



Factsheet: Eliminating Hexavalent Chrome From Cooling Towers

Board of Public Works
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Cooling towers are used by office buildings and manufacturing plants throughout the Los Angeles area to dissipate waste heat from air conditioning, industrial and power generation processes. Recirculating water transfer thermal energy from the building or industrial process to the atmosphere. Atmosphere air blown through the cooling tower carries away the heat.

Environmental problems arise when water escapes from the system in the form of droplets. Such water droplets carry with them various chemicals that are used in the system. Some of these chemicals are environmentally harmful. Hexavalent chromium is the one that is of the most concern and warrants immediate attention.

Hexavalent chromium-based ("chrome") compounds are among the most efficient and cheapest corrosion inhibitors available. The trouble is, hexavalent chromium is a suspected carcinogen, and is highly toxic. Chrome emissions from cooling towers in the South Coast Air Quality Management District (SCAQMD) alone could cause as many as 700 cancer cases over a 70 year exposure period.

SCAQMD has banned the use of hexavalent chromium water treatment chemicals in open water circulating systems that are potentially capable of emitting respirable hexavalent chrome. This prohibition is expected to reduce the risk of cancer cases due to cooling tower emissions to virtually zero. Additionally, elimination of hexavalent chromium-based treatment chemicals will eliminate the amount of hazardous and toxic wastes discarded through blowdown.

Cooling Tower Design

Most cooling towers are designed with recirculating water systems to conserve water resources and reduce costs of purchasing water. Cooling towers generally use open recirculating systems, although some employ closed systems. In open (wet) recirculating systems, warm water is brought into contact with air. Cooling takes place through evaporation. A simplified flow diagram of a typical open recirculating cooling tower system is shown in Figure 1. In closed (dry) recirculating systems, the warm water and air are separated by a solid surface, usually steel, which conducts heat from the warm water to the cooler air. Such systems require very large heat transfer areas. The cost of constructing such closed recirculating systems is about ten times that of wet direct contact systems (Kirk and Othmer 1979). They are thus not constructed unless there is an extreme scarcity of water. It is the more common open systems that are responsible for hazardous air emissions.

Cooling towers use either forced drafts or natural drafts to circulate water. The force draft tower uses

fans to move air. The difference in buoyancy of the air column in a very tall stack provides the driving force in a natural draft tower. Figure 1 [(see source document)] Both towers employ a set of louvers and baffles (called the "fill") over which warm water passes. The internal grid work of the fill material is designed to enhance splashing and film formation in order to give a large water-air interface. Depending on the tower characteristics, air may flow across this cascading liquid or counter current to it. Most cooling towers are equipped with drift eliminators that prevent water bubbles and droplets from leaving the water distribution portion of the tower. Several designs are in current use, most of which prevent water losses by redirecting the escaping bubbles and droplets back into the tower's basin (Drew 1977).

Water Loss And Cooling Tower Emissions

Although water is recirculated in open cooling systems, losses are considerable. They occur mainly through:

- a. **Evaporation into the exhaust air stream.** Evaporation provides for 80 percent of the cooling. Evaporated water does not contain chemicals, and so is not environmentally hazardous (SCAQMD 1989).
- b. **Cooling water blowdown.** Cooling water blowdown is a purge stream, which is necessary to prevent excessive build up of dissolved solids in the cooling water inventory. The makeup water to the cooling tower contains dissolved solids. Without blowdown, these solids would quickly build up to the levels resulting in excessive scaling of heat transfer surfaces. Cooling water blowdown is treated to remove chrome before being discharged.
- c. **Drift.** Water droplets and bubbles that escape from cooling tower stacks are referred to as drift. Drift is estimated to be in the range of 0.003% to 0.005% of circulating water (in gpm). Drift emissions are made up to large and small water droplets and bubbles. Large drops and bubbles are relatively heavy and may settle or condense in the vicinity of the cooling towers. Small bubbles and droplets travel further and can find their way into the human respiratory system. It is such respirable emissions that present a danger to human health and the environment.

The Need For Cooling Water Treatment

Circulating water chemical treatment is practiced to control scaling, erosion, corrosion and biological growth within the cooling towers, heat transfer units and associated piping. These phenomena are caused by dissolved and suspending solids and nutrients that promote the growth of microorganisms in the circulating water.

Scaling and fouling of heat exchange surfaces drastically reduce the heat transfer efficiency, resulting in sharp rises in energy transfer costs. Deposition of scale in heat exchanger tubes, on fill and drift eliminator ports results in clogging, higher pressure drops and alternation of fluid flow characteristics. This can lead to frequent shutdowns and increases in the generation of system cleaning wastes, maintenance and operating costs. Aeration of water in the cooling tower generates a highly corrosive environment for the tower components and associated equipment in contact with the water. Excessive corrosion causes additional maintenance and premature replacement of capital equipment. These operational problems cannot be controlled unless corrosion inhibitors, antiscalants, antifoulants, dispersants, surfactants, biocides and pH control chemicals are added to the circulating water (Table 1).

Table 1 [(see source document)]

Chromate compounds are among the most efficient and cheapest corrosion inhibitors available. However, they are highly toxic and suspected to cause cancer in human beings. Hence they must be replaced with non-chromate based chemicals. Some that have proved useful are the polyphosphates, organophosphates, zinc, molybdates and aromatic azoles. Unlike chromate inhibitors, these substitutes perform well only under specific conditions. This disadvantage can be overcome by employing blends of two or more inhibitors that can take advantage of the strengths of each. Table 2 compares the performance of some of these blends to that of a chromate-zinc blend. Note that while the chromate-zinc blend combination offers the best corrosion inhibition in most cases, other blends are close. To obtain the best results, several blends must be tested (for a specific water quality) and the one that best satisfies all performance requirements should be chosen.

Non-chromate chemicals may have some adverse impacts on the environment. For example, while zinc based chemicals are particularly dangerous to humans, they are highly toxic to marine life. Similarly, phosphate discharges into lakes and ponds may cause excessive algal growth leading to eutrophication problems. But in comparison to the highly toxic chromate inhibitors, the substitute chemicals are relatively innocuous and do not present the same environmental problems that chromates do. Nevertheless, the impact of substitute chemicals on the environment must be carefully analyzed before actually using them.

Table 2 [(see source document)]

It is encouraging to note that before the Rule went into effect, 85% of the cooling towers operating in the South Coast Air Quality Management District had already changed to non-chromate systems. The remaining 15%, however, have the potential to cause as many as 700 cancer cases in the years ahead if they are not modified (SCAQMD).

Economic Considerations

No major modifications to the cooling tower are required for changing from chrome to non-chrome systems although new test kits for analyzing and sampling will have to be used. Non-chrome chemicals, such as phosphates, react with metal surfaces and tend to remove existing chrome coatings from metal parts. This can lead to severe localized pitting. Therefore, existing chrome coatings on cooling tower and downstream components must be completely removed before chromate systems with cooling capacities of 500 and 3000 tons (T) are shown in Table 3. The costs shown in Table 3 include capital and maintenance costs, but do not include regulatory and operating costs. The capital costs includes new equipment and shortened life of towers using non-chromate chemicals. Non-chromate treatment costs can significantly vary depending upon the type of treatment used. The treatment costs shown in the table are average values and can vary as much as + 50%. Presently, non-chromate chemical treatment costs are far more expensive than chromate costs. However, with the increased consumption of non-chromate chemicals, the cost is bound to reduce significantly.

Table 3 [(see source document)]

Other Options

Currently, the best possible solution to the chromate problems appears to be replacement with non-chromate chemicals. However, in view of the potential hazards of many of the alternate chemicals, it may be wise to eliminate or reduce the emission of any treatment chemicals into the environment. This could be accomplished by:

- a. Makeup water pretreatment. Pretreatment of makeup water to cooling towers reduces the chemical treatment requirements for scale and corrosion control and can increase the number of times cooling water may be recycled before blowdown. Pretreatment reduces dissolved solids in the makeup water through precipitation and flocculation, softening and ion-exchange. Suspended solids are removed by clarification and filtration. Pretreatment may not be economical for "comfort" cooling towers (those used in office building air conditioning systems) but is advantageous for large industrial cooling towers.
- b. Using inert construction materials. Polyethylene (PE) and stainless steel (SS) are relatively non-reactive compared to carbon steel. Therefore PE and SS towers would require relatively lesser quantities of scale and corrosion inhibitors.
- c. Increasing the heat and mass transfer efficiency of cooling towers. Efficiency can be enhanced by improving the design of cooling towers. One example is to avoid designs where sunlight can shine directly on the water; adding to the cooling load an promoting biological growth. Increasing the efficiency will result in the usage of small towers that need less treatment chemicals.
- d. Increasing the efficiency of pollution control devices. Cooling tower emissions may be reduced by installing high efficiency drift (HED) eliminators (such as waveform and advanced interlaced monofilament eliminators) claim to reduce drift by 80%. However, even these eliminators are not capable of capturing most of the smaller respirable droplets and bubbles, which are the main source of health concerns.
- e. Use of wet-dry forced draft cooling towers (WDCT). In this type of tower, a dry cooling section is added to a conventional evaporative cooling tower. WDCT's combine the advantages of lower consumption of water and water treatment chemicals, reduced fogging problems in the winter, and economical cooling during summer. WDCT's are larger in size and cost about 25% to 100% more than wet forced draft cooling tower, and may not be viable alternative in the case of comfort cooling towers.

Regulatory Considerations

This SCAQMD has declared Rule 1404 to be effective starting January 1st 1990. This rule prohibits the use of hexavalent chrome-containing water treatment chemicals in open circulating waters of cooling towers. According to the rule, the concentration of hexavalent chrome in the cooling tower water of non-wooden towers is not to exceed 0.15 mg/l. The rule also requires biannual testing of the circulating water and accurate record keeping of test results.

Residual chromate chemicals may slowly desorb from wooden towers that were using chromium chemicals in the past. To account for this phenomenon, the law allows chrome concentrations up to 8 mg/l in wooden tower circulating waters until July 1st 1990. Thereafter, wooden towers must also comply with the 0.15 mg/l chrome concentration limit. The chromium chemicals can be desorbed quickly from the wooden towers using high pressure water flushing in combination with alkali/acid treatment techniques. Cooling tower chemical treatment suppliers claim that after appropriate treatment, the chromium concentration in the replaced systems can be reduced to less than 0.15 mg/l in less than six months (Atwater, 1990)

In addition to SCAQMD, other regulatory agencies such as EPA, Bureau of Sanitation and Occupational Health and Safety Administration (OSHA) can require use of various consumer and industrial hazardous chemicals. For example, cooling tower operators require National Pollution Discharge and Elimination

Systems (NPDES) and Industrial Waste Water permits before discharging cooling tower blowdown.

Disposal Of Hexavalent Chromium-Bearing Waters

Hexavalent chromium bearing recirculating waters and cooling tower sludges must be disposed of approximately before changing to non-chromium based systems. Recirculating water are currently disposed of in the same way as blowdown, by mixing with other building sanitary sewer waters. However, permissions must be obtained from the local sanitation district before disposing of recirculating waters in this way. While disposing the chromium bearing recirculating water into the sanitary sewer, care must be taken to exceed the hydraulic loading capacity of the existing sewer system and the discharge chromium concentrations permitted by the local sanitation district. Sludge that has collected in the cooling tower basin while operating the chromium system must be analyzed for chromium-concentrations. If the concentrations exceed State or Federal toxicity criteria, the sludge must be disposed of appropriately as a hazardous waste.

Conclusion

Open recirculating cooling towers emits droplets of water into the air that carry chemicals used for treating recirculating waters along with them. Treatment is performed to control scaling, erosion, corrosion and biological growth within the cooling tower, heat transfer units and associated piping. Hexavalent chromium based treatment chemicals have traditionally been used for this purpose because they are the most efficient and cheapest among commercially available treatment chemicals. But the problem is, hexavalent chromium is a suspected carcinogen. Chrome emissions from cooling towers in the SCAQMD alone could cause as many as 700 cancer cases over a 70 year exposure period.

In view of the environmentally harmful effects, SCAQMD has banned the use of hexavalent chromium based chemicals in open recirculating cooling towers. The ban is effective starting January 1st, 1990. Many other alternatives to hexavalent chromium based chemicals are commercially available. These products are currently comparatively expensive and some what less effective than chromium chemicals, however, the cost of such treatment is bound to be reduced.

References

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Roti, Joseph and Soeder, Kenneth. (1988) Technical Paper Number TP 88-03, Cooling Tower Institute 1988 Annual meeting.

Drew. (1977) Principles of Industrial Water Treatment, Published by Drew Chemical Corporation, Boonton, New Jersey.

Popejoy, Cliff. 1990 California Air Resources Board. Personal Communication.

South Coast Air Quality Management District (SCAQMD). 1989 Agenda #34 - Adopt Proposed Rule 1404, El Monte California.

Further Information

Several articles on various aspects of cooling tower chemical treatment have been published by the Cooling Tower Institute. A bibliography and price list of all these papers are available from the cooling

tower institute. Phone (713) 583-4087.

For more regulatory information on Ruse 1404, contact:

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