulants and flocculants in use. Many systems designed in the past, using archaic chemistry such as ferric chloride and calcium hydroxide, produce a high level of effluent suspended solids, which while perfectly acceptable for sewer discharge, is too high for reuse. We have found that application of modern organic polymers as coagulants, coagulant aids, and flocculants, can substantially decrease effluent suspended solids.

While the wastewater system is being looked at, the mixdown procedures, specific application points, and mixing of the various coagulants and flocculants into the wastewater stream should also be studied. In many cases, substantial performance improvements, and chemical cost reductions, can be obtained simply by moving an injection point or changing a mixer speed.

Equipment, such as sand and multi-media pressure filters, cartridge media, cross flow microfilters, and hydrocyclones have been employed as both polishing units at the end of the treatment process, and as bypass filters on the cooling tower system. Our company recommends installation of bypass filtration on all cooling systems operated at high cycles or with treated wastewater as makeup.

#### Process Case Histories

As promised at the beginning of this paper, we are now going to visit two successful instances of wastewater treatment and reuse back to the generating process.

#### Case History #1

Process: In the manufacture of incandescent electric lamps, colored lamps are produced by coating the exterior of the glass bulb with a fired colored ceramic glaze. These glazes are commonly applied as a liquid and due to the process, a liquid wastewater is produced. Since the ceramic glaze contains substantial amounts of lead, as a flux, and various other heavy metals, as colorants, the wastewater must be treated prior to discharge.

By careful selection of the coagulant and flocculant chemistry to minimize dissolved solids buildup, and installation of polishing cartridge filters, the treated wastewater has been totally reused in the above process since 1990. A special concern for reuse has been control of cadmium buildup in the reused water due to health and safety considerations.

#### Case History #2

Process: In the manufacture of seals for pumps and jet engines from various carbons and silicon carbide, the wet finish grinding process produces an intensely black wastewater containing many submicron size particles. As the surface finish is critical to production of acceptable parts, water for reuse has to comply with strict standards as to suspended solids content.

An innovative inclined plate clarifier was designed to operate with an all organic coagulant/flocculant chemistry to treat this process wastewater. Operating at a flow rate of 160 gpm, this treatment process has consistently produced an effluent with a turbidity below 0.5 ntu without use of any final filtration. This treated wastewater has been totally reused back to the finish grinding process since 1993. A special consideration in this reuse application has been control of biological growth within the recycle loop.

### Biography

Eugene Wei, District Manager, ProChemTech, B.Sc. and M.Sc. in Chemistry, former Far Eastern Manager, Dionex, and District Manager, Wright Chemical.

Timothy Keister, President, ProChemTech, B.Sc. in Ceramic Science, former Section Head, Water/Wastewater Control, Brockway Glass Company, Fellow, American Institute of Chemists.

This presentation is an adoption of one first given at the Association of Water Technologies, Spring Conference, Philadelphia, April 1994.

#### ProChemTech International

The company is a unique business that combines manufacture and application of chemical products for treatment of boiler, cooling, and waste waters with design, engineering, and manufacture of cooling and wastewater treatment systems. For potential reuse applications, the company is considered to be a "one stop" source as it combines all the areas of needed expertise in one integrated organization.