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13. ABSTRACT *(Maximum 200 words)*

THIS DOCUMENT CONSISTS OF A MAJOR REPORT ON INORGANIC CONTAMINANT REMOVAL FROM GROUND WATER. IN THIS PLAN, WES HAS BEEN REQUESTED BY THE OPM-CDIR TO CONDUCT A LITERATURE REVIEW AND PRELIMINARY LABORATORY TREATABILITY STUDIES ON VARIOUS SOURCE WATERS AT RMA. RECOMMENDATION IS THAT THE DETERMINATION OF SUITABLE TREATMENT PROCESSES BE BASED ON BOTH ENGINEERING AND ECONOMIC ANALYSIS AND THAT THE PROCESSES BE COMPATIBLE WITH THE ORGANIC CONTAMINANT TREATMENT PROCESSES UNDER STUDY (ACTIVATED CARBON ADSORPTION AND ULTRAVIOLET/OZONE OXIDATION). THE AMENDMENT TO THE TEST PLAN PRESENTS THE INORGANIC TREATMENT PROCESSES FOUND FROM THE LITERATURE TO BE APPLICABLE TO THE INORGANIC CONTAMINANTS IN RMA GROUND WATER AND OUTLINES THE BENCH SCALE STUDY TO BE CONDUCTED AT WES USING THE POTENTIAL PROCESSES. THE REST OF THE DOCUMENT IS CORRESPONDENCE AND REPORTS ON VARIOUS WATER TREATABILITY.

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TEST PLAN

for

Preliminary Study of Inorganic Contaminant Removal from RMA Groundwater

by

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ITARMS TASK NO: 1.05.21

February 1978

Prepared For: Office, Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, Maryland 21010

INTRODUCTION

1. Rocky Mountain Arsenal (RMA) has been the site of numerous military and non-military activities which have resulted in the introduction of both organic and inorganic contaminants into the groundwater. Previous treatability studies at RMA have concentrated on organic contaminants which were of particular concern to the Colorado State Health Department. Well monitoring at RMA has indicated that certain inorganic contaminants have migrated into the groundwater in concentrations above mandatory Federal and state standards. The potential exists for the migration of these contaminants off the arsenal as the groundwater flows towards the North Platte River.

2. The state has not fully addressed the inorganic contaminant problem associated with groundwater flow from RMA. However, it is anticipated that in the near future, the State of Colorado will request that RMA pursue inorganic contaminant mitigation measures. Such measures could include altering groundwater flow and/or groundwater removal, treatment, and recharge.

3. In order to obtain the data base necessary for the design of inorganic treatment systems, the OPM-CDIR has initiated funding for literature review and bench-scale treatability studies on inorganic contaminants identified in RMA groundwater. MERADCOM has been funded to review fluoride treatment systems and to conduct fluoride treatability studies on groundwater from the northern boundary area of RMA. The object of the MERADCOM study is to develop a design for a fluoride removal system to be used with the Calgon northern boundary pilot system, if needed.

4. The Waterways Experiment Station (WES) has been requested by the OPM-CDIR to conduct a literature review and preliminary laboratory treatability studies on various source waters at RMA. The OPM-CDIR has recommended that the determination of suitable treatment processes be based on both engineering and economic analyses and that the processes be compatible with the organic contaminant treatment processes under study (activated carbon adsorption and ultraviolet/ozone oxidation).

OBJECTIVES

5. The objectives of this study are as follows:

a. To develop an applicability matrix of treatment processes for inorganic contaminants identified in RMA groundwater as being above acceptable concentration limits.

b. To use this matrix in setting up bench-scale inorganic treatability studies on RMA groundwater from Pump Well (PW) 118.

c. To conduct additional laboratory bench-scale inorganic treatability studies on other RMA source waters as identified by the PMO.

d. To provide the information needed (as funds allow) for the design of field-scale units for testing onsite at RMA.

e. To develop a mathematical model of the most applicable process(es) for predictive determinations.

APPROACH

6. This study will be conducted in two phases involving three subtasks. The first phase will involve a literature and information review to determine the inorganic contaminants to be considered (Subtask 1) and any applicable treatment processes (Subtask 2). An applicability matrix of contaminants versus treatment processes will be developed.

7. The second phase of the study will be the laboratory bench-scale treatability studies (Subtask 3) using the treatment processes found to be most applicable. This work will be performed at WES.

METHODOLOGY

Subtask 1 - Identification of Contaminants

8. A number of inorganic groundwater contaminants have been identified from the RMA well monitoring program as being in excess of mandatory or suggested concentration standards. Table 1 presents a list of inorganic contaminants that have been identified in certain RMA wells as being in excess of mandatory or suggested standards. It should be noted that not all of the contaminants have been found in excess in every well. These contaminants will provide a starting point for the applicability study. A review of existing well monitoring data will be made to determine other inorganic contaminants that should be addressed in the study.

Subtask 2 - Applicability Study

9. An applicability study on inorganic treatment processes for the contaminants of concern will be conducted incorporating available literature and data provided by MERADCOM. The information obtained will be

discussed in a report which will be in the form of an amendment to this test plan. Also included will be a summary applicability matrix for ease in identifying potential treatment processes. The inorganic treatment processes will be reviewed on the basis of both engineering and economic factors. Evaluations of treatment processes will include such factors as the potential for multi-contaminant removal, removal potential versus contaminant concentration, and overall compatability with an organic/inorganic treatment system.

10. The review and evaluation of inorganic treatment processes will provide a basis for development of a laboratory bench-scale treatability scheme which will be presented in the test plan amendment for review by OPM-CDIR. Included will be recommendations and a detailed outline for a laboratory treatability program to provide both verification of feasibility and design information for high potential inorganic treatability processes.

Subtask 3 - Bench-Scale Study

11. Upon approval by OPM-CDIR, bench-scale treatability studies will be initiated at WES. Treatment studies will be conducted on RMA source water shipped to WES. Studies will begin on water from PW 118 as an extension of precipitation pretreatment work initiated in the field-scale UV/ozone system study.* Work can then proceed to other source waters as directed by OPM-CDIR providing funds are available. Details of the bench-scale treatability study will be included in the amendment to this test plan.

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*See "Test Plan for Field-Scale System Study (Ultraviolet/Ozone Process)" by Douglas W. Thompson, dated January 1978.

SCHEDULING

12. A time schedule for the inorganic treatment study is presented as Figure 1. Test plan development and review is scheduled for completion by 1 April 1978. The applicability study and development of the amendment to this test plan will be initiated in February 1978 and should be completed by 21 April 1978. Laboratory bench-scale treatability studies will begin in May 1978 and continue through the end of FY 78. A summary report on work completed in FY 78 is due 1 October 1978.

SAFETY

13. All laboratories and personnel will be periodically checked to determine that proper safety equipment is available and that proper operating procedures are being used.

Table 1

Inorganic Contaminants Identified at RMA With State of Colorado Drinking Water Aquifer Pollution Limits

Mandatory Limits (mg/ℓ)

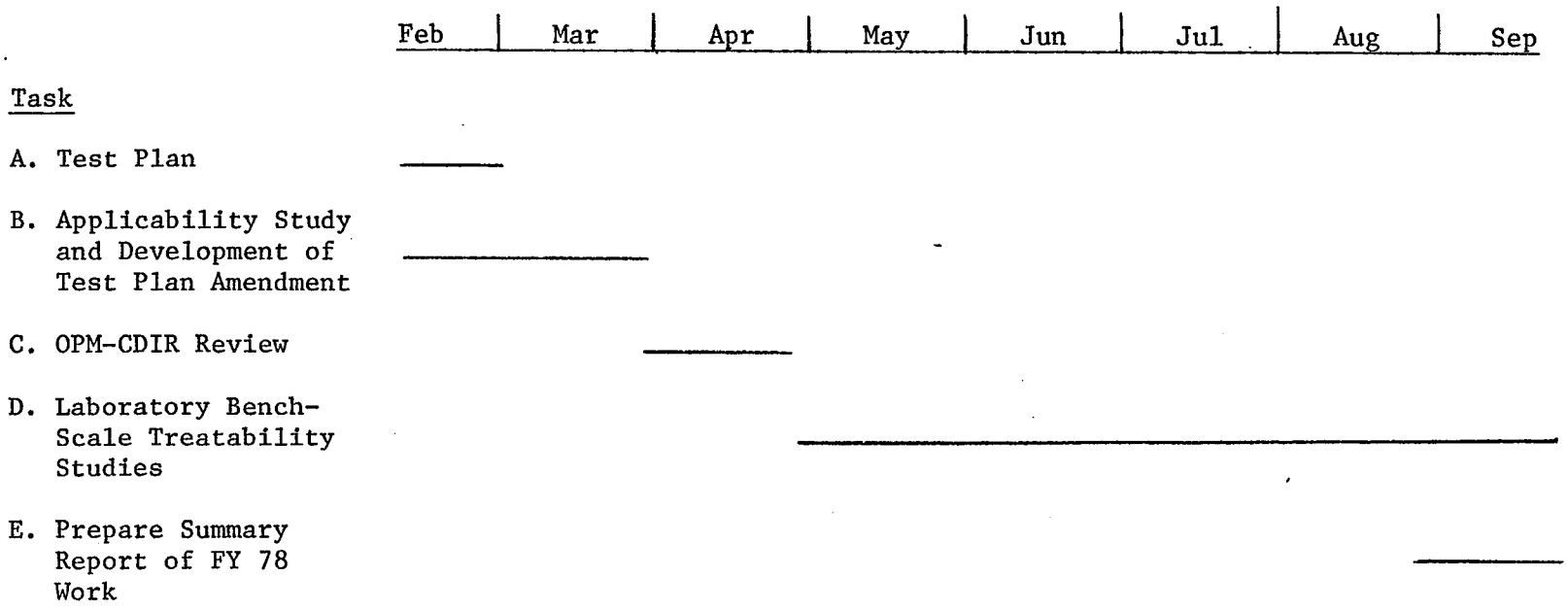
Parameter	Limit
Arsenic	0.05
Fluoride	2.4
Mercury	0.002
Nitrate (as N)	10

Suggested Limits (mg/ℓ)

Parameter	Limit
Chloride	250
Iron	0.3
Manganese	0.05
Sodium	250
Sulfate	250

Figure 1

Inorganic Treatment Study Schedule



81295R11
ORIGINAL

JULY 1978

AMENDMENT

TO

TEST PLAN

for

Preliminary Study of Inorganic Contaminant Removal from RMA Groundwater

Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

FILE COPY

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WORKING DRAFT

ITARMS TASK NO: 1.05.21

July 1978

Prepared For: Office, Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, Maryland 21010

INTRODUCTION

1. The Waterways Experiment Station (WES) has been requested by the Office of the Project Manager for Chemical Demilitarization and Installation Restoration (OPM-CDIR) to conduct a literature review and preliminary laboratory treatability studies on various source waters at RMA. The OPM-CDIR has recommended that the determination of suitable treatment processes be based on both engineering and economic analyses and that the processes be compatible with the organic contaminant treatment processes under study (activated carbon adsorption and ultraviolet/ozone oxidation).

2. The original test plan* presented the objectives, approach, methodology, and scheduling for the task. This amendment presents those inorganic treatment processes found from the literature to be applicable to the inorganic contaminants in RMA groundwater and outlines the bench-scale study to be conducted at WES using the potential processes.

LITERATURE REVIEW

3. Table 1 presents a list of inorganic contaminants that have been identified in certain RMA wells as being in excess of mandatory or suggested standards. A literature review was conducted with special emphasis placed on those contaminants found to be above mandatory limits of the State of Colorado. A summary of the information found follows.

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* See "Test Plan for Preliminary Study of Inorganic Contaminant Removal from RMA Groundwater" by Douglas W. Thompson, dated February 1978.

Table 1

Inorganic Contaminants Identified at RMA With State of Colorado Drinking Water Aquifer Pollution Limits

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Parameter	Limit
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Manganese	0.05
Sodium	250
Sulfate	250

Fluoride Removal

4. Most of the studies on defluoridation of water were done in the early 1930s with emphasis on the defluoridation of drinking water. These investigations led to the use of three methods of defluoridation that have proven practicable. Two involve use of activated alumina or bone char in the form of an insoluble granular media which removes the fluorides as water percolates through them. The media are periodically regenerated by chemical treatment when they become saturated. In the third method, magnesium is added to water in the form of dolomitic lime. It is removed, after absorbing the fluorides, by passing the water through settling basins and filters and is discarded.[1] These and various other methods of removing fluorides are discussed further.

Calcium phosphates

5. The chemical theory of the removal of fluorides by beds packed with calcium phosphates is based on the anion exchange properties of apatites. The carbonate radical in the apatite, $nCa_3(PO_4).CaCO_3$, is replaced by the fluorides in the water, forming an insoluble fluorapatite. In the regeneration of the material with sodium hydroxide the fluorapatite becomes a hydroxyapatite and the fluorides are removed in the form of soluble sodium fluoride. The hydroxyapatite subsequently becomes available as an exchange material by the replacement of its hydroxy radical with fluoride.

6. Bone char, the principal constituent of which is tricalcium phosphate, has been used in contact filters. It is reported to have an exchange capacity of 450 gr/cu. ft. with regeneration with caustic soda

and carbonic acid.[2] Sulfuric acid has also proved to be effective as a regenerant.[1]

7. One method of preparing bone for use as a fluoride-removing agent involves boiling to remove the fat and most of the protein. It is then crushed and boiled in a solution of sodium hydroxide. The caustic is removed by thorough washing and finally is neutralized with hydrochloric acid. The material is again washed and then dried and graded.[1]

8. A porous, granular type of tricalcium phosphate has been developed for use in contact filters. The exchange capacity has been determined to be 300 gr/cu ft.[3] Increases in sulfate and hardness of water decreases this capacity[4,3] Each 100 ppm increase in sulfates decreases this capacity by approximately 3%. The iron content also affects the system. Iron must be reduced to less than 0.10 mg/1 to prevent clogging. The particle size of the material also influences capacity and flow rate. In a water treatment plant using this process with an influent content of 2-14 mg/1 (average 8.3) the effluent concentration averaged 0.6 mg/1.

9. Regeneration is accomplished by washing with a 1% solution of sodium hydroxide (1 lb./cu.ft.) followed by a 0.7% by weight hydrochloric acid solution for neutralizing. However, a loss of 2.5 to 3% of tricalcium phosphate occurs per regeneration using hydrochloric acid[4]. Behrman and Gustafson[5] discovered that carbon dioxide used as a regenerant did not cause a loss of material, increased the useful life of the material and was not corrosive as is hydrochloric acid.

10. Goodwin and Litton[6] report the exchange capacity of calcium phosphate to be 275 gr./cu.ft. A commercial pilot plant using a calcium

phosphate bed reduced the fluoride concentration from 5 ppm to 0.42 ppm. The rated exchange capacity of this material was 358 gr./cu.ft.; actual exchange capacity for this plant was 346 gr./cu.ft. Tests indicated optimum flow rate to be 1.5 gal./min. for a 1.3 cu. ft. bed. Each regeneration required approximately 1 lb. caustic per cu. ft. of material. Approximately 0.65 lb. of phosphate was lost after fifty regenerations (83,700 gallons of water).

11. An alternate method to the use of a tricalcium phosphate contact tower is to remove fluoride by precipitating tricalcium phosphate in water by adding lime and then phosphoric acid to a pH of 7 to 7.5. This gives a mixture of hydroxyapatite ($3CaP_2O_8 \cdot Ca(OH)_2$) and tricalcium phosphate ($Ca_2P_2O_8 \cdot H_2O$). When tricalcium phosphate is precipitated in water by addition of phosphoric acid and lime a gelatinous floc is formed and fluoride removal is accomplished by adsorption and/or formation of a complex compound-fluorapatite. When the lime and acid are added so that the weight of the tricalcium phosphate is 200 times the fluoride present then essentially all the fluoride will be removed. One kg of tricalcium phosphate removes 6.05 gm of fluoride.[4]

Aluminum compounds

12. Aluminum sulfate and other aluminum salts have been used in combination with insoluble compounds in contact beds or as constituents of floc. The fluorides are removed by the formation of an aluminum fluoride complex or by adsorption on the floc.

13. Boruff[7] added hydrous aluminum sulfate to water, mixed for 30 min., allowed it to stand for 18-24 hours, and then removed the floc by

filtration. He reported increased dosage of aluminum sulfate gave increased removal of fluorides. A reduction from 2-3 mg/1 to 1 mg/1 required 2 gr./gal. and from 5 to 1 mg/1 required 10 gr./gal. (171 mg/1). He also noted good mixing, good flocculation, and pH control (optimum - 6.25-7.5) were needed for maximum removal. Fink and Lindsay[8] reported that the efficiency and capacity are dependent on the hydrogen ion concentration. As alkalinity increases capacity decreases. Boruff, Buswell and Upton[9] reported that "the cation associated with the fluoride ion in water greatly affects the completeness of its removal by alum floc." High concentrations of aluminum sulfate are needed for removal of even low concentrations of fluorides. For example, four ppm fluorides requires from 300 to 500 ppm of aluminum sulfate.[3] The varying amounts of aluminum sulfate are due to the differences in pH, flow rate, contact time and other parameters of the treatment processes. In one investigation 891 ppm aluminum sulfate was needed to reduce the fluoride content from 6.0 ppm to 1 ppm.[3] In another experiment 860 ppm aluminum sulfate reduced the fluoride content from 8.5 to 1 ppm.[3]

14. Contact beds have been prepared by reacting a number of compounds- sodium silicate, barium chloride, sodium phosphate, ferrous sulfate, titanium chloride - with an excess of aluminum ions thereby forming an insoluble material having fluoride-removing capacities. Another method utilizing aluminum salts involves pickling base exchange materials (natural or synthetic zeolites) or naturally adsorptive materials in aluminum salt solutions. In one study sawdust was used as the adsorptive material. Because of the long time (5 hours or more) required for the pickling process and the lower exchange capacities (compared to activated aluminum),

these methods have limited use.[3]

15. Dehydrated aluminum oxide (calcined aluminum, activated alumina) has been used in contact beds in various studies. In these investigations different exchange capacities have been reported - 416, 505, 514, 600 gr./cu.ft.[2] In the study by Savinelli and Black, regeneration with aluminum sulfate yielded a much higher exchange capacity (2000 gr./cu.ft.) than the other methods of regeneration. They also reported that the length of regeneration time and the alkalinity influenced the exchange capacity. Longer regeneration times up to 4 hours increased exchange capacities but beyond 4 hours there was no significant increase in the exchange capacity. As the alkalinity increased the capacity decreased. At the optimum pH of 5.6 the exchange capacity was 3400 gr./cu. ft.

Ion exchange processes

16. The ion exchange process works on the principle of exchange of an anion (such as chloride) with fluoride. This principle is also used in calcium phosphate removal of fluorides. One method utilized a complex metal chloride silicate formed from barium or ferric chloride and silicic acid.[3] Another method uses an organic resinious anion exchange material made from various diaminobenzenes or phenols and formaldehydes. The material is first conditioned with a 4% solution of soda ash, neutralized with a dilute acid, washed and soaked with a 4% solution of aluminum sulfate. The exchange capacity is 1240 gr./cu.ft.[3] However, its capacity was found to be derived entirely from the precipitated aluminum oxide formed in the column during alum regeneration and this floc restricted water flow.

17. Thompson and McGarvey[11] experimented with a strongly basic anion exchange resin in the chloride form. It behaves as a solid caustic with hydroxyl ions in solution and will absorb negatively charged ions. Its effectiveness depends on the concentration of fluorides and ratio of fluorides to total anions in the raw water. The higher the ratio, the greater its effectiveness.

Lime

18. Fluoride reduction with the use of lime has been observed and has been determined to be a function of the amount of magnesium removed. Between 6-65 ppm of magnesium must be removed to reduce the fluoride content by 1 ppm.[3,10] Employment of this method involves addition of magnesium in the form of dolomitic lime or activated magnesia.

19. Fluoride wastes are common to electronic tube, glass, nuclear fuel, aluminum and steel, metal finishing and electroplating and fertilizer industries. Westinghouse in its electronic tube manufacturing plants adds lime and a polyelectrolyte coagulant to their concentrated fluoride wastes. Fluoride is precipitated as calcium fluoride and is allowed to settle out in successive settling tanks. The clear liquid in the last tank is then diluted to bring the fluoride concentration from 10-30 ppm to drinking water standards. Periodically, the tanks are cleaned and the sludge hauled to a landfill. The feasibility of converting fluoride sludges to cryolite and calcium fluoride are being investigated.[12,13]

20. Paulson[14] reports that the most widely-used method for removal of fluorides from industrial wastewaters containing high fluoride concentrations involved precipitation by the addition of a soluble calcium

salt. Stoichemetrically 1.06 lbs. of calcium removes 1 lb. of fluorides. The required pH for optimum fluoride removal is 8-9 or greater than 12. Reaction time varies from 30 min. to 24 hours depending on the type of wastewater treated. This method reduces the fluoride concentration to 12-30 mg/l. For further reduction, other defluoridation techniques must be employed.

Absorbents

21. Absorbent material such as silica gel, activated carbon, Fuller's earths, bentonites and diatomacious earth have been found to reduce fluoride concentrations in varying amounts but all require very low pH (less than 3) or excessive quantities of material.[2,3] McKee and Johnston[15] reported low concentrations of fluoride are removed by activated carbon. The removal efficiency is a function of pH and the percent carbon in the filter. At a pH greater than 4 removal efficiencies were less than 50%. At a pH less than 3, removal efficiencies approached 100%.

Other methods

22. Other methods which have been studied include sodium aluminate and ferric salts used as coagulants and hydrated metallic oxides-ferric oxide, chromium borate, mixed oxides or iron and manganese, bauxite and bog iron ore-used in filtration. Zeolite has also been used in contact filters. Of these the most efficient is probably ferric oxide.[3]

Mercury Removal

23. Because metals exist in wastewater in many forms, soluble, insoluble, inorganic, metal organic, reduced, oxidized, free metal, precipitated, adsorbed, and complexed, treatment processes for metals removal

must be selected to remove the existing form of the metal, or the metal must be converted to a suitable form compatible with the removal process. In general, to be removed from wastewater, metals must be precipitated or otherwise attached to an insoluble form through adsorption or ion exchange.[16]

Chemical precipitation

24. Many heavy metals exhibit low solubility as the metal sulfide so that removal by sulfide precipitation using inorganic sulfide, hydrogen sulfide gas, or sulfide generated by anaerobic organic activity has been used for mercury removal from chloralkali plants and arsenic removal in the phosphoric acid industry. The major problem is the presence of excess sulfide ions in the effluent. In many cases this sulfide must be destroyed (usually by aeration) before discharged to prevent sulfide toxicity.[17] Because sulfide precipitation has not been widely used, there is not much data on operation or effluent quality.

25. Removal of mercury by conventional water treatment techniques include coagulation, clarification and filtration processes. Several coagulants have been tested by various investigators. Ferric chloride was found to be the most effective; at a 40 mg/l dose (pH 6.2 and influent concentration of 0.05 mg/l) 98% removal was obtained.[18] Ferric sulfate at a 20-30 mg/l dose gave 40-60% removal.[19] Lime at a 600 mg/l dose (pH 11.5, influent mercury concentration 0.5 mg/l) gave 70% removal.[16] Alum was found to be dependent on turbidity-10% removal at 3 Jtu and 60% removal at 100 Jtu.[19] As the turbidity of the raw water increased, mercury removal increased, indicating removal was due to mercury adsorbing onto suspended matter and being removed with the suspended matter.

26. Utilizing a water softening process, 60-80% removal of inorganic mercury by magnesium hydroxide at a pH of 10.6-11 was obtained.[19] Removal was thought to be related to mercury adsorption on the magnesium hydroxide floc. Methyl mercury was not removed by softening. At a lower pH (9.4) inorganic mercury removal was increased from 30 to 50% when iron coagulation was used.

27. A method for removing ionic mercury from wastewaters by co-precipitation with a polyelectrolyte complex of two oppositely charged polymers has been developed by Wing, et al.[20] One of the polymers, starch xanthate, contains functional groups capable of forming insoluble metal complexes. Poly vinylbenzyltrimethylammonium chloride (PVBTMAC) was selected as a cationic coprecipitant to aid in a more complete removal of metal ions.

28. Wing, et al[20] reports that removal of most metals with starch xanthate-PVBTMAC far exceeds that which can be attained by bases alone. Removal efficiencies are given in Table 2 below.

Table 2

Mercury Removal by Chemical Precipitation

Chemical	initial conc. (µg/l)	residual conc. (µg/l)
Xan-PVBTMAC	100,000	3.8
NaOH (pH 7)	100,000	10,000
NaOH (pH 9)	100,000	8,140

Wing et al[20] stated this process has other inherent advantages. They are:

a. Recovery is simple because treating the complex with mild acid releases the metal.

b. The volume of sludge is small compared to that from lime treatment.

c. The physical nature of the sludge is not gelatinous and the floc settles faster and can be removed easier.

d. Suspended solids need not be removed before treatment.

e. Effective over a pH range of 3 to 11.

f. Only a slight excess of reagent is necessary.

Wing et al[20] also reported that anionic polymers containing thiol groups may be effective in removing mercury since mercury forms an insoluble sulfide salt.

Ion exchange

29. Cheremisinoff and Habib[21] describe an ion exchange process using a strong base anion exchange resin produced by using a tertiary alkyl group. The wastewater is first adjusted to a pH 5-7 and then chlorinated. The metallic mercury in colloidal form is oxidized by chlorination and the water is then filtered through activated carbon to remove excess chlorine since the resins are sensitive to oxidizers. Mercury is reduced to 0.1 mg/l after passing through the ion exchangers and is further reduced to a few parts per billion after passing through an absorption tower. The absorber resin is not regenerable but the ion exchange resin is using a sulfide regenerant and it yields a rich eluate from which mercury may be recovered via chemical reduction.

contact time of only 6 min., APDC chelation of the mercury at pH 10 produced an effluent of less than 5 ppb. Precipitation-filtration was observed when APDC chelation of the mercury was employed.

34. Sulfurizing agents such as CS_2 improved mercury removals by activated carbon. In one study carbon was soaked with CS_2 and dried prior to adsorption. Water with a mercury concentration of 1 ppm (pH 10) was treated and resulted in a 50-fold increase of carbon capacity to 7.0 mg Hg removed/g (0.007 lb./lb.) carbon in the isotherm tests. In addition, removal was mostly independent of mercury concentration.

Other methods

35. Two processes, Osaka Soda Process by Crawford and Russell and the Ventron System, have been marketed and claim acceptable effluent reductions. In the Ventron System sodium borohydride ($NaBH_4$) is used as a reducing agent and the reduced mercury is removed through a cyclone clarifier yielding an effluent concentration below 10 ppb. The Osaka Soda Process oxidizes the mercury by chlorination followed by filtration which reduces the mercury concentration to 5 ppm. Ion exchange then reduces the concentration to 1/40th and an 'MR' resin gives a final effluent concentration of 2-5 ppb. The mercury can be recovered from the ion exchange by reduction with sodium amalgam while the 'MR' resin is discarded.

36. Other methods found to remove mercury are: charcoal activated with dithizone sulfurizing agent; mercapto-cellulose filter; a patented system designed for metals removal in the fabric dyeing industry which uses a prepared belt of peat', and sorption of mercury on waste wool fibers or chicken feathers.[17]

Arsenic Removal

Chemical precipitation

37. The same conventional water treatment processes used to remove mercury also remove arsenic. Among the various coagulants that have been tested ferric sulfate achieved highest removals, 90%.[16] Ferric chloride at a dose of 30 mg/l gave 82% removal.[23] Removal of the arsenic is via chemical binding with the iron ion rather than physical adsorption. However, coagulation alone did not reduce the arsenic content below World Health Organization standards. By oxidation with 15 mg/l chlorine and then coagulating with 50 mg/l of $FeCl_3$ only a trace of arsenic remained in the water. The chlorine appears to oxidize the $FeCl_3$ to a higher valence state so that chemical interchange between iron ion and arsenic occurs.[23] Other coagulants tested were aluminum sulfate-32% removal,[23] lime-20%[23] to 76-80%,[16] ferrous sulfate-24%.[23] A pilot plant was built using oxidation with chlorine, coagulation with ferric chloride and sand filtration with regeneration by sodium hydroxide. A natural arsenic water (1.72 mg/l) treated with 20 mg/l Cl_2 and 60 mg/l $FeCl_3$ followed by sedimentation and filtration produced a finished water arsenic free. The system was actively efficient for 2 months before sand regeneration with sodium hydroxide.[23]

Adsorption

38. Gulledge and O'Connor[24] tested arsenic removal from water by adsorption on aluminum and ferric hydroxides and reported the main variables affecting the adsorption process were pH and coagulant dosage. With increasing coagulant dosage there was a consistent increase in the removal

of arsenic (V) at all pH levels (see Table 3). A decrease in the adsorption of arsenic at pH 8 was noted on both aluminum hydroxide and ferric hydroxide. This phenomena was postulated to be the result of the change in the ionic form of the arsenic (V) from $H_2AsO_4^-$ to $HAsO_2^{-2}$. Alternately at the higher pH, the hydroxyl ion may begin to compete for the exchange site on the ferric and aluminum hydroxide precipitates (Table 3).

Table 3

Arsenic Removal by Ferric and Aluminum Hydroxides

Ferric Hydroxide			Aluminum Hydroxide		
pH	Dose (mg/1)	% removal	pH	Dose (mg/1)	% removal
5	10	96.5	5	10	59.0
5	50	99.0	5	50	91.7
6	10	97.1	6	10	74.5
6	50	98.4	6	50	93.6
7.5	10	94.0	7	10	64.5
7.5	50	97.5	7	50	92.0
8	10	88.6	8	10	18.5
8	50	96.5	8	50	65.5

Initial concentration of arsenic was .05 mg/1.

39. Nilsson[25] reported arsenic removal using aluminum sulfate and calcium hydroxide (Table 4).

Table 4

Arsenic Removal by Chemical Precipitation

Coagulant	Arsenic Concentration (ppm)	
	Influent	Effluent
aluminum sulfate	4.2	1.2-1.7
$Ca(OH)_2$	4.2	0.1-2.0

40. Bellack[26] while investigating fluoride removal with activated alumina noticed arsenic removal was also accomplished. Based on data from a pilot plant with a flow rate of 2.5 to 3 gpm the arsenic could be reduced from 0.06 mg/l to 0.005-.007 mg/l. When the effluent concentration reached 0.01 mg/l the column was regenerated using 4 bed volumes of 1% sodium hydroxide solution followed by 8 bed volumes of raw water then 1 bed volume of 0.05 N sulfuric acid and finally 1 bed volume of raw water. Bellack found that by reducing the pH of the water from 9.3 to 7.1 and increasing the caustic volume the removal efficiency increased. Since the removal is a cyclic process the effluent concentration will increase with time. When the effluent reached an arsenic concentration of 0.01 ppm regeneration procedures were instituted. The arsenic content was reduced from 0.106 ppm to an average of 0.006 ppm for the total amount of water treated before regeneration. The fluoride concentration of the effluent was found to be 0.4 ppm.

Nitrate Removal

41. Most of the work conducted in the past on nitrate removal has been associated with overall nitrogen removal from domestic wastewater. The principal technique used for nitrate removal has been biological denitrification where nitrate is reduced to nitrogen gas by heterotrophic organisms utilizing organic sources of carbon for energy and growth. The species of organisms responsible for denitrification include Pseudomonas, Achromobacter, Bacillus, and Micrococcus.[27]

Another nitrate removal technique which has received limited use is ion exchange. This technique is still considered to be under development.

Biological denitrification

42. Most of the work conducted on biological denitrification has indicated a need for an external source of carbon for the denitrifying organisms because most of the available carbon has been oxidized in previous treatment processes. Methanol has received wide application as a supplementary source of carbon. A number of relationships have been developed for estimating methanol requirements.[28,29,30]

43. English[31] investigated the effects of temperature and dissolved oxygen on methanol requirements for effective denitrification using two types of continuous flow reactors, packed column and suspended growth. The study indicated that the optimum methanol/nitrate nitrogen ratio for both reactors was between 2/1 and 3/1 at approximately 25°C. Using these ratios, a removal efficiency in excess of 90% was obtained. The study concluded that, based on retention time only, the packed column reactor (15 minutes retention) is a more efficient denitrifying unit than the suspended growth reactor (210 minutes retention).

44. Smith, et al[32] obtained 90% denitrification in pilot studies using packed columns with a surface loading of 7.0 gpm/ft^2 at an average temperature of 27°C. A contact time of 5 minutes was used for coarse sand and a contact time of 15 minutes was used for 3/4 inch stones. The optimum methanol/nitrate ratio was found to be 2.5/1.

45. In another study[33] using larger media, 1 to 2 inch aggregates, in an upflow process, nitrate reduction exceeding 90% was achieved using a contact time of from 1 to 2 hours. The optimum methanol/nitrate ratio was found to be 3/1.

Ion exchange

46. Information on the use of ion exchange for nitrate removal is limited. A nitrate specific ion exchange resin was reported developed which used selected primary amines in polystyrene.[34] Regeneration was achieved using 1N HCl. The report indicated that nitrate was adsorbed quantitively from feed solutions containing five times as much chloride ions as nitrate ions. High concentrations of other anions in a wastewater may severely limit the adsorbtive capacity of the resin with respect to nitrate ions.

Other Contaminants

47. Of the contaminants listed with suggested limits in Table 1, iron and manganese are the only two that are generally considered economically feasible to remove. The most popular removal techniques are oxidation and chemical precipitation. The other contaminants generally require more expensive removal techniques such as reverse osmosis, electrodialysis, distillation, or freezing. These processes are total removal processes and have not generally proven economically feasible for high volume treatment.

Results of Literature Review

48. Certain candidate removal processes for fluoride, mercury, arsenic, and nitrate are listed in Tables 5, 6, 7, and 8 respectively. Comments as to the advantages and disadvantages of each process are included. Table 9 compares relative efficiencies of the processes considered to be most likely candidates for fluoride, mercury, and arsenic. Nitrate is not included since it will probably require a separate treatment process if concentrations above the mandatory limit are found in the effluent from the total treatment system.

49. Based on the literature review, activated alumina or tricalcium phosphate treatment appear to be the most feasible processes presently proven for fluoride removal. Activated alumina has also been shown to efficiently remove arsenic. Tricalcium phosphate efficiently removes fluoride and may possibly remove mercury since mercury forms slightly insoluble complexes with phosphate, but will not likely be effective in removing arsenic. Lime is a possible candidate for removing high concentrations of fluoride, mercury, and arsenic, but generally will not result in concentrations below the mandatory limits. Activated carbon is not recommended as a pretreatment process since a pH of 3 must be obtained to promote high removal efficiencies for both fluoride and mercury. This low pH would not be advantageous to the UV/ozone system. A carbon system generally would not effect arsenic and would require neutralization of the effluent. Polyelectrolytes such as xanthate-PVBTMAC are highly efficient for mercury and other metals and could provide some fluoride removal by adsorption on the surface of a resulting precipitate.

Table 5

Fluoride Removal Efficiencies

Treatment	Efficiency	Comments
Calcium Precipitation (Lime or $CaCl_2$)	F	Minimum effluent concentrations generally above standard. Requires neutralization of water.
Alum Precipitation	F	High volume of sludge produced.
Activated Alumina	E	Disposal of regenerant Capacity is much higher than for other processes when regenerated with alum.
Ion Exchange (Anionic)	E	Disposal of regenerant Interferances by chlorides for certain resins.
Calcium Phosphate	E	May be effective in mercury removal Capacity decreased with high concentrations of sulfates
Tricalcium Phosphate	E	May be effective in mercury removal Capacity decreased with high concentrations of sulfates
Bone Char	E	May be effective in mercury removal Capacity decreased with high concentrations of sulfates
Reverse Osmosis	E	Total removal process therefore not economically feasible because of high total dissolved solids
Electrodialysis	E	Total removal process therefore not economically feasible because of high total dissolved solids
Ultrafiltration	E	Total removal process therefore not economically feasible because of high total dissolved solids
Distillation	E	Not economically feasible for high volume treatment
Freezing	E	Not economically feasible for high volume treatment

E = excellent F = fair P = poor

Table 6

Mercury Removal Efficiencies

Treatment	Efficiency	Comments
Activated Carbon	P	Low pH required
Ion Exchange (Cationic)	E	May require pH adjustment Regenerant disposal required
Chemical precipitation		Does not remove methyl mercury Must be proceeded by oxidation
Ferric Sulfate	F	May increase sulfate concentrations
Alum	E	Turbidity dependent
Lime	E	High pH required
Magnesium Hydroxide	F	High pH required
Ferric Chloride	E	May increase chloride concentrations
Polyelectrolytes	E	Starch xanthate-PVBTMAC far exceeds removal by bases alone Effective over wide pH ranges Low volume of sludge produced
Hydrogen Sulfide	E	Traces of sulfides in effluent
Reverse Osmosis	E	Total removal process therefore not economically feasible because of high total dissolved solids
Electrodialysis	E	Total removal process therefore not economically feasible because of high total dissolved solids
Ultrafiltration	E	Total removal process therefore not economically feasible because of high total dissolved solids
Distillation	E	Not economically feasible for high volume treatment
Freezing	E	Not economically feasible for high volume treatment

E = excellent F = fair P = poor

Table 7

Arsenic Removal Efficiencies

Treatment	Efficiency	Comments
Activated Carbon		
Activated Alumina	E	Also removes fluorides
Ion Exchange	F	
Chemical Precipitation		Cannot reduce to required standards
Ferric Chloride	E	Can reduce to required standards in combination with oxidation by chlorine Most effective of common coagulants
Ferric Sulfate	F	
Alum	F	
Lime	F	
Polyelectrolytes	E	
Ferric Hydroxide	E	
Hydrogen Sulfide	F	
Magnesium Hydroxide	F	
Reverse Osmosis	E	Total removal process therefore not economically feasible because of high total dissolved solids
Electrodialysis	E	Total removal process therefore not economically feasible because of high total dissolved solids
Ultrafiltration	E	Total removal process therefore not economically feasible because of high total dissolved solids
Distillation	E	Not economically feasible for high volume treatment
Freezing	E	Not economically feasible for high volume treatment

E = excellent F = fair P = poor

Table 8

Nitrate Removal Efficiencies

Treatment	Efficiency	Comments
Biological Denitrification	E	Requires removal of toxic substances in pretreatment process
Ion Exchange	F	Disposal of regenerant Interferences by chlorides and other anions

E = excellent F = fair P = poor

Table 9

Comparison of Removal Efficiencies of Candidate Processes

Treatment	Fluoride	Mercury	Arsenic
Lime	E at high influent concentrations	E at high influent concentations	E at high influent concentations
Activated Alumina	E	X	E
Iron Salts	X	E	E
Tricalcium Phosphate	E	*	X
Sulfides	X	*	*
Xanthate-PVBTMAC	X	E	*
Ozone Off-gas Oxidation and Dolomitic Lime	*	*	*

E = excellent
F = fair
* = possible
X = none

METHODOLOGY

50. The laboratory inorganic treatability studies will be conducted on a step-wise basis. Based on the literature review, the simplest and most economical processes will be investigated first. The results of the initial tests will be used to determine the need to conduct studies on more complicated and expensive processes. If no one process proves successful at removing the contaminants having mandatory limits, then process trains will be investigated. Analyses will be conducted for the various contaminants for all the processes studied in order to provide information on the removal or increase in concentration of contaminants in each treatment process.

Chemical Precipitation

51. A number of chemical precipitation processes will be investigated. RMA personnel will conduct studies on the use of air, oxygen, and oxygen/ozone for oxidation of metals. Each gas will be sparged into samples of Well 118 water for increasing periods of time and the precipitate volume generated will be recorded for each test. Precipitate volume will be plotted against time to determine optimum contact time for maximum precipitation for each gas. This information will be expressed as gas flow per unit volume of water.

52. Standard settling tests will be conducted to determine settling characteristics of the precipitate formed. Liquid and precipitate samples will be collected from these runs for metal analysis and organic analysis. These tests will indicate the metals being precipitated along with the amount of organic matter being removed with the precipitate.

53. Additional laboratory tests will be conducted using caustic, lime, and lime/soda ash to initiate precipitation of metals. These tests will be conducted using standard jar tests. A series of Well 118 samples will be placed on a gang stirrer and varying amounts of chemicals will be added to the samples. Results from these tests will indicate the optimum dosage rates for each of the chemicals.

54. After the optimum dosing rates have been determined, standard settling tests will be conducted to determine settling characteristics of the precipitate formed. Liquid and precipitate samples will be collected for analysis. These results will be used to determine the applicability of the different processes for inorganic removal from Well 118 water.

55. Another process to be investigated incorporates the addition of phosphoric acid and lime to form apatite. This mineral can incorporate anions such as fluoride and chloride as well as providing a surface for adsorption of other ions. Samples of Well 118 water will be subjected to chemical addition of varying amounts of phosphoric acid and lime in varying sequences. After the precipitate formed settles, samples will be obtained for analysis. Addition of polyelectrolytes will be investigated to help promote settling of the precipitate.

Activated Alumina

56. The next process investigated will be activated alumina. A series of isotherms will be conducted on Well 118 water using varying amounts of activated alumina. Samples of water will be stirred for 6 hours with activated alumina after which samples will be obtained for analysis. Results will be used to generate isotherm plots which will provide informa-

tion on the amount of contaminants adsorbed per unit weight of activated alumina.

Other Treatment Processes

57. At the conclusion of these tests, a review of the results will be made to determine if other studies are warranted. If these processes are not successful in reducing contaminant concentrations below mandatory limits, other treatment processes will be investigated. These processes will include first, those which are specific to the contaminants not successfully removed by previously studied processes, and finally expensive processes which involve non-specific removal of ions such as reverse osmosis, electrodialysis, ultrafiltration, distillation, and freezing.

Application of Information Obtained

58. The results obtained from the studies will be used to provide design and cost information for scaled-up systems. A design for a field-scale system based on the most applicable treatment process for use with either the field UV/ozone system or activated carbon system will be developed. Also, an attempt will be made to use the information obtained from the studies to develop a mathematical model or models of the most applicable process or processes.

Analysis

59. Inorganic and organic analyses will be conducted on samples as indicated previously. These analyses will include but not be limited to the following:

a. Organic

(1) DIMP

(2) DCPD

(3) Pesticides

(4) TOC (Total Organic Carbon)

b. Metals

(1) Iron

(2) Mercury

(3) Arsenic

(4) Manganese

(5) Calcium

(6) Magnesium

(7) Sodium

c. Others

(1) Chloride

(2) Fluoride

(3) Sulfate

(4) Nitrate

(5) Phosphate

Samples will be collected and analyzed according to Standard Methods.

60. The Analytical Laboratory Group (ALG) at WES will conduct most of the analysis on the various samples. The Material Analysis Laboratory Division (MALD) at RMA will provide back-up support and quality control testing.

SCHEDULING

61. The inorganic treatment study schedule was provided in the initial test plan. The bench-scale studies were scheduled to start in April 1978 and continue through September 1978 with a summary report being prepared during September 1978. The study as outlined should be complete by the end of September 1978.

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DEPARTMENT OF THE ARMY

ROCKY MOUNTAIN ARSENAL

Commerce City, Colorado 80022

SARRM-IR

2 Dec 77

SUBJECT: Draft Test Plan for Determination of Treatability of Various Source Waters with Activated Granular Carbon

Project Manager for Chemical Demil
and Installation Restoration
ATTN: DRCPM-DRR
Building E4585
Aberdeen Proving Ground, Maryland 21010

Subject Draft Test Plan is forwarded for your review and comment.

FOR THE COMMANDER

Irwin M. Glassman

IRWIN M. GLASSMAN
Director of IR

1 Incl
as

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Draft Test Plan for Determination of Treatability of Various Source Waters with Activated Granular Carbon	Office Symbol: DRCPM-DRR Date: 21 Feb 78

PURPOSE OF ACTION: Transmit format guidelines for preparation of IR Decon Tech test plan.

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

REFERENCES:

Ltr, SARRM-IR, RMA, 2 Dec 77, SAB (TAB B).

BACKGROUND & DISCUSSION:

1. REceipt by this office of vastly different quality test plans has prompted formulation of guidelines for preparation of Decontamination Technology test plans. These guidelines are compatible with ITARMS reporting/resource allocation requirements and as such will be incorporated into the revised RMA project plan and general Decontamination Technology ITARMS.

2. TAB B requested review of a draft test plan for determination of treatability of various source waters with activated granular carbon (task no. 1.05.11). Test plan guidelines are being transmitted to RMA to aid in finalizing their carbon plan.

RECOMMENDATIONS:

Approval and signature of 1st Ind (TAB A).

Review of these guidelines by the ITARMS coordinator, Mr. R. Snyder, to determine applicability for general IR implementation.

(Continue on Separate Sheet)

Coordinations				FRONT OFFICE APPROVALS		
Office	Name		INITIALS		INITIALS	Date
	D. Wynne	21 Feb 78	DW	C, PMD		
	A. Shafto			C, TSD		
	R. Snyder	21 Feb 78		PM CD		
	B. Aiken	21 Feb 78		PM IR	DW	21 Feb
	A. Anderson			Admin Ofcr		
				Exec Ofcr		
				DPM CDIR		
				PM CDIR		

Action Officer (Name, Telephone Ext & Signature)

D. CAMPBELL, 2556 Donald L Campbell

CDIR Form 6, 1 Jan 77

S: 1 Mar 78

DRCPM-DRR (2 Dec 77) 1st Ind
SUBJECT: Draft Test Plan for Determination of Treatability of Various Source Waters with Activated Granular Carbon

DA, Office of the Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, MD 21010

TO: Commander, Rocky Mountain Arsenal, ATTN: SARRM-IR, Commerce City, CO 80022 22 FEB 1978

1. The following comments are provided in accordance with basic correspondence.

a. The draft test plan provided represents a sound approach to apply the activated carbon process to contaminant migration source waters at Rocky Mountain Arsenal (RMA). Because this office has recently received many test plans of vastly different format and information content, Inclosures 2 and 3 (Format Guidelines for Preparation of IR Decontamination Technology Test Plans and sample plan) are provided for guidance in finalizing your granular carbon plan.

b. Specific comments are provided below.

(1) Para 3b(2): All isotherms with narrative interpretation should be forwarded to this office for review upon completion of the adsorption isotherm study.

(2) Para 3c(1): Periodic samples of influent and effluent column streams should be analyzed for characterization of organic and inorganic constituents. The organic fraction should be analyzed via a GC-MS "fingerprint" to guide analyses. The inorganic constituents should be determined via analysis specific to each contaminant. All information should be retained to eliminate future duplications of effort.

(3) Para 4: Investigation of treatability of Basin A source waters should be initiated as soon as possible after well no. 118 testing is initiated. Time-phased parallel activities should be pursued.

2. The final revised subject test plan should be forwarded to this office NLT 1 Mar 78 for approval. Until that time, efforts should be maintained in meeting scheduled milestones.

DRCPM-IRR (2 Dec 77) 1st Ind 22 FEB 1978
SUBJECT: Draft Test Plan for Determination of Treatability of Various Source Waters with Activated Granular Carbon

3. It is requested that all future Decontamination Technology Test Plans (ITARMS Task No. 1.05) either prepared by your office or forwarded through your office follow guidelines presented in Inclosure 2.

FOR THE PROJECT MANAGER:

2 Incl
wd incl 1
Added 2 incl
2-3. as

DAMON D. WINGFIELD
Colonel, CmlC
Assistant Project Manager for
Installation Restoration

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Test Plan for Preliminary Study of Inorganic Contaminant Removal from RMA Groundwater	Office Symbol: DRCPM-DRR
	Date: 2 Mar 78

PURPOSE OF ACTION: Transmit format guidelines to WES for preparation of IR Decon Tech test plans.

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

REFERENCES:

Draft copy of subject plan provided this office 23 Feb 78 (Incl 1).

BACKGROUND & DISCUSSION:

1. Receipt by this office of vastly different quality test plans prompted formulation of guidelines for preparation of Decon Tech test plans. These have been transmitted to RMA under separate cover on 22 Feb 78.

2. Test plan guidelines are being transmitted to WES to aid in finalizing their inorganic treatability plan.

RECOMMENDATIONS:

Approval and signature of TAB A.

We are giving WES a suspense date of 15 Mar.

(Continue on Separate Sheet)

Coordinations			FRONT OFFICE APPROVALS		
Office	Name	INITIALS		INITIALS	Date
	J. Zarzycki 2 Mar		C, PMD		
	D. Wynne 2 Mar		C, TSD		
	R. Snyder		PM CD		
	A. Anderson		PM IR	DEW	2 MAR 78
			Admin Ofcr		
			Exec Ofcr		
			DPM CDIR		
			PM CDIR		

Action Officer (Name, Telephone Ext & Signature)

DONALD L. CAMPBELL, 2556 Donald Campbell

CDIR Form 6, 1 Jan 77

WESSV 12 APR 78

SUBJECT: Test Plan Inorganic Groundwater Treatment

Project Manager
Chemical Demilitarization
and Installation Restoration
ATTN: Mr. Don Campbell
Aberdeen Proving Ground, MD 21010

Three copies of "Test Plan for Preliminary Study of Inorganic Contaminant Removal from RMA Groundwater" are inclosed for your review and approval (Incl 1).

FOR THE COMMANDER AND DIRECTOR:

1 Incl
as

F. R. BROWN
Engineer
Technical Director

DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

IN REPLY REFER TO: WESSV

12 APR 78

SUBJECT: Test Plan for Inorganic Groundwater Treatment

Project Manager
Chemical Demilitarization
and Installation Restoration
ATTN: Mr. Don Campbell
Aberdeen Proving Ground, MD 21010

Three copies of "Test Plan for Preliminary Study of Inorganic Contaminant Removal from RMA Groundwater" are inclosed for your review and approval (Incl 1).

FOR THE COMMANDER AND DIRECTOR:

F. R. Brown

F. R. BROWN
Engineer
Technical Director

1 Incl
as

D. CAMPBELL/ljm/2556

3 MAR 1978

DRCPM-DIR

SUBJECT: Test Plan for Preliminary Study of Inorganic Contaminant Removal from Rocky Mountain Arsenal Groundwater

Commander and Director
US Army Engineer Waterways
Experiment Station
ATTN: WESSV
PO Box 631
Vicksburg, MS 39180

1. Reference is made to draft copy of subject plan provided this office on 23 Feb 78 (Incl 1).

2. The draft test plan provided represents a sound approach to apply inorganic contaminant removal processes to contaminated source waters at Rocky Mountain Arsenal. Because this office has recently received many test plans of vastly different format and information content, Inclosures 2 and 3 (Format Guidelines for Preparation of IR Decontamination Technology Test Plans and sample plan) are provided for guidance in finalizing subject plan. The final test plan should be forwarded to this office NLT 15 Mar 78 for approval. Until that time, efforts should be maintained in meeting scheduled milestones.

3. It is requested that all future Decontamination Technology Test Plans (ITAPMS Task No. 1.05) either prepared by your office or forwarded through your office follow guidelines presented in Inclosure 2.

FOR THE PROJECT MANAGER:

3 Incl
as

DAMON D. WINGFIELD
Colonel, CmlC
Assistant Project Manager for
Installation Restoration

D. Campbell/ljm/2556

DRCPM-DRR (12 Apr 78) 1st Ind
SUBJECT: Test Plan for Inorganic Groundwater Treatment

DLC

DA, Office of the Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, MD 21010 24 APR 1978

DJW

TO: Commander and Director, US Army Engineer Waterways Experiment Station,
ATTN: WESSV, PO Box 631, Vicksburg, MS 39180

AWA

Subject Test Plan approved.

DDW

FOR THE PROJECT MANAGER:

Signed:

1 Incl
nc

DAMON D. WINGFIELD
Colonel, CmlC
Assistant Project Manager for
Installation Restoration

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Water Treatment Process Development for RMA	Office Symbol: DRCPM-DRR
	Date: 27 ~~Jul~~ 78

PURPOSE OF ACTION: Establish meeting dates and tentative agenda for DPM CDIR Briefing

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

REFERENCES:

1. Ltr, DRCPM-DRR, 5 Apr 78, subj: Management Plan for Installation Restoration Project at RMA (TAB B)

2. Mtg with DPM CDIR, 11-12 Apr 78, subj: Management Plan for Installation Restoration Project at RMA.

BACKGROUND & DISCUSSION:

1. In referenced meeting, DPM CDIR requested that a DPM CDIR decision point be inserted into the RMA IR program plan prior to progressing from individual water treatment process development (i.e., granular carbon, ultraviolet light/ozone, etc.) to combination process development. Individual treatability studies will be completed by the end of FY78. Therefore, a decision by the DPM CDIR has been tentatively set for 29 Sep 78.

2. Inclosed letter at TAB A establishes a date and agenda for a Technical Status Review on 19 Sep 78. The briefing will be for the PM CDIR staff to provide sufficient background in making the aforementioned program decision.

RECOMMENDATIONS:

Approval and signature of letter at TAB A.

Attendance at 19Sept78 review by DPMCDIR

(Continue on Separate Sheet)

Coordinations			FRONT OFFICE APPROVALS		
Office	Name	INITIALS		INITIALS	Date
	J. Zarzycki		C, PMD		
	D. Wynne		C, TSD		
	A. Anderson		PM CD		
			PM IR		1 Aug 78
			Admin Ofcr		
			Exec Ofcr		
			DPM CDIR		3 Aug
			PM CDIR		7 Aug

Action Officer (Name, Telephone Ext & Signature)
D. CAMPBELL, 2556 Donald Campbell

CDIR Form 6, 1 Jan 77

WATERWAYS EXPERIMENT STATION
ENVIRONMENTAL LABORATORY
TREATMENT PROCESS
RESEARCH BRANCH

UV/OZONE
PRODUCTS IDENTIFICATION STUDY

PROGRESS REPORT
2 Aug 78

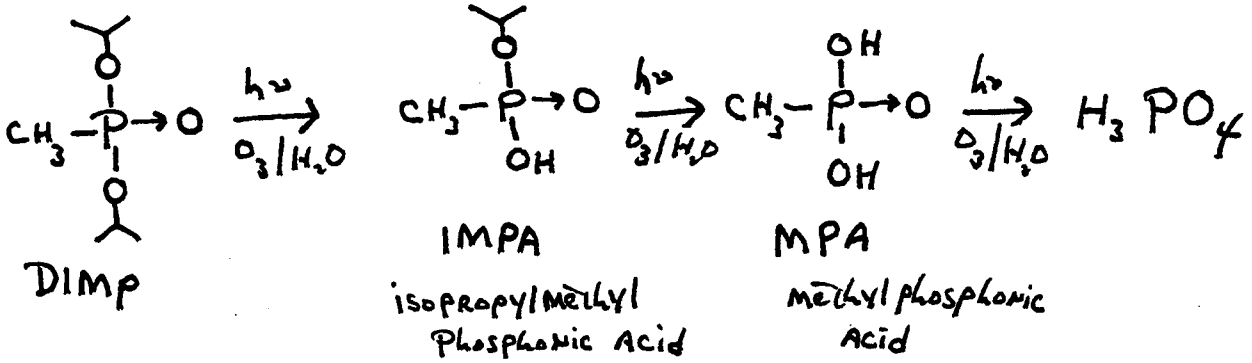
Robert E. Buhts
CPT, CE

The UV/O_3 products identification study is tasked with obtaining experimental evidence indicating the effect UV/ozone has on several chemical substances in water. The compounds studied thus far have been diisopropylmethylphosphonate (DIMP), dicyclopentadine (DCPD), Aldrin and Dieldrin.

The difficulties encountered to date involve the insolubility of the compounds in the reaction medium (water) and the hydrophilicity of the UV/ozone reaction products. It is hard to follow a chemical reaction unless an appreciable amount of initial reactant can be used. The investigatory process is further complicated when the reaction products take refuge in the solvent medium. The combined obstacle of low reactant and high product solubility is difficult to surmount.

Diisopropylmethylphosphonate

When DIMP is subjected to UV/ozone in aqueous media the expected reaction is



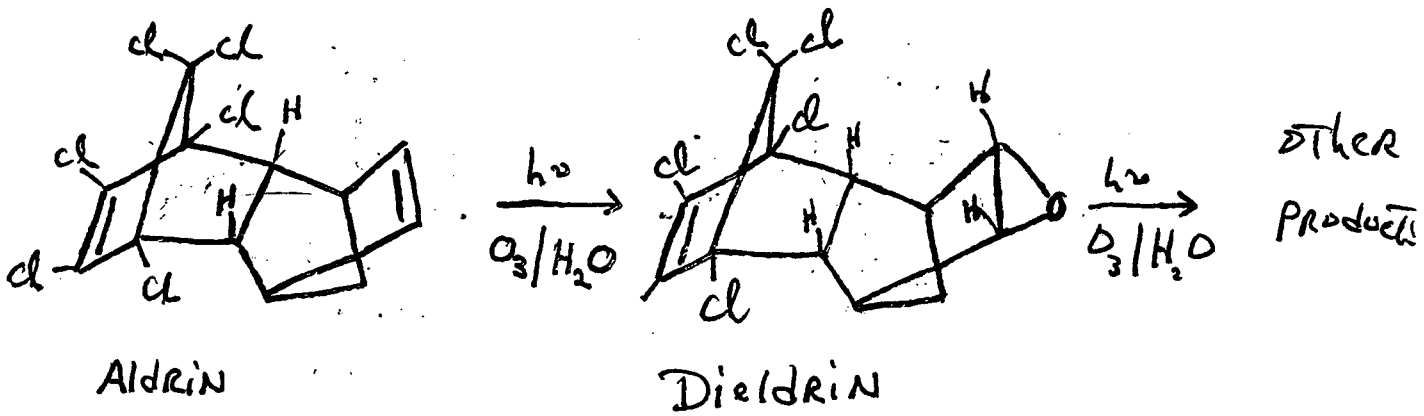
Experimentally, we have observed a rapid decrease in DIMP concentrations (72 ppm to 2.5 ppm in 2 hours). A corresponding buildup of phosphoric

acid is not observed until after 3 hours of reaction. The data indicates that the organophosphorous intermediates IMPA and MPA are being formed. MPA then undergoes a relatively slower reaction with UV/ozone and is converted to inorganic phosphorous.

Attempts are currently underway to determine the IMPA and MPA concentrations using ion chromatography. The additional organic products from this reaction would include isopropyl alcohol which would be oxidized to acetone and it in turn to acetic acid. Formic acid would also be produced from oxidation of the methyl group in MPA. Only acetic and formic acid would be detectable and both of these substances have been identified by Dr. Grabbe (formerly of MALD) as arising from UV/ozone oxidation of DIMP during previous studies.

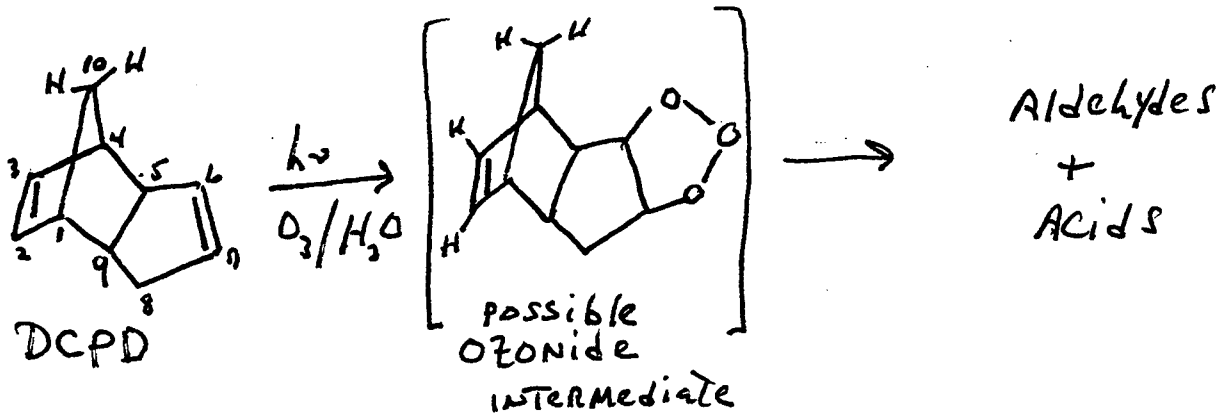
Aldrin and Dieldrin

We have established that UV/ozone oxidation of both compounds produces CO_2 as indicated by the formation of $BaCO_3$ upon bubbling the reaction off gases through $BaCl_2$ solution. A lowering of the reaction solution pH also indicates formation of carbonic acid (H_2CO_3) and perhaps hydrochloric acid (HCl). We have also determined that the initial UV/ozone product of Aldrin is Dieldrin:



Dicyclopentadiene (DCPD)

This insoluble and volatile compound reacts with ozone to produce a white aerosol above the reaction solution and a white precipitant within. The white solid formed is a mixture of aldehydes and acids. The initial ozonolysis reaction appears to focus on the cyclopentene ring in DCPD:



Preliminary results indicate that the bicyclic portion of the molecule remains intact during the early stages of the reaction. This would be expected since the 2-3 double bond is more sterically hindered than the 6-7 bond which reacts.

Laboratory work is continuing with particular emphasis being placed on the products formed during the first two hours of reaction time. Results on the UV/ozonation of p-chlorophenylmethylsulfone were unavailable for inclusion in this report.

It is doubtful that the Products I. D. Study will be entirely completed by 30 Sep 78. Significant slippage has occurred because of the projects' late start and the subsequent loss of Dr. Grabbe's services. I do anticipate, however, that a thorough characterization of the DIMP and DCPD reactions will be completed on schedule.

Table

Effectiveness of Lime and Soda-ash Treatment of RMA Groundwater

Water Quality Parameter	Pump Well No. 118*		
	Untreated	Excess Lime**	Soda-ash added after Lime
pH	7.0	10.5	10
Total Alkalinity†	870	110	380
Total Hardness†	2980	2200	425
Calcium Hardness†	1680	1340	110
Fluoride	4	0.4	0.3
Chlorides	3250	3250	3275 unchanged
Sulfates	1325	1512	1490 up
Calcium	675	488	22
Iron	17	0.05	<0.5
Magnesium	360	215	75
Manganese	26	0.13	0
Sodium	1750	1850	2650 up

* All values expressed in mg/l except pH

† As $CaCO_3$

** As CaO

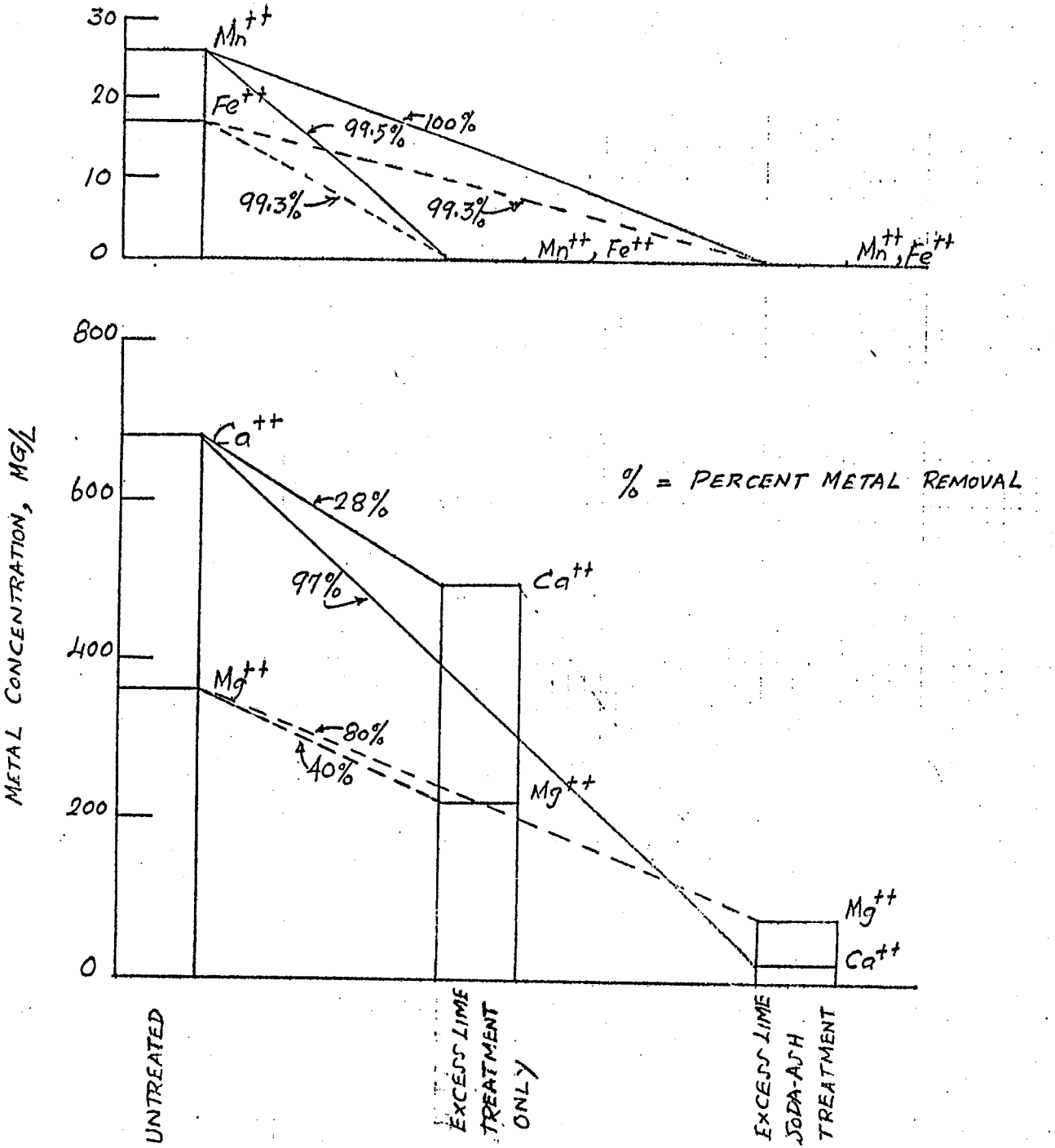


Figure . Theoretic metal removals [illegible]

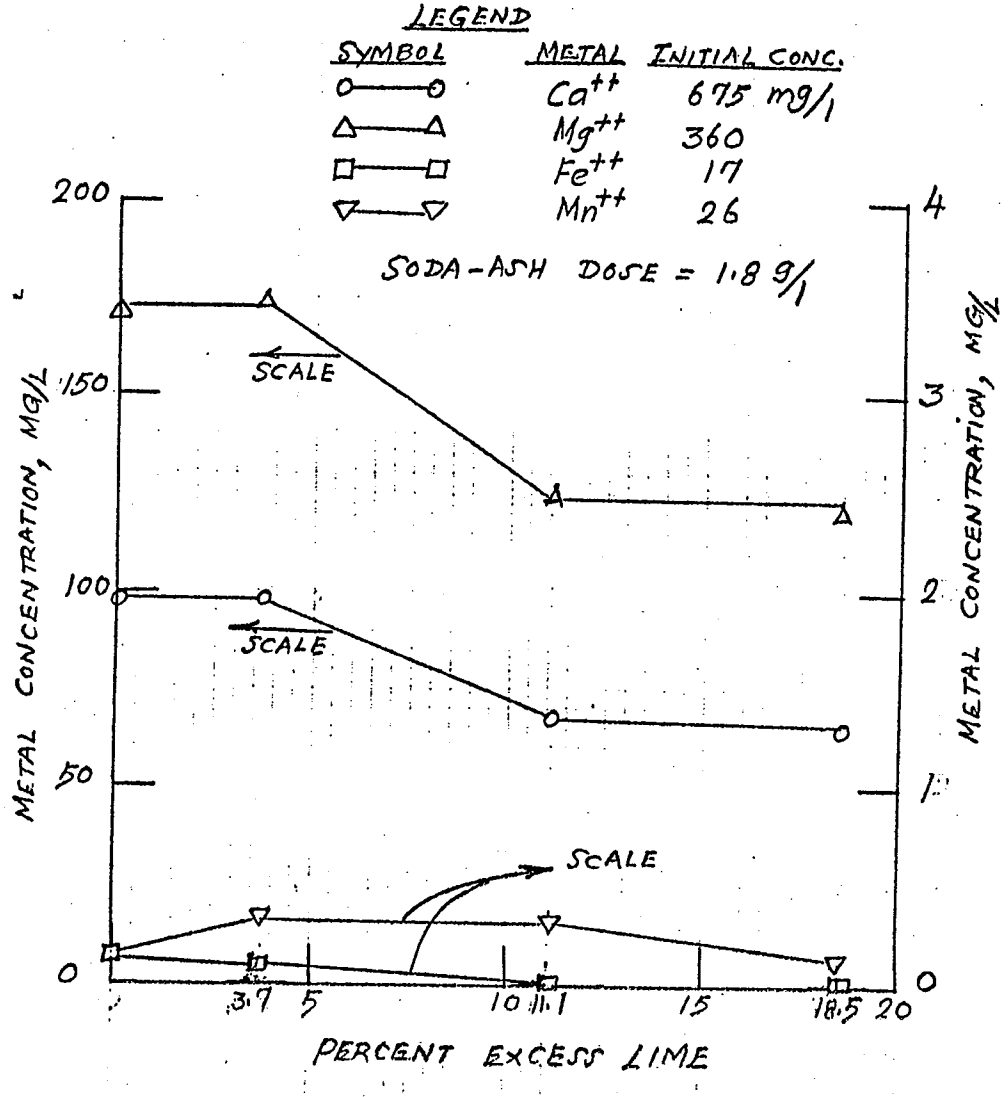


Figure . Effect of lime on inorganic metal removals from PW 118 Water

Table

Effectiveness of Lime-Soda ash and Caustic Treatment of RMA Groundwater

Water Quality Parameter	Pump Well No. 118[a]	
	Optimum Excess Lime[c] and 2.25 g/l Soda-ash	Caustic[d]
pH	10.2	10.2
Total Alkalinity[b]	900	220
Total Hardness[b]	745	1535
Calcium Hardness[b]	120	390
Fluoride	0.9	1.9
Chlorides	3200	3275
Sulfates	1500	1620
Calcium	50	150
Iron	0	0.2
Magnesium	150	290
Manganese	0	0.2
Sodium	2900	2550

(a) All values expressed in mg/l except pH

(b) As $CaCO_3$

(c) At an optimum lime dose of 1.5 g/l as CaO

(d) To raise the pH to 10.2

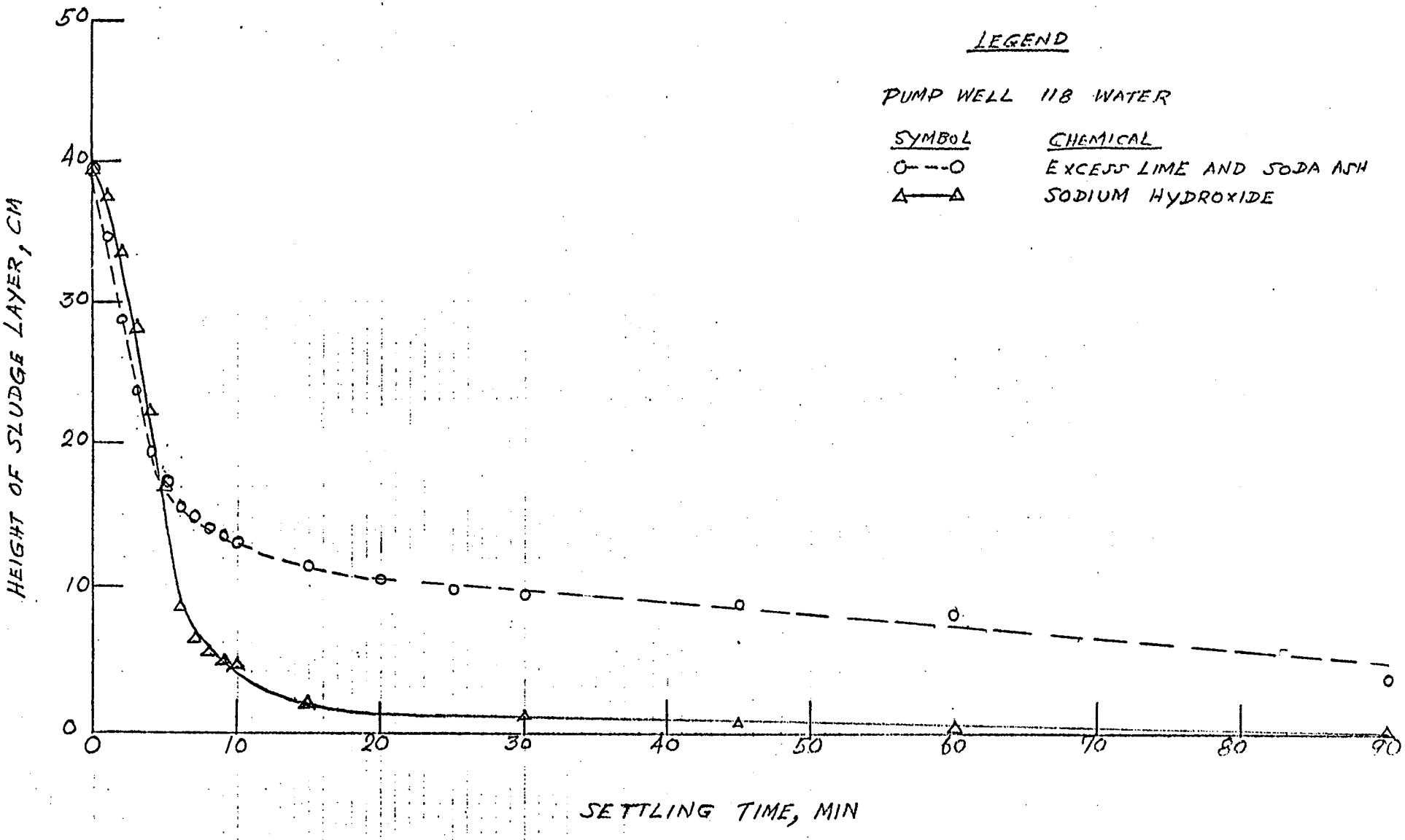


Figure . Settling properties of Chemically treated Sludges

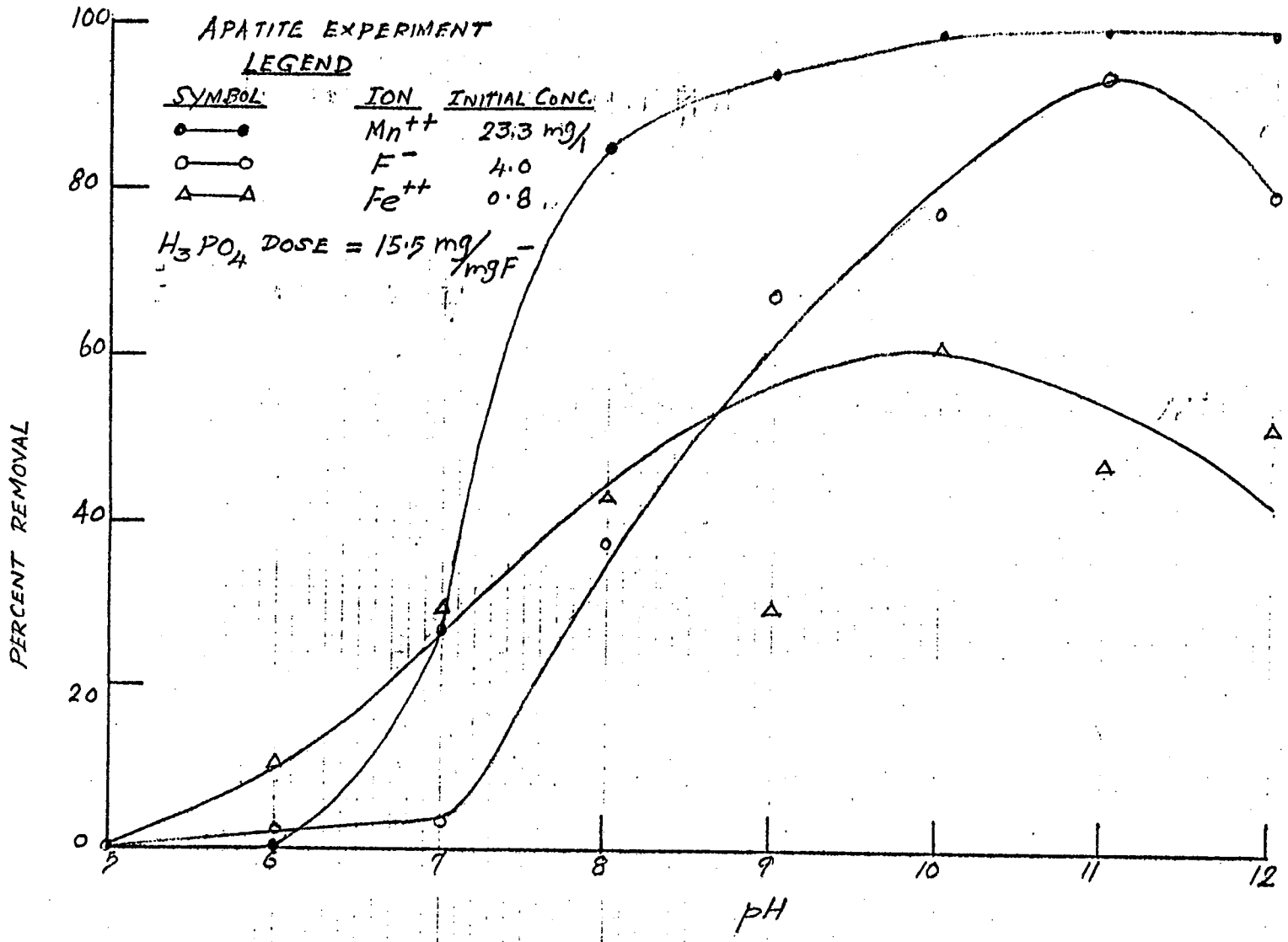


Figure . Effect of pH on Fluoride and heavy metal removals from PW 118 water at Stochiometric dose of Phosphoric acid

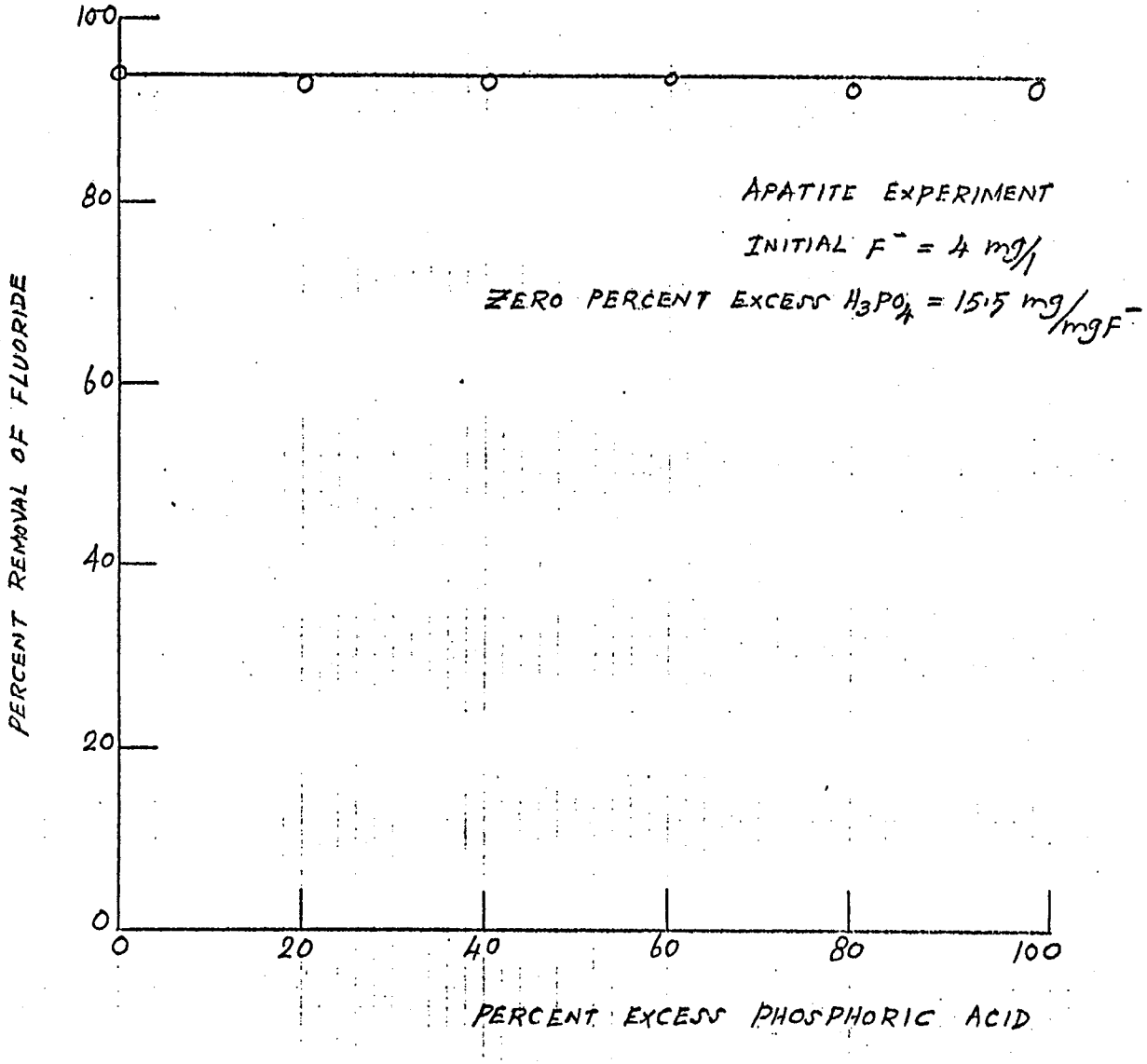


Figure . Effect of phosphoric acid dose on fluoride removal from PW 118 water at optimum pH 11

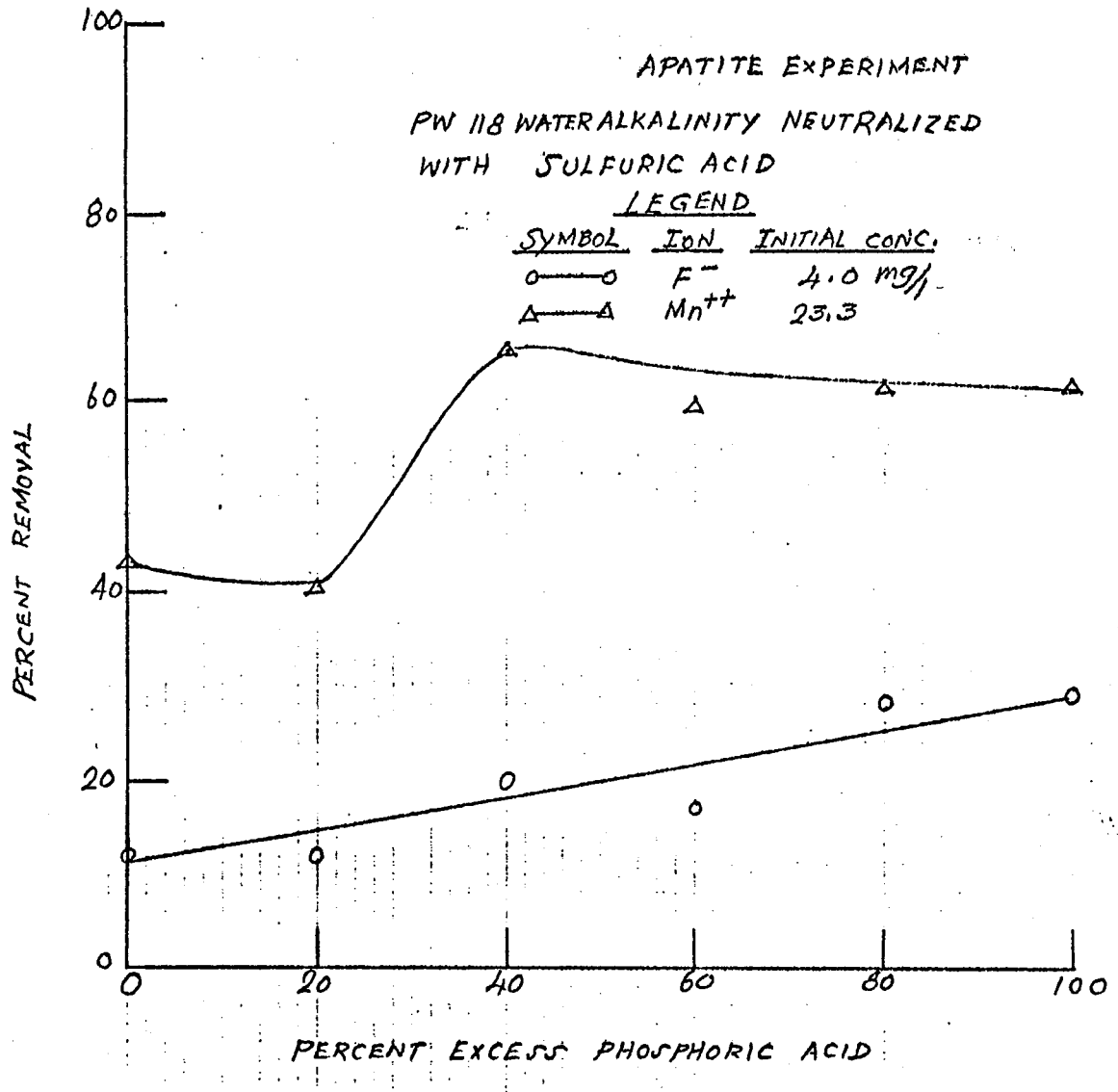


Figure . Effect of phosphoric acid dose on fluoride and manganese removals from PW 118 water at pH 6.5

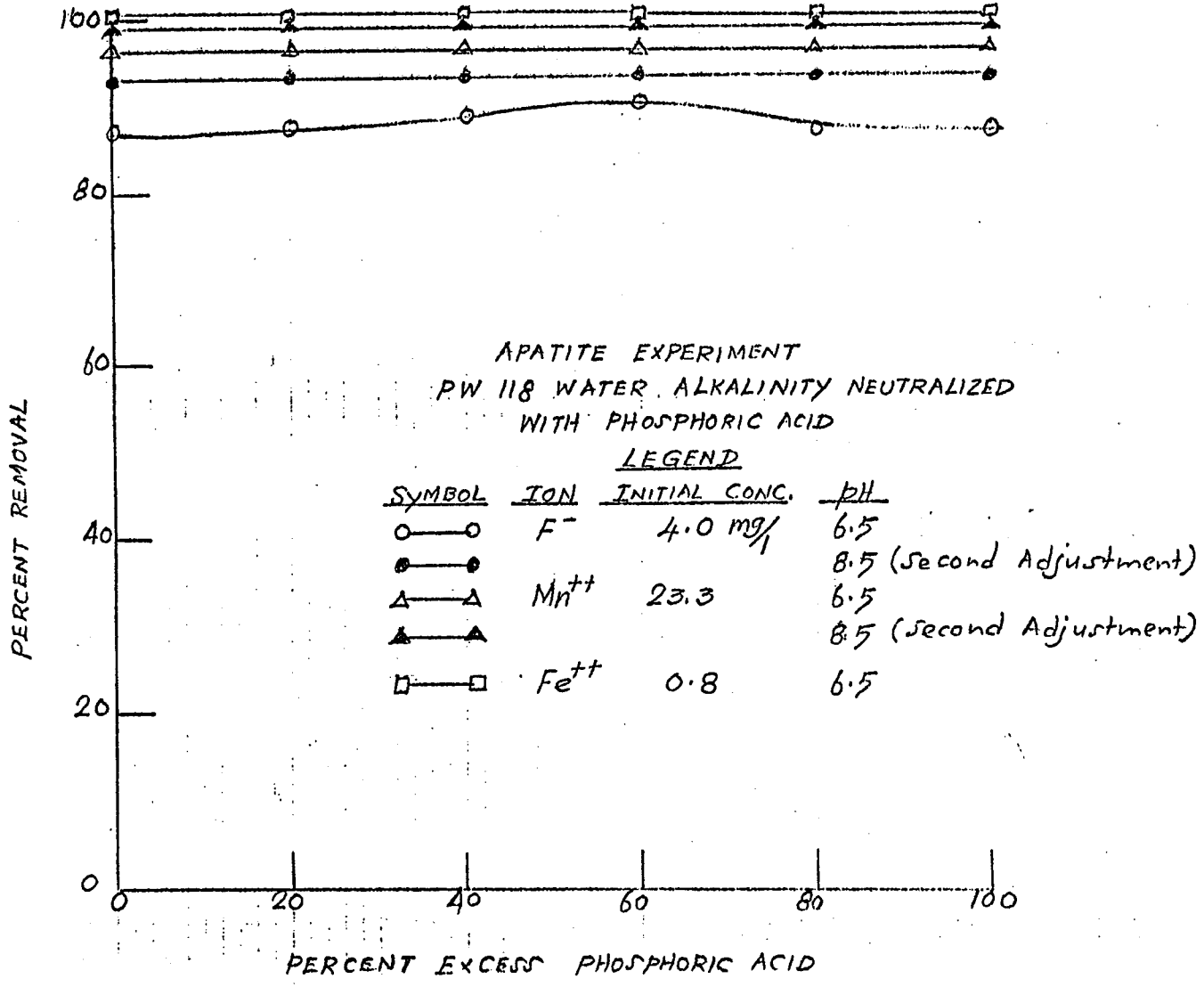
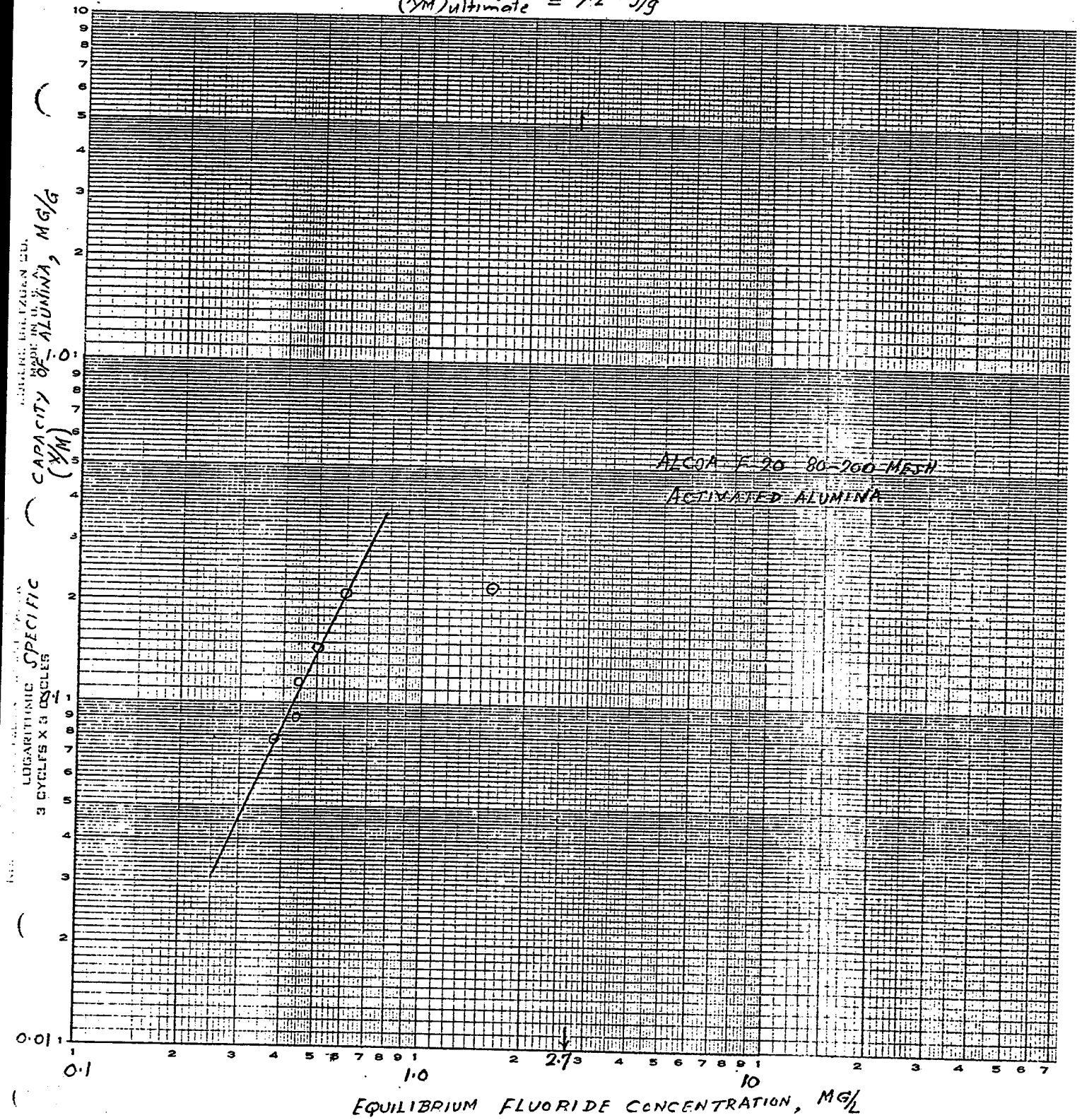


Figure . Effect of phosphoric acid dose on fluoride and heavy metal removals from PW 118 Water

$$\frac{X}{M} = 0.6\,C^{2.19}$$

$(X/M)_{ultimate} = 5.2\ mg/g$



(C)

Figure . Sorption isotherm for Fluoride in RMA WATER

D. CAMPBELL/1jm/2556

DRCPM-DRR

7 AUG 1978

SUBJECT: Water Treatment Process Development for RMA

Commander, Rocky Mountain Arsenal, ATTN: SARRM-CC, Commerce City, CO 80022
Commander and Director, US Army Engineer Waterways Experiment Station, ATTN: WESSV, PO Box 631, Vicksburg, MS 39180

1. Reference is made to letter, DRCPM-DRR, OPM CDIR, 5 Apr 78, subject: Management Plan for Installation Restoration Project at Rocky Mountain Arsenal.

2. Referenced letter transmitted above management plan to RMA requiring a PM CDIR decision on 29 Sep 78 for progressing from individual water treatment process development (i.e., granular carbon, ultraviolet light/ozone, etc.) to combination process development.

3. Request representatives from your office prepare a presentation for 19 Sep 78 to brief PM CDIR personnel on the results of subject water treatment development. A tentative agenda of discussion topics is attached (Inclosure).

4. Point of contact for this meeting is Mr. Donald Campbell of this office, AV 584-2556.

COL FRANK A. JONES, JR., PM

1 Incl
as

FRANK A. JONES, JR.
Colonel, CmlC
Project Manager for
Chemical Demilitarization
and Installation Restoration

CF:
Cdr, ARRCOM, ATTN: DRSAR-IS, Rock Island, IL 61299, wo incl

3. Lump sum payment for shipping, checkout, startup and training. $16,750.00

4. One-year contract for field services (includes annual replacement of UV bulbs). $17,550.00
(To be renewed annually)

These prices are based on current costs and do not include allowances for escalation, bonds, or taxes.

The installation cost is somewhat nebulous in that UCC is not familiar with small contractor charges in the Denver area. We would need to explore this cost thoroughly with local contractors before entering into a contract.

During our meeting in Denver you asked for comparative prices for a 10,000-GPD installation. Here again we assume building, water, and power availability. Budgetary prices on a similar basis as above are: monthly rental - $37,200; installation - $150,000; startup - $47,125; annual field service - $67,000.

It is a pleasure to offer this proposal for your review. If there are questions, or if I can help in any way, please do not hesitate to call.

Very truly yours,

W C Dedeke

W. C. Dedeke
Product Manager
Industrial Ozonation Systems

WCD/pc
Attachment

UNION CARBIDE CORPORATION
TECHNICAL CENTER
P.O. BOX 8361, SOUTH CHARLESTON, W. VA. 25303
TELEPHONE: 304-747-3758

Ozone Systems
ENVIRONMENTAL SYSTEMS

Iation Restoration
DRCPM - DRR
Attention: Mr. Don Cam
Aberdeen Proving Groun

August 11, 1978

Commander, Rocky Mountain Arsenal
SARRM - CC
Commerce City, Colorado 80240

Attention: Mr. Carl Loven

Dear Mr. Loven:

Union Carbide Corporation is pleased to submit this budgetary proposal to the U. S. Army at Rocky Mountain Arsenal. Union Carbide proposes to supply equipment to generate ozone, and a contactor capable of exposing water to ozone and UV light. It is our understanding the Army will utilize this equipment to treat groundwater for purposes of removing contaminants prior to recharge. The Army may also choose to use this equipment for other purposes, such as treating lagooned wastewater.

Union Carbide also proposes to provide installation of this equipment, in an existing building. It is assumed that space is available, and that adequate power is available from a nearby pole. It is further assumed that sufficient filtered water (@ 2500 GPH) at adequate pressure is available from a line inside the building that may be tapped for installation of our scope. I understand that this pipe is not owned by the Army.

Check-out and start-up services will be provided along with operator training, including safety training. An annual field service contract is also offered. This provides yearly change out of the UV lamps along with periodic visits to determine mechanical integrity of the system along with on-going safety review. This service can also be used to optimize the equipment or to determine applicability of alternate applications.

The budgetary estimate for the price of these offerings follows:

1. Monthly equipment rental based on 3-year lease. $ 9,975.00

2. Lump sum payment for installation. $89,000.00

Mr. Burdt/bjw/4331
15 Sep 78

DRCPM-DR-P (29 Aug 78) 1st Ind
SUBJECT: Water/Wastewater/Process Proposal

DA, Office of the Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, MD 21010 18 SEP 1978

TO: Commander, Rocky Mountain Arsenal, ATTN: SARRM-CCP, Commerce City, CO 80022

1. Subject proposal from Union Carbide Corporation has been evaluated for applicability to the Rocky Mountain Arsenal Installation Restoration project. The following review comments apply:

a. Adsorption by granular activated carbon has been demonstrated to be effective in treating contaminated groundwater for North Boundary of Rocky Mountain Arsenal Containment System. However, ongoing long range studies are being considered to define the role of UX-Ozone in RMA applications. Subject proposal does not appear to offer any technical or economic benefit beyond that presently being experienced in ongoing programs.

b. Suggest this proposal be put on file until your future treatment requirements, specifically UV-Ozone, are better defined.

2. Follow-on effort should consider Union Carbide as well as other companies with the expertise to meet the long range requirements as yet to be determined.

FOR THE PROJECT MANAGER:

1 Incl
nc

DAMON D. WINGFIELD
Colonel, CmlC
Assistant Project Manager
for Installation Restoration

not sent

DEPARTMENT OF THE ARMY
OFFICE OF THE PROJECT MANAGER FOR
CHEMICAL DEMILITARIZATION AND INSTALLATION RESTORATION
ABERDEEN PROVING GROUND, MARYLAND 21010

DRCPM-DR-P

Mr. W. C. Dedeke
Union Carbide Corporation
Technical Center
P. O. Box 8361
South Charleston, WV 25303

Dear Mr. Dedeke:

This letter acknowledges the receipt of your unsolicited proposal dated 11 August 1978.

This office has conducted a review of your proposal and, as a result, has determined that there is no interest at this time for the following reason:

> The principle technology being used by Rocky Mountain Arsenal for treatment of contaminated groundwater is adsorption by granular activated carbon.

Your proposal does not appear to offer any technical or economic benefit beyond that presently in use.

However, this office is currently conducting long range water treatability studies to better define the role of UV-Ozone in various Chemical Demilitarization and Installation Restoration projects. Your proposal will be maintained on file until future treatment requirements are defined.

Your continued interest in the Chemical Demilitarization and Installation Restoration mission is appreciated.

Sincerely yours,

FRANK A. JONES, JR.
Colonel, CmlC
Project Manager for
Chemical Demilitarization
and Installation Restoration

DISPOSITION FORM

For use of this form, see AR 340-15, the proponent agency is TAGCEN.

S - 13 Sep 78

REFERENCE OR OFFICE SYMBOL	SUBJECT
DRCPM-DR-P	Preliminary Review of Union Carbide Corp., Linde Div. Unsolicited Proposal - Water/Wastewater/Process Proposal

TO: DRCPM-DRR
DRCPM-DRD
DRCPM-DR-T

FROM: Unsolicited Proposal Coordinator, Prog Mgt Ofc

DATE: 7 Sep 78

CMT 1: Mr. Burdt/bjw/4331

1. Reference is made to:

   a. AMCR 70-2, 21 Aug 75, Unsolicited Proposals.

   b. CDIR Supplement 1 to AMCR 70-2, 24 Jun 77.

2. The attached unsolicited proposal is provided for your preliminary review to determine the extent of the Project Manager Office's interest. If a technical feasibility and cost evaluation is deemed necessary because of PMO interest, a Policy Statement and Memorandum of Understanding must be obtained from the proponent. If, as the result of the preliminary review, the PMO lacks further interest, the unsolicited proposal will be returned.

3. It is required, by reference 1b above, that the preliminary review be completed and technical information upon which to base a reply and/or other recommendations with respect to disposition of proposal be provided by COB 13 Sep 78. Notification to the proponent of the result of this review must be provided by COB 14 Sep 78.

. Proposal was provided the undersigned by Don Campbell, DRCPM-DRR, who is the technical POC.

STEPHEN R. BURDT
Unsolicited Proposal Coordinator

1 Incl
as

CF:
DRCPM-DR-P

DA FORM 1 FEB 62 2496 REPLACES DD FORM 96, WHICH IS OBSOLETE.

☆GPO—1975—665-422/1063

UNSOLICITED PROPOSAL

Use of Data Limited

(ARMCOM SUPPL 1 TO AMCR 70-2)

All Government personnel handling this proposal shall exercise EXTREME CARE to insure that the information contained herein is NOT DISCLOSED outside the Government and is NOT DUPLICATED, USED, OR DISCLOSED in whole or part for any purpose other than to evaluate the proposal, without the written permission of the submitter (except that if a contract is awarded on the basis of this proposal, the terms of the contract shall control disclosure and use).

This notice does not limit the Government's right to use information contained in the proposal if it is obtainable from another source without restriction.

This is a Government notice, and shall not by itself be construed to impose any liability upon the Government or Government personnel for any disclosure or use of data contained in this proposal.

UNSOLICITED PROPOSAL

Use of Data Limited

APPENDIX A - COVER SHEET FOR UNSOLICITED PROPOSAL

not submitted OBE

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Water/Wastewater/Process Proposal	Office Symbol: DRCPM-DRR
	Date: 14 Sep 78

PURPOSE OF ACTION: Respond to unsolicited proposal forwarded by RMA.

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

REFERENCES:

Letter, SARRM-CCP, RMA, 29 Aug 78, SAB (TAB B)

BACKGROUND & DISCUSSION:

1. Previous treatability studies for north boundary application have shown that granular activated carbon and UV-Ozone will effectively remove organic contaminants to below standards. Operating costs for both are similar. However, because of the quick response that could be demonstrated with a Calgon Corporation lease agreement and the vast R&D data base, granular carbon was selected for pilot application.

2. Mr. Jack Zeff, Westgate Corporation, recognized that UV-Ozone would be soon out of its infancy and would have more application if offered also via a lease arrangement. Therefore, he joined with Union Carbide Corp. in offering subject proposal.

3. 1st Indorsement, inclosed at TAB A, responds back to RMA concerning same. It does not appear that installation of UV-Ozone equipment in duplication of the Calgon system is feasible at this time. Benefits of short term lease agreements such as this might have application within the FY80 MCA project.

RECOMMENDATIONS:

Approval and signature of TAB A.

(Continue on Separate Sheet)

Coordinations			FRONT OFFICE APPROVALS		
Office	Name	INITIALS		INITIALS	Date
	J. Zarzycki		C, PMD		
	D. Wynne	D.W.	C, TSD		
	A. Shatte	A.S.	PM CD		
	S. Budt		PM IR		
	A. Anderson		Admin Ofcr		
			Exec Ofcr		
			DPM CDIR		
			PM CDIR		

Action Officer (Name, Telephone Ext & Signature)
DONALD L. CAMPBELL, 2556 Donald Campbell

CDIR Form 6, 1 Jan 77

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Union Carbide Corp., Linde Division - Unsolicited Proposal - Water/Wastewater/Process Proposal	Office Symbol: DRCPM-DR-P Date: 15 Sep 78

PURPOSE OF ACTION: Respond to unsolicited proposal forwarded by RMA.

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

REFERENCE: Comments by APMCD, APMIR, TSO rejecting unsolicited proposal.

DISCUSSION:

The attached unsolicited proposal was received from RMA, 6 Sep 78. Divisions have reviewed the proposal per attached comments.

Based upon their comments, the unsolicited proposal has been found to not require acceptance at this time. Further program studies are being conducted for boundary and source water treatment at which time the proposal could be considered. PMO will maintain in file.

The letter informs Union Carbide of the results of our review.

(Continue on Separate Sheet)

Coordinations			FRONT OFFICE APPROVALS		
Office	Name	INITIALS		INITIALS	Date
	[illegible] Lawson	[illegible]	C, PMD ✓	[illegible]	9/15
			C, TSD ✓	[illegible]	[illegible]
			PM CD ✓	[illegible]	11 Sep
			PM IR ✓	[illegible]	15 Sep 78
			Admin Ofcr		
			Exec Ofcr		
			DPM CDIR		
			PM CDIR		

Action Officer (Name, Telephone Ext & Signature)

STEPHEN R. BURDT, 4331

CDIR Form 6, 1 Jan 77

Chem. Abstracts	70+
Bio. Abstract	72+
NTIS	64+
Compendex	70+
Agricola	70+
Scisearch	74+
Enviroline	71+
Pollution Abstract	70+
Aquatic Science + Fisheries Abstract	75+
APTIC	66+
Biosis	72-77
Analytical Abstracts	1954-1976
Chemical Abstract	1907-1956
Federal Index	
CAB Abstracts	
USDA/CRIS	
MEDLINE	
TOXLINE	
Dissertation Abstracts	
SSIE	
BioResearch Indep	

Best DIMP removal in each.
Precip of metal in GC column - where AIR?

TECHNICAL STATUS REVIEW OF WATER TREATMENT
PROCESS DEVELOPMENT FOR ROCKY MOUNTAIN ARSENAL
19 Sep 78

AGENDA

TOPIC	PRESENTER
1. Introductory Remarks	OPM CDIR
2. Program Overview	OPM CDIR
3. Program Status	WES/RMA
a. Granular Carbon Organic Treatment	
b. Ultraviolet Light/Ozone Organic Treatment	
c. Inorganic Treatment	
d. Preliminary Organic/Inorganic Combination Testing	
4. Open Discussion	ALL
5. Concluding Remarks	OPM CDIR

REQUISITION ON WAREHOUSEMAN

(ER's 735–2–1 & 735–345–1)

REQUISITION NO.

DATE

REQUISITIONED BY *(Signature)*

ACCOUNT OF *(Responsible employee and location)*

Responsible Employee No. 7

TO BE USED FOR:

EED/EL

DELIVER TO *(Office location)*

Buhts

QUANTITY	UNIT	NOMENCLATURE OF ARTICLES	PRICE	AMOUNT
		Furnish all necessary labor, equipment, and		
		material to perform a computer assisted		
		literature search -		
		Chemical Abstracts 1970-71 Chemical Abstracts 1972-1976		
		Chemical Abstracts 1977 to date Toxicity of Drugs & Chemicals 1974 to date		
		Toxicity of drugs & Chemicals 1940 to 1973 Cancer literature 1963 to date		
		Bio-medical literature 1976 to date Bio-medical literature 1975		
		Bio-medical literature 1972-1974 Bio-medical literature 1969-1971		
		Bio-medical literature 1966-1968 CAS Registry Numbers and chemical nomenclature;		
		current for the following chemical compounds: Aldrin - 1, 2, 3, 4, 10, 10-hexachloro-1, 4,		
		4a, 5, 8, 8a-hexahydro-endo-1, 4:5, 8-dimethanonaphthalene		
		Dieldrin - 1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8,		
		8a-octahydro-endo-exo-1, 4:5, 8-dimethanonaphthalene		
		Dicyclopentadiene Diisopropylmethyl Phosphonate		
		Isopropyl Methyl Phosphonic Acid Methyl Phosphonic Acid		
		p-Chlorophenyl Methyl Sulfone p-Chlorophenyl Methyl Sulfoxide		
		p-Chlorophenyl Methyl Sulfide Nemagon 1, 2-dibromo-3-chloropropane		
		Any Reference containing one of the above		
		chemical compounds in combination with any of the following key words is desired:		
		Photolysis Photo-oxidation Oxidation ozonolysis (ozonation)		

ACCOUNTING CLASSIFICATION *(Appropriation, project, cost account and amounts)*

RECEIVED BY *(Signature of Responsible employee or Designee)*

PROPERTY VOUCHER NO.

REQUISITION ON WAREHOUSEMAN

(ER's 735-2-1 & 735-345-1)

REQUISITION NO. 7/2086

DATE 19 Sep 78

REQUISITIONED BY *(Signature)*	ACCOUNT OF *(Responsible employee and location)*
A. J. GREEN	Responsible Employee No. 7

TO BE USED FOR:	DELIVER TO *(Office location)*
EED/EL	Buhts

QUANTITY	UNIT	NOMENCLATURE OF ARTICLES	PRICE	AMOUNT
		hydrolysis biodegradation		
		degradation		
		Any Reference containing one of the chemical		
		compounds by itself or with one or more of the key words used in conjunction with one		
		or more of the following topics is desired: Environmental effects (of)		
		Environmental toxicity Human toxicity		

DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

DPM
CF: IR

IN REPLY REFER TO: WESEE

29 September 1978

MEMORANDUM FOR: CHARLES BARONIAN, APM-CDIR

SUBJECT: Influence of pH on Carbon Adsorption

1. Several questions concerning the influence of pH on carbon adsorption were raised at the technical status review meeting held at Edgewood Arsenal on 20 September 1978. This memorandum was prepared to address these questions and provide a general discussion of how pH affects the adsorption of organic compounds (particularly munition wastes) by activiated carbon.

2. The pH of a solution from which adsorption occurs influences the extent of adsorption for several reasons. First, since the extent of ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization. Next, since hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution.

3. Many organic molecules either exist as, or have the potential of existing as, ionic species. Organic acids and many pesticides exhibit the property of ionizing under appropriate pH conditions. Past observations relative to ionization effects on adsorption can be generalized as follows. As long as the compounds are structurally simple, adsorption is at a minimum for the charged species and at a maximum for the neutral species. The more complex the compound, the less important the effect of ionization becomes. Amphoteric compounds which have the capacity to be both an acid and a base have been found to have an adsorption maximum at the isoelectric point (that pH at which both the acidic end and the basic end of the compound are ionized and the compound bears a net charge of zero).

4. Activated carbon commonly carries a net negative surface charge. For this reason, adsorption of typical organic pollutants from water is increased with decreasing pH. In many cases this may result from neutralization of negative charges at the surface of the carbon with increasing hydrogen-ion concentration, thereby reducing hindrance to diffusion and making available more of the active surface of the carbon. In any case, the objective is to adjust the concentration of hydrogen or hydroxide ions so that any charge repulsion is minimized.

File
Decon Tech

WESEE 29 September 1978

SUBJECT: Influence of pH on Carbon Adsorption

5. In order to illustrate the influence of pH on carbon adsorption, I have inclosed (Incl 1) a reprint entitled "The Treatability of a Munitions-Manufacturing Waste With Activated Carbon". This paper discusses the effect of pH on the carbon adsorption of TNT. Figure 6 in the paper presents breakthrough curves for carbon columns using a feed water with pH 7.0 and one with pH 2.1. This plot indicates an approximate doubling of carbon capacity for TNT at pH 2.1.

6. In the case of TNT contained in wastewater at pH 11 (discussed at the meeting) a lowering of the pH should greatly increase the adsorptive capacity of the carbon for the TNT. Since this wastewater contains a number of compounds, it is difficult to predict the optimum pH for adsorption without conducting a series of isotherms. As mentioned, different compounds have different optimum pH levels for adsorption. Other factors such as mutual solubility effects and competition for adsorption sites may greatly effect the adsorptive capacity of the carbon for a particular compound.

7. In summary, the literature indicates varying amounts of adsorptive capacity increases with respect to pH adjustment. The best technique for determining the optimum pH appears to be the adsorption isotherm. The increase in adsorption efficiency must then be evaluated with respect to increased costs for chemicals and equipment required for pH adjustment.

Donald L Campbell
for DOUGLAS W. THOMPSON
Sanitary Engineer
Treatment Processes Research Branch

1 Incl
as

TEST PLAN
for
WATER TREATMENT SYSTEM
EVALUATION AT RMA

by

USAE Waterways Experiment Station
Treatment Processes Research Branch
Environmental Laboratory
Vicksburg, MS 39180

ITARMS TASK NO: 1.05.25

September 1978

Prepared For: Office, Project Manager for
Chemical Demilitarization and
Installation Restoration, Aberdeen
Proving Ground, Maryland 21010

INTRODUCTION

1. Groundwater at Rocky Mountain Arsenal (RMA) has been found to contain certain inorganic and organic contaminants as a result of various past and ongoing activities at the arsenal. Treatability work on groundwater was initiated by the Waterways Experiment Station (WES) in FY 77 and continued in FY 78. The groundwater initially studied was characteristic of that at the northern boundary of the arsenal. Activated carbon adsorption and UV/ozone oxidation were both found to effectively remove organic contaminants from this water. Due to the immediate availability of equipment, activated carbon was chosen for the pilot containment/treatment system at the northern boundary. A Calgon carbon system was installed in FY 78 and has operated successfully for several months. No requirement for inorganic treatment (except possibly for fluoride) has been needed at the northern boundary.

2. Interest in groundwater treatment near suspected contamination sources led to an initiation of treatability studies on water from Well 118 (near Basin F) in FY 78. A high concentration of inorganic contaminants was found in this water. Preliminary treatability studies with activated carbon and UV/ozone indicated an interference problem associated with the precipitation of metal hydroxides (particularly iron and manganese). The precipitate could plug the carbon beds lowering the efficiency of the adsorption process and it could interfer with the transmittance of the UV light thus lowering the efficiency of the oxidation process.

3. This preliminary work established a need for a very versatile treatment process system incorporating both organic and inorganic treatment that could be used on different source waters at RMA and on wastewaters from other Army installations. A treatment scheme was developed (Figure 1) incorporating pretreatment (for inorganics), primary treatment (for organics), post treatment (for contaminants not removed by the first two), and side-stream treatment and disposal for process water. A research and development program was initiated during FY 78 to develop processes suitable for use as pretreatment and primary treatment. This work was conducted on Well 118

water. Chemical addition and precipitation were chosen for the pretreatment process. Activated carbon and UV/ozone were chosen for the primary treatment process. Equipment for a field scale system was constructed and set up at RMA in order to evaluate different process trains. This evaluation and optimization of the treatment process will be conducted in FY 79. This test plan presents the combination system work to be performed.

OBJECTIVES

4. The objectives of this study are as follows:

   a. Assess the potential of the treatment system in removing inorganic and organic contaminants from various RMA source waters.

   b. Testing of individual inorganic/organic processes to determine optimal configurations of pretreatment, primary treatment, post treatment and side stream disposition unit operations on the identified source waters.

   c. Provide operating data and costs associated with various process trains.

   d. Refinement of operational models for the treatment processes based on the data obtained.

MATERIALS AND METHODS

Equipment

5. The equipment for the pretreatment process includes mixers, mixing tanks, chemical feed pumps, and modified ERDA lator (upflow clarifier), and a storage tank. The pretreatment unit has been constructed and checked-out and is ready for use.

6. The UV/ozone treatment unit to be used initially is a single vessel, mechanically-mixed reactor (Figure 2). The reactor vessel is constructed of stainless steel and contains a variable speed impeller mixer. The reactor has four quartz tubes placed so as to surround the mixer impeller. Various UV lamps can be placed in these tubes. The unit allows for variable control of temperature, pH, pressure, and recycle along with the standard operational parameters. The unit is completely contained, skid mounted and highly portable.

7. The equipment to be used for activated carbon evaluation includes jars and stirrers for adsorption isotherm testing and various size columns for use in determining breakthrough characteristics. Various types of carbon are available for evaluation.

8. All the equipment is configured so as to be portable and to permit the interconnecting of each unit operation. These alternate test configurations will be discussed in the next section.

Field System Operation

9. The field system operation will incorporate the evaluation of three different treatment scenarios: (a) pretreatment followed by carbon (b) pretreatment followed by UV/ozone, and (c) pretreatment followed by a combination of UV/ozone and carbon.

10. Initially, effluent from the pretreatment unit will flow to a storage tank. Water will be taken from the storage tank for both carbon and UV/ozone treatment tests so that water used in each test is identical. Work on carbon adsorption and UV/ozone treatment will be done simultaneously.

11. In the carbon studies, pretreated water will be subjected to standard isotherm testing with the tests being conducted at different pH levels to determine optimum pH levels, best carbon type, and adsorption capacity of the carbon for various organic contaminants. At the completion of the isotherm tests, small columns will be set-up for evaluation of breakthrough of the contaminants for the activated carbon. With this information and cost information from the vendors, an evaluation of efficiency and costs for this treatment scenario will be provided to the OPM-CDIR. This work will be conducted by RMA personnel with technical assistance being provided by WES.

12. For the UV/ozone studies, water will be taken from the storage tank and passed through the UV/ozone reactor. Operational parameters will be adjusted until optimum conditions can be determined. This will be achieved by use of a factorial type experiment that lends itself to statistical analysis. The study will begin with a series of runs designed to evaluate the correlation between the field unit and the laboratory unit. The runs will be made on pretreated Well 118 water due to the data available from the lab unit on this water. These correlation data will be used to determine

the correlation factors between the two units so that in the future, any laboratory work done can be applied to the field through use of the developed factors. With the operational information generated combined with equipment and power costs, an evaluation of efficiency of the process along with costs for this treatment scenario will be provided to the OPM-CDIR. This work will be conducted by WES personnel with operational support from RMA.

13. In the combined UV/ozone and carbon work, effluent from the UV/ozone reactor using various retention times will be obtained, adsorption isotherms and breakthrough column studies will be conducted on the effluent samples to determine the effect on the adsorptive rate and capacity of the carbon. When this work has been completed, the UV/ozone reactor and carbon columns will be configured in series and the operational studies will be initiated. The best retention times and carbon operational parameters found in the preliminary work will be used initially and then the operational parameters of both systems will be checked to insure optimum efficiency. In order to minimize the costs for the combination system, the flow rate through both systems must be maximized (reduction in capital costs) and the sum of the power costs for UV/ozone (dependent upon the retention time) and the regeneration costs for the carbon (dependent on the organic loading to the carbon bed) must be minimized. At the conclusion of this work, process efficiency and costs for this treatment scenario will be provided to the OPM-CDIR. This work will be conducted jointly by WES and RMA personnel with technical supervision being provided by the WES project engineer.

14. Some work will be required in the area of sidestream treatment and disposal. This work will include carbon regeneration studies and sludge disposal from the pretreatment unit. Any carbon regeneration studies will probably be done by a vender. This work would determine the compatability of the adsorbed organic contaminants with the regeneration process and the suitability of the carbon for reuse after regeneration. The sludge disposal work will incorporate studies on dewaterability, solids handling, leaching potential, and suitability for chemical fixation (if required). This work will probably be done at WES.

Sampling and Analysis

15. The field system will be instrumented to facilitate continuous monitoring of operating parameters. Parameters to be monitored include:

a. Ozone concentration (UV/ozone unit only)

b. pH

c. Liquid and gas flow rates

d. Temperature

16. As in previous studies, DIMP will probably be used as a representative constituent on which to base treatment efficiency. Analyses will be conducted as follows:

a. Organic

(1) DIMP

(2) DCPD

(3) Nemagon

(4) Pesticides

(5) Organosulfur compounds

(6) Organophosphorus compounds

(7) TOC (Total Organic Carbon)

(8) COD (Chemical Oxygen Demand)

b. Metals

(1) Iron

(2) Lead

(3) Mercury

(4) Arsenic

(5) Manganese

(6) Sodium

(7) Calcium

(8) Magnesium

c. Others

(1) Total dissolved solids

(2) Conductivity

(3) Chloride

(4) Fluoride

(5) Hardness

(6) Alkalinity

(7) Sulfate

(8) Nitrate

(9) Phosphate

The aforementioned analyses will be conducted throughout the study. Not all analyses will be conducted on every sample, but sufficient testing will be conducted to insure a thorough characterization of the different source water samples. Samples will be collected and analyzed according to Standard Methods.

17. The Analytical Laboratory Group (ALG) at WES will conduct metal analysis on the various samples. The Material Analysis Laboratory Division (MALD) at RMA will be responsible for organic analysis of samples except for COD. WES personnel will be responsible for any other analyses to be performed on site. Approximately 50 to 60 samples per week will be submitted to MALD for DIMP analysis while the field system is in operation. Approximately 10 to 15 samples per week will be submitted for analysis for the remaining organic species. Approximately 10 to 15 samples per week will be submitted to ALG for metal analysis and quality control. This analytical requirement supersedes any previously stated requirement.

SCHEDULING

18. A time schedule for operation of the water treatment system and combination studies at RMA during FY 79 is presented in Figure 3. The field studies on Well 118 are scheduled to continue through April 1979. The laboratory studies on Well 118 are scheduled to continue through December 1978. The laboratory work will then continue using water from the Basin A area; the work to be finished in late April 1979. The field studies on Basin A source water will be initiated in April 1979 and continue through the year. The work on Basin A area water can probably be initiated sooner if the Contamination Survey identifies a suitable well for procuring water at an earlier date than scheduled. Additional laboratory work will be conducted starting in April 1979 and continuing through the year on other source waters identified as a result of the Contamination Survey. Work is also scheduled in the expanded north boundary area if needed during the

May through September 1979 time frame. A final summary report on work completed in FY 79 is due 1 October 1979. Other data and information will be provided to the OPM-CDIR throughout the year as requested.

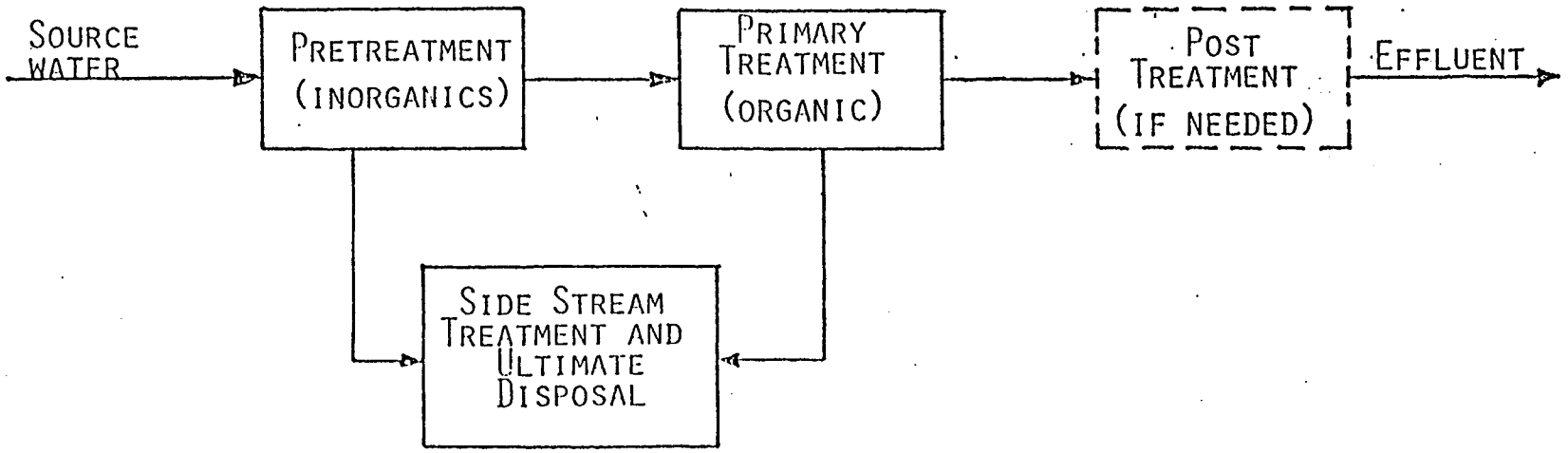


FIGURE 1. IR/RMA WATER TREATMENT SYSTEM

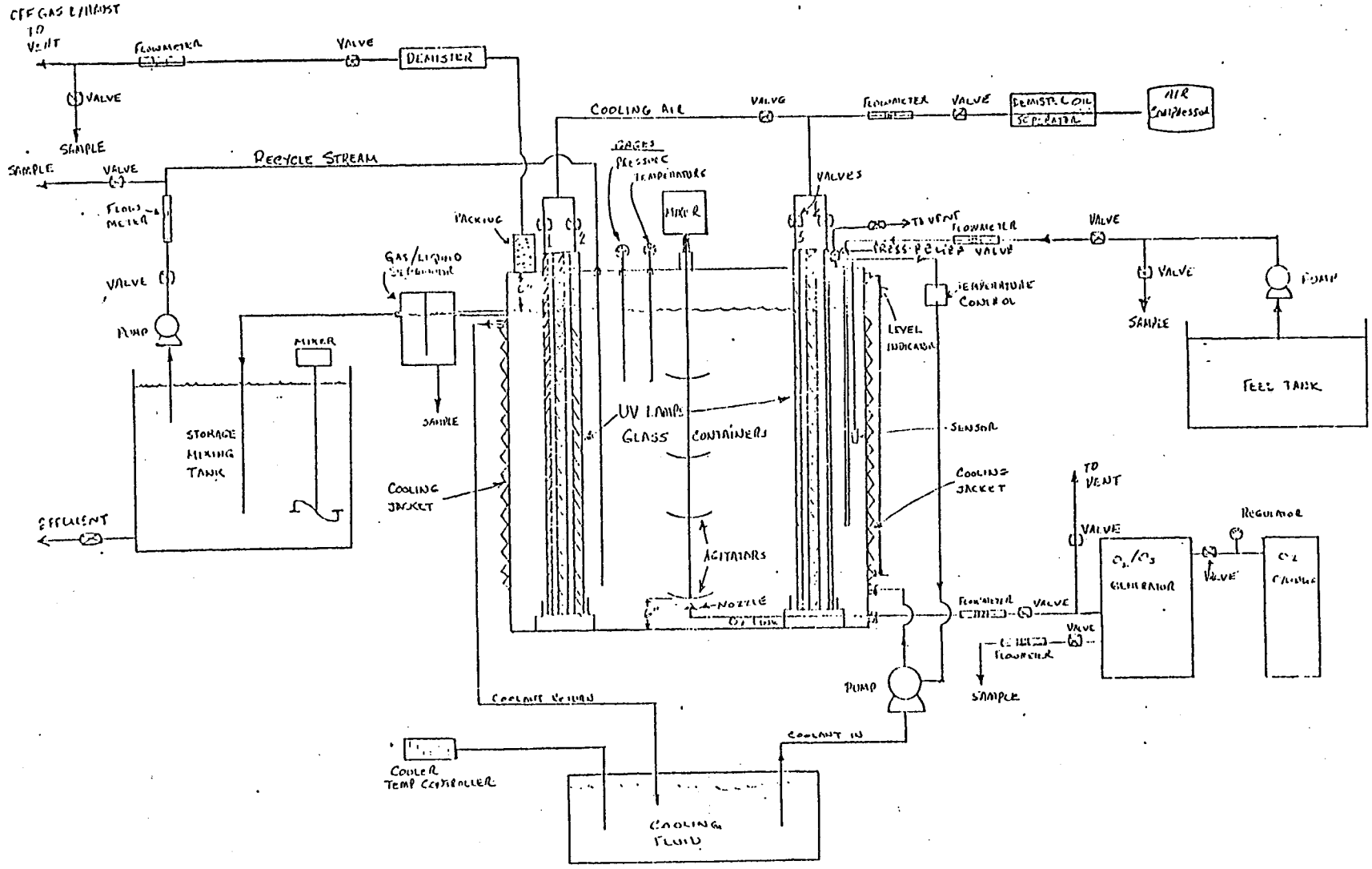


Figure 2. UV/Ozone Field Unit

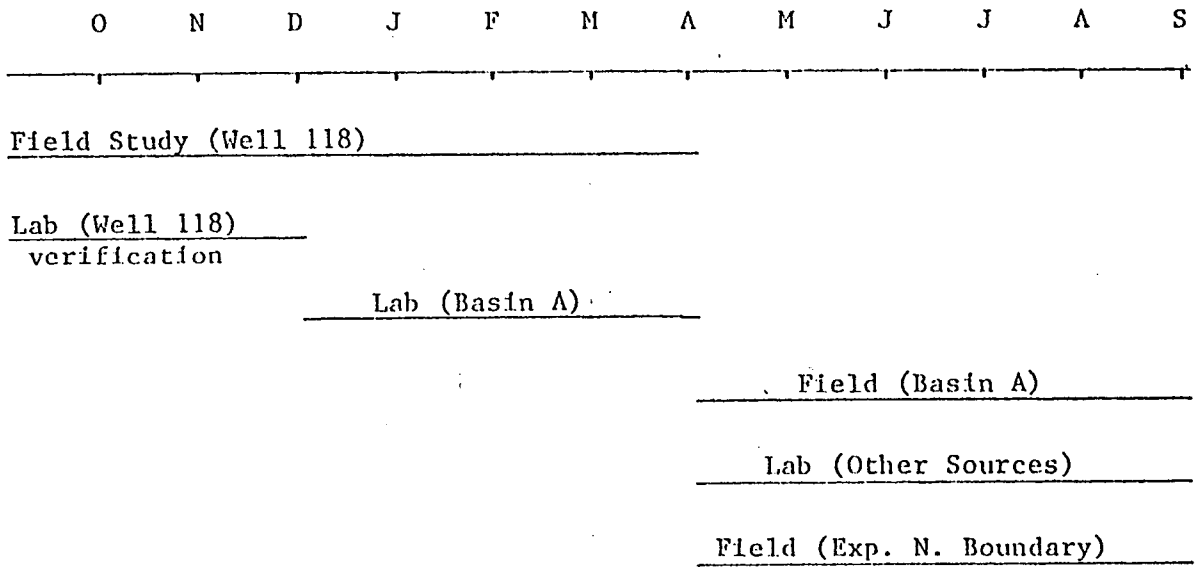


Figure 3. Combination Studies Schedule (FY 79)

DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

IN REPLY REFER TO: WESGC

5 OCT 1978

SUBJECT: Test Plan for Water Treatment Evaluation at RMA

Project Manager
Chemical Demilitarization and
Installation Restoration
ATTN: DRCPM-DR-P
Aberdeen Proving Ground, MD 21010

Subject test plan is inclosed for your information (Incl 1).

FOR THE COMMANDER AND DIRECTOR:

F. R. BROWN
Engineer
Technical Director

1 Incl
as

CF w/incl:
Commander
Rocky Mountain Arsenal
ATTN: SARRM-CC/Mr. Ed Berry
Commerce City, CO 80022

File RMA Decon Tech.

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Test Plan for Water Treatment Evaluation at RMA	Office Symbol: DRCPM-DRR
	Date: 16 Oct 78

PURPOSE OF ACTION: Approval of test plan.

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

REFERENCES:

Ltr, WESGC, WES, 5 Oct 78, subj: Test Plan for Water Treatment Evaluation at RMA, TAB B.

BACKGROUND & DISCUSSION:

1. Justification for source water treatability studies is primarily based upon the requirement to contain and treat groundwater in Basin A. However, at this time a clear definition of the Basin A problem is not possible.

2. Approval of these treatability studies is required to meet MCA milestones. In lieu of taking just any groundwater source in Basin A, treatment development efforts will continue on well 118 just north of Basin F. As soon as a representative Basin A source is found, program schedules will be shifted and laboratory study will begin.

RECOMMENDATIONS:

Approval and signature of TAB A.

(Continue on Separate Sheet)

Coordinations			FRONT OFFICE APPROVALS		
Office	Name	INITIALS		INITIALS	Date
	J. Zarzycki		C, PMD		
	D. Wyllie	DJW	C, TSD		
	A. Anderson		PM CD		
			PM IR		
			Admin Ofcr		
			Exec Ofcr		
			DPM CDIR		
			PM CDIR		

Action Officer (Name, Telephone Ext & Signature)

D. CAMPBELL, 2556 Donald L Campbell

CDIR Form 6, 1 Jan 77

DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

IN REPLY REFER TO:

17 Oct 78

Dear Don,

I had previously indicated that a preliminary UV/O_3 products identification report would be in the mail to you on 18 Oct. I am unable to meet this deadline and now expect to finish the report and have it to you by 30 Nov.

The project required my attention at RMA and Colorado University, Boulder (CUB), last week and I was unable to do much writing. At RMA, Richard Karn and myself examined several UV/O_3 runs on the mass spectrometer and a fair amount of data was obtained which requires interpretation. In addition, several UV/O_3 samples are awaiting mass spec analysis at CUB (their mass spec has been down for repairs the past two weeks). I have scheduled two more runs here at the WES with mass spec work to be done at RMA. CUB will also do two more runs in an attempt to pin down whether changing the wavelength of light used leads to different products.

I have targeted 10 Nov as the deadline for all experimental work and will write the report with the data available at that time. There is also a good likelihood that the computer performed literature search will be finished by then. Thanks for your understanding and patience.

Sincerely,

Bob Buhts

Robert E. Buhts
CPT, CE

D. CAMPBELL/ljm/2556

DRCPM-DRR (5 Oct 78) 1st Ind
SUBJECT: Test Plan for Water Treatment Evaluation at RMA

DA, Office of the Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, MD 21010 2 NOV 1978

TO: Commander and Director, US Army Engineer Waterways Experiment Station, ATTN: WESGC, PO Box 631, Vicksburg, MS 39180

1. Subject test plan approved.

2. Treatability studies on Basin A area waters must be emphasized throughout FY79. Scheduling noted in subject plan must be considered tentative contingent upon procurement of representative source waters in Basin A.

FOR THE PROJECT MANAGER:

Signed:
a. H. Anderson
for DAMON D. WINGFIELD
Colonel, CmlC
Assistant Project Manager for
Installation Restoration

wd incl

WESGC

29 DEC 78

SUBJECT: Transmittal of Report for Task 1.05.23

Project Manager
Chemical Demilitarization and
Installation Restoration
ATTN: DRCPM-DRR
Aberdeen Proving Ground, MD 21010

A final draft report, "Study of Inorganic Contaminant Removal from Rocky Mountain Arsenal (RMA) Groundwater," is inclosed for your review and comment (Incl 1). Work for this report was conducted with funds provided by Task 1.05.23. Incorporation of your comments and publication will be accomplished with funds provided by Task 1.05.25.

FOR THE COMMANDER AND DIRECTOR:

1 Incl
as

F. R. BROWN
Engineer
Technical Director

CF w/incl:
Commander
Rocky Mountain Arsenal
ATTN: SARRM-CC/Mr. Ed Berry
Commerce City, CO 60022

SUMMARY OF ACTION (Para 2-10, AR 340-15)	Suspense Control Number:
SUBJECT: Transmittal of Report for Task 1.05.23	**Office Symbol:** DRXTH-IR
	Date: 26 Mar 79

PURPOSE OF ACTION: Forward comments on report to WES

MEMORANDUM FOR RECORD (List references, describe briefly background & discussion and give recommendation.)

1. REFERENCES:

   None.

2. BACKGROUND AND DISCUSSION:

   Self-explanatory.

3. RECOMMENDATIONS:

   Approval and signature of Tab A.

(Continue on Separate Sheet)

Coordinations			FRONT OFFICE APPROVALS		
Office	Name	INITIALS		INITIALS	Date
	D. Wynne 28 Mar 79	DJW	C, PMD		
		✓	C, TSD	wg	2 Apr
			PM CD	✓	
			PM IR		
			Admin Ofcr		
			Exec Ofcr		
			DPM CDIR		
			PM CDIR		

Action Officer (Name, Telephone Ext & Signature)
D. CAMPBELL, 2556 Donald Campbell

CDIR Form 6, 1 Jan 77

RECOMMENDED CHANGES TO PUBLICATIONS AND BLANK FORMS

For use of this form, see AR 310-1; the proponent agency is the US Army Adjutant General Center.

Use Part II *(reverse)* for Repair Parts and Special Tool Lists (RPSTL) and Supply Catalogs/Supply Manuals (SC/SM).

DATE: 26 Mar 79

TO: *(Forward to proponent of publication or form) (Include ZIP Code)*
Commander and Director
US Army Waterways Experiment Station
ATTN: WESGC
P.O. Box 631, Vicksburg, MS 39180

FROM: *(Activity and location) (Include ZIP Code)*
USATHAMA
Aberdeen Proving Ground, MD 21010

PART I - ALL PUBLICATIONS (EXCEPT RPSTL AND SC/SM) AND BLANK FORMS

PUBLICATION/FORM NUMBER	DATE	TITLE
	Dec 78	Study of Inorganic Contaminant Removal from Rocky Mountain Arsenal (RMA) Groundwater

ITEM NO.	PAGE NO.	PARAGRAPH	LINE NO.*	FIGURE NO.	TABLE NO.	RECOMMENDED CHANGES AND REASON *(Exact wording of recommended change must be given)*
1	Cover					Must revise the report date to correspond to the actual publication date. Include distribution statement. Include new Agency name of USATHAMA.
2	i					Needs disclaimers.
3	iii					Needs executive summary. This may be the best place to explain change from PMCDIR to USATHAMA.
4	1	2				Change OPM CDIR to USATHAMA (same applies to all other references to OPM CDIR in basic text)
5	1	2				Expand MERADCOM to read "Mobility Equipment Research & Development Command". Include applicable standards for arsenic, fluoride, mercury and nitrate.
7	14	29	6-9			Statement appears to be a conclusion. Should also appear on p.21, para.48.
8	15	32	1-2			Statement appears to be a conclusion. Should also appear on p.21 para 48.

**Reference to line numbers within the paragraph or subparagraph.*

TYPED NAME, GRADE OR TITLE	TELEPHONE EXCHANGE/AUTOVON, PLUS EXTENSION	SIGNATURE
ANDREW W. ANDERSON Act C, Field Sys Div USATHAMA	584-3434	Signed: 3 APR 1979

DA FORM 1 FEB 74 2028 REPLACES DA FORM 2028, 1 DEC 68, WHICH WILL BE USED.

Mr. Campbell/jja/2556
Typed: 28 Mar 79

DRXTH-IR (29 Dec 78) 1st Ind
SUBJECT: Transmittal of Report for Task 1.05.23

US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD 21010 3 APR 1979

TO: Commander and Director, US Army Waterways Experiment Station,
ATTN: WESGC, P.O. Box 631, Vicksburg, MS 39180

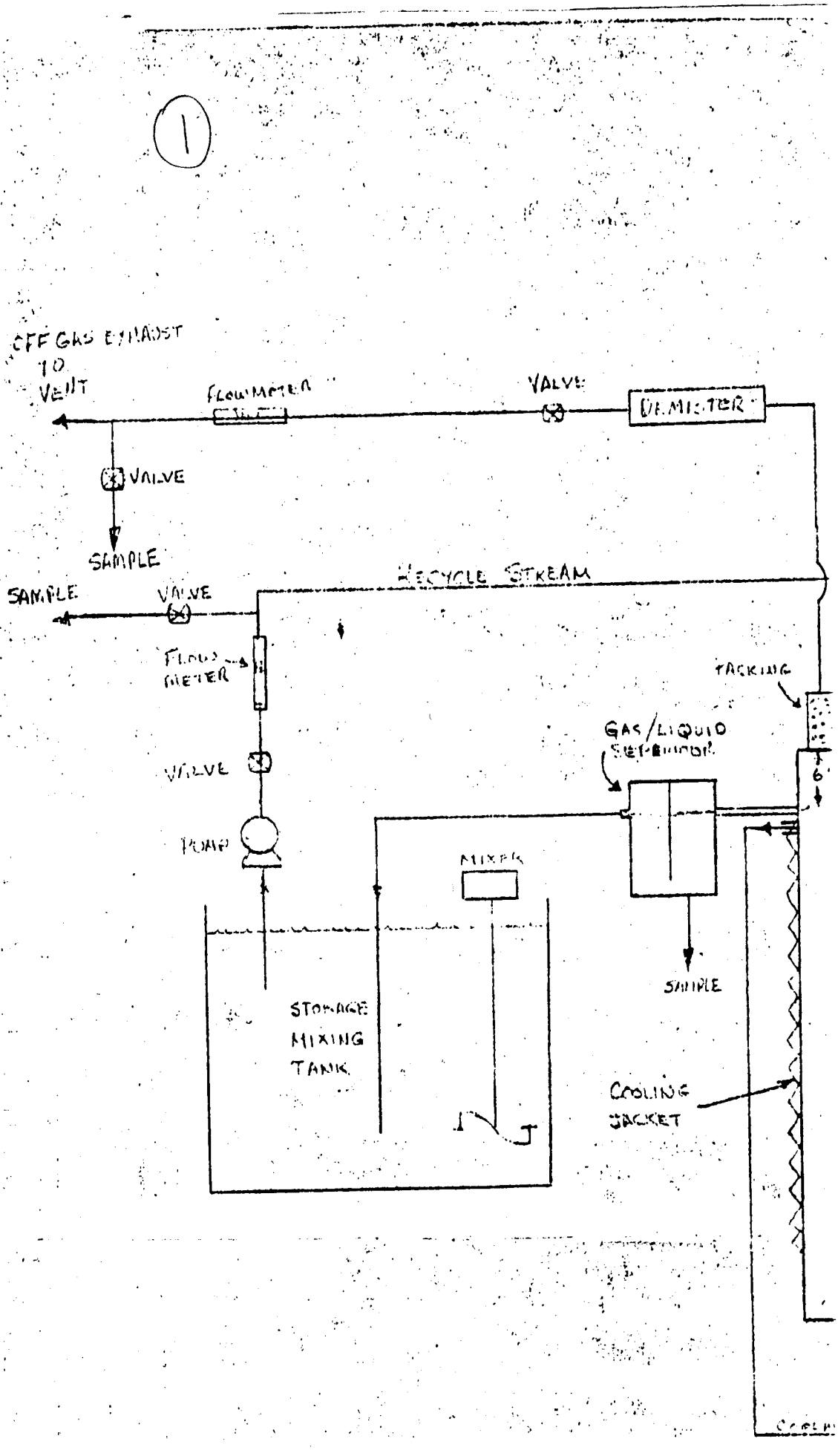
Subject report has been reviewed according to request in basic letter. Comments appear at inclosure 2. Request transmittal of 12 copies of the final report to this Agency for distribution to DDC. Incorporation of DD Form 1478 by WES is therefore required.

FOR THE COMMANDER:

Signed:

ANDREW W. ANDERSON
Acting Chief
Installation Restoration Division

1 Incl
wd incl 1
Added 1 incl
2. DA Form 2028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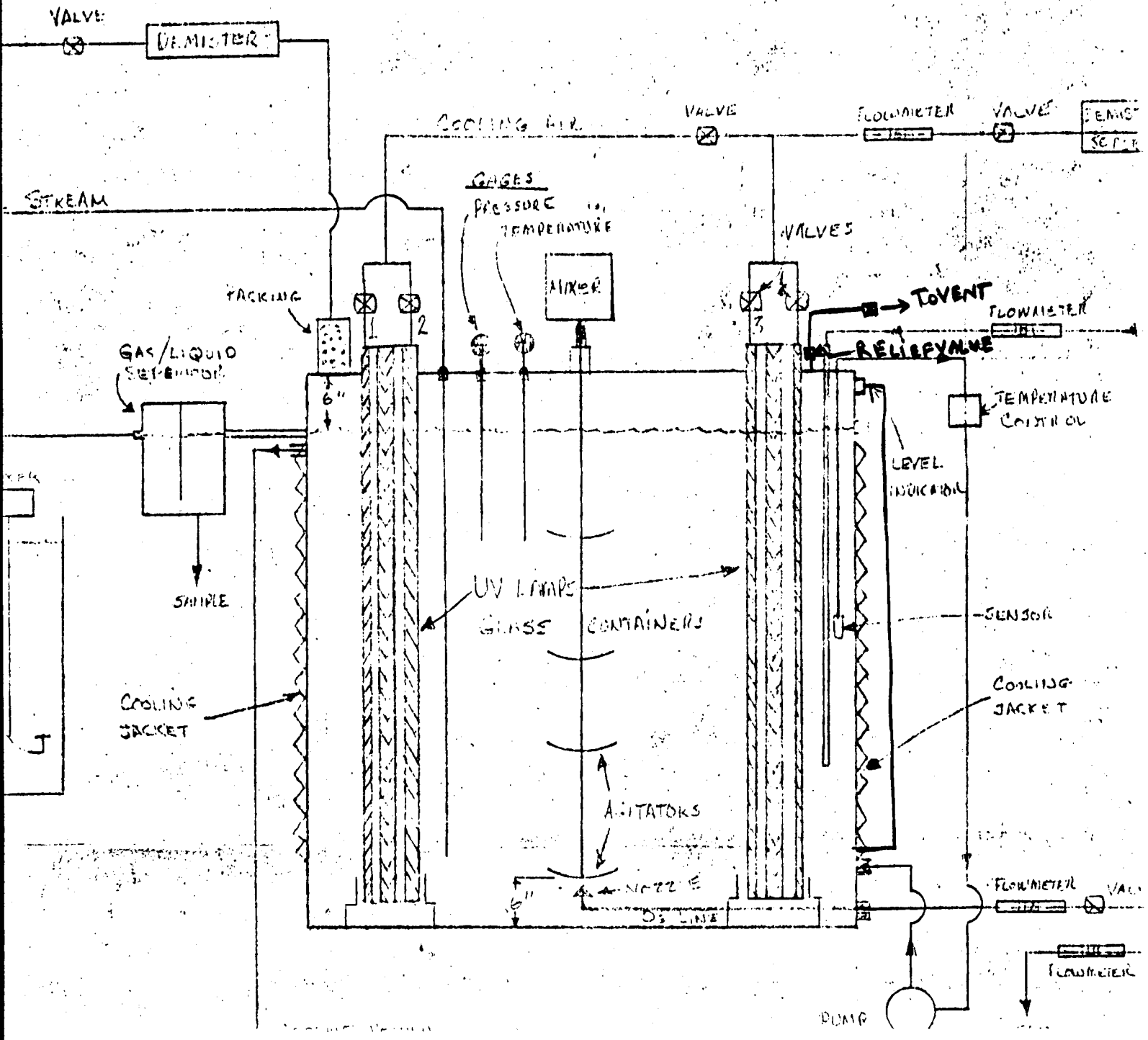
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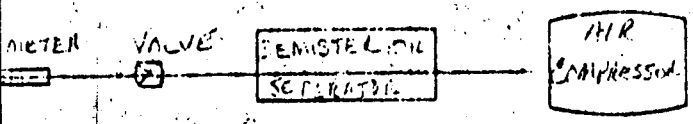
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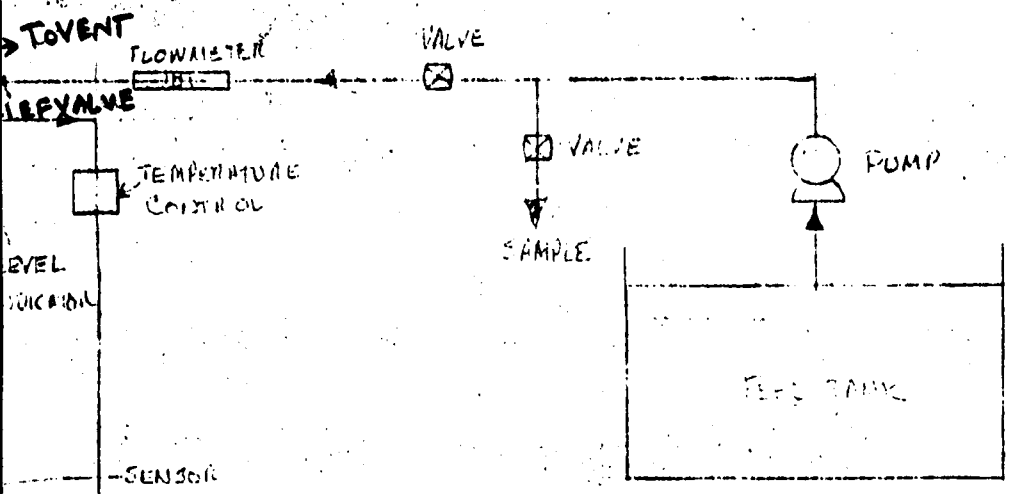
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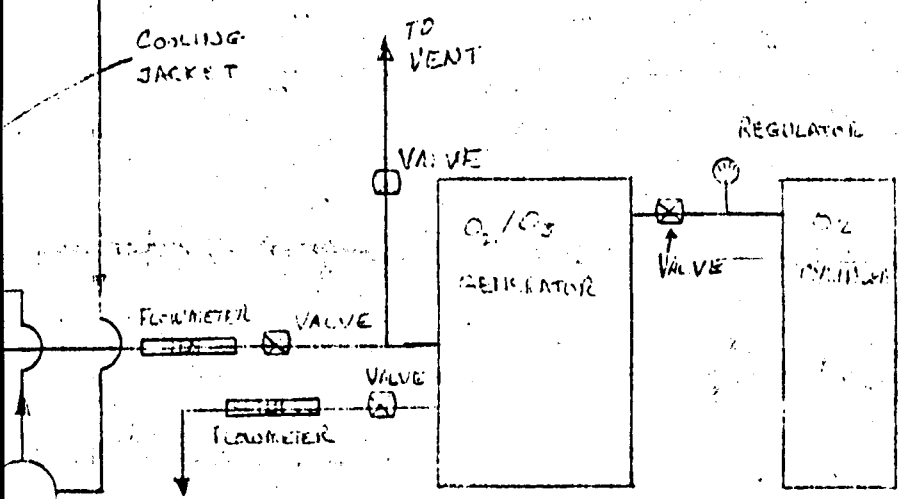
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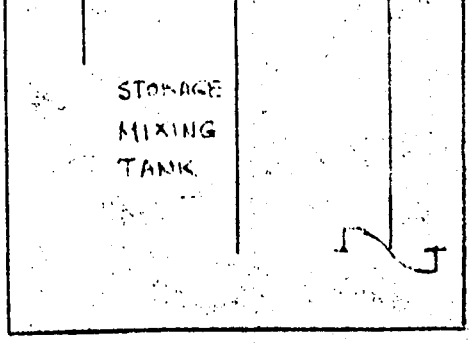

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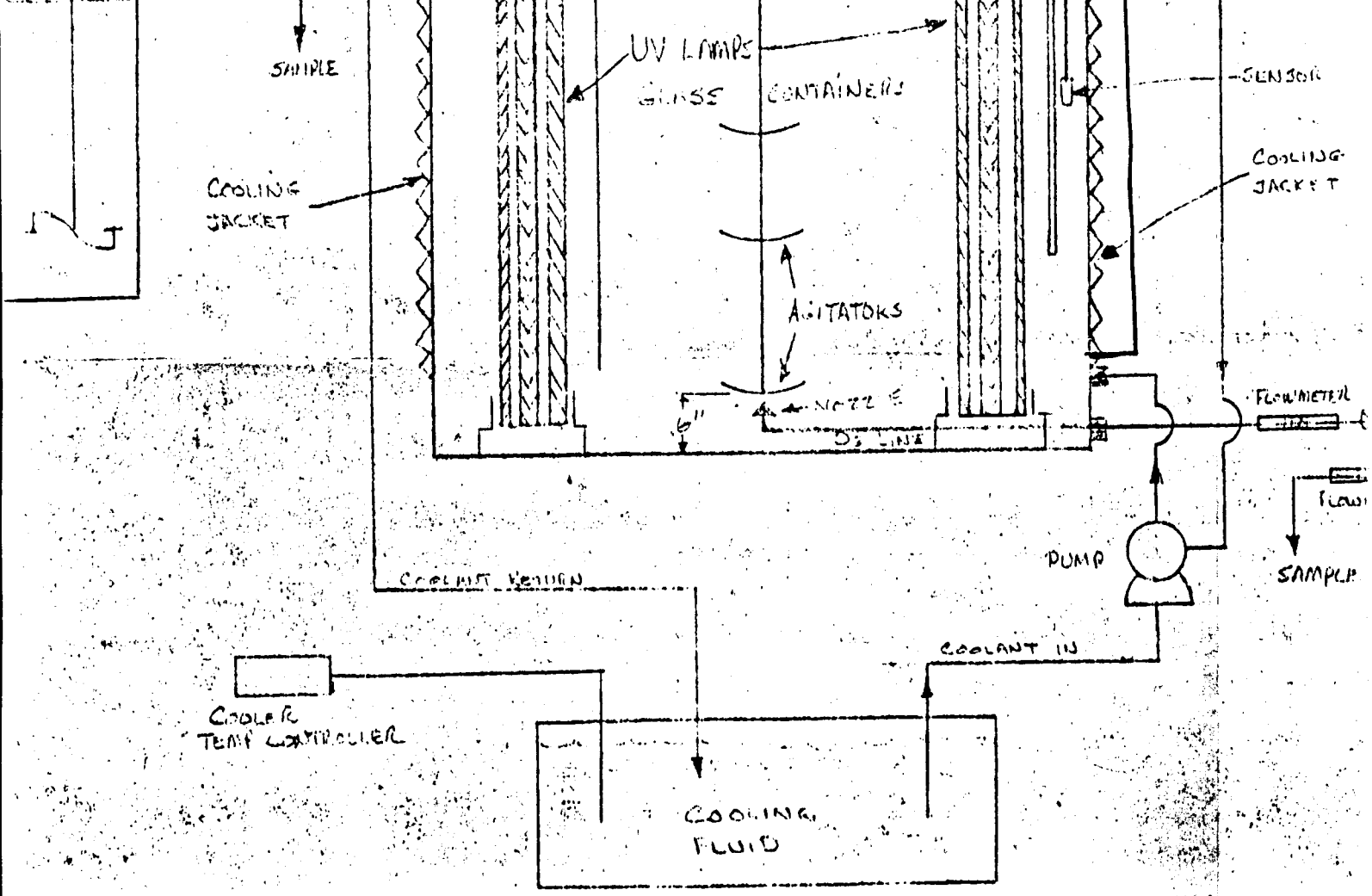
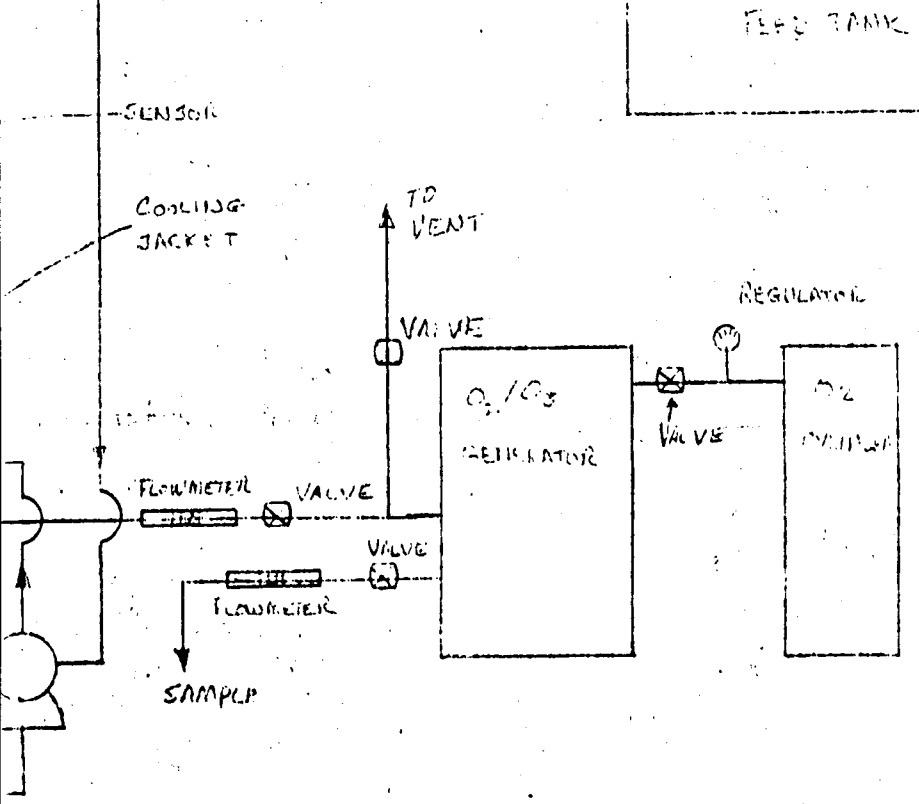


UV/O_3 SYSTEM: CONTINUOUS FIELD SCALE (NOT TO SCALE)



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