

**Fundamental's of Cooling Water Treatment
Annual Conference 2000
Panel Discussion**

Mike Trulear, ChemTreat, Inc. – Our educational panel discussion today concerns Fundamental's of Cooling Water Treatment. We have put this seminar together both for the experience water treater and for the non-water treatment contingent at CTI. You can look at this as Cooling Water Fundamentals 101. We have four excellent speakers who will cover different aspects of cooling water treatment.

They are Gary Geiger of BetzDearborn Inc., Tony Dallmier of Nalco Chemical Company, Ted Beardwood of Ashland/Drew, and Pete Zisson of Buckman Laboratories. Each will give a 20-minute prepared presentation on one aspect of cooling water treatment and then will address any questions that can be directed to the panel.

There are basically four different problems that we as water treaters try to prevent or minimize in a cooling water system. They are scale, corrosion of base metals, general fouling, and microbiological growth. Any well designed cooling water treatment program is designed to prevent these processes from occurring. Each presenter will give a prepared presentation on one aspect of cooling water control and treatment.

Our first speaker will be Gary Geiger. Gary will be talking about scale control and scale inhibition in cooling systems. Gary is the Cooling Water Technology Manager for BetzDearborn's North American Water Management Division. He has been with BetzDearborn for 26 years. His experience includes 16 years in the Research and Development Department as a Senior Research Scientist in the Cooling Water Group and as a manager of the General Process Group. Gary has developed many cooling water treatment programs and deposit control treatment for the process and refining industries. Gary holds a BS degree in chemistry from Temple University and has 11 U.S. and 14 foreign patents. Gary is a member of the National Association of Corrosion Engineers, The American Chemical Society and The Cooling Technology Institute.

Gary Geiger, Betz/Dearborn – As Mike indicated I am going to cover the area of scale and scale control. Before we begin I am going have a very basic discussion of cooling towers and their operation that will set the stage for the rest of the topics today.

The primary purpose of a cooling tower is to remove heat. It accomplishes this though the evaporation of water. Since water is constantly recycled in a cooling tower, water conservation is also achieved. The amount of water leaving the tower is very small and easily treated in most industrial waste plants or in municipalities, thus, reducing the impact of pollutants on the environment. The only product of a cooling tower, what it is producing, is very simple but is the heart of the industry – cold water. The cold water is circulated to the system where process heat is transferred to the water, which then returns to the top of the tower. The water is distributed across the tower and comes down through the fill while air is coming counter-current to the water. Evaporation occurs and pure water vapor leaves the top of the tower. The water vapor may contain some entrained cooling water droplet, which is known as drift. If the tower is well designed and maintained drift will be very small. Since evaporation occurs this water must be replaced with fresh water, which comes into the system to make up for what has evaporated. It is a good system, a simple system that works very well.

Problems arise when water enters these systems. With the make-up water, ions dissolved in the water enter the system. These minerals are in both surface water and ground (well) water. As water evaporates, the minerals concentrate. This cannot continue indefinitely since precipitation of the minerals will occur. Some water has to be removed to control this concentration effect in the system. This is called blowdown, which is a purge from the system. This allows the control of the ion concentration in the cooling water so that the chemistry of the system can be controlled. The number of times the various ions concentrate in the system is called cycles of concentration.

Blowdown is something that is physically removed from the system. It is an important function in controlling cycles but it is also responsible for the chemical cost. When a system is being treated, the only way chemicals are leaving the system is through blowdown. That is what you are paying for in chemical costs.

Make-up to a system is a combination of the evaporative losses and what is being removed by blowdown. Blowdown is that portion of the cooling tower water that is being removed voluntarily and also involuntarily. Involuntary losses may be drift, windage from the tower, or leaks in the system. So make-up is a combination of blowdown and evaporative losses.

That brings us to cycles of concentration. A cycle of concentration is a term that provides an estimate of the concentration of the minerals in the water. There are two ways to calculate this. You can do a hydraulic calculation, simply a ratio of the make-up to the blowdown. If you have a 100-gpm make-up and the blowdown 10 gpm, the cycles of concentration are 10. This is not always that accurate unless the makeup and blowdown rates are measured precisely. A second way is with chemical cycles. Chemical cycles are measured by monitoring the concentration of a specific ion. Take for instance chloride, which isn't good but one we can all relate to. In the cooling water you have a hundred parts per million of chloride, the make-up water contains 10, there are 10 cycles of concentration.

Cycles can be calculated by the ratio of make-up to blowdown or by ion balance. The important thing to remember is that by increasing cycles blowdown is reduced. Actually it should be the other way around. When blowdown is reduced cycles increase. Higher cycles lower chemical usage. That has a direct impact on your overall water treatment cost.

What is happening in a cooling tower? Dissolved solids concentrate. The conductivity of the water is going up and ions, such as chloride and sulfate, are increasing the corrosivity of the water, making it more aggressive to many of the alloys that are used in a cooling system. It also increases the deposition tendency. These ions are concentrating, they are starting to supersaturate, and the dissolved ions want to come out of solution and precipitate. If there is any particulate matter entering the cooling system or any solids scrubbed out of the air, they will concentrate in the system. The only way these solids are removed from the system is through blowdown. When blowdown is reduced the ability to remove contaminants is reduced. Finally, a cooling tower is an excellent place for microbial growth. A cooling tower has all the nutrients it needs and a nice warm environment, making one of our other concerns biological control.

To successfully treat a cooling water system three areas must be treated: corrosion, deposition, and microbiological control. You can't just treat for two really well and forget about the other. All three must be addressed simultaneously.

With regard to scale or deposit control, there are two mechanisms – scaling and fouling. This section will cover the scaling portion of it. Scaling is really minerals coming out of solution and forming a deposit on the surface. Fouling is a result of insoluble materials that is in the bulk circulating water i.e., clays, silts, iron oxide corrosion products, process leaks, heavy organics or even microbial matter.

Mineral scales form when solubility is exceeded. The cooling tower cycles up, minerals and suspended solids in the water concentrate and some of the mineral solubilities are exceeded and those minerals want to precipitate. The mechanism for scaling is very simple. Minerals are brought in with the water unless the water is pretreated to remove minerals. As those minerals start to concentrate they become super saturated. They exceeded their solubility and want to do something. Mother Nature wants to take over here and get back to some kind of steady state. So the mineral wants to come out of the solution or precipitate. That initial phase of precipitation is called nucleation. It is when crystals first start to form in to small microcrystalites – they are not very stable. They can form a well-formed crystal or they can go back into solution and another crystal could form. Once they form the crystal starts to grow and there is crystal growth. Once that occurs, and if it occurs at a metal surface, the crystal will grow and a scale deposit will form at the metal surface.

You can conceptualize this process easily. Put a beaker of cold water on a hot plate, turn on the heat, and let the water evaporate. Pure water is leaving as steam and the dissolved solids start to concentrate and finally precipitate. For the most part the water coming in to the cooling tower is stable. It has a lot of dissolved ions in it, cations, anions, mostly calcium, magnesium, some carbonate, dissolved CO₂, chloride, sulfate, and silica are very common. Stable water doesn't want to deposit. But if half the water is evaporated, the solids start to concentrate. That is like two cycles of concentration in the cooling tower. Continue that evaporative process, reducing the volume again by a half and that is four cycles of concentration. Now the water is starting to get pretty saturated with all of these different minerals and that is only four cycles of concentration. There are industrial cooling water systems that are operating at five or six cycles, some of them much higher – 7 to 10, 15 to 20 cycles. If you can imagine a graduate cylinder with a 100 milliliters of water, evaporating that water down to just 10 milliliters that is equivalent to 10 cycles and the water is now very concentrated with minerals. What wants to happen now is that these insoluble materials want to come out of the solution.

We define scale as an insoluble deposit that forms on a surface by the precipitation of the soluble species from the cooling water. Probably the most common scale is calcium carbonate. Calcium sulfate may be seen in some West Texas waters. Calcium phosphate is common because inorganic phosphate is used as a mild steel corrosion inhibitor, probably the number one inhibitor used today for steel protection. When a system operates in an alkaline pH range, magnesium silicate may become a problem. There is aluminum silicate or zinc phosphate from a corrosion control program, iron phosphates, calcium magnesium silicates, a lot of different scales all forming under different conditions of pH, conductivity, and temperature.

Actually we are dealing with solubility and what affects the scaling potential. The two biggest factors that effect scale and scale formation are temperature and pH. The higher the cycles, the higher the super saturation, so there is more potential for scale to form.

Velocity also has a big effect on deposition in process equipment. If scale wants to form it has to crystallize and then adhere to a surface. The higher the velocity the more sheer stress is placed on that deposit and in some cases; deposition can be eliminated by high velocity. Low velocities, of course, are detrimental and that is where most of our scaling problems occur.

In addition to solid seeding materials, clays, particulates scrubbed from the atmosphere by the cooling tower, can serve as nucleation sites for scale to form and cause scaling in the equipment.

System holding time is an important parameter. This goes right along with cycles. As cycles increase blowdown is reduced. That means the water is spending more and more time in the cooling system. So as the cycles go up holding time goes up and scaling potential increases.

Most of the materials dealt with have what is called inverse or retrograde solubility. As temperature increases, solubility decreases. With most minerals, for example sodium chloride, as the temperature increases the solubility increases and the amount of solids that can be maintained in solution increases. Inverse solubility is just the opposite. As the temperature increases the material's solubility decreases. What does this mean? A cooling water could be relatively stable. It may at be saturation or maybe slightly super saturated, there is a good deposit control agent in the water, and everything is alright. The water then passes by a heat transfer surface, the temperature increases, the water becomes supersaturated, and deposition occurs. This is not what you want. The heat exchanger removes process heat and mineral deposits interfere with that process.

Another factor is pH. The solubility of calcium carbonate, calcium phosphate, iron phosphate, and zinc salts decrease as pH increases. Today the trend is more toward alkaline pH operation. Operating above pH 8, acid feed can be reduced or eliminated. The trend has been upward in pH and is taking us into the area where scales are becoming more difficult to control and prevent.

Then why is scale a concern? Scale is a concern because it reduces heat transfer efficiency. It can force the shut down of a unit, requiring pulling a bundle, and cause a loss of production while the bundle is cleaned. Scale also restricts water flow and promotes under deposit corrosion.

Finally, scale does affect the cooling tower. High efficiency film fills are susceptible to deposition, scale being one of them. Scaling in film fill has been documented many times. In these cases, the cooling tower no longer performs its job of removing heat from the water, resulting in a significant loss of efficiency.

There are some pretty easy methods of controlling scale: increasing velocities through process equipment are a positive step and equipment redesign to operate at the lowest possible temperature to minimize scale formation. You could also just resign to accept the scaling and periodically acid clean or mechanically clean the equipment. You could

operate at low cycles. Stay below the supersaturating point as much as possible. You'll pay a penalty in water use and for the corrosion inhibitor, but it is a way of controlling scale. The makeup water could be pretreated, putting it through an RO or use a demin system. Using pure water will eliminate the scale potential, but it will cost a lot of money and a corrosion inhibitor is still required, so it isn't an option seen exercised very frequently.

Chemically, you can soften the water. This is frequently done often on the Gulf Coast. Cold lime softening removes some of the hardness ions that cause calcium scaling problems. For cooling systems operating at pH 8 or below, it will help to minimize scaling problems from calcium carbonate and some silicates.

Chemical agents such as sequestering agents or threshold inhibitors can also be used. This is by far the method of choice to control scale and deposition formation in industry today. A sequestering agent is a material that actually bonds with a cation and forms a soluble complex. The complex is not reactive so it won't form a scale or precipitate with a counter anion. The problem with sequestering agents is they require stoichiometric quantities. So many parts of calcium require so many parts of your sequestering agent, so with increased cycles chemical feeds must also increase, and it becomes a very cost ineffective way to control deposition. In some cases when you are dealing with low levels of iron or manganese, some of the rarer metals seen in make-up water, sequestering agents can be used to tie them up so they won't deposit.

Threshold inhibitors interfere with crystal formation. They distort the crystal, making it unstable. In some cases it may go back into solution. If it does not go back into solution it goes on to continue to crystallize. The crystals are not well formed; the crystal lattice isn't very strong and the crystals are friable. The deposits that they produce are very fragile and in many cases will be removed by a mechanical action of the water.

To give you an example of these materials, I think it was mentioned today, HEDP. There are a number of phosphonate materials; HEDP is probably the most widely used based on quantity. I know there are those who use other things but based on quantity in the US and probably in the world it is probably the number one inhibitor for calcium carbonate today. It is a very basic material. It is a phosphonate due to the PO₃ to carbon bond. It is used primarily for calcium carbonate and also has mild steel corrosion inhibition properties, and in certain situations it isn't bad for iron and manganese chelation.

Prior to the 1980's, the number one polymer used in cooling water was polyacrylic acid. If you polymerize acrylic acid, just make a chain of them and you have polyacrylic acid. It is a very effective dispersant for particulate matter and not a bad calcium carbonate inhibitor for its time, but not a very good calcium phosphate inhibitor. As time went on, polymers evolved and development of co-polymers began. One of these copolymers is a combination of acrylic acid and AMPS (an amino methyl propyl sulfonic acid) which is much different than polyacrylic acid. It was found that if AMPS was co-polymerized with acrylic acid the result was a polymer that was not only good for calcium carbonate but was an excellent calcium phosphate inhibitor. This was one of the first materials developed for inhibition of calcium phosphate deposits. Ter-polymers followed with quad-polymers not far behind. These have three and four monomers respectively. The functional groups as well as the ratio of the groups in the polymers and the molecular weight of the final material determine the properties of the polymer.

This brings us back to where we started. If you want to be successful or have a successful program and minimize your problems you have to address all three of the primary concerns. Scale control is but one of the concerns.

Trulear – Thank you very much Gary. You did an excellent job. As Gary went through the presentation it did bring many questions to mind. Think about, for instance, increased cycles of concentration. What does that do to holding time index in a cooling system when one of the ingredients that were talked about has to maintain things in solution for three days at may be three cycles of concentration and you take it to eight cycles? Holding time index may increase to 10 to 11 days. The ingredient has a much greater stress put on it. There are several questions that could be asked about that. How do you monitor these inhibitors? How do you make sure that they are in solution at the proper level you need to perform the function they were designed to perform?

If you look at the treatment triangle the box on the top is corrosion control and that is the topic for our next presenter, Pete Zisson from Buckman Laboratories. Pete is an industry specialist in the industrial water treatment group. He earned his BS degree in chemistry at Columbia University in 1975. Peter started his water treatment career shortly thereafter. For the last 15 years he has coordinated global water treatment for Buckman Laboratories.

Peter Zisson, Buckman Laboratories - Thank you Mike. I am going to review the problems associated with corrosion and what can be done to minimize corrosion. In general in industrial operations there are two metals that are of primary concern. They are steel and copper alloys. These are the most widely used components and most susceptible to corrosion. I am going to restrict my discussions to those materials. If you have questions about any exotic metallurgy they can addressed during the question and answer period.

There are many problems associated with corrosion and sometimes we don't think about many of them. There is premature equipment failure. Plants are expensive and need to be maintained. Downtime, loss of production, hazardous conditions – we saw a case of corrosion of wood in a cooling tower this morning that could have killed someone as the tower collapsed. This is true in a lot of cases with plants and with a lot of things we don't think about. Buried natural gas pipelines need to be protected from corrosion. If they explode they explode rather explosively! Most of all, corrosion costs money.

In 1989 it was estimated that corrosion cost to the industry was \$33 billion in the United States alone. A new cost of corrosion study is currently underway at NACE International. They are looking at everything from the cost of the corrosion of cooling systems to the cost of corrosion of reinforcing steel in roadways. It is an extremely costly problem and the more we can do to control it the better off our industries will be financially.

Corrosion is the deterioration of a metal due to its interaction with the environment. It is the result of some kind of difference on the metal surface and we will look at the differences that can occur, the different things that can initiate corrosion. We have to look at the basic corrosion cell. Corrosion is an electro-chemical phenomenon, in all cases be it microbiological, under deposit or any of the other factors can initiate it. It is

always an electro-chemical process. When we understand that process we can understand the mechanisms to inhibit that process.

Typically there are two types of corrosions seen in industrial settings. There is general or uniform corrosion, general wear of a pipeline; or second, there is localized corrosion often called pitting. Localized corrosion is the larger of the two because it can result in equipment failure at a much more rapid rate. Uniform corrosion on a heavy walled steel pipe at a rate of 5 mils per year may take 40 years before there is through wall penetration but under the right circumstances with pitting corrosion that pipe can perforate in a year.

I would like to spend a few minutes on the basic corrosion cell model. On a metal tube, there may be one area that is different than the rest of the tube. It could be just the microstructure of the metal itself, it could be a little bit of deposit, it could be a bacterium, but there is something different about that spot on the metal from the remainder of the metal. That difference is what keys off on corrosion and that is why deposit control/microbiological control from the triangle is so important.

Because of the presence of oxygen in the water there is a depolarization at the primary area and it demands electrons. The metal that is slightly different gives up electrons, which then creates hydroxyl ions by reacting with oxygen in the water. If the metal is steel, iron becomes soluble, leaves the metal surface, and goes into the water. As this proceeds there is a build up of iron oxide, a higher hydroxide is formed because of the hydroxyl ions, which are being made, and it is a self-accelerating system. The iron hydroxide creates additional deposits, which initiates more iron cells. It can also create fouling in other parts of the system, in fill, and in other areas of the cooling system.

The area where the iron dissolves is the anode and the area where the hydroxyl forms and the electrons exit into the water is the cathode. There are several ways we can inhibit the corrosion but in the case of water treatment the two principal ways are to use anodic or cathodic inhibitors. As their name implies an anodic inhibitor stops the reaction at the anode while a cathodic inhibitor stops the reaction at the cathode. A film forming material could also be used; if the water can't touch the steel there can be no corrosion. The problem is getting a film former that is uniform, has no holidays, is rugged, and works well.

In the case of stainless steel that film is actually a complex metal oxide film that forms on the surface due to minor corrosion. That is a dense film that is very corrosion resistant and prevents the continuation of the corrosion. This gives a clue in how we can anodically inhibit. Does everybody remember the days of chromate? There are probably a few who are young enough that wouldn't. Think about chromate and today we also use molybdate. When you look at austenitic steels what are the alloys added to the iron? The alloys are chromium and molybdenum. When the stainless steel forms that oxide it is a complex molybdenum chromium oxide forming on the surface. If we put those components in the water the same type of thing will happen. Those are anodic inhibitors.

TABLE 1

Corrosion Inhibitors	
Calcium	Nitrite

Orthophosphate	Azoles
Zinc	Silicate
Phosphonates	
Molybdate	
Polyphosphate	

Table 1 is a complete collection of inhibitors both anodic and cathodic. All of these types of products are used based on the specific application. Chromate is not included because environmental regulations. All of these materials will inhibit corrosion. Calcium carbonate is a cathodic inhibitor. Remember I talked about the formation of hydroxyl ions at the cathode and we know that calcium is inversely soluble with respect to pH. As the pH rises calcium is less soluble. So when there is a corrosion cell as the pH rises at the cathode a film of calcium carbonate is formed. It inhibits the flow of electrons and stops the corrosion cell. Once the corrosion cell stops, the pH drops back to the normal water pH and the calcium carbonate dissolves. This is an ideal situation if the conditions are right. Although we don't talk about it much as water treaters it is a significant inhibitor in the types of systems we operate today. It is not normally thought of as an inhibitor, but it really does make a big difference. If you look at some of the work that has been done on corrosivity of water as opposed to using a saturation index for calcium carbonate to simulate corrosivity of water you will find that one of the biggest factors as far as how corrosive is how much oxygen is in the water and one of the most significant factors of how less corrosive is by the amount of calcium in the water.

Now poly and ortho-phosphates also act as cathodic inhibitors. They form complexes with calcium at the cathode again as a result of the elevated pH. It is important when you are using phosphates to use some of the more exotic polymers that have been developed because you don't want that calcium phosphate to stay there. Once the corrosion has ceased you want that to dissolve in to the bulk water.

Orthophosphate also acts at the anode to form a complex in a similar manner of molybdates and chromates. The only reason orthophosphate isn't used as a component of stainless steel is because it makes it very brittle. Therefore it has to be excluded from the metal itself for structural rigidity purposes. From corrosion standpoint, allowing phosphate into steel systems improves corrosion resistance. Typically 2 –20 ppm are used depending on the type of program used and the water chemistry conditions.

Phosphonates used as calcium carbonate scale control agents also act as corrosion inhibitors at proper dosage levels. Again, they are forming calcium complexes at the cathode. In order for them to work calcium must be present in the water. Cathodic inhibitors that rely on calcium do not work in soft water because they need the calcium to form a complex.

There is a little bit of reaction but not significant at the anode and typically with a phosphonate like HEDP it is necessary to have about 6-10 ppm active, more than you would normally use for calcium carbonate inhibition, in order to have sufficient amount to be a good corrosion inhibitor. Effectiveness is going to vary depending on the hardness of the water, the pH of the system and the amount of iron in the circulating water.

Zinc is traditionally one of the most popular cathodic inhibitors. Zinc doesn't rely on calcium concentration so it can be used in soft water. Zinc forms a hydroxide, zinc hydroxide precipitant at the cathode as a direct result of the hydroxyl ions formed by the corrosion cell. The problem is that when the pH gets to about 8.3 the solubility of zinc is almost zero because at 8.3 free hydroxyl ions can exist in the bulk water. So you have to be very careful. In programs that operate at higher pHs there are zinc-stabilizing polymers just as there are phosphate-stabilizing polymers that allow the use of zinc. Depending on the pH of the system, anywhere from 0.25 ppm to 3 ppm of zinc might be used in the system.

One of the things to look at is a pH buffer. If we maintain the pH at a higher level, all of the anions are going to be acting to help, as cathodic inhibitors, all of the cations in the water. You can also use buffers such as borax (not used typically in cooling towers but is done in closed systems) to raise the pH up to the range of 9.5 – 10.0, which is the least corrosive condition for carbon steel.

Nitrite is another inhibitor typically not used in cooling towers because high concentrations are required, which becomes expensive when you have blowdown. It is also an excellent nutrient for microbiological activity, something to be avoided in the cooling towers. It is often used in closed systems to control corrosion where makeup is low. Typically at 500 – 1000 ppm you have to watch out for microbiological activity. It also provides an oxidative potential to help molybdate work on systems that don't have a lot of oxygen in them, it's an anodic inhibitor that works with the corrosion products at the surface.

Molybdate does not act the way chromate does. Chromate is a self-oxidizing inhibitor. Molybdate requires an oxidative potential. It is much more like orthophosphate in that manner but it is complexing at the anode just like phosphate and chromate. Sometimes if there are corrosion products on the surface it has some ability to penetrate through the porous deposit to get to the bare metal and help inhibit corrosion.

In closed water systems it is not necessary to make up a significant amount of water so it is possible to use high concentrations of corrosion inhibitors. In addition, with the low makeup water the ion buildup found in cooling tower water does not become a factor in closed systems.

Aromatic azols are organic chemicals that are used as corrosion inhibitors on copper alloys. They are a film forming inhibitor that reacts with cupric oxide to form a surface film. You have to be careful with oxidizing biocides because they can attack the film and cause additional corrosion. Remember, whenever there is a break in the film that area becomes cathodic and the rest of the area becomes anodic and a new corrosion cell is created.

So oxidation is used to create anodic inhibition and use chemicals for film strengthening.

We use cathodic precipitants and other things not typically used in cooling tower systems but are used in other areas for corrosion inhibition. For example, instead of allowing the iron to supply the electrons we can inject the electrons by setting up a current (cathodic protection). Cathodic protection is used to protect underground pipeline from corrosion. We can also attach a metal, like magnesium, to a steel surface so that the magnesium becomes the anode allowing the steel to remain cathodic. That

is called a sacrificial anode. It is anticipated the magnesium will dissolve over time. It has to be replaced from time to time, but it does protect the steel equipment.

Trulear – After these first two presentations, it's easy to understand why the process of water treatment becomes complex. Now there is an additional factor to include in the overall equation of water treatment. The next presentation is on "Generalized Fouling". Both Gary commented on fouling as did Peter in their presentations. Ted Beardwood from Ashland/Drew is going to bring it home and give more detail on generalized fouling. Ted is Technical Director for Drew Canada a division of Ashland Chemical. He is a member of the National Association of Corrosion Engineers, The American Society of Mechanical Engineers and a member of the Refrigeration Service Engineer Society. Ted has over 23 years experience and involvement in water treatment conditioning.

Ted Beardwood, Ashland/Drew - Thank you Michael. As we have heard from the other speakers, they have mentioned fouling in passing. I'm going to discuss things that lay down in the system that reduce the operational efficiency of the system. Also I will review some mechanical aspects, operational aspects and chemical aspects to look at the balancing of those. By the time we are done, unless we are dealing with composite material, any form of fouling eventually brings you full circle back to corrosion. You can always clean out foulants but you cannot turn around and put metal back on to the system surfaces. The underlying message here is corrosion.

The process itself starts out with some form of reaction in the bulk fluid. This may be some ion, which are driven to form a precipitate, something that was leaked into the system from a heat exchanger, or something that was scrubbed out of the air. In any case it leads to some form of reaction that may have nothing to do with pH or temperature. At this point in time there is a mechanism that transports it to the heat exchange surface itself. The attachment or formation of the deposit on heat transfer surface then occurs. What I mean by "formation" is mass transfer driven, sending suspended solids to the surface.

This is a dynamic operation. Materials lie down and come off of heat transfer surfaces continuously. There can be dissolution, erosion where the velocity itself re-entrains smaller particles, spalling or sluffage of large masses that are fractured if there is a fair amount of heat input. These areas are related to velocity, shear stress, or roughness factors of the metallurgy you are dealing with and the turbulence of the water.

Transport and removal of this material to the bulk water will occur. Again, it is a dynamic process; something laying down and pulling back into the water again. There can also be post fouling, meaning the material redeposit down stream in another heat exchanger, the cooling tower sump, the cooling tower deck, or even the fill can be laden with this debris. You want to take a look at whether or not you are generating suspended solids within the system or are they from the makeup water. This can be combated either one of the non-chemical or chemical approaches or both.

Forms of fouling can be generated by precipitation or crystallization, or particulate such as mud and silts, even impurities washed out of the air. Organic fouling may come from ground water, surface water, process leaks or from the intake air.

There can be corrosion fouling, where the corrosion products form a tubercle that increases the roughness factor on the heat exchanger surface, which momentarily gives

you improved heat transfer and then eventually acts as nucleation sites for the crystallization precipitation and entrapment of other fouling suspended solids.

There is combined fouling whereby biofouling results indirectly in corrosion. This then causes entrapment of inorganic debris and eventually leads to under deposit corrosion due to the apparent porosity of that deposit.

Microbiologically induced corrosion (MIC) or biofouling itself can then also entrap inorganic debris. This debris sets up under deposit corrosion cells. The deposit then reduces the ability of the corrosion inhibitor to get to the surface and the oxygen tension is changed at the surface. Oxygen tension in open cooling water systems is a friend. It is used to produce the gamma iron oxide protective film below the capping layer of inhibitors. Pitting can result in, insitu corrosion product production which then leads to under deposit corrosion and the list goes on. The bottom line with fouling is that the outcome will be under deposit corrosion; only the pathways are different.

There are several factors that effect fouling. The deposition probability of a particular foulant, which is tied to the velocity, the stickiness of the deposit, the water quality itself, the inorganics in that water and their solubility, organic materials that can absorb onto the surface, biological, pH and carbonate alkalinity rather than total alkalinity.

It should also be noted that the higher the surface temperature, that is approaching boiling conditions, and high flow rates, which are by the way your friend, will generate thermophoretic conditions which drives the deposits away from the heat transfer surface. Heat exchanger residence time is very important. You heard mentioned about the holding time index in the system, well there is also a holding time index for the heat exchanger. You start looking at numbers greater than 10-15 seconds hold up time at high temperatures you are into potential fouling conditions.

Low velocity on plate and frame heat exchangers of 4 ft. per second or 2 ft. per second on shell and tube lead to large asymptotic fouling occurring as the temperature goes up. So there are tricks that can be played with the heat exchanger not just from the standpoint of what it was designed for but where it operates to minimize fouling. Increasing the velocity will reduce the fouling capability with little regard to the skin temperature that is occurring within. Then there is deposit strength and the ability to remove it at these higher shear stresses that occur at higher velocities.

Metallurgy of the surface materials also plays an important part. We are talking about the charge on a surface. When Teflonⁱ first came out and the joke at the time was, "if nothing sticks to Teflon then how does Teflon stick to the metal." Actually, I don't know, but the bottom line is, it has the lowest surface charge, therefore it does not foul as easy and that number is above 20 ugrs/per square centimeter. Whereby stainless steel has 1800 ugrs/per square centimeter and titanium is 1300. So you are looking at a very broad band of surface charge in use and this is why anti-foulant coatings are sometimes used. Surface roughness also plays a part. Obviously carbon steel itself will foul easier than copper based materials and as mentioned earlier insitu corrosion products increase fouling due to increases in inherent roughness.

Foulants may enter a system from the make-up water and these materials can be inorganic impurities, organic impurities, suspended solids and macro and microbiological in nature. Foulants may also enter with the air, things such as acid rain, organic matter

being washed out of the air, sulfur, carbon, and nitrogen oxides. Of those last three sulfur itself may lead to a calcium sulfate fouling problem; the other three are nutrient sources to derive another foulant that will be spoken of in the next presentation. Dust and dirt, with or without absorbed microorganisms or spores is another problem. Vegetation and plant derived issues can happen whether you are dealing with pollen etc. and everything else entrapped tends to block and reduce heat transfer and reduce airflow and water flow. Insects and other wildlife create problems. Life cycle wastes derived from seagulls and birds in cooling towers not only create a problem with the biological fouling control of the cooling water but you should see what it does to membrane roofs. Life cycle wastes derived from rats are not uncommon. We've seen the microorganisms derived from the stomach of a rat that created some biological control problems within a system!

Foulants can come from process leaks. They may be reactive, whereby you end up actually polymerizing, or at the lower temperature of the cooling water leading to solidification when it gets into your cooling system. Inorganics as mentioned earlier will lead to the foulants; attachment of those precipitated crystalline structures. Suspended solids can come from the process side. It isn't uncommon to have some severe corrosion in the mining industry from Nash vacuum systems by not maintaining 25 psig on the screw seal on the compressor. This can lead to process side materials and slurries entering the cooling water, producing galvanic corrosion or under deposit corrosion.

Now that we have a bit of a picture of the debris that deposits within the system, now let's look at what caused the problem. Let's say you have a fouling problem. Typically people extract deposits. Deposits should tell the story, but all of those inorganic precipitates that are seen in the beginning, can be found on a non-heat transfer surface incorporated in your corrosion inhibitory film. Basically, a differential deposit analysis is required. That includes looking at the percent moisture and correcting the percent moisture. An example might be; 90% water moisture content, 7.5% iron. If the water is removed from the equation, there was actually 75% iron in the deposit analysis although it truly is only 7.5% of the deposit. That provides some ideas of where these deposits are from or what causes them. A high percentage moisture and high loss of ignition after you correct for the Freonⁱⁱ or hexane extractable are typically derived from microbiological activities where hexane extractable (oils and greases) are agglomerates that come from inleakage into the system. The highest percentage component in the deposit itself is probably one of the major indicators of what created the fouling problem. Now why would you want to know that? I am going to "generically" talk about some of the additives that prevent foulants from forming.

As far as hardness salts, phosphates, carbonates and sulfates are concerned, this is an inorganic deposit control issue, which has been discussed earlier or from make-up carry over from a pretreatment system, such as a cold lime softener. The latter comes back to filtration or getting control of the softener. Silica or silicates may deposit. Sometimes the type of silica deposit can determine the source. If it comes from the water itself it will tend to be a hard crystalline or an amorphous deposit versus a muck, which may in fact be sodium/magnesium aluminosilicate which is derived from sands and clays being washed out of the air. Iron and copper could be from corrosion within the system. Aluminum, iron, and manganese are typically from the pretreatment or pretreatment carry over.

	-itant			Repulsion	Sticking Agent	foulants	
Polyphosphate	✓	✓	(✓)				
Phosphonates	✓	✓	(✓)				
Surfactants							
Nonionic					✓	✓	
Anionic			(✓)	✓	✓	✓	
Cationic					✓		
Polymers							
• Homo, Co, Ter, Quadra							
Anionic							
- carboxylated							
- sulfonated							
- phosphonated							
Nonionic							
• Molecular Weights							
1,000-2,000	✓	✓	(✓)				
2,000-10,000	✓	✓	(✓)	✓		(✓)	
10,000-70,000		✓	(✓)	✓		✓	
>1,000,000						✓	
Blends							

Table 2 is a generic list of additives. Listed on the left hand side are the types of additive; across the top are their functional performance characteristics. When we look at something like a polyphosphate you can see that it is classified as good anti-precipitant, a crystal modifier and does provide inorganic antifouling. Of interest is when you take a look at surfactants and what the surfactants have to offer that can give you some performance that typically you normally have not used in the past. We are dealing with, mechanistically, heat exchanger surface charge repulsion, the ability to wet surfaces including cooling tower fill and how the material enhances the removal of suspended solids and reduces organic biological fouling.

There are a variety of polymers that vary in molecular weight and functional groups. What I've done is listed where the functional performance are applicable. When you start dealing with anodic polymers with over a million molecular weight used to disperse suspended solids or silt, you have to treat this at very low residuals unless you wish to increase fouling. When you look at the numbers for molecular weight, 1000-2000 molecular weight, it is around 2000 where dispersency really starts to kick in. That is why that one check mark is blocked out. It can act as both a dispersant and anti-precipitant/crystal modifier in that area, but as you go down towards a molecular weight of 1000 you are dealing more with an anti-precipitant and crystal modifier.

There are a number of mechanical methods that can be used to reduce fouling by removing the foulants from the system. These include: down flow or up flow filtration and centrifugal down flow, which has been in the marketplace now probably about 5

years. The centrifugal units use half as much backwash water and you don't have to backwash as frequently as other filtration methods.

In some filtration cases, cationic polymer may be added to enhance the filtration rate. Filtration will decrease the fouling potential within the system if there are suspended solids in the system. You heard someone talk about holding time index, you can form the precipitate but not form scale in the heat exchanger. As the colloidal precipitate in the water makes a number of passes through the heat exchanger, it will agglomerate increasing mass, over time. These suspended solids will build over time unless there is have a sufficient amount of dispersant in the water. Filters can remove suspended solids but are less effective on the untreated colloidal precipitates.

Another mechanical method to investigate is on-line mechanical and physical methods for prevention of fouling. Circulation of sponge rubber balls is one method, cage and brush flow reversal systems can also be used. You usually do these on systems that are running once through cooling water and devoid of a cooling tower. Reverse flow can be done to backwash a heat exchanger; pulsating flow is sometimes used where an additional pump is used to increase flow just to get a little bump and transitioning from high asymptotic fouling to lower saw tooth fouling. With these methods, fouling will slowly increase over time, and then you will reduce them again through the use of these mechanical and physical methods. Off line chemical cleaning is another way of going about it, in order to get you back to the original clean state, and the additives and solvents used are specific not only for the deposit analyzed but the metallurgy present.

One of the best methods to avoid fouling is to operate heat exchangers at the design point.

It is not uncommon for people to oversize heat exchangers. If you limit the excess surface area to 25% on a shell and tube heat exchanger you will not have severe fouling. If the oversize runs up to 40%, that heat exchanger is guaranteed to foul because you will change the operating characteristics of that heat exchanger to provide what you need on the process side. When you do that, it will foul. More and more additives will have to be used and in some cases be unsuccessful to prevent fouling. In the case of plate and frame heat exchangers the fouling allowance should be 15%. Anything above 25% is guaranteed to foul. I'm not going to get into the characteristics on spiral frame exchangers, but anybody who manufactures this equipment can provide proper allowances. Arrangement on plate and frame is very important where you are dealing with different types of temperatures. You can utilize the HTRI-ST5 computer program to give you an idea how to stage and size the equipment. If you do; check all this in the design phase of a system and there will be less fouling potential.

Increasing the flow through an exchanger increases the water velocity and that lowers surface temperature and reduces the amount of reaction fouling that occurs. It increases the sheer stress so attachment cannot occur as easily. It reduces the asymptotic fouling potential. If, for example, the fouling factor is 100-btu/per hr per sq. ft per degree Fahrenheit inverse, by increasing the velocity you will run lower fouling values. Instead of 100 you could be down around 50, which may be acceptable. Thirty-five is an acceptable limit for the backend condenser on a turbine used in the generation of electricity.

Keep the interfacial fluids surface temperature gradient as small as possible. What we mean is, the temperature between the surface of the heat exchanger and the bulk water, you keep that as small as possible. This removes the attachment factor so now even if a precipitate is produced it will not grow large enough to be a suspended solid that will settle.

Don't reduce flow through heat exchangers if at all possible. This is very bad. You oversize that heat exchanger, then you will pay a price if flow is reduced. If possible, recycle exchanger exit water to the inlet to maintain the velocity through the heat exchanger. This allows process side temperature to stay within the operating requirements without reducing water flow. The overall water temperature entering the heat exchanger is higher but the velocity is up. You now have dropped that interfacial temperature. Another possibility is to bypass some of the process fluid around the exchanger and blending it with the cooler exchanger outlet to obtain the desired process temperature.

Minimize the amount of sludge that can accumulate in the cooling tower sump. This is another place to house microorganisms and filterable materials which over time can become septic and reinoculate the system. In colder/winter climates, utilization of a hot water bypass around the cooling tower avoids pinching back heat exchangers. You not only avoid freeze out conditions but you also improve the process side cooling without getting into fouling conditions. Shutting down cooling tower fans may also accomplish this to some degree.

Finally, when you take a look at the degree of system fouling also look at the stressors that drove the fouling and evaluate the chemical treatment to match these stressors. There is a long list that you could investigate to determine what may have to be done and what can be done from a standpoint of operational characteristics, mechanical characteristics and then chemical polishing.

For extensive systems, a little bit of caution. Why worry about all the system when there is only one heat exchanger that is creating a problem. Satellites treat that heat exchanger. Operate at low levels of additive, like a once through system. You can validate your controls by using corrosion coupons, fouling and deposit monitors, scale coupons, ATP monitoring, (which can be related to overall total bulk counts for the system because they are system specific), microbiological dip slides, and biocide efficacy testing all can be used to evaluate a system or a particular exchanger. Scale coupons are really nothing more than coupons with holes perforated in them that increase the amount of energy input. Energy input leads to deposition

Trulear – A comment that Ted made several times in his presentation was balance. A key point I want to make at this time, with the types of technologies that we have talked about balance through out the cooling system is incredibly important. In some parts of a system corrosion control will be more of an issue, in other parts scale control and yet in other parts fouling. A well-administered program has to address all of these issues.

Our last topic is going to be microbiological control. Our final presenter is Dr. Anthony (Tony) Dallmier of Nalco Chemical Company. Tony is a group leader of the Global Microbial Control and the Food & Beverage Groups at Nalco. Tony has over 9 years of industrial water treatment experience. He has worked for Nalco since 1994. Prior to joining Nalco, Tony was employed by Great Lakes Chemical Corporation as a research scientist in biocide research. Tony received his BS and Ph.D. degrees from the University of Illinois at Urbana, Champaign. He is an active member of NACE, and of CTI including the Water Treatment Group. Tony was a contributor of the recent update of the CTI position paper on Legionella Control. In addition to CTI and NACE, Tony is also a member at the American Society of Microbiologist and the Institute of Food Technologist. He is an author and inventor of numerous publications and patents. It is often been said that more cooling system programs fail because of poor microbiological control than for any single reason.

Dr. Anthony Dallmier, Nalco Chemical Co. - Microbial control, as Mike said this is one of the underpinnings for good overall cooling water control. You'll see in just a few moments how that microbial control component pieces together, what Gary spoke about with scale, what Peter spoke about corrosion, and what Ted spoke about with fouling. Hopefully by the end of this talk you will get an appreciation that in order to control your overall cooling water program it is good practice to start with the microbial control component.

Just a brief overview of what I would like to present. Is biofouling a problem? We throw around numbers like 10 to the 3rd power and 10 to the 5th power. What do these numbers really mean and what is an effective level of control? Biofilms are the root cause of biological problems in cooling water systems. It is not those microorganisms, which float around in the bulk fluid; instead it is the surface fouling that really causes problems. Then I will speak very briefly about biological diversity and why that is important and then wrap up with some recommendations and a summary.

What is the cost of biofouling? In 1981 it was estimated that in Great Britain biofouling cost about .5% of the total GNP of Great Britain. In non-communist countries petroleum refining operations, biofouling cost over \$4 billion per year. Bringing that home to the US, heat exchanger biofouling alone is estimated to cost the industry into the billions. As mentioned earlier the microbial world is what I believe to be at the very heart of the triangle. This is similar to what you've seen already today, you see scale on one side of the triangle, corrosion and fouling on the others. At the very center of that is the microbial world. You'll notice that if you keep your microbial component under control the rest of the overall treatment program is much easier to manage. In a paper by Marley, presented a few years ago (TP94-05), they took a tower fill deposit and carefully analyzed it. They found that about 37% of that particular fill fouling deposit was due to biological fouling. Surprisingly, calcium scales constitute only 15% of the total deposit. In this laboratory study using a pilot-cooling tower, they demonstrated it took about a month to equilibrate the tower fill. The weight increased from about 2-lbs/per cubic ft just up to about 4.

It is commonly believed in the industry that silts and calcium scale cause all of the fouling. After a month Marley added sterilized silt to the system and found the fill weight did not increase over a period of about 3 or 4 months. It was only after a microbial population was inoculated into the system that a microbial film grew on surface and provided a glue for not only the silt but also other suspended solids in the system. The overall fill weight increased. Carrying that back to what Ted mentioned about fouling, the microbial world is indeed at the center of the water treatment control triangle.

I want to review very briefly the different microorganism classes present in cooling water. This is a very broad categorization of bacteria that are present. We have all heard of *Legionella* and *Pseudomonas*, and certainly those are two problematic bacteria, but there are many other types. For instance, sulfate-reducing bacteria may exist in your cooling water systems. Bacteria are prokaryotic which means that they do not possess a nucleus. They are typically single celled microscopic organisms. Bacteria are the predominant class of organisms, which constitute biofilms.

The next broad class would be the fungi, which are broken up into yeast and molds. This is a very diverse class; in fact there are more different types of fungi than there are bacteria. They can be either unicellular or multi-cellular. Fungi are eukaryotes, thus, they possess a nucleus. As far as cooling water control is concerned, spore-forming microorganisms like some of the fungi are much more difficult to kill than nonspore forming microorganisms. Fungi are closely associated with wood rot.

There are many different types of algae. You can typically think of algae as plants. They are eukaryotic meaning that they possess a nucleus. Algae are also photosynthetic meaning they need sunlight in which to live in cooling water systems. As with the fungi, algae can either be multi-cellular or unicellular. A major problem that algae present to cooling water operators are that they grow on uncovered distribution desks. Once they grow on desks they form mats, which then interfere with water flow across the distribution deck and down into the system. There are problems which algae cause that are symbiotic with other types of microorganisms present in the cooling water system. An example is that the algae can utilize phosphate, which typically cannot be assimilated or metabolized by many types of bacteria. The algae processes phosphorus and other additives in the system in such a way that bacteria can react with it. The bacteria lives, breaths, break opens and spills out their guts releasing nutrients that algae can live and breath on. So it is a very vicious cycle. In order to properly control a cooling water program you need to take a very holistic approach as far as the different classes of microorganisms. Remember these classes whenever we get to diversity.

The last class of microorganisms that I would like to mention is the protozoa. I mentioned that you can think of algae as a plant but the protozoa are recognized as being the first animals, thus the name proto meaning first; and zoa meaning animal. They are microscopic, eukaryotic organisms. There are more types of protozoa than bacteria, and they are recognized to be higher life forms. I should mention that protozoa are non-photosynthetic and they indicate an advanced biological problem. If you have protozoa present in your system bulk water microbiological reports, there is probably trouble.

Protozoa indicate an advanced population present in the system. Amoeba and other types of protozoa are known to harbor *Legionella*. *Legionella* can live within protozoa. It

takes a lot of biocide to kill a protozoan cell. Protozoa can be infested by *Legionella* then later pop open and release viable *Legionella* into your cooling water system. This is a definite warning sign that if you see protozoa in any of your microbiological reports you need to get after your microbial control program.

Lets put this into perspective. As I previously mentioned, some of the numbers that we microbiologists and others who have presented throw around are 10^3 or 10^4 . What do those really mean? If we take just a coke can of cooling water and measure the viable bacteria in that water there is essentially the equivalent population of the United States contained in that water. If you multiply that up to a 50,000-gallon tower you are going to get approximately 40,000 times the population of the entire world. So it is not realistic to think that you are going to sterilize the system (another inappropriate word is disinfect) because you are not going to achieve it. Don't fool yourself. You will not sterilize the system. The numbers are just too vast. Rather you want to manage the microbial population in your system to levels, which minimize the operational, and public health concerns such as *Legionella*.

What should you focus on as far as a microbial control program? As was mentioned by Ted we have process leaks, which come into a system. Those provide nutrients for different types of microorganisms. The system should be tightened to eliminate or minimize process leaks. Where do microorganisms enter a system? If the make-up water is dirty you might want to consider putting a side stream filter directly on the make-up water. Stop the inoculation at the source, where it comes in. Also you want to remove and prevent biofilms. Biofilms are the true target for proper biological control in a cooling water system. Lastly, you want to keep the biological diversity low.

Minimize inoculation sources and nutrient sources in cooling water systems. Ted mentioned sludge in the basin. If I were a bacterial cell I would head right there. I would have a lot to eat and the biocides will not get to me. It's a great place to hide. What you need to do in biological control is remove the hiding places in the system. Take away their food source. Step back from the cooling water control program and take an overall look. Walk through the system from make-up to blow down. Where could microorganisms be introduced? Is there a construction site next door that allows dust into the tower that is being scrubbed out? Are there process leaks that can be controlled? If you look at a system in that fashion the overall microbial control program will be much easier to implement.

Pseudomonas is a common genus of bacteria found in cooling water. The reason that *Pseudomonas* is such a problem is because it spits out all of this EPS (extra cellular polysaccharides) around the perimeter of the cell. That particular structure enables bacterial cells to lie down on surfaces. It is kind of a sticky, gluey type of material. Biofilms are the true microbial control target. In order to define a biofilm it's a matrix of an enclosed bacterial population inherent to each other and/or surfaces or interfaces. That's fine for scientist to say but what are biofilms? Let's just group them together – they're slime. You need to control those slime layers present in your cooling water system. They form in response to and for survival in hostile environments. It takes a lot of energy for a bacterial cell to produce a biofilm. Why do they do it? There are a number of reasons. First, it makes them easier to lie down on surfaces. Second, it forms a protective coating and it is much harder to kill a biofilm bacterial cell than it is a free-floating bacterial cell. This can be related to cholesterol. Now I'm not a physician, but cholesterol floating around in your blood stream, if it is just free floating isn't causing

you a lot of problems. It's when it deposits onto the walls of blood vessels to where it can form a blockage or a clot thus causing damage. The same is true for cooling water. The bacteria and other microorganisms that are floating around in the bulk water aren't really causing many problems. It is when they lay down on surface and causing surface fouling that they become a problem.

As I mentioned, biofilm bacteria are much harder to kill than the planktonic microorganisms. If you want a rough rule of thumb it takes about 10 times more biocide to kill biofilm bacteria than it does for the same planktonic bacterial cell, which has been removed from the biofilm or released out into the bulk water. Here is another factor. If the biocide addition reduced dip slide numbers, showing it to be working well, that isn't necessarily true; you could still have a large amount of biofilm contamination present throughout the system. Don't be fooled. There are ways that biofilms can be attacked. You can use products in conjunction with biocides such as bio-dispersants, bio-detergents, and bio-penetrants. These products almost always help. They help get the biofilms off of the surfaces, help get the rest of the fouling material off of the surfaces, and get the bacteria and other microorganisms out into the bulk water where the biocide has access to them. These supplements almost always help and should be a standard part of any cooling water control program where you are trying to minimize biofilm formation.

What are some of the problems that biofilms cause? They cause energy losses due to increase heat transfer and fluid frictional resistances. They cause increased capital cost because you need to put in excess capacity to account for the loss of energy from biofilms. They also present higher capital cost due to premature equipment replacement. I believe it was Ted that spoke about MIC (microbiological influenced corrosion) and indeed MIC is a very active component of the biological system such as SRB's and acid producing bacteria. Also it should be pointed out that biofilms have very poor thermal conductivity since they are almost all water. As Gary mentioned the scale deposits create a problem as far as heat transfer resistance and that is certainly true. Biofilm thermal conductivity is approximately 4 times less compared to calcium scale. So they are better insulators to heat transfer than calcium salts.

Biofilms also impart significant costs. Biofilms can greatly increase your condenser backpressure and some of the associated costs once the condenser backpressure goes above design. In the interest of time I won't present them but there are many other instances where the impact of biofilms has been published. Biofilms cause unscheduled maintenance or down time, quality control problems such as fouling of your process stream, and of course, as mentioned earlier, *Legionella* are known to reside in biofilms and protozoa. So biofilms can present a public health concern by protecting *Legionella* against a biocide program.

Let's go to monitoring. Some bulk water biological techniques – ATP (adenosine triphosphate) an energy molecule that all living organisms possess. Humans possess ATP. You can relate the ATP values to the microbial contamination present in your system. You can take the value the ATP gives you as a measurement of the total viable biomass present in your cooling water system. Also, there are standard microbiological tests such as dip slides. There is a test that can be run by service companies or sent to a microbiological lab to provide greater detail as far as the population present in a system. It is also important to measure the microbial contamination present on surfaces. There are various methods to do that. There are swab tests where you take a sterile

swab, swab a given sample area of your cooling water system, and then send the swab to a laboratory for an analysis. That surface population will almost always be higher than the bulk water numbers because the large majority, over 99%, of the total microbial population present in a system resides on surfaces. There are various online devices, some of which have been here at CTI for measuring surface fouling. You can look at system performance parameters such as measuring condenser backpressure or heat transfer resistance to find just how much fouling there is in a cooling water system.

Keeping biological diversity low is very important. Highly diverse microbial communities in cooling water systems are an indication of poor control. You want to keep your diversity low. You want to minimize the different classes of microorganisms. You don't want to allow different types of algae to be present, and certainly not the protozoa. So you want to minimize diversity.

If a sample is submitted for a bulk cooling water microbiological report, not a dip slide, but where you get a detailed analysis regarding the different types and numbers of microorganisms that are present. Here are a few warning signs. The first are anaerobes. If you take a bulk water sample that is highly oxygenated, the anaerobic bacteria don't want to be there because oxygen will poison them. They prefer to be under deposits. If you have a bulk water sample that came back with a high amount of anaerobes such as sulfate reducing bacteria and *Clostridia*, which are acid producing bacteria, there is a deposit somewhere. As Ted mentioned there is under deposit corrosion and that certainly could be going on here if you have anaerobes present. Then you need to go back and add bio-dispersants or bio-detergents to remove surface fouling from your system. There are higher life forms. We have talked about that with the protozoa. These indicate an advanced biological problem present in your system. There are algae. We talked about the vicious cycle with the nutrient cycling with the bacteria and other forms of microorganisms. I want to point out as far as monitoring of bulk samples, if you take a dip slide it will provide some meaningful information, but it doesn't provide anything as far as the diversity in the system. The sample should be sent to a biological testing facility where they can provide the different classes and numbers of microorganisms present.

Biological inoculation should be identified and managed. Certainly don't forget equipment like side stream filters. That is a commonly overlooked item that is neither treated nor backwashed properly. The manufacturer's cleaning recommendations should be followed or else the system will continuously re-inoculate itself. The same is true for basin sludge. Process leaks and other nutrient ingresses need to be eliminated. Realistic biocide levels should be used. Excessive biocide feed rates is an indication of unwanted nutrients entering the system. Again, tighten up the system and look for root causes in order to control the microbes present. Supplement with non-oxidizing biocides. I won't mention any particular biocide today, but there are advantages and disadvantages to all of them. It is important to apply the biocides and other agents close to the critical control point. For instance, if you have heat exchanger problems and fouling factors are going up, it doesn't make sense to dribble in a little biocide at the distal end of the basin. The biocide could be consumed as it sweeps across the basin, and never reach the heat exchanger. You need to apply your bio-control agent as close to the critical control point as possible. As mentioned bio-dispersants, bio-detergents and biopenetrants almost always help. They make the biocides work much better. It is important to trend the monitoring data. One number doesn't tell you anything. Relate it

back to the overall operational performance of the cooling water system as well as the bio-control program.

In summary remember biofouling is the centerpiece, the very heart of a good microbial control program. Remember the triangle. The system survey is crucial to identify and manage inoculation and nutrient ingresses present into your system. The true targets are biofilms, the surface foulants. It is nice to say I reduced the planktonic count, but you really need to go after the biofilms. They truly cause the problems. You need to keep your diversity low. Last but not least, you need to dose realistic levels of bio-control agents.

Trulear – I wanted to take a minute to thank the entire panel for an excellent job. You can see that a lot of work went in to putting these presentations together. There was a lot of coordination and at this point I would just like to thank everybody on the panel for doing a great job.

At this time we will open the floor for questions.

Q. Ken Mortensen, Marley Cooling Tower Company – I have a question for Gary on scaling. You mentioned calcium carbonate having reverse solubility with temperature. Is that true for calcium sulfate and calcium phosphate?

Geiger – It is certainly true for calcium phosphate. Calcium sulfate has normal solubility up to about a temperature of 140°F then it has reverse solubility.

Q. Brian Hayward, Chemworks Filtration – We do high efficiency filtration. I've learned a lot today and want to thank the speakers for the things they reviewed. I have been doing filtration for a long and learned a few things today that I didn't know before. One of the things we work on is this question of particles coming in with the make-up water; do you filter the water coming in or side stream it? From my experience, you can just necessarily say that you can filter the particulate from the incoming water because filters are only a certain percent efficient. When you look at the cycles on the tower, you are better off to filter the incoming water. At five cycles you can do dramatically better in the final TSS in the cooling water if you do a side stream on a similar size filter at a lower cost because incoming water requires full flow and you'll need to double the size of the filter, etc. We usually look at cycles and then try to determine where lowest TSS will be with the same expense on a filter. Unless you are down at 3 cycles, it is almost always better from our perspective to filter the tower water. I may not understand something that you folks know. So that is one question. Then on the sizing of the filters when you talked about the formula of 2% gives you 80% removal on 5 cycles – I think that formula assumes a 50% particle removal rate on a filter. One of the other formulas I saw assumed a 100%. When we do our work on filtration we have to look carefully at particle distributions, what's in the water, what the percent efficiency on a single pass through a filter is, then define what size filter you would need for a particular setup. I know this was generalizing; I'm not questioning that. I don't know if there is any comment on that or not.

The other thing is in the Laminar flow area at heat transfer surfaces, the Marley paper was terrific as far as the particles sizing in there being 5 micron and lower. I don't know if anyone has looked at the particle size distribution in the film formed on heat

exchangers or heat transfer surface. I don't know if anyone knows what the particle sizing is in that because that is critically important also.

Dallmier - That was a lot of questions. Let's come back to the 2-5%, 5 cycles 80% removal rule of thumb. As far as choosing where to filter, it has been my opinion based on the work that I have done in the past, if the suspended solids are generated within the system from reaction products or washing it out of the atmosphere, side stream filtration should be used. You are correct about particle size. A particle distribution test should be made, but you are correct on your particle size entering with the make-up water. It may be of no value to filter even though in time the particles get larger in the cooling water. It is a quick statement to say, "Is the bulk of your problem derived from the make-up water and are the chunks big enough to filter?"

Trulear – Brian, you mentioned in your experience that side stream filtration being a much more effective approach. I would agree, at least in our experience, that by properly sizing a side stream filter can be of amazing benefit as long as it is properly sized and operated.

Dallmier – I just want to add, since I am in the chemical business I generally look at things also as how many pounds of solids are generated. Based upon how many pounds of solids are generated I sometimes lean toward adding an anti-foulant rather than adding a side stream filter. All that being said however, it is never a good idea to use unclarified river water as cooling tower make-up.

Q. Raul Castillo, Dow Chemical – Are there any good inhibitors that would overcome galvanic corrosion due to dissimilar materials?

Zisson – About the only thing you can do if you have a dissimilar metal corrosion problem is to either coat the tube sheet, make sure you have a good coating, preferably with some impressed current cathodic protection to overcome coating holidays or to use sacrificial anodes. You're not going to be able to overcome with an inhibitor the potential that exists because of the dissimilar metals. All you can do is just shift to another metal or take the most reactive metal out of contact with the water.

Q. Castillo – The next question, on carbon steel tubes we typically acidize and pretreat to remove the mill scale but other owners say they don't do that at all. What are your recommendations?

Zisson – I'm in favor of an acid flush followed by a caustic polyphosphate passivation step, which should be done immediately after the acid flush. I do believe it is important to remove the mill scale because the sites where the mill scales exist tend to form anodes readily. When mill scale is removed, there is a more uniform surface and corrosion control is easier to accomplish.

Geiger – I would like to comment on your first question because I disagree with the answer that was given about galvanic couples. I don't think that is always the case. I think inhibitors do improve performance especially when you have a copper/steel galvanic couple. The copper alloy acts as the cathode and drives the corrosion of steel. With the azoles and substituted azoles a good film can be maintained on the copper surface, which really blocks the electrons from being transferred. If you can accomplish that the galvanic effect will be eliminated. One of the examples given was shown to be a

mild steel, stainless steel galvanic effect where you really corroded the steel. Yet in the industry that is a very prevalent couple. Stainless steel tubes with mild steel tube sheets are seen frequently. When read basic corrosion theory this is not desirable. You look at where they are on the galvanic series, and the steel wants to corrode. But it depends on what the pH is. At the more acid conditions that is a bad galvanic couple when you are down around pH 7. As you increase pH in the water and the programs seem to be more cathodic, that galvanic cell is reduced because the stainless steel wants to be the cathode and that is where most of your inhibitors want to work. Now it is not a good idea but it is not a recipe for failure.