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KERR-MCGEE CHEMICAL CORPORATION

HENDERSON, NEVADA FACILITY

WATER ISSUES MEETING

With The

DIVISION OF ENVIRONMENTAL PROTECTION

NEVADA DEPARTMENT OF CONSERVATION AND  
NATURAL RESOURCES

MAY 2, 1986

CARSON CITY, NEVADA

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FEB 28 1986

R.B. CHASE

STATE OF NEVADA  
DEPARTMENT OF CONSERVATION AND NATURAL RESOURCES  
DIVISION OF ENVIRONMENTAL PROTECTION  
Capitol Complex  
Carson City, Nevada 89710  
(702) 885-4670

February 26, 1986

Kerr-McGee Chemical Corporation  
P.O. Box 55  
Henderson, Nevada 89015

Dear Mr. Chase:

This letter is in response to several issues that need our mutual attention. Specifically, the "Geohydrological Investigation" report which you submitted to Mr. Tom Fronapfel on July 29, 1985; the need for some type of groundwater cleanup or mitigation program; the monitoring schedule proposed in your letter of November 15, 1985; the problem of unauthorized cooling tower overflows and ways of eliminating them; and the NPDES permit revision which Kerr-McGee applied for on April 24, 1985.

The Geohydrologic Investigation report has been reviewed by our hydrogeologist and has been found to be a very good report with respect to its content. Like all good reports, it has raised further questions. We are particularly interested in questions related to plume chemistry such as:

- . What is the chemical makeup of the plume?
- . What other toxic constituents were present in the process waters that contained the chromium?
- . What reactions are likely to be occurring between the plume and sediments?
- . Is there uptake of chromium or other constituents by the sediments?

We feel that some type of recovery or mitigation measures are in order and, at this time, are leaning toward a well field intercept system. Groundwater flow and contaminant transport should be modeled prior to final design of any cleanup or mitigation program. We are aware that some voluntary pumping was done with the three wells located near unit #5 and possibly well M-3, and that this pumping has been terminated. Has the effectiveness of this test pumping been evaluated? Is there a feasible way to process the contaminated water pumped from these wells?

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Law Department

Letter to Kerr-McGee Chemical Corporation

February 26, 1986

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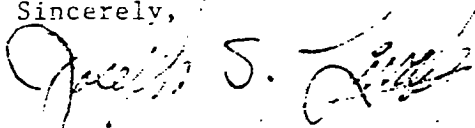
We agree with proposed monitoring schedule for chromium presented in your letter of November 15, 1985. It is possible, however, that more or different monitoring wells may be needed as a cleanup program develops.

Regarding the cooling tower overflows, we know that Kerr-McGee has been evaluating alternative ways of dealing with this problem. You should know that the DEP considers these overflow incidents to be violations of Nevada Revised Statute (NRS) 445.221 and your NPDES permit, and that a Finding of Violation and Order is being developed. Civil penalties are a possibility. In spite of this ominous note, we do want to work with you on finding a mutually acceptable solution to the problem.

Finally, we need to discuss various alternative approaches to the new permit, including how stormwater is to be handled.

Because of the variety of issues to be resolved, we feel that a meeting would be very beneficial. I am, therefore, proposing a meeting in Carson City between you and/or appropriate Kerr-McGee staff and DEP staff to discuss the issues raised in this letter (and any others that you feel are pertinent). We would like to meet sometime before the end of March. Please contact me regarding an acceptable date. Any questions regarding the content of this letter or the purpose of the meeting are, of course, also welcome.

Sincerely,



Joseph S. Livak  
Water Quality Enforcement Officer

JL/jh

cc: Steve Fuller, EPA

ENVIRONMENTAL GEOLOGY NOTES

APRIL 1977 • NUMBER 79

**ATTENUATION OF POLLUTANTS IN  
MUNICIPAL LANDFILL LEACHATE  
BY CLAY MINERALS:**

**PART 2 –  
HEAVY-METAL ADSORPTION**

*R. A. Griffin, R. R. Frost, A. K. Au,  
G. D. Robinson, and N. F. Shimp*

ILLINOIS STATE GEOLOGICAL SURVEY

Jack A. Simon, Chief • Urbana, IL 61801

TABLE 1. ANALYTICAL RESULTS OF CHARACTERIZATION STUDY OF HENDERSON GROUNDWATER

Units = mg/l

| Well # | Area        | Boron | Calcium | Chromium | Iron | Magnesium | Manganese | Sodium | Vanadium | Zinc |
|--------|-------------|-------|---------|----------|------|-----------|-----------|--------|----------|------|
| M-10   | Background  | 4.0   | 150     | 0.02     | 0.21 | 74        | 0.64      | 410    | <0.5     | <0.5 |
| M-12   | Units 4&5   | 3.7   | 480     | 16       | 0.27 | 191       | 0.35      | 390    | <0.5     | <0.5 |
| M-29   | Unit 6      | 5.6   | 460     | <0.02    | 0.43 | 4270      | 6400      | 950    | <5       | <0.5 |
| M-9    | Steam Plant | 200   | 380     | 31       | <0.1 | 287       | <0.5      | 3790   | <0.5     | <0.5 |

| Well # | pH          | Conductivity | Alkaline | TDS | TOC   | Chloride | Phosphate | Sulfate | Chlorate | Perchlorate |
|--------|-------------|--------------|----------|-----|-------|----------|-----------|---------|----------|-------------|
| M10    | Background  | 7.6          | 5180     | 135 | 2730  | 0.53     | 507       | 877     | Pending  | Pending     |
| M-12   | Units 4 & 5 | 7.5          | 27000    | 253 | 20400 | 1.6      | 2210      | 1450    | Pending  | Pending     |
| M-29   | Unit 6      | 6.3          | 34200    | 74  | 49800 | 1.4      | 526       | 30,400  | Pending  | Pending     |
| M-9    | Steam Plant | 7.7          | 36000    | 266 | 2040  | 2.6      | 3150      | 1,520   | Pending  | Pending     |

*Mid March 86*

ATTENUATION OF POLLUTANTS IN MUNICIPAL  
LANDFILL LEACHATE BY CLAY MINERALS

Part 2—Heavy-Metal Adsorption

*R. A. Griffin, R. R. Frost, A. K. Au,  
G. D. Robinson, and N. F. Shimp*

ABSTRACT

The potential usefulness of clay materials as liners for waste disposal sites depends to a large extent on the pH of the leachate solutions that pass through the landfill and on ionic competition during the ion adsorption process. Adsorption of the cationic heavy metals—lead, cadmium, zinc, copper, mercury, and chromium (III)—was found to increase as the pH increased, while adsorption of the anionic heavy metals—chromium (VI), arsenic, and selenium—decreased as the pH increased. The presence of leachate reduced by as much as 85 percent the amounts of the cationic heavy metals removed from solution, whereas leachate had relatively little effect on the amounts of the anionic heavy metals removed by the clays. Removal of the heavy-metal cations from solution was concluded to be primarily a cation exchange-adsorption reaction affected by pH and ionic competition, whereas removal of the heavy-metal anions is primarily an anion-adsorption reaction in which the monovalent ion is the predominant one being adsorbed.

Precipitation of the heavy-metal cations in leachate was an important attenuation mechanism at pH values of 5 and above. No precipitation of the heavy-metal anions was detected in the pH range 1.0 to 9.0.

Adsorption isotherms determined at various pH values were used to compute how thick a clay liner must be to remove lead from solutions of  $Pb(NO_3)_2$ , from 0.1 M NaCl, and from two landfill leachates at lead concentrations ranging between 10 and 1000 ppm and at pH values from 3 to 8. Where pH and ionic competition are unfavorable for the interaction of heavy metals and earth materials, some undesirable environmental consequences can occur.

## INTRODUCTION

As industry in the United States complies with the Clean Air Act and the Federal Water Pollution Control Act, it finds itself in the position of having to handle and dispose of huge volumes of solid wastes, sludges, and liquid concentrates of pollutants. The quantity of industrial wastes that must be placed in landfills is expected to double in the next 10 years, reaching 260 million dry tons per year (Gordon, 1975). The U.S. Environmental Protection Agency (EPA) estimates that about 10 percent of the nonradioactive industrial wastes will be classified as hazardous, although the definition of "hazardous" is still being clarified (U.S. EPA, 1973a). From 1948 to 1968, United States consumption of certain toxic metals increased 43 percent, and the EPA concluded that generation of hazardous wastes will, in general, continue to parallel industrial production rates in the future.

While the volumes of industrial wastes are doubling in the next 10 years, the available capacity of landfills for solid waste is declining throughout the nation. A recent survey of cities with populations over 10,000 revealed that 46.5 percent of the respondents stated that their present landfill sites would be filled to capacity in from 1 to 5 years (Early, 1974). Not only will acceptable disposal sites be difficult to find in the future, but their location will be approved only after certain geologic and hydrologic criteria are met. In addition, their operation will have to be conducted in an environmentally acceptable manner.

Before about 1965, few people were aware of the environmental degradation that could occur from the leachate generated in landfills. Walker (1969) and Hughes, Landon, and Farvolden (1971) described how leachate from solid-waste disposal sites has polluted some Illinois aquifers. Since officials have become aware of these problems, landfill disposal sites are not uncommonly approved for use with the provision that any leachate generated must be collected and disposed of in some harmless manner. This provision implies that adequate technology is available for the environmentally acceptable disposal of the leachate, but that is not entirely true. Davies (1973) reported that at one disposal site installation of a small lagoon to treat the collected leachate proved ineffective and created a surface-water problem that would otherwise not have existed. Such failures have caused considerable interest in land treatment of leachate. Spray irrigation has been discussed (Garland and Mosher, 1975) as a method of leachate disposal, and the effect of municipal wastes on crop yields has been studied by Giordano, Mortvedt, and Mays (1975).

The results of chemical analyses of 20 municipal leachates, reported by the U.S. Environmental Protection Agency (1974), showed that leachate was



similar to sewage sludge effluent in that it has a high content of organic matter, nitrogen, phosphorus, and potassium; high levels of heavy metals also were found.

The accumulation of these potentially toxic heavy metals in soils makes long-term application of municipal leachates to the land hazardous, because heavy metals enter the human food chain by accumulating in plants. However, a lack of basic data on the reactions of these metal ions with soil colloids in the presence of a complex solution matrix, such as leachate, has hampered efforts to determine what levels of application can be tolerated without degradation or loss of the soil for food crop production.

Efforts to dispose effectively of most industrial heavy-metal wastes without polluting the environment have thus far proved unfruitful. Traditionally, rivers or lakes have been used for the disposal of these potentially hazardous discharges. Industrial plants have also disposed of their wastes through recharge basins or diffusion wells (Welsch, 1955) and into sewer systems (Nassau County, N.Y., Department of Public Works Sewer Regulations, 1955). All of these disposal methods can contribute to contamination of surface and ground water (Davids and Lieber, 1951).

To minimize the problems caused by heavy-metal wastes in sewage treatment, laws have been enacted in some northern Illinois counties forbidding the disposal of such wastes into sanitary sewers. That prohibition has increased the pressure for permission to dispose of these wastes in the available sanitary landfill sites. However, unless they are specially designed, sanitary landfills also are a potential source of surface and ground-water pollution (Walker, 1969; Hughes, Landon, and Farvolden, 1971). For that reason a demand has arisen for information about the capacity of earth materials to adsorb heavy metals from landfill leachates (Fuller, 1975). Little information has been available as to whether industrial wastes containing heavy metals can be safely disposed of in landfills designed to contain municipal solid wastes.

This report presents the results of an investigation whose purpose was to determine the capacity of two major clay minerals for removing the heavy metals Pb, Cu, Zn, Cd, Cr, As, Se, and Hg from solution and the effect municipal leachates have on this capacity at various pH values. Other purposes of the investigation were to determine the mechanisms responsible for attenuation of these heavy metals and to evaluate the potential use of clay minerals as liners for waste disposal sites.

#### Acknowledgments

We gratefully acknowledge the U.S. Environmental Protection Agency's partial support of this work under Contract No. 68-03-0211, Cincinnati, Ohio, and we thank the American Colloid Company, Skokie, Illinois, for supplying the montmorillonite clay.

We also wish to thank W. A. White, R. R. Gadde, F. R. Bloom, J. M. Mellske, and P. L. Johnson, all of the Illinois State Geological Survey,

TABLE 1—CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES

| Component                                  | Range of all values given by Garland and Mosher (1975)<br>(mg/l) | Blackwell Forest Preserve leachate (Hughes et al., 1971)<br>(mg/l) | Du Page leachate used in sorption study<br>(mg/l) |
|--|--|--|---|
| Chemical oxygen demand (COD)               | 40 - 89,520  | 39,680.  | 1,362.  |
| Biological oxygen demand (BOD)             | 9 - 54,610   | 54,610.  | —   |
| Total organic carbon                       | 256 - 28,000   | —  | —   |
| Organic acids                              | —  | —  | 333.  |
| Carbonyls as acetophenone                  | —  | —  | 57.6  |
| Carbohydrates as dextrose                  | —  | —  | 12.   |
| pH   | 4 - 9  | 7.10   | 6.79  |
| Eh (oxidation potential) (m.v.)            | —  | -180.  | -155.   |
| Total dissolved solids                     | 0 - 42,276   | 19,144.  | 5,910.  |
| Electrical conductivity (mmhos/cm)         | 3 - 17   | 10.90  | 7.20  |
| Alkalinity (CaCO <sub>3</sub> )            | 0 - 20,850   | 3,255.   | 4,220.  |
| Hardness (CaCO <sub>3</sub> )              | 0 - 22,800   | 7,830.   | 1,100.  |
| Total phosphorus                           | 0 - 154  | 6.   | 0.1   |
| Ortho-phosphate                            | 6 - 85   | —  | —   |
| NH <sub>4</sub> -nitrogen                  | 0 - 1,106  | —  | 809.  |
| NO <sub>3</sub> +NO <sub>2</sub> -nitrogen | 0 - 1,300  | 1.70   | —   |
| Aluminum                                   | —  | 2.20   | 0.1   |
| Arsenic                                    | —  | 4.31   | 0.11  |
| Boron                                      | —  | —  | 33.   |
| Calcium                                    | 5 - 4,080  | —  | 49.   |
| Chloride                                   | 34 - 2,800   | 1,697.   | 1,070.  |
| Sodium                                     | 0 - 7,700  | 900.   | 822.  |
| Potassium                                  | 3 - 3,770  | —  | 516.  |
| Sulfate                                    | 1 - 1,826  | 680.   | 0.01  |
| Manganese                                  | 0 - 1,400  | 1.66   | 0.1   |
| Magnesium                                  | 16 - 15,600  | —  | 204.  |
| Iron                                       | 0 - 5,500  | 5,500.   | 4.40  |
| Chromium                                   | —  | 0.20   | 0.1   |
| Mercury                                    | —  | —  | 0.0008  |
| Nickel                                     | —  | —  | 0.3   |
| Silicon                                    | —  | —  | 15.1  |
| Zinc                                       | 0 - 1,000  | —  | 0.03  |
| Copper                                     | 0 - 10   | 0.05   | 0.1   |
| Cadmium                                    | 0 - 17   | 0.05   | 0.01  |
| Lead                                       | 0 - 5  | —  | 0.1   |

and the Survey's Analytical Chemistry Section, under the direction of R. R. Ruch, for assistance in parts of this research. We also thank G. M. Hughes of the Ontario (Canada) Ministry of the Environment.

#### LEAD ADSORPTION BY CLAY MINERALS

Lead was chosen for study because documented evidence shows that even low Pb levels in drinking water can cause death to human beings. In one case reported in Australia, for instance, 94 adults died of chronic lead poisoning because throughout childhood they had drunk water collected from house roofs that were painted with lead-pigmented paint (Henderson, 1955). Another reason for choosing Pb for study was the evidence (Broadbent and Ott, 1957) that organic chelates form with hydrolyzable metals such as Pb. The chelates may make Pb more mobile in soils or clay liners that contain municipal leachate than in soils or liners that contain effluents that do not have such high concentrations of organic compounds.

#### Experimental

The two clay minerals used in the study were kaolinite and montmorillonite. Complete chemical descriptions were given in Part 1 of this study (Griffin et al., 1976). The chemical characteristics of the two landfill leachates used are given in table 1. For comparison, table 1 also summarizes the chemical ranges of leachate that were given by Garland and Mosher (1975).

In the investigations of Pb removal, a known weight of clay was placed in a 125-ml Erlenmeyer flask. Between 0.100 and 1.000 g of clay was used to effect an estimated 20 to 50 percent change in the Pb concentration of the solution at equilibrium. A 50-ml aliquot of either deionized water or 0.1 M NaCl solution was pipetted into the flask. The pH of the solution was adjusted with either HNO<sub>3</sub> or NaOH throughout the determined pH range and the volume of acid or base added, usually less than 1 ml, was recorded. The flasks were tightly stoppered, and, as a result, the CO<sub>2</sub> liberated from the leachate solutions caused a slight positive pressure in the flask that helped to maintain anaerobic conditions during equilibration. (For a few minutes after acid was added, the stoppers were removed to relieve excessive pressure; the flasks were then restoppered.)

Rate studies indicated that 4 hours were necessary for Pb in leachate to equilibrate with kaolinite. This result agreed with that of Beevers (1966), who found that Pb(NO<sub>3</sub>)<sub>2</sub> solutions equilibrated in from 1 to 12 hours, depending on the clay mineral. The samples in this study were shaken for at least 24 hours in a constant temperature bath at 25° ± 0.5° C to insure equilibration. The equilibrium pH was recorded, the samples were centrifuged, and the solutions were analyzed for their Pb concentration by atomic absorption. The difference between the initial concentration and the equilibrium concentration was used to compute the amount of Pb removed from the solution at the

particular pH by a given clay mineral. This procedure was carried out for a range of initial Pb concentrations that varied between 10 and 1000 ppm.

The resulting data were plotted as amount of Pb removed from solution per gram of clay versus pH. From the resulting curves, adsorption isotherms were constructed for individual pH values throughout the pH range 3 to 6. Representative adsorption isotherms and plots of the data according to the Langmuir (1918) adsorption equation were constructed for various pH values to determine the maximum amount of Pb that could be adsorbed from the various solutions by the two clay minerals and to try to gain insight into the mechanisms of adsorption. The Langmuir equation in its linear form is:

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \quad [1]$$

where C = the equilibrium concentration of the metal ion,  
x/m = the amount of the metal ion adsorbed per unit mass of clay,  
1/b = the slope where b is the adsorption maximum, and  
k = the slope/intercept, where k relates to the energy of adsorption.

The ability of the two municipal leachates to complex metal ions, particularly Pb, was studied. The leachates were centrifuged at 1000 rpm for 10 minutes and then filtered through a Millipore membrane (0.45  $\mu$ m pore size) held in an anaerobic-bacteria filter holder under argon pressure. The leachate obtained after centrifugation and filtration was considered to contain only soluble organic material and was used in the complex formation studies. Successive aliquots of Pb were added to the leachate and equilibrated for several hours. The concentration of free and complexed lead ions in solutions was determined from pulse polarographic wave heights by using the methods and equipment described by Gadde and Laitinen (1973a).

Lead was removed from leachate solutions as a white precipitate at pH values greater than 6. The precipitate was separated from solution on a 0.45  $\mu$ m Millipore membrane, washed with deionized water, and dried at room temperature. The chemical compound was then identified from its X-ray diffraction pattern.

## Results

The results of Pb removal from 25° C solutions of Du Page leachate by kaolinite (fig. 1) and montmorillonite (fig. 2) clay minerals were plotted as a function of pH. Similar results obtained for Pb removed from Blackwell leachate by kaolinite are shown in figure 3. The data indicate that Pb removal from landfill leachate increases as pH values increase and as the concentration of Pb in solution increases. The increase in Pb concentration is indicated in the figures by increasing alphabetical order. The initial Pb concentration, micrograms of Pb added, weight of clay used, and volume of solution for each alphabetical designation are given in table 2. A blank (no clay) solution of leachate with Pb added was carried along through the experiment, and the results appear in figures 1, 2, and 3.

Data for Pb removal from leachate, plotted in increasing concentration, can be used to construct sorption isotherms by using the information given in table 2 for values from pH 3 to pH 6. To construct Pb sorption isotherms, a vertical line is first placed across the family of curves at the pH of interest. The amount of Pb removed from solution is found on the graph at the points where the vertical pH line intersects each curve. The equilibrium Pb concentrations that correspond to the chosen pH value are then computed from the amounts of Pb removed at each concentration, as determined from the graph and the information for each Pb curve given in table 2, by using the following relation:

$$\text{Equilibrium Pb} = \frac{\text{Pb added } (\mu\text{g}) - (\text{Pb removed } (\mu\text{g/g}) \times \text{wt of clay})}{\text{sample volume (ml)}}$$

Pb sorption curves were constructed by this method for several pH values from the data in figures 1, 2, and 3. Representative sorption curves from Du Page and Blackwell leachates are presented in figure 4, along with sorption isotherms obtained at pH 5.0 and 25° C for Pb sorption from Pb(NO<sub>3</sub>)<sub>2</sub> solutions and 0.1 M NaCl solutions.

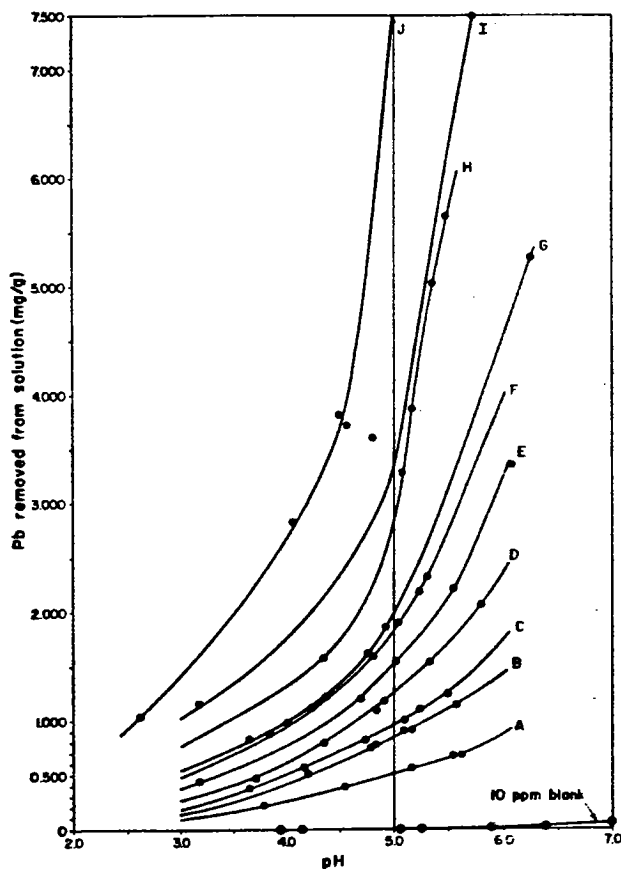


Fig. 1 - Amount of Pb removed from Du Page leachate by kaolinite at 25° C, plotted as a function of pH.

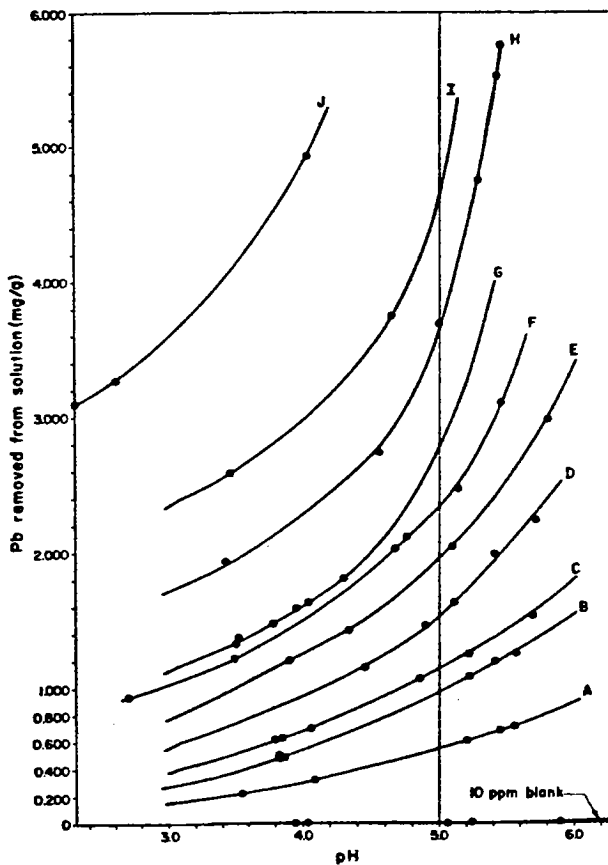


Fig. 2 - Amount of Pb removed from Du Page leachate by montmorillonite at 25° C, plotted as a function of pH.

The sorption curves for the two leachates show a sharp upswing occurring at equilibrium concentrations of approximately 200 ppm Pb. Qualitatively identical curves, also with a sharp upswing at about 200 ppm Pb, were obtained by using montmorillonite clay. The data in figure 2 may be used to support this finding. Sorption isotherms computed at pH 3.0 or 4.0 from figures 1, 2, and 3 did not exhibit the sharp upswing. A sharp upswing in a sorption isotherm is generally viewed as the initiation of precipitation of an insoluble compound. That the sharp rise in Pb removal at pH 5 occurred at about 200 ppm Pb under the CO<sub>2</sub> partial pressures in the flasks, while at pH 4.0 no sharp increase was observed, is consistent with solubility computations that assume PbCO<sub>3</sub> formation.

To predict the maximum amounts of Pb that could be sorbed by the two clays from the various solutions, the kaolinite sorption data plotted in figure 4 and the sorption data obtained for montmorillonite were plotted according to the Langmuir equation. The results appear in figure 5.

The Langmuir equation described the data obtained for Pb(NO<sub>3</sub>)<sub>2</sub> sorption by both kaolinite and montmorillonite and for Pb sorption from 0.1 M NaCl solutions by kaolinite throughout the entire concentration range studied. The results obtained for the leachates, however, were somewhat different. The Langmuir equation described the sorption up to Pb concentrations between 30 and 40 ppm, at which point a sharp change in slope occurred, dividing the curves into two distinct linear regions. The adsorption maximums computed from the slopes of the lines shown in figure 5 are given in table 3. From the values in table 3 a quantitative estimate of the sorption differences noted in figure 4 and a comparison of the sorption capacities of the two clays can be made. From the Pb(NO<sub>3</sub>)<sub>2</sub> solution, montmorillonite sorbed approximately 5 times more Pb than kaolinite, while from Du Page leachate it sorbed less than twice as much as kaolinite. This result indicates that the competitive ions contained in landfill leachate

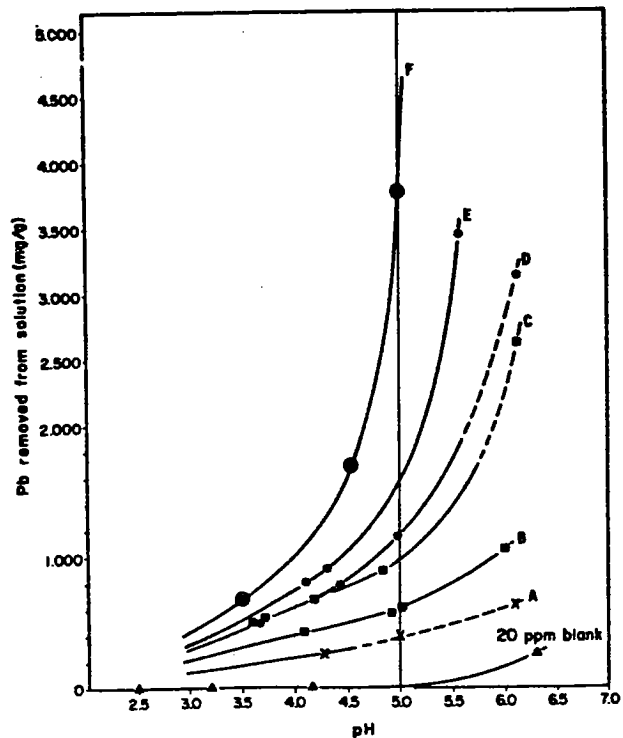


Fig. 3 - Amount of Pb removed from Blackwell leachate by kaolinite at 25° C, plotted as a function of pH.

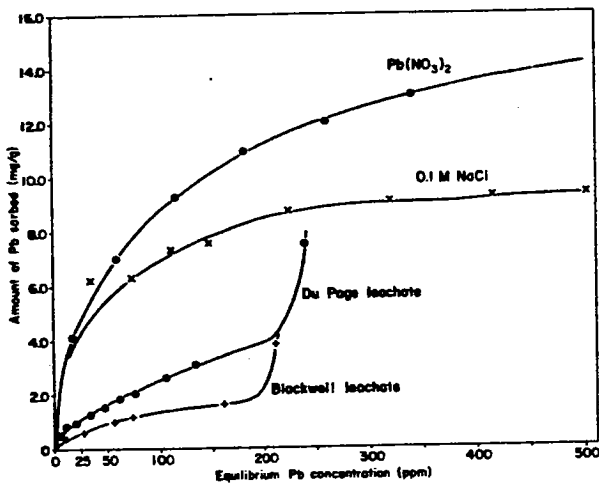


Fig. 4 - Amount of Pb sorbed per gram of kaolinite at pH 5.0 and 25° C, plotted as a function of the equilibrium Pb concentration.

lessened the relative sorption affinity of Pb for the montmorillonite proportionately more than it reduced Pb sorption by kaolinite.

### Discussion

The data presented above suggest that several mechanisms are responsible for removal of Pb from solutions of varying ionic composition and pH.

Precipitation was found to be an important mechanism in removing Pb from landfill leachates, as is shown by Pb removal from blank solutions that contained no clay (figs. 1, 2, 3). Losses of Pb from the Du Page leachate were observed at pH values above about 6 and in Blackwell leachate at pH values above 5. A white precipitate was observed forming in the leachate solutions at pH values above 6. When it was filtered out, it was identified by its X-ray diffraction pattern as a highly crystalline lead carbonate ( $PbCO_3$ ). The peaks were sharply defined, and no peaks other than those attributed to  $PbCO_3$

TABLE 2—PARAMETERS USED TO COMPUTE SORPTION CURVES FOR REMOVAL OF LEAD FROM 52 ml REACTION VOLUMES

|   | Curve | Initial Pb concentration (ppm) | Pb added ( $\mu$ g) | Clay weight (g) |
|---|-------|--------------------------------|---------------------|-----------------|
| Du Page leachate and kaolinite (fig. 1)       | A     | 9.62                           | 500                 | 0.500           |
|   | B     | 19.23                          | 1,000               | 0.500           |
|   | C     | 38.46                          | 2,000               | 1.000           |
|   | D     | 57.69                          | 3,000               | 1.000           |
|   | E     | 76.92                          | 4,000               | 1.000           |
|   | F     | 96.15                          | 5,000               | 1.000           |
|   | G     | 115.38                         | 6,000               | 1.000           |
|   | H     | 153.85                         | 8,000               | 1.000           |
|   | I     | 192.31                         | 10,000              | 1.000           |
|   | J     | 384.62                         | 20,000              | 1.000           |
| Du Page leachate and montmorillonite (fig. 2) | A     | 9.62                           | 500                 | 0.500           |
|   | B     | 19.23                          | 1,000               | 0.500           |
|   | C     | 38.46                          | 2,000               | 1.000           |
|   | D     | 57.69                          | 3,000               | 1.000           |
|   | E     | 76.92                          | 4,000               | 1.000           |
|   | F     | 96.15                          | 5,000               | 1.000           |
|   | G     | 115.38                         | 6,000               | 1.000           |
|   | H     | 153.85                         | 8,000               | 1.000           |
|   | I     | 192.31                         | 10,000              | 1.000           |
|   | J     | 384.62                         | 20,000              | 1.000           |
| Blackwell leachate and kaolinite (fig. 3)     | A     | 19.23                          | 1,000               | 1.000           |
|   | B     | 38.46                          | 2,000               | 1.000           |
|   | C     | 76.92                          | 4,000               | 1.000           |
|   | D     | 96.15                          | 5,000               | 1.000           |
|   | E     | 192.31                         | 10,000              | 1.000           |
|   | F     | 288.46                         | 15,000              | 1.000           |

were observed. The diffraction pattern is evidence that  $PbCO_3$  was the compound responsible for removing Pb from leachate solutions at the higher pH values, and it is presumed to be the cause of the apparent formation of a precipitate at concentrations of Pb greater than 200 ppm shown by the sorption isotherms (fig. 4).

Stumm and Morgan (1962) showed that the occurrence of metal hydroxyl species can affect the sorption of hydrolyzable metal ions. They found that the pH at which metal hydroxyl species formed corresponded to the pH at which metal ion sorption became significant. To check the effect of hydrolysis of the Pb ion on its sorption by clay at various pH values and in solutions where no precipitate formed to remove Pb, we used the distribution of various hydroxyl species in a  $4 \times 10^{-4}$  M  $Pb(NO_3)_2$  solution in the pH range 3 to 8 obtained by Gadde and Laitinen (1973b). They computed the species distribution by using the constants given by Olin (1960). The distribution of Pb hydroxyl species, along with data obtained for sorption by kaolinite from a solution with an initial concentration of  $4 \times 10^{-4}$  M Pb as  $Pb(NO_3)_2$ , is illustrated in figure 6.

It is evident in figure 6 that species other than  $Pb^{++}$  are relatively insignificant (< 1%) at pH values less than 6. Sorption at pH values below 6 are not related to the hydroxyl species of Pb but rather to the  $Pb^{++}$  ion. The low Pb sorption at low pH values is apparently due to increased competition for sorption sites, with  $H^+$  and its related competitive effects on Pb sorption caused by the dissolution of  $Al^{+++}$  ions from the clay crystal lattice (Grim, 1968). At pH values above 6, a sharp rise in Pb sorption occurred, coincident

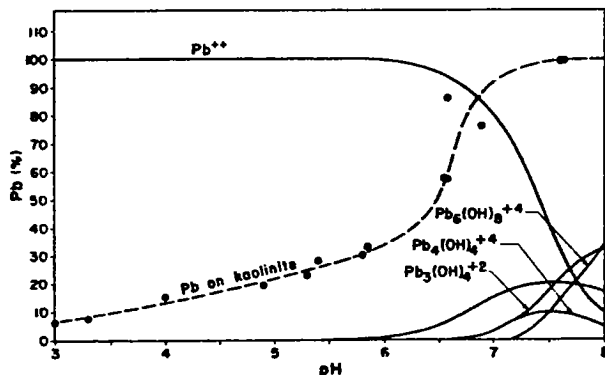


Fig. 6 - Distribution of Pb (II) species in  $4 \times 10^{-4}$  M  $Pb(NO_3)_2$  and uptake by 0.1 g kaolinite from 60 ml of solution.

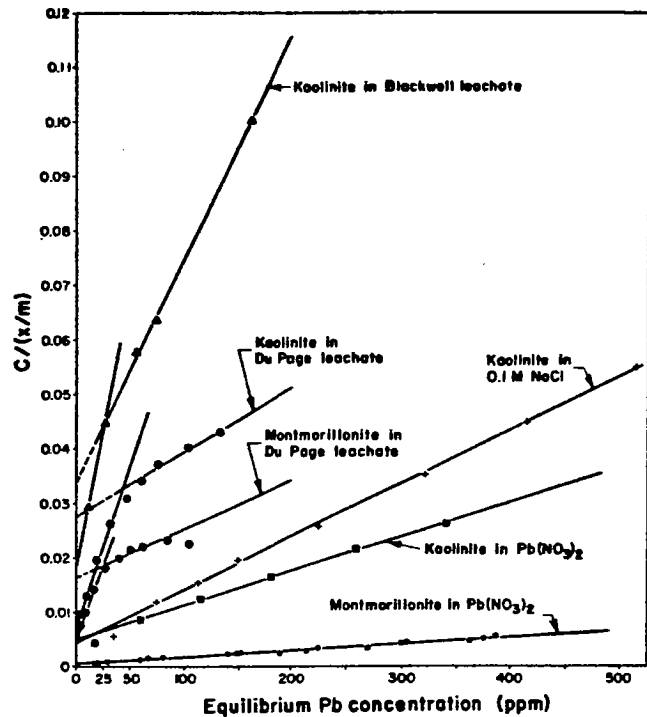


Fig. 5 - Lead sorption by kaolinite and montmorillonite at pH 5.0 and  $25^{\circ}$  C, plotted according to the Langmuir equation.

with the formation of hydroxyl Pb species. It therefore seems likely that at least a portion of the observed increase in Pb sorption with increasing pH and the rapid increase in the amount of Pb sorbed coincident to the formation of monovalent Pb-hydroxyl species are due to a cation exchange mechanism. Table 3 presents further evidence that cation exchange is the principal mechanism for Pb removal by clay minerals.

The sorption maximums for  $Pb(NO_3)_2$  solutions, computed from the slope of



TABLE 3—MAXIMUM REMOVAL OF LEAD FROM pH 5.0 SOLUTIONS AT 25° C,  
COMPUTED BY THE LANGMUIR EQUATION

| Clay and<br>solution              | Adsorption maximums |          |                                  |          |
|-----------------------------------|---------------------|----------|----------------------------------|----------|
|                                   | Micrograms/g        |          | Meq Pb <sup>++</sup> /100 g clay |          |
|                                   | Region 1            | Region 2 | Region 1                         | Region 2 |
| <b>Kaolinite</b>                  |                     |          |                                  |          |
| Pb(NO <sub>3</sub> ) <sub>2</sub> | —                   | 15,914   | —                                | 15.36    |
| 0.1 M NaCl                        | —                   | 10,240   | —                                | 9.88     |
| Du Page leachate                  | 1,680               | 8,530    | 1.62                             | 8.23     |
| Blackwell leachate                | 986                 | 2,401    | 0.95                             | 2.32     |
| <b>Montmorillonite</b>            |                     |          |                                  |          |
| Pb(NO <sub>3</sub> ) <sub>2</sub> | —                   | 82,428   | —                                | 79.56    |
| Du Page leachate                  | 1,811               | 11,133   | 1.75                             | 10.75    |

the Langmuir plots, for kaolinite and montmorillonite are 15.36 and 79.56 meq Pb<sup>++</sup>/100 g clay, respectively. These values can be compared to the cation exchange capacity (CEC) values of 15.1 for kaolinite and 79.5 meq/100 g for montmorillonite that were determined by the ammonium acetate method and reported by Griffin et al. (1976). The CEC values are within 2 percent of the Pb sorption maximums computed from the Langmuir equation—Pb<sup>++</sup> sorption is merely another method of measuring the cation exchange capacity of a clay.

Further evidence of a cation exchange mechanism is the reduction in Pb sorption in solutions containing 0.1 M NaCl and also in the two leachates as their total salt content increases. The decrease in Pb sorption is attributed to increasing competition for cation exchange sites by Na<sup>+</sup> in the 0.1 M NaCl solutions and to an increase in the divalent cation competition in the two leachates. For example, the Blackwell leachate contains much more Fe in solution than the Du Page leachate (table 1). Such high levels of competing ions could account for the very low Pb sorption observed in the presence of landfill leachate compared to Pb sorption in pure Pb(NO<sub>3</sub>)<sub>2</sub> solutions.

The results for Pb sorption from leachate (fig. 5), plotted according to the Langmuir adsorption equation, show a distinct two-slope character. A curve of this shape has been attributed to adsorption at sites of distinctly different adsorption energy (Griffin and Burau, 1974). However, in the present study, competition from other cations in solution seems to be responsible for the change in slope, because it was observed only in the multicomponent cation systems. Solutions of Pb(NO<sub>3</sub>)<sub>2</sub> or NaCl did not exhibit the sharp change in slope for Pb sorption that was observed for the leachates.

One of the assumptions of the Langmuir equation is that the adsorbent surface is homogeneous with respect to the energy of the adsorption sites. However, in a multicomponent cation system the sites are occupied by cations

with various retention energies relative to Pb—that is, Pb can displace cations such as  $\text{Na}^+$  much more easily than it can replace cations such as  $\text{Ca}^{++}$ . This displacement pattern probably affects the shape of the adsorption isotherm because the lower energy sites are preferentially filled—Pb first exchanges with a cation, or a group of cations, that have the lowest exchange energy. This phase of the sorption brings about the initial slope of the Langmuir plot. As the concentration of Pb in solution is increased, the chemical potential gradient is increased until it is sufficient to initiate exchange of the cation, or group of cations, with the next highest level of energy of retention relative to Pb. Initiation of this second energy level of exchange probably produces the sharp change in slope of the Langmuir plots in the leachate solutions (fig. 5).

The observed reductions in over-all Pb sorption can be attributed to the tendency of Pb to form metal-organic complexes with the organic compounds present in landfill leachate, as well as to competition for cation exchange sites. These metal-organic complexes can lower the activity of the Pb in solution, thus reducing the chemical potential gradient for sorption. Gadde and Laitinen (1973a) showed that Pb forms stable complexes with organic compounds found in soils and that these compounds were able to solubilize Pb present in different forms in the solid phase.

To determine the role of Pb-organic complexes in the observed Pb sorption reductions in leachates, the complexing capacity of Pb in the two leachates was measured. In the Du Page leachate, the extent of complexation (ppm complexed) was found to be 22 ppm at a Pb concentration of 200 ppm. It is clear from the above data that only about 11 percent of the Pb is complexed, and it would take more than 50 percent complexation to explain the reduction in Pb sorption in terms of an organic complexing mechanism.

The fact that formation of a Pb-organic complex cannot be used to explain more than a small fraction of the observed reduction in Pb sorption is emphasized by the results obtained from Blackwell leachate. Addition of successive aliquots of Pb to blanks and to the Blackwell leachate gave approximately the same incremental response ( $\mu\text{A}$ -current) in the wave for free lead ion. Up to 80 ppm total Pb, no apparent complexation of Pb was observed.  $\text{Fe}^{++}$ , or its weak complex with leachate, is presumed to have produced the large increase in polarographic current observed at a potential  $-1.4$  V. Apparently,  $\text{Pb}^{++}$  is either unable to compete with  $\text{Fe}^{++}$  or other cations present in large amounts in Blackwell leachate, or the leachate has little or no complexing capacity. The former explanation appears the more plausible.

We concluded that Pb removal from solution is primarily an exchange-adsorption reaction affected by pH and ionic competition. The formation of Pb-organic complexes was concluded to be of secondary importance in landfill leachates because competition from concentrations of other cations was high. At pH values above 6, removal of Pb from solution by clay can be expected to increase substantially, owing to either increased adsorption of Pb-hydroxyl complexes or the formation of  $\text{PbCO}_3$  in landfill leachates.

TABLE 4—THICKNESS OF A SQUARE METER OF A LINER CONTAINING 30 PERCENT CLAY NEEDED TO REMOVE LEAD FROM 762 LITERS (201 GALLONS) OF SOLUTION PER YEAR

| Clay and solution                 | Thickness (cm/m <sup>2</sup> ) of liner (30% clay) |     |   |            |      |    |             |      |   |
|-----------------------------------|--|-----|---|------------|------|----|-------------|------|---|
|                                   | 10 ppm Pb  |     |   | 100 ppm Pb |      |    | 1000 ppm Pb |      |   |
|                                   | at pH  |     |   | at pH      |      |    | at pH       |      |   |
|                                   | 3  | 5   | 8 | 3          | 5    | 8  | 3           | 5    | 8 |
| <b>Kaolinite</b>                  |  |     |   |            |      |    |             |      |   |
| Pb(NO <sub>3</sub> ) <sub>2</sub> | —  | <1  | — | 5.3        | 1.8  | <1 | —           | 10.0 | — |
| 0.1 M NaCl                        | —  | <1  | — | —          | 2.3  | —  | —           | 15.5 | — |
| Du Page                           | 15.9   | 2.1 | * | 28.9       | 6.4  | *  | 79.4        | *    | * |
| Blackwell                         | 19.8   | 4.0 | * | 49.6       | 11.3 | *  | 264.6       | *    | * |
| <b>Montmorillonite</b>            |  |     |   |            |      |    |             |      |   |
| Pb(NO <sub>3</sub> ) <sub>2</sub> | —  | <1  | — | —          | <1   | —  | —           | 1.93 | — |
| Du Page                           | 9.9  | 1.8 | * | 13.2       | 3.7  | *  | 18.0        | *    | * |

\*Precipitation as PbCO<sub>3</sub>

#### Application of Results to Design of Disposal Sites

How thick a proposed clay liner must be to remove all Pb from landfill leachates, from industrial waste streams of similar ionic strength to the leachates (0.1 M NaCl), or from Pb(NO<sub>3</sub>)<sub>2</sub> solutions at various pH values and Pb concentrations can be determined from the data collected in this study. The results of the computations are presented in table 4.

The table gives the thickness of a square meter of a liner, packed to a bulk density of 1.60 g/cc, that contains enough clay (30 percent) to remove all the Pb from 762 liters (201 gal) of solution. That particular volume is the amount of leachate generated from a typical sanitary landfill containing municipal solid waste 3 meters (10 ft) deep and having an annual net infiltration of 254 mm (10 in.) of rainfall (U.S. EPA, 1974). The thicknesses of the clay liner given in the table, therefore, are those needed per square meter of liner for total removal of Pb for a year at the given concentrations of Pb and pH values. They are, of course, the minimum thicknesses possible because they represent an idealized situation. The actual thickness necessary in a field application will be somewhat greater to allow for nonequilibrium conditions, physical dispersion, diffusion, and normal engineering safety factors.

Table 4 indicates that only relatively thin layers of clay, especially of montmorillonite, are necessary for removal of Pb unless the pH values are very acid and the Pb concentrations are high. The high sorption capacity of clay minerals and the reversible nature of exchange adsorption reactions have important environmental consequences. Soils and surface waters may change in ionic composition or pH as environmental conditions change. A sudden decrease

in pH may release large amounts of potentially toxic Pb into the aqueous phase, particularly in places where  $PbCO_3$  has accumulated. Cations, especially divalent and trivalent cations, compete with Pb and may exchange with it, thus allowing Pb to come into solution. These multiple interactions must be considered when the environmental impact of Pb is assessed and a disposal site is designed.

### COPPER, ZINC, AND CADMIUM ADSORPTION

The adsorption of copper, zinc, and cadmium from a landfill leachate by kaolinite and montmorillonite clay minerals was measured as a function of pH. Included in the study was an investigation of adsorption by earth materials of low concentrations of heavy-metal ions from deionized water solutions and their removal (adsorption plus precipitation) from a leachate in the pH range 2 to 8. Our results reveal the mobility of Cu, Zn, and Cd in soils irrigated with leachates and can be applied to the design of clay liners for municipal and industrial waste disposal sites.

#### Theoretical

In any adsorption study, the amount adsorbed by an adsorbent is usually measured as a function of adsorbate concentration in the medium surrounding the adsorbent. It is generally desirable to be able to fit the adsorption data to an adsorption isotherm equation so that "parameters" associated with the adsorption isotherm can be calculated and used for comparisons and correlation with other data. The Langmuir equation (equation [1]) has been used extensively in studies of adsorption of ions from solution by soils and clay minerals. The application of equation [1] to experimental data for Zn adsorption by soils (Shuman, 1975) has produced two linear regions of the plot. Following the lead of Syers et al. (1973), Shuman attributed the two regions to two types of adsorption sites. However, the adsorption model upon which equation [1] is based assumes that the surface of the adsorbent contains only one type of adsorption site. Therefore, there is only weak justification for arguing the existence of two sites on an adsorbent surface when a one-site model equation has been applied to the experimental data. In addition, equation [1] at low concentrations reduces to

$$x/m = kbC. \quad [2]$$

Therefore, equation [2] has no significance at low concentrations, even though  $C/(x/m)$  values can be calculated and plotted. If a two-site adsorption model is to be discussed, then the following equation should be applied to the experimental data:

$$(x/m)_{\text{total}} = \alpha \frac{k_1 b_1 C}{1 + k_1 C} + (1-\alpha) \frac{k_2 b_2 C}{1 + k_2 C} \quad [3]$$

where  $\alpha$  = fraction of sites with bonding-energy coefficient  $k_1$ . In practice, equation [3] is difficult to apply to experimental data.

The linear form of the Langmuir equation (equation [1]) holds best for the plateau region of the adsorption isotherm (high concentrations). This is true regardless of the equilibrium concentrations, because the deviations from the linear plot occur as the equilibrium concentration approaches zero. A close look at equation [1] confirms this point. At or near the plateau region of the adsorption isotherm,  $x/m$  is essentially constant, and hence the real plot is  $C/\text{constant}$  versus  $C$ , which must be a straight line. But at low concentrations, where  $x/m$  is increasing as  $C$  is increasing, values of  $C/(x/m)$  can change at a faster rate than they do at higher concentrations, at which  $C$  is the only variable changing to an appreciable extent. Therefore, all Langmuir plots (equation [1]) will probably show two or more straight-line segments if data points are obtained at sufficiently low and high concentrations.

The most important point ignored by the application of equation [1] to the adsorption of cations from solution by soils and clay minerals is that the adsorption process is primarily one of cation exchange, and for every cation adsorbed one or more cations must be desorbed. The latter can then compete for adsorption sites. Boyd, Shubert, and Adamson (1947) developed an adsorption equation for the simultaneous competitive adsorption of two equally charged cations, A and B. By formal analogy with the Langmuir (1918) equation for adsorption from a binary gaseous mixture, the following equation is obtained:

$$(x/m)_A = \frac{b K_A/K_B (C_A/C_B)}{1 + K_A/K_B (C_A/C_B)} \quad [4]$$

The linear form of equation [4] is

$$\frac{C_A/C_B}{(x/m)_A} = \frac{K_B}{K_A b} + \frac{C_A}{b C_B} \quad [5]$$

Where the concentration of A is low compared to the concentration of B, so that adsorption of A does not produce a detectable change in the concentration of B (e.g., adsorption on a Ca-saturated clay from solutions with a high Ca content), a plot of  $C_A/(x/m)_A$  versus  $C_A$  should be linear. The plot should also be linear when  $(x/m)_A$  approaches the cation exchange capacity (CEC), because  $C_B$  would then become a constant value and would not change as  $C_A$  changes. From equation [4] it can be seen that the amount adsorbed,  $(x/m)_A$ , must depend upon the ratio of the equilibrium concentrations of the exchanging cations and not upon the actual concentrations in solution. Where  $C_B \gg C_A$ ,  $(x/m)_A$  will become a linear function of  $C_A$ , and when  $C_A \gg C_B$ ,  $(x/m)_A$  will become a constant and independent of the concentration of A.

Equation [4] shows that, under appropriate experimental conditions, the amount of exchange-adsorption should be independent of the solution concentration of the cation adsorbed. If the migration of a cation through soils or clays is to be studied by measuring its adsorption from a pure solution, then a fixed weight of soil sample and a fixed solution volume should be maintained throughout the concentration range being studied. However, it is not sufficient to measure the exchange-adsorption from pure cation solutions. For example, to determine how far the Cu, Zn, or Cd in 250 ml of 200 ppm deionized water solutions will migrate down a clay column, the following procedure should be used. One gram of clay is placed in the 250 ml of solution (initial concentration, C);

adsorption will occur to give an equilibrium concentration,  $C_1$ . In the process,  $(200 - C_1) \times 0.25$  mg of cation is adsorbed, and an equivalent number of moles of exchangeable cations on the clay will be desorbed. Hence, the solution phase will now contain a mixture of cations, and the amount of exchange-adsorption of a particular cation will be less than the amount of exchange-adsorption measured from a pure solution with a concentration of  $C_1$ . This process should be carried out stepwise,  $C$  to  $C_1$ ,  $C_1$  to  $C_2$ , . . . ,  $C_{n-1}$  to  $C_n$ , until  $C_n \rightarrow 0$ . Thus, the amount of adsorption from solution concentration  $C_1$  will depend on the initial concentration of the solution from which  $C_1$  was derived.

### Experimental

The clay minerals and leachate used are the same as those used in the Pb adsorption test. After pH adjustment, all clay-leachate or clay-deionized water suspensions were shaken in a constant-temperature bath at  $25 \pm 0.5^\circ \text{C}$  for at least 24 hours to insure complete equilibration. The equilibrium pH values of the clay suspensions were measured, the clay suspensions centrifuged, and the supernatant solutions analyzed by atomic absorption spectroscopy for their Cu, Zn, or Cd concentrations. Blanks (*i.e.*, no clay) of leachate spiked with the heavy metals or deionized water solutions that had been prepared along with the clay suspensions also were analyzed to determine the initial Cu, Zn, or Cd concentrations present in the solutions. The amount of Cu, Zn, or Cd removed from solution by a given clay at a particular pH was calculated as (initial equilibrium concentration)  $\times$  (solution volume/sample weight) / 1000. The amount of Cu, Zn, or Cd removed from solution was plotted as a function of pH.

Three types of experiment were conducted on the removal of Cu, Zn, and Cd by the clay minerals from deionized water solutions of Cu, Zn, or Cd nitrates. In the first, 1.000 g of kaolinite or montmorillonite and 50-ml aliquots of the appropriate nitrate solution were placed in 125-ml Erlenmeyer flasks. The approximate concentrations chosen were 25, 50, 100, and 200 ppm Cu and 10, 40, 200, and 400 ppm Zn for both kaolinite and montmorillonite; 100, 200, and 500 ppm Cd for kaolinite; and 100, 500, and 1000 ppm Cd for montmorillonite. Three or four replicate clay suspensions were prepared for each concentration of Cu, Zn, or Cd. The pH values of the replicate clay suspensions were adjusted to various values in the pH range 4 to 6 with dilute  $\text{HNO}_3$  or dilute NaOH solutions. The use of NaOH was avoided if possible because Na ions can compete for adsorption sites.

In the second type of experiment, the weight of the clay sample and/or the volume of solution were chosen so that the total amount of Cu, Zn, or Cd in solution per gram of clay would be a constant. The quantities used were about 12.5 mg of Cu/g of kaolinite (*i.e.*, 250 ml at 25 ppm Cu/0.5 g) at 10, 25, 125, 200, and 500 ppm Cu; about 62.5 mg of Cu/g of montmorillonite (*i.e.*, 250 ml at 25 ppm Cu/0.10 g) at 25, 125, and 500 ppm Cu; about 20.0 mg of Zn/g of kaolinite (*i.e.*, 50 ml at 40 ppm Zn/0.10 g) at 10, 40, 200, and 400 ppm Zn; about 100 mg of Zn/g of montmorillonite (*i.e.*, 250 ml at 40 ppm Zn/0.10 g) at 10, 40, 200, and 400 ppm Zn; about 25.0 mg Cd/g of kaolinite (*i.e.*, 50 ml at 50 ppm Cd/0.10 g) at 20, 50, 200, and 500 ppm Cd; and about 125.0 mg Cd/g of montmorillonite (*i.e.*, 250 ml at 50 ppm Cd/0.10 g) at 50, 100, 200, and 1000 ppm Cd. Three or four replicate suspensions were prepared for each concentration of Cu, Zn, or Cd. The pH values of the replicate clay suspensions were adjusted to various values in the pH range 4 to 6.

In the third type of experiment, stepwise removal of Cu, Zn, or Cd from solution was studied. Some experiments of the second type that used 250-ml solutions were used as the first step in the third type of experiments. For the second step, the supernatant solutions from replicate clay suspensions in the first step were sampled for analysis and then mixed together. The combined solution was used with fresh clay samples to prepare three replicate clay suspensions, which were adjusted to various pH values in the pH range 4 to 6. The supernatant solutions from the second step were used in a third step, etc.

Experiments on the removal of Cu, Zn, or Cd from leachate were carried out by pipetting 50-ml aliquots of leachate into 125-ml Erlenmeyer flasks. Either the leachate had been spiked with Cu, Zn, or Cd nitrates to give the desired concentration prior to the previous step, or 2.0 ml of an appropriate stock solution was pipetted into the flasks containing the 50-ml aliquots of nonspiked leachate. Several replicates were prepared for each concentration of Cu, Zn, or Cd used. The pH values of the replicate spiked leachate solutions were adjusted to various values throughout the pH range 2 to 8. Samples of either kaolinite or montmorillonite were then weighed out and transferred to the flasks. The weight of clay used was chosen so that the amount of Cu, Zn, or Cd removed from the leachate solutions could be determined with some precision from the difference between the initial and final solution concentrations.

We had learned during preliminary experiments that when the pH of a clay-leachate suspension was adjusted to a particular value the pH of the suspension would rise when the suspension was shaken and that the removal of Cu, Zn, or Cd increased with increasing pH. Therefore, addition of the clay to the spiked leachate solutions after pH adjustments have been made avoids such potential problems as the possible irreversible removal of Cu, Zn, or Cd. The irreversible removal could occur if the pH of the prepared clay plus spiked leachate suspension were high and the pH of the suspension were then adjusted to a much lower value. The experimental procedure used should produce data on true equilibrium removal.

Several individual experiments also were carried out in which clay samples were placed in a mixture of 50-ml aliquots of pH 5 leachate or deionized water and 2-ml aliquots of different stock solutions. The pH of the resulting suspensions was repeatedly adjusted to 5.0 until equilibrium was obtained.

### Results and Discussion

The amount of Cu, Zn, or Cd removed from deionized water solutions was plotted against pH. Except in certain cases, very significant increases in the amounts removed were observed as the pH rose from 4 to 6. The initial concentration of Cu, Zn, or Cd in solution, the weight of the clay used, the final solution volume after pH adjustments, and the removal versus pH curves themselves can be used to construct "adsorption," or "removal" (adsorption plus precipitation) isotherms at different pH values by means of the following equation:

$$\text{Equilibrium concentration (ppm)} = \text{initial concentration (ppm)} - \frac{\text{amount removed (mg/g)} \times \text{wt of clay (g)} \times 1000}{\text{final solution volume (ml)}} \quad [6]$$

Isotherms were calculated from the data recorded for the deionized water solutions at pH 5.0, and the results are shown as isotherm types I, II, and III in figures 7 and 8.

The isotherms called type I (figs. 7 and 8) are those obtained when 1.00 g of kaolinite or montmorillonite was placed in about 50 ml of Cu, Zn, or Cd solution. The total Cu, Zn, or Cd present in 50 ml of solution at various concentrations is given in table 5. For kaolinite (CEC 15.1 meq per 100 g), 75.5  $\mu$ moles of a divalent cation per g would be required for complete exchange; for montmorillonite (CEC 79.5 meq per 100 g), 397.5  $\mu$ moles per g would be required for complete exchange. Therefore, as indicated in table 5, at low concentrations of Cu, Zn, or Cd, insufficient cations are present in 50 ml of solution for complete exchange of 1.00 g of clay (especially montmorillonite). The amount of Cu, Zn, or Cd that can be adsorbed is therefore necessarily limited by the number of Cu, Zn, or Cd ions initially present in solution. The number of Cu, Zn, or Cd ions actually adsorbed will depend on how extensively the desorbing Ca ions compete with the Cu, Zn, or Cd ions remaining in solution. The isotherms of type I in figures 7 and 8 represent the amount of Cu, Zn, or Cd adsorption by 1.00 g of clay from about 50 ml of solution.

The isotherms of type II in figures 7 and 8 were obtained when the weight of clay samples and/or solution volumes were adjusted so that the ratios (total number of Cu, Zn, or Cd ions to number of exchangeable cations on the clay samples) were held about constant (at least 2:1) and independent of the concentrations in the initial solution. Although an equilibrium concentration of Cu, Zn, or Cd ( $C_A$ ) could not be considered to be much greater than the concentration of desorbing Ca ions ( $C_B$ ), the ratio of

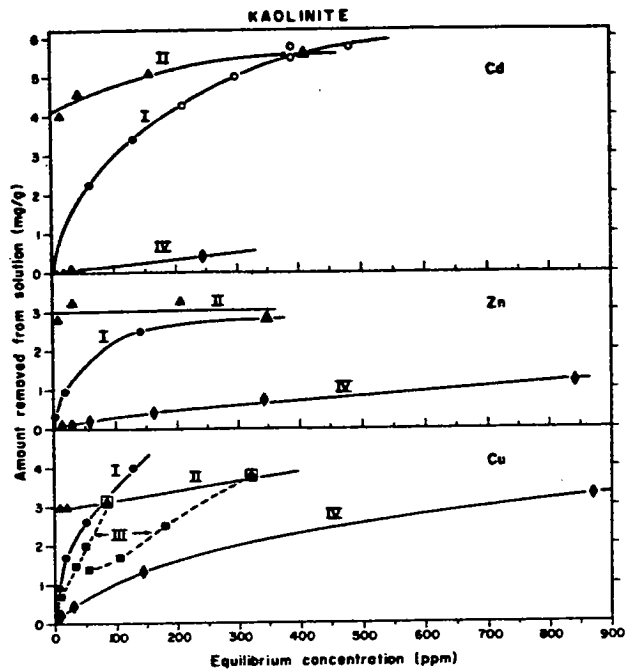


Fig. 7 - Amount of Cu, Zn, or Cd removed from solution per gram of kaolinite at pH 5.0 and 25°C, plotted as a function of the equilibrium concentration. Curve I—fixed weight of clay per fixed solution volume; Curve II—total amount of clay exchangeable ions per total amount of Cu, Zn, or Cd ions in solution held about constant; Curve III—stepped isotherms; Curve IV—Du Page leachate isotherms. Open symbol data points were obtained from clay suspensions adjusted several times to pH 5.0 instead of being calculated from removal curves at pH 5.0.

TABLE 5—TOTAL Cu, Zn, OR Cd IN 50 ML OF SOLUTION

| Initial concentration in solution (ppm) | Copper ( $\mu$ moles in 50-ml solution volumes) | Zinc ( $\mu$ moles in 50-ml solution volumes) | Cadmium ( $\mu$ moles in 50-ml solution volumes) |
|---|---|---|--|
| 4                                       | 3.15  | 3.06  | 1.78   |
| 10                                      | 7.87  | 7.15  | 4.45   |
| 25                                      | 19.7  | 17.9  | 11.1   |
| 40                                      | 31.5  | 30.6  | 17.8   |
| 50                                      | 39.4  | 38.2  | 22.2   |
| 100                                     | 78.7  | 76.5  | 44.5   |
| 200                                     | 157.4   | 153.0   | 89.0   |
| 400                                     | 314.8   | 306.0   | 178.0  |
| 500                                     | 393.4   | 382.5   | 222.5  |
| 1000                                    | 786.9   | 765.0   | 445.0  |



$C_A/C_B$  should be constant; hence, equation [4] says that  $(x/m)_A$  should be constant and independent of  $C_A$ . This is shown by the isotherms of type II in figures 7 and 8. The "scatter" in the experimental data points for the isotherms of type II is attributed to experimental errors caused primarily by problems in measuring accurately the small changes in the concentration that are due to adsorption. These errors must then be multiplied by large factors to compute the amount of metal removed per gram of clay.

The isotherms of types I and II, plotted according to the linear form of the Langmuir equation (equation [1]), are shown in figures 9 and 10. The Langmuir plots for the isotherms of type I (1.00 g clay per 50 ml solution) show a definite two-slope character; in fact, three linear segments of the Langmuir plot appear to exist for Cu-montmorillonite. The Langmuir plots (fig. 10) of the isotherms of type II for montmorillonite (the total amount of Cu, Zn, or Cd initially present in solution per g of clay was held about constant) show only a one-slope character throughout the concentration range investigated. The  $C/(x/m)$  values definitely approach zero as the equilibrium concentration approaches zero. This is precisely what should occur if the competitive Langmuir equation (equation [4]) is valid, because equation [4] says that, if the equilibrium ratio  $C_A/C_B$  is constant,  $(x/m)_A$  is independent of the actual concentration, and, therefore, as  $C_A$  approaches zero,  $C_A/(x/m)_A$  must approach zero.

The Langmuir plots (fig. 9) for the Cu and Cd isotherms of type II with kaolinite do show a two-slope character. It was observed during the Cu adsorption experiments that the pH of the Cu-kaolinite suspensions in deionized water decreased when the flask was shaken, thereby indicating that

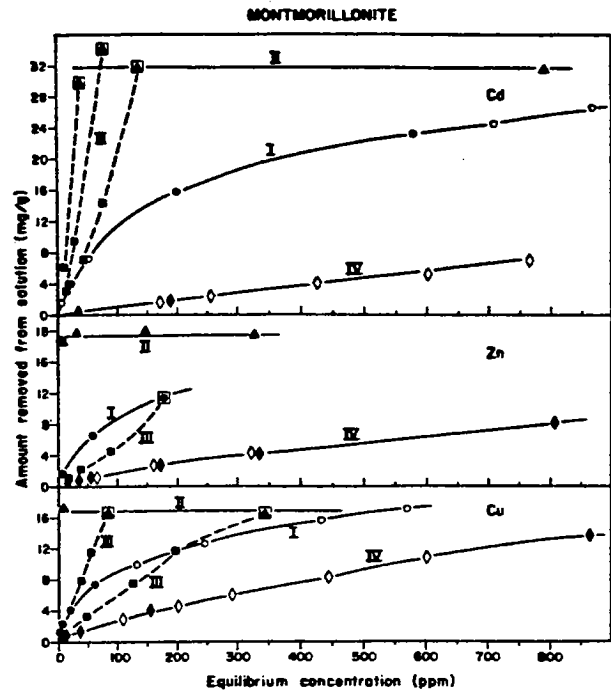


Fig. 8 - Amount of Cu, Zn, or Cd removed from solution per gram of montmorillonite at pH 5.0 and 25° C, plotted as a function of the equilibrium concentration. Numerals and symbols have same meaning as in figure 7.

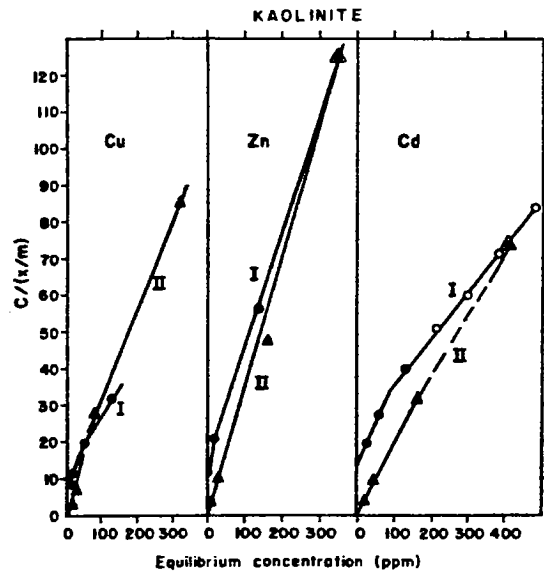


Fig. 9 - Cu, Zn, and Cd removal by kaolinite in deionized water solutions at pH 5.0 and 25° C, plotted according to the Langmuir equation. Numerals refer to corresponding isotherms in figure 7.

hydrolysis of the  $\text{Cu}^{+2}$  ion was occurring in solution (i.e.,  $\text{Cu}^{+2} + \text{H}_2\text{O} = \text{CuOH}^+ + \text{H}^+$ , etc.). Data on hydrolysis of cations (Mesmer and Baes, 1974) show that no appreciable concentrations of  $\text{CuOH}^+$  or  $\text{Cu}_2(\text{OH})_2^{+2}$  will exist in solutions of low Cu concentration below pH 7, but in the pH range 5 to 6 precipitation can occur from solutions of about 400 ppm Cu. Thus, precipitation is a reasonable explanation for the occurrence of the second slope in the Langmuir plot for Cu-kaolinite. Although similar arguments could be advanced for the Cd-kaolinite Langmuir plot, the Mesmer and Baes (1974) data indicate that, in the range of Cd concentrations used, hydrolysis and precipitation cannot be considered as contributing factors to the "adsorption" of Cd by kaolinite around pH 5.0.

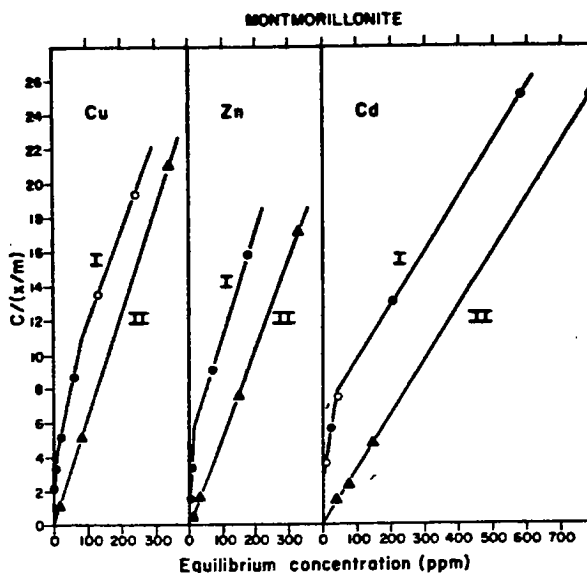


Fig. 10 - Cu, Zn, and Cd removal by montmorillonite in deionized water solutions at pH 5.0 and 25° C, plotted according to the Langmuir equation. Roman numerals indicate corresponding isotherms in figure 8.

Shuman (1975) obtained two-slope Langmuir curves when he plotted data for Zn adsorption by Georgia soils according to equation [1]. John (1972) found no significant correlation between the CEC values and Langmuir Cd adsorption maximums for 30 different soil samples. Both Shuman and John used a fixed weight of soil and a fixed volume of solution in the adsorption measurements. The results of our study indicate that both Shuman and John would have obtained somewhat different results and conclusions if they had equilibrated their soil samples with sufficient solution volumes of low Zn or Cd concentration so that the total Zn or Cd content of the solutions would exceed the CEC values of their respective soil samples. The appropriate solution volumes will necessarily depend on the CEC values of the soil samples (the larger the CEC values, the larger the solution volume that will be required) and what kind of exchangeable cations are present on the soil.

The isotherms of type III in figures 7 and 8 are "stepped" isotherms. These isotherms show the competitive effect of the desorbing exchangeable cations initially present on the clay minerals on the removal of other heavy-metal cations from solution. The isotherms of types I and II in figures 7 and 8 do not provide sufficient information for prediction of the migration of Cu, Zn, or Cd in pure solutions through the soil.

The adsorption data plotted by using the linear form (equation [5]) of the competitive Langmuir equation (equation [4]) are shown in figures 11 and 12. It was assumed that the number of ions (presumed to be all Ca, which is more reasonable for kaolinite than montmorillonite) desorbed from the clays into solution equals the amount of Cu, Zn, or Cd adsorbed from solution. It can be shown that

$$C_A \text{ (ppm)} / \Delta C_A \text{ (ppm)} = C_A \text{ (moles/l)} / C_{Ca} \text{ (moles/l)}$$

where  $C_A$  = equilibrium concentration of Cu, Zn, or Cd and  $\Delta C_A = C_{\text{Initial}} - C_A$ , so that  $(C_A/\Delta C_A)/(x/m)_A$  versus  $(C_A/\Delta C_A)$  was plotted in figures 11 and 12. For stepped isotherms, the  $\Delta C_A$  used included the  $\Delta C_A$  values from previous steps. Although the data show appreciable scatter, reasonably straight lines can be drawn through most of the data points, which include all data plotted for deionized-water solution isotherms I, II, and III in figures 7 and 8. Where some data points lie above the line drawn through the data points,  $C/\Delta C$  is generally small and the number of ions adsorbed ( $x/m$ ) is limited by the total number of ions initially present in solution. Negative deviations from the main linear region can occur when equation [1] is used for low concentrations. Positive deviations from the main linear region can occur when equation [5] is used for small values of  $C/\Delta C$ .

The adsorption maximums calculated from the Langmuir plots of type II in figures 9 and 10 and the competitive Langmuir plots in figures 11 and 12 are given in table 6.

The question arises as to why, if cation exchange is the primary adsorption mechanism, there is such poor correlation between the adsorption maximums calculated from the CEC values and the experimental adsorption maximums. Bittel and Miller (1974) have determined the selectivity coefficients for Cd/Ca on kaolinite and montmorillonite to be about 1 (i.e.,

TABLE 6—COMPARISON OF LANGMUIR ADSORPTION MAXIMUMS IN DEIONIZED WATER WITH CEC VALUES

| Source                                  | Copper<br>(mg/g) |      | Zinc<br>(mg/g) |      | Cadmium<br>(mg/g) |      |
|---|------------------|------|----------------|------|-------------------|------|
|   | K*               | M†   | K              | M    | K                 | M    |
| II - Langmuir plots<br>(Figs. 3 and 4)  | 3.08             | 18.5 | 2.86           | 19.2 | 5.0               | 31.2 |
| Langmuir plots<br>(Figs. 5 and 6)       | 3.33             | 21.0 | 3.00           | 23.6 | -                 | 50.0 |
| Calculated from CEC<br>values (table 1) | 4.80             | 25.3 | 4.94           | 26.0 | 8.45              | 44.8 |

\* Kaolinite. † Montmorillonite.

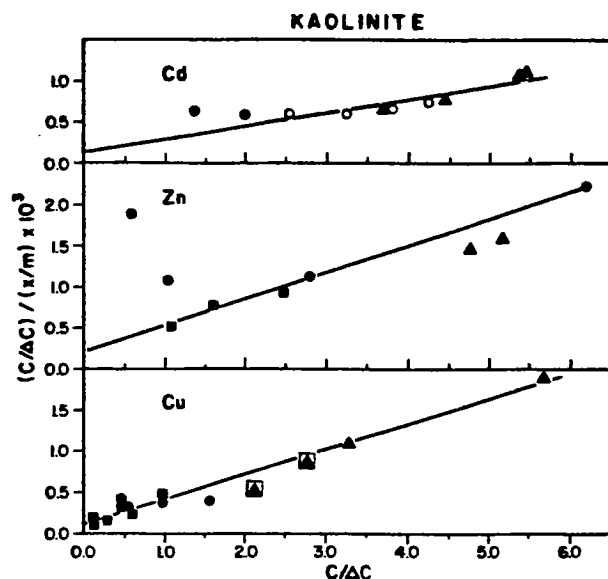


Fig. 11 - Cu, Zn, and Cd removal by kaolinite in deionized water solutions at pH 5.0 and 25° C, plotted according to the competitive Langmuir equation (equation [5]). The data-point symbols correspond to those used in figure 7.

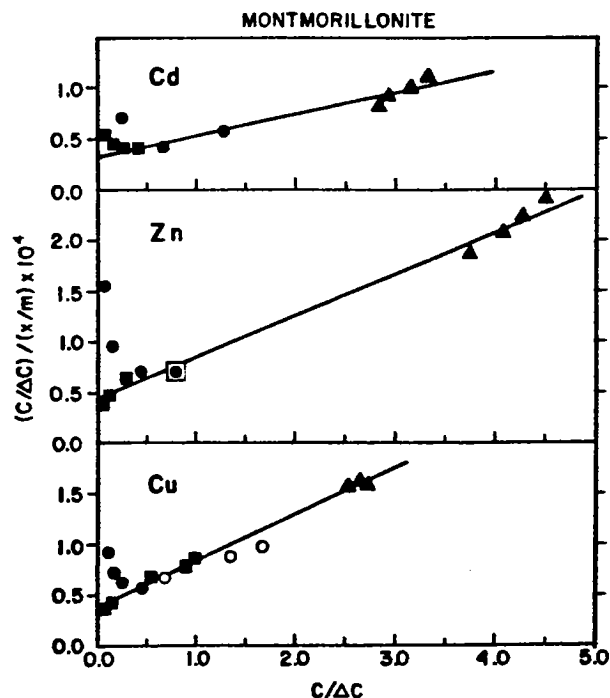


Fig. 12 - Cu, Zn, and Cd removal by montmorillonite in deionized water solutions at pH 5.0 and 25° C, plotted according to the competitive Langmuir equation (equation [5]). The open symbols have the same meaning as those in figure 7.

Ca and Cd ions compete on about an equal basis for adsorption sites), but they do not specify a pH for their experimental measurements. The data obtained in our study indicate that the selectivity coefficients for Cu, Zn, and Cd on Ca-saturated kaolinite and montmorillonite are less than 1 at pH 5 and approach 1 at higher pH. Therefore, the experimental adsorption maximums for Cu, Zn, or Cd would not approach the CEC values until the equilibrium ratio  $C/C_{Ca}$  was larger than was the case in any of our experiments, because the adsorption maximums will, of course, show definite pH-dependence. Prior to the onset of precipitation, which is dependent on both concentration and pH, decreasing competition from  $H^+$  and increasing concentration of hydrolyzed ions (e.g.,  $Cu_2(OH)_4^{+2}$ ,  $ZnOH^+$ , and  $CdOH^+$ ) are possible reasons for the "adsorption" to increase as pH increases.

Curves for pH versus the removal of Cu, Zn, or Cd from leachate by kaolinite and montmorillonite are shown in figures 13 and 14, respectively. The data listed beside each curve and in the figure captions were used in equation [6] to calculate the isotherms of type IV at pH 5.0 (figs. 7 and 8) so that direct comparisons could be made with the deionized-water isotherms. Figures 7 and 8 show that the removal from leachate is appreciably lower than the removal from deionized-water solutions. Boyd, Shubert, and Adamson (1947) gave a general expression for the exchange adsorption of a cation, A, from a mixture of equally charged cations in solution:

$$(x/m)_A = \frac{b K_A C_A}{1 + \sum_{\text{all } j} K_j C_j} \quad [7]$$

Equation [7] says that the exchange adsorption of any one cationic species at constant concentration will decrease as the concentrations of other cationic species increase. Thus, from solutions of high ionic strength, the amount of Cu, Zn, or Cd removed cannot easily approach the CEC of the soil or clay mineral, as is true in the case of exchange-adsorption from solutions of low ionic strength.

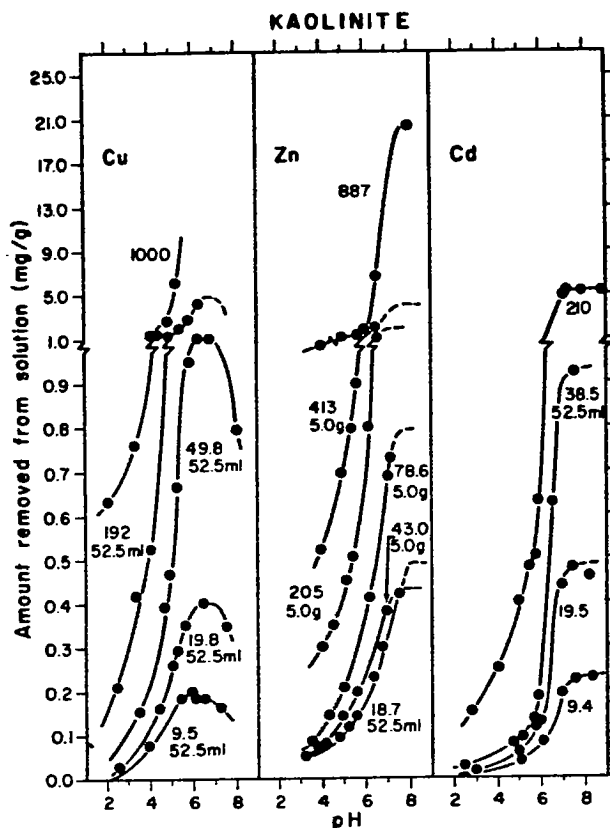


Fig. 13 - Amount of Cu, Zn, or Cd removed from Du Page leachate solutions by kaolinite at 25° C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained. Unless otherwise indicated, 2.0 g of clay and a total leachate solution volume of 50.5 ml were used to obtain each data point.

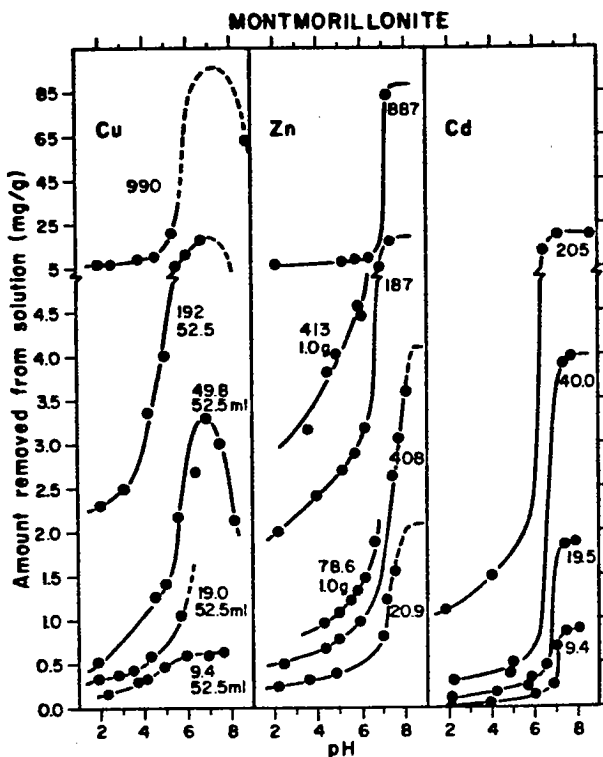


Fig. 14 - Amount of Cu, Zn, or Cd removed from Du Page leachate solutions by montmorillonite at 25° C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained. Unless otherwise indicated, 0.5 g of clay and a total leachate solution volume of 50.5 ml were used to obtain each data point.

and 14) and then decreases as the pH increases. This behavior is due to the amphoteric character of  $\text{Cu}(\text{OH})_2$  precipitates, which redissolve in basic solutions by forming  $\text{Cu}(\text{OH})_3^-$ , etc., ions.

The amount of Cu, Zn, or Cd removed from leachate has no significant apparent dependence on leachate volume, as can be seen from the leachate isotherms (figs. 7 and 8) on which data points obtained for different weights of clay sample but constant leachate volumes have been plotted on one isotherm curve. However, the amount removed could become dependent on the leachate volume if the clay sample is very large.

Equation [7] implies that at a given ionic strength, where  $\sum_{\text{all } j} K_j C_j$  is about constant and large compared to 1,  $(x/m)_A = \text{Constant} \times C_A$ . The isotherms for Cd (figs. 7 and 8) are linear to quite high concentrations.

The sharp rise in the removal curves shown in figures 13 and 14 can easily be interpreted, with the aid of information assembled by Mesmer and Baes (1974), as being caused primarily by precipitation of Cu, Zn, or Cd carbonates, hydroxides, or hydroxide-carbonates. Much less Zn and Cd is removed from the leachate by both kaolinite and montmorillonite than was removed from deionized water solutions at pH 5.0. The reduction of Zn and Cd is about the same for kaolinite and montmorillonite, but the reduction in the amount of Cu removed from the leachate is appreciably greater for montmorillonite than for kaolinite. This is because the Cu is removed by a combination of exchange-adsorption and precipitation. The amount of Cu removed by precipitation, for example 1 mg/g, will be about the same for leachate solutions at pH 5 whether kaolinite or montmorillonite is present in solution. However, the 1 mg/g is about 20 percent of the CEC for kaolinite while it is only about 4 percent of the CEC for montmorillonite. The decrease in removal from leachate, therefore, appears much greater for montmorillonite than for kaolinite although the actual decrease in Cu exchange-adsorption is probably proportionally the same for both clays. The removal of Cu from leachate reaches a maximum about pH 7 (figs. 13

The isotherms for Cu, Zn, or Cd removal from leachate were not plotted according to the linear form of a Langmuir adsorption isotherm equation, although, most assuredly, straight line plots would have been obtained and "adsorption" maximums could be calculated. The reasons for not plotting them were, first, none of the leachate isotherm plots have really reached the plateau region in the concentration range studied (up to 1000 ppm). Second, any adsorption maximums calculated from the Langmuir plots would be somewhat meaningless because the amount of exchange-adsorption from leachate is limited by competition, owing to the high ionic strength of the leachate rather than because all the adsorption sites have been occupied by Cu, Zn, or Cd ions as is implied with a Langmuir adsorption maximum. Third, if an adsorption maximum is calculated from the rising part of an isotherm, it represents the amount adsorbed at some higher hypothetical concentration that may or may not lie on the real adsorption isotherm. Finally, our purpose was to determine the maximum amount of Cu, Zn, or Cd that can be removed by kaolinite or montmorillonite from leachate at any concentration up to approximately 1000 ppm. As we have seen for removal from deionized water, with appropriate experimental conditions the amount removed is relatively independent of concentration and is proportional to the CEC values of the clays. It would presumably approach the CEC at higher (volume)/(weight of clay) ratios. But with leachate the ionic strength is not a variable to be adjusted, and the conditions cannot be created under which at low concentrations of Cu, Zn, or Cd the ratio of the (equilibrium concentration of Cu, Zn, or Cd)/(concentration of other cations) is large. The maximum amount removed must then be a function of the ionic strength of the leachate, the CEC of the clay sample, and the pH of the leachate. Therefore, the maximum amount removed at any concentration and pH from leachate (or for that matter any solution) is simply the value read from the removal isotherm itself at a designated concentration.

#### Summary and Conclusions

Under appropriate experimental conditions, the amount of Cu, Zn, or Cd exchange-adsorbed from deionized water by purified kaolinite and montmorillonite clay minerals is relatively independent of the equilibrium concentration of Cu, Zn, or Cd. However, the maximum amount of Cu, Zn, or Cd adsorbed in our experiments was related to, but not equal to, the CEC values of the clay minerals, probably because the desorbing Ca ions effectively competed with the Cu, Zn, or Cd ions present in solution. If cation-exchange adsorption experiments are carried out at constant (solution volume)/(sample weight) ratios for Cu, Zn, or Cd in deionized water, the amount of adsorption is necessarily limited by the total amount of Cu, Zn, or Cd that was initially present in solution at low concentrations. Therefore, the isotherm obtained really indicates the amount of Cu, Zn, or Cd removed by a fixed weight of sample from a fixed volume of solution versus concentration. At low concentrations a different isotherm can be obtained simply by using a different constant (solution volume)/(sample weight) ratio in the experiments. If the migration of Cu, Zn, or Cd from deionized water through soils or clays is to be studied by means of batch experiments, the experiments can be carried out in steps (i.e., repeated treatments of a solution with new soil or clay samples) for each initial solution concentration tested. That is desirable because of the increasing concentration of exchangeable cations in solution as exchange-adsorption of a particular cation from solution occurs in steps towards zero.

The three different types of isotherms obtained for the same range of Cu, Zn, or Cd concentration are easily interpreted in terms of a cation exchange-adsorption mechanism. Also, our data suggest that the correct "Langmuir" isotherm equation to apply to exchange adsorption data is equation [4], which covers the simultaneous competitive adsorption of two cations, not equation [1], which is for a single cation.

The adsorption of Cu, Zn, or Cd from leachate by kaolinite and montmorillonite clay minerals is presumed to occur via a cation exchange mechanism, but, because the ionic strength of the leachate is not variable in the adsorption experiments, the amount adsorbed cannot become independent of the concentration of Cu, Zn, or Cd in the leachate. There is therefore no way to predict the maximum amount of Cu, Zn, or Cd that will be adsorbed from a given leachate by a given soil or clay mineral at a given pH and at a particular concentration without actually measuring it. At pH 5.0, precipitation of Cu as a hydroxide-carbonate makes a very significant contribution to the total amount of Cu removed by kaolinite, but because montmorillonite has a higher amount of exchange-adsorption the contribution of precipitation to the total amount of Cu removed by montmorillonite is less significant. If the pH of the leachate is lower than about 6.5, precipitation makes no significant contribution to the total amount of Zn and Cd removed by kaolinite and montmorillonite.

The mobility of Cu, Zn, and Cd in soils or clay minerals is dependent upon solution pH and ionic strength as well as on the CEC of the soils or clay minerals. This is of little importance at sufficiently high (above 7) pH values, because precipitation is then more important than cation exchange in the removal of Cu, Zn, or Cd from solution. However, the mobility of Cu would apparently reach a minimum at pH 7 and would subsequently increase at pH values above 7. At pH 5 Cu, Zn, and Cd in leachate will be quite mobile in soils or clay minerals with low CEC values, especially when the ionic strength of the leachate is high. Thus, if adsorption data at pH 5.0 is obtained from a leachate very high in ionic strength or from a low CEC soil or clay mineral and the mobility of Cu, Zn, or Cd is estimated from the data, it can be stated that for higher pH values, higher CEC values, and/or for leachates with low ionic strength, the mobility would be less than it is at pH 5.0. These facts provide a safety factor for estimations of adsorption and/or mobility.

Treatment of a soil with a waste stream or leachate will alter the exchangeable cation distribution of the soil; for example, a soil with a high Ca content will become high in Na if treated with a waste stream or leachate that has a high Na content. Thus, in addition to the problem of heavy-metal toxicity to plants or heavy-metal accumulation in the food chain when waste streams or leachates are disposed of on agricultural land, other problems may be created.

#### CHROMIUM ADSORPTION STUDIES

Chromium compounds are widely used in the leather, textile, chemical manufacturing, metal finishing, and other industries. Approximately 30,000 tons of chromium-bearing wastes are discharged annually from the metal-finishing industries alone (U.S. EPA, 1973a). Such discharges have created problems of

environmental pollution. Chromium (VI) contamination of the village wells in Douglas, Michigan, was reported in 1947 (Davids and Lieber, 1951), and as early as 1952 chromium was found in high concentration in the ground water of Nassua County, New York (Welsch, 1955).

In trace amounts, chromium is an essential element in the diet of some animals and, presumably, human beings. However, at high concentrations, all compounds of chromium are toxic (Smith, 1972). The valence state of chromium has a considerable influence on its toxicity. It is well established that Cr(VI) compounds are the most toxic and are usually irritating or poisonous to all tissues (Baetjer, 1956).

The distribution and impact of chromium on aquatic ecological systems have not thus far been extensively studied, so that relatively little is known about the transfer of the metal from waste streams to earth materials and then to living systems. Because information about the chromium-leachate system is scant, the present study was designed to determine the effect pH has on Cr(VI) and Cr(III) adsorption by clay minerals and on their precipitation in deionized water and municipal leachate solutions. We also hoped for some insight into the factors that affect the mobility of chromium as it passes through soils or clay-mineral layers. These soil or clay layers may be useful as liners for waste disposal sites.

### Experimental

The clay minerals and leachate used in the study were described earlier. Various concentrations of Cr(VI) as potassium chromate ( $K_2CrO_4$ ) were added to both deionized water and Du Page leachate, and 50-ml aliquots were pipetted into Erlenmeyer flasks containing either 3 g of montmorillonite or 5 g of kaolinite. The weight of clay used was chosen so that the amount of Cr removed from the solutions could be determined with some precision from the difference between the initial and final solution concentrations. Several replicate suspensions were prepared for each concentration, and their pH values were adjusted with either  $HNO_3$  or  $NaOH$  to various values in the pH range 1.0 to 9.0.

In preliminary experiments, Cr(VI) adsorption was found to decrease as pH increased, and pH values of the Cr(VI)-clay suspensions rose when the flasks were shaken. Also, apparent irreversible Cr(VI) adsorption occurred if the Cr(VI)-clay suspensions had been equilibrated at a given pH value and again at a higher pH. Therefore, the flasks were shaken for about 2 weeks in a constant temperature bath at  $25 \pm 0.5^\circ C$ ; the pH values of the clay suspensions were measured each day, and acid or base was added when necessary to maintain the initial pH value. At least 1 day after the final pH adjustment, the pH values were recorded and the suspensions centrifuged. The supernatant solutions were then decanted into plastic bottles and their pH adjusted to  $< 2.0$  to prevent any Cr adsorption by the container. The equilibrium Cr concentrations  $C_{Eq}$  (ppm) in the supernatant solutions were determined by atomic absorption spectroscopy. The initial Cr concentration ( $C_I$ ) was determined in ppm by analyses of a blank sample (i.e., a sample without clay) prepared at the same time



as the clay suspensions. In our experiments,  $C_I$  concentrations ranging from 5 to 300 ppm Cr as Cr(VI) were used.

The amount of Cr(VI) adsorbed ( $x/m$ ) in mg/g clay at a given pH was calculated as

$$(C_I - C_{Eq}) \times V_E/1000$$

where  $V_E$  = final solution volume (ml)/weight of clay sample (g).

The amount of Cr(VI) adsorbed by a fixed amount of clay from a given  $C_I$  solution at various pH values was plotted against the pH values to obtain an adsorption-pH curve.

The experimental procedures for the Cr(III) adsorption studies were similar to those used in the Cr(VI) experiments. It was determined that 0.100 g of the clay minerals would give the desired precision in determining the change in Cr(III) concentrations at equilibrium. Chromium (III) nitrate ( $Cr(NO_3)_3 \cdot 9H_2O$ ) was used as a source of Cr(III). The study of Cr(III) adsorption was generally limited to the pH range of 1.5 to 4.5 because of Cr(III) precipitation around pH 5. Because of the precipitation, the pH of the leachate was adjusted to about 4 prior to spiking the leachate with Cr(III). An initial Cr(III) concentration range of 30 to 800 ppm was chosen for the experiments.

#### Results and Discussion

Adsorption isotherms at various pH values can be calculated from a family of adsorption-pH curves. The amount of Cr adsorbed ( $x/m$ ) in mg/g of clay at a particular pH value is read from an adsorption-pH curve for a particular  $C_I$ , and the equilibrium concentration,  $C_{Eq}$ , in ppm is calculated from the following equation:

$$C_{Eq} = C_I - \frac{(x/m) \cdot 1000}{V_E} \quad [8]$$

where all the parameters are as previously defined.

Interpretation of the adsorption data was aided by application of the Langmuir (1918) equation. In the derivation of the Langmuir equation it is assumed that (a) the surface is energetically homogeneous, (b) the adsorbate-adsorbate interaction on the surface is negligible, and (c) the adsorbed molecules do not influence neighboring sites. The Langmuir adsorption equation in its linear form (equation [1]) was used to describe the adsorption data.

#### Chromium (VI) Adsorption

No precipitation of Cr(VI) was observed in the pH range 1.0 to 9.0. Families of Cr(VI) adsorption-pH curves are presented in figures 15 and 16. Several characteristics of Cr(VI) adsorption by the clays appear. First, the adsorption of Cr(VI) decreases as pH increases. Second, no Cr(VI) is adsorbed by the clays near pH 8.5 and above. Third, the amounts of Cr(VI) adsorbed are

small compared to the amounts of exchangeable cations on the clay samples.

Diagrams showing the distribution of Cr(VI) species covering the experimental concentration range are presented in figure 17 and the curves were calculated by using the constants given in Butler (1964). Noteworthy is the rapid decrease in the fractions of  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  species above pH 5 and the corresponding increase in the fraction of  $\text{CrO}_4^{2-}$  species, which becomes the principal species present in solution at about pH 8.5 (fig. 17). Below pH 2 the fraction of  $\text{HCrO}_4^-$  ions decreases rapidly as the fraction of  $\text{H}_2\text{CrO}_4$  species increases.

The behavior of the Cr(VI) adsorption-pH curves in figures 15 and 16 implies that the  $\text{HCrO}_4^-$  ion is the principal ion being adsorbed by the clay minerals. Conversely, the lack of adsorption at pH values above 8.5 indicates that the  $\text{CrO}_4^{2-}$  ion is not adsorbed at all by either of the two clays. The mechanism of Cr(VI) adsorption by these clay minerals apparently cannot neutralize the two negative charges present on the  $\text{CrO}_4^{2-}$  ion. On the other hand,

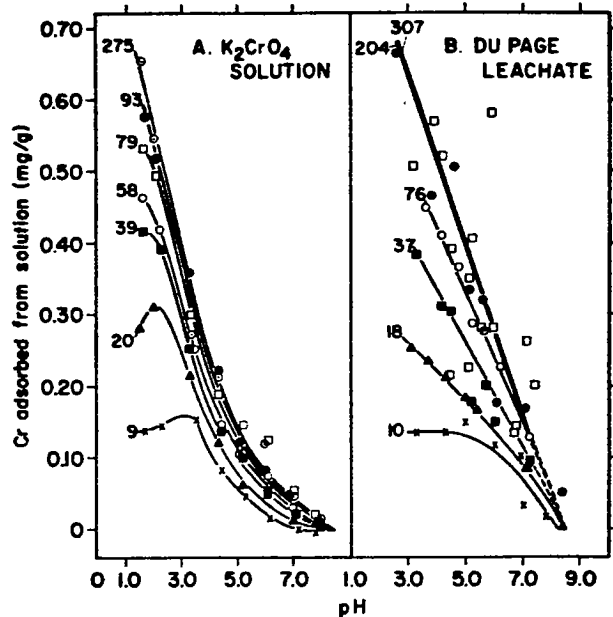


Fig. 15 - Chromium (VI) adsorption-pH curves for montmorillonite at 25°C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve, and the equivalence volume for each curve is 16.7 ml/g montmorillonite.

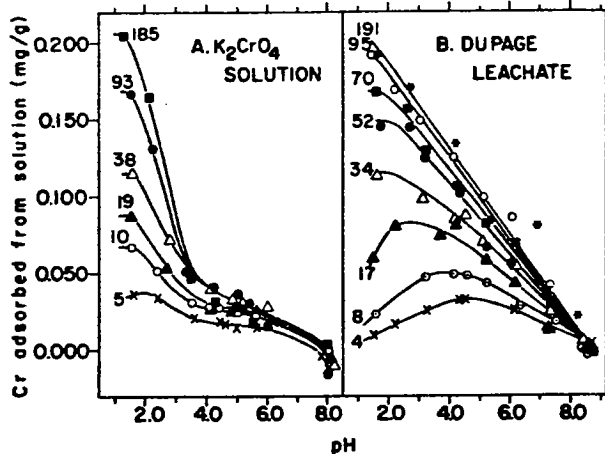


Fig. 16 - Chromium (VI) adsorption-pH curves for kaolinite at 25°C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve, and the equivalence volume for each curve is 10.0 ml/g kaolinite.

$\text{Cr}_2\text{O}_7^{2-}$  ions may be adsorbed at low pH values because of their more open structure ( $\text{CrO}_3^- - \text{O} - \text{CrO}_3^-$ ), which places the two negative charges an appreciable distance apart, in contrast to charges on adjacent oxygens that occur in the  $\text{CrO}_4^{2-}$  structure. The charge separation on the  $\text{Cr}_2\text{O}_7^{2-}$  ion may allow it to act essentially as two monovalent ions, with either each negative charge filling an adsorption site or one negative charge filling an adsorption site and the other negative charge being neutralized by a cation in solution. If the distribution of Cr(VI) species in solution is the only factor governing adsorption of Cr(VI) throughout the pH range 2 to 5, a plateau should be observed in the Cr(VI) adsorption-pH curves; however, the adsorption of Cr(VI) continues to rise with de-

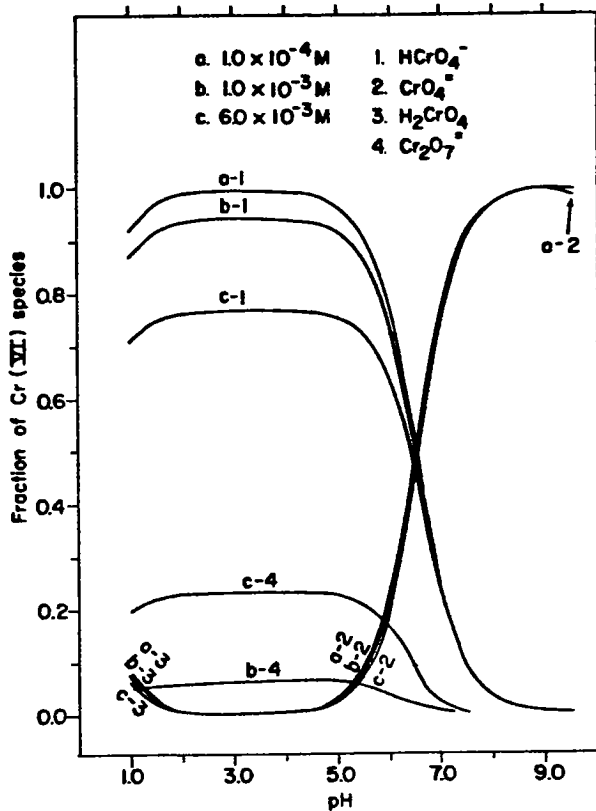


Fig. 17 - Distribution of Cr(VI) species for various Cr(VI) concentrations.

creasing pH to a pH value around 2. Therefore, in the low pH range the pH probably modifies the structures of the clay minerals to permit increased Cr(VI) adsorption to occur. Dissolution of clay minerals is known to occur at low pH levels (Hofmann et al., 1956). This can alter the surface structure and surface area of the clays, resulting in changes in their adsorption characteristics as the pH is lowered.

Adsorption isotherms were constructed from the Cr(VI) adsorption-pH curves in figures 15 and 16 by using equation [8] at pH values of 3.0, 4.0, 5.0, and 7.0. Sample adsorption isotherms, constructed at pH 4.0, are shown in figure 18. For both clay minerals, more Cr(VI) was adsorbed from Du Page leachate solutions than from pure  $K_2CrO_4$  solutions throughout the pH range 3.0 to 7.0. This result is contrary to what was expected. Evidently, anions (e.g.,  $Cl^-$  and  $HCO_3^-$ ) in the leachate do not compete favorably with  $HCrO_4^-$  ions, or adsorption would have decreased.

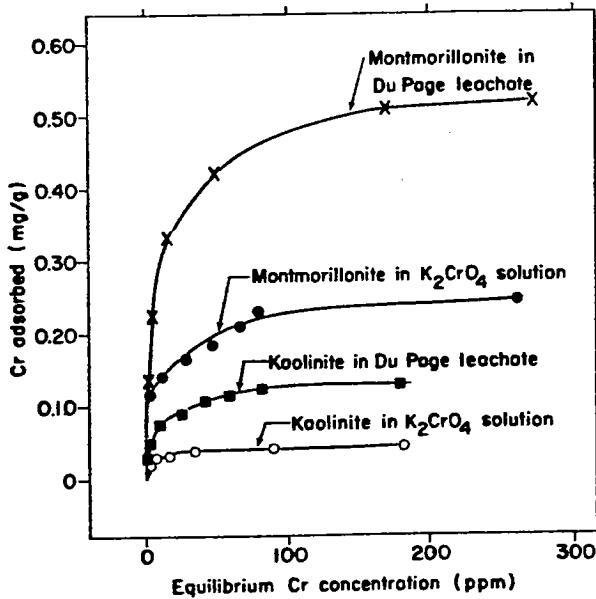


Fig. 18 - Adsorption isotherms for Cr(VI) at pH 4.0 and 25° C.

The effect of the  $Cl^-$  ion on the adsorption of Cr(VI) by clay was determined by adsorption experiments carried out with 20 ppm Cr(VI) in deionized water with, and without, 1000 ppm of  $Cl^-$  added as NaCl. No appreciable change in the adsorption of Cr(VI) was caused by the  $Cl^-$  ion. That more Cr(VI) was adsorbed from Du Page leachate than from pure  $K_2CrO_4$  solutions may be the result of the formation in the leachate solutions of polynuclear complexes, organic or inorganic in nature, which can be adsorbed by the clay. The high ionic strength of the leachate may also contribute to higher adsorption of Cr(VI) species by depressing the diffuse double layer surrounding the clay particles (van Olphen, 1963). More ions could then approach the clay surface and be adsorbed.

The adsorption isotherms for Cr(VI) at pH values of 3.0, 4.0, 5.0, and 7.0 were plotted according to the linear form of the Langmuir equation (equation [1]). All the Langmuir plots give linear regression  $r^2$  values of 0.99. The Langmuir plots at pH 4.0 are shown in figure 19. From the slopes of the Langmuir plots, adsorption maximums were calculated and are presented in table 7. The difference in the calculated adsorption maximums of montmorillonite and kaolinite reflects the difference in the probable number of available adsorption sites, based on comparison of the structural differences and the surface areas of the two clay minerals. The precise mechanism for anion adsorption by clay minerals is not known, but we, as others have, assume that anion exchange plays an important role in the adsorption process. However, the adsorption maximums presented in table 7 represent the maximum number of Cr(VI) ions adsorbed at some sufficiently high concentration of Cr(VI) ions in solution, whereas the adsorption isotherms in figure 18 represent the maximum number of Cr(VI) ions that can be adsorbed at any given concentration of Cr(VI) ions in solution.

**Chromium (III) Adsorption**

During preliminary experiments on Cr(III) adsorption by kaolinite, the removal curves shown in figure 20 were obtained. The curve labeled "blank" in figure 20 represents removal of Cr(III) from a solution containing no clay and shows that precipitation becomes a very important mechanism near pH 5.0. The precipitate formed was blue-gray, and X-ray diffraction patterns of the precipitate showed no definite crystalline structure. Because only HNO<sub>3</sub> and NaOH were used to adjust the pH of the Cr(NO<sub>3</sub>)<sub>3</sub> solution, we concluded that the precipitate formed is a chromic hydroxide, especially as Murray (1956) stated that chromic hydroxide is a hydrous oxide (Cr<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O) of indefinite composition

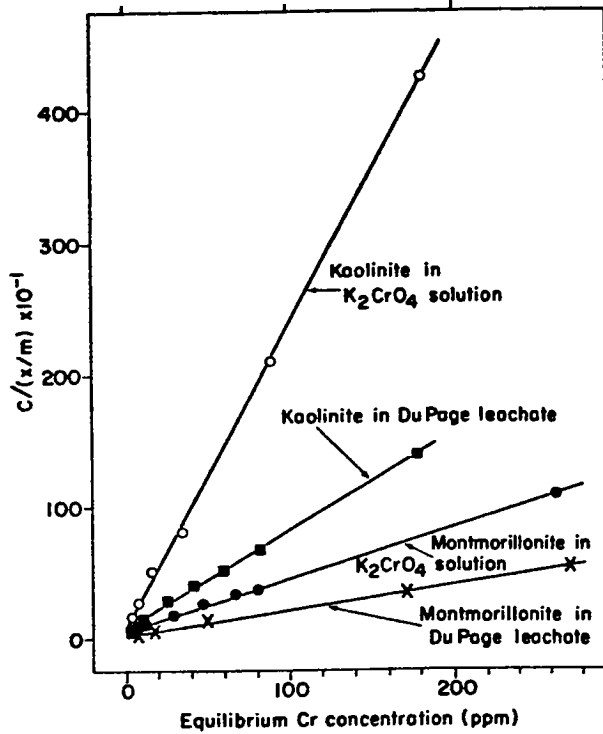


Fig. 19 - Langmuir plots of Cr(VI) adsorption data at pH 4.0 and 25° C.

TABLE 7—ADSORPTION MAXIMUMS FOR Cr(VI) BY MONTMORILLONITE AND KAOLINITE AT 25° C FOR VARIOUS pH VALUES

| pH        | Pure K <sub>2</sub> CrO <sub>4</sub> solution (mg/g) | Du Page leachate solution (mg/g) |
|-----------|--|----------------------------------|
|           | MONTMORILLONITE                                      |                                  |
| 3.0       | 0.400  | 0.667                            |
| 4.0       | 0.256  | 0.526                            |
| 5.0       | 0.147  | 0.417                            |
| 7.0       | 0.052  | 0.169                            |
| KAOLINITE |  |                                  |
| 3.0       | 0.093  | 0.189                            |
| 4.0       | 0.044  | 0.130                            |
| 5.0       | 0.032  | 0.115                            |
| 7.0       | 0.015  | 0.051                            |

Because only HNO<sub>3</sub> and NaOH were used to adjust the pH of the Cr(NO<sub>3</sub>)<sub>3</sub> solution, we concluded that the precipitate formed is a chromic hydroxide, especially as Murray (1956) stated that chromic hydroxide is a hydrous oxide (Cr<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O) of indefinite composition

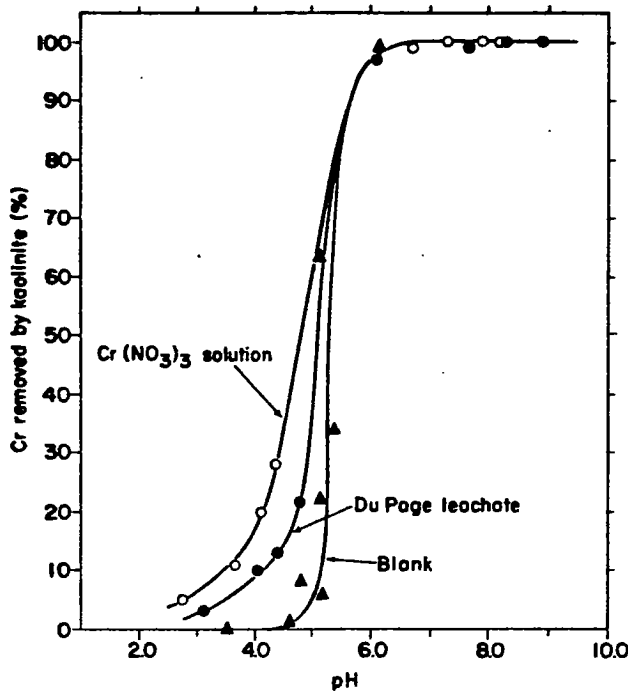


Fig. 20 - Removal of Cr(III) from solution by kaolinite. The curve labeled "Blank" represents Cr(NO<sub>3</sub>)<sub>3</sub> solution without kaolinite.

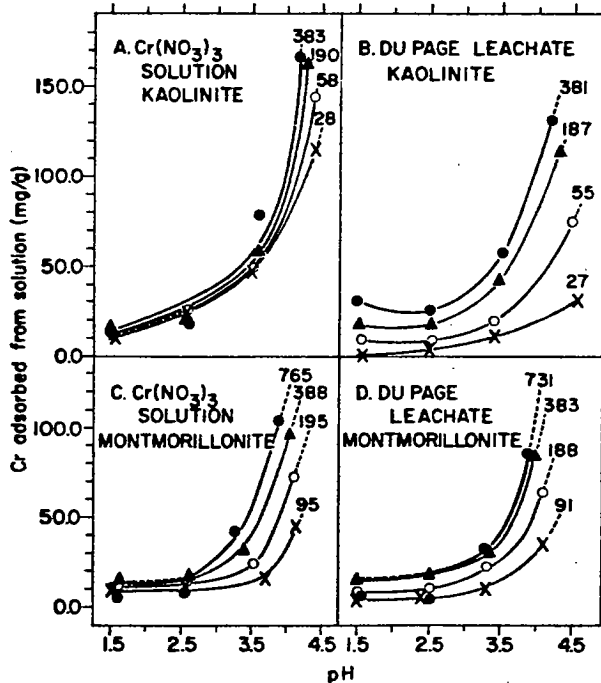


Fig. 21 - Chromium (III) adsorption-pH curves at 25° C. Initial Cr(III) concentrations (ppm) are indicated beside each removal curve, and the equivalence volume for each curve is 500.0 ml/g kaolinite.

that is blue gray when its water content is high.

Families of Cr(III) adsorption-pH curves for the pH range 1.5 to 4.5 are presented in figure 21. Cation exchange is generally accepted as the principal mechanism for cation adsorption by soils and clay minerals. Chromium (III) is known (Rollinson, 1956) to be extensively hydrolyzed in acid solutions to species such as Cr(OH)<sup>2+</sup>, Cr(OH)<sub>2</sub><sup>1+</sup> or Cr<sub>2</sub>(OH)<sub>4</sub><sup>2+</sup> or Cr<sub>6</sub>(OH)<sub>12</sub><sup>6+</sup>, and Cr<sub>6</sub>(OH)<sub>15</sub><sup>3+</sup>. Therefore, the increasing adsorption of Cr(III) as pH increases can be attributed, in part, to exchange-adsorption of hydrolyzed Cr(III) species other than Cr<sup>3+</sup> ions.

Adsorption isotherms were constructed from the adsorption-pH curves (fig. 21) by using equation [1] at pH values 2.5, 3.0, and 4.0. The isotherms constructed for pH 4.0 are shown in figure 22. As was expected, the adsorption of Cr(III) by the clay minerals is lower in Du Page leachate than in pure Cr(NO<sub>3</sub>)<sub>3</sub> solutions. However, significantly less reduction in adsorption of Cr(III) from Du Page leachate (3 percent to 14 percent) took place than was observed in tests of Pb, Cu, Zn, and Cd adsorption from Du Page leachate by the same clay minerals. The Cr(III) species existing in solution are so strongly adsorbed that the cations present in the Du Page leachate do not effectively compete with the Cr(III) species for exchange-adsorption sites.

The adsorption isotherm data for Cr(III) at pH values 2.5, 3.0, and 4.0 were plotted according to the Langmuir equation (equation [1]), and the Langmuir plots for the pH 4.0 adsorption isotherms are shown in figure 23. Adsorption maximums calculated from the slopes of the Langmuir plots in figure 23 are presented in table

8. The amounts of the various hydrolyzed Cr(III) species that could be adsorbed via a cation exchange mechanism by the montmorillonite and kaolinite clay minerals having CEC values of 79.5 meq/100 g and 15.1 meq/100 g, respectively, are presented in table 8. If cation exchange is the principal adsorption mechanism, the ratio of the adsorption maximums should be about equal to the ratio of the CEC values for the two clay minerals.

At pH 2.5 the adsorption maximum ratio is close to the CEC ratio (table 8), but the adsorption maximums themselves are higher than those based on exchange adsorption of  $Cr^{3+}$  ions. This implies that even at pH 2.5 some hydrolyzed Cr(III) species are being adsorbed. The question may arise as to the validity of using CEC values obtained from  $NH_4^+$  ion exchange at pH 7.0 to calculate the expected adsorption maximums at pH 2.5. However, as there is a general relative correlation between the adsorption maximums and CEC values, it is reasonable to use adsorption maximums calculated from CEC values for comparison purposes. At pH 4.0, the ratio of the adsorption maximum increases to about 13, and the amount of Cr(III) adsorbed by montmorillonite is even larger than would be expected from the exchange adsorption of the  $Cr_6(OH)_{15}^{3+}$ .

TABLE 8—ADSORPTION MAXIMUMS FOR Cr(III) BY MONTMORILLONITE AND KAOLINITE AT 25° C FOR VARIOUS pH VALUES (mg/g)

| pH 2.5                       | pH 3.0 |      | pH 4.0 |       | Values based on CEC for different species |                      |                                  |  |      |
|------------------------------|--------|------|--------|-------|---|----------------------|----------------------------------|--|------|
|                              | P*     | L†   | P      | L     | Cr <sup>3+</sup>                          | Cr(OH) <sup>2+</sup> | Cr(OH) <sub>2</sub> <sup>+</sup> | Cr <sub>6</sub> (OH) <sub>15</sub> <sup>3+</sup> |      |
| MONTMORILLONITE              |        |      |        |       |   |                      |                                  |  |      |
| 17.9                         | —      | 33.7 | 32.8   | 139.6 | 136.1                                     | 13.8                 | 20.7                             | 41.4   | 82.7 |
| KAOLINITE                    |        |      |        |       |   |                      |                                  |  |      |
| 3.3                          | —      | 5.0  | 5.0    | 10.7  | 14.7                                      | 2.6                  | 3.9                              | 7.8  | 15.6 |
| RATIO OF ADSORPTION MAXIMUMS |        |      |        |       |   |                      |                                  |  |      |
| 5.4                          | —      | 6.5  | 6.6    | 13.0  | 9.3                                       | 5.3                  | 5.3                              | 5.3  | 5.3  |

\*Pure solutions; †Du Page leachate solutions.

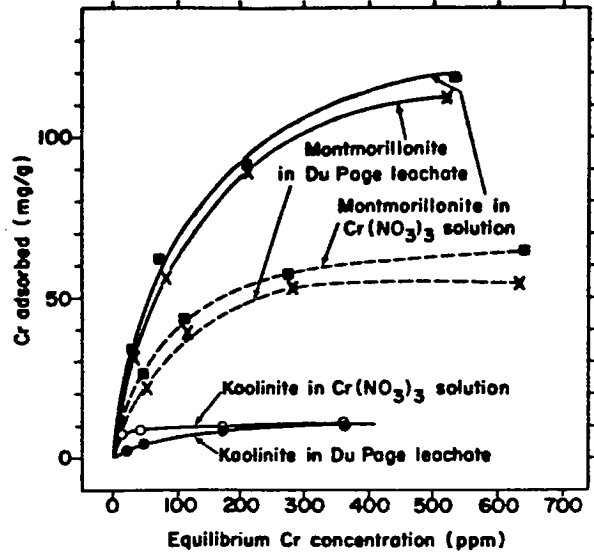


Fig. 22 - Chromium (III) adsorption isotherms at pH 4.0 and 25° C. The dashed curves were obtained from the "corrected" adsorption-pH curves.

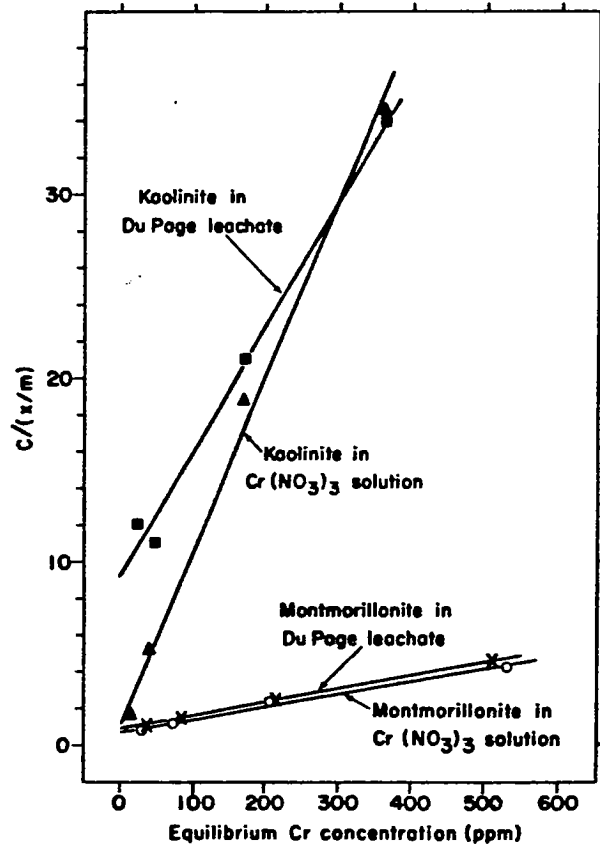


Fig. 23 - Langmuir plots of Cr(III) adsorption data at pH 4.0 and 25° C.

The high adsorption maximum ratio at pH 4.0 is the result of the large adsorption maximum obtained for montmorillonite, which appears to be caused indirectly by our experimental procedure. The rates of some of the Cr(III) hydrolysis reactions are very slow, and in one case reported (Laswick and Plane, 1959) about 107 days were required for Cr(III) solutions, even at elevated temperatures, to reach equilibrium. In our Cr(III) experiments, the clay mineral suspensions were adjusted to a particular pH value, such as 4.5. After a few hours, hydrolysis caused the pH of the suspensions to drop. The pH of the suspensions were readjusted to 4.5, but the pH again dropped because of hydrolysis. The pH of the suspensions were all readjusted to the desired pH value several times during a period of two weeks. They were then shaken for 2 days before a final pH value was measured, and the suspensions were centrifuged.

What appears to occur in the pH range 3.5 to 4.5 is as follows. Adsorption plus possible precipitation of Cr(III) takes place at the higher initial pH values to which the suspensions had been adjusted. But, when hydrolysis causes the pH of the suspensions to drop, desorption of Cr(III) species from the clay mineral or dissolution of any precipitate formed apparently does not occur fast enough to achieve true equilibrium in the clay suspension. The pH values of the montmorillonite suspensions showed greater decreases than those of the kaolinite suspensions, and apparently as a result much greater differences are produced between the calculated and true equilibrium adsorption maximums for montmorillonite than between those for kaolinite.

The adsorption-pH curves shown in figure 21 were replotted as the amount of Cr(III) adsorbed versus the highest pH values to which the clay suspensions were adjusted. The adsorption isotherms were calculated from the "corrected" adsorption-pH curves at pH 4.0 and are shown as the dotted isotherms for montmorillonite in figure 22. The "corrected" adsorption isotherms for kaolinite were almost superimposable on the isotherms shown in figure 22, and therefore were omitted. Adsorption maximums from pure  $\text{Cr}(\text{NO}_3)_3$  solutions, calculated by Langmuir plots of the "corrected" isotherms at pH 4.0, are 72.2 mg/g for montmorillonite and 10.0 mg/g for kaolinite. Thus, the "corrected" adsorption maximums agree with an exchange-adsorption mechanism involving hydrolyzed Cr(III) species. As Laswick and Plane (1959) pointed out, the changes that Cr(III) species undergo are generally quite slow, making the interpretation of some experiments difficult.

### Conclusions

The results of the chromium study indicate that landfill disposal of Cr(III) wastes probably would not initiate pollution problems. Above pH 6, Cr(III) should be immobile because of precipitation. Below pH 4, Cr(III) species are strongly adsorbed by both kaolinite and montmorillonite and would have a relatively low mobility through soils or clay minerals used as landfill liners. Between pH 4 and 6, the combination of adsorption and precipitation should render Cr(III) quite immobile.

In the pH range 1.5 to 4.0, 30 to 300 times more Cr(III) than Cr(VI) is adsorbed by the clay minerals; at higher pH values the ratio (Cr(III) removed)/(Cr(VI) removed) becomes even larger because of increased Cr(III) removal

and decreasing adsorption of Cr(VI). Cr(VI) adsorption decreases markedly as the pH is raised into the alkaline range, and the Cr(VI) would become very mobile at high pH. Since Cr(VI) is the most toxic and mobile form of Cr, landfill disposal of Cr(VI) wastes potentially can cause serious pollution problems, even if the landfill has a thick clay liner. The results of this study suggest that a conversion of Cr(VI) wastes to Cr(III) by a process such as that devised by Shiga (1975) may be necessary to prevent pollution of water resources by Cr(VI) wastes disposed of in a landfill.

#### ARSENIC AND SELENIUM ADSORPTION STUDIES

Arsenic and selenium are toxic (U.S. EPA, 1973b) and their potential for creating pollution problems is high. The U.S. Environmental Protection Agency cites several instances in which land disposal of arsenic wastes has poisoned drinking water wells (U.S. EPA, 1973a). Selenium has reportedly polluted ground water as much as 2 miles from a dump on Long Island (Garland and Mosher, 1975).

Arsenic and selenium waste streams may be liquids, suspensions, or sludges. Samples from waste streams from copper, lead, and zinc smelting, from the manufacturing of duplicating and photographic equipment, and from pharmaceutical industries have been analyzed and found to contain from 1000 to 30,000 ppm As and from 3000 to 50,000 ppm Se (Lehman, 1973). These waste streams may be disposed of on land in lagoons, in landfills, or by spreading. Land spreading of municipal wastewater effluents (U.S. EPA, 1975) and sewage sludges that may contain low concentrations of As and Se is now being considered as a viable alternative to treating the waste to remove the toxic elements.

The purpose of this study was to provide some basic data regarding the effect pH has on the removal of As and Se from landfill leachate by kaolinite and montmorillonite, the common clay minerals found in soils. The results of the study are applicable as to whether As and Se wastes can be safely disposed of in landfills properly designed to contain municipal solid waste. Information concerning the mobility of As and Se through soils can be useful in the design of land disposal systems for As and Se wastes.

#### Experimental

The clay minerals and leachates used in this study are those described in the introductory paragraphs. Appropriate stock solutions of As(V) and As(III) were prepared by dissolving reagent grade  $\text{Na}_2\text{HAsO}_4$  or  $\text{NaAsO}_2$  in deionized water. Se(IV) stock solutions were prepared by dissolving pure selenium metal in a minimum amount of 1:1  $\text{HNO}_3$ . The solution was heated gently to speed up the dissolution. All stock solutions were adjusted to about pH 5 before use.

Fifty-ml aliquots of leachate were pipetted into 125-ml Erlenmeyer flasks containing from 1.00 to 5.00 g of either kaolinite or montmorillonite. The weight of clay used was chosen so that the amount of As(V), As(III), or



Se(IV) removed from the leachate solutions could be determined with some precision from the difference between the initial and final concentrations of the solutions. Several replicates of each clay suspension were prepared. The pH values of the replicate clay suspensions were adjusted with HNO<sub>3</sub> or NaOH to pH values ranging from 1 to 9. The clay suspensions were shaken overnight before 2.0 ml of an appropriate stock solution of either As or Se at pH 5 was pipetted into the flasks. Of several possible experimental procedures, the procedure used gave the most satisfactory results.

The As or Se clay suspensions were shaken in a bath at a constant temperature of 25 ± 0.5° C for at least 24 hours to insure complete equilibration. The equilibrium pH values of the clay suspensions were measured, the clay suspensions centrifuged, and the supernatant solutions analyzed for their As or Se concentration by atomic absorption spectroscopy. A N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame was used for As analyses and an air-C<sub>2</sub>H<sub>2</sub> flame was used for Se analyses. Blanks (i.e., no clay) were prepared along with the clay suspensions and were analyzed to determine the initial As or Se concentration. The amount of As or Se removed from solution by a given clay at a particular pH was determined as the (initial - equilibrium concentration) × (total solution volume after pH adjustments) ÷ (sample weight). The amount of As or Se removed from solution was then plotted as a function of pH. From the initial concentration of As or Se in solution, the weight of clay used, the final solution volume after pH adjustments, and the removal versus pH curves themselves, "adsorption" isotherms were constructed at different pH values by use of equation [6].

### Results and Discussion

#### Arsenate (As(V)) and Arsenite (As(III)) Adsorption

Curves for the removal of As(V) from leachate by kaolinite and montmorillonite versus pH are shown in figure 24. The amount of As(V) removed from solution reaches a maximum at about pH 5. The distribution of As(V) species in solution as a function of pH is shown in figure 25A. Comparison of figure 24 with figure 25A shows that the As(V) removal curves follow the monovalent H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> species curve reasonably well. It was

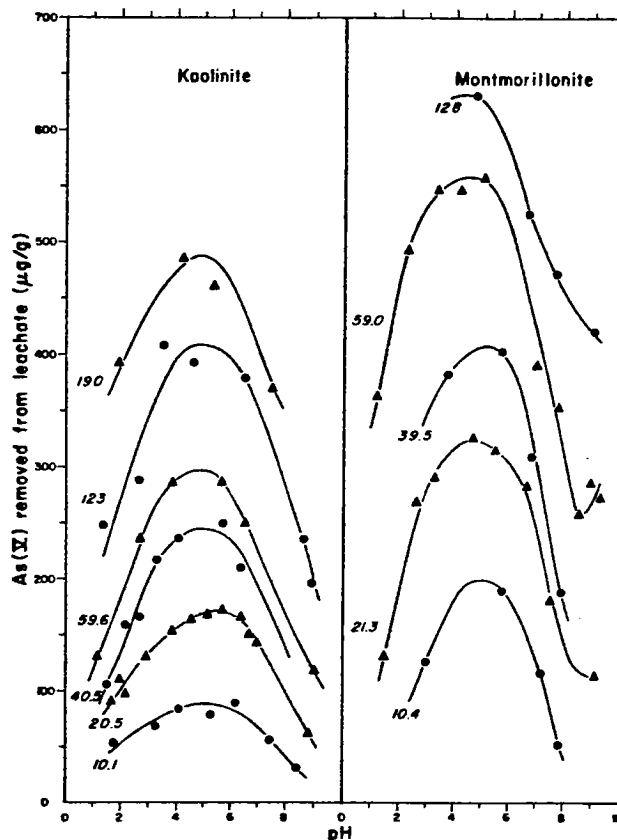


Fig. 24 - Amount of As(V) removed from Du Page leachate solutions by kaolinite and montmorillonite at 25° C, plotted as a function of pH. Initial solution concentrations of As(V) are given in ppm on the curves. Each datum point was obtained by using either 4 g of kaolinite or 1 g of montmorillonite in a total solution volume of 52.5 ml.

concluded, therefore, that the  $H_2AsO_4^-$  ion is the principal As(V) ion being adsorbed by the clay minerals. The nonadsorption or depressed adsorption of the  $HAsO_4^{2-}$  ion is apparently due to the occurrence of negative charges on adjacent oxygen atoms in the tetrahedral  $HAsO_4^{2-}$  ion, which results in repulsion of the ion from the clay surface.

Curves for the removal of As(III) from leachate by kaolinite and montmorillonite are plotted versus pH in figure 26. In general, an increase in adsorption of As(III) is observed as pH increases in the range 3 to 9. The montmorillonite removal curves in figure 26 show a peak about pH 7. There is some question as to what As(III) species are present in the leachate solutions and which is actually being adsorbed. In a study (Everest and Popiel, 1957) of As(III) adsorption by an anion exchange resin, the concentration of  $As_3O_5^-$  or  $As_3(OH)_{10}^-$  species was low and the amount of exchange adsorption was small. Other As(III) species that apparently exist in solution are  $As_2O_4^{2-}$  ( $As_2(OH)_8^{2-}$ ),  $As(OH)_3$ ,  $As(OH)_4^-$ , and  $AsO_2OH^-$ , the latter two species becoming important above pH 9. Whatever As(III) species are present in solution, the fraction of the total As(III) in solution that is present as monovalent As(III) species will increase as pH increases. Therefore, the amount of As(III) adsorption should increase as pH increases (fig. 26). There is no apparent explanation for the peaks observed about pH 7 on the montmorillonite removal curves in figure 26. Although no peaks appear on the kaolinite removal curves in figure 26, they

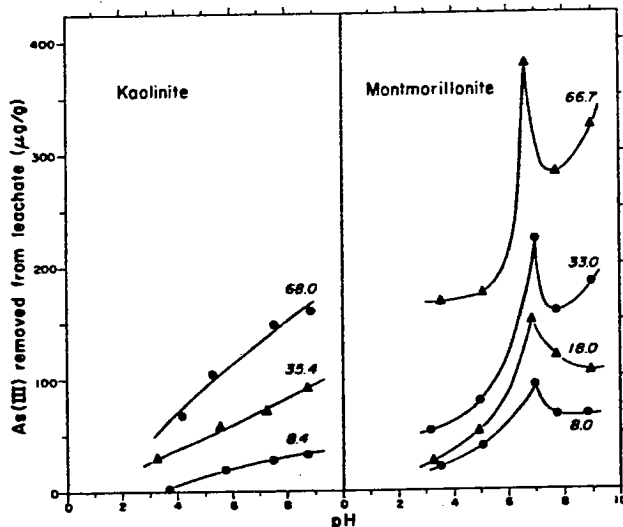


Fig. 26 - Amount of As(III) removed from Du Page leachate solutions by kaolinite and montmorillonite at 25° C, plotted as a function of pH. Numbers on curves give the initial solution concentration of As(III) in ppm. Each datum point was obtained by using 4 g of clay in a total solution volume of 52.5 ml.

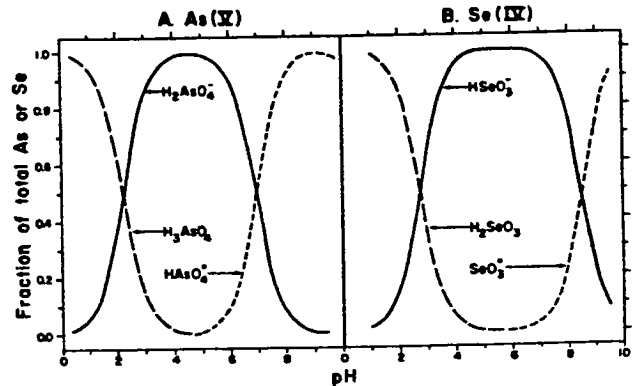


Fig. 25 - Distribution of forms of As(V) and Se(IV).

might have appeared if more data points were obtained in the pH range 6.5 to 7. When removal curves (not shown) for As(V) and As(III) from deionized water solutions that were obtained at a single concentration for each clay mineral are compared with the corresponding leachate removal curves, the anion competition present in the leachate is seen to suppress the clay mineral adsorption of As(V) slightly and adsorption of As(III) by some 30 to 50 percent.

When removal curves (not shown) for As(V) and As(III) from deionized water solutions that were obtained at a single concentration for each clay mineral are compared with the corresponding leachate removal curves, the anion competition present in the leachate is seen to suppress the clay mineral adsorption of As(V) slightly and adsorption of As(III) by some 30 to 50 percent.

Isotherms calculated from the removal curves in figures 24 and 26 at pH 5.0 are shown in figure 27. The higher adsorption of As(V) and As(III) by montmorillonite compared to their adsorption by kaolinite simply reflect the differences in structure and surface area of the two clay minerals. Anion exchange sites

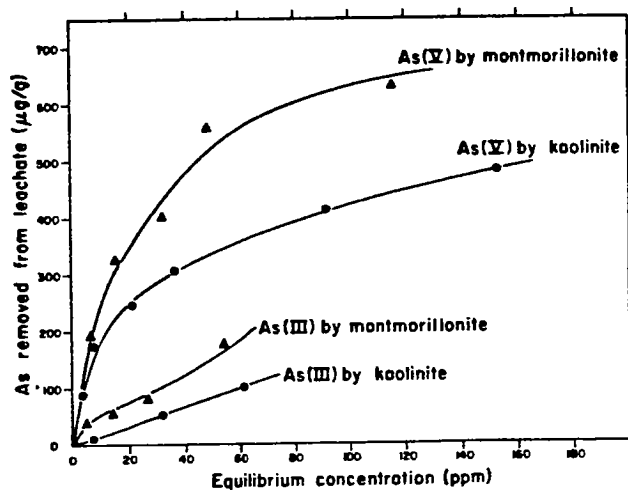


Fig. 27 - Amount of As(V) or As(III) removed from Du Page leachate solutions at pH 5.0 and 25° C per gram of clay, plotted as a function of the equilibrium As concentration.

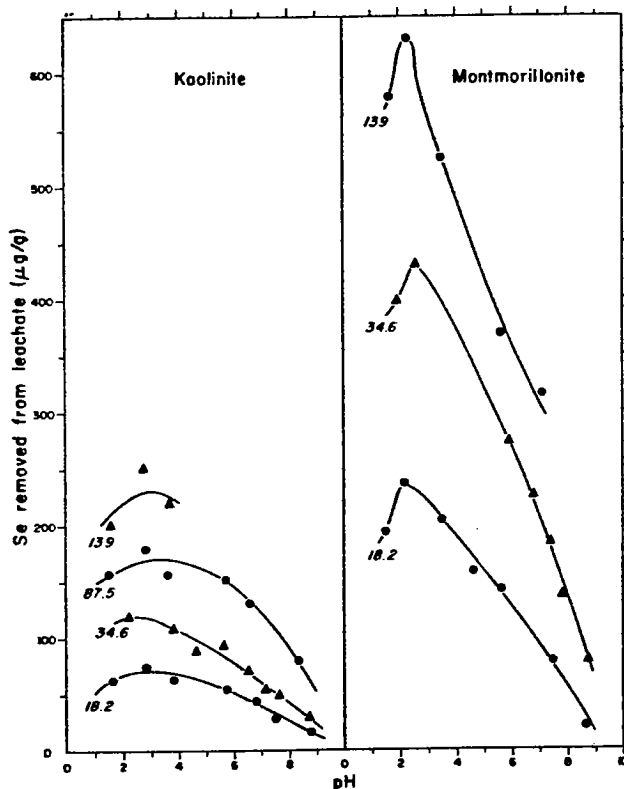


Fig. 28 - Amount of Se(IV) removed from Du Page leachate solutions by kaolinite and montmorillonite at 25° C, plotted as a function of pH. Numbers are the initial solution concentration of Se(IV) in ppm. Each datum point was obtained by using either 5 g of kaolinite or 1 g of montmorillonite in a total solution volume of 52.5 ml.

are thought to exist primarily at the broken edges of clay minerals (Grim, 1968).

Montmorillonite clay was found to adsorb approximately twice as much As as kaolinite. Surface area data, as measured by N<sub>2</sub> gas adsorption, suggest that the montmorillonite has roughly twice as much edge area as the kaolinite. The tetrahedral H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> ion can align itself with the silica tetrahedral of the clay lattice and can form an extension of the crystal lattice, which has a relatively high bond strength. The arsenate ion can be compared to the large As<sub>3</sub>(OH)<sub>10</sub><sup>-</sup> ion, which is not tetrahedral and thus is unable to align itself as effectively on the clay edges. It was therefore concluded that the principal adsorption mechanism was anion exchange of the monovalent species of each elemental form.

#### Selenite (Se(IV)) Adsorption

Curves for the removal of Se(IV) from leachate by kaolinite and montmorillonite versus pH are shown in figure 28. The removal of Se(IV) goes through a maximum in the pH range 2 to 3 and then decreases as the pH increases. The distribution of Se(IV) species in solution as a function of pH is shown in figure 25B. As for As(V), the monovalent HSeO<sub>3</sub><sup>-</sup> ion appears to be the species predominantly adsorbed by the clay minerals. It is evident from the data in figure 28 that the adsorption of Se from solution is rapidly reaching zero removal at approximately pH 10, which is the value at which the HSeO<sub>3</sub><sup>-</sup> species disappears from solution (fig. 25B). The HSeO<sub>3</sub><sup>-</sup> ion has a trigonal-pyramidal configuration, as opposed to a tetrahedral configuration for the H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> ion, which may account for its reduced adsorption. The configuration of the HSeO<sub>3</sub><sup>-</sup> ion must therefore be an inhibiting factor in its adsorption by the clay minerals. On the other hand, pH must be playing a signifi-

cant role in modifying the clay mineral surface structure so that increasing adsorption occurs with decreasing pH until it reaches the point where a significant fraction of the total Se(IV) in solution is present as  $H_2SeO_3$  molecules. At this point, adsorption starts to decline sharply as the pH is lowered below a value of 2.

When removal curves (not shown) for Se(IV) from deionized water solutions that were obtained at a single concentration for each clay mineral are compared with the corresponding leachate removal curves, they showed that the leachate slightly suppresses the adsorption of Se(IV) by the clay minerals. This suppression is presumed to be due to competition for anion exchange sites between the  $HSeO_3^-$  ion and the high concentrations of anions present in leachate (table 1).

Isotherms calculated from the removal curves in figure 28 at pH values 3.0, 5.0, and 7.0 are shown in figure 29. Adsorption of Se(IV) by montmorillonite is higher than adsorption by kaolinite, reflecting the structural and surface area differences between the two clay minerals, as previously discussed.

### Conclusions

The results of this study indicate that pH has a pronounced effect on the amounts of As(V), As(III), and Se(IV) adsorbed from leachate by clay minerals. It was concluded that the principal adsorption mechanism was anion exchange, and that, as the species distribution diagrams showed, the monovalent species of each element studied accounted for most of the adsorption and for the strong pH dependency of the adsorption process.

The results also suggest that optimum As removal from waste streams would be achieved by converting any As(III) to As(V) and then disposing of the waste in montmorillonitic soils at pH 5. Optimum Se(IV) removal would be achieved by disposal in a montmorillonitic soil at a pH of 2 to 3. A high mobility, and hence potential pollution hazard, would be expected from land disposal of As(V) or Se(IV) wastes under alkaline conditions.

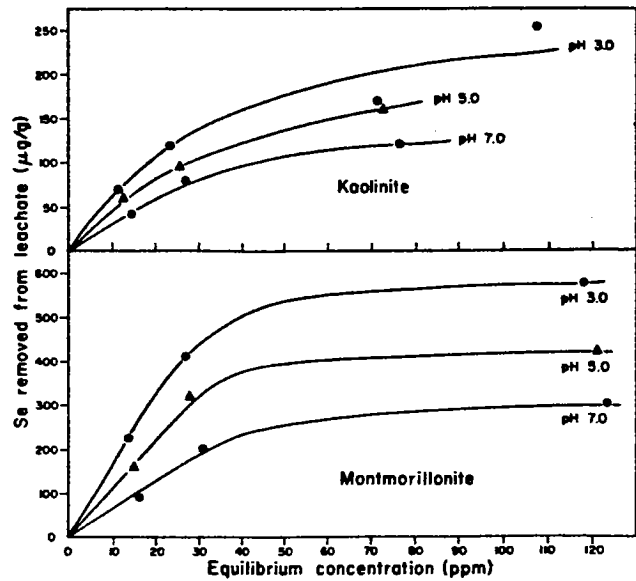


Fig. 29 - Amount of Se(IV) removed from Du Page leachate solutions at 25° C and several pH values per gram of clay, plotted as a function of the equilibrium Se concentration.

## MERCURY ADSORPTION STUDIES

As mercury has been the subject of many publications, its occurrence and toxicity will be discussed here only briefly. Mercury is widely distributed in the air, soil, and water in low concentrations (Klein, 1972). However, Hg-related technology has at times redistributed this Hg in the environment, and it is this redistribution that we must concern ourselves with because it often results in dangerously high Hg concentrations (Goldwater, 1971).

The main source of Hg contamination of the environment has been industry (D'Itri, 1972a), and much of this contamination can be attributed to the discharge of industrial waste water into rivers and streams (Turney, 1972; Derryberry, 1972). Much of the mercury in waste, both organic and inorganic, disposed of in this manner can be directly or indirectly converted by anaerobic microbes into mono- or di-methylmercury (D'Itri, 1972a; Greeson, 1970), both of which are extremely toxic.

As a result of studies on Hg contamination and poisoning, the disposal of industrial mercurial wastes is carefully controlled. However, the potential for contamination still exists where gaps in knowledge preclude enlightened disposal practices. The possibility of contamination also exists at municipal landfill sites that accept wastes containing mercury. The leachate generated from these sites is anaerobic and therefore has the ability to convert mercurial wastes into their toxic forms. Mercury is incorporated into many industrial or consumer products, such as paints, pharmaceuticals, paper products, fluorescent lamps, and mercury batteries. The indiscriminate disposal of these products in landfills by an uninformed population presents a potential threat to the environment from Hg contamination (D'Itri, 1972b).

Very little research has been done on the chemical behavior of Hg in municipal leachates. The information that is available to date is inadequate for making an evaluation of the migration of Hg in landfills. Our studies on the adsorption of Hg from leachate by clay minerals were initiated to determine whether clay minerals used as landfill liners can attenuate Hg that may be present in leachates.

### Experimental

To determine the amount of Hg removed from solution, a series of samples was prepared that consisted of  $\text{HgCl}_2$  solution,  $\text{HgCl}_2$  in Du Page landfill leachate, and  $\text{HgCl}_2$  in Du Page landfill leachate with clay (kaolinite or montmorillonite) added. The latter two series of samples were also used to determine the amounts of organic and inorganic Hg removed from solution.

The amounts of organically bound Hg and inorganic Hg in solution were determined by the flameless atomic absorption spectroscopy (AA) technique described by Griffin and Shimp (1976).

Eight samples were prepared for each solution in each experiment. Before addition of Hg, 50-ml aliquots of either deionized H<sub>2</sub>O, Du Page leachate, or Du Page leachate and 1.000 g of kaolinite were added to 125-ml Erlenmeyer flasks. Each solution was then adjusted by using 0.1N, 1N, 3N, and/or conc. HNO<sub>3</sub> to pH values between 1 and 9 (each set of samples spanned this range). The samples were placed in a shaking waterbath at 25 ± 0.5° C and allowed to equilibrate overnight. The pH values were checked after 20 to 24 hours, and 2-ml aliquots of 25 ppm Hg stock solution were added to each flask, giving a total volume of ≈52 ml and a Hg concentration of approximately 0.96 ppm. The samples were again placed in the shaking waterbaths and allowed to equilibrate overnight. After 20 to 24 hours the final pH values of the samples were recorded, and each sample was transferred to a 50-ml centrifuge tube and centrifuged at 20,000 rpm for 5 minutes. The supernatant solutions were decanted, acidified, and analyzed by flameless AA for their Hg content.

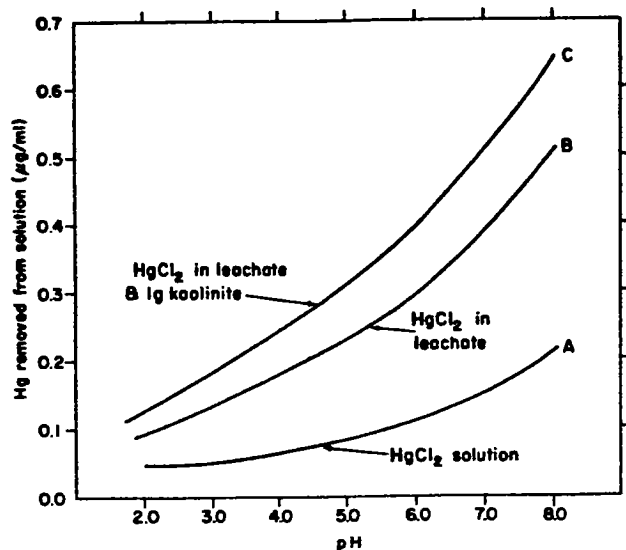


Fig. 30 - Removal of Hg from Du Page landfill leachate and from pure HgCl<sub>2</sub> solutions, plotted as a function of pH at 25° C. The initial Hg concentration is 0.96 ppm. The final volume is ≈52 ml.

The amount of Hg removed from solution by a given clay at a particular pH was determined by using equation [6]. The amount of Hg removed from solution was then plotted as a function of pH.

### Results and Discussion

Examples of results obtained for Hg removal from various solutions, plotted as a function of pH, are presented in figure 30. The figure shows that Hg is removed from solution, even in a presumably sterile and pure HgCl<sub>2</sub> solution (curve A). In the short time available for this study we were not able to isolate satisfactorily all the reasons for such removal of Hg. Three possible removal mechanisms are adsorption onto the walls of the glassware and plastic bottles, precipitation, or volatilization. At the lower pH values the Hg removal is thought to have been by adsorption onto the glassware, although standard solutions may be satisfactorily stored at pH 2. We presumed that the adsorption in the sample solutions occurred at the higher initial pH values and that the Hg did not have sufficient time to totally desorb from the vessel walls after the pH was adjusted to lower values. The increase in removal in the higher pH range (5 to 8) is apparently the result of both precipitation and adsorption. Volatilization was not considered as an important mechanism for the Hg losses observed from the HgCl<sub>2</sub> solutions, since they were presumably sterile and stoppered.

Curve B illustrates the loss of Hg from a leachate solution. The removal of Hg from solution here is probably due to the same mechanisms responsible for losses from the pure  $\text{HgCl}_2$  solutions with increased adsorption or increased precipitation. However, volatilization losses of organic Hg compounds caused by microbial transformations in the leachate are also possible.

Curve C in figure 30 shows the total amount of Hg removed from leachate with 1 g of kaolinite present. The amount of Hg removed by 1 g kaolinite is taken as the difference between curve C and curve B. This is plotted as curve B in figure 31.

Figure 31 shows a breakdown of various forms of Hg removal from leachate solutions. The amount of organic and inorganic Hg removed by clay was determined by placing an aliquot from each sample into each of two BOD bottles. One set was digested by the general procedure, while the second set was analyzed undigested. A set of leachate blanks was treated in the same manner. There were then four separate sets in all, a digested blank ( $\text{HgCl}_2$  in leachate), an undigested blank, a digested sample ( $\text{HgCl}_2$  in leachate with 1 g kaolinite), and an undigested sample.

The total organic Hg in solution was determined by taking the difference between the digested and undigested blanks. The amount of organic Hg in solution with 1 g kaolinite present was always less than the total organic Hg determined from the blanks. This difference was taken as the amount of organic Hg removed because of the presence of the clay. Figure 31 illustrates the relative amounts of organic Hg (curve C) and inorganic Hg (curve D) removed by 1 g kaolinite, plotted as a function of pH. These results can be compared with the total Hg removed by 1 g kaolinite in curve B and with the total Hg removed from solution by all mechanisms in curve A.

The results given in figure 31 show that Hg removal is pH-dependent. As the pH is raised within the range 2 to 8, the amount of Hg removed increases.

The data reveal that approximately two-thirds of the total Hg removed by 1 g kaolinite was organic Hg (curve C), while about a third of the Hg removed by the clay was inorganic Hg (curve D). The total Hg removed from solution (curve A) is apparently the result of several mechanisms operating simultaneously—adsorption by clay, volatilization, and precipitation. When the amount of Hg removed as a result of the presence of clay was determined, it accounted for approximately 20 to 30 percent of the total Hg removed from

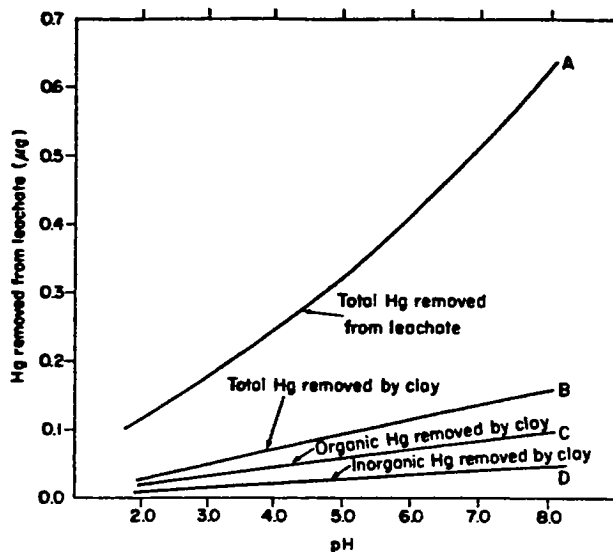


Fig. 31 - Removal of various forms of Hg from Du Page landfill leachate solutions by kaolinite, plotted as a function of pH at 25° C.

solution. It therefore appears that precipitation and volatilization account for the largest amounts of Hg removed in this study. The relative amounts of Hg lost by volatilization and precipitation are not known. In any event, large amounts of Hg are lost from leachate solutions in both the presence and absence of clay.

In an unreplicated experiment, the removal of Hg from solution by montmorillonite was found to be approximately 5 times greater than the removal of Hg from solution by kaolinite. Since this experiment has not been repeated, the results are tentative. However, this ratio resembles the ratio of the cation exchange capacities (CEC) of these two clay minerals. As this result is consistent with those for the previous heavy-metal cations studied, it was concluded that the difference in adsorption between montmorillonite and kaolinite was due to the cation exchange of the various ionic forms of Hg that may be present in leachate solutions of variable pH.

### Conclusions

The results of the Hg study indicate that removal of Hg from leachate solutions is enhanced by clay minerals and is pH-dependent. Substantial amounts of Hg were removed from leachate by the clays, and these amounts were concluded to be in proportion to the clays' respective CEC values. Two-thirds of the Hg removed by the clays was organic and about one-third inorganic.

Large amounts of Hg were removed from solution, both in the presence and absence of clay. These results lead to the conclusion that adsorption by clays was not the major mechanism. Rather, precipitation and/or volatilization accounted for between 70 and 80 percent of the Hg removed from the leachate solutions and were concluded to be the predominant attenuation mechanisms in these experiments.

The results of this study suggest that maximum removal of Hg from leachate would be achieved by disposal under alkaline conditions. They also suggest that montmorillonitic clays or soils will remove substantially more Hg than kaolinitic clays or soils.

### SUMMARY

The results of these studies of the heavy metals indicate that pH has a pronounced effect on the amounts adsorbed from landfill leachates by clay minerals. It was concluded that the principal adsorption mechanism is cation and anion exchange, a mechanism that led to the strong pH dependency of the adsorption process. In addition, species distribution diagrams led to the conclusion that it is the monovalent species of each element that is principally adsorbed by anion exchange.

A comparison of the relative amounts of heavy metals removed at pH 5.0 from 100 ppm equilibrium concentration solutions of the metals studied, both cationic and anionic, is presented in table 9. The table indicates that



the cationic heavy metals are generally adsorbed to a greater degree than the anionic forms. However, this ranking is somewhat pH-dependent, because the greatest anion adsorption occurs in acid solutions and the greatest cation adsorption in alkaline solutions. The ranking therefore changes somewhat at different pH values.

A significant point shown in table 9 is the importance of the valence state of an element to the amount of that element removed from solution by clay minerals. Cr(III) species are removed to a much greater extent than Cr(VI) species. The clay minerals removed 30 to 300 times more Cr(III) from solution than Cr(VI). The table also shows more extensive removal of As(V) than of As(III). These results indicate that safer disposal of certain elements may be achieved if, prior to deposition at the landfill or disposal site, the element is converted to the form that would be most strongly attenuated.

The information derived from the studies of the various elements indicate that the amounts of heavy metals removed from leachate by clay minerals depends to a large degree on the element and the form of the element involved, the pH of the leachate, the adsorption capacity of the particular clay mineral in the liner, and the ionic strength of the leachate.

The adsorption capacity of the clay minerals and the reversible nature of exchange-adsorption reactions have important environmental consequences. For example, if industrial wastes containing heavy metals are placed in a landfill, changes in the ionic composition or pH of the leachate can occur. A change in pH may release large amounts of potentially toxic heavy metals into the aqueous phase, especially in places where precipitates may have accumulated. Other ions in the waste compete with the heavy metals and may exchange with them, thus allowing metal ions to come into solution. These multiple interactions must be considered when a disposal site is designed and when the environmental impact of adding heavy-metal wastes to municipal landfills is assessed.

TABLE 9—REMOVAL OF HEAVY METALS FROM SOLUTIONS BY KAOLINITE AT pH 5.0

| Element | Amount removed at equilibrium concentration of 100 ppm (micromoles/g) |                  |
|---------|---|------------------|
|         | Pure solutions  | Du Page leachate |
| Cr(III) | 769*  | 576*             |
| Cu      | 55.1  | 15.7             |
| Pb      | 42.3  | 12.1             |
| As(V)   | †   | 5.3              |
| Zn      | 33.6  | 3.8              |
| As(III) | ‡   | 2.0              |
| Cd      | 26.7  | 1.9              |
| Cr(VI)  | 0.62  | 1.9              |
| Se      | †   | 1.9              |

\*Precipitation contributes to removal at pH 5.0.

†Removals from 40 ppm solutions were approximately the same as removals from leachate.

‡Removals from 40 ppm solutions were 30 percent greater than removals from leachate.

## REFERENCES

- Baetjer, A. M., 1956, Relation of chromium to health, in J. U. Marvin [ed.], Chromium: Reinhold, New York, p. 76-104.
- Beevers, J. R., 1966, A chemical investigation into the role of sorption processes in ore genesis: Australia Bureau of Mineral Resources, Geology, and Geophysics Rept. 106, 32 p.
- Bittel, J. E., and R. J. Miller, 1974, Lead, cadmium and calcium selectivity coefficients on a montmorillonite, illite, and kaolinite: Journal of Environmental Quality, v. 3, p. 250-253.
- Boyd, G. E., J. Schubert, and A. W. Adamson, 1947, The exchange adsorption of ions from aqueous solutions by organic zeolites, I—Ion exchange equilibria: Journal of American Chemical Society, v. 69, p. 2818-2829.
- Broadbent, F. E., and J. B. Ott, 1957, Soil organic matter—Metal complexes, I—Factors affecting various cations: Soil Science, v. 83, p. 419-427.
- Butler, J. N., 1964, Ionic equilibrium—A mathematical approach: Addison-Wesley, Reading, Massachusetts, p. 360-363.
- Davids, H. W., and M. Lieber, 1951, Underground water contamination by chromium wastes: Water and Sewage Works, v. 98, no. 12, p. 528-534.
- Davies, R., 1973, Special report on solid wastes, leachate control: Canadian Water and Pollution Control, v. 111, no. 12, p. 15-31.
- Derryberry, O. M., 1972, Investigation of mercury contamination in the Tennessee Valley region, in R. Hartung and B. D. Dinman [eds.], Environmental mercury contamination: Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p. 76-79.
- D'Itri, F. M., 1972a, The environmental mercury problem: Chemical Rubber Co. Press, Cleveland, Ohio, p. 17-64.
- D'Itri, F. M., 1972b, Sources of mercury in the environment, in R. Hartung and B. D. Dinman [eds.], Environmental mercury contamination: Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p. 5-25.
- Early, A. B., 1974, Coal conversion technology and solid waste disposal—Time to take stock: Paper presented at U.S. Environmental Protection Agency Symposium, "Fuel conversion technology," St. Louis, Missouri, May 13-16.
- Everest, D. A., and W. J. Popiel, 1957, Ion-exchange studies of solutions of arsenites: Journal of Chemical Society, v. 1957, p. 2433-2436.
- Fuller, W., 1975, Attenuation of pollutants in landfill leachate by soils, in Proceedings of Research Symposium, "Gas and leachate from landfill: Formation, collection and treatments," New Brunswick, N. J., March 15, 16: U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio.

- Gadde, R. R., and H. A. Laitinen, 1973a, Study of the interaction of lead with corn root exudate—A pulse polarographic study: *Environmental Letters*, v. 5, p. 91-102.
- Gadde, R. R., and H. A. Laitinen, 1973b, Study of the sorption of lead by hydrous ferric oxide: *Environmental Letters*, v. 5, p. 223-235.
- Garland, G. A., and D. C. Mosher, 1975, Leachate effects from improper land disposal: *Waste Age*, v. 6, no. 3, p. 42-48.
- Giordano, P. M., J. J. Mortvedt, and D. A. Mays, 1975, Effect of municipal wastes on crop yields and uptake of heavy metals: *Journal of Environmental Quality*, v. 4, p. 394-399.
- Goldwater, L. J., 1971, Mercury in the environment: *Scientific American*, v. 224, no. 5, p. 15-21.
- Gordon, M., 1975, Is industry managing its wastes properly?: *Environmental Science and Technology*, v. 9, p. 415-416.
- Greeson, P. E., 1970, Biological factors in the chemistry of mercury, in Mercury in the environment: U.S. Geological Survey Professional Paper 713, p. 32-34.
- Griffin, R. A., and R. G. Bureau, 1974, Kinetic and equilibrium studies of boron desorption from soil: *Soil Science Society of America Proceedings*, v. 38, p. 892-897.
- Griffin, R. A., and N. F. Shimp, 1976, Attenuation of pollutants in municipal landfill leachate by clay minerals: Final report for contract 68-03-0211, U.S. Environmental Protection Agency, Cincinnati, Ohio.
- Griffin, R. A., Keros Cartwright, N. F. Shimp, J. D. Steele, R. R. Ruch, W. A. White, G. M. Hughes, and R. H. Gilkeson, 1976, Attenuation of pollutants in municipal landfill leachate by clay minerals, Part 1—Column leaching and field verification: *Illinois State Geological Survey Environmental Geology Note* 78, 34 p.
- Grim, R. E., 1968, *Clay mineralogy*: McGraw-Hill, Inc., New York, p. 213-221.
- Henderson, D. A., 1955, Chronic nephritis in Queensland: *Australasian Annals of Medicine*, v. 4, p. 164.
- Hofmann, U., A. Weiss, G. Koch, A. Mehler, and A. Scholz, 1956, Intracrystalline swelling, cation exchange, and anion exchange of minerals of the montmorillonite group and of kaolinite, in A. Swineford [ed.], *Clays and clay minerals*: National Academy of Sciences—National Research Council Pub. 456, Washington, D. C., p 273-287.
- Hughes, G. M., R. A. Landon, and R. N. Farvolden, 1971, Hydrogeology of solid waste disposal sites in northeastern Illinois: U.S. Environmental Protection Agency, Solid Waste Management Series, Report SW-12d, 154 p.
- John, M. K., 1972, Cadmium adsorption maxima of soils as measured by the Langmuir isotherm: *Canadian Journal of Soil Science*, v. 52, p. 343-350.
- Klein, D., 1972, Some estimates of natural levels of mercury in the environment, in R. Hartung and B. D. Dinman [eds.], *Environmental mercury contamination*: Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p. 25-29.

- Langmuir, I., 1918, The adsorption of gases on plane surfaces of glass, mica and platinum: *Journal of American Chemical Society*, v. 40, p. 1361-1403.
- Laswick, J. A., and R. A. Plane, 1959, Hydrolytic polymerization in boiled chromic solutions: *Journal of American Chemical Society*, v. 81, p. 3564-3567.
- Lehman, J. P., 1973, Guidance for conducting chain of evidence research: U.S. Environmental Protection Agency, Office of Solid Waste Management Programs, Hazardous Waste Management Division, Washington, D. C.
- Mesmer, R. E., and C. F. Baes, 1974, The hydrolysis of cations: A critical review of hydrolytic species and their stability constants in aqueous solution: Oak Ridge National Laboratory, NSF-EATC-3, Pt. 3, p. 141.
- Murray, C. U., 1956, The physical and chemical properties of compounds of chromium, *in*, J. U. Marvin [ed.], *Chromium*: Reinhold, New York, p. 113-250.
- Olin, A., 1960, Studies on the hydrolysis of metal ions: Application of the self-medium method to the hydrolysis of lead (II) perchlorate solution: *Acta Chemica Scandinavia*, v. 14, p. 814.
- Rollinson, C. L., 1956, Olation and related chemical processes, *in*, J. C. Bailar, Jr., and D. H. Busch [eds.], *Chemistry of the coordination compounds*: Reinhold, New York, p. 448-471.
- Shiga, Shoji, 1975, Treatment of waste water containing Cr (VI) ions: *Chemical Abstracts*, v. 82, 102850n [Japanese].
- Shuman, L. M., 1975, The effect of soil properties on zinc adsorption by soils: *Soil Science Society of America Proceedings*, v. 39, p. 454-458.
- Smith, R. G., 1972, Five of potential significance, *in*, D. H. K. Lee [ed.], *Metallic contaminants and human health*: Academic Press, New York, p. 139-162.
- Stumm, W., and J. J. Morgan, 1962, Chemical aspects of coagulation: *Journal of American Water Works Association*, v. 54, p. 971.
- Syers, J. K., M. G. Browman, G. W. Smillie, and R. B. Corey, 1973, Phosphate sorption by soils evaluated by the Langmuir adsorption equation: *Soil Science Society of America Proceedings*, v. 37, p. 358-363.
- Turney, W. G., 1972, The mercury pollution problem in Michigan, *in*, R. Hartung and B. D. Dinman [eds.], *Environmental mercury contamination*: Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p. 29-31.
- U.S. Environmental Protection Agency, 1973a, Report to Congress on hazardous waste disposal: U.S. Environmental Protection Agency Publication SW-115, Washington, D. C.
- U.S. Environmental Protection Agency, 1973b, 1972 water quality criteria: U.S. Environmental Protection Agency Publication R3-73-033, Washington, D. C.

U.S. Environmental Protection Agency, 1974, Summary report—Gas and leachate from land disposal of municipal solid waste: U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1975, Land treatment of municipal wastewater effluents: Technology Transfer, October, p. 4-9.

van Olphen, H., 1963, An introduction to clay colloid chemistry: Interscience, New York, p. 251-279.

Walker, W. H., 1969, Illinois ground water pollution: Journal of American Water Works Association, v. 61, p. 31-40.

Welsch, W. F., 1955, Ground water pollution from industrial wastes: Sewage and Industrial Wastes, v. 27, p. 1065-1069.

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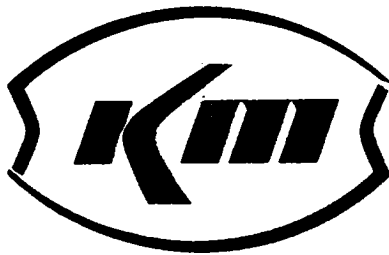
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***KERR-MCGEE CORPORATION***



GROUNDWATER MITIGATION PROGRAM  
KERR-MCGEE CHEMICAL CORPORATION  
HENDERSON, NEVADA FACILITY

October, 1985

**Engineering Services**


GROUNDWATER MITIGATION PROGRAM

KERR-McGEE CHEMICAL CORPORATION  
HENDERSON FACILITY

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## SUMMARY

The Kerr-McGee Henderson Facility proposes a groundwater corrective action program which will intercept and treat the chromium contaminated groundwater. The mitigation program consists of an interceptor well field to be installed downgradient from the source areas near the 5 mg/l chromium concentration limit. The interceptor field will span a buried stream channel that principally controls the migration of the plume in this area and will assure that the major portion of the contaminated groundwater will be intercepted and treated. The recovery system will be approximately 1400 feet long, consist of 10 interceptor wells (each producing about 7.5 gallons/minute), and will remove and treat 75 ( $\pm 25$ ) gpm of chromium contaminated groundwater. The interceptor wells will be placed so overlapping cones of depression prevent migration of the plume past the interceptor well field. The groundwater pumped from the aquifer will be sent to a treatment facility where the chromium will be removed. The treated groundwater will then be re injected back into the aquifer through recharge trenches installed downgradient of the interceptor field. A monitoring well network will be installed to monitor the effectiveness of the intercept system and rate of aquifer cleanup.

## CONCLUSIONS

- 1) An interceptor well field can be installed across the channel north of AP ponds that will effectively capture chromium contaminated groundwater that flows from upgradient areas. A well field of approximately 10 wells spaced roughly 150 feet apart and spanning the ancient stream channel 600' north of the AP ponds will intercept the contaminant plume. Each well will discharge at a rate of 7.5 gallons/minute (75 (±25) gpm total from all wells).
  
- 2) All captured groundwater can effectively be treated to remove chromium. All treated groundwater will be recharged back into the Near-Surface aquifer through recharge trenches installed downgradient from the interceptor wells.

## INTRODUCTION

Kerr-McGee describes in this report a corrective action program to intercept and treat the chromium contaminated groundwater at a location down-gradient from the Facility sources. Recovered groundwater will be processed through a treatment system which will reduce the chromium. The treated groundwater will be reinjected back to the Near-Surface aquifer through recharge trenches.

Geohydrological information supporting this program was previously submitted to the Nevada Division of Environmental Protection on July 31, 1985.

## GROUNDWATER MITIGATION PROGRAM

### Past Mitigation Programs

Beginning in August, 1983, Kerr-McGee initiated a trial program to recover impacted groundwater and recycle it back through the process. Well M-3 was pumped until July, 1984 when excessive rainfall collected in Facility ponds prevented recycling of recovered groundwater and the well was shut down. This well was successful in capturing impacted groundwater immediately adjacent to this well and creating a decline in the chromium levels.

In early 1983 ponds S-1 and P-1 were drained and taken out of service and are currently undergoing closure. This effectively eliminated a potential source area of impact to the groundwater system.

The repair of Units 4 and 5 is progressing by sealing all cracks in the concrete basement floor, effectively eliminating leakage from these areas.

To further reduce the source of chromium contamination, the basements under Units 4 and 5 have been regulated to insure that liquids are restricted to the drainage system and do not flow onto or remain on the basement floor.

#### Proposed Groundwater Interception System

The data gathered to date indicates that the installation of a groundwater recovery well system approximately 600 feet north of the AP impoundments (shown in Plate 1) will provide control and recovery of chromium contamination. The basis for installing the recovery system in this area is to intercept the groundwater with the highest chromium concentrations in an area which exhibits favorable hydrogeological properties. Groundwater having chromium concentrations greater than 5.0 mg/l will be intercepted while lower concentrations downgradient from the recovery area will be allowed to attenuate toward background levels.

A geological cross-section approximately 300 feet south of the recovery area is shown in Figure 1 (section A-A'). The cross-section is along the same east-west line as the proposed recovery program. As shown by section A-A', the recovery well system will span a buried stream channel system developed on the Muddy Creek surface. Referring to Plate 1, the recovery well field will trend in an east-west direction and will be approximately 1400 feet long. The length of the recovery system will cross the entire width of the chromium plume and capture or recover contaminated groundwater that occurs upgradient or south of this recovery well area. The outline of the chromium plume is shown in Plate 1. Details of chromium concentrations for June/July, 1985 are presented in Plate 2.

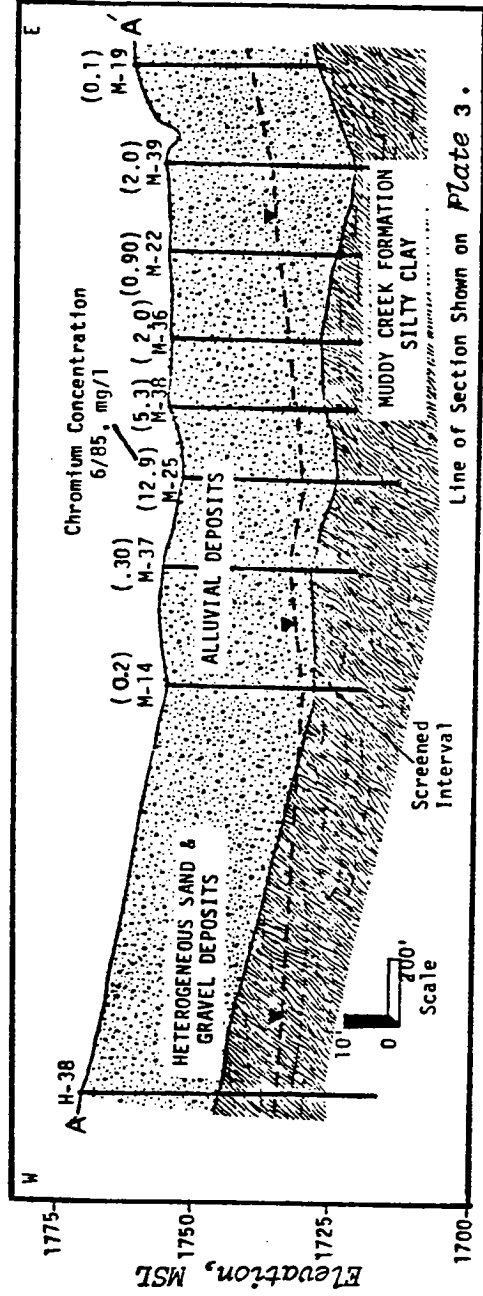


FIGURE 1. GEOLOGICAL CROSS SECTION (EAST-WEST) THROUGH THE INTERCEPTOR WELL AREA, HENDERSON FACILITY.

The aquifer properties of this buried channel system were used to simulate a recovery well field. Aquifer coefficients typical to this channel system are: transmissivity (range 2000-5000 gpd/ft; average 3000 gpd/ft) and storage coefficient (.053). Maximum drawdown in the recovery wells was set at four feet. A recovery well field across the channel system was simulated (using Theis equation) and an effective well spacing of 150 feet was determined. In other words, after pumping for 10 days a minimum drawdown of 1 foot in the aquifer at a distance of 150 feet from this well will be produced by cone of influence or capture. Therefore, all recovery wells will have overlapping cones of at least 1 foot as a design safety factor. To effectively capture the plume over this channel width will require approximately 10 recovery wells (Plate 1) each pumping at a rate of about 7.5 gallons/minute. This pumping rate creates a maximum drawdown of approximately 4 feet in the recovery wells. The total discharge from the recovery system should be 75 ( $\pm 25$ ) gallons/minute. All recovered groundwater will be sent through a treatment system which removes chromium.

The numbers described above are best estimates upon available site specific data. Field pumping tests will be conducted on each of the recovery wells to further refine the exact well spacings, number of wells and pumping rates.

All interceptor or recovery wells will be installed at least 15 feet into the Muddy Creek formation and screened throughout the saturated alluvial sediments and the upper 10 feet of Muddy Creek formation. The recovery wells will be screened within the upper portions of the Muddy Creek formation to insure capture of any chromium moving through fine sand and silt



lenses in the upper part of the formation. A typical recovery well design is shown in Figure 2.

#### Chromium Removal System

The contaminated groundwater removed from the recovery or interceptor system will require treatment prior to discharge into a reinjection or recharge field. A report on the groundwater treatability studies will be submitted at a later date. The report indicates that the chromium contaminated groundwaters could successfully be treated to remove the chromium.

#### Proposed Treated Groundwater Reinjection/Recharge System

Once the groundwater has been removed from the aquifer, the resulting treated water will be returned to the groundwater system at a point downgradient (Plate 1) from the recovery field. The treated groundwater will be recharged back to the alluvial or "Near Surface" aquifer through recharge trenches.

The recharge system will be placed downgradient of the recovery line to create a hydraulic barrier to groundwater flow along the edge of the cone of depression for the recovery field. Placing the recharge system at this location will insure little recycling of the groundwater back through the interceptor wells. Placing the recharge system upgradient from the well field or within the plume would actually inhibit the migration of the plume.

Based upon infiltration tests conducted by Stauffer Chemical Corporation, the recharge rate which the formation will accept was determined to be 7.2 cubic feet of water per day per square foot of surface area (Hall,

1985). Calculated losses from the Alpha Ditch indicates a recharge rate of 1.5 cubic feet of water per day per square foot. Assuming an infiltration rate of 5 cubic feet/day/ft<sup>2</sup> and a ditch with a wetted perimeter of 7 feet, approximately 3850 square feet of recharge area would be needed to handle 100 gallons/minute (19,233 ft<sup>3</sup>/day). Based upon these numbers, two recharge trenches each 600 feet long and having a wetted perimeter of 7 feet (assuming a 2-foot water level in the trench) would be installed approximately 150 feet downgradient (Plate 1). The two trenches would be 50 feet apart, 600' long, 3 feet wide and 5 feet deep as shown in Figure 2. The bottom 2 feet of the trench would contain a 4" perforated drain pipe surrounded by a clean gravel filter blanket. The remainder of the trench will be backfilled with excavated soils. The coarse-grained nature of the backfilled soils should eliminate any significant capillary rise. All treated groundwater may be filtered to remove excessive suspended particles.

#### GROUNDWATER INTERCEPT AND RECHARGE SYSTEM MONITORING PROGRAMS

An important part of any groundwater mitigation program is the ability to accurately monitor the effectiveness of the program.

The groundwater monitoring programs that will be implemented as part of this program involve both the chemical characterization and physical measurement of the groundwater system. The details of these two monitoring programs are discussed below along with a description of the proposed monitoring well network.

### Monitor Well Network

The groundwater monitoring program for the intercept and recharge system will accurately monitor: 1) the rate and magnitude of chemical change in the groundwater in both the upgradient and downgradient directions and 2) the physical configuration of the groundwater system to insure proper function of the intercept and recharge systems.

The upgradient groundwater monitoring well network for the recharge and intercept systems will involve the monitoring of previously drilled wells M-37, M-25, M-36, and M-39 as shown on Plate 1. The downgradient monitoring network for the recharge and interceptor fields will involve the installation of five monitoring wells and use of existing well M-18 as shown on Plate 1. In addition to these wells, five wells will be installed for the purpose of water-level measurements. All five wells will monitor the effectiveness of the interceptor field. The details of this network are shown on Plate 1. Plate 3 shows the location of all monitoring wells at the Henderson Facility.

### Chemical Monitoring Program

All wells involved in the interception of the groundwater (interceptor wells) and all upgradient and downgradient monitoring wells associated with the interceptor and recharge system will be monitored on a quarterly basis. Groundwater samples from these wells will be analyzed for specific conductance, pH, and chromium. In addition to the program associated with the intercept and recharge system, groundwater samples will be collected annually from all Kerr-McGee M-series wells and selected Stauffer wells (on Kerr-McGee property) and analyzed for the constituents noted above.

All chemical analytical results will be monitored to track the progress of the cleanup and note any changes in the plume configuration. KMCC reserves the right to change the frequency and number of wells monitored if data indicates the system can be adequately monitored after the reduction.

Water Level Monitoring Program - It is important to monitor the configuration of the groundwater surface to insure that an effective cone of depression or influence is maintained to insure full capture of the chromium plume. In efforts to closely monitor water levels, two continuous water level recorder installations will be evaluated. One recorder is proposed to be installed within the middle of the intercept system and a second recorder installed slightly downgradient of the recharge or reinjection area. In addition, <sup>1</sup>water levels will be measured on all M-series wells, the intercept wells, and monitoring wells associated with the recovery and recharge program on a quarterly frequency. Data developed from this program will be reviewed to insure proper well field management to produce the desired drawdown within the intercept system.

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<sup>1</sup>5 wells will be installed within interceptor well area to verify the cone of depression.

## REFERENCES

Hall, L. E., March, 1983; 1982 Hydrogeologic Investigation in Support of the Groundwater Intercept System at Stauffer Chemical Company, Henderson, Nevada; Inhouse Report.



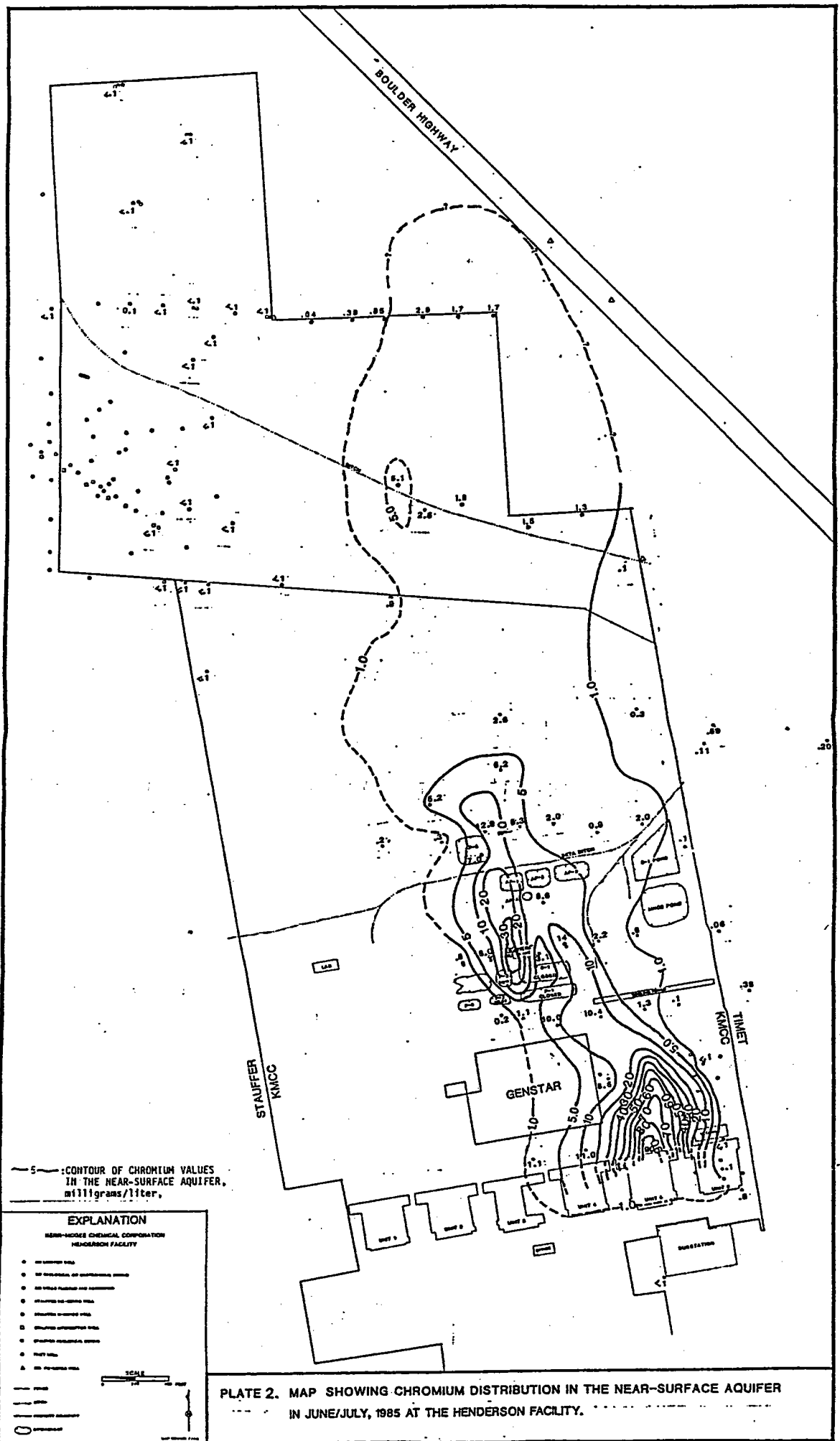


PLATE 2. MAP SHOWING CHROMIUM DISTRIBUTION IN THE NEAR-SURFACE AQUIFER IN JUNE/JULY, 1985 AT THE HENDERSON FACILITY.





## CHROMIUM-REMOVAL STUDIES

### KERR-McGEE CORPORATION TECHNOLOGY DIVISION

#### Pilot Plant Studies

The KMC Technology Division performed laboratory studies on several processes for removal of Chromium VI from the groundwater at the Henderson Facility during 1985. Groundwater samples from facility wells were used to duplicate actual conditions. Processes studied included ion exchange, activated carbon absorption, ferrous sulfate reduction, and metallic iron reduction. Ion exchange and carbon absorption were adversely affected by the elevated chloride and chlorate concentrations of the groundwater being tested. These species acted as eluants.

Ferrous sulfate and metallic iron reduction was found effective for chromium removal with metallic iron reduction considered most feasible as a low-maintenance operation.

In 1985, the Technology Division operated a pilot plant at the Henderson Facility to test the metallic iron system. The pilot plant processed groundwater from monitor well M-11. At 65-100 mg/l Cr<sup>+6</sup> and 17 g/l chlorate, this well represented the most concentrated constituent conditions.

The pilot demonstration unit was operated successfully for two weeks. Test results indicate that a Chromium VI concentration of 100 mg/l can be reduced to below .05 mg/l by pH adjustment, contact with metallic iron, and precipitation of Chromium III followed by filtration.

Metallic iron was in the form of coarse steel wool. The pilot plant was operated in both downflow and upflow configurations with the upflow configuration producing the least operating and bed-plugging problems (see Figures 1 and 2). Varying flow rates, pH levels, and iron replacement rates were studied (see Table I). For the solution concentration tested, a flow rate of one bed volume per hour and a pH of 3 provided chromium concentration reduction to 0.02 mg/l with an iron consumption rate of 5.5 to 7 pounds per 1,000 gallons of feed water (approximately one pound of chromium).

The operation of this pilot plant demonstrated the feasibility of Cr removal from the Henderson Facility groundwater and provided parameters for design of a large-scale facility. Other metallic ions besides chromium would be expected to be removed in the precipitation and filtration processes, although detailed information on exact amounts is not available at this time.

## Evaluation of Other Technologies

Since that study KMC Technology Division has evaluated a number of commercial processes for removal of Chromium VI from Henderson groundwater. A summary of the proposals received is presented in attached Table II.

The processes may be grouped together by type. The Pollution Technology Systems, the Manchester Corporation, and the Kerr-McGee Technical Center processes are of the same type: chemical reduction to Cr(III) followed by precipitation as metal hydroxide. The Pollution Technology System unit uses modular construction, which allows for process-sized equipment on the shelf which can be put together at a lower cost than we could design and build from scratch. This highlights the advantage of modular construction of a process unit for this type application.

The Manchester Corporation design is heavily instrumented and appears able to run with little operator attention. However, improvements over other systems in terms of removal efficiency were not addressed.

The Sanitech system uses the DeVoe Holben process in which a biologically produced reduction agent is used to treat groundwater.

Of the information available for evaluation, neither the Sanitech nor the Lancy (not discussed) process provided adequate detail for necessary evaluation, including how the processes work and operate.

Andco Environmental Processes, Inc., has provided a detailed proposal for an electrochemical system for removal of chromium and other heavy metals from the Henderson groundwater. The electrochemical process generates ferrous iron by passing a direct current through a cell containing carbon steel electrodes. The ferrous ion reduces hexavalent chromium to trivalent chromium and coprecipitates any other dissolved metals present.

KM Technology Division has recommended the Andco Environmental process for further testing as it appears the most promising of those evaluated. The unit would not require pH adjustment and would coprecipitate other dissolved metals. Andco has 150 of its units in commercial operation. Contact with one of these users indicates a low maintenance unit with little operator attention.

Figure 1  
Pilot Plant in Downflow Configuration

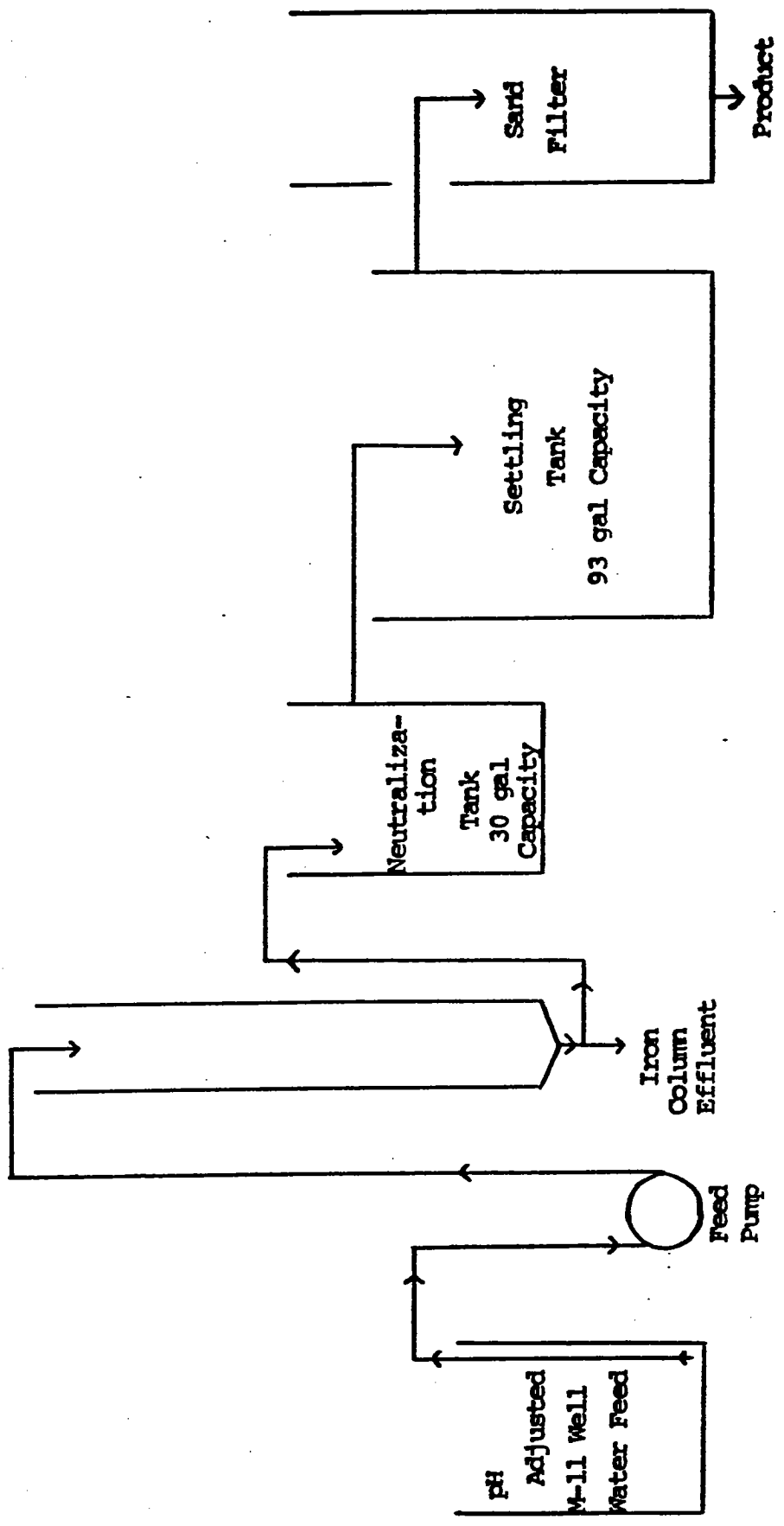
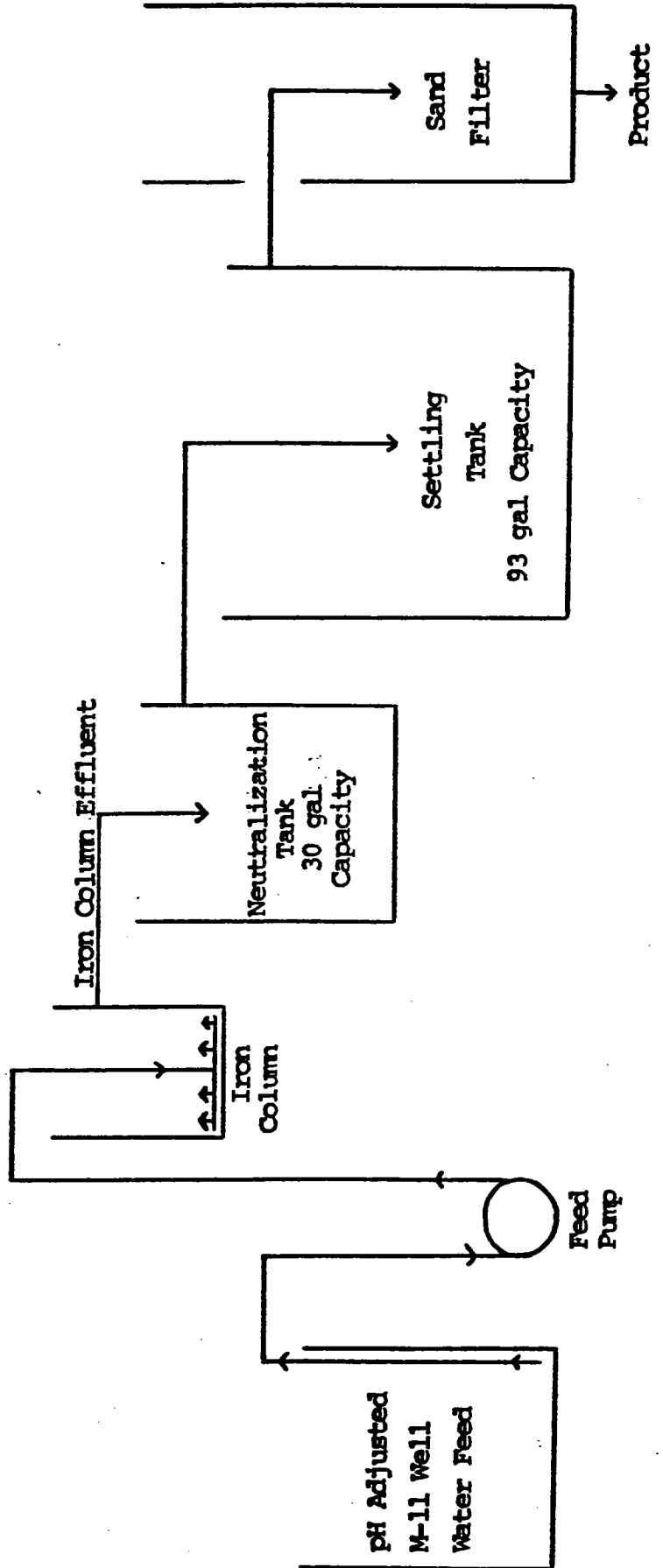
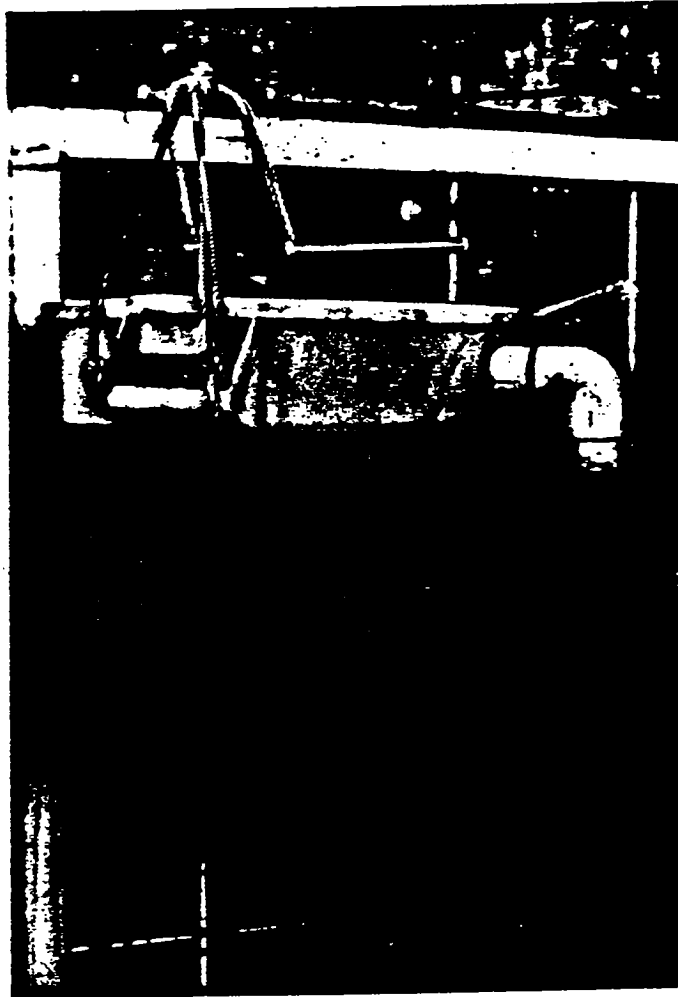


Figure 2  
Pilot Plant in Upflow Configuration





Neutralization Tank    Settling Tank    Sand Filter



**Iron Reduction Vessel  
In Upflow Configuration**

TABLE I

TABLE I

| DATE/TIME            | Height (cm) | PACKING     |                               | Mass (Kg) | Density (GM/CM <sup>3</sup> ) | PH  | FIBER       |              | Cr (%) | IRON COLONY |           | NEUTRALIZATION |        |
|----------------------|-------------|-------------|-------------------------------|-----------|-------------------------------|-----|-------------|--------------|--------|-------------|-----------|----------------|--------|
|                      |             | Weight (cm) | Bed Vol (BV-OM <sup>3</sup> ) |           |                               |     | Rate (G/hr) | Rate (BV/hr) |        | Effluent PH | Fe (Mg/L) | Cr (%)         | Cr (%) |
| 5-8-85 (Downflow)    | 15.2        | 83.8        | 15,290                        | 4.5       | 0.30                          | 1.8 | 60          | 15           | 100    |             |           |                | >10    |
| 5-9                  | 1130        | 83.8        | 15,290                        | 4.5       | 0.30                          | 1.8 | 60          | 15           | 100    |             |           |                | 10.4   |
|                      | 1730        | 83.8        | 15,290                        | 4.5       | 0.30                          | 1.8 | 40          | 10           | 100    |             |           |                | 2.4    |
|                      | 1800        | 83.8        | 15,290                        | 2.3       | 0.15                          | 1.8 | 41          | 10           | 96     | 136         | 0.5       |                | 0.3    |
| 2100                 | 83.8        | 15,290      | 2.3                           | 0.15      | 1.8                           | 41  | 10          | 98           | 120    | 0.1         |           | 3.3            |        |
| 5-11 No Sample Taken | 15.2        | 83.8        | 15,290                        | 2.3       | 0.15                          | 1.8 | 41          | 10           |        |             |           |                |        |
| 5-12                 | 1300        | 25.4        | 18,530                        | 4.5       | 0.24                          | 1.8 | 40          | 8            | 100    | 192         | 0.1       |                | 0.9    |
|                      | 1730        | 25.4        | 18,530                        | 4.5       | 0.24                          | 1.8 | 32          | 6.5          | 98     | 240         | 0.1       |                | 0.1    |
| 5-13 (Upflow)        | 1300        | 25.4        | 18,530                        | 4.5       | 0.24                          | 1.8 | 43          | 9            | 98     | 224         | 0.08      |                | 0.04   |
|                      | 1900        | 25.4        | 18,530                        | 4.5       | 0.24                          | 1.8 | 43          | 9            | 98     | 256         | 0.1       |                | 0.04   |
|                      | 0840        | 25.4        | 18,530                        | 4.5       | 0.24                          | 1.8 | 42          | 9            |        |             |           |                | 0.46   |
| 5-14                 | 1040        | 25.4        | 18,530                        | 4.5       | 0.24                          | 1.8 | 42          | 9            |        |             |           |                | 6.0    |
|                      | 1730        | 27.9        | 23,930                        | 8.4       | 0.35                          | 1.8 | 40          | 6            |        |             |           |                | 0.21   |
|                      | 1830        | 27.9        | 23,930                        | 8.4       | 0.35                          | 1.8 | 40          | 6            |        | 128         |           |                | 6.0    |
| 5-15                 | 1145        | 20.3        | 17,400                        | 5.9       | 0.34                          | 1.8 | 40          | 9            |        |             |           |                | 1.03   |
|                      | 1245        | 20.3        | 17,400                        | 5.9       | 0.34                          | 1.8 | 40          | 9            |        | 124         |           |                | 16     |
|                      | 1445        | 20.3        | 17,400                        | 5.9       | 0.34                          | 1.8 | 40          | 9            |        | 31          |           |                | 3.0    |
| 5-16                 | 1645        | 20.3        | 17,400                        | 5.9       | 0.34                          | 1.8 | 20          | 4.4          |        | 172         |           |                | 19     |
|                      | 1845        | 20.3        | 17,400                        | 5.9       | 0.34                          | 1.8 | 20          | 4.4          |        | 124         |           |                | 24.5   |
|                      | 1030        | 20.3        | 17,400                        | 4.5       | 0.25                          | 3.0 | 19          | 4            | 86     |             |           |                | 23.5   |
| 5-17                 | 1430        | 20.3        | 17,400                        | 4.5       | 0.25                          | 3.0 | 19          | 4            |        | 4           |           |                | 54     |
|                      | 1630        | 20.3        | 17,400                        | 4.5       | 0.25                          | 3.0 | 19          | 4            | 92     |             |           |                | 60     |
|                      | 0900        | 20.3        | 17,400                        | 4.5       | 0.25                          | 2.5 | 20          | 4            | 96     |             |           |                | 33     |
| 5-18                 | 1400        | 20.3        | 17,400                        | 4.5       | 0.25                          | 2.5 | 20          | 4            |        | 32          |           |                | 29     |
|                      | 1900        | 20.3        | 17,400                        | 4.5       | 0.25                          | 2.5 | 20          | 4            | 94     |             |           |                | 35     |
|                      | 1000        | 38.1        | 37,840                        | 8.4       | 0.22                          | 2.5 | 20          | 2            | 88     |             |           |                | 12     |
| 5-19                 | 1415        | 38.1        | 37,840                        | 8.4       | 0.22                          | 2.5 | 20          | 2            |        | 64          |           |                | 0.6    |
|                      | 1815        | 38.1        | 37,840                        | 8.4       | 0.22                          | 2.5 | 21          | 2            | 96     |             |           |                | 1.9    |
|                      | 0930        | 38.1        | 37,840                        | 8.4       | 0.22                          | 3.0 | 8           | 0.8          |        | 44          |           |                | 0.05   |
| 5-20                 | 1830        | 38.1        | 37,840                        | 8.4       | 0.22                          | 3.0 | 8           | 0.8          | 100    |             |           |                | 0.03   |
|                      | 0900        | 38.1        | 37,840                        | 8.4       | 0.22                          | 3.0 | 8           | 0.8          | 102    |             |           |                | 0.02   |
|                      | 1500        | 38.1        | 37,840                        | 8.4       | 0.22                          | 3.0 | 8           | 0.8          | 100    |             |           |                | 0.04   |

**TABLE II**

**SUMMARY OF PROPOSALS FOR CHROMIUM REMOVAL FROM HENDERSON GROUNDWATER**

| <u>Company Submitting Proposal</u>         | <u>ANDCO Environmental Processes</u>       | <u>Pollution Technology Systems</u>     | <u>Lancy International Inc.</u>                    | <u>Sanitech Inc.</u>  | <u>Manchester Corporation</u>            |
|--|--|---|--|---|--|
| <u>Process Type</u>                        | Electrochemical (sacrificial Fe electrode) | Cr(VI) reduction with FeSO <sub>4</sub> | Cr(VI) reduction followed by sulfide precipitation | Pre-treat to convert Cr(VI) to Cr(III), Ion Exchange Removes Cr | Cr(VI) reduced with Sodium metabisulfite |
| <u>Reductant</u>                           | Fe   | FeSO <sub>4</sub>                       | Unspecified  | Unspecified   | Sodium Metabisulfite                     |
| <u>Precipitation Agent</u>                 | None                                       | NaOH                                    | Sulfide  |   | Mg(OH) <sub>2</sub>                      |
| <u>Qualitative Assessments</u>             |  |   |  |   |  |
| 1. Quality of Design Information Presented | Good                                       | Good                                    | Fair   | Poor  | Very Good                                |
| 2. Quality of Cost Estimate Presented      | Good                                       | Good                                    | Average  | Poor  | Very Good                                |
| 3. Detail Presented                        | Good                                       | Good                                    | Poor   | Poor  | Very Good                                |



**GROUNDWATER:**

**1. Mitigative Actions Taken**

- A. Remove holding ponds P-1 and S-1. These ponds stored solutions containing the contaminant constituents of interest.
- B. Seal process building floors; leakage to groundwater stopped.

GROUNDWATER CHROMIUM CONCENTRATION TRENDS

KERR-MCGEE CHEMICAL CORPORATION  
HENDERSON FACILITY

MAY 2, 1986



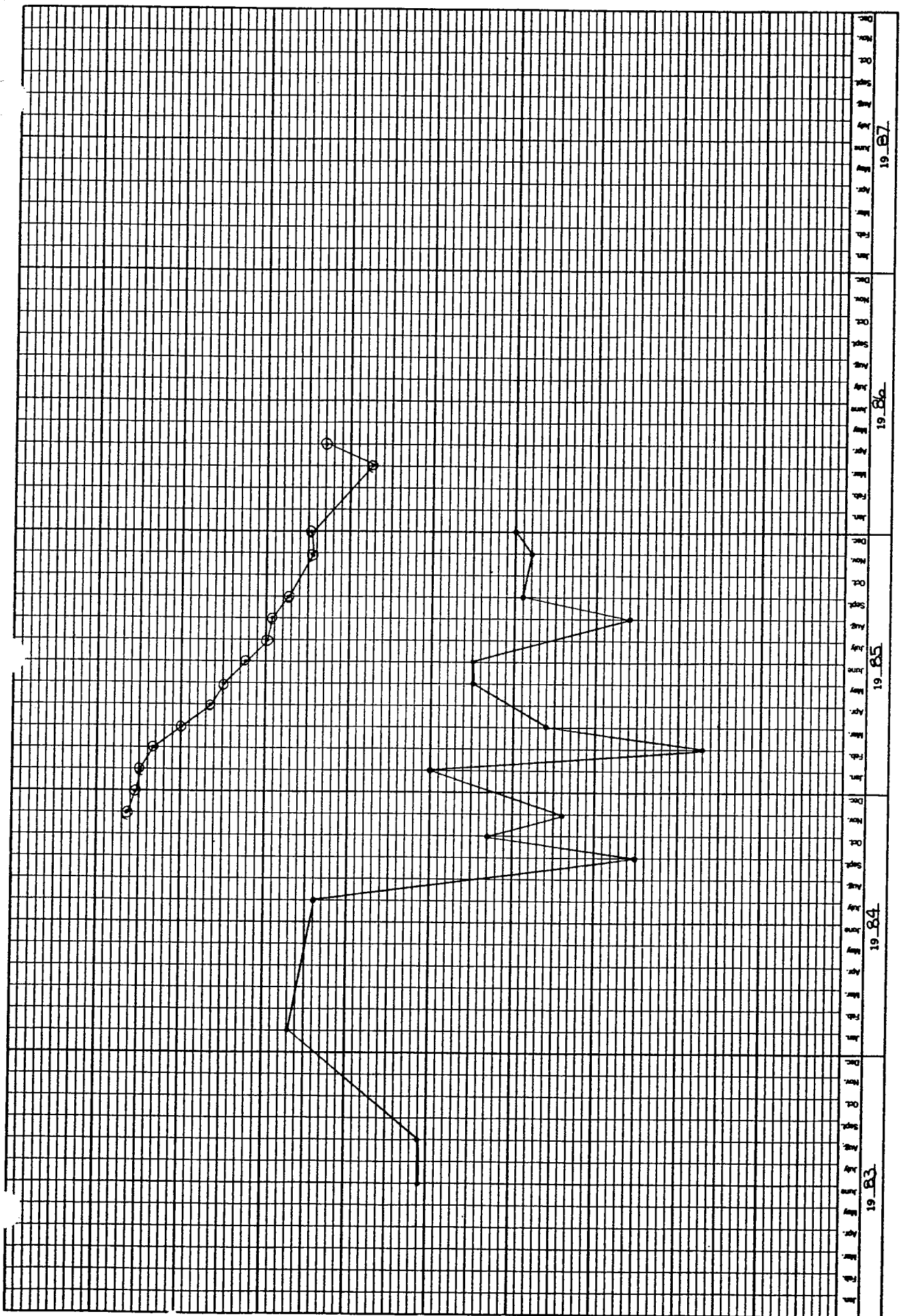








1741  
1745  
1744  
1743  
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1741



CHROMIUM CONCENTRATION (ppm)

M-8

WATER ELEVATION (FT) 0-0-0



1744

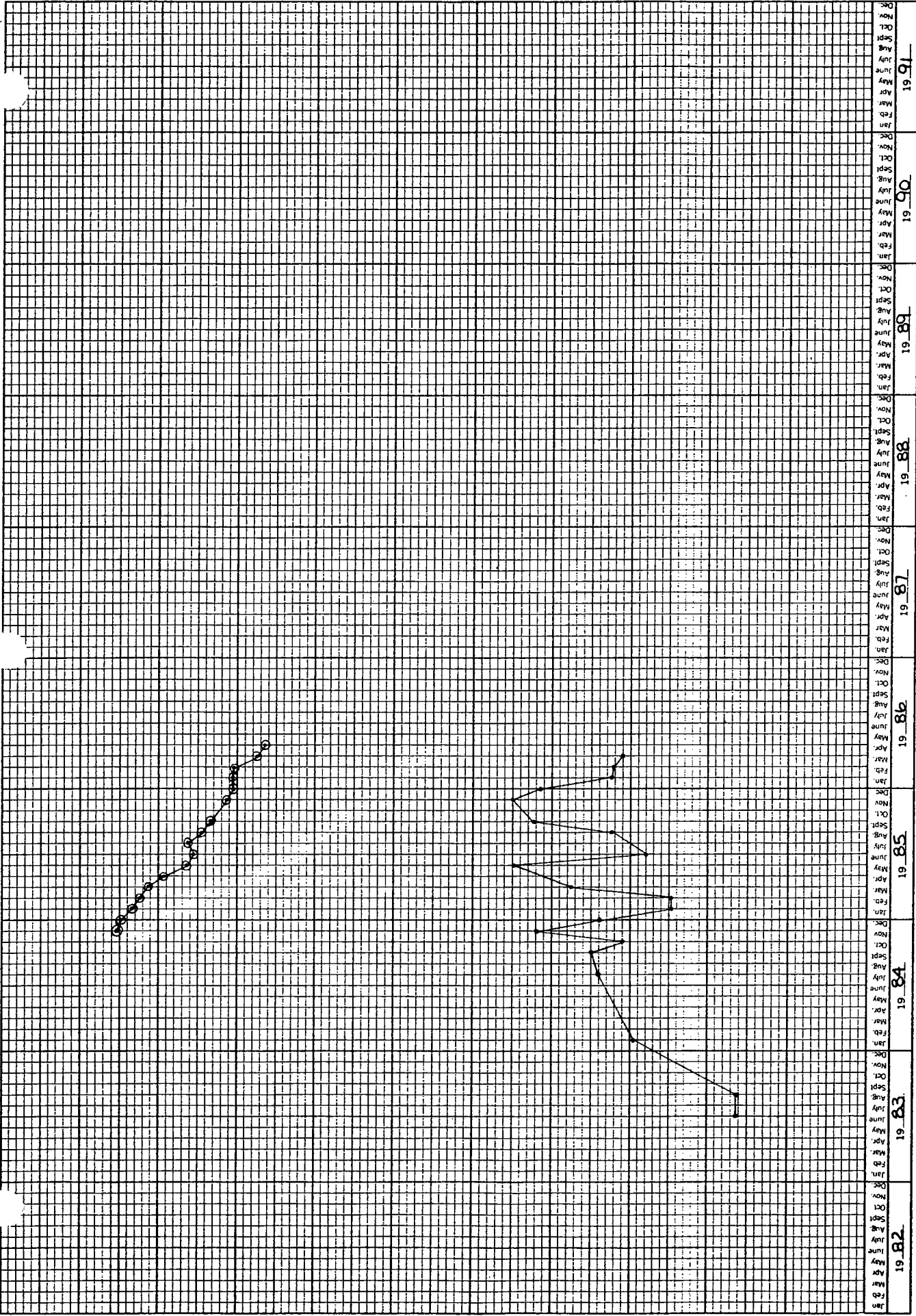
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1740

60  
50  
40  
30  
20  
10  
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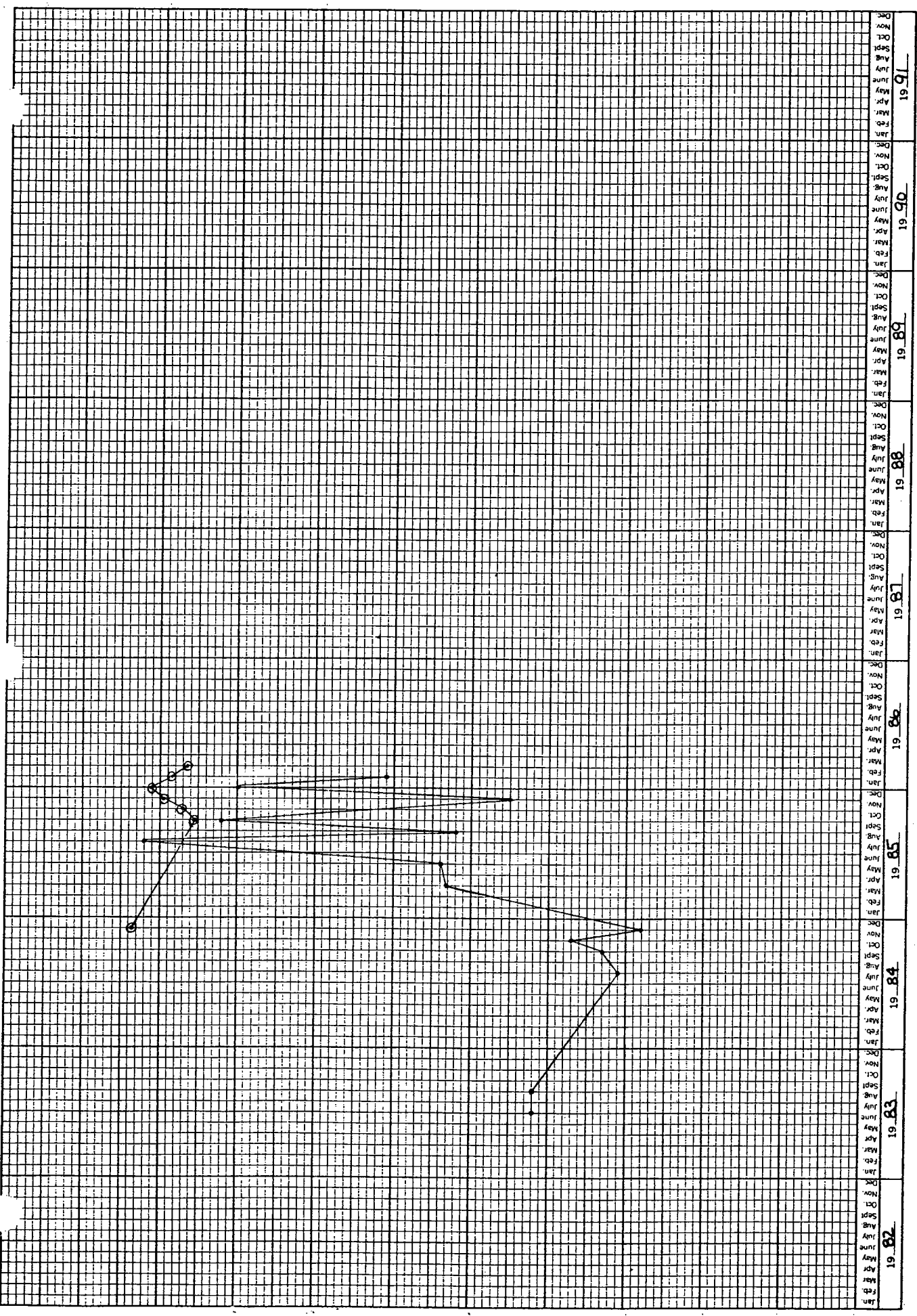
CHROMIUM CONCENTRATION (ppm)

M-9

WATER ELEVATION (FT)

0-0-0

130  
120  
110  
100  
90  
80  
70  
60  
50  
40



177  
176  
176  
1767  
1766

CHROMIUM CONCENTRATION (ppm)

M-11

WATER ELEVATION (FT)

| Year | Month | Year | Month | Year | Month | Year | Month | Year | Month | Year | Month | Year | Month | Year | Month | Year | Month | Year | Month |
|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|
| 1982 | Jan   | 1983 | Jan   | 1984 | Jan   | 1985 | Jan   | 1986 | Jan   | 1987 | Jan   | 1988 | Jan   | 1989 | Jan   | 1990 | Jan   | 1991 | Jan   |

50

40

30

20

10.0

1764

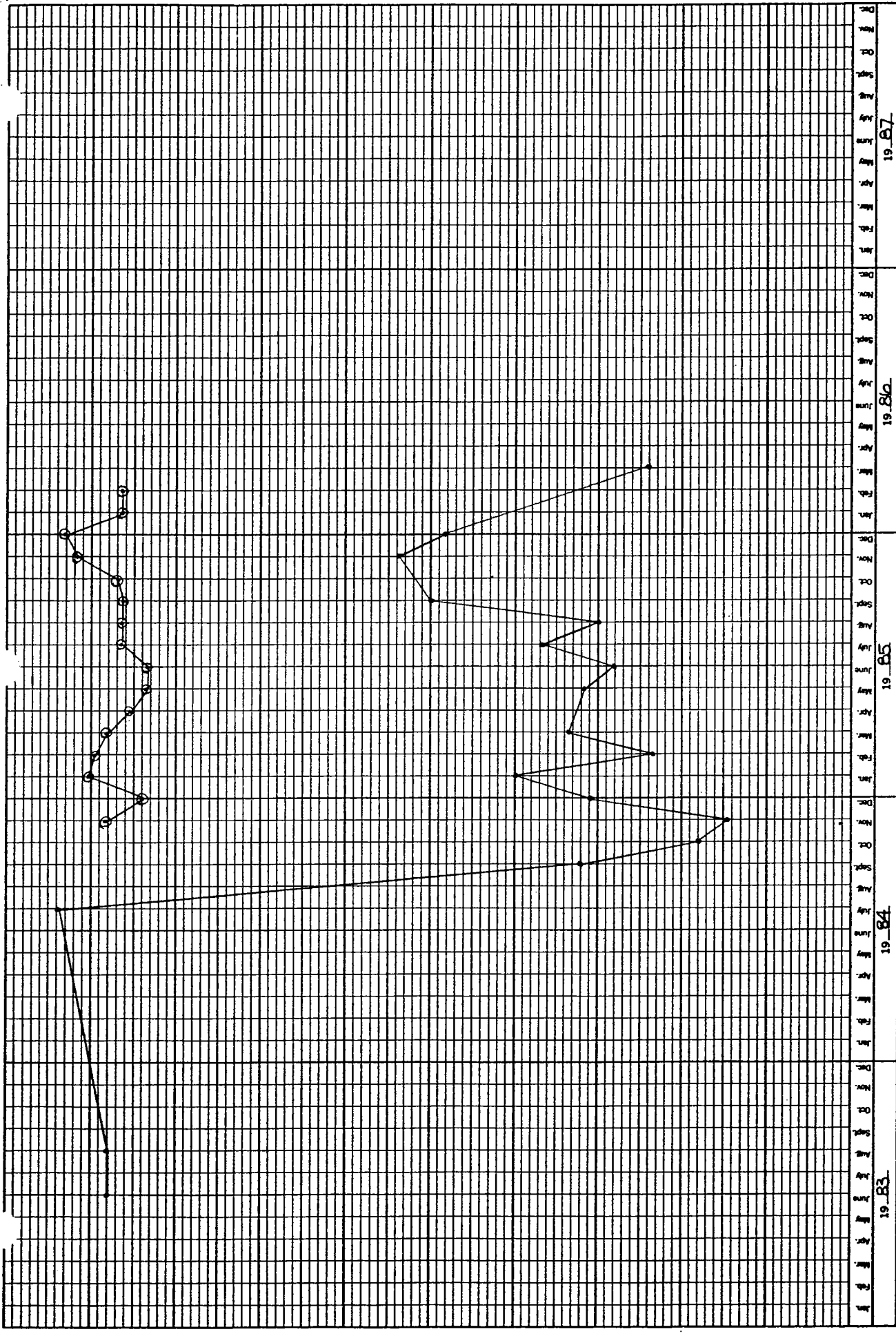
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1767

1766

1765

1764



CHROMIUM CONCENTRATION (ppm)

M-12

WATER ELEVATION (FT)

19.83

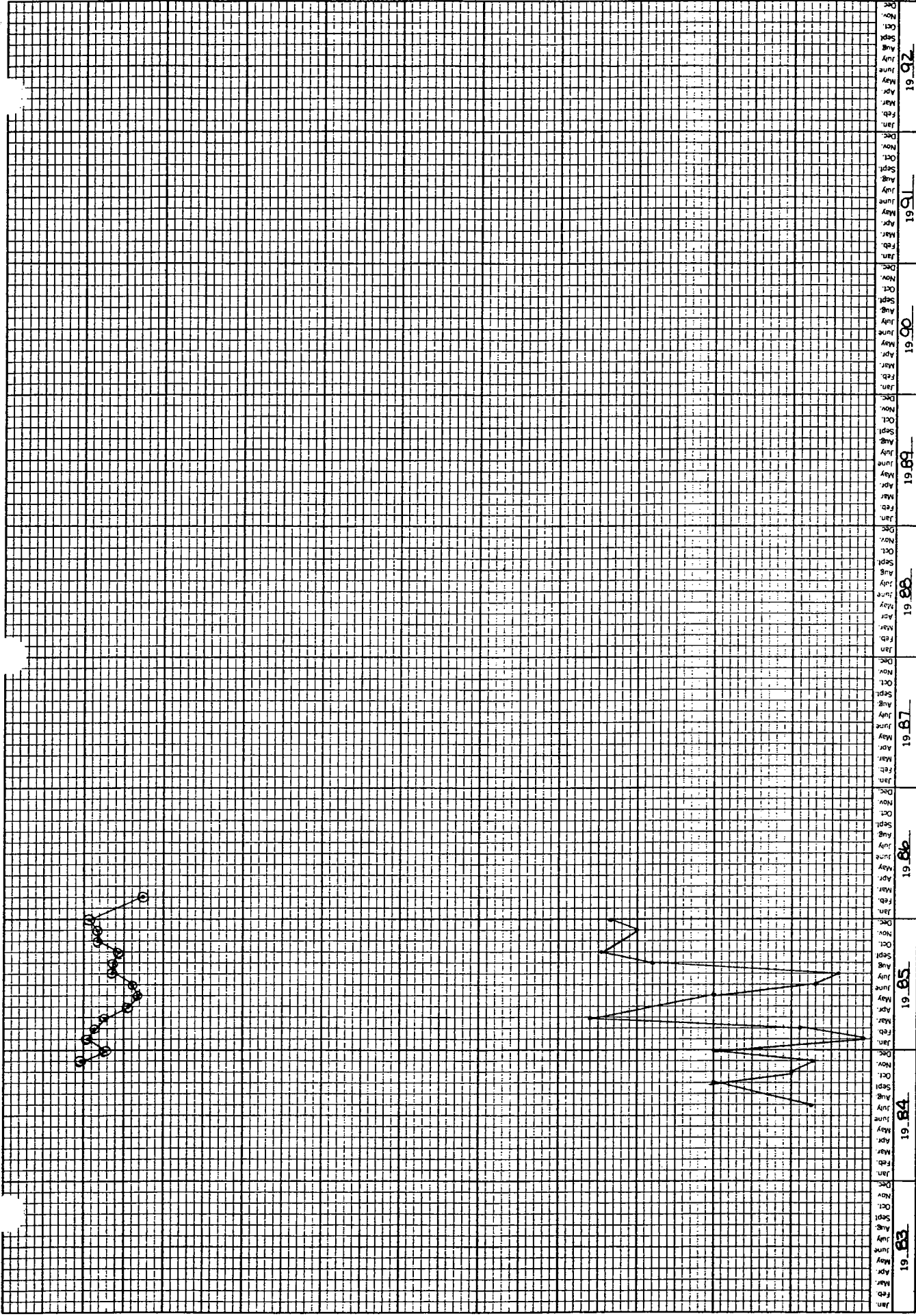
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19.85

19.86

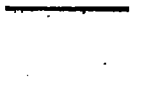
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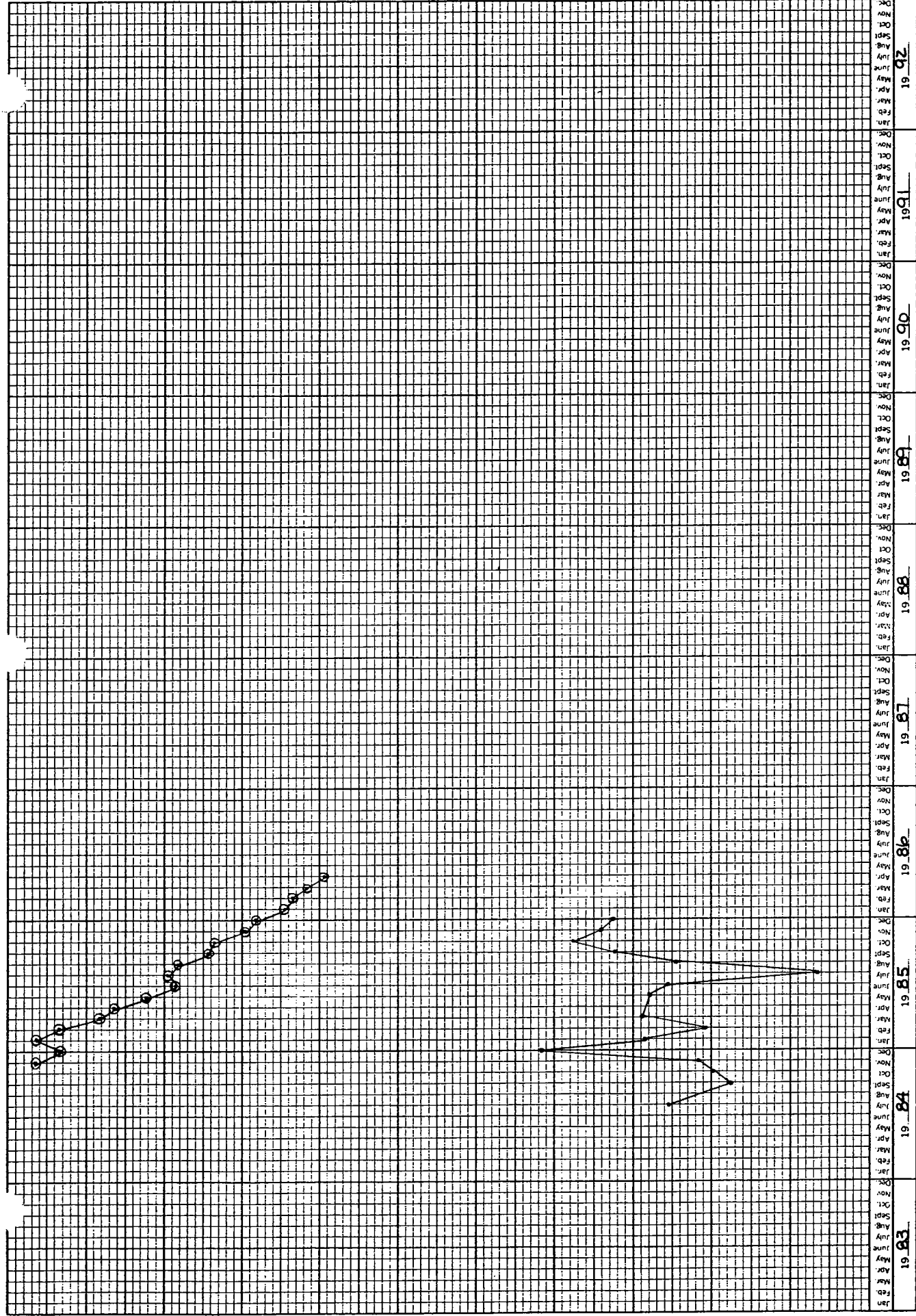
CHROMIUM CONCENTRATION (PPM) M-13 WATER ELEVATION (FT) 00-0

| Year | Month | Year | Month | Year | Month | Year | Month | Year | Month | Year | Month |
|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|
| 1983 | Jan   | 1984 | Jan   | 1985 | Jan   | 1986 | Jan   | 1987 | Jan   | 1988 | Jan   |
| 1983 | Feb   | 1984 | Feb   | 1985 | Feb   | 1986 | Feb   | 1987 | Feb   | 1988 | Feb   |
| 1983 | Mar   | 1984 | Mar   | 1985 | Mar   | 1986 | Mar   | 1987 | Mar   | 1988 | Mar   |
| 1983 | Apr   | 1984 | Apr   | 1985 | Apr   | 1986 | Apr   | 1987 | Apr   | 1988 | Apr   |
| 1983 | May   | 1984 | May   | 1985 | May   | 1986 | May   | 1987 | May   | 1988 | May   |
| 1983 | Jun   | 1984 | Jun   | 1985 | Jun   | 1986 | Jun   | 1987 | Jun   | 1988 | Jun   |
| 1983 | Jul   | 1984 | Jul   | 1985 | Jul   | 1986 | Jul   | 1987 | Jul   | 1988 | Jul   |
| 1983 | Aug   | 1984 | Aug   | 1985 | Aug   | 1986 | Aug   | 1987 | Aug   | 1988 | Aug   |
| 1983 | Sep   | 1984 | Sep   | 1985 | Sep   | 1986 | Sep   | 1987 | Sep   | 1988 | Sep   |
| 1983 | Oct   | 1984 | Oct   | 1985 | Oct   | 1986 | Oct   | 1987 | Oct   | 1988 | Oct   |
| 1983 | Nov   | 1984 | Nov   | 1985 | Nov   | 1986 | Nov   | 1987 | Nov   | 1988 | Nov   |
| 1983 | Dec   | 1984 | Dec   | 1985 | Dec   | 1986 | Dec   | 1987 | Dec   | 1988 | Dec   |
| 1989 | Jan   | 1990 | Jan   | 1991 | Jan   | 1992 | Jan   |      |       |      |       |
| 1989 | Feb   | 1990 | Feb   | 1991 | Feb   | 1992 | Feb   |      |       |      |       |
| 1989 | Mar   | 1990 | Mar   | 1991 | Mar   | 1992 | Mar   |      |       |      |       |
| 1989 | Apr   | 1990 | Apr   | 1991 | Apr   | 1992 | Apr   |      |       |      |       |
| 1989 | May   | 1990 | May   | 1991 | May   | 1992 | May   |      |       |      |       |
| 1989 | Jun   | 1990 | Jun   | 1991 | Jun   | 1992 | Jun   |      |       |      |       |
| 1989 | Jul   | 1990 | Jul   | 1991 | Jul   | 1992 | Jul   |      |       |      |       |
| 1989 | Aug   | 1990 | Aug   | 1991 | Aug   | 1992 | Aug   |      |       |      |       |
| 1989 | Sep   | 1990 | Sep   | 1991 | Sep   | 1992 | Sep   |      |       |      |       |
| 1989 | Oct   | 1990 | Oct   | 1991 | Oct   | 1992 | Oct   |      |       |      |       |
| 1989 | Nov   | 1990 | Nov   | 1991 | Nov   | 1992 | Nov   |      |       |      |       |
| 1989 | Dec   | 1990 | Dec   | 1991 | Dec   | 1992 | Dec   |      |       |      |       |



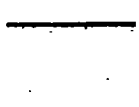


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173  
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CHROMIUM CONCENTRATION (PPM) WATER ELEVATION (FT)

M-15



1743

1742

174

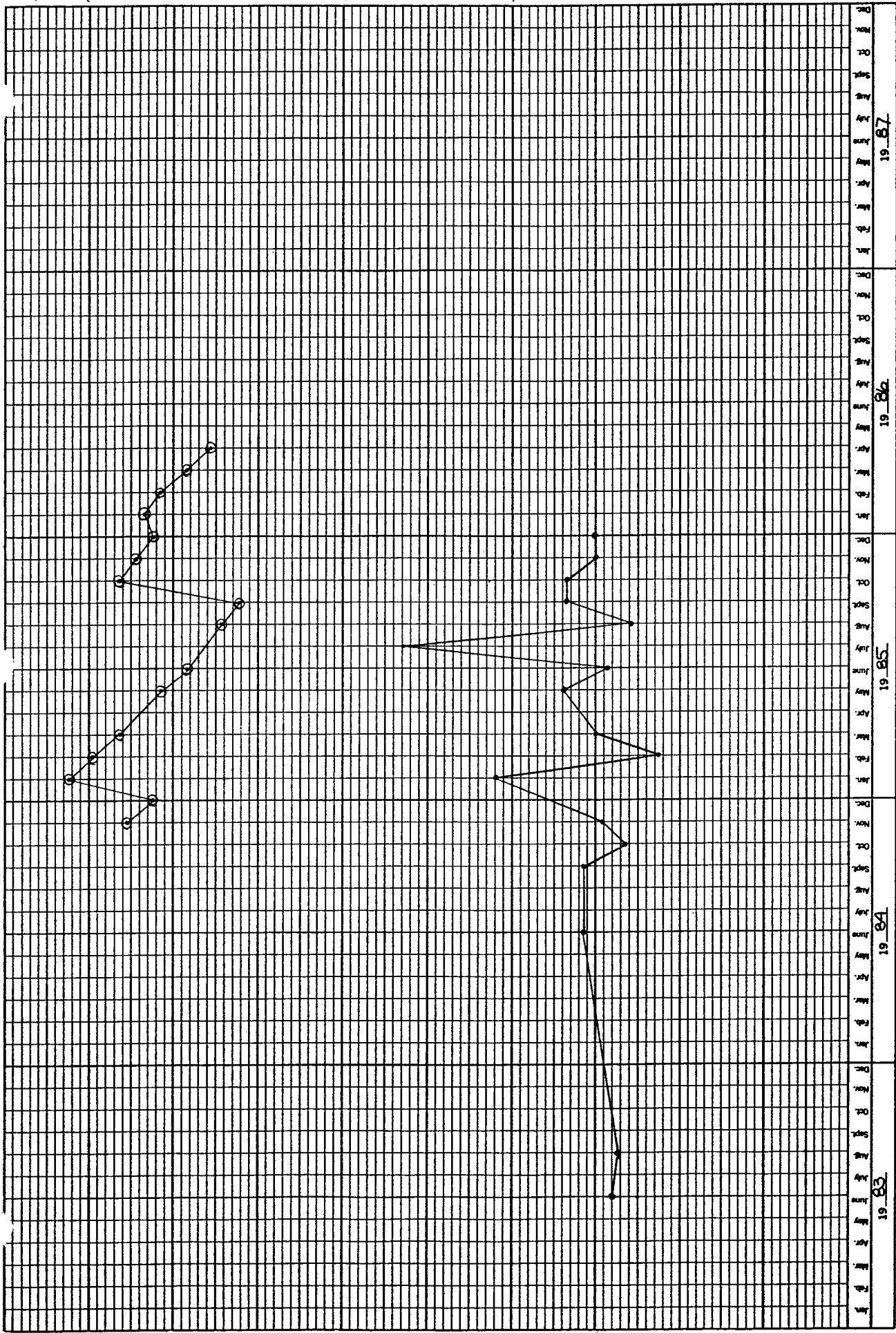
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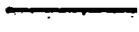
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---●--- CHROMIUM CONCENTRATION (ppm)

○--- WATER ELEVATION (FT)

M-17



173

1738

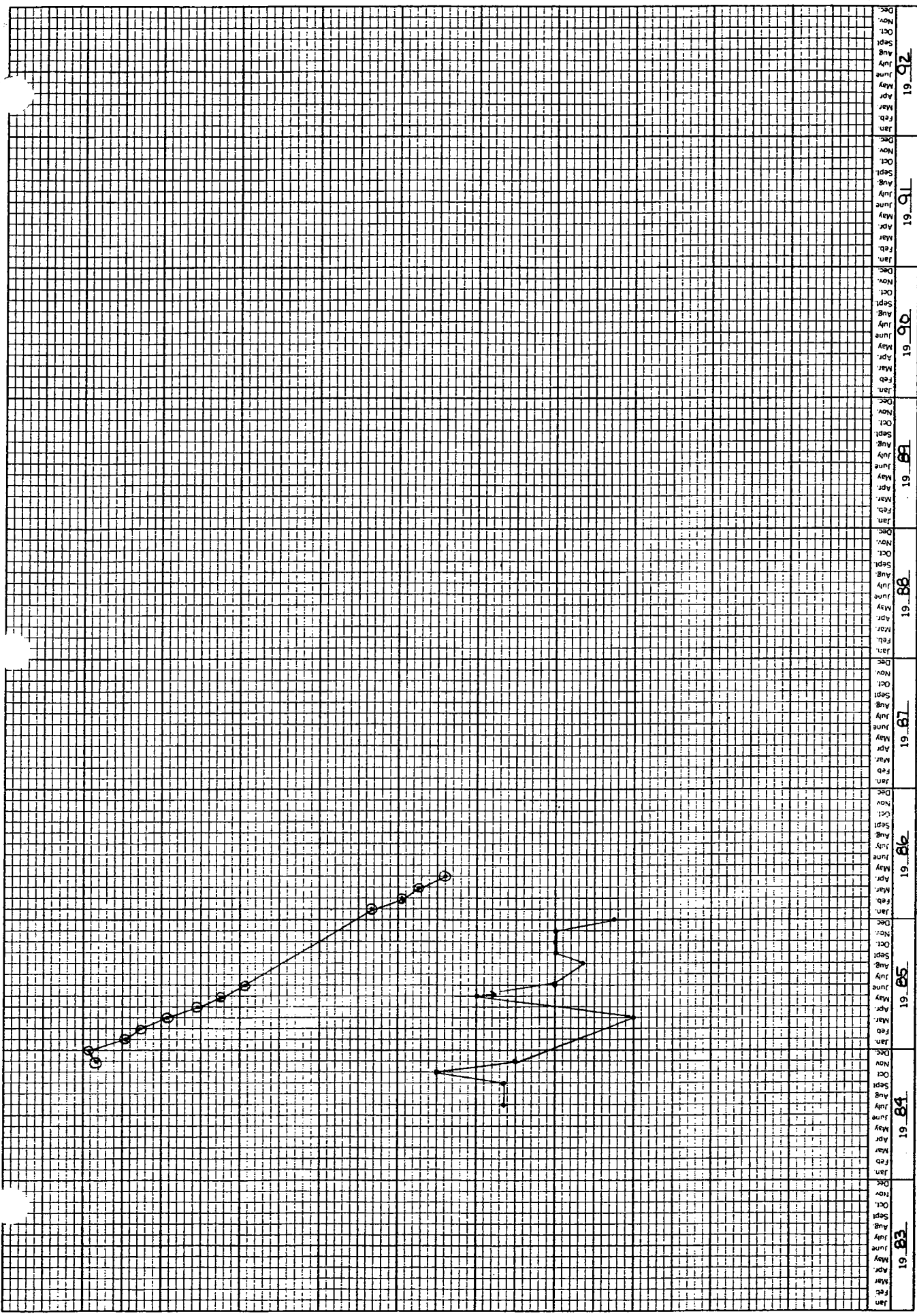
1737

1736

1735

1734

1733



CHROMIUM CONCENTRATION (ppm)

M-22

WATER ELEVATION (FT)

19 92

19 91

19 90

19 89

19 88

19 87

19 86

19 85

19 84

19 83



170

1704

1705

1704

1703

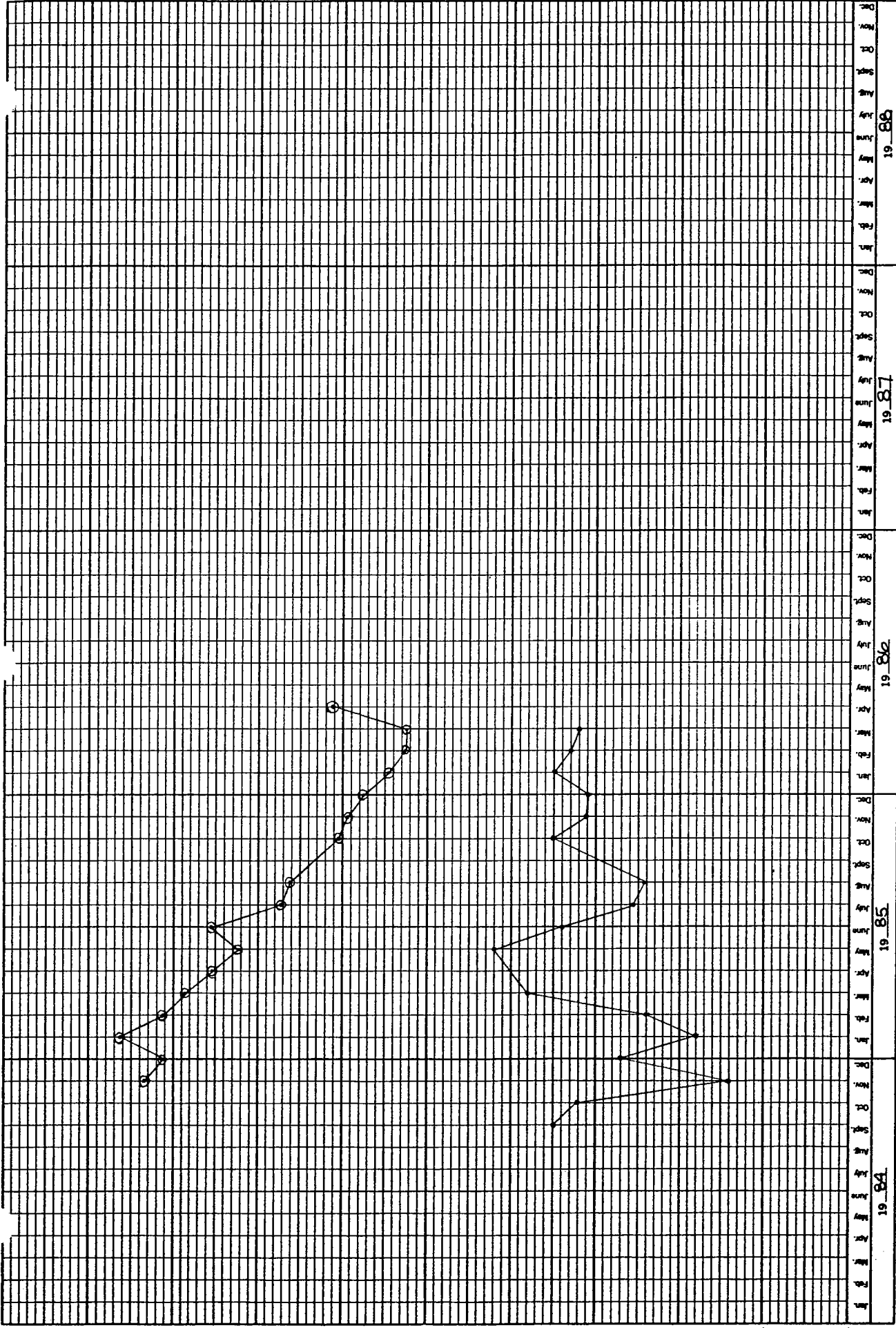
1702

19\_84 19\_85 19\_86 19\_87 19\_88

CHROMIUM CONCENTRATION (ppm)

M-23

WATER ELEVATION (FT) 000



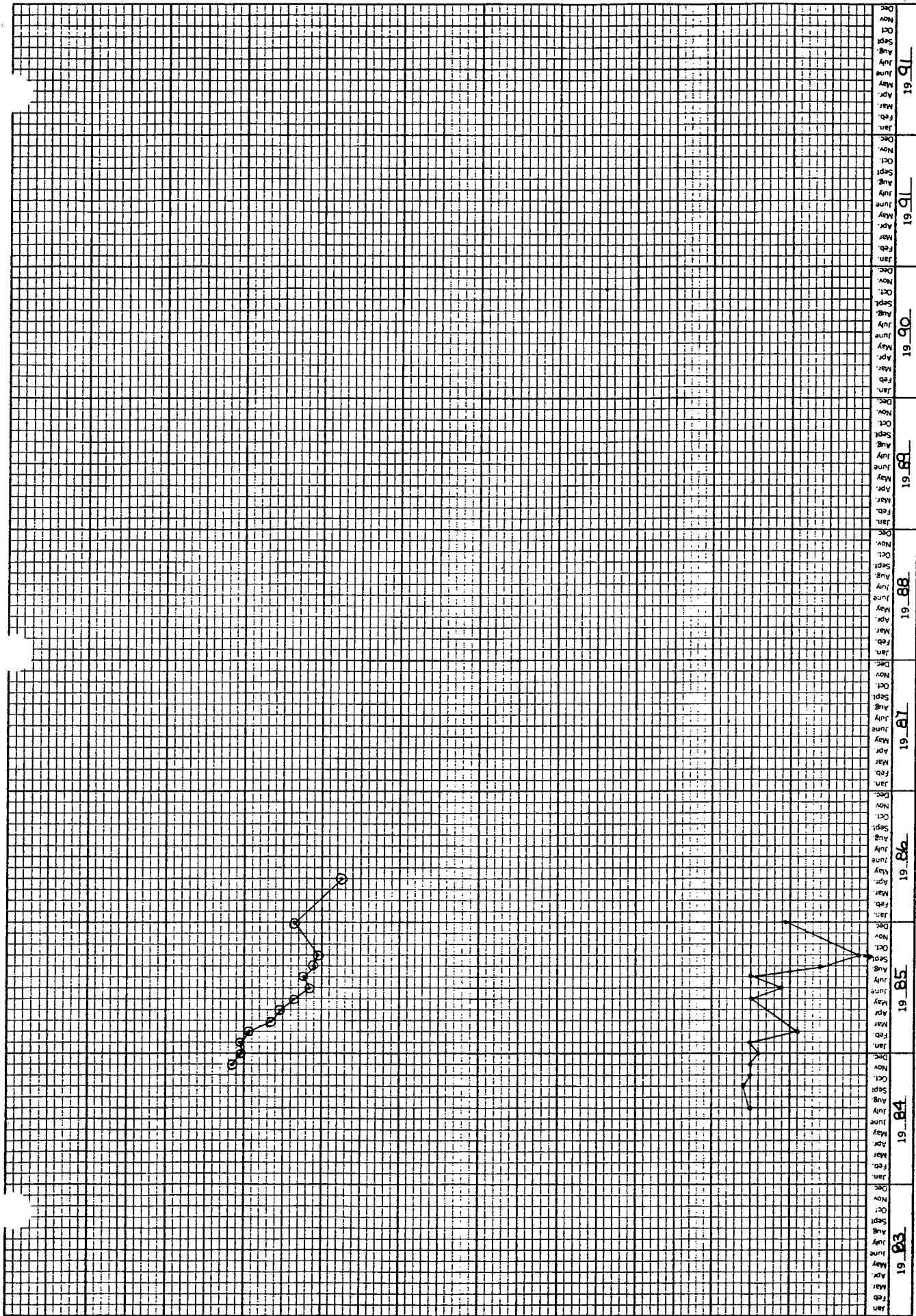
1750

1749

1748

1747

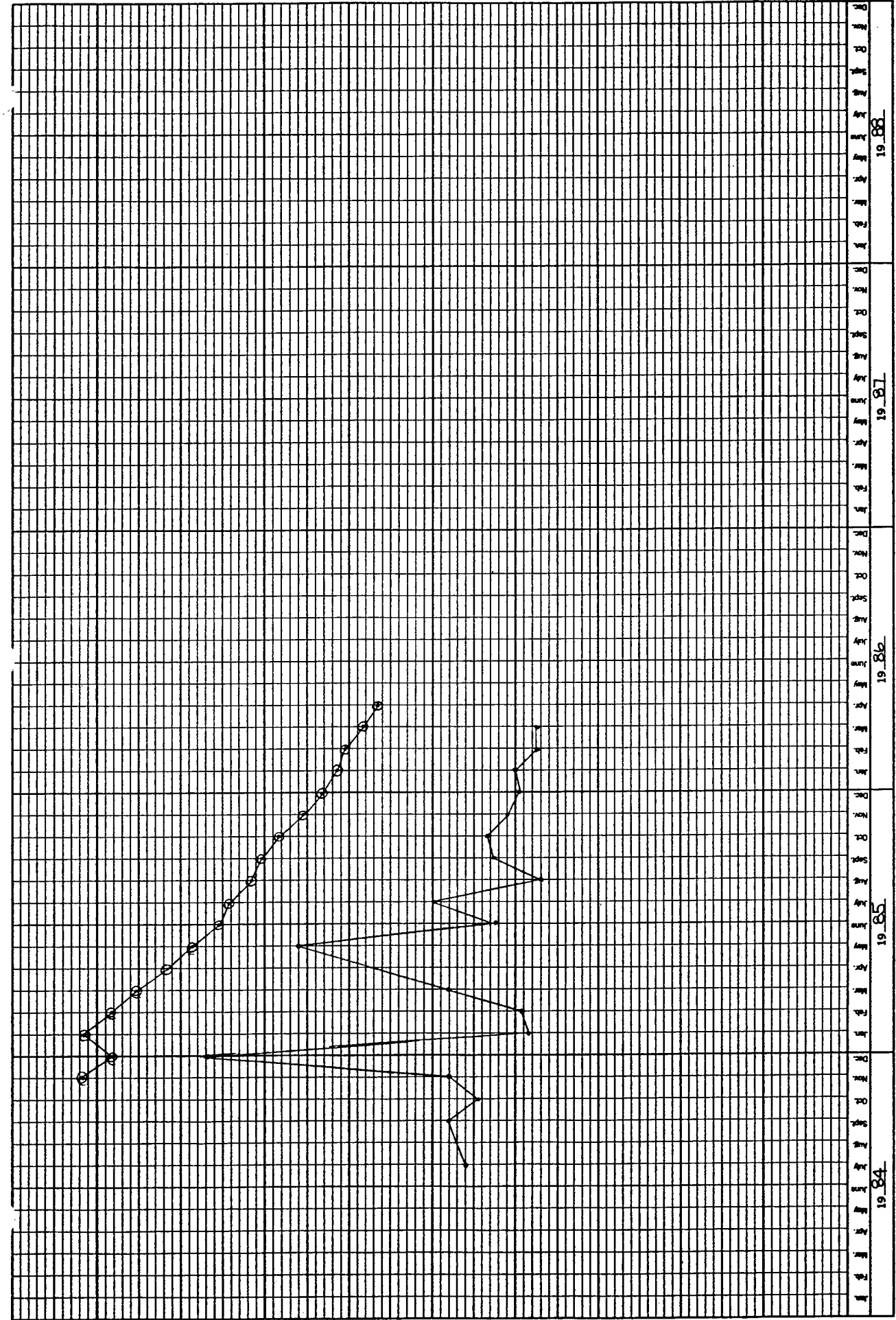
1746



CARBON DIOXIDE CONCENTRATION

M-24

WATER ELEVATIONS (FT) 000



1734

1733

1732

1731

1730

1729

1728

20.0

15.0

10.0

5.0

19.84

19.85

19.86

19.87

19.88

CHROMIUM CONCENTRATION (ppm)

M-25

WATER ELEVATION (ft)



1751

1750

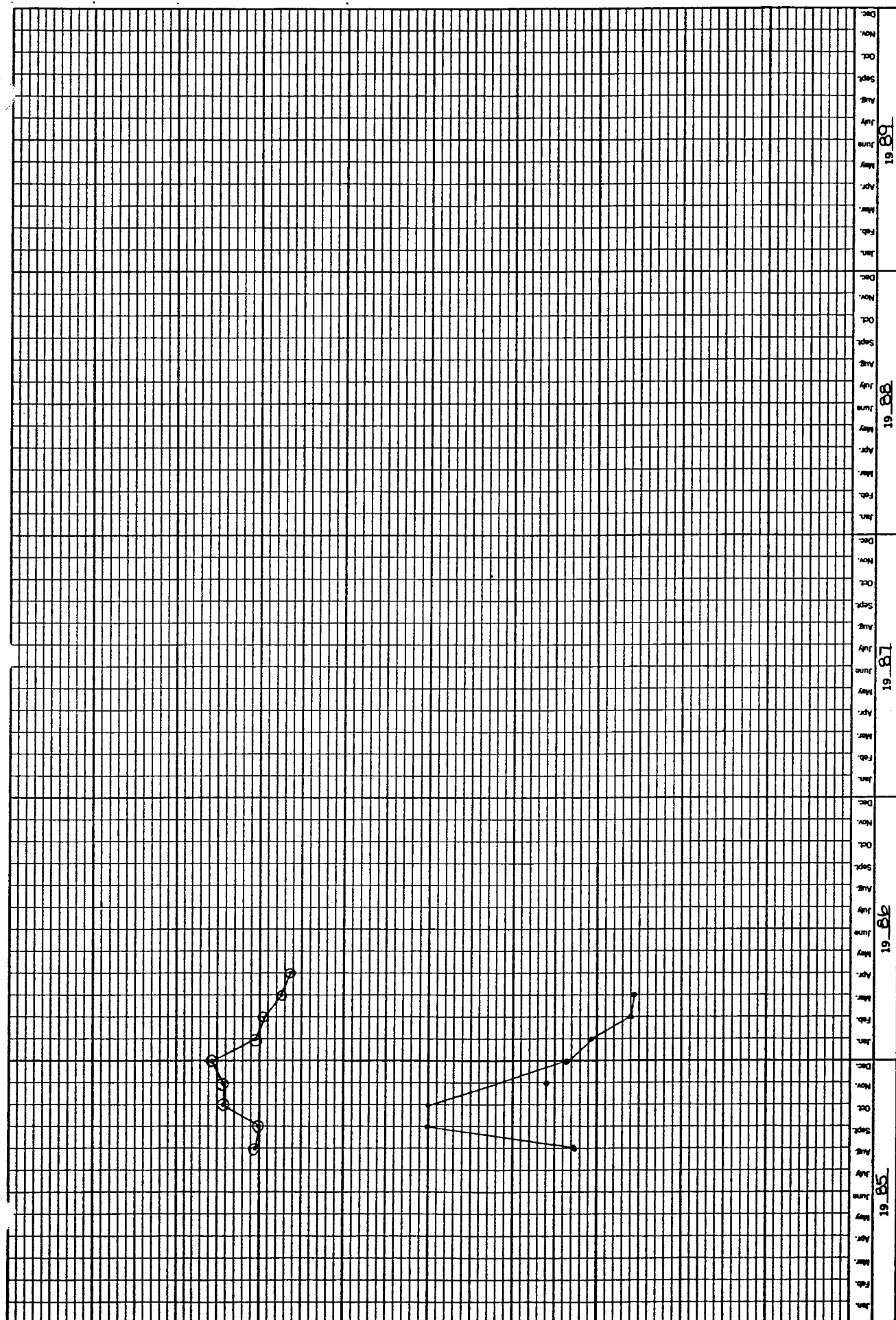
1749

1748

15.0

10.0

5.0



CHROMIUM CONCENTRATION (ppm)

M-31

WATER ELEVATION (FT)

19 85

19 86

19 87

19 88

19 89

174

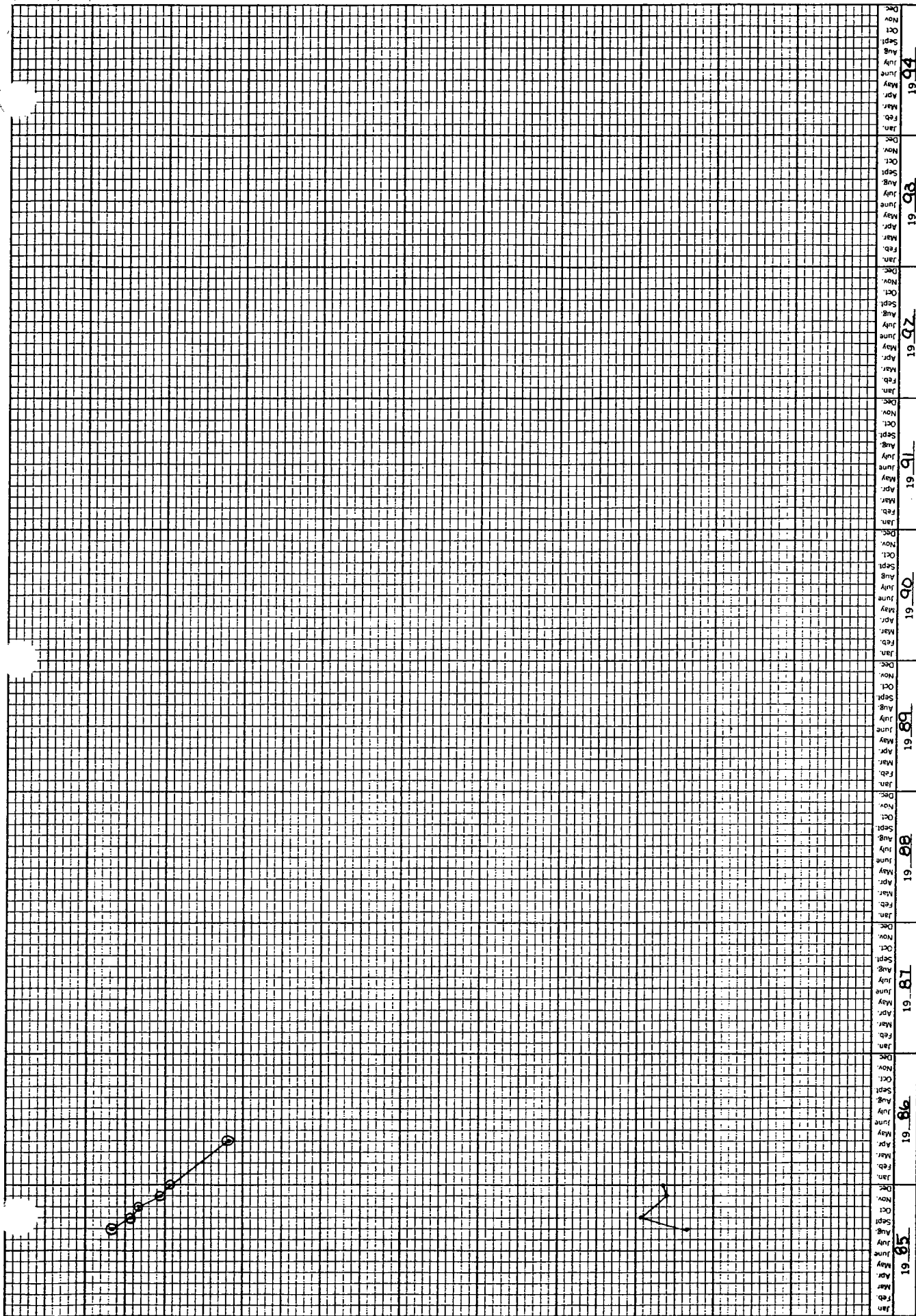
176

174

1742

1741

1741



CHROMIUM CONCENTRATION (PPM)

M-34

WATER LEVEL (FT)

19 85 19 86 19 87 19 88 19 89 19 90 19 91 19 92 19 93 19 94

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

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Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

Dec Nov Oct Sept Aug July June May Apr Mar Feb Jan

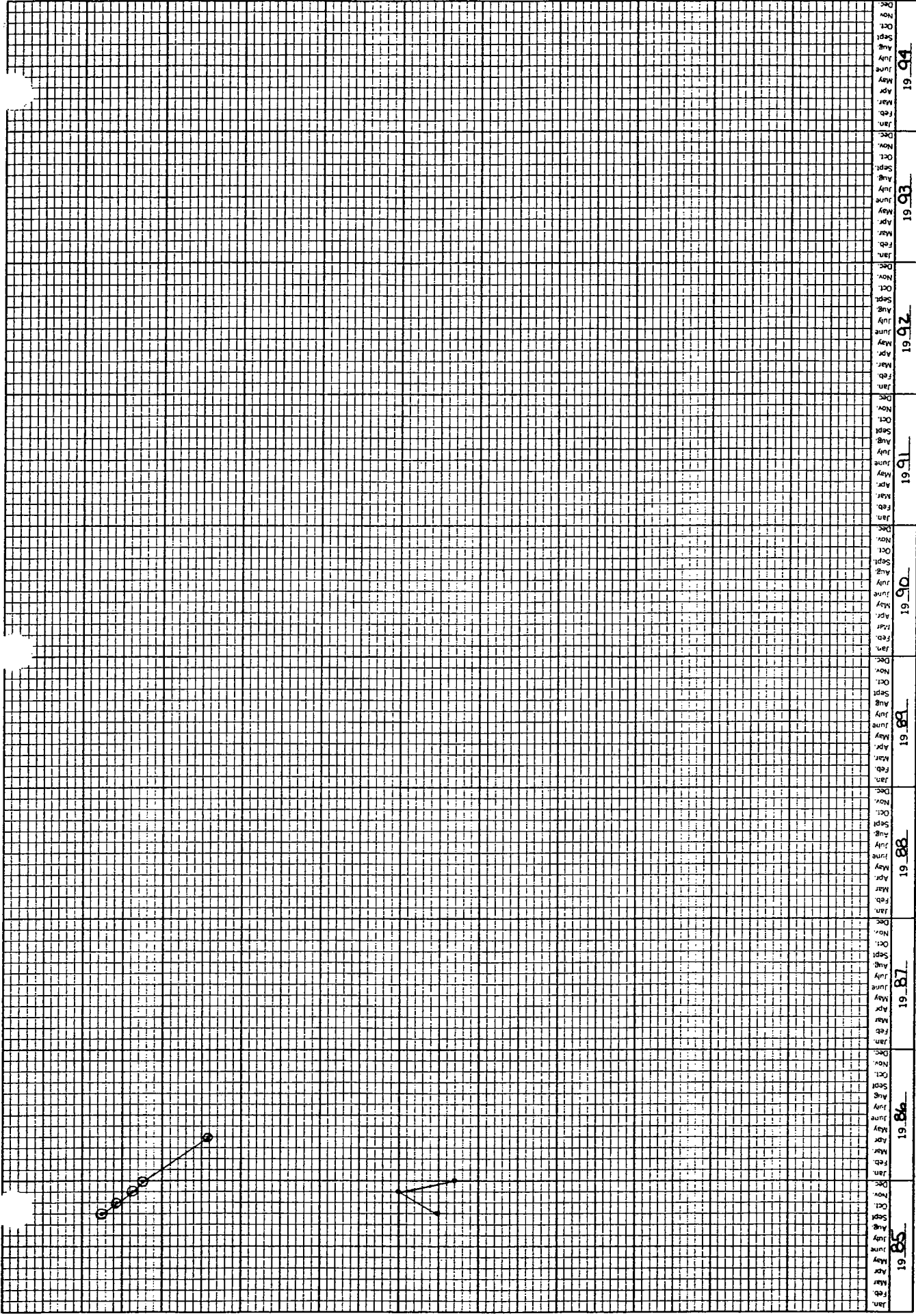
174

174

174

174

174



CHROMIUM CONCENTRATION (PPM)

M-35

WATER ELEVATION (FT)

000

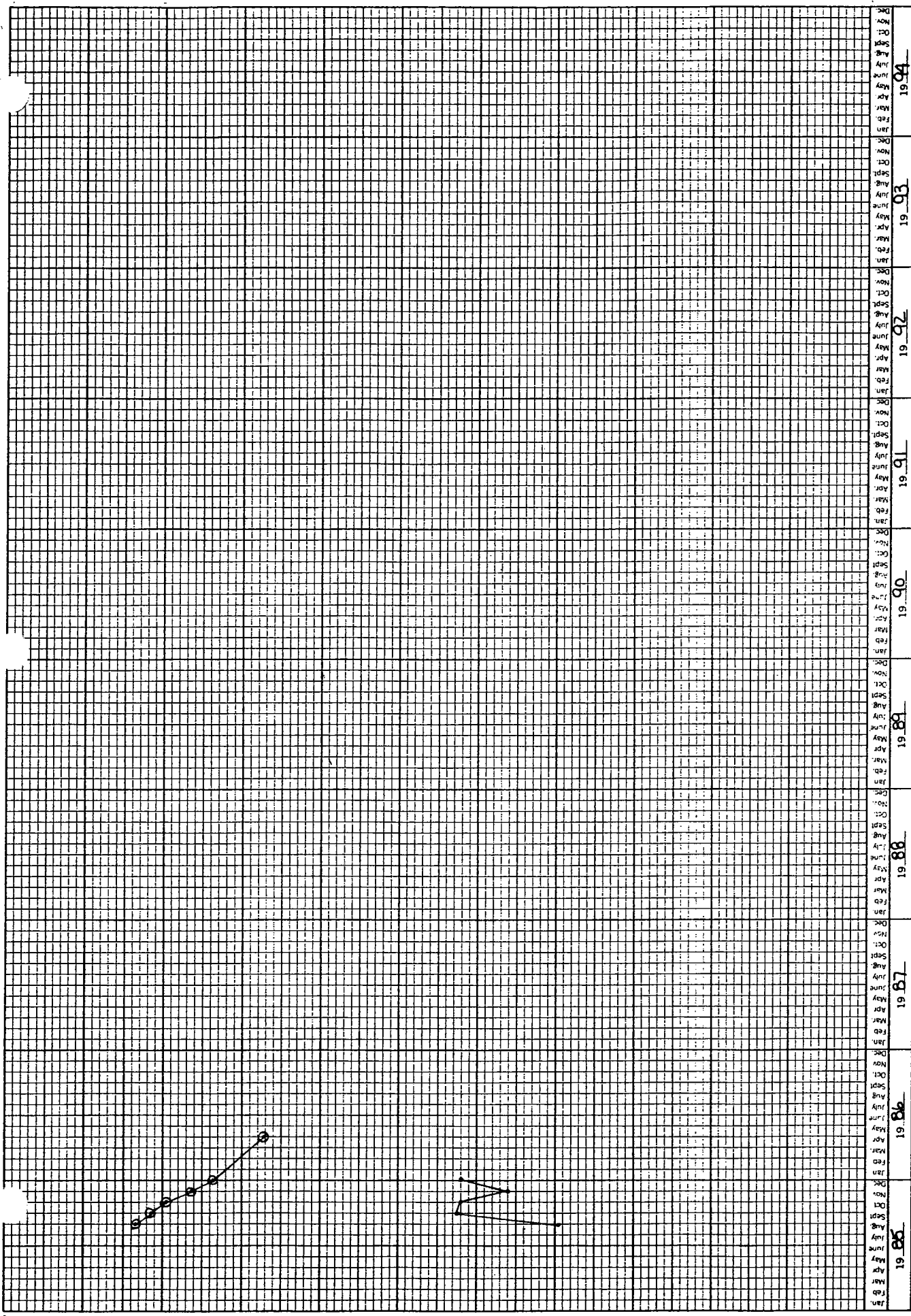
1735

1734

1733

1732

1731



CHROMIUM CONCENTRATION (ppm)

M-36

WATER ELEVATION (ft)

3.0

2.0

1.0

1986 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1986 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1987 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1987 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1988 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1988 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1989 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1989 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1990 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1990 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1991 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1991 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1992 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1992 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1993 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1993 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec  
 1994 Jan Feb Mar Apr May June July Aug Sept Oct Nov Dec



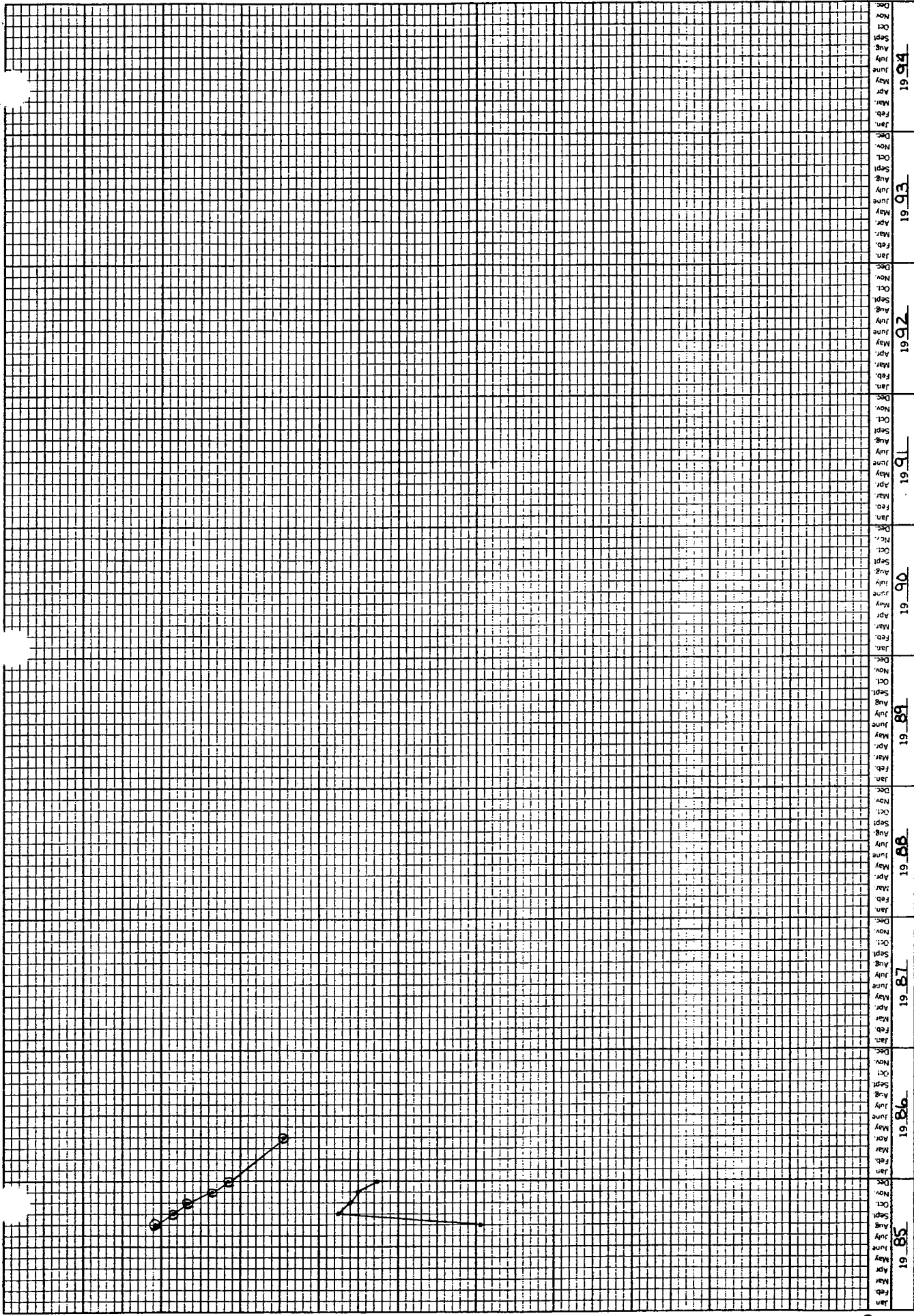
1732

1734

1733

1732

1731



CHROMIUM CONCENTRATION (PPM)

M-38

WATER ELEVATION (FT)



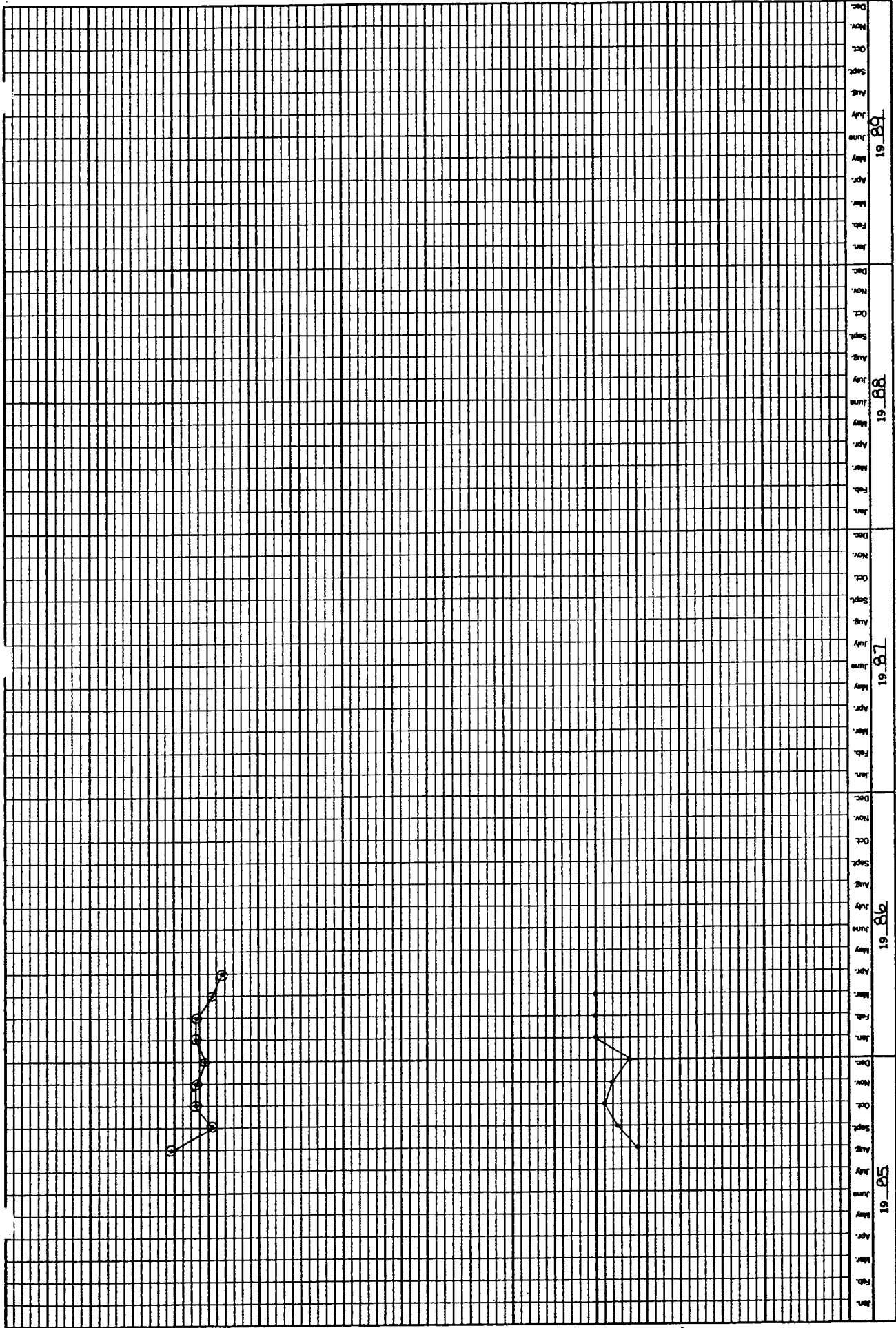
1691

169C

1689

168E

1687



WATER ELEVATION (FT)

M-42

CHROMIUM CONCENTRATION (ppm)



1681

1684

1683

1687

1681

0.5

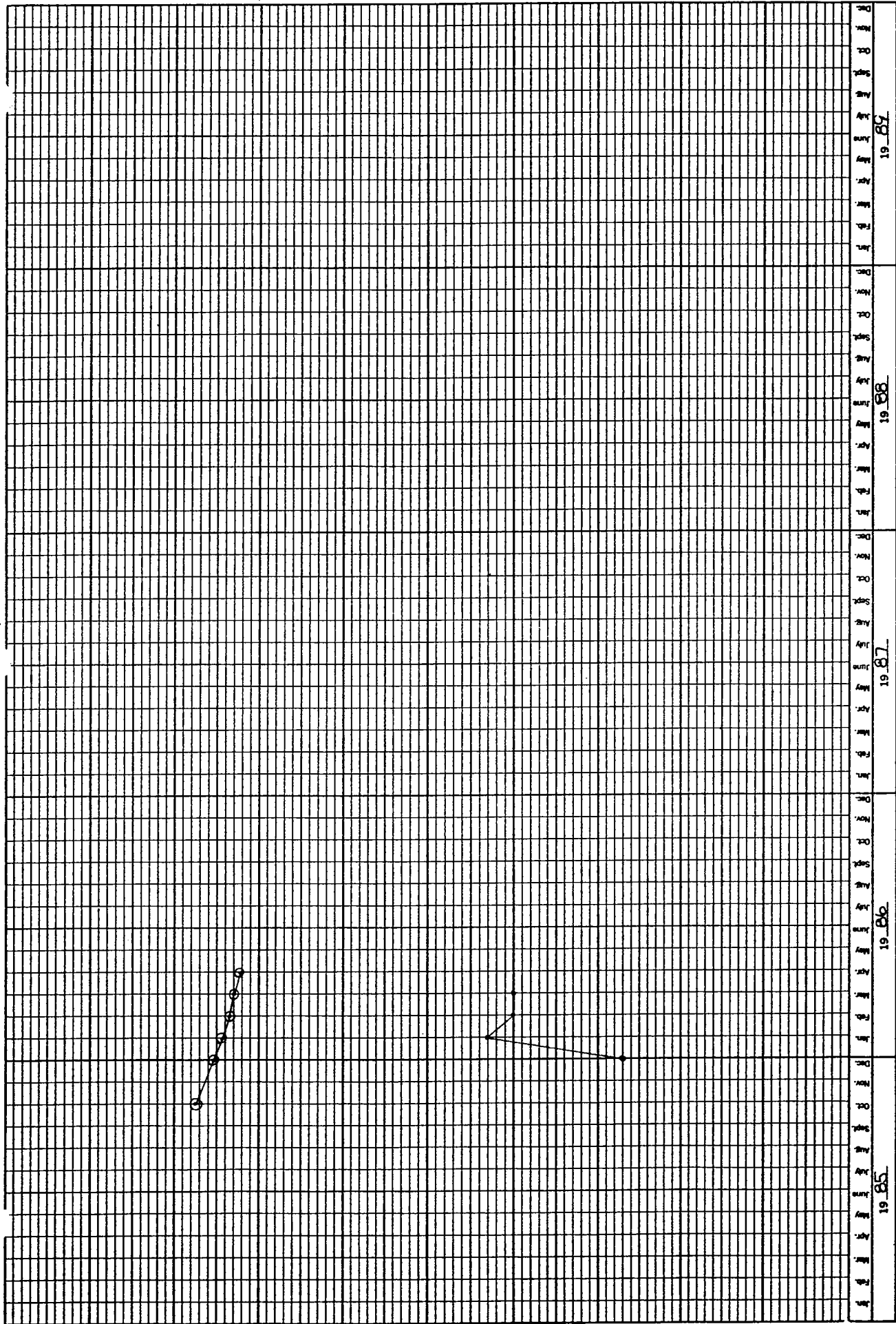
0.4

0.3

0.2

0.1

0



---○--- CHROMIUM CONCENTRATION (ppm)

M-44

--- WATER ELEVATION (FT) ---

1985

1986

1987

1988

1989

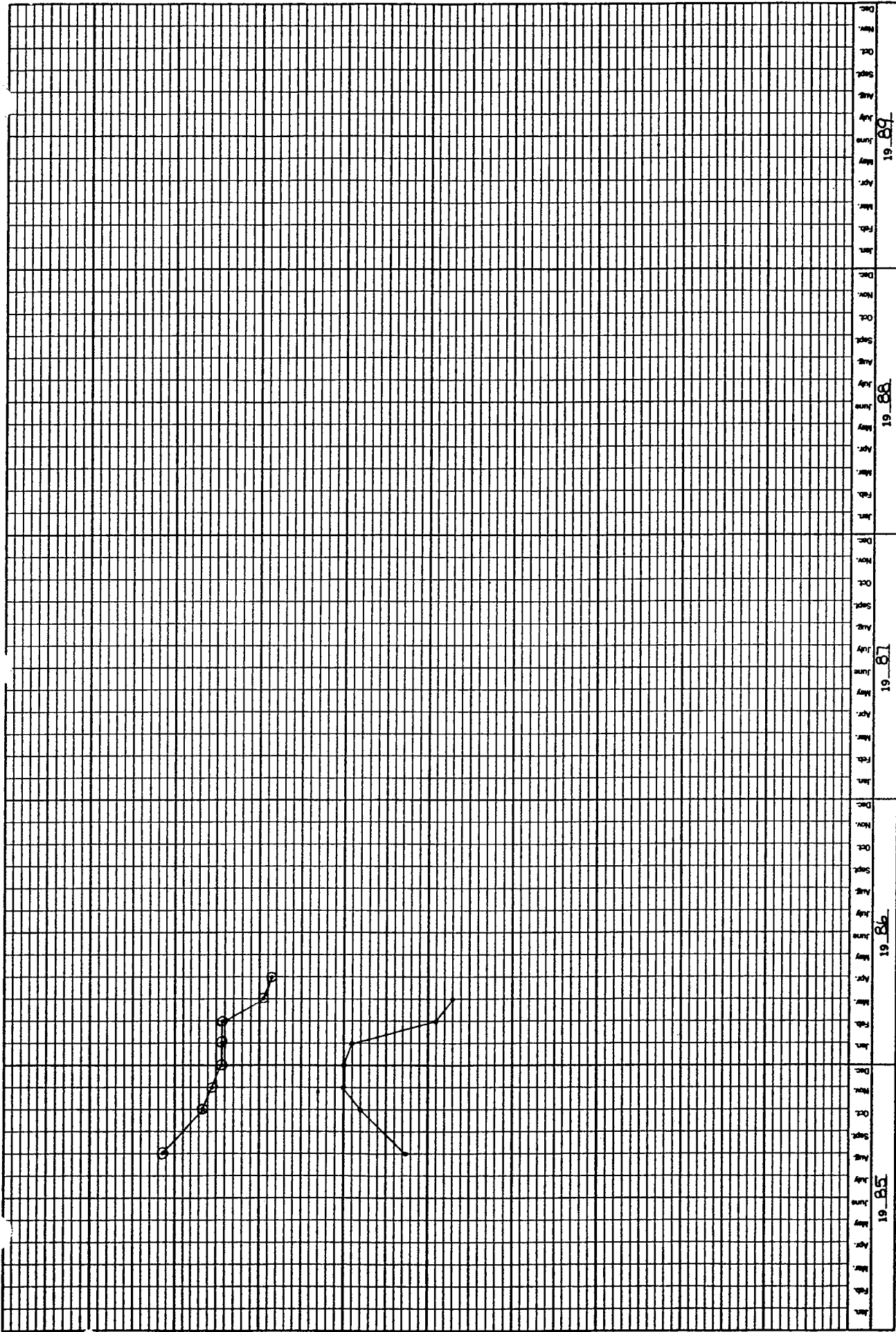
1704

1702

1702

1701

1700



---○--- CHROMIUM CONCENTRATION (ppm)

M-47

WATER ELEVATION (FT) 0-0-0

19 85

19 86

19 87

19 88

19 89

MONITOR WELL INVENTORY  
KERR-MCGEE HENDERSON FACILITY

| MONITOR WELL NUMBER | REFERENCE CASING ELEV., MSL | GROUND ELEV., MSL | *CASING STICKUP FT. | *DRILLED WELL DEPTH FT. | **MEASURED WELL DEPTH FT. TOC | *SCREENED INTERVAL, FT | CASING TYPE AND SIZE IN. | DATE WELL DRILLED | *DEPTH TO TOP OF MUDDY CREEK FT | ELEV. OF MUDDY CREEK MSL | *DEPTH TO GW FT. 6/85 | WATER-TABLE ELEVATION MSL. 6/85 | SATURATED AQUIFER THICKNESS FT. 6/85 | CHROMIUM CONCENT. mg/l 6/85 | GM COND.-2 umhos/cm 6/85 | **DEPTH TO WATER, FT TOC. 6/85 |
|---------------------|-----------------------------|-------------------|---------------------|-------------------------|-------------------------------|------------------------|--------------------------|-------------------|---------------------------------|--------------------------|-----------------------|---------------------------------|--------------------------------------|-----------------------------|--------------------------|--------------------------------|
| KH Wells            | ---                         | ---               | ---                 | ---                     | ---                           | ---                    | ---                      | ---               | ---                             | ---                      | ---                   | ---                             | ---                                  | ---                         | ---                      | ---                            |
| M-1                 | 1792.68                     | 1791.38           | 1.30                | 50.0                    | 45.38                         | 33.5-43.5              | 5" Steel                 | 11/81             | 40.0                            | 1751.4                   | 43.4                  | 1748.0                          | -3.4                                 | 1.2                         | 16,200                   | 44.70                          |
| M-2                 | 1780.02                     | 1778.60           | 1.42                | 44.0                    | 40.69                         | 30-40                  | 5" Steel                 | 11/81             | 39.0                            | 1739.6                   | 35.2                  | 1743.4                          | 3.8                                  | 3.1                         | 8,800                    | 36.64                          |
| M-3                 | 1780.46                     | 1779.76           | 0.70                | 44.5                    | 40.44                         | 30-40                  | 5" Steel                 | 11/81             | 41.0                            | 1738.8                   | 37.2                  | 1742.5                          | 3.8                                  | 8.0                         | 13,300                   | 37.92                          |
| M-4                 | 1781.45                     | 1780.05           | 1.40                | 45.0                    | 41.34                         | 30-40                  | 5" Steel                 | 11/81             | 36.0                            | 1744.1                   | 35.3                  | 1744.8                          | 0.7                                  | 0.6                         | 5,200                    | 36.69                          |
| M-5                 | 1747.86                     | 1747.01           | 0.85                | 43.0                    | 40.25                         | 29-39                  | 5" Steel                 | 6/1/82            | 25.5                            | 1721.5                   | 32.6                  | 1714.4                          | -7.1                                 | <0.1                        | 10,100                   | 33.46                          |
| M-6                 | 1729.15                     | 1728.04           | 1.11                | 43.0                    | 39.90                         | 25-35                  | 5" Steel                 | 6/2/82            | 32.0                            | 1696.0                   | 33.2                  | 1698.9                          | -1.1                                 | <0.1                        | 9,500                    | 34.26                          |
| M-7                 | 1729.81                     | 1728.81           | 1.00                | 37.0                    | 35.23                         | 25-35                  | 5" Steel                 | 6/3/82            | 29.5                            | 1699.3                   | 28.7                  | 1700.2                          | 0.9                                  | <0.1                        | 8,300                    | 29.66                          |
| M-8                 | 1780.00                     | 1778.80           | 1.20                | 45.0                    | 40.96                         | 30-40                  | 5" Steel                 | 6/14/82           | 43.0                            | 1735.8                   | 35.3                  | 1743.5                          | 7.7                                  | 14.0                        | 7,100                    | 36.49                          |
| M-9                 | 1778.92                     | 1778.57           | 0.35                | 45.0                    | 39.83                         | 30-40                  | 5" Steel                 | 6/15/82           | 35.0                            | 1743.6                   | 35.1                  | 1742.4                          | -1.1                                 | 32.0                        | 25,000                   | 36.48                          |
| M-10                | 1834.76                     | 1832.70           | 2.06                | 75.0                    | 69.45                         | 43-63                  | 5" Steel                 | 5/83              | 38.0                            | 1794.7                   | 55.2                  | 1777.6                          | -17.1                                | <0.1                        | 3,200                    | 57.21                          |
| M-11                | 1814.45                     | 1812.28           | 2.17                | 60.0                    | ~58.0                         | 33-53                  | 5" Steel                 | 5/83              | 36.5                            | 1775.8                   | 43.7                  | 1768.6                          | -7.2                                 | 90.0                        | 25,100                   | 45.82                          |
| M-12                | 1814.90                     | 1812.37           | 2.53                | 65.0                    | 49.90                         | 37-47                  | 5" Steel                 | 5/83              | 34.5                            | 1777.9                   | 44.7                  | 1767.7                          | -10.2                                | 11.0                        | 21,000                   | 47.22                          |
| M-13                | 1814.23                     | 1812.33           | 1.90                | 55.0                    | 54.76                         | 28-48                  | 5" Steel                 | 5/83              | 37.5                            | 1774.8                   | 46.0                  | 1766.3                          | -8.5                                 | 1.1                         | 6,900                    | 47.90                          |
| M-14                | 1759.43                     | 1757.03           | 2.40                | 37.0                    | 39.24                         | 22-37                  | 2" PVC                   | 5/83              | 28.0                            | 1729.0                   | 25.4                  | 1731.6                          | 2.6                                  | 0.2                         | 4,000                    | 27.80                          |
| M-15                | 1750.31                     | 1747.93           | 2.38                | 41.0                    | 42.55                         | 26-41                  | 2" PVC                   | 5/83              | 34.0                            | 1713.9                   | 16.7                  | 1729.3                          | 15.4                                 | 6.2                         | 15,100                   | 21.05                          |
| M-16                | ---                         | 1759.42           | ---                 | 37.0                    | ---                           | 22-37                  | 2" PVC                   | 5/83              | 30.0                            | 1729.4                   | ---                   | ---                             | ---                                  | ---                         | ---                      | ---                            |
| M-17                | ~1769.90                    | 1767.15           | 2.75                | 42.0                    | 37.00                         | 27-42                  | 2" PVC                   | 5/83              | 35.0                            | 1732.2                   | 26.3                  | ~1740.8                         | ~8.6                                 | 6.6                         | 9,100                    | 29.07                          |
| M-18                | 1738.93                     | 1737.78           | 1.14                | 28.0                    | 29.80                         | 14-24                  | 2" PVC                   | 8/10/83           | 25.0                            | 1712.8                   | 8.1                   | 1723.7                          | 16.9                                 | 0.3                         | 6,500                    | 9.25                           |
| M-19                | 1766.93                     | 1763.63           | 3.30                | 40.0                    | 41.20                         | 14.5-34.5              | 2" PVC                   | 8/10/83           | 33.0                            | 1730.6                   | 21.8                  | 1741.8                          | 11.2                                 | 0.1                         | 14,200                   | 25.11                          |
| M-20                | 1798.21                     | 1795.79           | 2.42                | 35.0                    | 46.55                         | 20.4-40.4              | 2" PVC                   | 8/11/83           | 39.5                            | 1756.3                   | 33.7                  | 1762.1                          | 5.8                                  | <0.1                        | 6,000                    | 36.07                          |
| M-21                | 1790.50                     | 1788.37           | 2.13                | 43.0                    | 44.74                         | 18-38                  | 2" PVC                   | 8/11/83           | 37.0                            | 1751.4                   | 38.8                  | 1749.6                          | -1.8                                 | 0.20                        | 3,800                    | 40.94                          |
| M-22                | 1758.91                     | 1756.72           | 2.19                | 35.0                    | 36.70                         | 11-31                  | 2" PVC                   | 8/11/83           | 30.0                            | 1726.7                   | 19.4                  | 1737.3                          | 10.6                                 | 0.90                        | 8,100                    | 21.60                          |
| M-23                | 1717.61                     | 1715.04           | 2.57                | 43.0                    | 44.47                         | 9.4-37.4               | 2" PVC                   | 8/11/83           | 37.5                            | 1677.5                   | 9.8                   | 1705.2                          | 27.7                                 | 2.5                         | 15,100                   | 12.37                          |

| MONITOR WELL NUMBER | REFERENCE CASTING ELEV. MSL | GROUND ELEV. MSL | *CASTING STICKUP FT. | *DRILLED WELL DEPTH FT. | **MEASURED WELL DEPTH FT. TO TOP | *SCREENED INTERVAL, FT | CASING TYPE AND SIZE IN. | DATE WELL DRILLED | *DEPTH TO TOP OF MUDDY CREEK FT | ELEV. OF MUDDY CREEK MSL | *DEPTH TO GW FT. 6/85 | WATER-TABLE ELEVATION MSL, 6/85 | SATURATED AQUIFER THICKNESS FT, 6/85 | CHROMIUM CONCENT. mg/l 6/85 | GW COND. umhos/cm 6/85 | **DEPTH TO WATER, FT TOC, 6/85 |
|---------------------|-----------------------------|------------------|----------------------|-------------------------|----------------------------------|------------------------|--------------------------|-------------------|---------------------------------|--------------------------|-----------------------|---------------------------------|--------------------------------------|-----------------------------|------------------------|--------------------------------|
| M-24                | 1788.54                     | 1786.34          | 2.20                 | 40.0                    | 42.69                            | 25-40                  | 2" PVC                   | 5/14/84           | 36.0                            | 1750.3                   | 37.9                  | 1748.4                          | -1.9                                 | 1.1                         | 4,200                  | 40.13                          |
| M-25                | 1756.81                     | 1753.79          | 3.02                 | 40.0                    | 41.47                            | 25-40                  | 2" PVC                   | 5/14/84           | 28.0                            | 1725.8                   | 21.9                  | 1731.9                          | 6.1                                  | 12.9                        | 14,000                 | 24.94                          |
| M-26                | ---                         | 1748.94          | ---                  | 40.0                    | ---                              | 25-40                  | 2" PVC                   | 5/14/84           | 35.0                            | 1713.94                  | ---                   | ---                             | ---                                  | ---                         | ---                    | ---                            |
| M-27                | 1741.28                     | 1739.46          | 1.82                 | 35.0                    | 30.92                            | 20-35                  | 2" PVC                   | 5/14/84           | >40.0                           | <1699.5                  | 13.2                  | 1726.4                          | >26.9                                | 2.6                         | 10,100                 | 14.88                          |
| M-28                | 1811.27                     | 1811.1           | -0.24                | 50.5                    | 47.61                            | 30-50                  | 2" PVC                   | 7/23/85           | 31.0                            | 1780.5                   | 43.0                  | 1768.5                          | -12.0                                | <0.1                        | 6,700                  | 42.78                          |
| M-29                | 1806.60                     | 1806.24          | 0.36                 | 42.0                    | 41.74                            | 42-27                  | 2" PVC                   | 7/12/85           | 21.0                            | 1785.2                   | 36.1                  | 1770.1                          | -15.1                                | 0.1                         | 34,600                 | 36.48                          |
| M-30                | 1810.68                     | 1810.88          | -0.20                | 46.50                   | 43.32                            | 45-30                  | 2" PVC                   | 7/17/84           | 25.0                            | 1785.9                   | 39.0                  | 1771.9                          | -14.0                                | 0.6                         | 5,500                  | 38.80                          |
| M-31                | 1787.92                     | 1785.54          | 2.38                 | 45.0                    | 47.60                            | 30-45                  | 2" PVC                   | 6/85              | 35.0                            | 1750.5                   | 35.0                  | 1750.5                          | 0.0                                  | 10.4                        | 11,000                 | 37.36                          |
| M-32                | 1787.48                     | 1785.63          | 1.85                 | 45.0                    | 46.76                            | 30-45                  | 2" PVC                   | "                 | 34.0                            | 1751.6                   | 33.4                  | 1752.3                          | 0.6                                  | 1.3                         | 8,900                  | 35.22                          |
| M-33                | 1786.98                     | 1785.03          | 1.95                 | 45.0                    | 46.78                            | 30-45                  | 2" PVC                   | "                 | 35.0                            | 1750.0                   | 32.2                  | 1752.8                          | 2.8                                  | 0.1                         | 7,200                  | 34.15                          |
| M-34                | 1776.10                     | 1774.25          | 1.85                 | 40.0                    | 41.83                            | 25-40                  | 2" PVC                   | "                 | 35.0                            | 1739.3                   | 29.3                  | 1745.0                          | 5.7                                  | 2.2                         | 7,800                  | 31.10                          |
| M-35                | 1775.01                     | 1773.11          | 1.90                 | 40.0                    | 42.33                            | 25-40                  | 2" PVC                   | "                 | 33.5                            | 1739.6                   | 27.1                  | 1746.1                          | 6.4                                  | 0.6                         | 6,500                  | 28.95                          |
| M-36                | 1758.88                     | 1756.03          | 2.85                 | 35.0                    | 37.85                            | 20-35                  | 2" PVC                   | "                 | 27.5                            | 1728.5                   | 21.2                  | 1734.0                          | 6.3                                  | 2.0                         | 13,100                 | 24.08                          |
| M-37                | 1759.58                     | 1757.43          | 2.15                 | 35.0                    | 37.18                            | 20-35                  | 2" PVC                   | "                 | 27.0                            | 1730.4                   | 23.1                  | 1734.3                          | 3.9                                  | 0.3                         | 20,000                 | 25.27                          |
| M-38                | 1759.08                     | 1756.48          | 2.60                 | 35.0                    | 37.44                            | 20-35                  | 2" PVC                   | "                 | 28.0                            | 1728.5                   | 21.9                  | 1734.6                          | 6.1                                  | 5.3                         | 9,100                  | 24.52                          |
| M-39                | 1760.22                     | 1757.62          | 2.60                 | 40.0                    | 42.60                            | 20-35                  | 2" PVC                   | "                 | 34.0                            | 1721.6                   | 19.4                  | 1738.3                          | 14.6                                 | 2.0                         | 8,500                  | 21.97                          |
| M-40                | 1797.89                     | 1795.49          | 2.40                 | 45.0                    | 47.40                            | 30-45                  | 2" PVC                   | "                 | 32.0                            | 1763.5                   | 37.5                  | 1758.0                          | -5.5                                 | 2.5                         | 11,200                 | 39.93                          |
| M-41                | 1695.60                     | 1693.03          | 2.57                 | 35.0                    | 37.52                            | 5-35                   | 2" PVC                   | 7/85              | 24.5                            | 1668.5                   | 4.5                   | 1688.6                          | 20.0                                 | 1.7                         | 10,100                 | 7.04                           |
| M-42                | 1696.24                     | 1693.64          | 2.60                 | 35.0                    | 37.02                            | 4.4-34.4               | 2" PVC                   | "                 | 26.0                            | 1667.7                   | 3.5                   | 1690.1                          | 22.4                                 | 2.9                         | 11,000                 | 6.16                           |
| M-43                | 1696.16                     | 1693.52          | 2.64                 | 35.0                    | 37.56                            | 4.9-34.9               | 2" PVC                   | "                 | 24.5                            | 1669.0                   | 4.9                   | 1688.6                          | 19.6                                 | 0.85                        | 10,500                 | 7.53                           |
| M-44                | 1696.74                     | 1694.19          | 2.55                 | 35.0                    | 37.65                            | 5.1-35.1               | 2" PVC                   | "                 | 20.0                            | 1674.2                   | 10.0                  | 1684.2                          | 10.0                                 | 0.38                        | 9500                   | 12.58                          |
| M-45                | 1697.13                     | 1694.73          | 2.40                 | 35.0                    | 36.59                            | 4.2-34.2               | 2" PVC                   | "                 | 27.0                            | 1667.7                   | 15.3                  | 1679.4                          | 11.9                                 | 0.04                        | 4625                   | 17.74                          |
| M-46                | 1716.08                     | 1713.34          | 2.74                 | 45.0                    | 46.89                            | 4.2-44.2               | 2" PVC                   | "                 | 41.0                            | 1672.3                   | 8.7                   | 1704.6                          | 32.3                                 | 1.8                         | 9600                   | 11.46                          |
| M-47                | 1715.04                     | 1712.50          | 2.54                 | 45.0                    | 42.59                            | 0.1-40.0               | 2" PVC                   | "                 | 42.0                            | 1670.5                   | 9.2                   | 1703.3                          | 32.8                                 | 5.1                         | 12,900                 | 11.79                          |
| M-48                | 1719.05                     | 1716.60          | 2.45                 | 35.0                    | 38.59                            | 6.1-36.1               | 2" PVC                   | "                 | 32.0                            | 1684.6                   | 7.3                   | 1709.3                          | 24.7                                 | 1.3                         | 11,900                 | 9.78                           |
| M-49                | 1718.89                     | 1716.35          | 2.54                 | 45.0                    | 46.50                            | 4.0-44.0               | 2" PVC                   | "                 | 36.0                            | 1680.4                   | 8.5                   | 1707.9                          | 27.5                                 | 1.5                         | 6400                   | 11.02                          |
| M-50                | 1793.87                     | 1791.27          | 2.60                 | 60.0                    | 62.15                            | 39.6-59.6              | 2" PVC                   | "                 | 40.0                            | 1751.3                   | 43.5                  | 1747.8                          | -3.5                                 | 10.0                        | 7200                   | 46.08                          |
| M-51                | 1695.34                     | 1692.66          | 2.68                 | 35.0                    | 36.62                            | 3.9-33.9               | 2" PVC                   | "                 | 26.0                            | 1666.7                   | 4.0                   | 1688.7                          | 22.0                                 | 1.7                         | 10,000                 | 6.68                           |
| M-52                | 1798.72                     | 1795.84          | 2.88                 | 45.0                    | 47.38                            | 34.5-44.5              | 2" PVC                   | "                 | 32.0                            | 1763.8                   | 38.5                  | 1757.3                          | -6.5                                 | 1.5                         | ---                    | 41.38                          |

NOTE: All data collected from wells M-41 through M-52 were collected in late July, 1985.









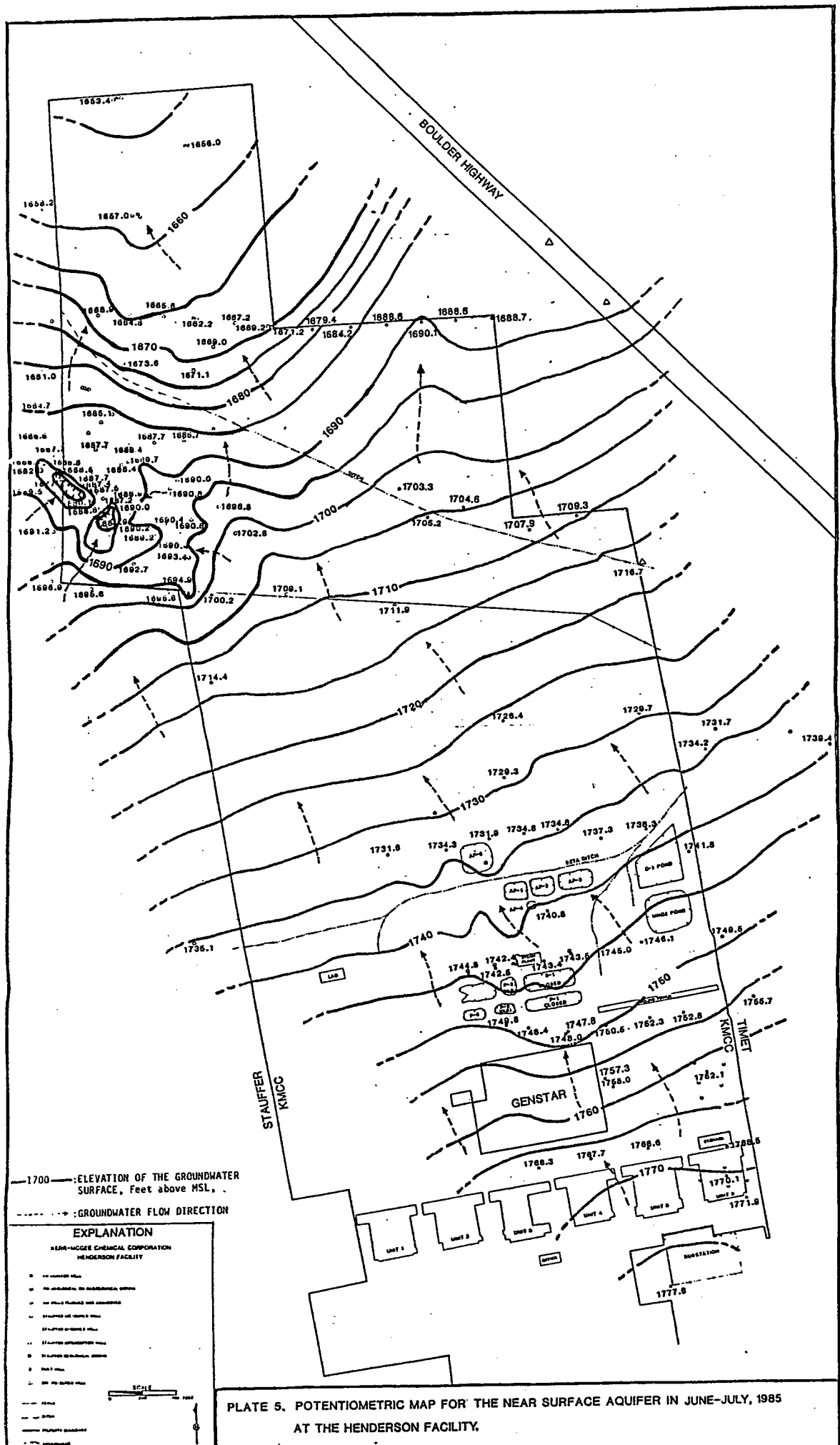
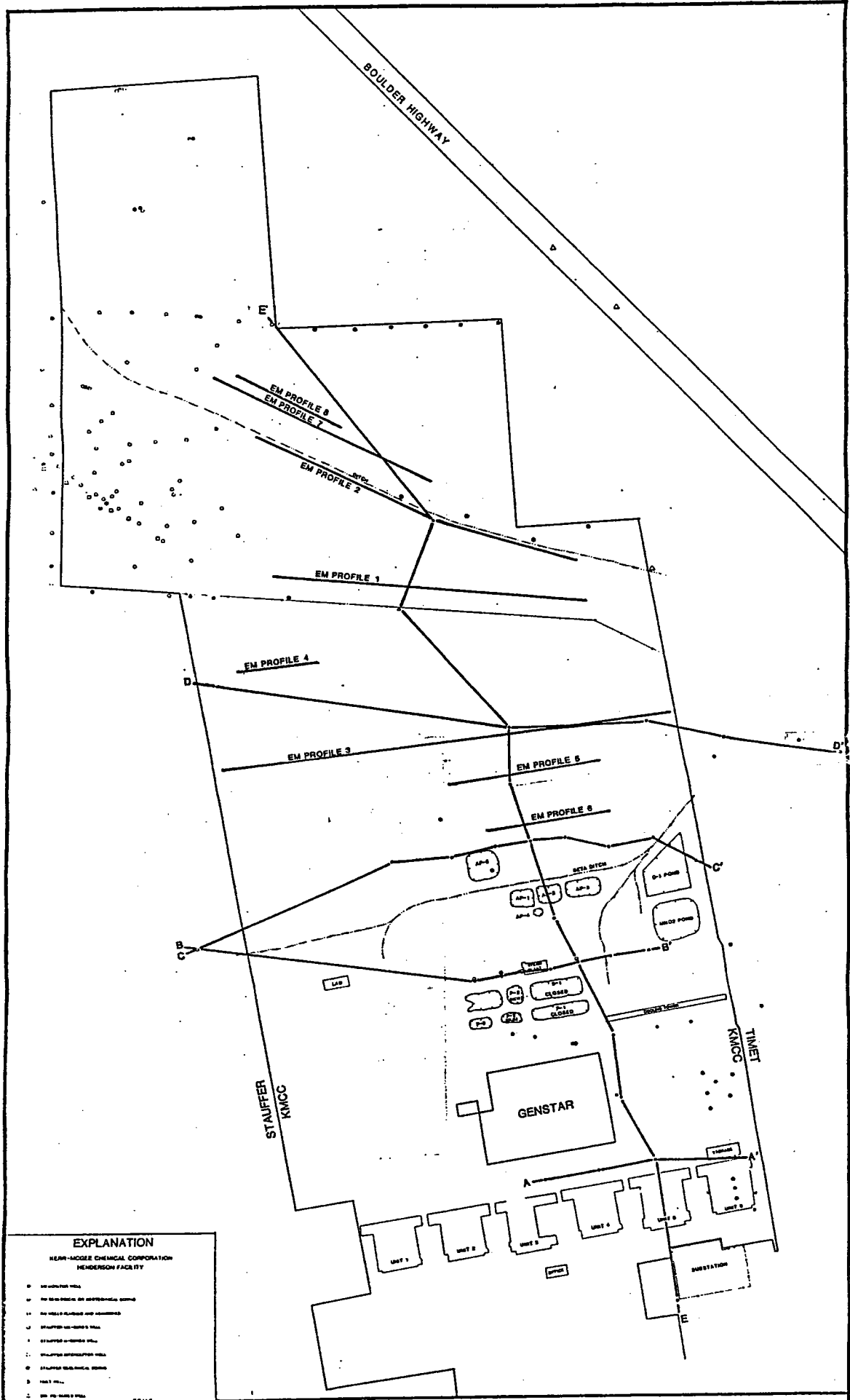


PLATE 5. POTENTIOMETRIC MAP FOR THE NEAR SURFACE AQUIFER IN JUNE-JULY, 1985 AT THE HENDERSON FACILITY.









**EXPLANATION**  
 KERN-MOORE CHEMICAL CORPORATION  
 HENDERSON FACILITY

- 20" WATER WELL
- 16" WATER WELL OR OBSERVATION POINT
- 12" WATER PUMPING AND OBSERVATION
- STAUFFER 20" WATER WELL
- STAUFFER 16" WATER WELL
- STAUFFER OBSERVATION POINT
- 16" WATER WELL
- 20" WATER WELL

--- ROAD  
 --- RAILROAD  
 --- PROPERTY BOUNDARY  
 --- OBSERVATION POINT

SCALE  
 0 20 40 FEET

MAP SCALE 1:1000

PLATE 9. MAP SHOWING LOCATIONS OF THE GEOLOGICAL CROSS SECTIONS AND EM PROFILE LINES AT THE HENDERSON FACILITY.

## HENDERSON GROUNDWATER TOXIC CONSTITUENTS

### ANALYSES

Attached are groundwater characteristic results requested by NDEP in their February 26, 1986 letter. Areas which have groundwater with high conductivity were sampled. Those areas included Unit 6 (well M-29), Units 4 and 5 (well M-12), and the steam plant (well M-9). A well upgradient of the KMCC facility (well M-10) was also sampled. Also attached are data from samples collected in January, 1985 from wells M-9, M-10, and M-23, as well as the process electrolytic cells.

1. Elevated levels of chromium, TDS, chlorate, and perchlorate are noted north (downgradient) of Units 4 and 5. Cell liquor from these units are high in  $\text{Cr}^{+6}$ , Cl, and TDS.
2. Elevated levels of magnesium, manganese, TDS, sulfate, and lowered pH are noted under Unit 6. Manganese and sulfate in an acidic solution can be found in Unit 6.
3. Elevated levels of boron, chromium, sodium TDS, chloride, chlorate, and perchlorate are found in groundwater in the facility steam plant area downgradient of the process buildings and retention ponds P-1 and S-1. These compounds can be attributed to groundwater flow from Units 4 and 5 and possibly from past leakage from now closed ponds S-1 and P-1.



HENDERSON, NEVADA  
GROUNDWATER DATA

| <u>Parameter</u> | <u>Well<br/>M-23</u> | <u>Well<br/>M-10<br/>Background</u> | <u>Well<br/>M-9</u> | <u>Cell Liquor</u> |
|------------------|----------------------|-------------------------------------|---------------------|--------------------|
| Cr <sup>+6</sup> | 3.8                  | <.01                                | 39                  | 2500               |
| Cl               | 2680                 | 460                                 | 5340                | 71,000             |
| SO <sub>4</sub>  | 1960                 | 780                                 | 2030                | 2510               |
| TDS              | 12,000               | 2660                                | 22,800              | 650,000            |
| Ag               | .08                  | <.02                                | .05                 | <2.0               |
| As               | .27                  | <.11                                | .31                 | <11                |
| B                | 13                   | 3.0                                 | 43                  | 16                 |
| Ba               | .04                  | .031                                | .046                | <.15               |
| Cd               | .028                 | <.015                               | .019                | <1.5               |
| Co               | .051                 | <.011                               | .035                | <1.1               |
| Cu               | .047                 | <.015                               | .024                | <1.5               |
| Fe               | .079                 | <.033                               | 2.1                 | <3.3               |
| Mg               | .30                  | 76                                  | .51                 | 85                 |
| Mn               | .11                  | .34                                 | .34                 | <.70               |
| Na               | 1700                 | 530                                 | ---                 | 150,000            |
| Pb               | .24                  | <.05                                | .17                 | <5                 |
| Se               | .15                  | <.1                                 | .16                 | <10                |
| V                | .18                  | <.025                               | .012                | <2.5               |
| Zn               | .26                  | <.005                               | .73                 | <.5                |
| F                | <0.5                 | <.2                                 | <1                  | <.2                |

Note: All analyses are in units of mg/l.  
Samples collected in January, 1985.



**KERR-McGEE CHEMICAL CORPORATION**

POST OFFICE BOX 88 • HENDERSON, NEVADA 89015

January 27, 1986

Certified Mail No. P 673 531 439

Mr. Joe Livak  
State of Nevada  
Division of Environmental Protection  
201 South Fall Street  
Carson City, NV 89710

bcc: B. Ritchey-TIMET  
L. G. Christiansen  
P. S. Corbett  
S. M. Crowley  
B. L. Hoffman  
J. H. Stallings  
J. C. Stauter  
R. F. Wohletz

Dear Mr. Livak:

Kerr-McGee Chemical Corporation operates a main recirculated water cooling tower which supplies cooling for Titanium Metals and KMCC.

In the past, we have experienced cooling tower overflows which resulted in recirculated water discharges from our property through the Beta ditch eastern weir. The recirculated water is noncontact, yet it is treated to prevent corrosion and scale. KMCC recognizes its responsibility to minimize unpermitted discharges, and we have taken several steps related to the cooling tower to achieve this goal.

1. Installation of an alarm for loss of power to the recirculation pumps was completed in 1985. This was done to reduce the necessity of the Fisher valve opening to supply emergency cooling. If power fails to one recirculation pump, the plant is alerted and can power up a replacement pump, if available. This situation has occurred at least once since the alarm's installation. Appropriate actions were taken before the cooling tower overflowed.
2. KMCC has requested that Titanium Metals not return emergency cooling water to the cooling tower without prior arrangements. Without prior arrangements, Titanium Metals would need to obtain appropriate agency approval to discharge it through the storm sewer. After recirculated water line breaks, both Titanium Metals and KMCC are required to make up emergency cooling water from Lake Mead stabilized water. If this additional water returned to the tower is more than the makeup required by evaporation, an overflow occurs. Discharging the emergency cooling water directly should not cause an adverse environmental impact since the discharged water would be once-through, noncontact, Lake Mead stabilized cooling water rather than treated cooling tower water. There have been a number of oral and written communications between the management of the two plants on this subject.

Mr. Joe Livak  
Page 2  
January 27, 1986

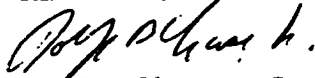
3. Several exhaustive searches have been conducted at the KMCC plant to determine points where Lake Mead stabilized water can be used as emergency cooling water in the event of recirculation water failure. Points where crossties are available have been "tagged out." This means that before the valving sequence can be changed to allow for emergency cooling water, the environmental engineer must be notified. Each time there is an overflow due to return of excess water to the tower, each crosstie is checked. To date, none have been shown to be the cause of an overflow.
4. Installation of an alarm system to warn of a high level in the recirculated water wells is in progress. This alarm will alert KMCC of a rising level in either the cold or hot well and, further, of an impending cooling tower overflow. Before the overflow occurs, there can be an investigation of the reason(s) for excess flows returning to the tower and possible prevention of the overflow.
5. KMCC is committed to the reduction of all water added to the recirculated water system. This includes any known water sources and any unknown ones that may be discovered.
6. A total abandonment of the present tower is tentatively scheduled for the year 1988. Until that time, all that is practical and feasible will be done to ensure that the incidents of tower overflows will be kept to a bare minimum.

We understand that Titanium Metals is constructing a new cooling tower which will allow them to discontinue use of KMCC's cooling tower. The tentative date for severing this connection with the KMCC tower is March 1, 1986.

Again, KMCC is committed to reducing unpermitted cooling tower overflow discharges. If you have any questions or can offer any advice, please feel free to call S. M. Crowley at (702) 565-8901, Ext. 234.

Sincerely,

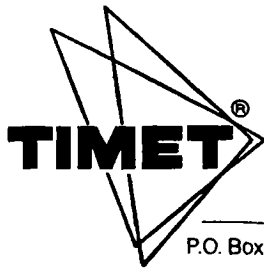
KERR-McGEE CHEMICAL CORPORATION



R. B. Chase, Jr.  
Plant Manager

RBC:jc

cc: Wendell McCurry



FIRST IN TITANIUM

Henderson Plant

P.O. Box 2128, Henderson, NV 89015

(702) 564-2544

March 31, 1986

Ms. Susan Crowley  
Kerr-McGee  
8000 West Lake Mead Drive  
Henderson, NV 89015

Dear Susan:

Our Production Department was notified on March 13 by Kerr-McGee that the return to their cooling tower was high and in danger of overflowing. Production conducted a search and found a 3/4 inch hose discharging stabilized water into the recirculating water system at the rate of 10 to 12 gpm.

A conversation between Pat Corbett (Kerr-McGee) and Mike Thompson (TIMET) on Friday, March 14 indicated the problem was no better. TIMET found a 1-1/2 inch domestic water line open to the recirculating water supply system. The line was closed off promptly at 1500 hours. In addition, to help alleviate the problem, recirculating water to the oil heat exchangers on 82, 83 and 84 off gas blowers was drained to TIMET's pond system for about four hours.

Production received no further word from Kerr McGee concerning this particular incident.

Mark Small, Ph.D  
Supervisor of Environmental Quality

MS/jk

cc: B. J. McNair  
J. M. Partridge  
R. W. Ritchey  
P. C. Roybal  
S. M. Thompson  
D. A. Wruck



RECEIVED

MAR 14 1986

STATE OF NEVADA  
DEPARTMENT OF CONSERVATION AND NATURAL RESOURCES  
DIVISION OF ENVIRONMENTAL PROTECTION

R.B. CHASE

Capitol Complex  
Carson City, Nevada 89710  
(702) 885-4670  
March 11, 1986

Kerr McGee Chemical Corporation  
Attn: Rolf B. Chase, Plant Manager  
P.O. Box 55  
Henderson, Nevada 89015

Dear Mr. Chase:

The enclosed Finding of Alleged Violation is issued by the Administrator of the Division of Environmental Protection, pursuant to Nevada Revised Statutes (NRS) 445.317 and 445.324. The Finding was developed as a result of our review of a chronic history of cooling tower overflows which KMCC has reported in accordance with Part II.A.2 of Permit NV0000078.

Enforcement action in the form of a compliance order normally accompanies a Finding, but in this case enforcement action is being deferred, pending the outcome of our meeting scheduled for April 4, 1986.

If you have any questions concerning this matter, please contact me at (702) 885-4670.

Sincerely,

A handwritten signature in black ink, appearing to read "Joseph S. Livak".

Joseph S. Livak  
Water Quality Enforcement Officer

Enclosures

Certified Mail# P 055 338 464  
Return Receipt Requested

cc: Roland Westergard  
L.H. Dodgion  
Marta Adams  
Nevada Environmental Commission  
EPA, Region IX

IN THE MATTER OF  
KERR-MCGEE CHEMICAL CORPORATION }  
HENDERSON, NEVADA }

FINDING OF ALLEGED VIOLATION

I. This Finding is made on the basis of the following facts, to wit:

A. The State of Nevada Department of Conservation and Natural Resources, Division of Environmental Protection, under the authority of Nevada Revised Statutes (NRS) 445.214 subsection 1 has the power and duty to administer and enforce the provisions of NRS 445.131 to 445.354 inclusive and all rules, regulations and standards promulgated by the Commission and all orders and permits promulgated by the Department.

B. NRS 445.221 "Unlawful discharge of a pollutant without a permit."

Except as authorized by a permit issued by the Department under the provisions of NRS 445.131 to 445.354 inclusive and regulations promulgated under such sections by the Commission, it is unlawful for any person to discharge from any point source any pollutant into any waters of the State.

C. Permit No. NV0000078 issued by the Department on September 21, 1981 contains general and specific conditions including: Part I.A.1 which states, in part: "The permittee shall contain all process waste spills and prevent them from entering the discharge ditch."

D. Nevada Administrative Code (NAC) 445.1353 -- Lake Mead Water Quality Standard: "The method of controlling phosphorus for Lake Mead at this time is application of 1 mg/l total phosphorus as a limit on discharge of effluent (30-day average) for point sources ... into Lake Mead or its tributaries". The chloride standard is  $\leq$  400 mg/l.

E. During the period beginning September 20, 1984 and ending February 11, 1986, Kerr McGee Chemical Corporation reported twenty three (23) unauthorized discharges of noncontract cooling water from the cooling tower overflow basin to the Beta Ditch, a tributary of the Las Vegas Wash. Pollutant concentrations, based on grab samples, and estimated volumes of each discharge were reported as follows:

| <u>Date of incident</u> | <u>NaCl<br/>(mg/l)</u> | <u>PO<sub>4</sub><br/>(mg/l)</u> | <u>Volume<br/>(gallons)</u> |
|-------------------------|------------------------|----------------------------------|-----------------------------|
| September 20, 1984      | 467                    | NR                               | 48,000                      |
| September 26, 1984      | 761                    | NR                               | 200                         |
| November 19, 1984       | 1,056                  | NR                               | 92,000                      |
| December 13, 1984       | 500                    | NR                               | 63,000                      |
| December 19, 1984       | 909                    | NR                               | 50,400                      |

**FINDING OF ALLEGED VIOLATION**  
**KERR MCGEE CHEMICAL CORPORATION**  
 Page 2

|                    |        |    |           |
|--------------------|--------|----|-----------|
| December 26, 1984  | NR     | NR | 390,600   |
| January 2, 1985    | 1,240  | NR | 6,000     |
| January 5, 1985    | NR     | NR | 13,950    |
| January 6, 1985    | NR     | NR | 12,000    |
| January 25, 1985   | 254    | NR | 4,176,000 |
| April 22, 1985     | 12,320 | NR | 800       |
| June 19, 1985      | 1,910  | NR | 900,000   |
| June 29, 1985      | NR     | NR | 16,800    |
| July 23, 1985      | 650    | 16 | 4,953,000 |
| August 2, 1985     | 1,112  | 30 | 352,800   |
| August 28, 1985    | 2,534  | NR | 125,400   |
| September 24, 1985 | 1,000  | 11 | NR        |
| November 22, 1985  | 684    | 25 | 67,400    |
| December 9, 1985   | 1,000  | 30 | 3,018     |
| December 23, 1985  | 548    | 11 | 1,354,320 |
| December 26, 1985  | 600    | 8  | 23,800    |
| December 31, 1985  | 616    | 11 | 1,680     |
| January 20, 1986   | 234    | 8  | 6,492,000 |

II. On the basis of the facts listed above, the Administrator of the Division of Environmental Protection finds that Kerr McGee Chemical Corporation is in violation of NRS 445.221 and permit No. NV0000078 for the unauthorized discharge of pollutants to waters of the state; and NAC 445.1353 for exceeding the water quality standard in effect for Lake Mead.

Dated

3/12/86

  
 Joseph S. Livak  
 Water Quality Enforcement Officer



**KERR-McGEE CHEMICAL CORPORATION**

POST OFFICE BOX 55 • HENDERSON, NEVADA 89015

May 1, 1986

Mr. Joe Livak  
State of Nevada  
Division of Environmental Protection  
Capitol Complex  
201 South Fall Street  
Carson City, NV 89710

Re: NPDES Permit No. NV 0000078  
Kerr-McGee Chemical Corporation  
Henderson, Nevada Facility  
Amended Permit Application

Dear Mr. Livak:

On April 24, 1985, an NPDES permit application was submitted to the NDEP for the Kerr-McGee Chemical Corporation (KMCC) Henderson, Nevada Facility. The application, submitted in response to the December 10, 1984 NDEP request, incorporated all stormwater point source discharge locations as well as an outfall point for cooling tower discharges during upset conditions.

Since the time of the submittal, programs to substantially reduce the incidences of cooling tower discharges have been instituted. These programs will remain in effect until the scheduled cooling tower replacement in August, 1988. The actions are reflected in the attached amended facility NPDES permit application.

The amended application incorporates the following:

- o The existing permitted discharge point 001 is being retained for discharge of once-through noncontact cooling water. Once-through cooling water from the Manganese Leach plant is being piped to this point for discharge. No process fluids are discharged.

An additional flow diagram is submitted showing the discharge of noncontact cooling water from the Manganese Leach plant to point 001.

Pages V-1, V-2, and V-3 have been revised to reflect discharge of this once-through cooling water.



Mr. Joe Livak  
Page 2  
May 1, 1986

- o Proposed discharge point 004 includes stormwater discharges from adjacent properties owned and/or operated by Genstar, State Industries, TIMET, and Stauffer Chemical Corporation. The September 26, 1984 amendments to the NPDES permit regulations provide for separate permits for stormwater discharges affected by more than one company. KMCC requests that Nevada DEP evaluate the discharges from each of the listed companies and issue separate NPDES permits for their discharges.
- o As committed in the April 24, 1985 submittal, KMCC will sample the stormwater outfalls during the first runoff event, analyze for appropriate constituents, and submit the results to the NDEP. To date, there have been no rainfall incidents sufficient to produce runoff. Therefore, information provided on effluent characterization at the proposed discharge points is based on knowledge of operations and the potential presence of process-related chemicals.
- o The cooling tower Water Balance Diagram has been amended to show that upset discharges will be routed to Mn-1 Pond rather than 001. Discharges to the pond will be recycled to the cooling tower. The diagram also shows elimination of the connection with TIMET noncontact cooling water, effective July 1, 1986.

Should you have any questions regarding the attached amended application, please contact Ms. Susan Crowley at (702) 565-8901, Ext. 234.

Sincerely,

KERR-McGEE CHEMICAL CORPORATION



R. B. Chase, Jr.  
Plant Manager

RBC:jc  
Attachments

cc: US EPA, Region IX

|                                      |   |  |
|--------------------------------------|---|--|
| <b>FORM 1</b><br><b>GENERAL</b>      | <b>U.S. ENVIRONMENTAL PROTECTION AGENCY</b><br><b>GENERAL INFORMATION</b><br><i>Consolidated Permits Program</i><br><i>(Read the "General Instructions" before starting.)</i> | <b>I. EPA I.D. NUMBER</b><br>F N V D 0 0 8 2 9 0 3 3 0 D   |
| <b>II. POLLUTANT CHARACTERISTICS</b> | PLEASE PLACE LABEL IN THIS SPACE  | <b>GENERAL INSTRUCTIONS</b><br>If a preprinted label has been provided, affix it in the designated space. Review the information carefully; if any of it is incorrect, cross through it and enter the correct data in the appropriate fill-in area below. Also, if any of the preprinted data is absent (the area to the left of the label space lists the information that should appear), please provide it in the proper fill-in area(s) below. If the label is complete and correct, you need not complete items I, III, V, and VI (except VI-B which must be completed regardless). Complete all items if no label has been provided. Refer to the instructions for detailed item descriptions and for the legal authorizations under which this data is collected. |

**INSTRUCTIONS:** Complete A through J to determine whether you need to submit any permit application forms to the EPA. If you answer "yes" to any questions, you must submit this form and the supplemental form listed in the parenthesis following the question. Mark "X" in the box in the third column if the supplemental form is attached. If you answer "no" to each question, you need not submit any of these forms. You may answer "no" if your activity is excluded from permit requirements; see Section C of the instructions. See also, Section D of the instructions for definitions of bold-faced terms.

| SPECIFIC QUESTIONS   | MARK 'X' |    |               | SPECIFIC QUESTIONS   | MARK 'X' |    |               |
|--|----------|----|---------------|--|----------|----|---------------|
|  | YES      | NO | FORM ATTACHED |  | YES      | NO | FORM ATTACHED |
| A. Is this facility a publicly owned treatment works which results in a discharge to waters of the U.S.? (FORM 2A)   |          | X  |               | B. Does or will this facility (either existing or proposed) include a concentrated animal feeding operation or aquatic animal production facility which results in a discharge to waters of the U.S.? (FORM 2B)  |          |    | X             |
| C. Is this a facility which currently results in discharges to waters of the U.S. other than those described in A or B above? (FORM 2C)  | X        |    | X             | D. Is this a proposed facility (other than those described in A or B above) which will result in a discharge to waters of the U.S.? (FORM 2D)  |          |    | X             |
| E. Does or will this facility treat, store, or dispose of hazardous wastes? (FORM 3)   |          | X  |               | E. Do you or will you inject at this facility industrial or municipal effluent below the lowermost stratum containing, within one quarter mile of the well bore, underground sources of drinking water? (FORM 4)   |          |    | X             |
| G. Do you or will you inject at this facility any produced water or other fluids which are brought to the surface in connection with conventional oil or natural gas production, inject fluids used for enhanced recovery of oil or natural gas, or inject fluids for storage of liquid hydrocarbons? (FORM 4) |          | X  |               | H. Do you or will you inject at this facility fluids for special processes such as mining of sulfur by the Frasch process, solution mining of minerals, in situ combustion of fossil fuel, or recovery of geothermal energy? (FORM 4)  |          |    | X             |
| I. Is this facility a proposed stationary source which is one of the 28 industrial categories listed in the instructions and which will potentially emit 100 tons per year of any air pollutant regulated under the Clean Air Act and may affect or be located in an attainment area? (FORM 5)                 |          | X  |               | J. Is this facility a proposed stationary source which is NOT one of the 28 industrial categories listed in the instructions and which will potentially emit 250 tons per year of any air pollutant regulated under the Clean Air Act and may affect or be located in an attainment area? (FORM 5) |          |    | X             |

**III. NAME OF FACILITY**  
 KERR-MCGEE CHEMICAL CORPORATION

**IV. FACILITY CONTACT**

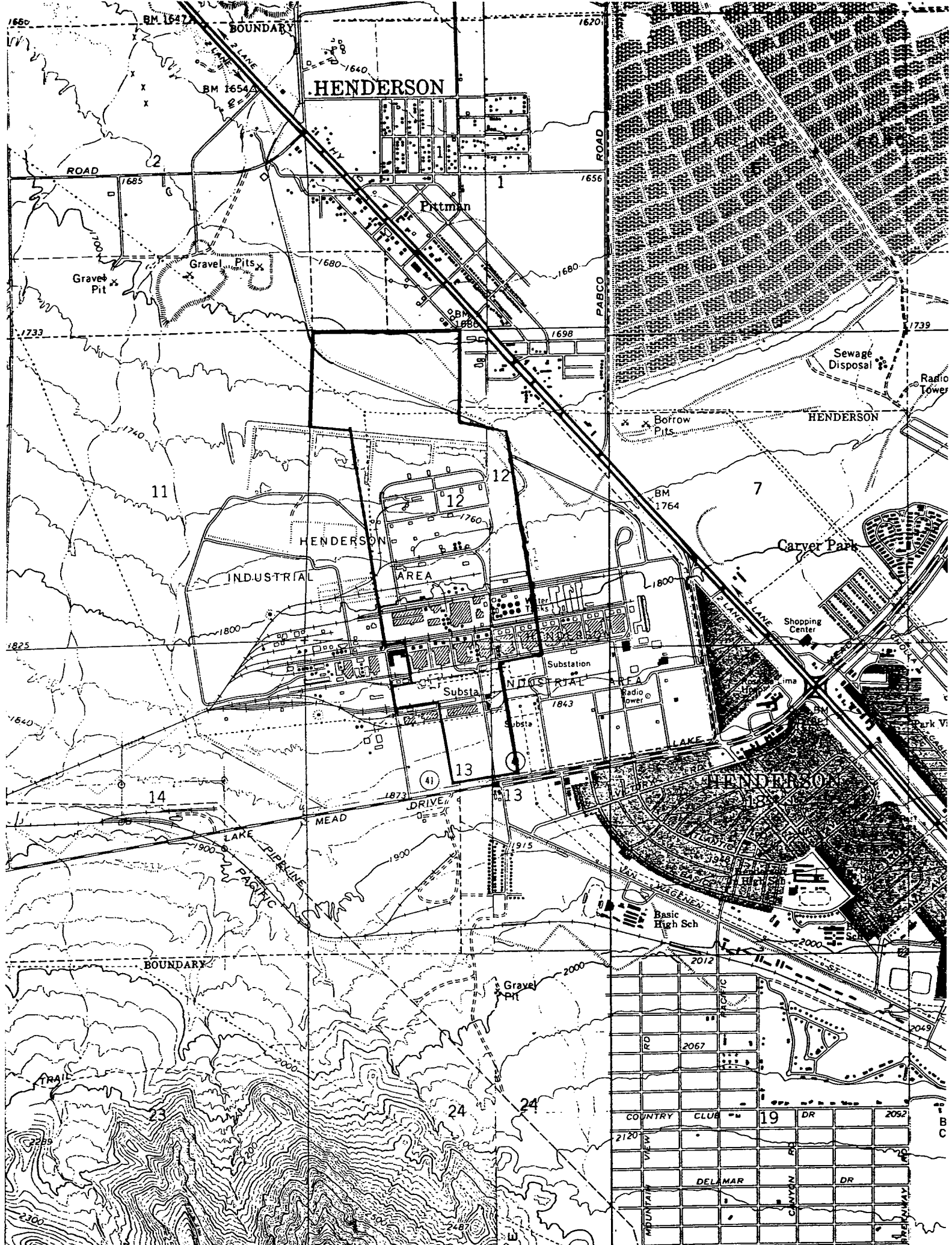
|  |                            |
|--|----------------------------|
| A. NAME & TITLE (last, first, & title) | B. PHONE (area code & no.) |
| CROWLEY, SUSAN M.                      | 702 565 8901               |

**V. FACILITY MAILING ADDRESS**

|                       |  |          |             |
|-----------------------|--|----------|-------------|
| A. STREET OR P.O. BOX |  |          |             |
| P. O. BOX 55          |  |          |             |
| B. CITY OR TOWN       |  | C. STATE | D. ZIP CODE |
| HENDERSON             |  | NV       | 89015       |

**VI. FACILITY LOCATION**

|   |  |             |                 |                           |  |
|---|--|-------------|-----------------|---------------------------|--|
| A. STREET, ROUTE NO. OR OTHER SPECIFIC IDENTIFIER |  |             |                 |                           |  |
| LAKE MEAD DRIVE                                   |  |             |                 |                           |  |
| B. COUNTY NAME                                    |  |             | C. CITY OR TOWN |                           |  |
| CLARK   |  |             | HENDERSON       |                           |  |
| D. STATE  |  | E. ZIP CODE |                 | F. COUNTY CODE (if known) |  |
| NV  |  | 89015       |                 |                           |  |



HENDERSON

Pittman

HENDERSON

INDUSTRIAL AREA

Substation

Substa

13

HENDERSON

Basic High Sch

Carver Park

Sewage Disposal

BM 1764

BM 1647

BOUNDARY

Gravel Pit

Gravel Pits

11

14

BOUNDARY

23

24

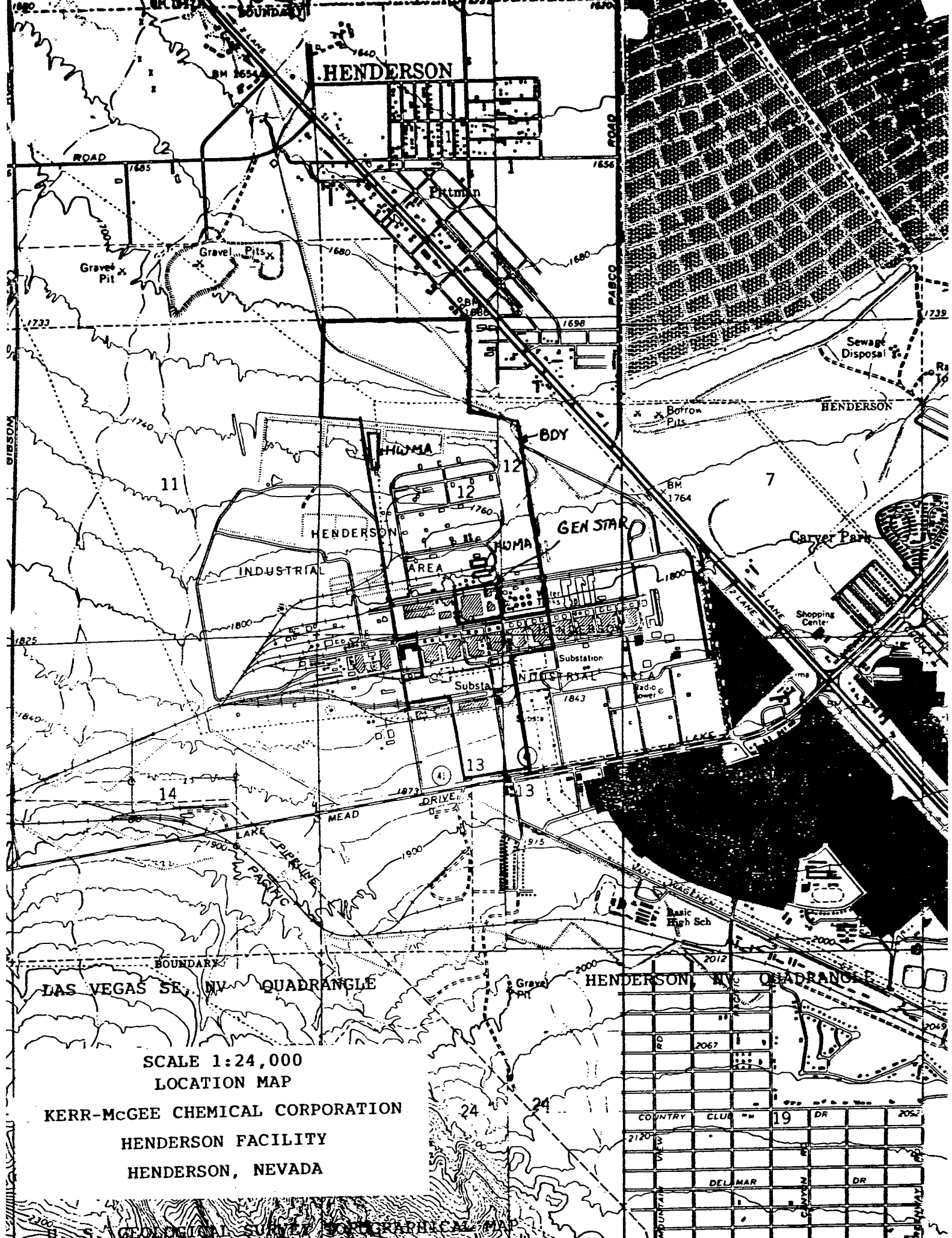
19

COUNTRY CLUB

DELMAR

CAVAYON

B  
C



HENDERSON

INDUSTRIAL AREA

GEN STAR

Carver Park

Shopping Center

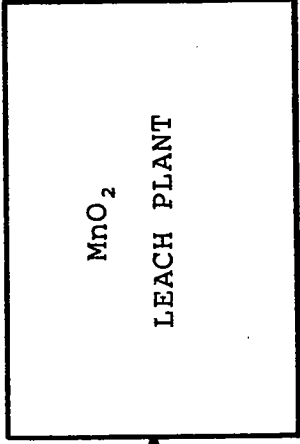
Basic High Sch

SCALE 1:24,000  
LOCATION MAP

KERR-McGEE CHEMICAL CORPORATION  
HENDERSON FACILITY  
HENDERSON, NEVADA

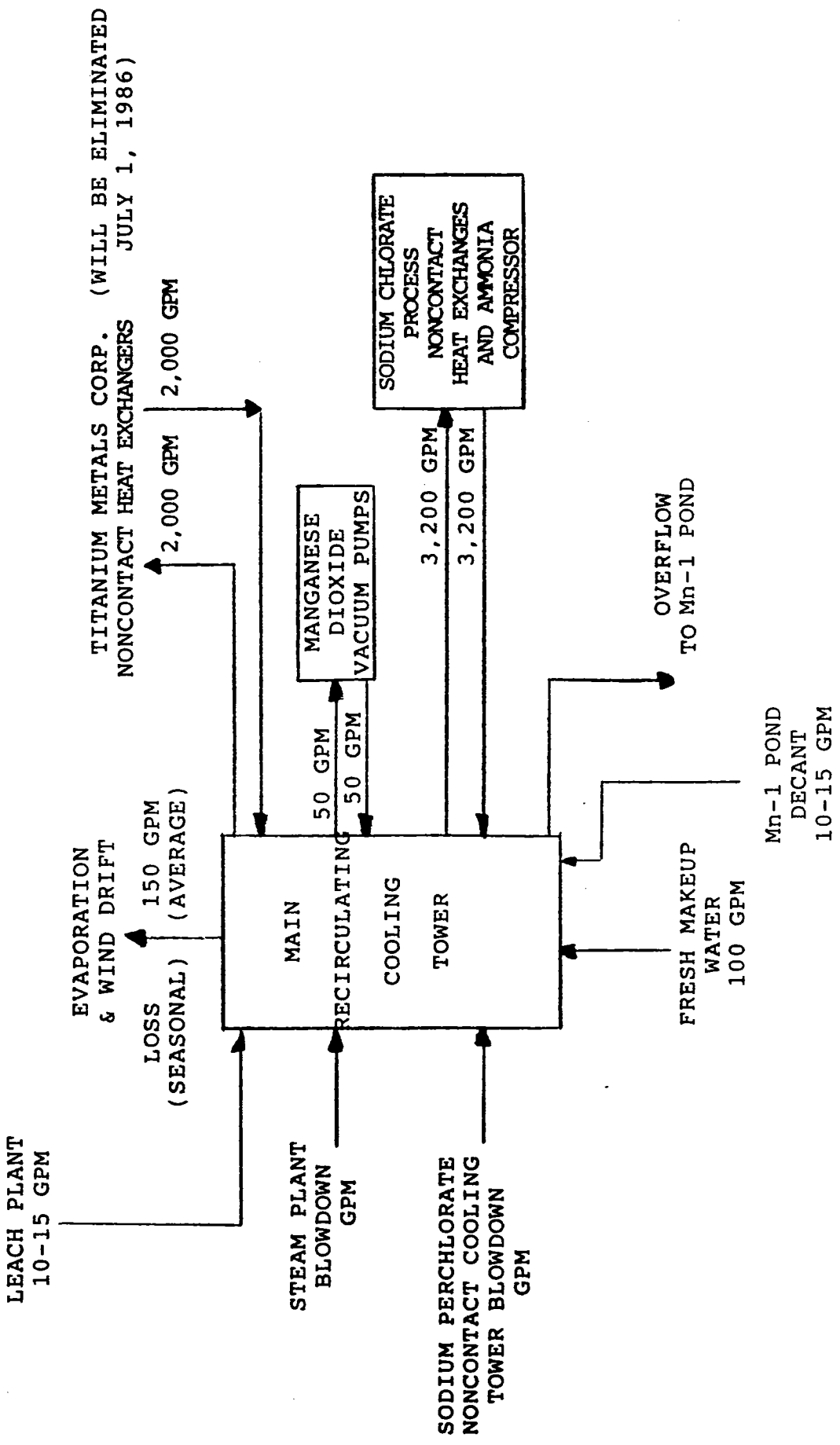
HENDERSON, NV QUADRANGLE

|         |      |    |    |      |
|---------|------|----|----|------|
| COUNTRY | CLUB | 19 | DR | 2052 |
| 2120    | 3    |    |    |      |
| DELMAR  | 2    | DR |    |      |



LAKE MEAD  
STABILIZED WATER  
20-35 GPM

ONCE-THROUGH  
COOLING WATER  
TO BETA DITCH  
20-35 GPM





**V. INTAKE AND EFFLUENT CHARACTERISTICS**

A, B, & C: See instructions before proceeding – Complete one set of tables for each outfall – Annotate the outfall number in the space provided.  
 NOTE: Tables V-A, V-B, and V-C are included on separate sheets numbered V-1 through V-9.

D. Use the space below to list any of the pollutants listed in Table 2c-3 of the instructions, which you know or have reason to believe is discharged or may be discharged from any outfall. For every pollutant you list, briefly describe the reasons you believe it to be present and report any analytical data in your possession.

| 1. POLLUTANT | 2. SOURCE | 1. POLLUTANT | 2. SOURCE |
|--------------|-----------|--------------|-----------|
| None         |           |              |           |

**VI. POTENTIAL DISCHARGES NOT COVERED BY ANALYSIS**

A. Is any pollutant listed in Item V-C a substance or a component of a substance which you do or expect that you will over the next 5 years use or manufacture as an intermediate or final product or byproduct?

YES (list all such pollutants below)  NO (go to Item VI-B)

B. Are your operations such that your raw materials, processes, or products can reasonably be expected to vary so that your discharges of pollutants may during the next 5 years exceed two times the maximum values reported in Item V?

YES (complete Item VI-C below)  NO (go to Section VII)

C. If you answered "Yes" to Item VI-B, explain below and describe in detail the sources and expected levels of such pollutants which you anticipate will be discharged from each outfall over the next 5 years, to the best of your ability at this time. Continue on additional sheets if you need more space.



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 001

PLEASE PRINT OR TYPE IN THE UNSHADED AREAS ONLY. You may report some or all of this information on separate sheets (use the same format) instead of completing these pages. SEE INSTRUCTIONS.

V. INTAKE AND EFFLUENT CHARACTERISTICS (continued from page 3 of Form 2-C)

PART A - You must provide the results of at least one analysis for every pollutant in this table. Complete one table for each outfall. See instructions for additional details.

| 1. POLLUTANT                       | 2. EFFLUENT                                   |  | 3. UNITS (specify if blank) |         | 4. INTAKE (optional)                              |                    |
|------------------------------------|---|--|-----------------------------|---------|---|--------------------|
|                                    | a. MAXIMUM DAILY VALUE (1) mass concentration | b. MAXIMUM 30-DAY AVERAGE VALUE (2) mass concentration | c. CONCEN-TRATION           | d. MASS | e. LONG TERM AVERAGE VALUE (1) mass concentration | f. NO. OF ANALYSES |
| a. Biochemical Oxygen Demand (BOD) |   |  |                             |         |   |                    |
| b. Chemical Oxygen Demand (COD)    |   |  |                             |         |   |                    |
| c. Total Organic Carbon (TOC)      |   |  |                             |         |   |                    |
| d. Total Suspended Solids (TSS)    |   |  |                             |         |   |                    |
| e. Ammonia (as N)                  |   |  |                             |         |   |                    |
| f. Flow                            | VALUE   |  |                             |         | VALUE   |                    |
| g. Temperature (water)             | VALUE   |  |                             |         | VALUE   |                    |
| h. Temperature (air/water)         | VALUE   |  |                             |         | VALUE   |                    |
| i. pH                              | MINIMUM                                       | MAXIMUM  |                             |         | STANDARD UNITS                                    |                    |

Analyses pending--will be supplied as available

PART B - Mark "X" in column 2-a for each pollutant you know or have reason to believe is present. Mark "X" in column 2-b for each pollutant you believe to be absent. If you mark column 2-b for any pollutant which is limited either directly, or indirectly but expressly, in an effluent limitations guideline, you must provide the results of at least one analysis for that pollutant. For other pollutants for which you mark column 2-a, you must provide quantitative data or an explanation of their presence in your discharge. Complete one table for each outfall. See the instructions for additional details and requirements.

| 1. POLLUTANT AND CAS NO. (if available) | 2. MARK 'X' (a) present (b) absent | 3. EFFLUENT                                   |  | 4. UNITS          |         | 5. INTAKE (optional)                              |                    |
|---|------------------------------------|---|--|-------------------|---------|---|--------------------|
|   |                                    | a. MAXIMUM DAILY VALUE (1) mass concentration | b. MAXIMUM 30-DAY AVERAGE VALUE (2) mass concentration | c. CONCEN-TRATION | d. MASS | e. LONG TERM AVERAGE VALUE (1) mass concentration | f. NO. OF ANALYSES |
| a. Bromine (74809-47-8)                 | X                                  |   |  |                   |         |   |                    |
| b. Chlorine, Total Residual             | X                                  |   |  |                   |         |   |                    |
| c. Color                                | X                                  |   |  |                   |         |   |                    |
| d. Fecal Coliform                       | X                                  |   |  |                   |         |   |                    |
| e. P Surbide (1009-43-8)                | X                                  |   |  |                   |         | 0.3 ppm   | 1                  |
| f. Nitro-White (as N)                   | X                                  |   |  |                   |         | <1 ppm  | 1                  |

ITEM V-3 CONTINUED FROM FRONT

| 1. POLLUTANT AND CAS NO. (if available)       | 2. MARK 'X'<br>a. USES LISTED ON 40 CFR 146.101<br>b. USES LISTED ON 40 CFR 146.102 | 3. EFFLUENT            |          | 4. UNITS                |          | 5. INTAKE (approx) |          |
|---|---|------------------------|----------|-------------------------|----------|--------------------|----------|
|   |   | 6. MAXIMUM DAILY VALUE |          | 7. MAXIMUM 30-DAY VALUE |          | 8. APPROX VALUE    |          |
|   |   | (1) concentration      | (2) mass | (1) concentration       | (2) mass | (1) concentration  | (2) mass |
| 3. Nitrogen, Total Organic (as N)             | X   |                        |          |                         |          |                    |          |
| 4. Oil and Grease                             | X   |                        |          |                         |          |                    |          |
| 5. Phosphorus (as P), Total (1723-14-0)       | X   |                        |          |                         |          | .3 ppm             | 1        |
| 6. Radioactivity                              |   |                        |          |                         |          |                    |          |
| (1) Alpha, Total                              | X   |                        |          |                         |          |                    |          |
| (2) Beta, Total                               | X   |                        |          |                         |          |                    |          |
| (3) Radium, Total                             | X   |                        |          |                         |          |                    |          |
| (4) Radium 226, Total                         | X   |                        |          |                         |          |                    |          |
| 7. Solids (as SO <sub>4</sub> ) (1450-79-8)   | X   |                        |          |                         |          | 290 ppm            | 1        |
| 8. Sulfide (as S)                             | X   |                        |          |                         |          |                    |          |
| 9. Oil/Fat (as SO <sub>3</sub> ) (14298-48-3) | X   |                        |          |                         |          |                    |          |
| 10. Surfactants                               | X   |                        |          |                         |          |                    |          |
| 11. Aluminum, Total (14279-60-8)              | X   |                        |          |                         |          |                    |          |
| 12. Barium, Total (17440-39-3)                | X   |                        |          |                         |          |                    |          |
| 13. Boron, Total (17440-42-8)                 | X   |                        |          |                         |          | .13 ppm            | 1        |
| 14. Cobalt, Total (17440-49-4)                | X   |                        |          |                         |          |                    |          |
| 15. Iron, Total (17439-69-8)                  | X   |                        |          |                         |          | 0.02 ppm           | 1        |
| 16. Magnesium, Total (17439-98-4)             | X   |                        |          |                         |          |                    |          |
| 17. Molybdenum, Total (17438-98-7)            | X   |                        |          |                         |          | 120 ppm            | 1        |
| 18. Manganese, Total (17439-98-8)             | X   |                        |          |                         |          |                    |          |
| 19. Vanadium, Total (17440-31-8)              | X   |                        |          |                         |          |                    |          |
| 20. Zinc, Total (17440-67-8)                  | X   |                        |          |                         |          |                    |          |

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CONTINUED FROM PAGE 2 OF FORM 20

**PART C -** If you are a primary industry and this outfall contains process wastewater, refer to Table 20-2 in the instructions to determine which of the GC/MS fractions you must test for. Mark "X" in column 2-0 for all such GC/MS fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2-0 (secondary industries, nonprocess wastewater effluents, and nonregulated GC/MS fractions), mark "X" in column 2-b for each pollutant you know or have reason to believe is present. Mark "X" in column 2-a for each pollutant you believe is absent. If you mark column 2-b for any pollutant, you must provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for each of these pollutants which you know or have reason to believe that you discharge in dinitrophenol, or 2-methyl-4, 6-dinitrophenol, you must provide the results of at least one analysis for each of these pollutants which you know or have reason to believe that you discharge in concentrations of 100 ppb or greater. Otherwise, for pollutants for which you mark column 2b, you must either submit at least one analysis or briefly describe the reasons the pollutant is expected to be discharged. Note that there are 7 pages to this part; please review each carefully. Complete one table (a-f 7 pages) for each outfall. See instructions for additional details and requirements.

| 1. POLLUTANT AND CAS NUMBER (if available) | 2. MARK 'X' (TEST RESULTS) |     | 3. EFFLUENT |     | 4. UNITS |     | 5. INTAKE (optional) |     | 6. NO. OF ANAL. YES | 7. NO. OF ANAL. YES |
|--|----------------------------|-----|-------------|-----|----------|-----|----------------------|-----|---------------------|---------------------|
|  | 2-a                        | 2-b | 3-a         | 3-b | 4-a      | 4-b | 5-a                  | 5-b |                     |                     |
| <b>METALS, CYANIDE, AND TOTAL PHENOLS</b>  |                            |     |             |     |          |     |                      |     |                     |                     |
| 1M. Antimony, Total (7440-36-0)            | X                          |     |             |     |          |     |                      |     |                     |                     |
| 2M. Arsenic, Total (7440-38-2)             | X                          |     |             |     |          |     |                      |     |                     |                     |
| 3M. Beryllium, Total (7440-41-7)           | X                          |     |             |     |          |     |                      |     |                     |                     |
| 4M. Cadmium, Total (7440-43-0)             | X                          |     |             |     |          |     |                      |     |                     |                     |
| 5M. Chromium, Total (7440-47-3)            | X                          |     |             |     |          |     |                      |     |                     |                     |
| 6M. Copper, Total (7440-45-0)              | X                          |     |             |     |          |     |                      |     | 0.06 ppm            | 1                   |
| 7M. Lead, Total (7440-31-1)                | X                          |     |             |     |          |     |                      |     |                     |                     |
| 8M. Mercury, Total (7439-97-8)             | X                          |     |             |     |          |     |                      |     |                     |                     |
| 9M. Nickel, Total (7440-02-0)              | X                          |     |             |     |          |     |                      |     |                     |                     |
| 10M. Selenium, Total (7782-49-2)           | X                          |     |             |     |          |     |                      |     |                     |                     |
| 11M. Silver, Total (7440-37-4)             | X                          |     |             |     |          |     |                      |     |                     |                     |
| 12M. Thallium, Total (7440-28-0)           | X                          |     |             |     |          |     |                      |     |                     |                     |
| 13M. Zinc, Total (7440-66-3)               | X                          |     |             |     |          |     |                      |     | 0.04 ppm            | 1                   |
| 14M. Cyanide, Total (57-13-1)              |                            | X   |             |     |          |     |                      |     |                     |                     |
| 15M. Phenols, Total                        |                            | X   |             |     |          |     |                      |     |                     |                     |

**DO NOT**  
 16. 17. 18. Total Chlorides (1700-01-0) X  
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| 1. POLLUTANT AND GAS NUMBER (if available)  | 2. MARK 'H' (if available) |                | 3. EFFLUENT                                |  | 4. UNITS               |           | 5. INTAKE (if applicable)                           |                  |
|---|----------------------------|----------------|--|--|------------------------|-----------|---|------------------|
|   | USE                        | TYPE           | MAXIMUM DAILY VALUE (i) mass concentration | WASTEWATER VALUE (ii) mass concentration | CONCENTRATION          | MASS      | LONG TERM AVERAGE VALUE (i) concentration (ii) mass | NO. OF ANAL. YRS |
|   | (if available)             | (if available) | (i) mass concentration                     | (ii) mass concentration                  | (i) mass concentration | (ii) mass | (i) concentration (ii) mass                         | (i) mass         |
| <b>SCREEN FRACTION - VOLATILE COMPOUNDS</b> |                            |                |  |  |                        |           |   |                  |
| 1V. Acetone (107-02-8)                      |                            |                | X  |  |                        |           |   |                  |
| 2V. Acrylonitrile (107-13-1)                |                            |                | X  |  |                        |           |   |                  |
| 3V. Benzene (71-43-2)                       |                            |                | X  |  |                        |           |   |                  |
| 4V. Ethyl Chloride (84-74-8)                |                            |                | X  |  |                        |           |   |                  |
| 5V. Bromoform (75-26-2)                     |                            |                | X  |  |                        |           |   |                  |
| 6V. Carbon Tetrachloride (50-33-8)          |                            |                | X  |  |                        |           |   |                  |
| 7V. Chloroethane (108-90-7)                 |                            |                | X  |  |                        |           |   |                  |
| 8V. Chloroethene (126-02-1)                 |                            |                | X  |  |                        |           |   |                  |
| 9V. Chloroethane (78-00-3)                  |                            |                | X  |  |                        |           |   |                  |
| 10V. 2-Chloroethylvinyl Ether (110-78-8)    |                            |                | X  |  |                        |           |   |                  |
| 11V. Chloroform (67-68-3)                   |                            |                | X  |  |                        |           |   |                  |
| 12V. Dichlorobromomethane (78-37-4)         |                            |                | X  |  |                        |           |   |                  |
| 13V. Dichlorodifluoromethane (78-11-8)      |                            |                | X  |  |                        |           |   |                  |
| 14V. 1,1-Dichloroethane (78-34-3)           |                            |                | X  |  |                        |           |   |                  |
| 15V. 1,2-Dichloroethane (107-06-2)          |                            |                | X  |  |                        |           |   |                  |
| 16V. 1,1-Dichloroethene (78-38-4)           |                            |                | X  |  |                        |           |   |                  |
| 17V. 1,2-Dichloropropane (78-87-8)          |                            |                | X  |  |                        |           |   |                  |
| 18V. 1,3-Dichloropropane (84-73-8)          |                            |                | X  |  |                        |           |   |                  |
| 19V. Ethylbenzene (100-81-4)                |                            |                | X  |  |                        |           |   |                  |
| 20V. Methyl Bromide (74-83-8)               |                            |                | X  |  |                        |           |   |                  |
| 21V. Methyl Chloride (74-87-3)              |                            |                | X  |  |                        |           |   |                  |

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**CONTINUED FROM PAGE 1A**

| 1. POLLUTANT AND CAS NUMBER (if available)               | 2. MAXIMUM DAILY VALUE (a) mass concentration (b) concentration | 3. EFFLUENT       |                        | 4. UNITS        |        | 5. INTAKE (inhalation)                   |                  |
|--|---|-------------------|------------------------|-----------------|--------|--|------------------|
|  |   | (1) concentration | (2) mass concentration | % CONCENTRATION | % MASS | AVERAGE VALUE (1) concentration (2) mass | NO. OF ANAL. YRS |
| <b>ORGANIC FRACTION - VOLATILE COMPOUNDS (continued)</b> |   |                   |                        |                 |        |  |                  |
| 22V. Methylene Chloride (75-09-2)                        | X   |                   |                        |                 |        |  |                  |
| 23V. 1,1,2,2-tetrachloroethane (78-34-5)                 | X   |                   |                        |                 |        |  |                  |
| 24V. Trichloroethylene (127-18-4)                        | X   |                   |                        |                 |        |  |                  |
| 25V. Toluene (108-88-3)                                  | X   |                   |                        |                 |        |  |                  |
| 26V. 1,2-Trans-Dichloroethylene (106-60-6)               | X   |                   |                        |                 |        |  |                  |
| 27V. 1,1,1-Trichloroethane (71-83-2)                     | X   |                   |                        |                 |        |  |                  |
| 28V. 1,1,2-Trichloroethane (78-00-5)                     | X   |                   |                        |                 |        |  |                  |
| 29V. Trichloroethylene (79-01-6)                         | X   |                   |                        |                 |        |  |                  |
| 30V. Trichlorofluoromethane (78-69-4)                    | X   |                   |                        |                 |        |  |                  |
| 31V. Vinyl Chloride (78-01-4)                            | X   |                   |                        |                 |        |  |                  |
| <b>ORGANIC FRACTION - ACID COMPOUNDS</b>                 |   |                   |                        |                 |        |  |                  |
| 1A. 2-Chlorophenol (95-67-8)                             | X   |                   |                        |                 |        |  |                  |
| 2A. 2,4-Dichlorophenol (120-63-2)                        | X   |                   |                        |                 |        |  |                  |
| 3A. 2,4-Dimethylphenol (108-67-9)                        | X   |                   |                        |                 |        |  |                  |
| 4A. 4,6-Dinitro-O-Cresol (834-87-1)                      | X   |                   |                        |                 |        |  |                  |
| 5A. 2,4-Dinitrophenol (81-58-5)                          | X   |                   |                        |                 |        |  |                  |
| 6A. 2-Nitrophenol (88-76-5)                              | X   |                   |                        |                 |        |  |                  |
| 7A. 4-Nitrophenol (102-07-7)                             | X   |                   |                        |                 |        |  |                  |
| 8A. p-Chloro-m-Cresol (95-80-7)                          | X   |                   |                        |                 |        |  |                  |
| 9A. p-Fluorophenol (87-68-5)                             | X   |                   |                        |                 |        |  |                  |
| 10A. Phenol (108-95-3)                                   | X   |                   |                        |                 |        |  |                  |
| 11A. 2,4,6-Trichlorophenol (88-06-2)                     | X   |                   |                        |                 |        |  |                  |

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| 1. POLLUTANT AND CAS NUMBER (if available)    | 2. MARK 'X' IF: |         | 3. EFFLUENT            |                   | 4. UNITS                   |                   | 5. INTAKE (upland)         |                   |  |
|---|-----------------|---------|------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|--|
|   | USE             | ST. USE | B. MAXIMUM DAILY VALUE |                   | C. LONG TERM AVERAGE VALUE |                   | D. LONG TERM AVERAGE VALUE |                   |  |
|   | WATER           | AIR     | (1) WASTE              | (2) CONCENTRATION | (1) WASTE                  | (2) CONCENTRATION | (1) WASTE                  | (2) CONCENTRATION |  |
| DCMS FRACTION - BASE/NEUTRAL COMPOUNDS        |                 |         |                        |                   |                            |                   |                            |                   |  |
| 16. Acenaphthene (83-87-9)                    |                 |         |                        |                   |                            |                   |                            |                   |  |
| 26. Acenaphthylene (208-96-8)                 |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 39. Anthracene (120-12-7)                     |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 49. Benzidine (92-87-8)                       |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 59. Benzene (6) Anthracene (83-84-3)          |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 69. Benzene (6) Pyrene (103-52-8)             |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 79. 3,4-Benzofluoranthene (200-90-2)          |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 89. Benzene (6H) Paraffin (101-32-3)          |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 99. Benzene (6) Fluoranthene (207-08-9)       |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 109. Bis (2-Chloro-ethyl) Methane (111-91-1)  |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 119. Bis (2-Chloro-ethyl) Ether (111-44-4)    |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 129. Bis (2-Chloro-propyl) Ether (102-60-1)   |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 139. Bis (2-Ethylhexyl) Phthalate (117-91-7)  |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 149. 4-Bromo-phenyl Phenyl Ether (101-59-3)   |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 159. Butyl Benzyl Phthalate (85-87-7)         |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 169. 2-Chloro-naphthalene (91-60-7)           |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 179. 4-Chloro-phenyl Phenyl Ether (7085-78-9) |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 189. Chrysene (218-01-6)                      |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 199. Dibenz (a,h) Anthracene (83-70-3)        |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 209. 1,2-Dichlorobenzene (95-90-1)            |                 |         | X                      |                   |                            |                   |                            |                   |  |
| 219. 1,3-Dichlorobenzene (841-73-1)           |                 |         | X                      |                   |                            |                   |                            |                   |  |

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| 1. POLLUTANT AND CAS NUMBER (if available)                 | 2. MARK 'N' (see 101.10-101.10-1) | 3. EFFLUENT  |   | 4. UNITS           |         | 5. INTAKE (upstream) |  |                      |
|--|-----------------------------------|--|---|--------------------|---------|----------------------|--|----------------------|
|  |                                   | 6. MAXIMUM DAILY VALUE (1) mass concentration (2) mass | 7. LONG TERM AVERAGE VALUE (1) concentration (2) mass | 8. CONCEN- TRATION | 9. MASS | 10. NO. OF ANAL. YRS | 11. AVERAGE VALUE (1) concentration (2) mass | 12. NO. OF ANAL. YRS |
| <b>GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS (continued)</b> |                                   |  |   |                    |         |                      |  |                      |
| 27B, 1,4-Dichloro- benzene (100-45-7)                      |                                   | X  |   |                    |         |                      |  |                      |
| 23B, 3,3'-Dichloro- benzidine (91-94-1)                    |                                   | X  |   |                    |         |                      |  |                      |
| 24B, Diethyl- 2-Naphthyl- sulfone (84-68-2)                |                                   | X  |   |                    |         |                      |  |                      |
| 26B, Diurethyl- Phthalate (131-11-3)                       |                                   | X  |   |                    |         |                      |  |                      |
| 24B, Di-N-Butyl- Phthalate (84-74-2)                       |                                   | X  |   |                    |         |                      |  |                      |
| 27B, 2,4-Dinitro- toluene (121-14-2)                       |                                   | X  |   |                    |         |                      |  |                      |
| 26B, 2,6-Dinitro- toluene (89-20-2)                        |                                   | X  |   |                    |         |                      |  |                      |
| 29B, Di-N-Octyl- Phthalate (117-92-0)                      |                                   | X  |   |                    |         |                      |  |                      |
| 30B, 1,3-Dibenzyl- hydrazine (or Azobenzene) (122-06-7)    |                                   | X  |   |                    |         |                      |  |                      |
| 31B, P-Naphthothene (206-64-0)                             |                                   | X  |   |                    |         |                      |  |                      |
| 29B, Fluorene (86-73-7)                                    |                                   | X  |   |                    |         |                      |  |                      |
| 28B, Hexachlorobenzene (116-74-1)                          |                                   | X  |   |                    |         |                      |  |                      |
| 34B, Methyl- chlorobutadiene (87-68-3)                     |                                   | X  |   |                    |         |                      |  |                      |
| 26B, Hexachloro- cyclopentadiene (17-47-4)                 |                                   | X  |   |                    |         |                      |  |                      |
| 36B, Hexachloro- ethane (87-72-1)                          |                                   | X  |   |                    |         |                      |  |                      |
| 27B, Indene (117-90-1) / styrene (103-30-5)                |                                   | X  |   |                    |         |                      |  |                      |
| 26B, Isophorene (84-63-1)                                  |                                   | X  |   |                    |         |                      |  |                      |
| 40B, Naphthalene (91-20-3)                                 |                                   | X  |   |                    |         |                      |  |                      |
| 40B, Microbenzene (98-56-3)                                |                                   | X  |   |                    |         |                      |  |                      |
| 41B, N-Nitro- octylmethylamine (82-75-8)                   |                                   | X  |   |                    |         |                      |  |                      |
| 43B, N-Nitrodi- N-propylamine (821-64-7)                   |                                   | X  |   |                    |         |                      |  |                      |

CONTINUE ON REVERSE

| 1. POLLUTANT AND CAS NUMBER (if available)                | 2. WARM 'R' (see 401.150-159) |               | 3. EFFLUENT                                       |  | 4. UNITS         |         | 5. INTAKE (if known)                         |                       |  |
|---|-------------------------------|---------------|---|--|------------------|---------|--|-----------------------|--|
|   | WARM 'R' NO.                  | WARM 'R' NAME | 6. MAXIMUM DAILY VALUE (1) mass (2) concentration | 7. MAXIMUM 30-DAY VALUE (1) mass (2) concentration | 8. CONCENTRATION | 9. MASS | 10. AVERAGE VALUE (1) mass (2) concentration | 11. NO. OF ANAL. YRS. |  |
| <b>OCAS FRACTION - BASE/NEUTRAL COMPOUNDS (continued)</b> |                               |               |   |  |                  |         |  |                       |  |
| 439. N-Nitro-methylbenzylamine (88-30-8)                  |                               |               | X   |  |                  |         |  |                       |  |
| 448. Phenanthrene (85-01-8)                               |                               |               | X   |  |                  |         |  |                       |  |
| 458. Pyrene (129-00-0)                                    |                               |               | X   |  |                  |         |  |                       |  |
| 468. 1,2,4-Trichlorobenzene (120-82-1)                    |                               |               | X   |  |                  |         |  |                       |  |
| <b>OCAS FRACTION - PESTICIDES</b>                         |                               |               |   |  |                  |         |  |                       |  |
| 1P Aldrin (500-00-2)                                      |                               |               | X   |  |                  |         |  |                       |  |
| 3P D DMC (319-84-6)                                       |                               |               | X   |  |                  |         |  |                       |  |
| 3P P DMC (316-85-7)                                       |                               |               | X   |  |                  |         |  |                       |  |
| 4P T DMC (58-49-9)  |                               |               | X   |  |                  |         |  |                       |  |
| 5P H DMC (316-86-8)                                       |                               |               | X   |  |                  |         |  |                       |  |
| 6P Chlordane (53-74-9)                                    |                               |               | X   |  |                  |         |  |                       |  |
| 7P 4,4'-DDT (50-79-3)                                     |                               |               | X   |  |                  |         |  |                       |  |
| 8P 4,4'-DDE (79-57-9)                                     |                               |               | X   |  |                  |         |  |                       |  |
| 9P 4,4'-DDD (79-54-8)                                     |                               |               | X   |  |                  |         |  |                       |  |
| 10P Dieldrin (60-57-1)                                    |                               |               | X   |  |                  |         |  |                       |  |
| 11P D Dieldrin (115-29-7)                                 |                               |               | X   |  |                  |         |  |                       |  |
| 12P D Dieldrin (115-29-7)                                 |                               |               | X   |  |                  |         |  |                       |  |
| 13P Dieldrin (1031-07-8)                                  |                               |               | X   |  |                  |         |  |                       |  |
| 14P Fenitrothion (79-90-8)                                |                               |               | X   |  |                  |         |  |                       |  |
| 15P Fenitrothion (79-90-8)                                |                               |               | X   |  |                  |         |  |                       |  |
| 16P Fenitrothion (79-90-8)                                |                               |               | X   |  |                  |         |  |                       |  |
| 17P Fenitrothion (79-90-8)                                |                               |               | X   |  |                  |         |  |                       |  |

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EPA Form 3810-2C (Rev. 4-84)



EPA ID. NUMBER (copy from Item 1 of Form 1) **NVD 008290330** **001**  
 OUTFALL NUMBER

CONTINUED FROM PAGE V-8

| 1. POLLUTANT AND GAS NUMBER (if applicable) | 2. MARK 'X' (if applicable) | 3. EFFLUENT                                    |  | 4. UNITS          |               | 5. INTAKE (if present)                  |   |
|---|-----------------------------|--|--|-------------------|---------------|---|---|
|   |                             | MINIMUM DAILY VALUE (1) mass (2) concentration | MAXIMUM DAILY VALUE (1) mass (2) concentration | NO. OF ANAL. YRS. | CONCENTRATION | ANNUAL VALUE (1) mass (2) concentration | LONG TERM ANNUAL VALUE (1) mass (2) concentration |
| OCRES FRACTION - PESTICIDES (continued)     |                             |  |  |                   |               |   |   |
| 17F. Heptachlor Epoxide (1074-97-3)         | X                           |  |  |                   |               |   |   |
| 18P. PCB-1242 (83469-31-8)                  | X                           |  |  |                   |               |   |   |
| 19P. PCB-1254 (11087-98-1)                  | X                           |  |  |                   |               |   |   |
| 20P. PCB-1231 (11104-28-3)                  | X                           |  |  |                   |               |   |   |
| 21P. PCB-1232 (11141-16-8)                  | X                           |  |  |                   |               |   |   |
| 22P. PCB-1248 (12672-38-6)                  | X                           |  |  |                   |               |   |   |
| 23P. PCB-1260 (11094-82-8)                  | X                           |  |  |                   |               |   |   |
| 24P. PCB-1016 (12674-11-2)                  | X                           |  |  |                   |               |   |   |
| 26P. Toxaphene (8001-38-2)                  | X                           |  |  |                   |               |   |   |

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EPA Form 3610-2C (Rev. 4-84)  
 (PR Doc. 84-5327 Prod. 8-28-84; 848 ms)  
 BILLING CODE 6460-60-C

Outfall 004 will also intercept the discharges from KMCC outfalls 001 and 002, Genstar Lime storm-water, State Industries, Timet, and Stauffer Chemical Corporation. KMCC's willingness to propose and accept the location of this outfall is dependent on the following:

- 1) The discharges of Genstar, State Industries, Timet, and Stauffer Chemical Corporation must be subject to individual NPDES permits, and these permits must contain effluent limitations at levels such that the permitted discharges will not cause KMCC's permitted discharge to violate its NPDES permit limitations.
- 2) The final NPDES permit must contain the following language: "An exceedance of an effluent limitation at outfall 004 will not be considered a violation of this permit or of the Federal Water Pollution Control Act of 1972 if it was caused by another company's effluent. Determination of the source of the exceedance shall be made by analyzing samples taken at relevant locations. The samples must be taken by KMCC within one hour after the exceedance is first recorded at outfall 004 to qualify as evidence for purposes of this paragraph."

The runoff area for outfall 004, not including the 002 area described above, is estimated at 25 acres. There is no treatment applied to this discharge.

Outfalls 002, 003, and 004 are located on the map provided. The outline around the ammonium perchlorate plant delineates the isolated area from which plant runoff is diverted to ponds for recycle/reuse.

**KERR-McGEE CHEMICAL CORPORATION**

**Henderson, Nevada**

**EPA No. NVD 008290330**

**NPDES Permit No. NV 0000078**

**¶ 122.21(f)(9)(i)**

**STORMWATER POINT SOURCE IDENTIFICATION**

**Outfall 002**      Outfall 002 is the monitoring point for the stormwater collection system serving the area surrounding buildings 1, 2, 3, and the western half of 4, and includes the approach road to the plant administration building and area. The sodium chlorate recovery operation in this area does not impact on discharges of outfall 002. The storm drain system has been sealed in the process operation area and barriers placed to prevent runoff from the area. The 002 collection area is depicted on the attached map and encompasses approximately 29 acres.

The stormwater runoff is collected and discharged into the unnamed ditch which flows into the Las Vegas Wash. No treatment is applied to these discharge waters.

**Outfall 003**      This discharge point monitors the stormwater collection system serving the area surrounding the eastern half of building 4 and buildings 5 and 6. Building 5 contains sodium chlorate, sodium perchlorate, boron trichloride, boron tribromide, and elemental boron processing operations. Building 6 contains a manganese dioxide electrolysis operation. These process areas are isolated from the stormwater collection system.

Outfall 003 discharges to the stormwater collection system that also serves Titanium Metals Corporation (Timet). The runoff area served by the KMCC outfall is estimated to be 24 acres. No treatment is applied to these discharge waters.

**Outfall 004**      Outfall 004 will monitor the noncontaminated stormwaters collected from the ammonium perchlorate unit area which is located in the northern section of the KMCC Henderson Plant. This plant produces dry granular ammonium perchlorate which is stored in lined and sealed 55-gallon drums on asphalt pads. The processing areas and vessels are isolated by containment foundations which prevent commingling of process and nonprocess areas.

**KERR-McGEE CHEMICAL CORPORATION**

**Henderson Facility**

**Henderson, Nevada**

**NPDES Permit No. NV 0000078**

**¶122.21(f)(9)(i)**

**STORM WATER POINT SOURCE OUTFALL DESCRIPTIONS**

| <u>Outfall<br/>No.</u> | <u>Operation</u>   | <u>Type<br/>Flow</u>   | <u>Treatment<br/>Type</u> |
|------------------------|--|------------------------|---------------------------|
| 002                    | Storm Water Runoff<br>Buildings 1, 2, 3,<br>and 1/2 of 4   | Group I<br>Storm Water | None                      |
| 003                    | Storm Water Runoff<br>Buildings 6, 5,<br>and 1/2 of 4 (Dis-<br>charges into TIMET<br>property)                     | Group I<br>Storm Water | None                      |
| 004                    | Storm Water Runoff<br>Ammonium Perchlo-<br>rate Plant and<br>Auxiliary Building,<br>Maintenance and<br>Steam Plant | Group I<br>Storm Water | None                      |

**¶122.21(f)(9)(ii) - Group I SWPS Pollutant Data**

All outfalls in Group I SWPS require all available quantitative data on the following pollutants for each SWPS discharge:

- a) Oil and Grease
- b) Total Organic Carbon
- c) Chemical Oxygen Demand
- d) GC/MS fractions as follows:
  - 1) Volatile Compounds
  - 2) Acid Compounds
  - 3) Base/Neutral Compounds

Under the present KMCC Henderson permit No. NV 0000078, these pollutants have not been required for analysis purposes. Furthermore, since no rainfall has occurred that has caused sufficient runoff, no information is available for these pollutants.

¶ 122.21(f)(9)(iii)

For any Group I SWPS, a list for each discharge point of any of the following pollutants which are known or expected to be present in the discharge is required. See the chart below for this information.

| <u>Pollutant</u>       | <u>Group I SWPS</u>    |                       |                        |                       |                        |                       |
|------------------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|
|                        | <u>002</u>             |                       | <u>003</u>             |                       | <u>004</u>             |                       |
|                        | <u>Believe Present</u> | <u>Believe Absent</u> | <u>Believe Present</u> | <u>Believe Absent</u> | <u>Believe Present</u> | <u>Believe Absent</u> |
| Oil and Grease         |                        | X                     |                        | X                     |                        | X                     |
| Total Organic Carbon   |                        | X                     |                        | X                     |                        | X                     |
| Chemical Oxygen Demand |                        | X                     |                        | X                     |                        | X                     |
| Volatile Compounds     |                        | X                     |                        | X                     |                        | X                     |
| Acid Compounds         |                        | X                     |                        | X                     |                        | X                     |
| Base/Neutral Compounds |                        | X                     |                        | X                     |                        | X                     |

**TOXIC AND HAZARDOUS MAT I.S INVENTORY**  
 For Chemicals Purchased or Used over 1000 pounds per year

Company Name KERR-MCGEE CHEMICAL CORPORATION Plant Location (city or state) Henderson, Nevada

Permit No. NVD 0000078

| Chemical Name       | Annual Qty. Purchased or used, <u>lbs.</u> tons | Avg. Qty. Stored <u>lbs.</u> tons | Method of Storage (1)   | Usage (2) | Potential for Aqueous Contact (3) |     | Secondary Containment (4) |
|---------------------|---|-----------------------------------|-------------------------|-----------|-----------------------------------|-----|---------------------------|
|                     |   |                                   |                         |           | (a)                               | (b) |                           |
| Sodium Hydroxide    | 815   | 100                               | a                       | i         | c                                 |     | a                         |
| Hydrochloric Acid   | 13,750  | 372                               | a                       | b         | d                                 |     | a                         |
| Sulfuric Acid       | 1,237   | 22                                | a                       | h         | c                                 |     | a                         |
| Hydrogen Sulfide    | 67  | 45                                | d                       | h         | d                                 |     | d                         |
| Sodium Bichromate   | 34.5  | 5                                 | f (bags)                | h         | d                                 |     | e                         |
| Strontium Carbonate | 44  | 7                                 | f (bags)                | h         | d                                 |     | e                         |
| Ammonia             | 1,872   | 100                               | a                       | b         | d                                 |     | d                         |
| Manganese Ore       | 10,591  | 5,000                             | f (contained open pile) | b         | d                                 |     | a                         |
| Sulfur Dioxide      | 12  | 4                                 | f (one-ton cylinder)    |           | d                                 |     | a                         |
| Chlorine            | 439   | 50                                | d                       | b         | d                                 |     | d                         |
| Bromine             | 11  | 3                                 | c                       | b         | d                                 |     | c                         |
| Boron Carbide       | 37  | 14                                | c                       | h         | d                                 |     | e                         |
| Boric Oxide         | 62  | 32                                | f (bags)                | b         | d                                 |     | e                         |

**Notes:**

- (a) Tanks - above ground
  - (b) Tanks - below ground
  - (c) Drums
  - (d) Rail Cars
  - (e) Tank Trucks
  - (f) Other see chart
- (a) Solvent
  - (b) Raw Material
  - (c) Intermediate Material
  - (d) Final Product
  - (e) Co/By-Product
  - (f) Catalyst
  - (g) Contaminant
  - (h) Other additive/treatment
- (a) High
  - (b) Medium
  - (c) Low
  - (d) None
- (a) Concrete tank
  - (b) Earthen berms or
  - (c) None
  - (d) None required (i.e. underground tank, gaseous material)
  - (e) Other curbing

**TOXIC AND HAZARDOUS MATERIALS INVENTORY**  
 For Chemicals Purchased or Used over 1000 pounds per year

Company Name KERR-MCGEE CHEMICAL CORPORATION Plant Location (city or state) Henderson, Nevada

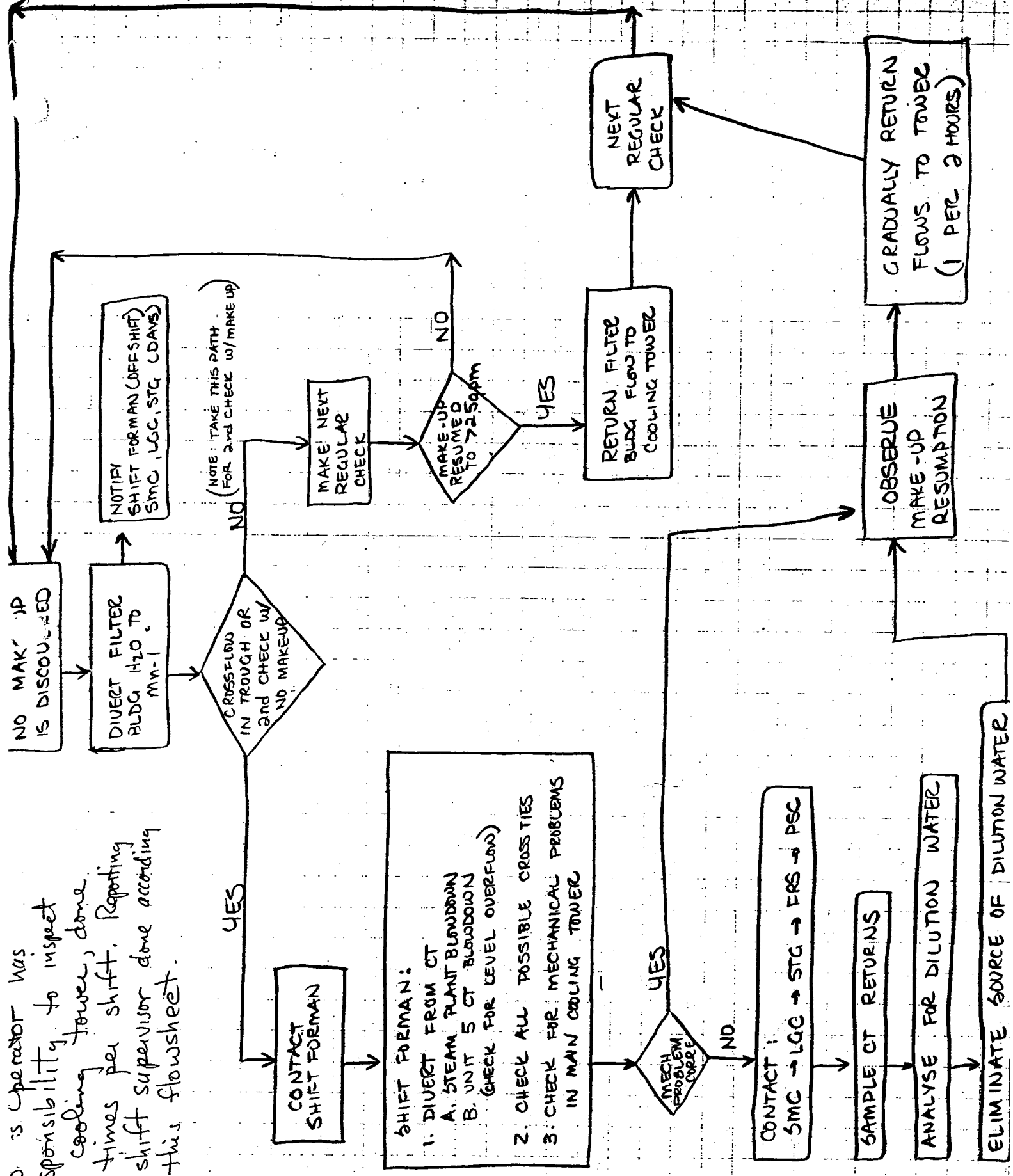
Plant Name \_\_\_\_\_ Permit No. NVD 0000078

| Chemical Name  | Annual Qty. Purchased or used, tons | Avg. Qty. Stored tons | Method of Storage (1) | Usage (2) | Potential for Aqueous Contact (3) | Secondary Containment (4) |
|--|-------------------------------------|-----------------------|-----------------------|-----------|-----------------------------------|---------------------------|
| Magnesium  | 19.9                                | 6.5                   | c                     | b         | d                                 | a                         |
| Sodium Chloride  | 14,917                              | 260                   | a                     | b         | b                                 | a                         |
| Soda Ash   | 269                                 | 15                    | f (bags)              | h         | c                                 | a                         |
| Sodium Chlorate  | 25,000                              | 1,000                 | a                     | c/d       | b                                 | a                         |
| Sodium Perchlorate   | 18,000                              | 1,800                 | a                     | c/d       | b                                 | a                         |
| Ammonium Perchlorate   | 14,000                              | 7,000                 | c/a                   | d         | b                                 | a                         |
| Manganese Sulfate  | 14,000                              | 800                   | a                     | c         | b                                 | a                         |
| Anolyte (MnSO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub> ) | 9,000                               | 40,000                | a                     | c         | c                                 | a                         |

- Notes:**
- (a) Tanks - above ground
    - (b) Tanks - below ground
    - (c) Drums
    - (d) Rail Cars
    - (e) Tank Trucks
    - (f) Other \_\_\_\_\_
  - (a) Solvent
    - (b) Raw Material
    - (c) Intermediate Material
    - (d) Final Product
    - (e) Co/By-Product
    - (f) Catalyst
    - (g) Contaminant
    - (h) Other \_\_\_\_\_
  - (a) High
    - (b) Medium
    - (c) Low
    - (d) None
  - (a) Concrete tank farm
    - (b) Earthen berms or
    - (c) None
    - (d) None required (i.e. underground tank, gaseous mat.)
    - (e) Other \_\_\_\_\_



Pro: Operator was responsible to inspect the cooling tower, done 3 times per shift. Reporting to shift supervisor done according to this flowsheet.



NOTE: TAKE THIS PATH FOR 2nd CHECK W/ MAKE UP

CONTACT SHIFT FORMAN

SHIFT FORMAN:  
 1. DIVERT FROM CT  
 A. STEAM PLANT BLOWDOWN  
 B. UNIT 5 CT BLOWDOWN  
 (CHECK FOR LEVEL OVERFLOW)  
 2. CHECK ALL POSSIBLE CROSS TIES  
 3. CHECK FOR MECHANICAL PROBLEMS IN MAIN COOLING TOWER

MECH PROBLEM CORRECTED?

CONTACT SMC -> LGC -> STG -> FRS -> PSC

SAMPLE CT RETURNS

ANALYSE FOR DILUTION WATER

ELIMINATE SOURCE OF DILUTION WATER

NOTIFY SHIFT FORMAN (OFFSHIFT) SMC, LGC, STG, (DAYS)

CROSSFLOW OR IN TROUGH OR AND CHECK W/ NO MAKE-UP

MAKE NEXT REGULAR CHECK

MAKE-UP RESUMED TO > 2.50pm

RETURN FILTER BUDG FLOW TO COOLING TOWER

NEXT REGULAR CHECK

GRADUALLY RETURN FLOWS TO TOWER (1 PER 2 HOURS)

OBSERVE MAKE-UP RESUMPTION

