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13. ABSTRACT (Maximum 200 words) AS PART OF AN OVERALL NORTH BOUNDARY CONTAINMENT SYSTEM, THE PROJECT MANAGER'S OFFICE HAS OUTLINED TASKS TO BE PERFORMED. THE TASK OF DEVELOPING A FLUORIDE REMOVAL PROCESS WAS BROKEN INTO TWO STAGES; 1) A LITERATURE SEARCH TO DETERMINE AND COMPARE METHODS, AND 2) A TESTING PLAN TO QUANTIFY THE PARAMETERS OF THE MOST PROMISING METHOD. THE OBJECTIVE OF THIS STUDY IS TO DETERMINE IF THE ACTIVATED ALUMINA ADSORPTION METHOD IS A TECHNICALLY AND ECONOMICALLY FEASIBLE METHOD OF REMOVING FLUORIDE FROM THE NORTH BOUNDARY GROUND WATER.

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ROCKY MOUNTAIN ARSENAL
CONTAMINATION CONTROL DIRECTORATE
PROCESS DEVELOPMENT AND EVALUATION DIVISION

FLUORIDE REMOVAL TEST PLAN
TASK NO. 1.05.15

by

DENNIS M. PRUSINSKI

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APR 78

1. Introduction - As part of an overall north boundary containment system the Project Manager's Office has outlined program tasks to be performed. These tasks seek to solve the problem of contaminates migration across the north boundary at Rocky Mountain Arsenal, and thus address the Cease and Desist Orders issued by the Colorado Department of Health in April 1975. This paper addresses the task of developing a fluoride removal process.

The task of developing a fluoride removal process was broken into two stages; (1) a literature search to determine and compare methods, and (2) a testing plan to quantify the parameters of the most promising method. The literature search revealed activated alumina adsorption to be the most efficient up to 10 ppm levels of fluoride (these levels are above those found on the north boundary at RMA). While the important parameters (pH, flow rates) were listed, the values were ranged rather than quantified. The effects of different types of activated alumina were not listed possibly due to the non-availability of these different types of activated alumina at the time. This testing plan seeks to find the optimal values of flow rates, pH and type of activated alumina plus the backwash efficiency. The testing plan was designed so that the optimal values for these parameters can be scaled-up to a full sized pilot plant used in series with the Calgon Activated Carbon Adsorption Plant.

2. Objective - The objective of this study is to determine if the activated alumina adsorption method is^a technically and economically feasible method of removing fluoride from the north boundary groundwater. Although treatment of untreated Well 118 water resulted in cementation effects (binding and plugging of activated alumina by organics), it is believed the lower contaminate concentration plus pretreatment of the north boundary water will allow the activated alumina adsorption method to successfully remove fluoride to acceptable levels. If the tests of the activated alumina method for removing fluorides are successful, then the analysis of the resulting data will allow the scale-up figures for a pilot plant to be determined.

This pilot plant could be series coupled to the activated carbon adsorption system (the Calgon plant) at the north boundary.

3. Approach - The first sub task is sampling the groundwater wells on the north boundary, specifically the dewatering wells to the Calgon plant, since activated carbon pretreatment is needed to prevent cementation effects, so that the fluoride levels being dealt with can be determined. The next sub task is collecting water from a representative dewatering well and pretreating the well water with the activated carbon adsorption process. The third sub task involves testing the three parameters affecting fluoride removal efficiency by the activated alumina adsorption method, these parameters are: (1) flow rate (thus contact bed time), ~~and~~ (2) pH levels, and (3) type of activated alumina used. The fourth sub task is that of determining the efficiency of fluoride removal after spent alumina has been recharged. The results of these tasks will not only determine optima operating parameters for a pilot fluoride removal treating plant in line with the activated carbon adsorption treatment plant, but lay the basis for a comparison with other methods and/or materials. The product is ultimately north boundary groundwater that will meet the Colorado Health Department standards for fluoride levels as addressed in the Cease and Desist Order. The subproduct is a method which will lead directly to a north boundary pilot plant capable of reducing fluoride levels to the Colorado Health Department (and other agencies) acceptable standards.

4. Methodology -

Sub task #1 - Finding baseline fluoride levels.

a. Purpose - The purpose behind sampling the north boundary dewatering wells is to determine with a high degree of confidence the range of fluoride levels present in the dewatering wells ^{which will} ~~to~~ feed the Calgon plant.

b. Equipment - A water sample bailer, a step ladder and 1 liter sample jars were the only physical pieces of equipment needed to pull samples from the north boundary dewatering wells.

c. Experiment - The samples will be analyzed at the MALD facility for pH and fluoride levels. The results will be cataloged with reference to date, time of day, location, pH and fluoride levels found. The results will be tested statistically to determine if the dewatering wells remain stable as to pH and fluoride levels from one week to the next, and to set a baseline range for the pH and fluoride levels. A representative well will also be found ^{statistically} where a 1000 gallon north boundary testing water can be pumped. (???)
from which

d. The samples will be 1 liter, taken twice daily twice a week over a three week period. These samples will be taken from the six dewatering wells plus two control wells located roughly 100 yards to the left and right from the dewatering wells' line. This test will be called "The North Boundary pH and Fluoride Levels Baseline". Close contact is required with SIAO and MALD personnel and facilities.

e. Standard chemical tests will determine the pH and fluoride levels. The results of the MALD tests will be treated with the Bayesian Estimation ^{OR} ~~method~~ method against the following hypothesis: (1) one of the six dewatering wells represents the mean of the group (2) the pH and fluoride levels remain stable over long periods (months) of time, and (3) the pH and fluoride levels remain in a specified (1st Bayesian Estimate) range.

Sub Task #2

a. Purpose - To collect north boundary water for use in activated alumina columns to test fluoride removal efficiency.

b. Scope - Tanker and pump to take 1000 gallons from the dewatering well most representative of all six dewatering wells. Assistance needed from Bldg 802 personnel and RMA motor pool personnel. Sub task entitled "Drawing North Boundary User Sample Water".

Sub Task #3

a. Purpose - The purpose of this task is to determine the optima flow rates, pH levels and type of activated alumina in the activated alumina adsorption columns.

- e. Define any modifications in procedures or design that need further evaluation.
- f. Provide additional data for use in refining and calibrating a mathematical model of the UV/ozone treatment process.
- g. Obtain the necessary information for design of a pilot plant along with an estimate of treatment costs for the various source waters.

MATERIALS AND METHODS

Equipment

8. The UV/ozone field scale system will include a precipitate removal unit, any one of three separate reactor units, and a ozone generator. Additional equipment such as flow meters, thermometers, and a ozone measuring system will be obtained and used to provide complete monitoring of all operational parameters.

9. The precipitate removal system will be designed based on information obtained in the study being conducted by RMA. The final unit design will probably include a contactor system using air or exhaust gas from the UV/ozone reactor vessel and a particulate removal system such as a clarifier or filter. The precipitate removal system will be an add-on device to facilitate its use only as needed on particular source waters.

10. Three separate reactor units with different configurations will be investigated. These three units will provide the versatility needed in the study due to the variation in characteristics of the source waters being tested. None of the units as configured are commercially available but the designs will incorporate off-the-shelf available components to decrease costs and delivery times. Construction costs will be covered by funds appropriated during FY 77; FY 78 funds will be used

to conduct studies at RMA. The designs for these three units have not been completed, but a general discussion of the units will be given in this plan.

11. The first reactor unit will consist of six separate stages each containing a gas sparger and a UV lamp. Each stage will be constructed from a six-foot section of eight-inch ID stainless steel pipe. A single UV lamp will be placed down the center of the pipe. Mixing will be accomplished by means of the sparged gas mixture. The unit is designed for use of cocurrent or countercurrent flow. This unit is similar to a test unit used by OTSG in their work on hospital wastes but will have additional features such as precipitate removal ports and variable flow capability. The author has visited Ft. Detrick where the hospital waste test program was conducted.

12. The second reactor unit will be a single mechanically mixed reactor. The reactor vessel will be constructed of stainless steel and will contain a variable speed impeller mixer. Two to four UV lamps will be inserted in the reactor vessel so as to surround the mixer.

13. The third reactor unit will use the dissolved air/pressure relief principle for gas introduction. The unit will consist of pressure vessels where the ozone/oxygen mixture will be introduced under pressure into a side stream of the water to be treated. This side stream will then pass through a pressure relief valve into a reaction chamber with the remainder of the water. Very small gas bubbles are formed as a result of the decrease in pressure. The unit will provide for water recirculation and will have UV light sources in both the pressure vessel and in the reactor chamber. The unit will be constructed of stainless steel.

14. All three units will be configured so as to be extremely adaptable. The units will allow for variable control of temperature, pH, and pressure along with the standard operational parameters. The three units will have similar volumes of approximately 300 to 350 liters. The units will be skid mounted and highly portable.

15. These three units incorporate three different types of gas introduction, since it is anticipated that the effectiveness of a particular gas introduction system will vary with the type of water being treated. Sparged gas systems are inclined to clog when used to treat water with high concentrations of metals in a reduced state. In waters with high organic contaminant concentrations, the mass transfer of ozone across the air/liquid interface can become a limiting factor. In this case, a decrease in gas bubble size will generally result in a better ozone mass transfer rate due to the increase in area of the air/liquid interface.

16. The problems previously discussed indicate that one type of reactor unit will probably not efficiently treat all types of source water. The use of three separate reactor units allows for better optimization of the treatment process on a variety of source waters.

Investigation of Precipitation in Water from PW 118

17. The precipitation study being conducted by RMA (under the technical direction of WES) will include three major tasks. These tasks have been tentatively identified as follows: (1) a measure of precipitate generation with respect to gas sparging time, (2) a chemical characterization of the precipitate, and (3) an investigation of the

physical settling characteristics of the precipitate. The information gathered will be used to design the precipitate removal system to be used in the UV/ozone field scale system.

18. Precipitate Volume vs Time. A determination will be made of precipitate volume generated with respect to sparging time for the following gases: (1) air, (2) oxygen, (3) oxygen/ozone mixture. Each gas will be sparged 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.

19. Chemical Characterization. Sparging tests will be conducted using times obtained in the first procedure. After settling, the liquid will be decanted and an additional test run made with ozone to determine how much more precipitate is formed. Liquid and precipitate samples will be collected from these runs for metals analysis and organic analysis. These tests will indicate the metals being precipitated along with the amount and identity of organic matter being removed with the precipitate.

20. Physical Settling Characteristics. A standard settling chamber* with side sampling ports will be used in determining settling characteristics. Gas will be sparged into the chamber for the appropriate time and then the gas shut off to allow the precipitate to start settling. Samples will be taken periodically from the sample ports and suspended

*Camp, T. R., "Sedimentation and the Design of Settling Tanks," Trans. ASCE, 111 (1946), 895-936.

solids analysis conducted on each sample. The percent removal of solids will be computed for each sample and plotted against time and depth.

21. All information generated in this study will be furnished to WES personnel for evaluation. WES will be responsible for final design approval and construction of a unit to be incorporated into the UV/ozone field scale system.

Field Scale System Operation

22. The UV/ozone field scale study will begin with a series of break-in and calibration runs conducted on PW 3 source water. Initial operating parameters will be determined by extrapolation from existing data.

23. A factorial type experiment will be conducted using a variety of parameter settings. Experimental runs on each source water will be made with various reactor units until the optimum unit can be determined. At that point, a series of additional runs will be made on the source water in order to optimize operational parameters associated with the unit.

24. Water from PW 118 will be tested first due to the availability of data from previous studies. Other source water as identified by the PMO will then be tested. It is anticipated that three to four runs per unit per week can be conducted at RMA.

25. The data generated in this study will be used to assess the effectiveness of the UV/ozone treatment process in removing organic contaminants from various source waters at RMA. This assessment will include estimated costs for treatment of the source water.

Sampling and Analysis

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

- a. Ozone concentration in the feed gas.
- b. Oxygen concentration in the influent and effluent.
- c. pH of influent and effluent.
- d. Liquid and gas flow rate.
- e. Temperature.

27. As in previous studies, DIMP (diisopropylmethylphosphonate) 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) Pesticides
- (4) Organosulfur compounds
- (5) Organophosphorus compounds
- (6) TOC (Total Organic Carbon)
- (7) COD (Chemical Oxygen Demand)

b. Metals

- (1) Iron
- (2) Lead
- (3) Mercury
- (4) Arsenic

(5) Manganese

(6) Sodium

c. Others

(1) Total dissolved solids

(2) Conductivity

(3) Chloride

(4) Fluoride

(5) Bromide

(6) Hardness

(7) Alkalinity

(8) Sulfate

(9) Nitrite

(10) Nitrate

(11) 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.

28. 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 TOC and 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. Approximately 10 to 15 samples

per week will be submitted for analysis for each of the other organic species. Approximately 10 to 15 samples per week will be submitted to ALG for metal and other analysis.

Scheduling

29. A time schedule for operation of the UV/ozone field scale system during FY 78 is presented in Figure 1. Test plan development is scheduled for completion by January 1978. The RMA test plan for the precipitation study is scheduled for completion by 20 January 1978. The initial phase of the precipitation study is scheduled for start-up at that time and should be completed by 1 April 1978. The remainder of the precipitation study will be conducted concurrently with the field studies from June to September. The procurement of field scale equipment is scheduled from January through May 1978. Starting in June, the field scale system will be in operation at RMA. A final summary report on work completed in FY 78 on the field scale system is due 1 October 1978.