

SLAC-PUB-6097
March 1993
(M)

**CHEMICAL APPROACHES TO
ZERO BLOWDOWN
OPERATION ***
(TP93-05)

G. E. Geiger
Betz Industrial
1 Quality Way
Trevose, PA 19053

J. Ogg
Stanford Linear Accelerator Center
Stanford University
Stanford, CA 94309

and

M. R. Hatch
Betz Industrial
622 Contra Costa Blvd
Pleasant Hill, CA 94523

*Work supported by Department of Energy contract DE-AC03-76SF00515.

*Presented at the 1993 Cooling Tower Institute Annual Meeting,
New Orleans, Louisiana, February 17-19, 1993*

ABSTRACT

Zero blowdown operation was evaluated at a cooling tower at the Stanford Linear Accelerator Center in an attempt to eliminate cooling water discharge. Testing was performed with and without acid feed for pH control using a state-of-the-art treatment which contained polymer, phosphonate, and azole. Supplemental addition of a proprietary calcium carbonate scale inhibitor was also evaluated.

INTRODUCTION

In August, 1990 the California Regional Water Quality Control Board ordered the Stanford Linear Accelerator Center to develop a plan to meet new limits for surface water discharge. At that time, the five cooling towers discharged approximately 25,000 gpd of water directly into small streams running off-site. The Accelerator Center is operated by Stanford University under contract with the Department of Energy.

The new limits, effective by December 1, 1991, prohibited discharge of heavy metals to a few parts per billion. For example, copper was limited to 20 µg/L.

The new discharge limits could not be met using conventional water treatment technology and blowdown to surface waters. On-site disposal by evaporation ponds and landscape irrigation was not acceptable for cost and environmental reasons.

Discharge to the sanitary sewer system was clearly the practical solution. The less stringent discharge limits for sewer blowdown could be met with using conventional water treatment.

At best, obtaining permission to discharge to the sanitary sewers would take months. At worst, permission could not be obtained. To assure the continued and uninterrupted operation of the laboratory, successful operational experience with zero blowdown was mandatory.

One tower was set up on zero blowdown in February, 1991, to provide operational experience before the mandatory compliance date of December, 1991. Concurrently, action to obtain a sewer permit was underway.

Conventional chemical treatment technology incorporating specific improvements was retained for the

zero blowdown test rather than changing to a different technology such as ozone.

Ozone was rejected for both cost and capability considerations. Ozone required new and expensive equipment and upgrading of the old and overloaded electrical system. In contrast, changes needed for the improved chemical treatment were minimal. Furthermore, there was concern about the capability of ozone to prevent fouling in the 25 year old, one mile long cooling loop.

SYSTEM DESCRIPTION

The cooling system for the linear accelerator is two miles long and contains 30 mechanical alcoves. Each alcove contains exchangers that employ both shell-side and tube-side cooling. The cooling system provides indirect cooling for a closed water system that maintains the magnets on the linear accelerator at a constant temperature of 130 °F.

Cooling is supplied by two identical cooling towers, designated CT-1201 and CT-1202. The cooling towers have a recirculation rate of 6,000 gpm and operate with a 10 °F ΔT. Return water temperatures are, at most, 100 °F. The systems have a volume of 120,000 gal. The towers service two separate cooling systems that contain low carbon steel, stainless steel, copper/nickel, and copper metallurgy. Water velocities are as low as 0.5 fps. The hottest bulk water temperature is about 113 °F.

The CT-1202 system was selected for the zero blowdown trial, while the CT-1201 system served as the control. The CT-1201 system is treated with a conventional inorganic phosphate program that utilizes high levels of orthophosphate to passivate mild steel. An azole is also added for the protection of yellow metal. The cooling tower operates at 10 to 15 cycles. Acid feed provides pH control. Corrosion rates are typically 1–3 mpy for mild steel and 0.1 mpy for copper/nickel (90:10).

Both systems use an identical treatment program for microbiological control. Sodium hypochlorite solution is fed continuously to maintain a 0.2–0.5 ppm free chlorine residual. A non-oxidizing biocide is shot fed periodically.

At the beginning of the trial, selected heat exchangers along the accelerator were cleaned and photographed to serve as references for future inspections.

TREATMENT PROGRAM

Treatment Considerations

When voluntary blowdown was eliminated, the research facility expected that the cooling tower would highly concentrate the circulating water. The maximum cycles achieved by the tower would be limited only by drift and windage losses.

The treatment program was designed to operate at 20 cycles of concentration, which was believed to be the theoretical maximum for the 1202 tower, and without acid feed for pH control. At 20 cycles the recirculating cooling water would contain approximately 500 ppm calcium hardness (as CaCO_3), 220 ppm magnesium hardness (as CaCO_3), 500 ppm M alkalinity (as CaCO_3), and 120 ppm silica (as SiO_2). At these conditions the Langelier Saturation Index (LSI) would exceed 2.5 when the pH of the circulating water exceeded 8.7. In the absence of pH control, calcium and magnesium silicates also represent potential scale forming deposits.

Scale Control

Control of calcium carbonate, calcium silicate, and magnesium silicate precipitation and deposition is complicated by the long system retention times. Long retention times are experienced at high cycle operation with systems having low heat loads (low cooling tower range). The retention time is about 36 days (75% depletion) at 20 cycles when the cooling tower is operating at a $10^\circ\text{F } \Delta\text{T}$. Retention times in excess of 10 days are considered severe for typical industrial applications.

Long retention times exacerbate scale control. This is because deposit control agents (threshold inhibitors) affect the kinetics of the precipitation reaction by delaying the formation of scale crystals and retarding crystal growth. High treatment concentrations are required to maintain a metastable state with regard to crystal growth.

The most formidable problem associated with operating at high cycles of concentration is the prevention of mineral scale, specifically calcium carbonate and silicates. High cycle/high pH operation also presents treatment-related problems. This is because many of the commonly used scale inhibitors (polymers and phosphonates) form insoluble salts with calcium that can act as foulants. More importantly, precipitation of the deposit control additive can result in a loss of scale control.

Corrosion Control

Corrosion control is not nearly as problematic as scale control because of the naturally lower corrosiveness of alkaline pH waters that are supersaturated with calcium carbonate and silicate salts. Both materials suppress the cathodic corrosion reaction by forming films at the metal surface that interfere with oxygen reduction. Although film formation can suppress corrosion, it is generally insufficient for overall protection.

Surface films tend to be porous, which result in the formation of differential oxygen cells that cause localized corrosion. The localized corrosion generally manifests itself as pitting corrosion.

Treatment Components

The treatment program designed for the 1202 cooling system included:

- acrylic acid/allyl ether copolymer: to inhibit scale forming salts and provide fouling control for particulate matter (clays, silt, and metal oxides)
- phosphonate (hydroxyethylidene diphosphonic acid, HEDP): to inhibit corrosion of ferrous alloys and to control deposits
- azole (tolyltriazole): to inhibit corrosion of copper alloys

The phosphonate was selected based on its hydrolytic stability, ability to inhibit mild steel corrosion, and ability to prevent calcium carbonate precipitation and deposition. As a class, phosphonates are the most effective calcium carbonate inhibitors; they provide much greater inhibition than acrylate-based polymers.

Partial degradation of the phosphonate by hypochlorite was anticipated. However, the degree of degradation cannot be projected with any certainty at the long retention times encountered with high cycles.

Phosphonates are susceptible to oxidation by chlorine, which attacks the carbon-phosphorus bond. Destruction of the bond releases orthophosphate and results in the loss of calcium carbonate deposit control and the potential for calcium phosphate scaling. Additionally, at high pH and high calcium hardness conditions, phosphonates can form insoluble salts with calcium. Thus, phosphonates can become potential foulants.

The polymeric dispersant must assume a multifarious role when high cycles are to be achieved at highly alkaline pH conditions. The polymer must prevent fouling by particulate solids, which enter the system from airborne contamination, corrosion products, and precipitates that form in the bulk recirculating water. Additionally, the polymeric dispersant must be capable of inhibiting the precipitation of both calcium phosphate and calcium phosphonate and must be immune from precipitation with calcium.

Treatment Approach

A two product approach was used to allow adjustment of the polymer independently of the phosphonate and azole. A combination of the copolymer, phosphonate, and azole in one product (designated 35K) and the copolymer alone in the second product (designated 40K) was applied. Polymer was included in the 35K product to ensure adequate deposit control if the feed of the 40K product was accidentally discontinued.

The product feed rate to the makeup water was calculated so it achieved 200 ppm 35K and 100 ppm 40K when the recirculating water was at 20 cycles. The 35K feed rate was increased when cycles were below 20 to maintain sufficient phosphonate and azole for corrosion inhibition. No adjustment in treatment feed rate was made when cycles exceeded 20. This permitted the treatment concentration in the recirculating water to increase proportionally with cycles and, hence, scaling potential.

Treatment performance was monitored with corrosion coupons, corrosion rate meters, and a portable deposition monitor. The deposition monitor was attached to the return water riser of the cooling tower. It employed an Admiralty brass heat transfer surface and operated with a water velocity of 2–3 feet per second (fps) and a surface temperature of 110–120 °F.

TRIAL SUMMARY

Phase I

Phase I determined the pH control range for the treatment program.

Operation with Uncontrolled pH (pH ≥ 9)

The 35K/40K treatment program was initiated in February 1991 at Cooling Tower 1202. The cooling tower was operated without pH or cycles control.

Cycling was limited for the first few months by the low heat load on the system.

During the first four months of the trial (February to June) calcium levels increased from 170 ppm to 521 ppm, the pH went from 7.9 to 9.0, and the conductivity increased from 1170 to 2560 μ mhos. At the same time the cycles increased from 6 to 17, based on calcium hardness.

The total phosphate in the cooling tower water was 15–22 ppm, corresponding to a 35K dosage of about 250–360 ppm. (The 35K program contains 6% phosphonate, as PO_4^{3-} .) Of the total phosphate, 35–50% was present as orthophosphate after the chlorine degradation of the phosphonate. The 35K/40K dispersant combination completely prevented the precipitation of hardness salts and calcium phosphate. The cooling tower, corrosion coupons, and test heat exchanger surface remained free of scale deposits.

Mild steel and Admiralty brass corrosion rates averaged 0.4 mpy and 0.1 mpy, respectively. Corrosion coupons were free of any signs of localized corrosion.

After three months of operation, reference heat exchangers were opened for inspection. The exchangers on the zero blowdown tower were as clean as the day the test started. The exchangers on the control tower were acceptable, but not perfectly clean. Corrosion control was judged to be excellent with both sets of exchangers.

By mid-June, the cycles began to increase rapidly and precipitation of calcium carbonate was detected by calcium losses in the circulating water. Cycles based on calcium hardness were lower than those based on magnesium or sulfate. The water analyses showed the cycles of concentration to be 19, based on calcium, and 23–27, based on magnesium and sulfate. Total phosphate levels were up to 26 ppm, with 7.6 ppm present as orthophosphate.

The first signs of scaling were evident in July when a very thin white deposit was noticed on the cooling tower fill. At this time cycles exceeded 40 (based on magnesium and sulfate levels). Cycles based on alkalinity, calcium (492 ppm), and silica (145 ppm) concentrations were 19, 20, and 23, respectively (see Table 1). The pH of the recirculating water was 9–9.2 and the conductivity was 4430 μ mhos. The total phosphate level was 31 ppm, with 11.2 ppm present as orthophosphate. Filtered (0.2 μ m) and unfiltered orthophosphate and phosphonate analyses did not indicate any sign of precipitation in the circulating water.

These results clearly demonstrated that the copolymer was preventing precipitation of calcium phosphate and calcium phosphonate. However, at the high hardness and high pH conditions encountered at 40 cycles, even high dosages of the phosphonate (19.8 ppm HEDP) were incapable of preventing calcium carbonate scaling of the cooling tower. This could only mean that the scale control capability of phosphonate had been exceeded.

At 40 cycles the theoretical LSI is about 3.3 (pH 9.0–9.2 and 100 °F). The retention time of the system is 75 days when the cooling tower operates with a 10 °F ΔT .

Corrosion control between May 5 and August 8 was excellent. Test coupon corrosion rates were 0.3 mpy for mild steel and 0.0 mpy for Admiralty brass. Corrosion coupons were free of deposits and localized corrosion.

Operation at pH 8.0 to 8.5

In an attempt to eliminate scaling of the cooling tower, acid feed was initiated for pH control in early July. The pH of the recirculating water was controlled at 8 to 8.5 by the addition of sulfuric acid. This precluded basing cycles on sulfate concentration.

By early August, it was apparent that reducing the pH to 8–8.5 would not stop scaling of calcium carbonate or silicate salts. Furthermore, extremely high treatment dosages (480 ppm of 35K and 240 ppm of 40K) did not provide complete prevention of deposition.

From July to mid-August the calcium hardness held constant at about 600 ppm and the magnesium was 429–472 ppm. This corresponded to 24 cycles, based on calcium, and 42–49 cycles, based on magnesium. Total phosphate and orthophosphate concentrations averaged 29 and 15 ppm, respectively. Differences between the phosphate values of filtered and unfiltered circulating water samples were <1 ppm. This indicates that complete control of calcium phosphate and calcium phosphonate precipitation was being maintained, even in the presence of calcium carbonate precipitation and deposition.

Paper thin scale deposits were evident on both the cooling tower and the deposition monitor. The cooling tower fill deposit was almost pure calcium carbonate (93%). Seventy-five percent of the deposit on the heat transfer surface of the deposition monitor contained calcium silicate/magnesium silicate, magnesium silicate, and silica.

In mid-August the pH of the cooling system was reduced further to 7.5–8.0. The 1202 cooling system was inspected just after the pH was reduced to assess the condition of the process heat transfer equipment. All of the heat exchangers were free of scale, with the exception of one that had a soft deposit. No corrosion problems were identified during the inspection.

The soft deposit was about $1/16$ of an inch thick, and it uniformly coated the heat transfer surface. The deposit was very similar in composition to that of the deposition monitor. The primary constituents were silica, magnesium silicate, and calcium/magnesium silicate (62%). About 9% of the deposit was calcium phosphate. The deposit contained 23% LOI (loss on ignition), of which approximately 15% consisted of diatoms and small flocs of decomposing bacterial rods.

The loss of calcium from the circulating water was attributed to the scaling of the cooling tower fill and not to process equipment.

Operation at pH 7.5 to 8.0

Testing at the lower pH condition was performed between mid-August and early December. During this time, the calcium concentration of the circulating water increased steadily from 624 ppm to 1112 ppm. The conductivity increased from 5790 to 8200 μmhos , and cycles of concentration exceeded 40 (see Table 2 for water analysis).

Performance was excellent during this test period. The scaling previously noticed did not occur at these lower pH's. The corrosion coupons and test heat exchanger surface remained free of deposits during the entire test. New slats installed in the cooling tower did not show any signs of fouling. Treatment concentrations averaged about 400 ppm of 35K and 200 ppm of 40K. The total phosphate concentration averaged 24 ppm, with 14 to 16 ppm present as orthophosphate. Corrosion results remained exceptional at 0.5 mpy for mild steel and 0.2 mpy for Admiralty brass.

Phase II

Phase II concentrated on improving the 35K/40K treatment program to allow operation at zero blowdown without pH control.

Experience with the 35K/40K products demonstrated that about 20 cycles could be treated with uncontrolled pH (pH 8.8–9.2) without encountering scaling. High dosages of dispersant were unable to

prevent calcium carbonate and silicate salt precipitation and deposition at 40 cycles when the pH exceeded 8.

The 35K/40K program was supplemented by the addition of a newly developed oligomeric scale control agent. The proprietary oligomer was developed specifically for high cycle cooling waters operating at alkaline pH. It is a non-phosphorus material that is not affected by chlorine and does not form insoluble precipitates with hardness cations.

Feed of the oligomeric material was initiated in early December as a supplement to the existing program. The plan was to evaluate the material in stages. The first phase would be determined if the pH could be increased to 8-8.5 without reducing cycles. If the program was successful, acid feed would be terminated and the system would be operated without pH control. The final phase of testing would assess the performance of the oligomer and polymer (40K) in the absence of phosphonate.

Operation at pH 8-8.5

The cooling system was operated at over 40 cycles from early December 1991 to March 1992; acid feed was used for pH control. During this period, the calcium hardness was 700-1,200 ppm. Phosphonate concentrations were 8-10 ppm. An almost equal amount of orthophosphate was present from reversion (see Table 3).

Scaling was not observed on the corrosion coupons, deposition monitor, or the cooling tower. System equipment did not experience any noticeable decrease in heat transfer performance.

Corrosion rates were 0.4 mpy for mild steel, 0.1 mpy for copper, and 0.1 mpy for copper/nickel (90/10).

Uncontrolled pH

In late March, acid feed for pH control was discontinued. The pH of the system equilibrated at 9-9.2 and cycles remained at over 40. Calcium concentrations were 900-1,200 ppm and the M alkalinity was 700-750 ppm. The circulating water was now operating with a LSI over 3.2. (See Table 4 for water analyses.)

After three months of operation, scaling was not observed on monitoring equipment or in the cooling tower. No loss in heat transfer efficiency occurred.

The phosphonate containing product (35K) was discontinued in June to determine if the combination of oligomer and polymer would provide both corrosion and scale inhibition. At the time this paper was written, the phosphonate and orthophosphate concentrations have been reduced to 2.0 and 3.2 ppm, respectively.

Because of the long system retention time, intermittent blowdown had to be initiated to reduce the phosphonate and orthophosphate concentrations. Blowdown was sent to the sanitary sewer system. By this time the other four towers operating with blowdown had already been shifted to the sanitary sewer.

The system is still operating at over 40 cycles without any indications of scaling. Corrosion results remain good (< 1 mpy for steel and < 0.2 mpy for copper), but an accurate assessment cannot be made until the phosphonate and inorganic phosphate are completely purged from the system.

Testing is ongoing to fully evaluate a non-phosphorus approach to zero blowdown. Hopefully, this work will lead to a program that is both effective and environmentally acceptable.

CONCLUSIONS

- On-site testing has shown that zero blowdown is a viable option with chemical treatment programs at this research facility.
- In the absence of pH control, calcium carbonate scale could not be completely controlled by high dosages of HEDP and polymer at the high cycles and long retention times experienced during zero blowdown operation.
- Programs utilizing phosphonate for deposition and/or corrosion inhibition will require a good calcium phosphate inhibitor if chlorine is used for microbial control.
- A proprietary oligomeric material extended the pH application range of phosphonate/polymer. The addition of the oligomer eliminated the need for acid addition for pH control. Testing indicates that the oligomer alone or in combination with a polymeric dispersant may provide acceptable performance at zero blowdown conditions in the absence of pH control. However, additional testing is necessary to corroborate these contentions.

Table 1: First Indication of Precipitation with Uncontrolled pH (7/10/91)

	Makeup	CT-1202	Cycles
pH	8.2	8.9	
Specific Conductance, μ mhos	134	4430	
Alkalinity, "P", as ppm CaCO ₃	0	90	
Alkalinity, "M", as ppm CaCO ₃	38	731	19
Sulfate, ppm	13.6	679	50
Chloride, ppm	<10	1060	
Total Hardness, as ppm CaCO ₃	34.6	913	
Calcium Hardness, as ppm CaCO ₃	25.0	492	20
Magnesium Hardness, as ppm CaCO ₃	9.6	417	43
Total Iron, ppm	<0.05	0.83	
Sodium, ppm	9.8	911	
Total Phosphate, as ppm PO ₄	<0.4	31	
Orthophosphate, as ppm PO ₄	<0.2	11.2	
Silica as ppm SiO ₂	6.3	145	23

Table 2: Water Conditions at pH 7.5 – 8.0 (11/01/91)

	Makeup 11-01-91	CT-1202 11-01-91	CT-1202 10-11-91
pH	7.1	7.6	7.2
Specific Conductance, μ mhos	87	7560	6450
Alkalinity, "P", as ppm CaCO ₃	0	0	0
Alkalinity, "M", as ppm CaCO ₃	24	129	106
Sulfate, ppm	<10	2380	2200
Chloride, ppm	<10	1750	1640
Total Hardness, as ppm CaCO ₃	25	1500	1530
Calcium Hardness, as ppm CaCO ₃	19.1	888	966
Magnesium Hardness, as ppm CaCO ₃	5.3	604	552
Total Iron, ppm	<0.05	1.7	1.6
Sodium, ppm	8.6	1499	1390
Total Phosphate, as ppm PO ₄	<0.4	23	24
Orthophosphate, as ppm PO ₄	<0.2	16.3	15.5
Silica, as ppm SiO ₂	<5	123	125

Table 3: Water Chemistry at pH 8–8.5 with Oligomer Top-Off (5/18/92)

	Makeup	CT-1202
pH	6.2	8.5
Specific Conductance, μ mhos	74	8060
Alkalinity, "P", as ppm CaCO ₃	0	55
Alkalinity, "M", as ppm CaCO ₃	20	700
Sulfate, ppm	<10	1470
Chloride, ppm	<10	2060
Total Hardness, as ppm CaCO ₃	22	1690
Calcium Hardness, as ppm CaCO ₃	18	1190
Magnesium Hardness, as ppm CaCO ₃	4.2	496
Total Iron, ppm	<0.05	0.6
Sodium, ppm	7.1	1690
Total Phosphate, as ppm PO ₄	<0.4	16.8
Orthophosphate, as ppm PO ₄	<0.2	8.2
Silica as ppm SiO ₂	5.2	156

Table 4: Water Chemistry with Oligomer Top-Off and Uncontrolled pH (7/10/92)

	Makeup	CT-1202
pH	6.6	9.2
Specific Conductance, μ mhos	117	8060
Alkalinity, "P", as ppm CaCO ₃	0	113
Alkalinity, "M", as ppm CaCO ₃	28	729
Sulfate, ppm	<10	1590
Chloride, ppm	14.6	2170
Total Hardness, as ppm CaCO ₃	27	1270
Calcium Hardness, as ppm CaCO ₃	21	989
Magnesium Hardness, as ppm CaCO ₃	6	334
Total Iron, ppm	0.14	0.84
Sodium, ppm	10.2	1530
Total Phosphate, as ppm PO ₄	<0.4	9.5
Orthophosphate, as ppm PO ₄	<0.2	4.9
Silica, as ppm SiO ₂	<5	156