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CONTAMINATION OF WHITE OAK CREEK

WITH ACTIVE WASTES FROM CLINTON LABORATORIES

by

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THE CONTAMINATION OF WHITE OAK CREEK
WITH ACTIVE WASTES FROM CLINTON LABORATORIES

On April 26, 1944 an examination was made of the active waste disposal system at Clinton Laboratories. This examination included an assay of the mud along the sides and on the bottom of White Oak Creek. The material was found to be quite strongly active at a number of points, and measurably active at the mouth of the creek where it empties into the Clinch River. This situation had arisen as a result of the discharge of active wastes into the creek starting March 6th, 1944. The fact that this might cause an undesirable condition if continued was the reason why studies of the situation, of which this is a part, were undertaken.

The samples were collected from the top 0.5 cm of the mud on the creek bottom and sides at points indicated on the map. The samples were passed through a 100 mesh sieve and the coarse inclusions discarded. The total activity was determined on suitable aliquots. Two sets of samples were taken. The first on April 26, 1944 and the second five days later. During this period no activity was discharged into the creek. The data are presented in Table I. For comparison, measurements made July 4, 1944 by P. L. Eisenacher are included.

Assay: Soil

Samples A, B, D, E, and F, were assayed for radioactive constituents as follows: from .0350 gm to 3.000 gm of soil, depending upon its activity was treated with a mixture of HF and H₂SO₄. 50 mgs each of barium and strontium, and 10 mgs each of zirconium, columbium, ruthenium, tellurium, cesium, lanthanum, yttrium and cerium were added and the mixture was evaporated to dryness.

The residue was fused with K₂CO₃. The fused mass was taken up in water and the insoluble material was centrifuged out and washed. The combined supernatant liquid and washings were neutralized with HCl and treated with HF. The resulting fluoride precipitate was centrifuged out and set aside. The supernatant liquid was discarded.

The residue from the carbonate fusion was treated with HCl and then made basic with carbonate-free NH₄OH. The hydroxide precipitate was centrifuged out and combined with fluoride precipitate described above. The supernatant liquid was treated with (NH₄)₂CO₃ reagent for the separation of barium and strontium as carbonates.

The combined NH₄OH precipitate and fluoride precipitate was digested with HF and the resulting insoluble fluorides were separated out and set aside for the rare-earth analysis. The HF filtrate was treated with H₂S and the precipitate of tellurium and ruthenium were separated out and discarded. The filtrate was fused with H₂SO₄ diluted and made basic with NH₄OH. The resulting precipitate was fused with K₂CO₃. The residue was brought into solution with HF followed by fusing with H₂SO₄. Zirconium was precipitated as the phosphate in the presence of 20% H₂SO₄ and H₂O₂. The columbium in the K₂CO₃ filtrate was purified by precipitation with CH₃CO₂H.

The rare earth fraction was fused with H_2SO_4 and then precipitated again as the fluoride. Cerium was separated by means of the iodate method. The Y+Pr fraction was precipitated as hydroxides from the iodate filtrate.

Since it was not practical to isolate cesium, ruthenium and tellurium from the same sample used for the above elements, these three elements were determined on a separate sample.

Holdback carriers were added and the sample fused with Na_2CO_3 . The filtrate from the carbonate fusion was saturated with HCl and NaCl precipitate discarded. The filtrate from the HCl treatment was made basic with $(NH_4)_2CO_3$ and the filtrate evaporated to dryness and ignited. The residue was taken up in H_2O and the cesium precipitated by fuming with $HClO_4$.

The fusion residue was digested with HF. The HF filtrate was treated with H_2S and the tellurium and ruthenium precipitated. Tellurium was isolated by reduction to the metal with SO_2 . Ruthenium was isolated by distillation with $HClO_4$.

All isolated samples were weighed and the activities corrected for percent recovery. The activities, corrected to 0 filter thickness, are presented in Table II.

W-6 Solution

Aliquots were taken from each of five, well agitated, three gallon samples of W-6. The mixed sample was centrifuged and the clear filtrate and small precipitate assayed separately. The method of assaying was essentially similar to that described above. The results at 0 thickness are given in Table II. The W-6 precipitate activities are based on the amount of precipitate from 1 cc of W-6 solution.

Product Assay

The filtrate and precipitate from W-6 storage tank was treated with hydroxylamine hydrochloride and the product precipitated as the fluoride with HF, after adding 5 mgms. lanthanum as carrier. The fluoride precipitate was dissolved in concentrated HNO_3 , diluted and reprecipitated as above. This was repeated three more times and the final precipitate transferred to a Pt dish and counted.

Soil samples A and B were fused with sodium carbonate; the melt was taken up in water and acidified. 5 mgms lanthanum was added and the mixture treated with aqua regia. The samples were centrifuged and the residue extracted with hot aqua regia. The residue left from the third treatment was found to be alpha inactive. The combined filtrates were evaporated to a small volume, made basic with NaOH and heated to boiling. The resulting precipitate was centrifuged, washed and taken up in HCl. The fluoride was precipitated and purified as the W-6 assay. The results for both W-6 and the soil samples are given in Table II.

Discussion

The data in Table I show that fission products are fixed on soils of the type occurring along White Oak Creek. This finding is in harmony with the known facts concerning the fixation of cations on clays.

Clay particles for the most part are aluminosilicate crystals of the layer lattice type. From the work of Pauling it has been possible to formulate idealized structures for the principle clay minerals in which the unit packages are built up of superimposed sheets of silica tetrahedra and alumina octahedra. In nature the clay minerals very often differ from the ideal structures as a result of isomorphous substitutions of aluminum for silicon in the silica tetrahedra, and the substitution of iron, magnesium, etc., for aluminum in the alumina octahedra. The ideal structures for the principle clay minerals are electrically neutral. The clay crystals in which isomorphous substitutions have taken place are negatively charged. Thus generally the clay platelets behave as large anions and are accompanied by cations which are held to the particle by electrovalent bonds. In soils the amount of cations required for electrical neutrality may vary from 1 to 100 milliequivalents per 100 gms of soil.

For most cations the binding force between the ions and the clay particle is sufficiently weak to admit of ion exchange. That is, cations held on the surface of the particles may exchange for cations in the surrounding solution. The extent of the exchange is determined by the relative binding forces between the exchanging ions and the particle. Exchange experiments with montmorillonitic clays show increasing binding force with increasing atomic weight and charge. Since the fission products are of relatively high atomic weight and most of them polyvalent, exchange adsorption should play an important part in the fixation of those elements behaving as cations.

An additional phenomena, characteristic of clay colloids, also must be considered. When positively charged colloids are mixed with negatively charged clay particles, mutual flocculation may occur with the subsequent settling out of the suspended material. Because the discharge liquors and the creek are alkaline (pH 8.3) certain of the fission products may be initially present as insoluble particles, possessing a positive charge. If the fission products are precipitated, exchange may occur in time, depending upon solubility products, bond forces, etc. Experiments are planned to determine whether or not such a process occurs.

The relatively small amount of activity found in the water phase may be due to incomplete fixation of the cations by the clay, the presence of colloidal soil particles in the water, or the fact that some of the fission products may be behaving as anions.

The data in Table I indicate that the activity per gram of soil decreases rapidly with increasing distance from the settling basins. Since the activity is closely associated with the clay, it accumulates wherever clay accumulates.

On the other hand, this process results in a dilution of the activity with inert clay. This dilution would, of course, increase with distance from the settling basins. However, the noted decrease with distance of the activity per gram of clay is due not only to dilution with inert clay, but also to decay owing to the appreciable time of transport. It should be pointed out that the mud-flats occurring along the stream with low specific activities may nevertheless constitute large accumulations of overall activity.

It is difficult to make a direct comparison between the samples collected by the authors (4/26/44 and 5/1/44) and those collected by Eisenacher (7/4/44) because the self-absorption differs so greatly. Since most of the beta activity is fairly soft (i.e. Zr and Cb), self-absorption is a paramount factor. Taking this into consideration, the decrease in activity does not appear to be as great as would be expected on the basis of decay and dilution with inert clay.

An assay of both W-6 storage solution and five soil samples (Table II) shows that zirconium and columbium constitute 80- 85% of the total activity. This is in essential agreement with the results reported by Martens for the W-6 discharge solution, when corrections are made for the differences in filter thicknesses. The chemical wastes are neutralized with Na_2CO_3 to pH 8 before release to the storage tanks W-5 and W-6. For ten days previous to the collection of the first samples, the wastes were treated with 500 pounds of CaCl_2 per day in W-6. This treatment effected the removal of a large fraction of the activity on the resulting precipitate. The supernatant fluid in W-6 was led off to be mixed with cooling water and emptied into the settling basins. The mixture of the liquor with cooling water produced an additional precipitate which accumulated noticeably on the bottom of the basins and on the bottom of the ditch leading to White Oak Creek.

An assay of the suspension in the settling basins after centrifugation revealed that the bulk of the activity was associated with the precipitate. This finding shows that the decontamination of the waters released to the creek could be accomplished by the efficient removal of suspended matter.

The supernatant liquid from W-6 contains substantial amounts of fission products which are not ordinarily present in alkaline filtrates such as the rare earths, zirconium and columbium. Evidently the precipitation of some of these elements in the presence of F^- , PO_4 , CO_3 etc. results in the formation of highly dispersed particles. An additional factor may be the formation of soluble complexes.

The Na_2CO_3 - CaCl_2 treatment is evidently quite effective in removing barium and strontium. On the basis of data presented by W. Q. Smith concerning the composition of wastes entering W-6, the relative content of these elements in the W-6 discharge solution had been lowered considerably. Possibly the insolubility of the carbonates and the presence of traces of barium and strontium in the CaCl_2 are responsible for this.

As previously pointed out, not all elements are fixed by soils to the same degree. Barium, strontium, and cesium are fixed by soil particles and held by moderately strong forces. Recent studies with the rare earths and thorium indicate that these are very readily fixed by quite strong bonding forces and are difficult to exchange off even by prolonged leaching with electrolytes.

The exchange properties of zirconium and columbium would be dependent upon their mode of occurrence, i.e. free ions, charged oxides, etc. The same holds true for protactinium. At pH's dealt with here, both ruthenium and tellurium are present for the most part as anions and as such would not be fixed by clay.

TABLE I

Sample No.	Distance in miles	$\mu\text{c}/\text{gram soil}$			$\mu\text{c}/\text{cc water}$	
		4/26/44	5/1/44	7/4/44	4/26/44	
1,A	0	1.95	3.57			
2	.063	4.28		4.26×10^{-3}		
3	.13	1.44		1.06×10^{-4}		
4	.14	.0375			1.56×10^{-4}	
5	}	.364			1.19×10^{-4}	
6,B		.15	.292	.129	2.96×10^{-3}	0
7			.300			7.03×10^{-3}
8			1.39			2.92×10^{-4}
9	.23	.096			0	
10,C	.50	.037	.168		0	
11	.66	.408				
12,D	.88	.765	.179			
E	1.37		.027			
13	}	.011				
14,F			9.19×10^{-3}	7.27×10^{-3}		
15		2.00	11.2×10^{-3}			
16			5.97×10^{-3}			7.08×10^{-6}
17	2.19	1.59×10^{-3}			4.72×10^{-6}	
G	2.59		2.00×10^{-3}			
H	2.65		1.28×10^{-3}			

Activities for samples collected 4/26/44 and 5/1/44 are for equivalent filter thickness of 15 $\mu\text{g}/\text{cm}^2$

Activities for samples collected 7/4/44 are for equivalent filter thicknesses varying from 95 to 290 $\mu\text{g}/\text{cm}^2$

TABLE II

(Values Corrected to 0 Filter Thickness)

Element	Counts/min/cc		Counts/min/gra. soil				
	W-6 Filtrate	W-6 ppt.	A	B	D	E	F
Ba+Sr	84.0 .27%	26.8 3.67%	1.15×10^4 .94%	242 .68%	360 .88%	67.2 .98%	17.4 1.42%
Zr	18100 58.4%	140 19.2%	6.03×10^5 49.2%	19200 54.0%	19200 46.7%	3230 47.2%	535 43.7%
Cb	7920 25.6%	243 33.3%	4.43×10^5 36.1%	9850 27.7%	14400 34.9%	2230 32.6%	427 34.8%
Ce	1470 4.73%	166 22.7%	9.95×10^4 8.12%	4120 11.6%	5280 12.8%	943 13.8%	172 14.2%
Y+Pr	67.2 .22%	57.6 7.89%	4.75×10^4 3.88%	1390 3.91%	1940 4.71%	373 5.46%	73.0 5.96%
Ru	522 1.69%	7.20 .99%	7.98×10^3 .65%	318 .90%			
Te	1330 4.29%	58.2 7.98%	2.42×10^3 .20%	76.2 .21%			
Cs	432 1.39%	4.80 .66%	1.12×10^4 .91%	338 .95%			
U _{K1}	1010 3.27%	26.8 3.67%					
Product	6.0	<.03	780	70.8			

