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Memo to file: Documentation of discussions with various people concerning LANL and Zia operations specific to cooling towers and the use of Chromium

Kay Birdsell, 3/23/06

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Documentation of discussion with William (Bill) Radzinsky, who works in FM-MSE (Facility Maintenance Division, Maintenance Support and Engineering)
Topic of discussion: Historic chromate use in LANL cooling towers

Pat Longmire and Kay Birdsell met with Bill on 2/24/06 to discuss past use of chromates in LANL cooling towers. Also included, follow-up phone conversation between Kay and Bill on 3/9/06.

General information obtained from Bill:
Chromates were used only at larger cooling towers because it is labor intensive to use them. Bill thinks that only the cooling towers for the TA-3 power plant, TA-2 Omega West Reactor and a facility at TA-41 used them. Cooling water is first acidified (most likely with sulfuric acid) to lower the pH (maybe to as low as 4 to 5), which inhibits scaling. Potassium dichromate is then added to inhibit corrosion or oxidation of the metal parts. It acts to coat the pipes so that pitting and corrosion doesn't occur. It works with most metals (steal, iron, brass, copper pipes). LANL used Betz 177, which contains phosphate, chromate and zinc. Phosphate and zinc were in the form of $Zn_3(PO_4)_2$ and were added as additional corrosion inhibitors to coat the copper and brass components within cooling towers. Bill had a copy of the Betz Handbook of Industrial Water Conditioning, and it recommended 300-500 ppm Cr as a good dosage; the concentration needs to be high to get desired coating. However, Bill also gave us a few pages from a report entitled "Water Treatment: Chromate Discharge to Canyon" (LASL, 1969; see attached) that gives concentrations of 30-40 ppm for hexavalent chromate additives used at TA-3 Power Plant cooling towers. Betz 177 comes as a solid sphere or brick shape that dissolves as water circulates. The LASL (1969) document includes plans for a chromate recovery system.

Note - Bill said that we may be able to find the product sheet for the Betz 177 (Betz is still in business) to get ratio of phosphate/chromate/zinc. However, this information can be inferred from the LASL, 1969 document.

Phone conversation on 3/9/06 – I asked Bill if a significant mass of chromate was lost from the cooling water due to coating of the metal parts (i.e., Did a fairly thick coating build up thus removing some of the mass from the cooling tower blowdown?). He said no, that "coating" is not really an accurate description. The chromate works in a very dynamic process to build and repair a very thin film on the metal parts (similar to an oxide film on stainless steel and probably only a few molecules thick). He said that this process requires a high concentration of chromate to insure that the film stays intact, but that it basically uses the chromate in this dynamic process in such a way that it wouldn't create an overall loss of chromate from the cooling water.

TA-3 Power Plant (TA-3-22 Steam Plant):
Bill said that the TA-3 power plant had the largest chromate usage at LANL; largest discharge volumes; most likely source. The steam plan was built in 1951 (gave me a page with steam plant information, see attached). Chromates were likely used from

I asked Mr. Robinson if he could give us information on some of the water treatment chemicals. He asked me for a list. I gave him: Phx 313 biocide, phx 302 biocide, phx 307 biocide, phx 315. phx 292, phx 250, phx 212, phx Cu, phx 32. He said that the 300's are all biocides, 200 anti-corrosives. He will try to find MSDS sheets for all of these and give me a call back. This goes so far back that the sheets may not be available; might have them in his own files.

Info about TA-3 Power Plant:
Mr. Robinson is the man who wrote the 1969 memo "Water Treatment: Chromate Discharge to Canyon." This memo suggested that the TA-3 Power Plant should switch to Phoenix 292 as its anti-corrosion chemical rather than using $K_2Cr_2O_7$. I asked him if the power plant followed that recommendation. He said "No." The TA-3 Power Plant had its own operations separate from operations of the rest of the LASL. They used the Betz products and did not ever use any products from Phoenix Industrial. He confirmed what Bill Radzinski had said about the chromate addition being very labor intensive. He said that there was an around-the-clock water technician for the power plant.

Info about TA-2, Omega West Reactor (OWR):
Mr. Robinson did recall that OWR switched for using chromium to a Phoenix product, although he was pretty sure it wasn't the Phx 292. He said he worked with a fellow named Robinson there. He recalls that the cooling tower was wooden.

Other operations:
Mr. Robinson confirmed what Bill Radzinski said about smaller operations at LASL not using chromium. He said that he worked with E-4 (Presley Foyt and Everett Miller, whose names are on the purchase orders) to supply water treatment chemicals for other (~107) cooling tower/heat exchangers and (~50) small boilers. These used the Phoenix products, which were supposed to be safe. He also said that Phoenix Industrial worked with the explosives group at TA-16 (HX group?) to confirm that all water treatment chemicals were suitable for operations based on toxicity and reactivity.

An aside story:
The silica concentrations in our water are so high that they were troublesome in terms of water treatment. Mr. Robinson worked with Hal Halvadil, a chemist from Hooker Chemical to come up with an ammonium biflourate solution to remove silica deposits. They came up with a great solution that was used to clean all of the piping in SM-66. Operations at that building were so bad because of silica deposits that they were thinking of scrapping the building. However, they treated the pipes over a weekend and removed all of the deposits so that the building was saved. The ammonium biflourate was neutralized and sent through the RLWTF at TA-50. (He thinks that the LANL folks published a paper on this – probably Ev Miller was one of the authors and a guy with a name like Cunningham.)

Retired LASL folks that we could talk to:
Presley Foyt, 1410 N. 11th St. Temple TX, 76501, (254)778-7167 Jimmy Parsons, lives in WR on Chris Cr. (winters in mesa)
Ev Miller, retired to Bend OR
Chuck Reynolds
Lon Alexander

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LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS, NEW MEXICO

SUBJECT: WATER TREATMENT,
CHROMATE DISCHARGE TO CANYON

MAY 12, 1969

(1) Rudy Velasco
(2) Guy Elder → Wes Nichols

I. ENCLOSURES

A. Materials Protection article reprint, March, 1969 "Cooling Tower Chromates--Recovery or Disposal?" B. J. Kelly, Nalco Chemical Co., Chicago, Ill.

B. Crane Company - Cochrane Division, Chicago, Ill. Bulletin No. 17.16 - Crane-Flo Chromate Recovery Systems

C. Crane Company Bulletin No. 17.22 - Chromate Recovery Systems; Cooling Towers

D. Crane Company correspondence; Subject: Chromate Recovery Systems

E. PHOENIX 292 Technical Information Bulletin

II. CONSULTING CONFERENCES

A. As part of the continuing consulting phase of our water treatment Contract No. 42432, the following meetings were held to discuss the discharge of hexavalent chromate ($CrO_4^=$) to the canyon. These conferences were held during the week of April 14, 1969 at the time of Phoenix Industrial's quarterly inspection visit.

1. TA-42

Mr. E. E. Wingfield, AEC
Mr. John Schoroer, AEC
Mr. William Kenndy, H-6, LASL
Mr. C. W. Christenson, H-7, LASL
Mr. C A. Reynolds, E-4, LASL
Mr. E. L. Miller, E-4, LASL
Mr. L. Robinson, Phoenix Industrial, Chgo.

2. Power Plant

Mr. Westley Nichols, Zia Co.
Mr. E. L. Miller, E-4, LASL
Mr. H. P. Foyt, E-4, LASL
Mr. L. Robinson, Phoenix Industrial.

C. Water Treatment Balances Maintained

1. Betz 177 - Hexavalent Chromate ($CrO_4^=$): 30-40 ppm
2. Phosphate from Betz 177: 15-20 ppm
3. Phosphate from bulk Hexametaphosphate: 10-15 ppm
4. pH: 6.0 to 6.3

D. Daily Control Tests

1. pH
2. Chromate ($CrO_4^=$)
3. Phosphate
4. Hardness
5. Heat transfer

E. System Metals

1. Condensers: 90-10 Copper-Nickel tubes
2. Steel piping
3. Some bronze valves
4. Some Muntz metal

F. System Cleaning

1. Heat transfer tests are performed daily. The entire system was cleaned only once. Japaneese inhibited sulfamic acid was used. The present condition of the system is reported to be clean.

The original design consisted of a single anion column and is described in detail in the Crane Company Bulletins No. 17.16 and 17.22 under "Enclosures" in this report.

The Crane Company, manufacturers of the recovery system used in the Nalco Chemical Company approach, report very poor results and have indicated that they (Crane) are no longer interested in supplying systems for this recovery method. (A letter from Crane Company is found under "Enclosures" in the report.)

In an article appearing in the March, 1969 issue of Materials Protection magazine (copy under "Enclosures") Mr. B. J. Kelly of Nalco Chemical Company describes a revised recovery system using dual anion exchange columns connected in series.

In order to effectively evaluate the described revised system, I personally visited an operating plant utilizing this recovery system and discussed its operation with the managing personnel. (Diagram appears in Figure No. 1)

A summary of their comments follows:

1. pH control is critical. Automatic acid control must be constantly monitored to maintain stability.

2. Resin loading is poor. Units tend to channel badly.

3. Hexavalent chromate reduction ranges from 30-40 ppm in the tower water to approximately 10 ppm in the recovery system effluent. This does not meet the State of Illinois anti-pollution requirements and this water must be diverted to a large holding pond where it is slowly fed into other plant waste water before disposal to the stream.

4. Regeneration of the system is complicated and the resulting chemical waste is also difficult to dispose of.

5. Chromate is recovered at the cost of 50¢ per pound.

B. Chromate Destruction System

A typical cheromate destruction plant flow diagram appears in Figure No. 2. This system when properly designed will produce an effluent water free of chromate. However, the system has some problems.

1. pH of primary reaction-mixing vessel must be maintained between 2.0 to 3.0.

2. Proper mixing in the reducing tank is critically important.

3. Holding time must exceed 15 minutes.

4. In the winter months, cold temperatures slow down all reactions and reduce plant put-thru.

5. Discharge usually contains Phosphate.

6. Sludge disposal is expensive.

7. Chromate is destroyed at the cost of $1.00 per pound.

C. Non-Chromate, Non-Phosphate Inhibitor System

1. LASL Experience

One Hundred and five (105) evaporative condensers, evaporative water condensers, air washers, and cooling towers have been successfully treated for over a year with PHOENIX mixed organo chelates.

This treatment not only has produced corrosion rates of less than one (1) mill per year but has been removing old accumulated scale over an extended period of time.

Blowdown from all systems is biodegradable.

2. Power Plant Water Tests

Six (6) gallons of power plant water was tested in our laboratory in March of this year. Results showed that PHOENIX 292 can provide corrosion results of less than one mill per year.

VI. OPERATING ECONOMICS OF WATER TREATMENT PROGRAMS

A. Cost of Present Zia Co. Power Plant Water Treatment

Using the information supplied by the power plant personnel, we have approximated costs of the current treatment program (Betz) with the costs of the proposed PHOENIX 292 treatment program.

The following figures are based on 2.5 concentrations now carried by the power plant. We have assumed a makeup of 400,000 gallons of water per day or 277 gallons per minute.

1. Betz 177 (50% CrO_4) at 100 lbs./day
   100 lbs./day X .28/lb. = $28.00/day.

   Hexametaphosphate at 20 lbs./day
   20 lbs./day X .12/lb. = $2.40/day.

   Total cost per day: $30.40
   Total cost per year: $10,800

B. Cost of Proposed PHOENIX Treatment Program

To treat the system with PHOENIX 292 would require:

36 lbs./day X .80/lb. = $28.80/day

$28.80/day X 360 days = $10,400 per year

Information supplied by the power plant personnel shows a makeup of 277 gallons per minute. The report of chemicals added and the balances maintained seem to confirm this makeup figure. Consequently, we have assumed this figure to be correct. However, the recirculation rate of 21,000 gallons per minute given us for this makeup and temperature drop of 20°F. is far too high. We have adjusted the reported circulation rate to 8000 gallons per minute.

Using the standard formula for the calculation of cooling tower makeup, we have calculated makeup rates for 2.5, 3.0, and 4.0 concentrations.

Formula used:

$$\text{Makeup (GPM)} = \text{recirculation rate (GPM)} \times \text{evaporation rate (1\% for every 10°F.)} \times \frac{\text{concentration ratio}}{\text{concentration ratio} - 1}$$

2.5 Concentrations (current operations)

$$\text{Makeup} = 8000 \text{ GPM} \times 2\% \times \frac{2.5}{2.5 - 1}$$

Makeup = 265 GPM

3.0 Concentrations

$$\text{Makeup} = 8000 \text{ GPM} \times 2\% \times \frac{3.0}{3.0 - 1}$$

Makeup = 240 GPM

4.0 Concentrations

$$\text{Makeup} = 8000 \text{ GPM} \times 2\% \times \frac{4.0}{4.0 - 1}$$

Makeup = 212 GPM

If we can operate the power plant at 4 concentrations the following water savings are possible.

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TECHNICAL INFORMATION BULLETIN

PHOENIX 292

DESCRIPTION

A specially formulated cooling water treatment containing a blend of near-neutral chelants, surface active agents and dispersants. An excellent corrosion inhibitor for systems containing steel, copper, aluminum (above 2900), cast iron, stainless steel and inconel.

GENERAL SPECIFICATIONS

pH	5.0 to 5.5
Form	White powder
Specific gravity of 1% solution	1.0 (approx.)
Solubility in water	50% by weight

RECOMMENDED USE

Recommended as a corrosion inhibitor for recirculating water systems containing steel, copper and its alloys. The chemical balances produced by this organo-chelate permit high calcium levels over a broad pH range so that blowdown can be held to a minimum.

PHOENIX 292 is biodegradable and non-toxic; it produces a waste water which is not harmful to fish or animals.

DIRECTIONS FOR USE

Treatment levels will vary according to the chemical make-up of the supply water and the corrosion load. Dosage ranges between 2 to 50 ppm based on blowdown.

PHOENIX 292 prevents corrosion by forming a monomolecular film on metal surfaces. In systems containing old scale or corrosion products, PHOENIX 292 will remove them gradually over an extended period of time.

Feeding equipment and chemical storage tanks for concentrate should be lined with polyethylene, rubber or be made of stainless steel.

PHOENIX 292 is not recommended for magnesium or zinc.

PHOENIX 292 is safe to handle and is non-toxic, however, we recommend flushing with water if contact is made with skin or eyes. Do not take internally.

SHIPPING

Available in polyethylene-lined, 100-lb, non-returnable fibre drums. F. O. B. Chicago, Illinois.

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