

Different Aspects of Cooling Water Systems:

Introduction

Due to the worldwide competitive nature of industrial activity today, all industrial manufacturers must maintain strict control over various sources of production cost. Cooling water is a commonly neglected area of the production process which is often responsible for substantial cost increases due to downtime, equipment damage, loss of process control, and increased energy usage. Other items which relate to treatment and control of cooling water: such as water and sewerage costs, environmental regulations, and lack of sufficient fresh makeup water; can also have substantial impacts on all aspects of manufacturing operations. Neglect of cooling water results from two items: first, the manufacturer often does not appreciate that cooling water is a vital part of the production process; and second, the fact that misinformation, "snake oil" products, and marketing "hype" are common when cooling water treatment is the issue under discussion.

Any discussion of cooling water treatment must begin with an objective statement of what is expected from the cooling water system. In manufacturing plants, the cooling water system must provide reliable production equipment cooling with maximum heat transfer efficiency. The following four basic requirements are derived from this objective.

- 1. Minimize problems from corrosion, scale, deposition, and growth to obtain maximum efficiency.**
- 2. Implementation and control must be "do-able" with a minimum input of labor and money.**
- 3. Cost effective as possible considering the total water system capital and operating costs.**
- 4. Must be environmentally acceptable.**

These four requirements form the basis for the following discussion of cooling water control and treatment.

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WATER CHEMISTRY CONTROL

One of the most interesting observations we have made over the years is that operational control of cooling water treatment programs is invariably neglected and is thus the single most common cause of program failure. The best possible combination of corrosion, scale, and deposition control chemicals, with effective biocides, is completely worthless if not consistently and correctly applied to the cooling water.

Cycles

Cooling water chemistry control begins with cooling water cycles of concentration (C), or the number of times that the dissolved salts in the fresh makeup water (MU) are concentrated by evaporation from the cooling system. This parameter is commonly obtained by measuring the conductivity of the cooling water (CW) and dividing it by the measured conductivity of the makeup water. Please note that cycles can also be calculated using other parameters, such as chlorides and dissolved solids, which are common to both the makeup and cooling water and are not expected to be effected in any great degree by chemical additions or precipitations.

$$C = \text{CW conductivity} / \text{MU conductivity}$$

Control of cycle is critical in systems using non-softened makeup water as no chemical treatment program can cope with the increased potential for scale formation resultant from excessive levels of hardness salts in cooling water caused by very high cycle operation.

Why Cycle?

One question that occasionally surfaces is "why use chemical treatments to operate at additional cycles when often no scale will form when operating at lower cycles". The best answer is that operation at increased cycles substantially lowers both the makeup and blow down requirements, cutting the cost of fresh water and sewage disposal. With corrosive waters, increasing the cycles so that the water is rendered less corrosive is a "cheap" means to improve control of corrosion. Another point is that operation at increased cycles permits use of effective corrosion inhibitors that may be too costly to employ at the higher blow down rates resultant

from low cycle operation. Typically, the most economical cycles to operate at are in the range of 3 to 6.

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Cycles - Economics

Maximum economic cycle is that cycle value where the total operating cost for the entire program is lowest. This value has to be determined based on the cost of water, blow down, and chemical treatment for each specific application. One unique set of operational parameters consisting of cycles, inhibitor chemistry, inhibitor dosage, makeup, and blow down can be found for each makeup water/plant combination that will give the lowest total operating cost program.

The first step in selection of maximum economic cycles, and many times the basic treatment program, is to calculate the calcium carbonate saturation index (SI) of the makeup water. The SI is utilized to ascertain if the makeup water is scaling (+), or non-scaling (-), prior to cycling. The makeup water is then cycled, over a typical range of 2 to 10 cycles, and the resultant SI, makeup rate, blow down rate, inhibitor chemistry needed, and chemical dosages calculated to determine the maximum economic cycles.

Value judgment is called for in selection of the inhibitor chemistry and dosage. Higher cycles reduce all costs, but also increase the potential for scale, corrosion, deposition, and biological fouling problems.

The calculation of maximum economic cycles is complex and can usually be justified only for larger plants. In the majority of cases, use of a chemistry that will permit 3 to 6 cycles operation will result in a total operating program cost close to the desired minimum cost optimum. Specific product selection for control of scaling is then based upon the SI at the selected cycle.

Cycle - Control

Two methods have been found to yield the best control of cycles.

The first, which is required when makeup water chemistry varies substantially or the plant has uncontrolled water losses, is to use an automatic control system based on measuring the conductivity (proportional to the level of dissolved salts in the water) of the cooling water. When the conductivity reaches the determined control level, an automatic valve is activated and high dissolved salt content water is drained from the cooling water system. Replacement of this drained water or blow down (BD) with fresh water lowers the conductivity of the cooling water, which causes the automatic valve to be deactivated.

Another means to control cycles automatically utilizes the makeup proportional method, where the amount of makeup water added to the cooling system is measured and a

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proportional amount of blow down drained from the system via operation of an automatic valve controlled by a makeup water meter activated timer. Thus to operate at ten cycles, for every 1000 gallons of makeup water added to the cooling water system, approximately 100 gallons of blow down would have to be drained. The equation for this is:

$$BD = MU/C$$

While this method is only applicable when the makeup water is of fairly consistent quality and the plant is low leakage, it is less costly to install and maintain than conductivity based system and yields the same degree of control. An additional advantage is that there is no conductivity electrode which requires routine maintenance.

As maintaining a set cycles value is the basic control function in cooling water treatment, only high quality, easy to maintain equipment should be used so as to obtain the most accurate, consistent, and reliable control possible.

Chemical Feed Control

Many methods have been used over the years to control the addition of chemical inhibitor products to cooling systems. Common practices have included manual batch feed; timer controlled feed; constant feed; "feed/bleed", where chemical is injected simultaneously with blow down; proportional feed; and active control feed, where a relevant parameter is measured and inhibitor feed used to maintain a set point.

Critical evaluation of these various methods over the years has shown that the best chemical inhibitor control method is that using proportional feed. This is based upon the fact that all chemical products, with the exception of biocides, are dosed according to the amount of blow down from the cooling system, which is directly proportional to the amount of makeup added.

Proportional chemical feed systems are quite simple, being based upon metering the amount of makeup water added to the cooling water system and activating a chemical metering pump via a timer to add an amount of inhibitor proportional to the amount of makeup added. As with control of cycles, only high quality equipment which provides the basic control function should be used.

The various "computerized" and "on-line" control systems now being marketed have no technical advantage over the basic control methods just discussed. In fact, due to the increased complexity of such systems, they are often less reliable than basic controls and are always more expensive to purchase and maintain.

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While active control feed systems should have a technical advantage over proportional control systems, i.e. they are "measuring" the control parameter in real time and maintaining control, in practice the systems on the market utilize an easy to measure tracer compound added to the inhibitor. Several cases have been documented where the tracer level has been within control limits, but the actives in the inhibitor were not due to selective precipitation and/or absorption within the cooling system. Our comments concerning high cost and poor reliability apply even more to this type of control system at the present time.

Calculation of Parameters

Calculation of the various operating parameters for a cooling system is very important as to initial sizing and subsequent monitoring of control system performance. We have found the following equations to be the most accurate for obtaining values for system evaporation (E), blowdown (BD), windage (W), and makeup (MU) as m³/day.

Evaporation is easily calculated by:

$$E = C.R. \times \Delta T \times 24 / 653 = \text{m}^3/\text{day}$$

Blow down is calculated using the evaporation determined from the heat load on the cooling system with the following equation.

$$B = E / \text{maximum } C - 1$$

The maximum cycle value will be set based upon the determined lowest total operating cost for the water treatment program as already discussed.

Windage is commonly calculated using the following equation.

$$W = 0.5 \% \text{ of Recirculation rate.}$$

Makeup is simply the sum of evaporation, blow down, and windage, and can be checked using mass balance techniques.

$$M = E + B + W$$

The measured cycles and makeup of a cooling system can be used to determine the thermal load on a system by using the above equations. Comparison of measured parameters against calculated values should be done on a routine basis to ensure that cooling systems are within design limits and to locate "problems" in the system before they become production problems.

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Biocide Control

The critical point concerning control of biocide feed is to remember that the dose makes the poison, i.e., there is a dosage (toxic threshold) below which a biocide will not work. Simply put, biocides do not work unless a critical dosage is reached and maintained for a set time period. The critical dosage point and time required for effective microbiological control varies substantially with the specific biocide in use and the overall condition of the cooling water system.

In addition to the critical dosage and time factor, one must also be aware of the fact that microorganisms are very fast to adjust to such things as "toxics" in their environment. Use of many biocides on a constant basis merely results in establishment of a resistant flora in the cooling system being treated.

These facts being noted, the best method for addition of biocide materials is on a slug, or intermittent, dosage basis using the system volume to establish initial dosage. Slug dosage can be accomplished either manually, or via automation using timers and pumps. Excellent results can be obtained by either addition method, though safety considerations in handling of toxic biocides are increasing usage of the automatic feed systems. Larger cooling systems can obtain substantial biocide chemical cost reductions by using the recently developed on-site chlorine dioxide and hypochlorite/bromite solution.

Operator Attention

While automatic systems for control of cycles, chemical feed, and biocide addition will improve the probability for success of any cooling water treatment program, a certain level of attention by plant operations personnel is required. Such items as replacement of empty chemical drums and finding / repair of water leaks can only be done by an operator. We recommend a daily check of the conductivity and makeup meter readings, along with a visual and operational check of the chemical feed pumps and drums.

Chemical tests of the cooling water should be made and logged at least once a week by the operator to ensure that proper levels of treatment chemicals are being maintained in the cooling water. Larger plants may benefit from an increased amount of testing due to the potential costs of upsets.

A technical representative of the treatment chemical supplier should visit the plant at least once a month to check operation of the automatic systems, undertake his own chemical tests (using his reagents) of the cooling water, and assist the plant operator with resolution

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of any problems. We have found that service is usually better if the treatment chemical supplier has also supplied the chemical control and any pretreatment equipment used on the cooling water system.

CORROSION

Water, while an excellent transporter of heat and quite inexpensive, is also an excellent ionic type solvent that will dissolve more, or less, of just about all known materials. Given this chemical fact, the chemistry of all cooling water treatment programs must begin by addressing corrosion, which is basically an electrochemical oxidation process which results in destruction of the basic metals from which most cooling systems are constructed.

Uncontrolled corrosion is often responsible for downtime from physical equipment failure, or plugging of cooling water passages from deposition of corrosion products. More subtle effects, often not linked to corrosion, are loss of production speed and/or process control and decreased energy efficiency, from deposition of corrosion products on heat transfer surfaces where the deposit acts as an insulator to decrease thermal conductivity.

Factors

Many factors affect the uncontrolled corrosion rates that could be expected in a given cooling water system.

Such items as the presence of dissolved gases, chloride and sulfate levels, pH, alkalinity, scaling tendency, and protective ions such as phosphate and nitrate; must all be taken into consideration along with such engineering factors as water temperatures, presence of galvanic couples, and water velocity in the design of corrosion control chemistry.

Test Control Method

The effectiveness of the corrosion inhibitor portion of a cooling water treatment program should be monitored by regular use of corrosion monitoring coupons to determine actual corrosion rates within the cooling water system. Electronic corrosion rate meters have been developed to the point where they are fairly accurate and quite valuable in many cases. Their major problems are that they are substantially costlier than corrosion coupons and do not give long term rate data. While not as good as direct corrosion monitoring, a complete chemical analysis of the makeup and cooling water can often be used by a skilled technician to spot problems such as excessive corrosion of copper alloys, or zinc, in the system. Corrosion rates above those noted are cause for immediate remedial action.

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An acceptable cooling water treatment program should be able to reduce corrosion rates to the following average levels reported as mil/yr:

Mild Steel < 5 **Copper Alloys** < 0.4

Attainment of these control levels, which equate to a corrosion rate reduction of 85% to 95% over uncontrolled level, can be difficult due to the factors already noted.

Inhibitor Chemistry

Purchasing agents have often been quoted as saying "all water treatment chemicals are the same, so we will buy the cheapest ones." This statement sums up some of the misinformation that abounds on water treatment chemistry. While it is true that most suppliers have products with similar chemistries and can duplicate each other's' products,

It is the application of specific products to particular plant makeup water and cooling system design that differentiates success from failure.

WATER QUALITY

Soft Water

In cooling systems operated using naturally soft, or softened, makeup water, control of corrosion is the major challenge for the water treatment program. The common water treatment industry practice of using makeup water hardness and alkalinity to provide the bulk of corrosion control action does not work with these types of makeup water.

In fact, the most commonly used corrosion inhibitors, phosphates and phosphonates, do not work if less than 50 mg/l calcium hardness is present in the cycled cooling water. This often overlooked fact has been responsible for many documented problems where this chemistry was applied to soft water makeup systems with horrible results.

As soft water makeup can be used to achieve zero discharge for water use reduction or environmental reasons, this specific problem will become more common. Many schemes for reuse/recycle of treated industrial wastewaters, particularly in the electronics industry, will provide a soft water for use as cooling tower makeup. Plants using soft waters as cooling system makeup are advised to guard against this misuse of technology and utilize a water treatment program supplier who has demonstrated knowledge in the use of soft water makeup.

The use of softening to render a hard water source suitable for use as cooling tower

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makeup should be evaluated very carefully as to the potential for increasing "white rust" corrosion of new galvanized steel components. Due to the normally high level of alkalinity associated with hard waters, softening may accelerate white rust corrosion by factors exceeding 100 times. We recently inspected a new softened makeup cooling tower system and found that over 50% of the galvanizing had been removed from the cooling tower in less than thirty (30) days.

SCALE

Deposition of scale is a chemical precipitation process where dissolved salts in the cooling water "out" surfaces in contact with the water due to their solubility limits being exceeded. The most common scale formers, calcium salts, exhibit reverse solubility in that they become less soluble as the temperature of the water increases. This property causes scale formation in the most sensitive area, the heat transfer surfaces of production equipment.

Since the thermal conductivity of scale is substantially less than metal, heat removal from the equipment is reduced and production speeds must be lowered to compensate. In extreme cases, enough material precipitates to physically block the cooling water passages, resulting in the effected equipment being removed from production for either chemical (acid) or mechanical cleaning.

Scale formation on the condensers of chillers reduces the efficiency of these units for removal of heat from chilled water systems, thus increasing the power needed to obtain a given volume of chilled water. Various studies have shown a non-linear electrical power cost increase with increased scale thickness, for instance 0.5 mils of calcium scale results in a power cost increase of 3.5 %, while 1.5 mils increase power cost to approximately 12.5%.

Control

Scale can be controlled, or eliminated, by application of one, or more, proven techniques. Typical measures taken to control scale start by controlling cycles; followed with chemical scale inhibitor treatment, pH adjustment by acid addition, or softening of cooling water system makeup.

As noted, cycles are best controlled by installation of a high quality system for automatic blow down based on conductivity or metered makeup. Chemical scale inhibitors function by either selective adsorption on growing scale crystals, converting the crystal structure into a non-scaling type which does not form a hard scale, or chemical reaction with the scale forming ions, converting them into non-scale forming materials.

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As with corrosion inhibitors, mixtures of scale control chemicals have been found to generally provide superior performance to single component products. Thus most formulated products will often contain two, or more, materials, typical formulations usually contain one, or more, phosphonates combined with polyacrylate.

As a general rule, typical chemical scale inhibitors can be utilized if the Langelier Saturation Index (SI) value of the cycled cooling water does not exceed 2.0. Cycled cooling water SI values exceeding 2.0 normally require use of exotic chemistries, pH adjustment by acid addition, or makeup water softening. Our firm, as well as some others, has reported operation of cooling systems, with newer treatment chemistries, scale free at cycled SI values from 2.8 to 3.5 without pH adjustment.

pH Adjustment

Control of scale with pH adjustment by acid addition functions via chemical conversion of the scale forming materials to more soluble forms. Thus, calcium carbonate is converted to calcium sulfate (using sulfuric acid for pH adjustment), a material several times more soluble. Normally, it is not desirable to add sufficient acid to convert all of the scale forming materials due to a substantial increase in the corrosivity of the cooling water if this is accomplished.

Of course, addition of excessive acid to the cooling water results in depressed pH values and extremely rapid corrosion of all system metals.

The SI and another index, the Ryznar Saturation Index (RSI), are utilized for system setup when pH adjustment by acid addition is used for scale control. Both indexes are merely convenient means of reducing the integrated parameters of calcium, alkalinity, pH, dissolved solids, and temperature to a single value, which indicates the tendency of water to form a calcium scale or promote corrosion. Thus,, a positive SI number (RSI less than 5.0) indicates a scale forming water, while a negative SI number (RSI greater than 7.0) indicates a scale dissolving, or corrosive, water

Normal practice is to maintain a slightly positive SI number, +0.2 to +0.5, (RSI between 5.0 and 6.0) when utilizing pH adjustment by acid addition and add some chemical scale inhibitor to cope with the resultant slight tendency to scale. Instances have been reported where scale has been

controlled with makeup calcium water hardness values up to 3000 mg/l as CaCO₃ with a combination of pH adjustment by acid addition and chemical scale inhibitors.

An important point to remember is that acid addition to cooling water should only be undertaken with an automatic pH control system and well trained operators. This caution

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is included; as serious corrosion damage will occur in a short period of time if excessive acid is added to the cooling water. Only high quality pH controllers equipped with acid pump lockout timers should be considered for this critical application. Daily plant control testing is required with use of pH control systems.

While not yet common usage, scale can be completely eliminated by softening all cooling system makeup water. It has been our experience that using softened makeup water for scale control is the safest, most cost effective method available. Normally, the added cost of softened makeup water is balanced by the decreased chemical and water usage resultant from the increased cooling system cycles made possible by the soft water.

The increased general corrosiveness of the softened water is countered by the high pH values (8.5 to 9.5) developed when the cooling system is cycled up with softened makeup. This, in combination with a good chemical corrosion inhibitor program, usually results in lower corrosion rates than the same cooling system using chemical scale inhibitors or pH control by acid addition. Note that specific inhibitor technology for control of white rust must be utilized with softened makeup water.

DEPOSITION

Deposition is a general term for all the things that can cause problems in a cooling water system that are NOT due to scale, corrosion, or biological activity. We find that such deposition can result from scrubbing of airborne material from the ambient air by the cooling tower, process contamination of cooling water by such things as leaking oil coolers, and suspended material in the makeup water.

Deposition effects process operations much like scale, the deposits act as a thermal insulator to decrease heat transfer efficiency in production equipment. Deposition can also cause physical blockage of cooling water passages and increase corrosion rates by blocking corrosion inhibitor access to the base metal, i.e., under deposit corrosion.

Control

Measures taken to control deposition depend on the cause of the problem. Process contamination problems are best corrected by elimination of the process leakage, while most suspended solids deposition can be controlled by addition of dispersant/surfactant chemicals to the cooling water. These materials function by charge neutralization of the suspended particles and emulsifying binding agents, breaking up existing deposits and preventing agglomeration of the particles to form new deposits.

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Severe suspended solids deposition should be treated with a combination of chemical dispersants/surfactants and an element filter, hydro- cyclone, or media filter, in a side stream configuration. Due to zero excess water loss operation, and lower cost, a hydro-cyclone set up to discharge via system blow down is oftentimes preferred over a media filter.

We have found that if a cooling system is to be operated at over six (6) cycles, some form of bypass filtration is required to prevent deposition and resultant under deposit corrosion problems. In dusty environments, such of bypass filtration may be required, regardless of the chemistry or cycles operated at.

BIOLOGICAL FOULING

Microbiological growth within a cooling water system, if not controlled, can result in formation of biological fouling layers on all surfaces in contact with the cooling water. The biological fouling effects process operation much like the previously discussed scale and deposition, the biological fouling acting as a thermal insulator to decrease heat transfer efficiency in the production equipment. Biological fouling usually results in substantial corrosion rate increases due to formation of anaerobic areas under the fouling layer, which creates galvanic couple corrosion, and formation of metabolic byproducts, such as hydrogen sulfide, which actually attack the base metals.

Severe cases of biological fouling have resulted in complete cooling system failure due to the biomass physically plugging cooling water passages in production equipment and cooling towers.

Waterborne diseases, such as Legionnaire's Disease, are also a major health and safety concern with operation of many cooling water systems. Systems which are not maintained in a clean and biologically controlled state can often be sources of such infections, which can sicken, or even kill, exposed employees.

Chemistry

Present practice for control of biological fouling is to periodically dose the cooling system with a biocide to kill as many of the organisms present as possible. Again, the critical point concerning control of biological fouling is to remember that the dose makes the poison. Simply put, a biocide will not work unless a critical dosage is reached and maintained for a set time period. The critical dosage point and time required for effective microbiological control varies substantially with the specific biocide in use and the overall condition of the cooling water system.

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The biocides commonly used can be broadly broken into two major classes, **oxidizing and non-oxidizing**

Oxidizing biocides function by chemical oxidation of the cellular structure of the organism, which effectively destroys it and kills the organism. Due to the destructive form of attack, it is impossible for any organism to show, or develop, significant immunity to an oxidizing biocide. Oxidizing biocides are usually quite cost effective due to their low unit cost, rapid effect on the target organism, and low effective dosage.

Unfortunately, **oxidizing biocides** do have some drawbacks.

- Some can decrease cooling water pH in an uncontrolled manner (gas chlorine and chlorine dioxide generators).
- Most increase the corrosive nature of the cooling water.
- Some, such as chlorine, produce undesirable by products from an environmental standpoint.
- Corrosion and scale control chemicals can be inactivated by contact with specific oxidizers.
- None of the oxidizing biocides have any dispersant effect for removal of dead microbiological growth and/or penetration of organic slime layers.
- Process contamination can neutralize many oxidizers.
- Some oxidizers are sensitive to water pH as to effectiveness.

Non-oxidizing biocides function by interference with the metabolism of the organism in a variety of ways, which by preventing normal processes kills the organism. Due to the large variety of organisms, those that are immune to a particular non- oxidizing biocide will rapidly replace those that are killed by a single dosage. Following doses will become progressively less effective as the organism population shifts to those varieties that are immune to the particular biocide employed.

Due to this natural effect, it is recommended that at least two different non- oxidizing biocides, or a oxidizing and a non-oxidizing biocide, be utilized in biological control programs on an alternating basis.

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Non-oxidizing biocides can be quite costly due to the high effective dosage required with some products, long contact times required with some products, and their often high unit cost.

Non-oxidizing biocides do have advantages in that most function in the presence of process contamination, no effect on corrosivity is evident from their use, corrosion and scale control chemicals are usually not effected by them, often they can be targeted at a specific class of problem organism, and several have a definite dispersant effect for removal of dead microbiological growth.

Typical practice for successful cooling water treatment will employ both an oxidizing and non-oxidizing biocide, with usage alternated on a weekly, or biweekly, basis.

Note should also be made concerning several "all in one" products, which package a non-oxidizing biocide with inhibitor chemistry for control of corrosion, scale, and deposition in one drum. Our experience has been that these products are almost worthless for effective control of biological fouling due to the inability to alternate biocides, adjust biocide dosage independent of the other inhibitors, and the particular chemistry of the biocide mandated by the other components in the product.

Control

Control of biocide feed is somewhat subjective in that a visual determination of microbiological growth is generally used to determine if the biocide program is effective.

Portable "dip stick" indicators to test organism density are available and will likely be utilized.

Local Service

The local service representative of the supplier is also very important to the success, or failure, of any water treatment program due to intimate involvement in chemistry specification, program control, and troubleshooting. The user is advised to carefully screen the supplier representatives and obtain one who has both a technical background and experience in the cooling water treatment field as applied to industrial plants.

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