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**Mound Laboratory Activities on the
Removal of Plutonium and Uranium
from Wastewater Using Bone Char**

Doye E. Blane and Elton L. Murphy

September 30, 1976

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Miamisburg, Ohio

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U. S. Government Contract No. EY-76-C-04-0053

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Introduction

Pilot plant studies sponsored by the Division of Military Application (DMA) to treat Mound Laboratory's low risk waste streams with bone char columns have been completed. This project was to accomplish the following: (1) acquire engineering data such as flow rates, adsorption capacity, and optimum particle size for designing a tertiary treatment system, and (2) optimize the primary waste treatment process using coagulants and flocculants.

Bone char, a natural product made from granulated cattle bone, is a form of calcium hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] and contains a small amount of carbon. It is characterized by a high porosity and good resistance to abrasion and crushing.

Because plutonium and other actinides can be precipitated as phosphates from weakly acidic, neutral or alkaline solutions, it appeared possible to use an insoluble phosphate adsorbent such as bone char to remove them from waste streams.

Preliminary column studies and a description of Mound Laboratory's radioactive low-level waste treatment facility can be found in a previous report.¹

Data and Results

FLOW RATE STUDIES AT 1.5 GAL/MIN

The final pilot studies using bone char were conducted on the filtrate or effluent from a sandfilter in the Waste Treatment Facility. The sandfilter effluent was pumped through a 15- μ filter which was followed by a column of bone char (Figures 1 and 2). A diagram of the column used in these studies is shown in Figure 3. Previous column studies included in the aforementioned report¹ were carried out with bone char in the 75-104 μ particle size range. This material size was obtained by grinding, sieving and hydraulic separation, a tedious task. It was decided to conduct the final studies on the "as received" bone char for a two-fold purpose: (1) to exclude the sizing operation and, (2) to possibly eliminate the higher pressure drops across the bed experienced with the smaller particle sizes. In the current study, "as received" bone char was used and the particle size distribution is shown in Figure 4. From this graph, it can be seen that the average particle size is about 1.1 mm.

Initial column studies on the sandfilter effluent were begun with 110 lbs of "as received" bone char whose bed dimensions were 24 in. high by 15 in. diameter. A flow rate of 1.4 to 1.6 gal/min was maintained.

As shown in the flow diagram (Figure 2) the sandfilter effluent (pH = 6.5-7.5) was pumped through a filter (15 μ), then into the bone char column. Samples were taken before and after the filter and after the column. A 10-ml sample of each was counted for 100 min in a Packard Model 2211 Liquid Scintillation Spectrometer. Data from this particular run is compiled in Table 1. Over 22,000 gal of the sandfilter effluent were pumped through the column with an average decontamination factor (DF) of 5.8. It can be discerned that the DF varies proportionally to the radioactive concentration of the column feed solution. However, there appears to be a lower limit of decontamination in the range of 0.1 to 0.3 dis/min/ml for the plutonium in the waste stream. It should also be noted that the 15- μ filter had a negligible effect on the removal of alpha-emitting radionuclide. The pressure drop across the bed was near zero at this flow rate.

Another run was attempted at 10 gal/min through a fresh 24-in. high bed, but had to be terminated because the pump capacity was too low and overheated due to the higher pressure drop. The old bed was replaced with a fresh one which was only 12 in. high and the flow was reduced to 5 gal/min.

FLOW RATE STUDIES AT 5 GAL/MIN

During this run the pressure drop ranged from 8 to 10 psig. Over 100,000 gal of sandfilter effluent were pumped through 60 lbs of bone char before saturation as plotted in Figure 5. The DF's averaged from 3 to 4 for approximately 60% of the run. In order to determine the adsorptive capacity of the bone char, the amount of plutonium adsorbed by the bed was plotted versus volume (Figure 6) and the area under the plot calculated. This value was determined to be 8,673 dis/min of plutonium per gram of bone char (3.9×10^{-3} $\mu\text{Ci/g}$). The feed solution had a concentration range of 0.3 to 1.9 dis/min/ml. In a small scale study using 1.88 g of bone char, 3.45 gal of waste water averaging 3.8 dis/min/ml was necessary to saturate the bed. From this data, the total capacity of the bone char was calculated to be 5.1×10^{-3} $\mu\text{Ci/g}$.

FIGURE 1 - Ecne char pilot unit and sandfilter.

FIGURE 2 - Flow diagram of bone char pilot plant.

FIGURE 3 - Diagram of bone char column.

FIGURE 4 - Particle size distribution of bone char.

Table 1

PILOT RUN WITH A 24 IN. HIGH BY 15 IN. DIAMETER BONE CHAR COLUMN*

Sandfilter Filtrate (dis/min/ml)	After 15- μ Filter (dis/min/ml)	After Column (dis/min/ml)	Volume Through Bed (gal)	DF**
2.4	2.3	0.20	472	11.5
1.5	1.4	0.32	1087	4.4
3.8	3.7	0.34	1755	10.9
3.0	2.8	0.33	2325	8.5
0.97	0.92	0.28	3998	3.4
0.74	0.67	0.28	5273	2.4
1.0	1.0	0.14	10,367	7.1
0.44	0.43	0.11	13,608	3.9
0.81	0.78	0.30	16,188	2.6
1.1	1.0	0.33	19,938	3.0
0.73	0.80	0.14	22,963	5.7

*Conditions: Flow = 1.4 - 1.6 gal/min
pH = 6.5 - 7.5

Average DF = 5.8

**Decontamination Factor (DF) = $\frac{\text{Initial dis/min/ml}}{\text{Effluent dis/min/ml}}$

FIGURE 5 - Radioactivity in sandfilter and column effluents.

FIGURE 6 - Radioactivity removed at 5 gal/min flow rate.

Alpha-pulse-height analyses were made on samples of the sandfilter and the column effluents to determine if plutonium-238 was the only alpha-emitting isotope removed by the bone char. Results of this analysis (Table 2) showed that uranium-233 was also present and bone char had nearly equal affinity for this radionuclide. This result should have been expected because actinides form insoluble phosphate compounds.

Figure 7 is a typical alpha-pulse-height spectrum of the waste stream showing the various radionuclides present. The two peaks on the extreme right are that of plutonium-236 and the less distinguishable one on the extreme left is uranium-236. Both isotopes were used as tracers.

As shown by the spectrum, plutonium-238 is the major contaminant (second peak from the right) in the waste stream with smaller amounts of plutonium-239 (to the left of plutonium-238) and uranium-233.

FLOW RATE STUDIES AT 10 GAL/MIN

Because of pumping capacity, an earlier pilot study at a 10-gal/min flow rate had to be terminated. A pump with a higher capacity was used and the results of this study through a 24-in. bed are shown in Figure 9. Another modification was made by increasing the holes in the dispersion plate from 0.031 in. to 0.078 in. to accommodate the increased flow rate. This modification decreased the pressure drop across the 24-in. bed to about 18-20 psig.

Table 2

ALPHA PULSE-HEIGHT RESULTS ON THE SANDFILTER AND COLUMN EFFLUENTS

Before Bone Char Column	After Bone Char Column	Decontamination Factor
Pu-238 (0.68 dis/min/ml)	Pu-238 (0.20 dis/min/ml)	3.4
U-233 (0.24 dis/min/ml)	U-233 (0.08 dis/min/ml)	3.0

FIGURE 7 - Alpha-pulse height spectra showing radionuclides in waste stream.

Before

After

FIGURE 8 - Alpha-pulse height spectra before and after the bone char column.

The column feed ranged from 0.29 to 0.45 dis/min/ml and the concentration average was about 0.4 dis/min/ml, while the radioactivity level in the column effluent ranged from 0.1 to 0.27 dis/min/ml with an average of 0.2 dis/min/ml. As shown by the graph, over 55,000 gal of sandfilter effluent was pumped through the column before saturation and the decontamination factor averaged about 2 for 90% of the run.

Comparing the longevity of this run with that in Figure 5, the latter had a total volume of over 100,000 gal before saturation which is nearly double the total volume from the 10-gal/min run. This difference can possibly be explained by the increased amount of radioactivity in the column feed which averaged at least 2 to 3 times higher than the feed in 10-gal/min run.

Figure 8 shows alpha-pulse-height spectra of the sandfilter effluent before entering the column and the column effluent. The peaks on the right of each photo are that of plutonium-236 which was used as a tracer and the most distinguishable one to the left of the plutonium-236 is plutonium-238. Less distinguishable are the uranium-233 peaks which are to the left of the plutonium-238.

Flow rates of 5 and 7.5 gal/min were made on the 24-in. bed used in the 10-gal/min flow rate study but little differences in the DF's were noted. It appeared that a lower limit for the removal of the radioactivity had again been reached. This limit appears to be about 0.4 dis/min/ml and at this point the bone char capacity for the radionuclides drops off to almost zero.

COLUMN DESIGN FOR TERTIARY TREATMENT

The criteria used in designing the full-scale treatment system was based on data obtained primarily from the 10-gal/min pilot study at a 24-in. bed height with an inner diameter of 15 in. A column with a cross-sectional area of 6.1 ft² will be necessary to treat the maximum flow of 50 gal/min from the sandfilter. This cross-sectional area was obtained by increasing the area of the pilot column 5-fold. However, two columns with an inner diameter of 2 ft would have a total cross-sectional area of 6.28 ft² which is more than adequate to accommodate a 50-gal/min flow.

The 24-in. bed yielded DF's of 2 or more (Figure 9) up to approximately 50,000 gal total throughput of sandfilter effluent.

FIGURE 9 - Radioactivity removed at 10 gal/min flow rate.

Therefore, columns with the same bed height and 5 times the cross-sectional area should theoretically handle 250,000 gal of sandfilter effluent with an equivalent radioactivity level before the DF drops below 2. For a bed height 1.75 times the theoretical one mentioned above, approximately 440,000 gal should be the total throughput before the DF falls below 2.

From studies at the same flow rate but at different bed heights (residence times), the controlling factor appeared to be the velocity of the stream rather than bed height, so it is assumed that an increase in bed height at the same flow rate will increase the total throughput volume proportionally without altering the DF significantly.

The design for the full-scale treatment of 50 gal/min flow will be two columns whose bed dimensions are 3.5 ft high by 2 ft in diameter. A diagram of one of the columns is shown in Figure 10. Each of the columns will contain approximately

500 lbs of bone char and at least 440,000 gal of sandfilter effluent can be treated with a DF of 2 when the feed concentration is at 0.4 dis/min/ml. It is estimated that the beds will be changed at about 3-month intervals or four times a year. A flow diagram of the bone char tertiary treatment system is illustrated in Figure 11. Pressure drops across the bed at the 1 and 2 ft bed heights and 10 gal/min flow showed the pressure varied proportionally to the bed height. It is estimated that the drop across a bed 3.5 ft high will be in the 40-50 psig range. Compaction of the bed will probably account for the pressure drop being closer to 50 psig.

Conclusion

Data previously mentioned were used to design two bone char columns 3.5 ft high by 2 ft in diameter. These columns, a tertiary treatment system, will be used to maintain an alpha-counting level in the range of 0.1 to 0.2 dis/min/ml or less in Mound Laboratory's low-level radioactive effluent stream.

Future Plans

Preliminary studies have been initiated using bone char columns as a primary treatment on high-level caustic scrub and residual solutions. Small scale column studies have yielded DF's in the 10^4 to 10^5 range with "as received" bone char. Primary treatment of the solutions with bone char yielded a waste stream which could be treated in the low-level Waste Treatment Facility thereby decreasing solid waste generation. Currently, about thirty-five 55-gal drums of solid waste are generated each month to absorb 350 gal of high-level caustic solution. In the low-level Waste Treatment Facility less than one drum of sludge would be generated in treating 350 gal of waste solution. Therefore, it is estimated that a 30:1 reduction in solid waste generation can be realized using the bone char columns as a primary treatment. About one year absorption life is expected from a 100-lb bone char column (less than one 55-gal drum of solid waste).

FIGURE 10 - Column design for tertiary waste treatment.

Reference

1. D. E. Blane and E. L. Murphy, Mound Laboratory Activities on the Removal of Radionuclides from Wastewater Using Bone Char, MLM-2244 (September 15, 1975), 17 pp.

FIGURE 11 - Flow diagram for full-scale tertiary treatment of sandfilter effluent.

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