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13. ABSTRACT *(Maximum 200 words)*
A FULL-SCALE CALGON ADSORPTION UNIT WAS INSTALLED AT RMA AND BEGAN OPERATION IN JULY, 1978. THE PURPOSE OF THIS UNIT WAS TWO-FOLD: (1) INSURE OPERATION IN COMPLIANCE OF CEASE AND DESIST ORDERS ISSUED BY STATE OF COLORADO DEPT. OF HEALTH, APRIL 7, 1975 AND (2) EVALUATE THE APPLICABILITY OF GRANULAR ACTIVATED CARBON OVER A THREE YEAR PERIOD FOR POTENTIAL USE IN DESIGNING AN EXPANDED SYSTEM CAPABLE OF ELIMINATING THE FLOW OF RESTRICTED TRACE ORGANICS OFF OF THE ARSENAL. IT IS THE PURPOSE OF THIS REPORT TO REVIEW THE OPERATION OF THE ADSORPTION SYSTEM AND THE RESULTS OBTAINED IN LIGHT OF PREVIOUS TREATABILITY STUDIES PERFORMED BY CALGON CORP. AND RMA PERSONNEL IN CONJUNCTION WITH RECOMMENDATIONS PROPOSED IN THE FY 1979 TECHNICAL REVIEW AND IMPLEMENTED BY RMA. TO ASSIST RMA PERSONNEL IN DEFINING FUTURE DESIGN PARAMETERS, THE RESULTS OF A COMPUTER ANALYSIS ON ALL DATA OBTAINED TO DATE IS PRESENTED FOR EVALUATION.

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CALGON CORPORATION
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REMOVAL OF TRACE ORGANICS FROM GROUNDWATER USING GRANULAR ACTIVATED CARBON

ROCKY MOUNTAIN ARSENAL
DENVER, COLORADO

ANNUAL TECHNICAL REVIEW
FY 1980

ACTIVATED CARBON DIVISION
CALGON CORPORATION

By

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Technical Services Co-ordinator

I. INTRODUCTION:

In accordance with recommendations put forth in the Department of Army's report on Carbon Adsorption Treatment of Contaminated Groundwater at Rocky Mountain Arsenal [1] dated 15 October, 1977, a full scale Calgon Adsorption unit was installed at Rocky Mountain Arsenal (RMA) and began operation in July, 1978. The purpose of this unit was two fold:
1) insure operation in compliance of Cease and Desist orders issued by the State of Colorado Department of Health on April 7, 1975 and
2) evaluate the applicability of granular activated carbon over a three year period for potential use in designing an expanded system capable of eliminating the flow of restricted trace organics off of the Arsenal.

As mentioned above, one of the prime objectives of the Program of Installation Restoration is "... To acquire technology to develop and implement containment and treatment systems...(at RMA)". It is the purpose of this report to review the operation of the Adsorption System and the results obtained in light of previous treatability studies performed by Calgon Corporation [1, 2] and RMA personnel [1] in conjunction with recommendations proposed in the FY 1979 Technical Review [3] and implemented by RMA. To assist RMA personnel in defining future design parameters, the results of a computer analysis on all data obtained to date is presented for evaluation.

Once again, Calgon Corporation would like to extend its' appreciation to RMA personnel, specifically the Project's Development Evaluation Division, for the cooperation during the past year. The overwhelming success of the current Adsorption System is directly attributable to the efforts by all personnel involved.

II. CONCLUSION & RECOMMENDATIONS:

- Based on a maximum allowable DIMP concentration of 500 ppb in the effluent at breakthrough, the carbon usage rate for the one full cycle in FY 1980 (August, 1979 - May, 1980) was 0.93 lb. carbon/1,000 gallon wastewater. This compares with a 1.1 lb. carbon/1,000 gallons obtained from the pilot studies conducted at RMA.[1]

- Computer analysis indicate that the adsorption mass transfer zone at contact times from 15 minutes to 95 minutes is less than 1 ft. in length at average influent concentrations of 400 ppm - 2400 ppm DIMP (Table 2). The difference in contact times (15 minutes vs. 95 minutes) gave insignificant benefits with regards to bed saturation - 98.4% saturated @ 15 minutes vs. 99.3% saturated at 95 minutes.

- Maintenance downtime during FY 1980 averaged less than 1% based on a 365 day operating year.

- Analyses performed by RMA clearly show that the monitoring of the effluent DIMP concentration is all that is necessary to insure compliance of all regulated substances (Fig. 2 & 3).

- For any future expansion, it is recommended that a separate sump be provided for the filter backwash water. The overflow or supernatant of this sump should be directed to the influent sump. Based on observed influent solids (approximately .2 mg/l) it is estimated that less than 400 lbs. of a 20% solid solution will be produced annually for ultimate disposal.

- Data developed by RMA shows that TOC is not an important criteria in determining bed life. TOC was one area suggested in the FY 1979 annual report to investigate as a potential cause for shorter than expected bed life. However, it has since been determined that anomallies in the initial TOC analytical method, gave erroneous results. In conjunction with this, all problems of shortened bed lifes have been rectified by the installation of the siphon break.

Discussion:

A. System Description[4]

1. Plant Facilities

The influent water is pumped from the dewatering wells to the feed sump located at the adsorption site. The wells, pumps and conveyance system to the feed sumps is provided by Rocky Mountain Arsenal.

The water conveyed to the feed sump is pumped at a controlled rate through the Adsorption System. A flow control system operates controlling flow to the Adsorption System on the basis of the water level in the feed sump. The sump, feed pumps and flow control system are provided by Calgon. Equipment for the Adsorption System consists of two (2) lined carbon steel pressure filters 4 ft. diameter, two (2) lined carbon steel adsorbers 10 ft. diameter by 11 ft. sidewalls and associated appurtenances to provide for filtration of the influent, adsorption of the dissolved organic contaminants and transfer of Activated Carbon into and out of the adsorber.

The influent is pumped at a controlled rate downflow through the two (2) filters in a parallel mode. Each filter contains four (4) feet of filter media consisting of a blend of graded coal and sand.

Each lined carbon steel filter vessel is rated for 100 psig at 150°F. The filters are operated in parallel until such time that backwashing is required. Backwashing may be effected manually or on a preset time interval. A high pressure drop alarm is provided to signal premature filter plugging indicating the need to manually initiate the backwash sequence. The backwash sequence is effected by isolating and backwashing one filter at a time with filtered water from the on-stream filter for a preset time period. When the backwashing operation is complete, the filter is automatically returned to service. Solids laden backwash water is conveyed to the influent sump. Periodically, RMA personnel remove settled sludge from the influent sump.

The filtered water flows under pressure to the adsorption section of the Adsorption System. This consists of two (2) single stage adsorbers. Each adsorber is rated for 75 psig at 150°F and is designed to contain 20,000 lbs. of Activated Carbon

The system is designed such that only one adsorber will be in service at a time. The filtered water passes downflow through the adsorber in service. The treated effluent from the adsorber is conveyed to the battery limits for disposal by RMA.

When the carbon in the adsorber becomes exhausted, the Spent Carbon is replaced with Activated Carbon. Fresh Activated Carbon is delivered to RMA in specially designed trailers. The Activated Carbon is transferred from the Calgon trailer to the adsorber by filling the trailer with treated water to slurry the Activated Carbon and pressurizing the trailer with compressed air. The treated water for the transfer is treated by the Adsorption System and stored in the empty adsorber prior to the arrival of the Calgon trailer. Once this operation is complete, the Adsorption System can be placed back in service. Calgon supplied an air compressor system to provide compressed air for the carbon transfer operations as well as any compressed air required for instrumentation or valve operators.

The Spent Carbon is transferred from the exhausted adsorber to the empty Calgon trailer as a water slurry by pressurizing the adsorber with compressed air. The slurry water is drained from the Calgon trailer to the feed system for treatment in the Adsorption System. The Calgon trailer removes the Spent Carbon from RMA.

Shown in Table I are the design conditions and performance capabilities of the system installed at RMA.

2. Operations & Maintenance

A major factor on deciding to install the Calgon unit at the RMA facility was its ease of operation and minimal manpower requirement. [1] Once again during FY 1980 downtime amounted to less than 1% based on a 365 day operating year. The only item of significance was the installation of the anti-siphon connection on the adsorber effluent. In addition to this, normal minor maintenance was performed on flow recorders, integrators, pump seals, etc.

It should be mentioned that the flow integrator which provides the total flow treated, operated sporadically during FY 1980. As this number (i.e. gallons treated) is the basis of any technical evaluation, the compensation for this failure should be documented. There are three independant sources which can be utilized to obtain the total gallons treated at any time. These are:

1) Flow Integrator
2) Strip Charts
3) De-watering Well Flow Integrators

For purposes of the following Technical evaluation, the summation of the de-watering well flow integrators was utilized. This figure showed that 21,654,900 gallons of water was treated during FY 1980. Naturally, this assumes that all water removed from the aquifer was treated and subsequently re-injected. The Calgon flow integrator showed 15,950,361 gallons treated -- a difference of 5,104,539 gallons. However, the third independent source of flow, though not integrated, showed normal flows during times when the Calgon integrator was not functioning. Additionally, no known problems were experienced with the de-watering well integrators.

B. System Performance

Presented in Figures 1, 2 and 3 are the operating curves for the one full adsorption cycle during FY 1980. In conjunction with this, Table 2 summarizes all work performed with granular activated carbon (GAC) at RMA. It is Calgon's opinion that the current system is indicative of future performance, and is suitable for utilization in obtaining design parameters for any future expansion.

In addition to providing technical expertise on the Adsorption System currently at RMA, it has been Calgon's goal to place in perspective the operating parameters, specifically carbon usage, of the full scale system with pilot work conducted prior to RMA's decision to utilize GAC in a full scale system. At the end of FY 1979, this was impossible due to the problem of bed-siphoning, which resulted in premature bed change-outs. However, this problem was rectified, and beginning in August, 1979, a true evaluation could be made.

Data is available on contact times ranging from 15 minutes to 95 minutes, a 6X order of magnitude -- a rare convenience. In addition to this wide range of contact times there is a similar bracketing with regards to influent concentrations (i.e. 400 ppm DIMP - 2400 ppm DIMP). As concentration is the second most important criteria, once again an extreme amount of reliability is introduced by covering these concentration ranges. The third design criteria is hydraulic loading. No great significance is placed on this providing the loading does not exceed 4 gpm/ft.^{2}. However, an added luxury is provided in that data is available over the range 0.7 - 1.8 gpm/ft.^{2}, which shows that the above assumption is true. Two additional points should be made with regards to the data. Bench work was performed in 5" diameter Plexiglas columns. It is Calgon's experience that dynamically, these provide a one-to-one scale-up. Or more simply put, there is no significant difference between a 5" diameter carbon adsorber and a 10 ft. diameter carbon adsorber providing all other operating parameters are equal. The second point is that all analyses generated for the two cycles in FY 1979 are not considered in this discussion due to the introduction of air into the beds, and hence no subsequent predictable performance. Computer analyses utilizing the data from these beds is included more to show that there were anomallies present in light of all the other work done.

The most significant result with regards to Table 2 is the length of the mass transfer zone. All work indicates that the zone is less than 1 ft. A typical industrial application exhibits mass transfer zones from 4 ft. - 7 ft. in length. However, for all intents and purposes, groundwater applications typically show pure component characteristics relative to their adsorbability. In very adsorbable compounds, such as DIMP, this translates to a very "sharp" breakthrough curve, as evidenced in Fig. 1. One can lengthen or shorten the mass transfer zone by changing the system hydraulics. As can be seen for FY 1980, the contact time was 95 minutes and the mass transfer zone was 3.2 inches. This can also be related to surface loading in a similar manner. The ramifications of this are many. From an equipment standpoint, considerable savings are realized due to the fact that only a single carbon bed is necessary. Any application which utilizes two or more carbon beds in series is doing so to insure maximum utilization of the carbon due to the partial saturation in the adsorption zone. With very short mass transfer zones, only a negligible amount of increased carbon utilization is realized. This can clearly be seen in Table 2 by comparing the bed saturations for various contact times. From a design standpoint, the relative insensitivity of saturation with respect to contact time provides savings in the sizing of equipment. Much larger vessels are needed as the contact time increases. In summation, one can see that the adsorption characteristics for the RMA application, as evidenced, allow a simple cost effective approach in any future design work.

With regards to the carbon usage rates, it has been Calgon's experience that field studies should provide a one-to-one scale-up, providing influent characteristics remain constant with time. As can be seen from Table 2, with the implementation of the siphon break (FY 1979), carbon usage rates were comparable to original pilot work -- approximately 0.95 lbs. carbon/1,000 gallons treated. The random effects of bed siphoning can also be seen. During the first cycle of FY 1979 carbon usage rates were over twice the predicated amount, and cycle two shows a 40% increase in usage.

The relative independance of concentration of DIMP with carbon usage rates (Table 2) indicates a fairly horizontal carbon isotherm (Fig. 4). One can conjecture that if an isotherm were performed at higher DIMP concentrations, a more horizontal line than seen in Fig. 4 would be obtained. Essentially, this states that the capacity of DIMP for carbon over a limited concentration range remains fairly constraint. This is a frequent occurrence in many industrial applications.

TABLE 1[5]

SYSTEM DESIGN AND PERFORMANCE CAPABILITIES

Parameter	System Design Performance Value	System Design Capabilities
Flow		
Average Daily	252,000 GPD	288,000 GPD
Instantaneous Peak	200 GPM	200 GPM
Pump Discharge Pressure		System Relief @75 psig
Temperature	$35^{o}F$ - $100^{o}F$	150^{O}Fht. Maximum
pH - Influent	7.0 - 8.0	6.0 - 9.0
Suspended Solids	20 mg/l	See Contract Note 2
Total Organic Carbon	Average Daily Concentration 9 mg/l	Instantaneous Maximum 25 mg/l
Diisopropyl Methyl Phosphonate	Average Daily Concentration 400 ug/l	Instantaneous Maximum 3,500 ug/l
Chlorides	Average Daily Concentration 500 mg/l	Average Daily Concentratic 1,000 mg/l
Organo-Sulfur Compounds as P-Chlorophenyl Methyl	Average Daily Concentration 200 mg/l	Instantaneous Maximum 1,000 mg/l
Dicyclopentadiene	Average Daily Concentration 500 mg/l	Instantaneous Maximum 3,000 mg/l
Oil & Grease	) SEE CONTRACT NOTES	
Other Organic Chemicals and Solvents	)	
Water Stability	)	

TABLE 2

	Original Pilot Work					FY 1979		FY 1980
	Bog Water	Col #1	Col #2	Col #3	Col #4	Cycle 1	Cycle 2	
Contact Time Min.	15	15	30	45	60	91.2	69.0	94.5
Flow, GPM	0.25	0.25	0.25	0.25	0.25	54.8	72.5	52.9
GPM/ $Ft.^2$	1.83	1.83	1.83	1.83	1.83	0.70	0.92	0.67
Avg. Inf. DIMP, MG/L	420	1,200	2,225	2,388	2,400	1,218	1,024	1,105
Carbon Usage lbs./1,000 gal.	0.9	0.95	1.05	1.10	1.10	1.90	1.29	0.93
Length of Mass Transfer Zone In	9.3	9.7	10.0	10.7	Ins. Data	34.6	Ins. Data	3.2
Unused Capacity in Transfer Zone %	0.505	0.195	0.121	0.119	Ins. Data	0.193	Ins. Data	0.257
% Bed Saturation	96.1	98.4	98.9	98.9	Ins. Data	94.4	Ins. Data	99.3

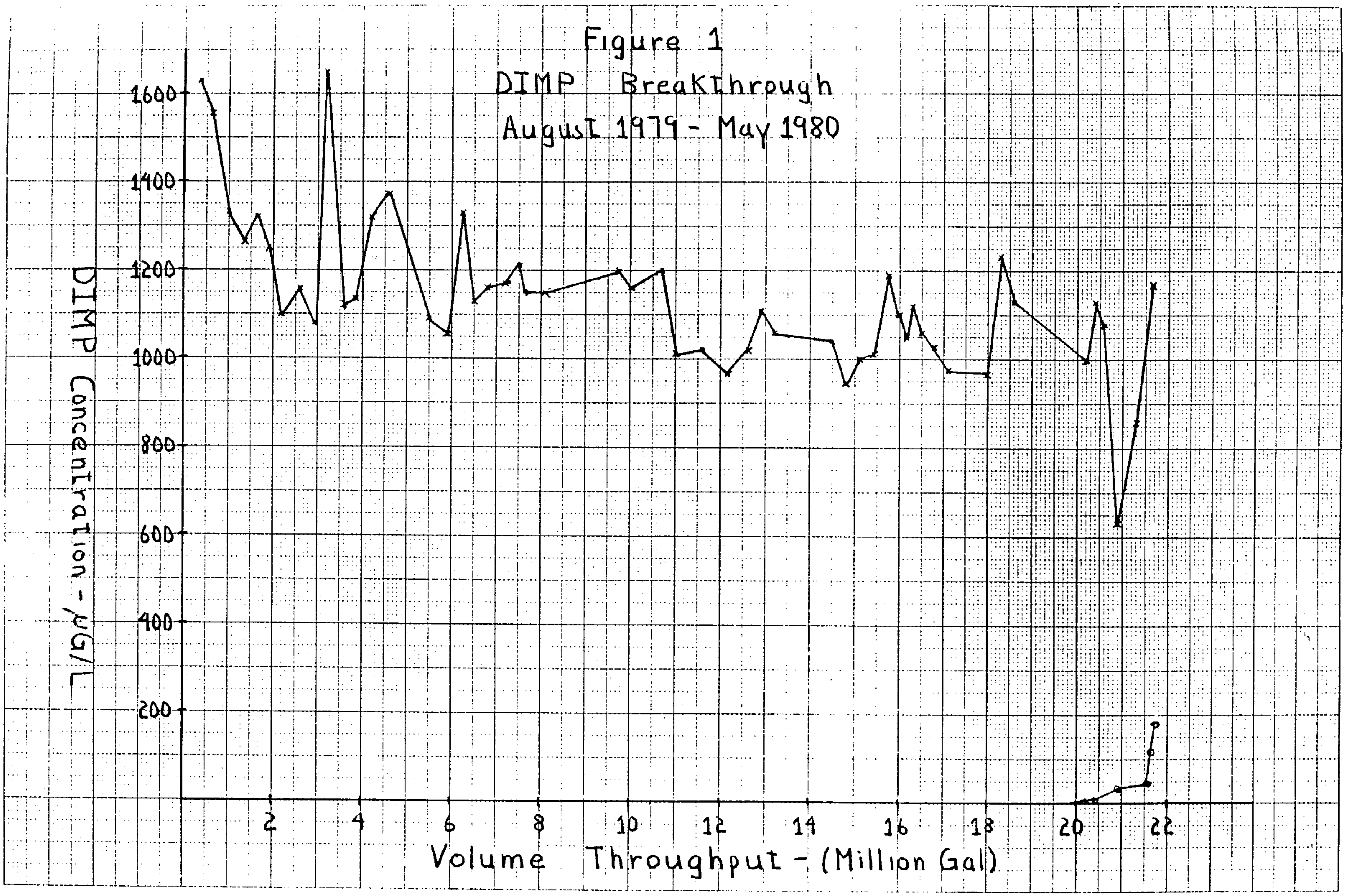
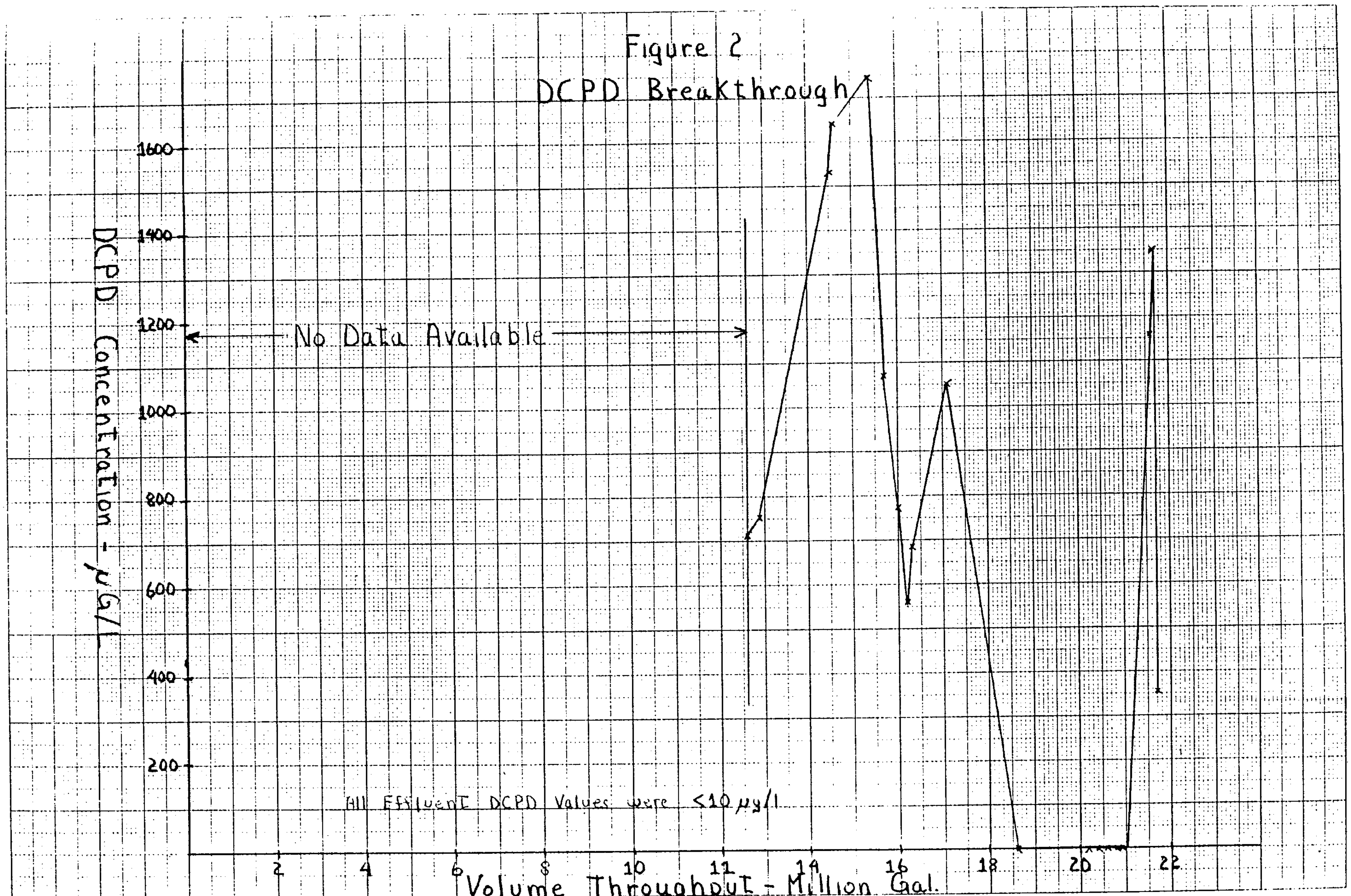


Figure 1
DIMP BreakThrough
AugusT 1979 - May 1980
DIMP Concentration - µG/L
1600
1400
1200
1000
800
600
400
200
2
4
6
8
10
12
14
16
18
20
22
Volume Throughput - (Million Gal)
47 1240



47 1240

K+E 20 X 20 TO THE INCH KEUFFEL & ESSER CO.

Figure 3

Component Breakthrough Curves

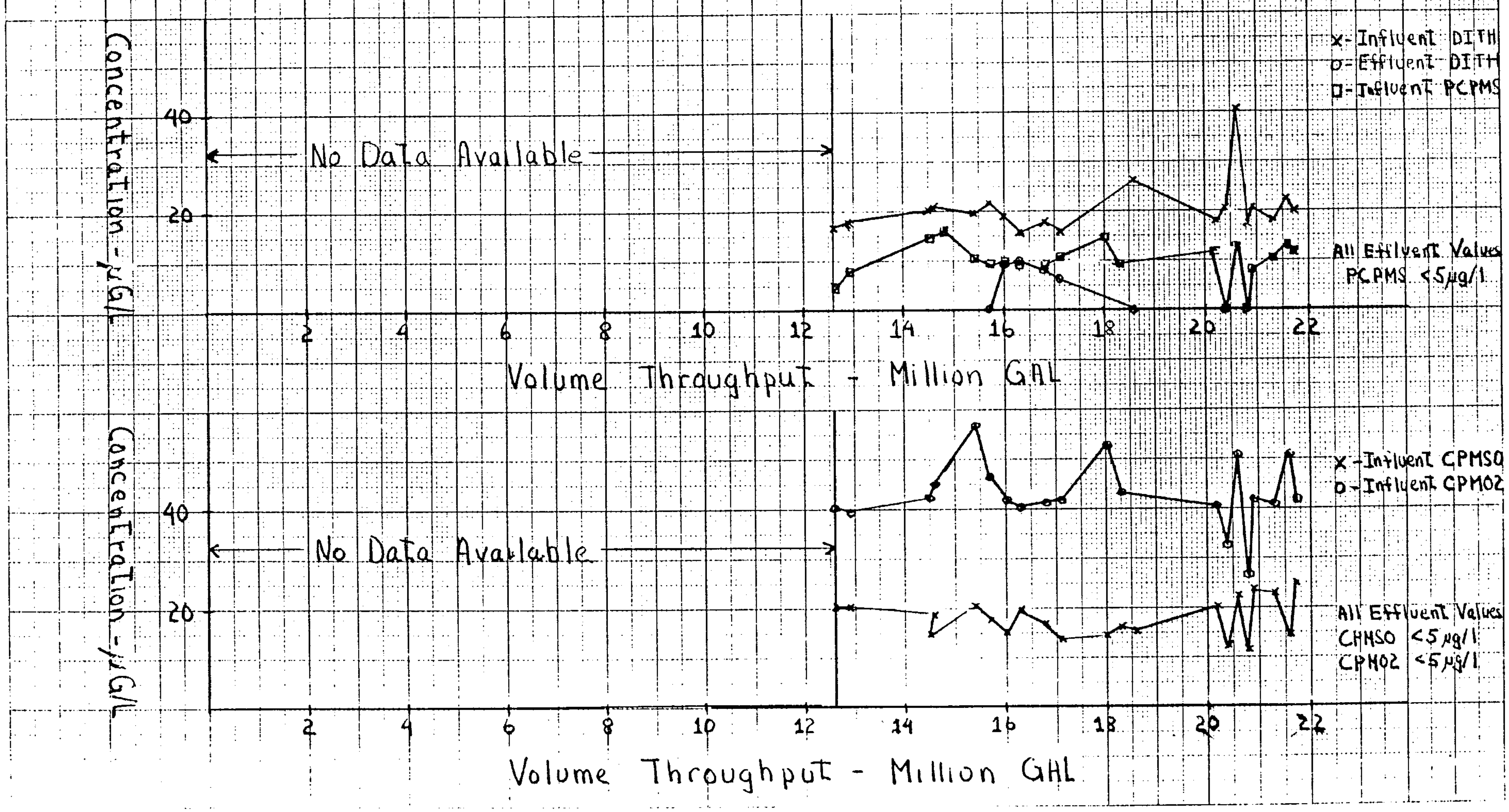


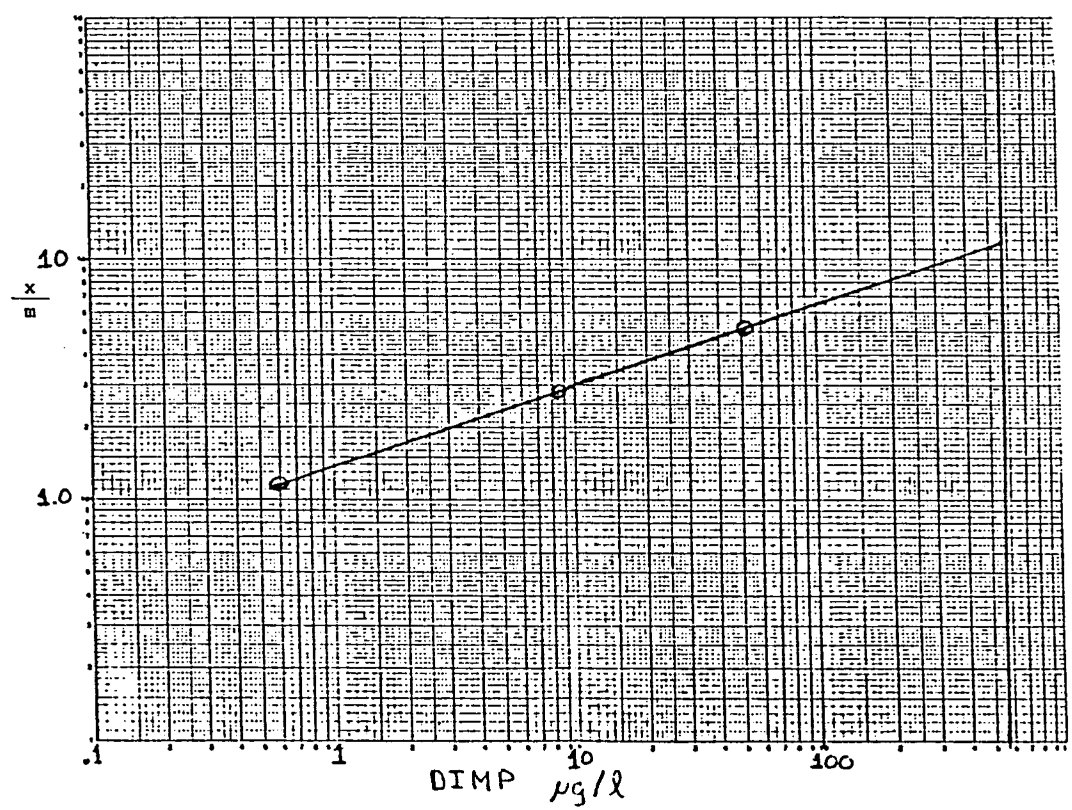
FIGURE 4

CALGON
SUBSIDIARY OF MERCK & CO., INC.

Date	August 6, 1976			pH	8.3
Name of Plant	Rocky Mountain Arsenal	Type Carbon	React	TOC	7 mg/l
Location	Denver, Colorado	Sample Volume	500 ml	SS	< 5 mg/l
Specific Contaminant	DIMP	Pretreatment	Filtration	Color	
Temperature	Ambient	Agitation Time	1 hr.		

Grams Carbon (m)	(c) Remaining ppb	μg	Mg Adsorbed (x)	$\frac{x}{m}$
Control	570	285		
50	51	25.5	259.5	5.19
100	8.5	4.25	280.75	2.81
250	.6	.3	284.7	1.14

By ____________



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2. "Removal of Trace Organics from Groundwater Using Granular Activated Carbon - Preliminary Report", Calgon Corporation, 1/25/77.

3. "Removal of Trace Organics from Groundwater Using Granular Activated Carbon - Annual Technical Review FY 1979", Calgon Corporation, L. E. Hood, July, 1979.

4. Contract No. DAAA05-78-C-0005, Exhibit A, Calgon Corporation/ Department of Army.

5. "Physicochemical Processes for Water Quality Control", W. J. Weber, Wiley Interscience, 1972.

APPENDIX

Calculation of Mass Transfer Zone

All values shown in Table 2 were calculated based on the below analyses. Figure 5 below is an idealized breakthrough curve.

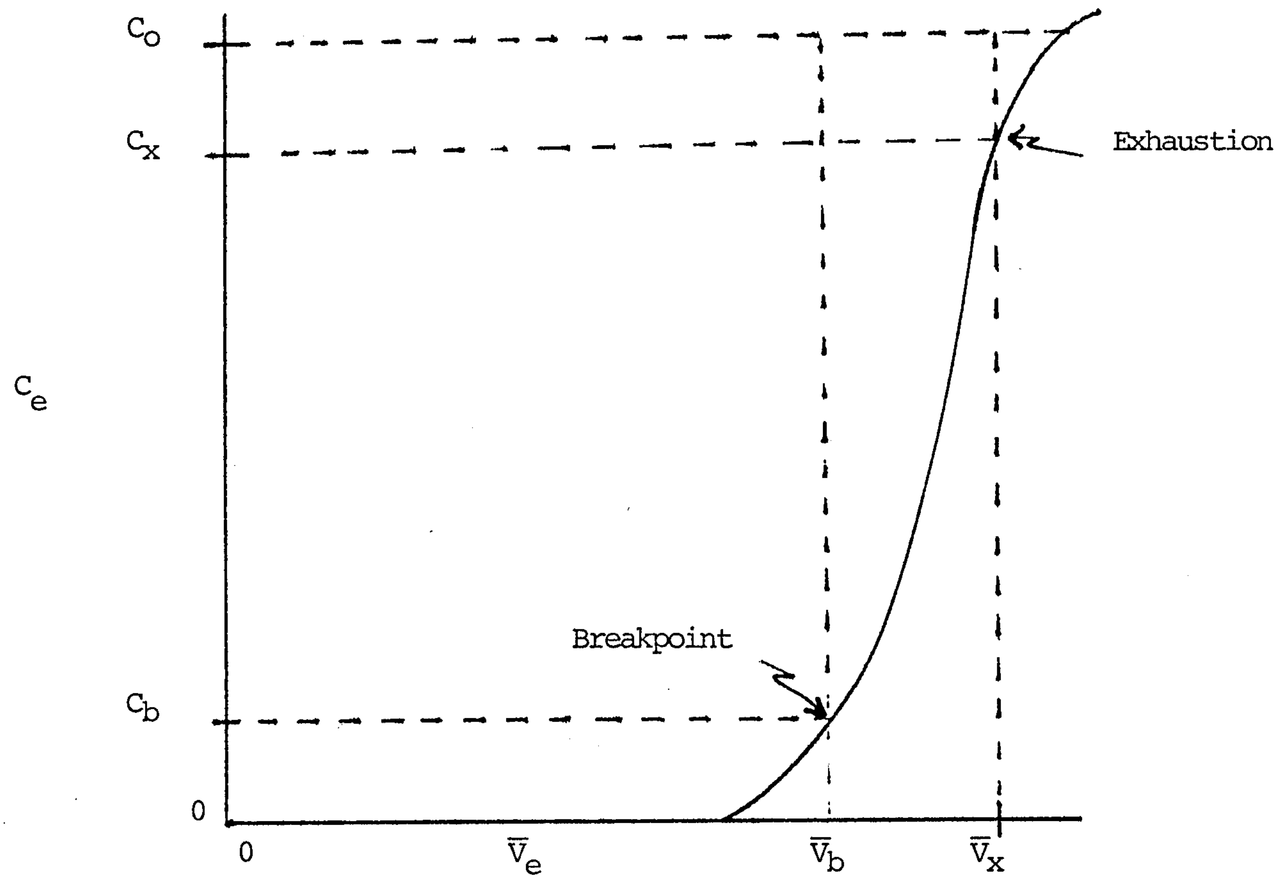

Figure 5

Where: C_o = Avg. Inf. DIMP concentration

C_x = DIMP concentration @ exhaustion = 500 ppb

C_b = DIMP concentration @ breakpoint = 50 ppb

$\overline{V}_b$ = Volume throughput (GAL) @ C_b

$\overline{V}_x$ = Volume throughput (GAL) @ C_x

One can define a fractional capacity, f, of the carbon in the adsorption zone at breakpoint to continue to remove solute from solution as:

$$f = \frac{\int_{V_b}^{V_x} (C_o - C)\, d\,\bar{V}_e}{(\bar{V}_x - \bar{V}_b)\, C_o}$$

Having obtained, f, it can be shown that the length of the mass transfer zone, f, for which the formation time of the zone is very small is given by:

$$\frac{\delta}{D} = \frac{\bar{V}_x - \bar{V}_b}{\bar{V}_b + f\,(\bar{V}_x - \bar{V}_b)}$$

δ = length of transfer zone

D = depth of carbon bed

Additionally, the percent saturation of the bed is defined by:

$$\%\ \text{saturation} = \frac{D + \delta\,(f-1)}{D} \times 100$$