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OFFICE MEMORANDUM

TO : Distribution

Reviewed/Lab Counsel
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WRD 616-06-9pp

DATE: March 7, 1972

FROM : L. P. Reinig

SUBJECT: PRELIMINARY REPORT - CHROMATE PROBLEM

SYMBOL : ENG-353

Transmitted herewith is a preliminary version of Dr. Pomeroy's report in connection with the chromate problem, power plant cooling towers. The report is preliminary only in the sense that it may require editing in some fashion for clarification and minor corrections but Dr. Pomeroy has assured me his opinion is not subject to change. You will note that the distribution is somewhat limited. Please feel free to consult with anyone whom you feel might be of assistance, and I request that you have your comments or suggestions ready for discussion with Dr. Pomeroy at a meeting which we will arrange early next week. Dr. Pomeroy will be here Monday through Wednesday. During that period I hope we can consolidate any comments or suggestions that you might develop in the meantime or at the meeting so that the report can be typed while Dr. Pomeroy is here and a final review be made with interested parties before he leaves; thus permitting printing and submittal of the final report to us shortly after he returns to his office in Pasadena later next week.

I particularly call your attention to page 5, item 4, which supports Dr. Pomeroy's recommendation. It may be desired by some of you to contact Harold Roland to dicuss the experience at his installation, and if so, his telephone number could be obtained from Dr. Pomeroy's office, (213) 795-7553.

In the meantime I will be in touch with you to arrange a meeting with Dr. Pomeroy to discuss your comments.

L. P. Reinig

LPR/lt
Attach.

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Cooling Towers of the LASL Electric Generating Facility

Cooling towers for the electric generating facility of LASL, operated by Zia Company, use the entire effluent flow of the TA-3 sewage treatment plant, plus a minor amount of water from the municipal supply, for make-up. The average water balance of the towers (average of typical winter and summer days, heat dissipation by the towers being about 10% greater in the summer than in the winter) is as follows:

Make-up	512,000	gallons per day (metered)
Evaporation	338,000	" " " (calculated)
Blowdown	128,000	" " " (metered)
Windage loss	46,000	" " " (difference)
Circulation rate	18,990	gallons per minute (metered)
Windage loss, % of circulation	0.164%	(calculated)
Chromate usage, as CrO_4	35.9	pounds per day (records)

The water is treated with acid to maintain the pH at 6.0, chromate to hold a concentration of 30 to 35 mg/l as CrO_4 (15 to 18 mg/l as Cr), a small amount of polyphosphate and a smaller amount of zinc. The feed water is given nominal chlorination as it enters, and a slug of 12 pounds of chlorine is added three times a day.

The blowdown is discharged to Sandia Canyon. There is a chance that chromate may eventually appear in downstream well waters. It is not certain that this will happen. If the water percolates through sediments containing organic matter, or sulfide, the chromate will be removed, but since there is no assurance that this will happen, the continued discharge as at present must be considered impermissible. The following alternatives may be considered.

1. Continue the tower operation as at present; construct a plant to reduce chromate with sulfur dioxide, then precipitate it as $Cr(OH)_3$. The

method is well established, and plans for such a plant have been quite fully developed by Zia. The cost is estimated at $95,000.

The regulations of the New Mexico Water Quality Control Commission specify that a discharged waste water shall not carry more than 0.01 mg/l of total chromium. Complete reduction of hexavalent chromium can be achieved, but there is not a reasonable expectation that all of the trivalent chromium will be removed from the water by settling. In fact, experiments at the site under the direction of Wesley Nichols show quite conclusively that it will not. The $Cr(OH)_3$ precipitate remains partly dispersed and does not completely settle, probably in part because of the dispersing action of the added polyphosphate and constituents in the sewage effluent.

It does not necessarily follow that the waste cannot be discharged with a small amount of chromium hydroxide in it. Regulations, however carefully drawn, require interpretation in the light of circumstances, because no regulations can anticipate all of the questions that will arise. Effluents discharged from facilities at Los Alamos percolate into the ground, and do not reach a usable groundwater basin until after passing through at least hundreds of feet of earth. If an effluent carries an inert, insoluble material that cannot pass through the earth, is the discharge of that insoluble material forbidden on the basis of regulations intended to prevent pollution of the groundwater? If the water were put through a filtering layer of sand spread on top of the ground, with a membrane and pipes to catch the underdrainage, and it were shown to be free of possibly harmful substances, the discharge would not be forbidden. If the effluent is put not onto an artificial sand bed, but onto natural earth of similar filtering capability, and if it were shown that the percolating water were free from possibly harmful substances, would the discharge be any less acceptable? We think not.

The concern has been expressed that if trivalent chromium accumulates in the soil, it may at some future date be reoxidized to chromate. There

need be no fear on this account. Chromium, while not abundant, is not a rare element. The average chromium content of the rocks of the earth's crust is about 200 ppm. One cubic yard of average rock contains about a pound of chromium. Except under unusual conditions, it is in the trivalent form. The only natural soluble hexavalent chromium compounds known are the chromate and dichromate of potassium found in a few places in the nitrate beds of Chile. There are three insoluble chromates, all containing lead, the most common being crocoite, $PbCrO_4$. The presence of lead probably facilitates the oxidation of chromium because of the insolubility of the products, but just how the oxidation comes about is not known. Despite the widespread occurrence of chromium, there is no authentic case of natural occurrence of chromate in ground water.

It is concluded that the effluent of a chromate reduction plant could be discharged into the canyon. It would probably be necessary for LASL to collect and analyse samples of the percolating water at some depth, and to demonstrate complete removal of the chromium.

A possible problem would remain from the escape of chromate in the spray or windage. This subject will be considered later.

2. Continue to operate the tower installation as at present; use one of the other possible ways to reduce chromate. A chemical sometimes used for the purpose is sodium dithionite, $Na_2S_2O_4$. This compound will reduce chromate even in neutral solution. Because of the convenience and simplicity of the operation, dithionite is sometimes used in small installations, but it is quite expensive and therefore is uneconomical where the requirement is more than a few pounds a day.

Ferrous sulfate has been used, but its applicability is limited to places where spent liquor from steel pickling is available.

Chromate is easily reduced by sewage, provided that the amount is not too great and provided that the sewage is retained long enough for

anaerobiosis to proceed. It would be ineffective to return it to the relatively small flow of the TA-3 sewerage system. The distance to a possible point of connection to the larger system serving the town, and other complications, make that route impractical also.

There are other possible ways to reduce chromate, but they have not been demonstrated in full scale practice.

3. <u>Remove chromate from the blowdown by anion exchange, and re-use it</u>. Chemical Separations Corporation (Chem-Sep) has offered a continuous-flow system, and has presented a comparison of annual costs. The comparison is based upon a blowdown rate considerably larger than the actual average rate of 128,000 gallons per day. The actual amount of chromate recovered with the proposed unit would be about 34 pounds per day as CrO_4. At the estimating cost used by Chem-Sep, 75¢ per pound of CrO_4, the value of the recovered chemical would be about $800 per month. The net cost of operation would be less than for the chromate reduction process, but there would, nevertheless, be a net operating cost of about $300 a month.

The price for the proposed unit is $75,000, with a probable installed cost of $100,000. The price might be less if it can be designed for a somewhat smaller capacity, corresponding more closely to the actual blowdown rate.

The proposal guarantees removal of chromate to 0.05 mg/l. If it is necessary to hold the concentration to 0.01 mg/l, this could be accomplished by use of a small amount of sodium dithionite.

Any one contemplating such an installation would like to see one of the units in actual use with cooling tower blowdown. According to a letter from the company to Dean Miller, Chief Engineer of Zia Company, the first such unit will be placed in service this month (March, 1972) on the east coast. Similar Chem-Sep equipment is in use for various

ion-exchange tasks, but there is the possibility that operating predictions may not be fully borne out in a different application, especially in a situation where the water supply is sewage effluent.

Any plan that concerns itself only with blowdown treatment leaves untouched the potential problem of windage, so it may be that neither reduction nor ion exchange will fully solve the chromate problem. But if treatment of the blowdown is to be practiced, the Chem-Sep unit must be carefully evaluated, because it may well prove superior to the reduction process.

4. Discontinue the use of chromate, using other inhibitors instead. The choice would probably be polyphosphates with zinc, and perhaps a dispersing agent, but there are other possibilities. Consideration might be given to the compounds furnished by Phoenix Company for use elsewhere in LASL, but it would be well to allow more time for evaluation of those chemicals in the other system. Of particular concern is the possible dezincification of yellow brasses by strong chelating agents. The tube sheets of the condensers are made of Muntz metal, a relatively high zinc brass. The sheet no doubt is quite thick, and the attack, if any, would be slow, but one would not want to take a chance without a more careful evaluation of probable effects.

Since Betz Company, with a great deal of experience in this field, has been supplying the chemicals for the steam and electric generating plant, Zia will probably follow their recommendations.

Chromate, generally now used in combination with phosphates, is the chemical of choice for cooling tower control in large power plants, but the opinion that chromate is indispensible is extreme. Many plants have used other inhibitors for years, and more are switching from chromate now because of water pollution problems. A pertinent example is at Burbank, California, where the water supply of the cooling tower is the effluent of a sewage treatment plant. In the opinion of Harold Roland,

Chief Steam Engineer, the effluent is comparatively non-corrosive, attributed to the high phosphate content of the effluent; water conditioning aims mainly at preventing fouling. Because of the tendency of the phosphate to form a sludge, a dispersing chemical is used, and an unspecified organic corrosion inhibitor. Shock dosages of chlorine are used to control biological growths. The effluent has a relatively high concentration of dissolved minerals. The towers run with a concentration ratio of $2\frac{1}{2}$.

A somewhat greater corrosion rate is likely if chromate is replaced by other inhibitors, but it can be kept to acceptable levels in the LASL plant.

5. Use the water for irrigation. With chromate in it, the water should not be sprayed on vegetation, but it could be used for furrow and probably broad irrigation. This would not necessarily satisfy the Water Quality Protection Commission. Furthermore, irrigation would not be a complete method of disposal anyway, since there are seasons when irrigation would be impractical. If the objective is to save water, and to permit the watering of plantings in the area, the project should be considered independently of a scheme designed to provide an assured, satisfactory route of disposal of the blowdown 100% of the time.

6. Use the water in connection with the operation of a refuse disposal landfill. The amount of water is much greater than could be absorbed by the landfill. As in the case of irrigation, use of water for this purpose would not lessen the need for a satisfactory means for disposing of the total flow.

7. Remove minerals from the blowdown and reuse it. The methods commonly used for producing fresh water from brackish water include distillation, electrodyalysis, and reverse osmosis. In these three methods, low mineral water is extracted from the brackish water, leaving the minerals in more concentrated form in a waste stream. A practical

limitation on these methods is that the minerals separate as solids: calcium carbonate, calcium sulfate, silica, and others. The solids separate on the heat-exchange surfaces and membranes. In most cases, the extraction of water is continued only until it approaches the point where the solids cause operating difficulties. Dispersing agents are often used to retard the formation of scale.

The operation of a cooling tower is in fact another such process, only in this case the water that is extracted and serves a useful purpose is that part which absorbs its latent heat of vaporization and passes into the atmosphere. If one wanted to save some part of the water that now leaves the system as blowdown, there would be no better way to do it than to evaporate more of it in the cooling tower. Practical considerations, however, have presumably already determined how far the evaporation can be carried.

A fourth method for treating brackish waters is ion exchange. In this operation, one obtains a waste stream that contains not only the salts that were in the water, but also the chemicals used for regeneration. From the over-all viewpoint of conserving the water supply of an area, it must be recognized that the adding of salts to water destroys at least a part of the utility of that water, because it cannot be subsequently evaporated to the same degree as it could without the mineral addition. Unless the regeneration brines are conveyed to the ocean or to an inland surface or subsurface basin where they cannot affect usable waters, the over-all operation does not save water but actually decreases the available water resource.

Comparisons

Alternatives 5, 6, and 7 are functionally inadequate to aid in the solution of the chromate problem.

Alternatives 1, 2, and 3 could solve the problem of chromate in the

blowdown, but would leave untouched the question of windage loss. Actually, there is no serious liklihood that chromate in the windage loss would ever harm usable waters. There is no evidence that trees or annual vegetation in the vicinity have been affected by chromate in the air. Where the fall-out of chromate is low, a biologically active soil will reduce and remove it. The amounts of chromate that would percolate downward would be diluted to the level that they would not diminish the beneficial uses of the water, in the not very likely case that they would ever reach such waters.

Despite this reasoning it must be recognized that the popular demand for the ultimate in security against any possible deterioration of the water may force LASL to take protective measures against airborne chromate. The amount of chromate carried from the tower by the air is about 12 pounds per day as CrO_4.

If an area around the towers for a distance of about 100 feet were paved, a significant part of the windage chromate could be caught and washed back into the towers. Farther away, to whatever distance is feasible, organic matter might be worked into the soil, providing a medium that would reduce and hold the chromium. With these measures, it is reasonable to hope that 80% or more of the chromate could be intercepted.

When one considers the capital and operating costs for any one of the chromate removal schemes, and the possible difficulties due to windage loss of chromate, and weighs these factors against the possible increase of corrosion if the use of chromate is stopped, in the light of experience elsewhere, it is concluded that the balance is unequivocally in favor of stopping chromate use.

It is recommended that the use of chromate in the cooling towers of the power plant be discontinued.