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**Removal of Plutonium from High-Level
Caustic Waste Solutions Using
Bone Char - Pilot Study**

Doye E. Blane and William R. Herald

October 2, 1978

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Miamisburg, Ohio 45342

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MONSANTO RESEARCH CORPORATION

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for the

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Abstract

Pilot studies have been completed using 275- μ m bone char as an adsorbent for the removal of plutonium, in concentrations ranging up to 8 mg/liter, from caustic waste solutions. These waste solutions were adjusted to an approximate pH of 8 before they were passed through columns of the bone char. Overall decontamination factors of about 5×10^9 were obtained.

A tentative design of a caustic waste treatment system utilizing cartridge filters and bone char columns was made. Its advantages and possible cost saving benefits are assessed.

Introduction

This project is a continuation of experimental work [1] on the use of bone char in removing radioactive contaminants from the Mound Facility waste streams. Previous studies [1,2] showed bone char to be a good adsorbent for the removal of plutonium in low concentrations; this study, however, entailed an investigation of caustic waste solutions with plutonium concentrations ranging up to 8 mg/liter. The objective of this Division of Military Application (DMA) sponsored study was to determine the feasibility of reducing plutonium concentration levels in the caustic waste stream such that processing in the Waste Water Treatment Facility was possible.

Bone char

Bone char is the commercial name given a natural product made from granulated cattle bone and is a form of calcium hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$. This material is obtained in granular form from the Kerr-McGee Chemical Corporation. Chemical components and physical properties

are listed in Tables 1 and 2. Additional information on the chemical behavior of bone char can be found in other Mound reports [2].

TABLE 1
CHEMICAL COMPOSITION OF BONE CHAR*

COMPONENTS	PERCENT
CARBON	7.0 - 8.5
Ca	24.3 - 25.0
ACID INSOLUBLE ASH	0.2 - 0.7
Fe	0.4 - 0.6
Al	0.02 - 0.03
Mg	0.5 - 0.7
P	14.8 - 15.2
WATER SOLUBLE	1.0 - 1.2

*COURTESY OF KERR-McGEE CHEMICAL CORP.

TABLE 2
TYPICAL PHYSICAL PROPERTIES OF BONE CHAR

PROPERTY	
BULK DENSITY (LBS./FT ³)	38 - 40 (0.641 gm/cc)
AVERAGE PARTICLE SIZE (mm)	1.1
SURFACE AREA (M ² /g)	110 - 120
PORE VOLUME (cc/g)	0.25 - 0.30

Caustic waste solutions

These waste solutions emanate primarily from the following three sources: (1) a 4% NaOH corrosive vapor scrubber solution from the corrosive vapor system constituting about 90% of the total volume; (2) filtrates from the NH_4OH precipitation of plutonium constituting about 8% of the volume, and (3) scrubber solutions for off-gases from an incinerator, analytical solutions, and other miscellaneous caustic solutions, constituting approximately 2% of the total volume. These sources generated about 1600 gal of caustic waste during calendar year 1977.

Characteristics of the waste stream are radioactivity levels in the range of 0.5 to 1.3 mg of plutonium/liter (maximum near 8 mg/liter) with a pH of 8 to 13 and a moderate amount of suspended solids. The current method of disposal of the

generated caustic waste is absorption of 10 gal in 150 lb of Fuller's Earth-type absorbent (Florco) contained in a 55-gal TRU package. A flow sheet of the caustic waste solidification is shown in Figure 1 and a picture of the Waste Solidification Facility (WS) is shown in Figure 2. During 1977 over 160 drums of solid caustic waste were produced for burial.

Experimental procedures and conditions

A pilot system was assembled (see Figure 3) containing a small micro-pump, two cartridge filters (100 and 1 μm), flow-meter, and four bone char columns (2 in. i.d. x 20 in. high bed). The first three columns contained granular bone char as received (1.1 mm average particle size) and the last column contained 275- μm

FIGURE 1 - Plutonium-238 high level liquid waste flowsheet.

FIGURE 2 - Waste solidification facility.

FIGURE 3 - Flow diagram of pilot system.

(average particle size) bone char. The 275- μ m bone char was obtained by grinding the granular material, sieving on a standard sieve (U. S. Standard Sieve Series No. 50), and washing with tap water to eliminate "fines". A picture of the pilot system is shown in Figure 4. Two pilot runs were made; the first with the above system as described and a second with 275- μ m bone char in all four columns.

Approximately 100 gal of caustic solution were retained in a holding tank in the WS Facility for each pilot study. This solution was adjusted to an approximate pH of 8 with concentrated HNO_3 and sampled for the initial feed concentration of plutonium. The flow was maintained at 10-12 ml/min in the first pilot study with periodic sampling before and after the filters and after each column. In the second study, the same procedure and conditions prevailed except the flow rate was 20 ml/min and a different particle size bone char was used.

Determinations of the amount of plutonium in the samples were made with a Packard "Tri-Carb" liquid-scintillation spectrometer. Packard "Instagel" scintillation cocktail was used in the sample preparation. Five milliliters of sample plus 15 ml of the "Instagel" were combined and counted from less than 1 to 5 min, depending on the total sample count.

Data and results

First pilot study

In the first batch of caustic solution, the average plutonium concentration was 3.25×10^7 dis/min/ml (0.85 mg/liter) with

an initial pH of 9.6. Flow was started through the system and sampling was initiated after the first 10 gal. Figure 5 is a plot of the data from the first pilot run. The effluent from the fourth column ranged from 5.3×10^2 dis/min/ml to 1.3×10^3 dis/min/ml during the experimental study. As can be seen from Table 3, the decontamination factor (DF) after 98 gal was 3.9×10^4 . It was concluded that the plutonium concentration in the effluents from this pilot system was too high for the Waste Treatment Facility and another study was initiated using bone char of a smaller particle size.

TABLE 3
DATA FROM 1ST PILOT RUN

CONDITIONS: pH $\approx$ 8
FLOWRATE = 10-12 ml/MIN

AFTER 98 GALLONS (370 LITERS) THROUGH SYSTEM	
FEED	- 5.0×10^7 DIS/MIN/ML
AFTER FILTERS	- 4.1×10^6 DIS/MIN/ML
AFTER 1ST COLUMN	- 11,392 DIS/MIN/ML
AFTER 2ND COLUMN	- 3,655 DIS/MIN/ML
AFTER 3RD COLUMN	- 2,211 DIS/MIN/ML
AFTER 4TH COLUMN	- 1,295 DIS/MIN/ML

OVERALL DF = 3.9×10^4

Second pilot study

In the second pilot run, the initial plutonium concentration was approximately 8 mg/liter ($\sim 3 \times 10^{11}$ dis/min/ml). This plutonium concentration was achieved by adding acidic waste solutions with higher plutonium concentrations to the caustic plutonium waste solutions. After this addition, the pH was still strongly basic, about 13. Further pH adjustments were made with concentrated HNO_3 until the overall basicity was approximately a pH of 8. The flow rate was maintained at 20 ml/min. The pressure drop across the filters (100 and 1 μ m) averaged about 2

FIGURE 4 - Pilot system.

FIGURE 5 - First pilot run of caustic waste solution through bone char.

psig for the entire run and the drop across the four columns was approximately 8 psig. It should be emphasized that the bone char had been thoroughly washed to remove "fines". Nevertheless, a second washing was necessary because pressure drops near 35 psig occurred during the initial check-out of the pilot system. Figure 6, a plot of the data collected during the second pilot run, shows that the filters removed 99+% of the initial plutonium (DF's near 10^5). (In the first run, the filters removed about 90%.) The most drastic removal of radioactivity by the columns occurred in the first column with DF's around 10^4 . A closer look at the adsorption system is shown in Table 4 after 97 gal have been passed through the columns. The overall DF at this point was 4.8×10^9 .

During the first pilot run, effluent samples counting near 1200 dis/min/ml were run through an ultrafiltration

TABLE 4
DATA FROM 2ND PILOT RUN

CONDITIONS: pH ≈ 8
FLOWRATE = 20 ml/MIN
INITIAL PLUTONIUM CONCENTRATION
~ 8 mg/liter (~ 3×10^{11} DIS/MIN/ML)

AFTER 97 GALLONS (367 LITERS) THROUGH SYSTEM
AFTER FILTERS - 6.9×10^6 DIS/MIN/ML
AFTER 1ST COLUMN - 355 DIS/MIN/ML
AFTER 2ND COLUMN - 130 DIS/MIN/ML
AFTER 3RD COLUMN - 84 DIS/MIN/ML
AFTER 4TH COLUMN - 63 DIS/MIN/ML

OVERALL DF ≈ 4.8×10^9

FIGURE 6 - Second pilot run of caustic waste through bone char.

membrane (2000 M.W. cut off) and over 50% of the plutonium was removed. Other studies [3] have shown that considerable amounts of plutonium can be removed from column effluents by centrifugation. So even though the objectives were accomplished in the second pilot study, further removal of plutonium is possible by ultrafiltration or reverse osmosis.

Full-scale column design

Several factors were considered in this tentative design of a caustic waste treatment system. First, the size of the components were limited so that they could be assembled in an existing facility without major modification and additionally sized so that upon disposal they could be packaged in 55-gal TRU drums without violating any existing or anticipated regulations.

The two cartridge filters will contain at least five or six elements (20 in. long) 100 and 1 μ m, respectively. Ideal conditions would be to procure low cost filters so that the entire package, housing and elements, could be disposed of intact thereby decreasing chances of radioactive contamination.

The cross-sectional area of the bone char columns is arbitrary and depends on the desired flow rate for the system. However, a column with a 6-in. diameter (0.2 ft² cross-sectional area) will handle a flow of 2.9 gal/hr based on a flow of 20 ml/min in the 2-in. diameter column pilot system. Since a bed height of 6.7 ft maintained the column effluent below 100 dis/min/ml for 97 gal, three columns in series (6 in. i.d. x 28 in. long each) with a total bed height of 7 ft should theoretically have a total throughput of about 850 gal

before the effluent count exceeds 100 dis/min/ml. Therefore, three columns in series (6 in. i.d. x 28 in. long each) with a flow rate of 2.9 gal/hr should theoretically maintain the column effluent below 100 dis/min/ml for 850 gal of caustic waste. Figure 7 is a diagram of one of the proposed columns. The pilot columns contained about 9.6 lb of 275- μ m bone char and the proposed system will utilize about 95 lb. Pressure drops across the proposed system should not exceed 15 psig for 850 gal but, of course, are dependent on the amount of suspended solids and the degree to which the sized bone char is free of "fines". Figure 8 is a flow diagram of the proposed caustic waste treatment system. A pump and flow-meter in the 0.1 gal/min (~380 ml/min) range would be more than adequate to maintain the desired throughput. Engineering estimates of the cost of installation of

FIGURE 7 - Column design for proposed treatment system.

FIGURE 8 - Flow diagram of full-scaled bone char system.

the proposed system is in the area of \$20,000. This system can be installed in the fume hoods of the WS Facility.

Advantages of proposed system

The estimated volume of solid waste generated from the proposed system after 1700 gal of caustic waste are treated is as follows: (1) four filter changes for the 100- μ m filter generating four 55-gal drums of waste; (2) one filter change for the 1- μ m filter producing one 55-gal drum of waste; and (3) two complete column changes for two 55-gal drums of waste generated. For a conservative cost-saving estimate, the above amount of generated waste is doubled for a total of 14 drums. During 1977 over 1600 gal of caustic waste were processed yielding over 160 55-gal drums of waste. At an estimated cost of \$150/drum for materials and shipping, this amounted to \$24,000, whereas 14 drums of waste would cost \$2,100. In addition there would be the intrinsic saving in at least a 10:1 reduction in the volume of solid waste to be buried. Other advantages to be realized from the proposed system is less manpower for its operation (thus lower operating cost) and the possible recovery of plutonium.

Conclusion

It has been shown that a caustic treatment system utilizing columns of bone char is feasible. This proposed system has economic advantages over the current disposal method and offers a 10:1 reduction in the volume of solid waste to be buried.

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