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SHORT-TERM PILOT COOLING TOWER TESTS

Dan F. Suci
Richard L. Miller

U.S. Department of Energy

Idaho Operations Office • Idaho National Engineering Laboratory

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ABSTRACT

Two major problems are associated with the use of cooled geothermal water as coolant for the 5 MW(e) pilot plant at Raft River. They are: (1) a scaling potential owing to the chemical species present in solution, and (2) the corrosive nature of the geothermal water. Tests were conducted to obtain data so that methods can be devised to either reduce or eliminate effects from these problems. Data show that scaling can be prevented, but only by using a high concentration of dispersant. Pitting data, however, are not as conclusive and seem to indicate that pitting control cannot be realized, but this result cannot be substantiated without additional experimentation. Results also demonstrate that chromate can be removed by using either chemical destruction or ion exchange. Whichever method is used, EPA discharge limits for both chromate and zinc can be achieved. A preliminary economic analysis is presented.

SUMMARY

The Raft River 5 MW(e) pilot power plant will use cooled geothermal water as make-up for the cooling tower. This requires that silica be removed before use and water be treated with corrosion inhibitors. The experiments reported here were designed to test the effectiveness of three compounds for removal of silica, a chromate-zinc corrosion inhibitor, a polyacrylate dispersant for scale control, and three methods for controlling chromate in effluent waste water.

Results of tests to reduce the silica level in the geothermal make-up water showed that, of the chemicals tested, $MgCl_2$ was the best to use in the present pretreatment system in place of the dolomitic lime. This selection was based upon effectiveness in reducing silica, cost, and the tendency not to form scale.

Tests showed that while the chromate levels tested controlled general corrosion, pitting corrosion was very high and sufficient to lead to tube perforation within 1 to 2 years of operation. These conclusions, however, are based upon only one week's exposure to corrosion compounds and may be misleading, since pitting corrosion frequently accelerates with time. Further, extremely high levels of chromate were required to achieve any kind of protection. Such levels would result in an extremely costly system to operate without chromate recovery and may represent an unacceptable environment around the tower. Based upon this limited test data, it has been concluded that an acceptable water treatment system has not yet been established for the 5 MW(e) pilot power plant.

Bench tests show that the chromate destruct system can use either sodium bisulfite (currently specified for the 5 MW(e) system) or ferrous sulfate to reduce chromate and zinc to acceptable levels in the tower blowdown stream. Electrochemical reduction was inconclusive. Chromate recycle recovery is possible and will almost certainly be necessary because of the high operating (chemical) cost when a destruct system is employed.

Recommended nominal^a operating conditions for the water treatment system, assuming no changes in the equipment permitted, are:

Pretreatment

Make-up water temperature [nominal, 333 K (140°F)^a
minimum recommended temperature
is 327 K (130°F)]

Make-up water rate to pretreatment system 22.4 l/s (356 gpm)

Chemical feed rates:

MgCl₂ 0.08 l/s (1.3 gpm)

Ca(OH)₂ 0.08 l/s (1.3 gpm)

Na₂CO₃ 0.08 l/s (1.3 gpm)

pH range 10.2 - 10.6

Pretreatment sludge discharge rate 0.09 l/s (1.5 gpm)

Tower water treatment

Maximum allowable silica level in 100 ppm as SiO₂
cooling water

Biocide/slimicide addition rate (as defined by FSEC)

Dispersant addition rate 0.001 l/s (0.03 gpm)

Chromate and zinc 0.002 l/s (0.03 gpm)

pH range 6.2 - 6.8

Blowdown treatment

Blowdown rate 1.9 l/s (30 gpm)

Blowdown sludge discharge rate 0.06 l/s (1 gpm)

These chemical feeds and operating conditions will yield the following:

Cooling tower cycles of concentration 8

- a. Nominal conditions are based upon heat rejection of 45 MW and plant effluent temperature of 140°F. Other operating conditions will require different requirements.

Approximate silica content of cooling water	100 ppm SiO_2
Chloride content of cooling water	9000 ppm
Chromate level	450 ppm CrO_4^{-2}
Zinc level	15 ppm Zn^{+2}
Estimated general corrosion rate	$38-55 \frac{\text{mg}}{\text{dm}^2 \text{ day}}$ (7 - 10 mpy)
Estimated pitting rate	60 $\mu\text{m}/\text{week}$
Estimated condenser life.	35 weeks

The corrosion rates are linear extrapolations of one-week corrosion data. The recommended conditions are based upon operating the system with the minimum number of cycles of concentration permitted by the equipment; the limiting equipment is the 2.0 l/s (32 gpm) capacity of the chromate destruct system.

It is recommended that the system be modified for recycling/recovery of chromate. Reuse of chromate will be cost effective since the estimated yearly cost of this material is about \$300,000.

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SHORT-TERM PILOT COOLING TOWER TESTS

1. INTRODUCTION

The Raft River 5 MW(e) pilot power plant is located in a region where neither ground nor near-surface aquifer water is available for make-up to the plant's evaporative cooling tower. Therefore, the plant will use cooled geothermal water, discharging from the power plant, as coolant to circulate between the condenser and the wet (open-loop, evaporative) cooling tower. This application requires that (1) silica be removed by means of a pretreatment process, and (2) the effluent be subsequently treated with biocides, corrosion inhibitors, and antiscalants, with the choice of corrosion inhibitor dependent upon condenser tube material selection. Based upon recommendations by Garrett Energy Research and Engineering (consultant and water treatment system designer for the architect-engineer, Facilities Systems Engineering Co.) and EG&G's water consultant, Cyrus W. Rice (Division of NUS), as well as discussions with personnel from major suppliers of water-treatment chemicals, low-carbon steel was selected for use as condenser tube material. Advantages relate to lower condenser costs as well as corrosion control by chromate.

The initial water treatment system was designed to use dolomitic lime (58 wt% Ca(OH)_2 and 37 wt% MgO) to remove silica and a chromate-zinc system for corrosion control. In addition, a Crane-Cochrane UNIPAC I chemical destruct unit, using sulfuric acid, sodium bisulfite, and lime, was to be used to remove chromium and zinc from the blowdown water prior to its discharge.

The initial make-up system was designed to reduce the incoming silica level to 10-15 ppm to provide make-up required for ten cycles of concentration. The system could treat 21.8 l/s (346 gpm) of make-up water and 2.0 l/s (32 gpm) of blowdown water, respectively.

However, Suciú and Miller¹ found, while conducting jar tests on the precipitation of silica from Raft River geothermal water, that reduction of silica did not occur to the extent predicted. They concluded that the data upon which the 5 MW(e) water treatment system was designed could not be

extrapolated to predict precipitation of silica from geothermal water, and therefore tested several other chemicals to determine their efficiency in precipitating silica.

The tests reported here were conducted to establish a new basis for the water treatment program. Three test cooling towers were designed, built, and installed at the Raft River site and used to study the effectiveness of three substitutes for the dolomitic lime originally prescribed for reduction of silica. In addition, the 5 MW(e) chromate destruct method was tested, and alternate means of chromate control using either ion exchange or electro-chemical methods were evaluated.

The specific objectives of these tests were to:

1. select an alternative to dolomitic lime for reducing silica levels within the make-up fluid using the existing pretreatment system;
2. determine concentration of dispersant required to prevent scaling at various cycles of concentration;
3. establish chromate levels necessary to prevent excessive corrosion, considering various cycles of concentration;
4. evaluate chromate destruct and recycle; and
5. recommend operating parameters under two conditions:
(a) no changes to the presently designed system, and
(b) with limited changes to the present system.

2. COOLING TOWER TESTS EXPERIMENTAL PROCEDURE

2.1 Pretreatment of Geothermal Water

Geothermal water was collected from Raft River Geothermal Wells Numbers 1, 2, and 5, mixed in a 300-gallon thickener tank in proportions of 2:1:1, respectively, and then cooled to 333 K (140°F).

The mixture was flash mixed during addition of either $\text{Mg}(\text{HCO}_3)_2$, MgCl_2 , or MgSO_4 , followed by lime to remove silica and soda ash to remove calcium. This mixture was slow stirred for twenty minutes after which the flocculent was allowed to settle for approximately one hour. Subsequently the water was pumped through a dual-medium filter of sand and anthracite and then gravity-fed into appropriate tanks for make-up to the cooling towers.

2.2 Cooling Tower/Condenser Recirculating System

The recirculating system used is shown in Figure 1. The chemical feeds were controlled by both pH and conductivity just as in actual practice, and the make-up addition was controlled by using a float mechanism within the tower basin. The pH and conductivity were regulated using a microprocessor (LSI 11) which operated appropriate valves at pre-determined set points.

2.3 CORROSION COUPONS

Carbon steel specimens were examined as follows:

- (a) scales were inspected visually,
- (b) corrosion rates were determined by means of weight loss, and
- (c) pit depths were determined microscopically.

2.4 CORROSION PROBES

Corrosion probes were inserted in the recirculating line and a Rohrbach model 1136 Corrator was used to monitor the instantaneous corrosion rates.

INEL-A-14 445

Figure 1. Cooling tower condenser system.

3. CORROSION TEST RESULTS AND DISCUSSION

Test data are shown in Tables 1, B-1, -2, and -3 of Appendix B and indicate that (1) acceptable general corrosion rates can be achieved by using 100 ppm hexavalent chromate, and (2) unacceptable pitting occurs for all levels of chromate tested. Data also indicate that scale deposition can be prevented, but only by using an extremely high concentration of dispersant, i.e., 50-60 ppm.

Table 1 summarizes test results and related expected costs for 5 and 8 cycles of concentration, respectively. Inhibitor antiscalant is unacceptable both in terms of performance and operating expense. The high levels of chromate also may pose environmental problems owing to chromate drift from cooling towers.

The general corrosion rates, indicated by probes, correlate well with weight loss data from metal coupons. In a majority of tests, the corrator indicated that the mode of corrosion was predominantly pitting, with a few tests showing the mode to be general corrosion. However, the magnitude of the pitting that occurred was not anticipated. There appears to be no correlation between the corrator pitting reading and the actual extent of pitting.

TABLE 1. RESULTS AND COSTS OF PRETREATMENT FOR SCALE AND CORROSION CONTROL (DATA FOR FIVE AND EIGHT CYCLES OF CONCENTRATION)

System	Five Cycles	Eight Cycles
Make-up flow rate	24.3 l/s (386 gpm)	22.2 l/s (352 gpm)
Blowdown flow rate	3.9 l/s (62 gpm)	1.9 l/s (30 gpm)
Chloride conc.	6000 ppm	9,000 ppm
Chromate conc.	335 ppm	400 ppm
Dispersant conc.	50 ppm	65 ppm
General corrosion rate	18.1 $\frac{\text{mg}}{\text{dm}^2 \text{ day}}$ (3.3 mpy) ^a	8.2 $\frac{\text{mg}}{\text{dm}^2 \text{ day}}$ (1.5 mpy)
Maximum pit depth	29 μm	29 μm
Lifetime of heat exchanger before perforation ^b	1.4 years	1.4 years
Pretreatment cost	\$0.12 /kl	\$0.12 /kl
(A) MgCl_2 , Ca(OH)_2 , Na_2CO_3	(\$0.45/1000 gal)	(\$0.45/1000 gal)
(B) sulfuric acid	\$0.02 /kl (\$0.08 /1000 gal)	\$0.02 /kl (\$0.08 /1000 gal)
Chromate addition	0.003 l/s (0.05 gpm)	0.002 l/s (0.03 gpm)
Dispersant addition	0.001 l/s (0.02 gpm)	0.001 l/s (0.02 gpm)
Chromate cost	\$600 /day	\$240 /day
Dispersant cost	\$200 /day	\$100 /day

a. Mils per year.

b. Based on a linear extrapolation of one week's test data; long-term pitting data are needed to generate reliable expected lifetime results.

4. CHROMATE REMOVAL SYSTEMS

Because chromium and zinc are toxic heavy metals, the Idaho Department of Health and Welfare requires that they be removed from the blowdown water prior to discharge. The maximum allowable discharge concentrations of these metals are 0.05 ppm of chromium as chromate and 0.1 ppm of zinc. A Crane-Cochrane UNIPAC I chemical destruct unit, using sulfuric acid, sodium bisulfite, and lime, is employed for this purpose in the 5 MW(e) plant.

Two chromate destruct methods were evaluated experimentally. One represented the system as designed for the 5 MW(e) plant, the other was an electrochemical method.

Fewer cycles of concentration require greater use of chromate. Because of the high cost of chromate, tests were conducted to determine the effectiveness of recovering the chromate for recycling purposes.

4.1 Chemical Destruct System Experimental Design

To determine the effectiveness to be expected from the UNIPAC I unit, blowdown samples were collected and analyzed for chromium and zinc. Equal volumes of blowdown were placed into a series of beakers and their pH adjusted to 3.0 by using sulfuric acid. Additions of varying concentrations of reducing agent followed. The samples were stirred and allowed to stand for 10 minutes, then treated with lime for final pH adjustment. The resultant flocculant was allowed to settle; the chromate and zinc concentrations in the supernatant were then determined using atomic absorption spectroscopy.

4.2 Electrochemical Destruction

A blowdown sample was placed into a 1000 cm³ beaker, and the beaker then fitted with two electrodes (carbon steel and zirconium), as shown in Figure 2. When the circuit was closed, the carbon steel electrode dissolved, the iron subsequently oxidized, and the chromium was reduced

from the hexavalent to the trivalent state which then precipitated as the hydroxide at the given pH. Residual chromium content in the liquid was then determined.

4.3 Chromate Recovery System

Blowdown samples (a total of 33 were collected) were placed into a 50-cm³ column containing a known amount of Rohm and Haas IRA-94 ion-exchange resin, and the pH subsequently adjusted to 4.0. Chromate was recovered by eluting with a 5 wt% sodium hydroxide solution (the resin was regenerated with a 5 wt% sulfuric acid solution). The zinc was recovered in a subsequent column (loaded with Rohm and Haas DP-1 resin) by eluting with a 5 wt% sulfuric acid solution and the resin was regenerated with a 5 wt% sodium hydroxide solution. For details see Figure 3.

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Figure 2. Chromate electrochemical destruction system.

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Figure 3. Chromate recovery ion exchange system.

5. TEST RESULTS AND DISCUSSIONS

5.1 Chemical Reduction of Chromate

Three chemical destruct systems were studied. They were: (1) sodium metabisulfite, (2) sodium bisulfite, and (3) ferrous sulfate. Data are tabulated in several tables in Appendix C and graphically displayed in Figures 4 and 5 for these systems. Both the sodium bisulfite and ferrous sulfate systems reduce chromate and zinc to acceptable levels, but the sodium metabisulfite system did not and was subsequently rejected.

5.2 Electrochemical Reduction of Chromate

Data concerning the electrochemical reduction of chromate are inconclusive owing to concentration polarization within the cell; that is, the current density becomes diffusion-controlled. Hence, the overall reduction becomes dependent on the first-order diffusion process, which is exponential, and cannot be clarified without further investigation. Data are listed in Table 2 and graphically shown in Figure 6.

5.3 Chromate Recovery via Ion Exchange

Chromate recovery by means of ion exchange should meet required levels, if a second column is added. Approximately 64 g of chromate can be recovered per litre of resin (4 lb/ft^3). This value, however, decreases with time, owing to mechanical breakage and fouling of the resin, to approximately 48 g of chromate per litre of resin (3 lb/ft^3).

Owing to the high levels of chromate and zinc required, their recovery is more economical than their destruction.

5.4 Blowdown Treatment Costs (Chemical Precipitation)

The costs for treating blowdown for chromate removal are based on 200 ppm hexavalent chromate, and are given in Table C-1, Appendix C.

Figure 4. Chromate reduction with sodium bisulfite in blowdown.

Figure 5. Chromate reduction with ferrous sulfate in blowdown.

TABLE 2. ELECTROCHEMICAL PRECIPITATION OF CHROMATE^{a,b}

<u>Time (min)</u>	<u>Chromium (6+) Conc. (ppm)</u>
0	278.5
10	249
20	221
30	199
40	168
50	155
60	130
70	108
80	92
90	72
100	62
120	47
130	34
140	22

- a. Reduction of chromate electrolytically, using a sacrificial carbon steel electrode, is $\text{Fe} + \text{CrO}_4^{-2} + 4\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + \text{Cr}(\text{OH})_3 + 2\text{OH}^-$
- b. For a current of approximately 1.0 ampere.
-

Figure 6. Chromate electrochemical reduction.

5.5 Chromate and Zinc Recovery Via Ion Exchange

Mechanisms are as follows:

For chromate

(a) loading

(b) recovery

(c) conditioning

For zinc

(a) loading

(b) recovery

(c) conditioning

The resins used, as previously stated, were Rohm and Haas resins IRA-94 and DP-1. The blowdown sample composition is as follows:

Cr^{6+} = 390 ppm, Zn^{+2} = 155 ppm, Ca = 1220 ppm (as $CaCO_3$),
 SO_4^{-2} = 1440 ppm, and Cl^- = 4185 ppm. Sample conductivity was 12,000 μS .

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Because the pilot cooling tower tests were of short duration, long-term corrosion projections based on data obtained are not reliable. However, data indicate that pitting protection is inadequate.

Scale deposition is controllable by using high concentrations of antiscalant. In addition, if calcium and sulfate concentrations are reduced there is a corresponding reduction in the amount of required antiscalant.

EPA discharge limits for both chromium and zinc for reinjected fluid can be met by using either chemical destruction or ion exchange.

6.2 Recommendations

6.2.1 Recommendations for Additional Experimentation

Test programs should be set up to determine effects of alternate treatment schemes regarding corrosion control of carbon steel. More specifically, these programs should include studies of the following:

- (a) effects of higher pH of the recirculating water in the tower.
- (b) effects of nonmetallic corrosion inhibitor systems.
- (c) effects related to prefilming with chromate and high-quality water prior to introduction of geothermal water.
- (d) effects related to use of alternative antiscalants for scale control.

- (e) effects of varying the zinc to chromate ratio

Alternatively, it would be prudent to investigate other heat-exchanger materials, especially materials requiring little or no corrosion protection.

6.2.2 Recommendations for the 5 MW(e) Pilot Power Plant Design

Recommendations are as follows:

- (a) that the magnesium chloride-lime-soda ash system be used for pretreatment of make-up water,
- (b) that chromate be recovered by means of ion exchange
- (c) that if chromate is removed instead of recovered, removal be by means of the ferrous sulfate reduction system,
- (d) that the cooling tower/condenser system be run at the maximum concentration allowed by the present equipment. This is eight cycles and is determined by the chromate destruct unit which limits blowdown to 2.0 l/s (32 gpm). (This may result in a shorter than desired lifetime for the heat exchanger, but would be cost-effective in the long run.)

6.2.3 Supplemental Recommendations

Use of a carbon steel heat exchanger at Raft River is costly owing to the large quantities of chemicals needed to make the system functional. Nonetheless, some savings in chromate costs can be achieved by feeding the blowdown directly back into the warm lime softener. However, this would increase solids in the cooling tower and may further shorten the already short life expectancy of the heat exchanger.

Another possibility is to treat all the make-up water by reverse osmosis and recover chromate by ion exchange. This would lower chemical cost and considerably extend the lifetime of the heat exchanger, but initial capital cost is estimated at \$900K.

7. REFERENCES

1. D. F. Suciu and R. L. Miller, Removal of Silica from Raft River Geothermal Water. (In preparation)

APPENDIX A

COOLING TOWER CALCULATIONS

APPENDIX A. COOLING TOWER CALCULATIONS

To determine flowrates through a cooling tower the following relation holds:

$$M = E + B + W \quad (1)$$

where

M = the make-up water,

E = the evaporation,

B = the blowdown (amount of water drained off),

W = losses due to windage.

Because windage losses are small as compared to other terms it is conventionally combined with the blowdown, thus (1) becomes

$$M = E + B. \quad (2)$$

By comparing the concentrations of some soluble species, e.g., chloride, the degree of concentration, conventionally termed cycles of concentration, C_y , is given by

$$C_y = Cl_c / Cl_m \quad (3)$$

where

Cl_c = chloride concentration in recirculating water

and

Cl_m = chloride concentration in make-up water.

A mass balance yields

$$M \times Cl_m = B \times Cl_c. \quad (4)$$

Rearrangement gives

$$M/B = Cl_c/Cl_m \quad (5)$$

The cycles of concentration can now be expressed in terms of in-flow and out-flow by substituting (5) into (3) to give

$$C_y = M/B. \quad (6)$$

Combining (2) and (6) gives

$$C_y = (E + B)/B. \quad (7)$$

Solving for B yields

$$B = E/(C_y - 1). \quad (8)$$

Substitution into (2) gives

$$M = E + E/(C_y - 1) \quad (9)$$

or

$$M = (E \times C_y)/(C_y - 1). \quad (10)$$

Given the evaporation from a cooling tower, the make-up and blowdown flow rates may then be calculated as a function of cycles of concentration.

APPENDIX B

CORROSION AND SCALING DATA

TABLE B-1. DATA FROM COUPONS EXPOSED TO WATER TREATED WITH MAGNESIUM
BICARBONATE AND LIME

Average Chloride Conc. (ppm)	Cycles Based on Chloride	Average Chromium (6+) Conc. (ppm)	Dispersant Conc. (ppm)	Corrosion Rate		Number of Pits Counted	Average Pit Depth (μ m)	Maximum Pit Depth (μ m)	Comment
				$\frac{\text{mg}}{\text{dm}^2 \text{ day}}$	(mpy)				
3,187	4	80	12	59.6	10.9	14	36	50	Coupons covered with scale
3,707	4.6	80	12	89.7 52.5	16.4 9.6				Coupons covered with scale
4,000	5	103	16	38.8 48.1	7.1 8.8				Coupons covered with scale
5,525	7	150	22	17.5 17.5 16.9	3.2 3.2 3.1				Coupons covered with scale
5,113	6.4	275	42	13.1	2.4	16	27	37	Coupons covered with scale
5,426	6.8	306	45	12.6 20.8	2.3 3.8	14 14	15 19	27 31	Scale on 90% of coupon
5,510	7	450	65	9.3 9.3	1.7 1.7	17 14	20 18	32 25	Light scale on flat surface, large amount on edges

TABLE B-2. DATA FROM COUPONS EXPOSED TO WATER TREATED WITH MAGNESIUM CHLORIDE, LIME, AND SODA ASH

Average Chloride Conc. (ppm)	Cycles Based on Chloride	Average Chromium (6+) Conc. (ppm)	Dispersant Conc. (ppm)	Corrosion Rate		Number of Pits Counted	Average Pit Depth (μm)	Maximum Pit Depth (μm)	Comment
				$\frac{\text{mg}}{\text{dm}^2 \text{ day}}$	(mpy)				
3,171	2.6	50	7	10.4	1.9	15	22	39	Coupons covered with scale
4,679	3.9	75	11	26.8 49.8	4.9 9.1				Coupons covered with scale
5,216	4.3	75	11	77.1	14.1	25	26	53	Coupons covered with scale
5,431	4.5	110	16	24.1 18.6	4.4 3.4				Coupons covered with scale
7,323	6.1	170	25	41.0 31.2	7.5 5.7				Thin film of scale on 90% of surface
7,100	5.9	300	45	37.2 20.8	6.8 3.8	16 13	27 17	53 22	Heavy scale on edges, spotted on flat surface
5,960	5	335	50	19.2 15.9	3.5 2.9	17 16	20 21	29 26	No scale observed
8,700	7.2	400	65	7.7 8.2	1.4 1.5	17 12	20 19	29 28	Very thin film on coupon edge, none on flat surface

TABLE B-3. DATA FROM COUPONS EXPOSED TO WATER TREATED WITH MAGNESIUM SULFATE, LIME AND SODA ASH

Average Chloride Conc. (ppm)	Cycles Based on Chloride	Average Chromium (6+) Conc. (ppm)	Dispersant Conc. (ppm)	Corrosion Rate		Number of Pits Counted	Average Pit Depth (μm)	Maximum Pit Depth (μm)	Comment
				$\frac{\text{mg}}{\text{dm}^2 \text{ day}}$	(mpy)				
3,635	4.5	80	12	12.6	2.3				Scale ^a on coupons, tower coated with scale
2,412	3.0	70	10	16.4	3.0				Scale on coupons, tower coated with scale
2,570	3.2	90	13	20.8	3.8				Scale on coupons, tower coated with scale

a. Scale deposits were determined as calcium, silica, and sulfate.

APPENDIX C

CHROMATE REMOVAL SYSTEMS DATA

TABLE C-1. BLOWDOWN TREATMENT COST

<u>Chemical Destruct</u>	<u>Sodium Bisulfite System (\$/kilolitre)</u>	<u>Ferrous Sulfate System (\$/kilolitre)</u>	<u>Cycles of Concentration</u>	<u>\$/day</u>	<u>\$/year</u>
Sulfuric acid	0.03	0.03	5 8	10 5	3,600 ^a 1,800
Sodium bisulfite (NaHSO ₃)	0.55		5 8	185 90	67,600 32,800
Ferrous sulfate (FeSO ₄)		0.13	5 8	44 21	16,000 7,700
Lime	0.01	0.01	5 8	3 2	1,100 700
Chromate lost	2.00	2.00	5 8	675 330	240,000 120,000
Total cost	2.59	0.88	5 8	872 425	318,000 155,000
		2.17	5 8	731 356	267,000 130,000
Chromate ^b recovery			5 8	55 17	20,000 6,200

a. Chemical destruct for 5 cycles would require an additional UNIPAC I unit costing approximately \$50K.

b. Chromate recovery unit estimated costs: \$150K to treat blowdown at 5 cycles, \$110K to treat blowdown at 8 cycles.

TABLE C-2. DATA FROM BLOWDOWN TREATMENT WITH SODIUM BISULFITE^a

Initial Zinc Conc. (ppm)	Initial Chromium (6+) Conc. (ppm)	pH	NaHSO ₃ to CrO ₄	Time Prior to Sample Collection (min)	pH 9.0		pH 12.0	
					Chromium (6+) (ppm)	Zinc (ppm)	Chromium (6+) (ppm)	Zinc (ppm)
35	155	3.0	1.28	10	89	0.5	84	0.1
35	155	3.0	1.28	10	42	0.1	33	ND
35	155	3.0	3.85	10	1.3	0.3	0.2	ND
35	155	3.0	5.13	10	1.6	0.2	0.2	ND
35	155	3.0	6.41	10	1.4	0.1	0.1	ND

a. These data are shown graphically in Figure 4

b. ND = None Detected

TABLE C-3. DATA FROM BLOWDOWN TREATMENT WITH FERROUS SULFATE^a

Metal Zinc Conc. (ppm)	Initial Chromium (6+) Conc. (ppm)	pH	FeSO ₄ to CrO ₄	Time Prior to Sample Collection (min)	pH Adjusted to 10.5	
					Chromium (6+) (ppm)	Zinc (ppm)
30	119	3.0	0.6	10	92.5	ND
30	119	3.0	1.3	10	58	ND
30	119	3.0	1.9	10	20.1	ND
30	119	3.0	2.3	10	1.2	ND
30	119	3.0	2.6	10	0.8	ND
30	119	3.0	2.9	10	0.1	ND
30	119	3.0	3.2	10	0.1	ND

- a. Three samples of blowdown with Cr⁺⁶ = 134 ppm were acidified to pH 3.0 and Na₂S₂O₅ added in ratios of 3, 4, and 5 parts Na₂S₂O₅ to one part CrO₄, pH raised to 10.4 with final Cr⁺⁶ concentrations of 2.4, 1.8, and 1.6(ppm); system deemed unacceptable.

These data are shown graphically in Figure 5.

- b. ND = None detected

TABLE C-4. RESIDUAL Cr⁶⁺ and Zn²⁺ AFTER ION EXCHANGE

Sample Number	Chromium (6+) (ppm)	Zinc (2+) (ppm)
1	2.35	0.65
2	2.05	0.55
3	1.55	0.25
4	1.25	0.15
5	1.45	0.10
6	1.20	0.05
7	1.30	0.05
8	1.15	0.05
9	1.15	0.05
10	1.25	ND ^a
11	1.35	ND
12	1.30	ND
13	1.45	ND
14	2.70	ND
15	1.70	ND
16	1.60	ND
17	1.40	ND
18	1.60	ND
19	1.60	ND
20	1.80	ND
21	3.50	ND
22	1.90	ND
23	2.00	ND
24	2.05	ND

TABLE C-4. (continued)

<u>Sample Number</u>	<u>Chromium (6+) (ppm)</u>	<u>Zinc (2+) (ppm)</u>
25	2.65	0.05
26	2.40	0.05
27	2.45	0.05
28	2.50	0.05
29	2.65	0.10
30	2.95	0.15
31	2.90	0.20
32	2.95	0.30
33	3.00	0.40

a. None detected

TABLE C-5. RECOVERY OF CHROMATE WITH A 5 WEIGHT PERCENT
SODIUM HYDROXIDE SOLUTION

<u>Sample Number</u>	<u>Chromium (6+) (ppm)</u>	<u>Zinc (2+) (ppm)</u>
1	2140	20
2	4360	80
3	2260	60
4	442	220
5	138	15
6	81	10
7	53	5
8	42	7
9	33	3
10	26	3
11	21	3
12	19	0.2
13	17	0.2
14	15	0.2
15	12	0.18
16	10.7	0.17
17	10.2	0.15
18	9.6	0.13
19	9.7	0.14
20	15.9	ND ^a

TABLE C-5. (continued)

<u>Sample Number</u>	<u>Chromium (6+) (ppm)</u>	<u>Zinc (2+) (ppm)</u>
21	7.3	ND
22	6.9	ND
23	6.0	ND
24	5.7	ND
25	5.2	ND
26	4.9	ND
27	4.7	ND
28	4.9	ND
29	3.8	ND
30	3.4	ND
31	3.2	ND
32	3.0	ND
33	2.9	ND
34	2.8	ND
35	2.7	ND
36	2.6	ND
37	3.4	ND
38	3.3	ND
39	3.2	ND

a. No data taken.

TABLE C-6. RECOVERY OF ZINC WITH A 5 WEIGHT PERCENT
SULFURIC ACID SOLUTION

Sample Number	Chromium (6+) (ppm)	Zinc (2+) (ppm)
1	7.15	900
2	2.26	950
3	0.77	420
4	0.38	300
5	0.35	230
6	0.27	210
7	0.25	130
8	0.25	100
9	0.20	80
10	0.18	70
11	0.20	54
12	0.16	48
13	0.14	38
14	0.18	34
15	0.15	28
16	0.17	24
17	0.15	20
18	0.14	18
19	0.24	20
20	0.28	40
21	ND	103
22	ND	4.7
23	ND	2.4
24	ND	1.3

a. No data taken.

APPENDIX D

CHEMICAL ANALYSIS

APPENDIX D. CHEMICAL ANALYSES

Four basic instruments and/or methods were employed for the analyses. They are: (a) atomic absorption spectroscopy, (b) visible spectroscopy, (c) specific ion probe, and (d) titration for alkalinity. Chemical standards and chemical reagents used were all purchased from outside vendors whose analytical methods have received prior EPA approval. Below is given a listing of the analytical methods used and the respective chemical species determined.

(a) Atomic Absorption Spectroscopy

zinc
chromium
iron
calcium
magnesium
sodium

(b) Visible Spectroscopy

silica
sulfate

(c) Specific Ion Probe

chloride
fluoride

(d) Titration

alkalinity

The pH and conductivity of the recirculating water were monitored continuously using a Balsbal 2200 pH meter and a Balsbal 910 conductivity meter, respectively.