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PROCESS FOR REMOVING RADIOACTIVE WASTES FROM LIQUID STREAMS

By

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PROCESS FOR REMOVING RADIOACTIVE WASTES FROM LIQUID STREAMS

ABSTRACT

A process is under development at Mound Laboratory to remove radioactive waste (principally plutonium-238) from process water prior to discharge of the water to the Miami River. The contaminated water, as normally received, is at a pH between 6 and 9. Under these conditions, plutonium in all its oxidation states is hydrolyzed; however, the level of the radioactive solids varies from about 50 ppm down to about 50 ppb and the plutonium remains in a colloidal or sub-colloidal condition. The permissible concentration for discharge to the river is about 50 parts per trillion.

Pilot plant tests show that 95-99% of the radioactive material is removed by adsorption on diatomaceous earth. The remainder is removed by passage through a bed of either dibasic or tribasic calcium phosphate. Ground phosphate rock is equally effective in removing

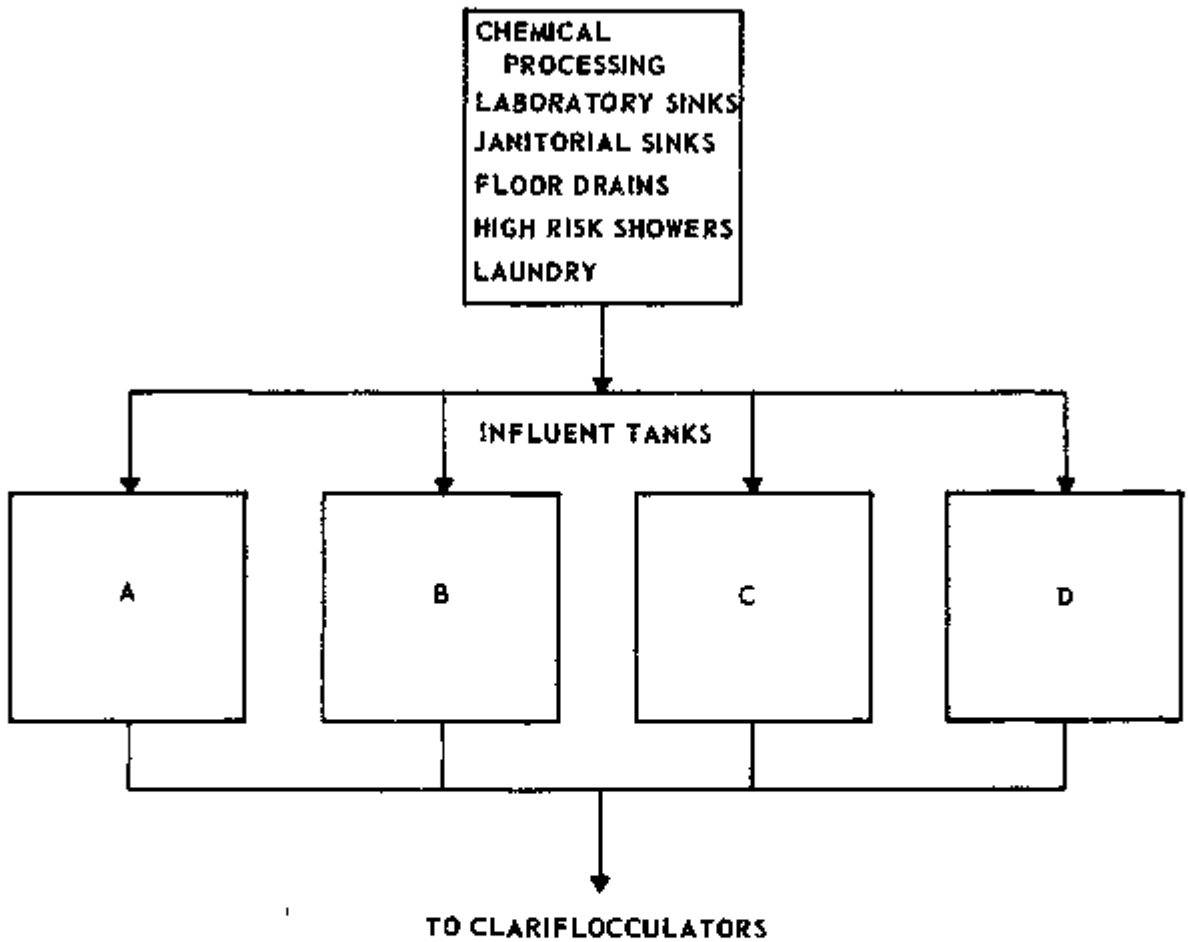
the radioactive material if the flow rate is controlled to permit sufficient contact time. Parameters for optimizing the process are now under study.

Future plans include application of the process to wastes from reactor fuels reprocessing.

The waste disposal system at Mound Laboratory is the same one that was put in service when the laboratory first opened its doors in October, 1948. At that time, our most important radioactive product - and, consequently, our chief radioactive waste product - was polonium-210. Two years of development work preceded the installation of the waste disposal system and all of this effort was directed towards the removal of polonium from our waste water prior to its being discharged into the Miami River.

One of the first decisions made was that the waste disposal system should be a general service facility, separate from the sanitary and storm sewer systems, but otherwise imposing no restrictions on scientists, chemical operators, decontamination workers or craftsmen as to the kind of radiochemical waste they might add to the system. In this respect, it was the first of its kind in the United States and, probably, in the world.

Let me take a few minutes to describe the present system and how it operates.


CHEMICAL PROCESSING
LABORATORY SINKS
JANITORIAL SINKS
FLOOR DRAINS
HIGH RISK SHOWERS
LAUNDRY
INFLUENT TANKS
A
B
C
D
TO CLARIFLOCCULATORS

SLIDE #1

(Slide #1)

The waste collection system consists of underground pipes carrying waste water from the chemical processing areas, from laboratory sinks, janitorial sinks, floor drains, showers in the high risk locker rooms and from the laundry. All of this waste is combined in a single 8-inch pipe which carries it to one of four 30,000-gallon influent tanks. Automatic level controls close off the flow when a tank has been filled to the desired level and the flow is directed into the next available tank.

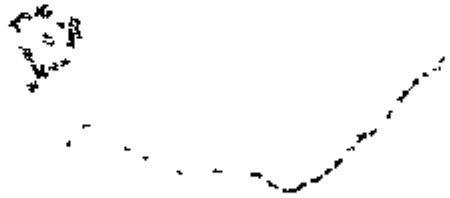
Because of the high dilution factor, the influent water is usually at a pH between 6 and 8. If it is not, it is adjusted to that pH with sodium hydroxide or sulfuric acid. After about 30 minutes of agitation, a sample is drawn and taken to the laboratory where the type of treatment to be used is determined.

This is a kind of black art, heavily dependent upon the experience and intuition of the chemist in charge.

ACTIVATED CARBON

$CaCl_2$
$BaCl_2$
$Fe_2(SO_4)_3$
(Na_2S)

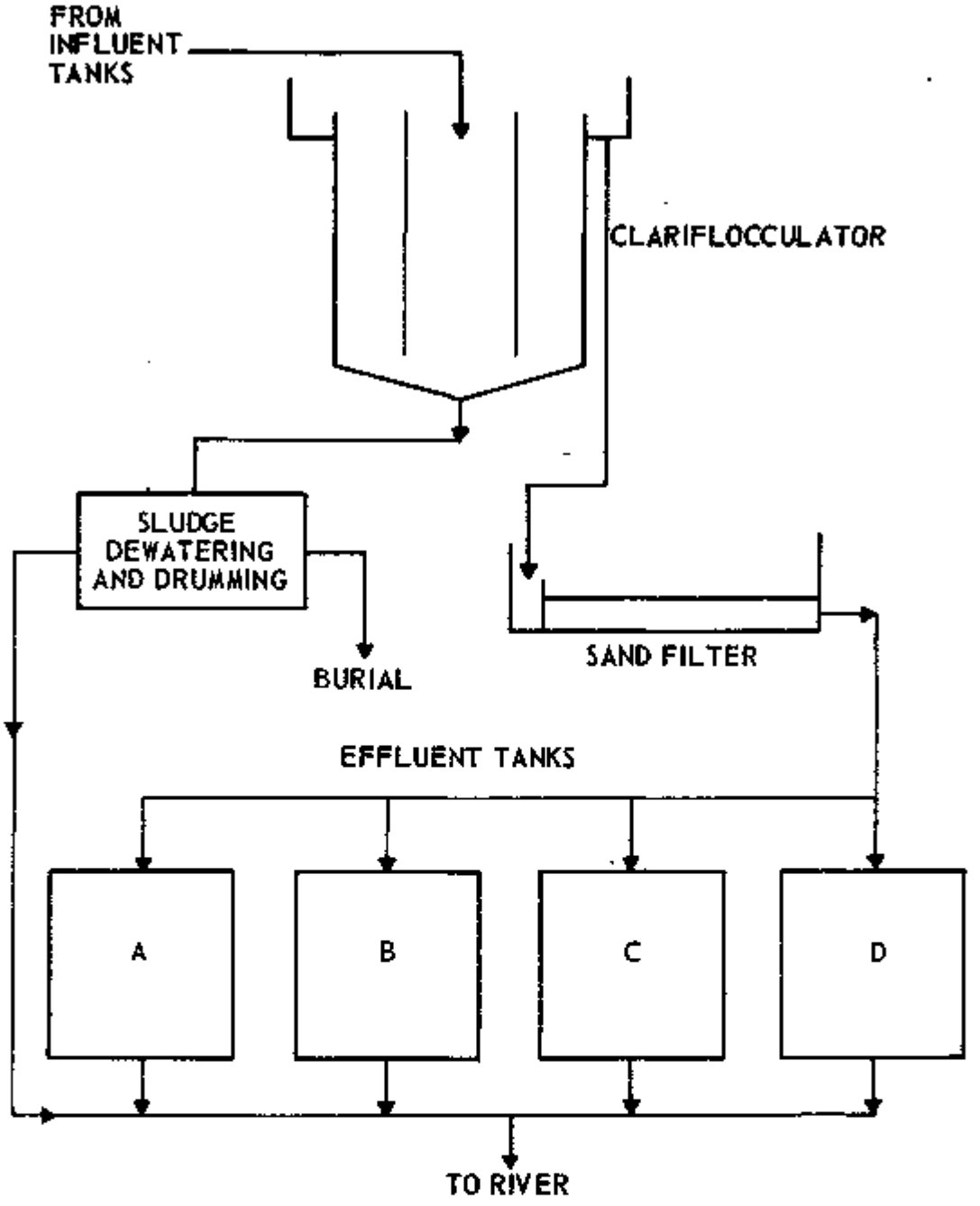
SLIDE #2



(Slide #2)

The chemist counts a sample of the influent water for alpha and beta activity and then determines which reagents must be added and in what quantities to bring the activity down to the desired level. Solutions of one or several of the following reagents are tested: activated carbon, calcium chloride, barium chloride and ferric sulfate. (At one time, sodium sulfide was also added to bring down the polonium, but this reagent is no longer used.)

Once the proper proportions have been determined, the solutions are metered into the influent tank and mixed. After thorough agitation, the water is pumped to the mixing trough of one of the two clariflocculators.


FROM
INFLUENT
TANKS
CLARIFLOCCULATOR
SLUDGE
DEWATERING
AND DRUMMING
BURIAL
SAND FILTER
EFFLUENT TANKS
A
B
C
D
TO RIVER

SLIDE #3

At this point, aluminum sulfate is added and the pH is adjusted to 8.8 with sodium hydroxide. A sludge collects at the bottom of the flocculator and the overflow from the clarifier passes to a mixing tank, where it is adjusted to pH 6.5-7 with acidified carbon. It then passes through the sand filter and into one of four 30,000-gallon effluent tanks.

Here, the water is again sampled and the residual alpha and beta activity is determined. If the activity is below the radioactivity concentration guide (RCG), the water is discharged to the river. This is usually the case, but occasionally, the activity is still too high, in which case the water is returned to one of the influent tanks and the entire procedure is repeated.

$$^{209}Bi + {}^{1}_{n} \rightarrow {}^{210}Bi \rightarrow {}^{210}Po + \beta$$

SLIDE #4

(Slide #4)

Up to now, the only radioisotope I have mentioned is polonium-210, an alpha-emitter with a half-life of 138.4 days. The RCG for polonium is 1.5 disintegrations per minute per milliliter and this is the value of the alpha activity we shoot for as the acceptable limit for discharging water to the river.

However, the polonium is made by neutron-irradiation of natural bismuth and even the purest bismuth we can obtain contains trace impurities which are also activated. The beta-emitting impurities which have been positively identified in the polonium process waste are shown on the next slide.

NUCLIDE	HALF-LIFE	RCG (μCi/ml)
^{210}Bi	5.0 d	4×10^{-5}
^{59}Fe	45.6 d	6×10^{-5}
^{60}Co	5.3 y	5×10^{-5}
^{75}Se	120.4 d	3×10^{-4}
^{110m}Ag	255 d	3×10^{-5}
^{124}Sb	60.4 d	2×10^{-5}
^{203}Hg	46.9 d	2×10^{-5}
^{132}Te	77.7 h	3×10^{-5}
^{129m}Te	34.1 d	3×10^{-5}
^{127m}Te	109 d	6×10^{-5}
^{125m}Te	58 d	2×10^{-4}

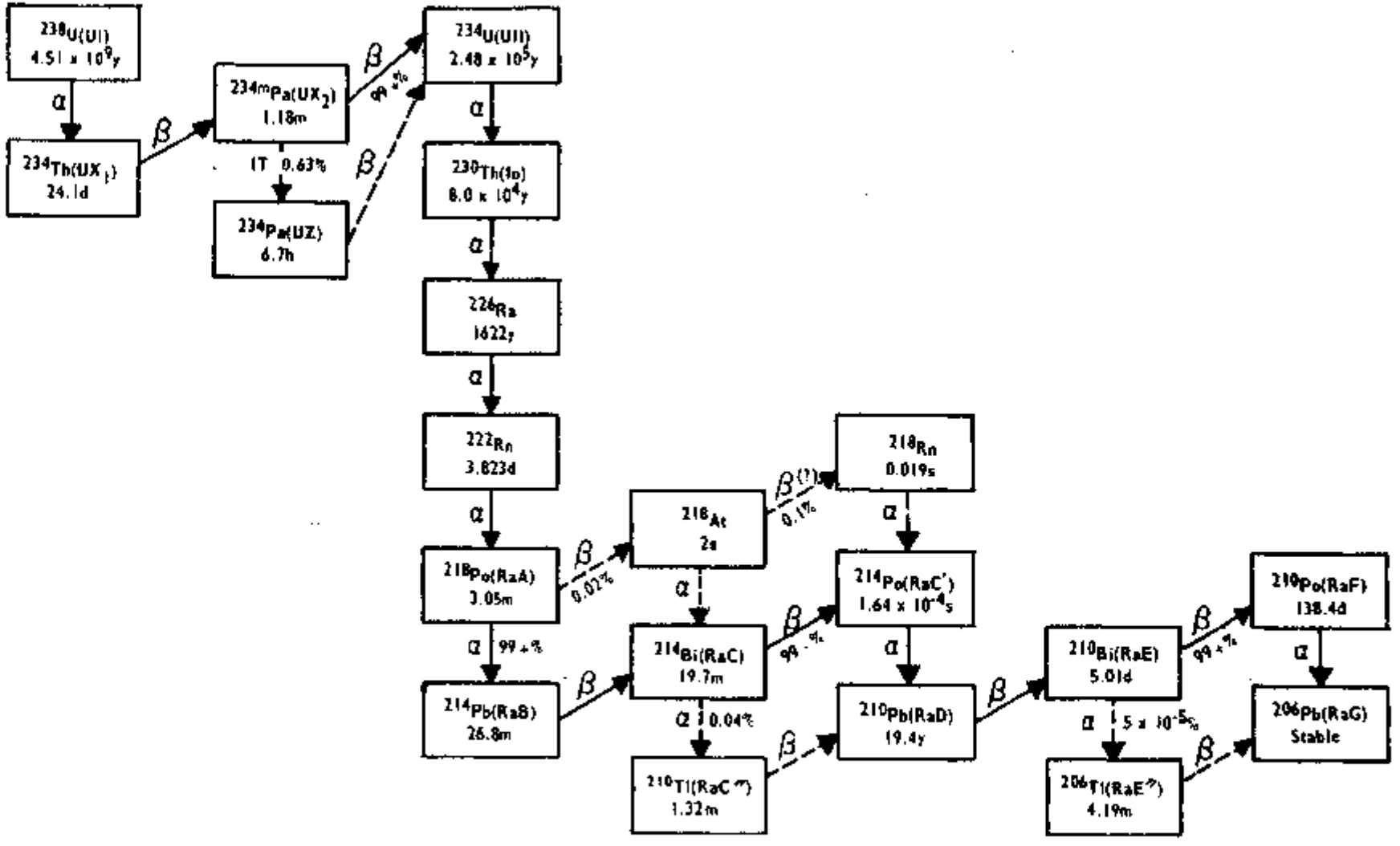
SLIDE #5

(Slide #5)

Since it is impractical to analyze each batch of influent and effluent water for specific beta emitters, we assume the worst possible case - that all of the beta activity comes from the nuclide with the lowest RCG.

The lowest RCG in this table is the one given for mercury-203 - 2×10^{-5} μCi/ml or 44 d/m/ml. However, an analysis of our waste water indicated the possibility that cesium-134 might also be present. Cesium-134 is a beta-emitter with a 2-year half-life and an RCG of 9×10^{-6} μCi/ml (or 20 d/m/ml). Therefore, even though it has never been positively identified in our wastes, we have taken the conservative position that cesium-134 is our worst possible case and limit the beta activity of water we discharge to the river to 20 d/m/ml.

SLIDE #6


238U(UI) 4.51 x 10^9 y
α
234Th(UX1) 24.1d
β
234mPa(UX2) 1.18m
IT 0.63%
234Pa(UZ) 6.7h
β
β 99.8%
234U(UII) 2.48 x 10^5 y
α
230Th(Io) 8.0 x 10^4 y
α
226Ra 1622 y
α
222Rn 3.823d
α
218Po(RaA) 3.05m
α 99+%
214Pb(RaB) 26.8m
β
β 0.02%
218At 2s
α
214Bi(RaC) 19.7m
α 0.04%
210Tl(RaC'') 1.32m
β(?) 0.1%
218Rn 0.019s
α
214Po(RaC') 1.64 x 10^-4 s
α
210Pb(RaD) 19.4y
β
β 99.9+%
210Bi(RaE) 5.01d
α 1.5 x 10^-4%
206Tl(RaE'') 4.19m
β
β 99.9+%
210Po(RaF) 138.4d
α
206Pb(RaG) Stable

$^{235}U(AcU)$ $7.1 \times 10^{8}y$
$^{231}Th(UY)$ 25.64 h
^{231}Pa $3.25 \times 10^{4}y$
^{227}Ac 21.77y
$^{227}Th(RdAc)$ 18.73d
$^{223}Fr(AcK)$ 22m
$^{223}Ra(AcX)$ 11.435d
^{219}At 0.9m
$^{219}Rn(An)$ 3.92s
^{215}Bi 8m
$^{215}Po(AcA)$ $1.83 \times 10^{-3}s$
^{215}At $10^{-4}s$
$^{211}Pb(AcB)$ 36 lm
$^{211}Bi(AcC)$ 2.16m
$^{211}Po(AcC')$ 0.52s
$^{207}Tl(AcC'')$ 4.79m
$^{207}Pb(AcD)$ Stable
α
β
1.4%
$1.4 \times 10^{-3}\%$
3%
97%
99.4%
$5 \times 10^{-4}\%$
99.7%
0.3%

SLIDE #7

232Th
1.39 x 10^10 y
α
228Ra(MsTh1)
5.75y
β
228Ac(MsTh2)
6.13h
β
228Th(RdTh)
1.91y
α
224Ra(ThX)
3.64d
α
220Rn(Tn)
51.5s
α
216Po(ThA)
0.158s
α
212Pb(ThB)
10.64h
β
212Bi(ThC)
60.5m
α 36.2%
208Tl(ThC'')
3.10m
β
β 63.8%
212Po(ThC')
3.04 x 10^-7 s
α
208Pb
Stable

SLIDE 8

(Slide #6)

But that is not all. Soon after Mound Laboratory opened its doors, we began working with radium-226 and ionium as well as polonium. Pretty soon we were processing nearly all the naturally occurring radioelements including, to name just a few,

(Slide #7)

actinium and protactinium,

(Slide #8)

thorium-232 and thorium-228.

Today, polonium represents a negligible fraction of the alpha radioactivity in our influent waste stream, while plutonium-238 and the impurities we separate from it contribute far more radioactivity than all other radioisotopes combined. All of these nuclides, together with their long- and short-lived decay products eventually find their way into our composite waste stream, and they are all treated by essentially the same process that was originally developed for polonium.

The miracle is that it has worked. Up to now, our effluents have continued to meet the same specs - 1.5 alpha d/m/ml and 20 beta d/m/ml - which were established for polonium-210, even though much higher RCG's would have been justified by the changing nature of the waste stream. The RCG for plutonium-238, for example, is 11 alpha d/m/ml - more than 7 times higher than for polonium.

In a way, this kind of success can be a handicap. There is a natural reluctance to tinker with a process that seems to be working well enough. Consequently, for more than 20 years, the waste disposal process originally developed for polonium-210 was not significantly modified or even seriously examined.

In the meantime, another problem was becoming increasingly important - not only to Mound Laboratory, but to the entire AEC complex and supporting services. The water we were sending to the river was clean enough to satisfy the various regulatory agencies, but what about the tons of radioactive sludge being accumulated in various burial grounds?

COST OF DRUM	$ 9
CEMENT FOR SOLIDIFICATION	$ 8
LABOR	$ 2
SHIPPING & BURIAL	$ 8
TOTAL PER DRUM	~$21
TOTAL PER YEAR	~$50,000

SLIDE #9

(Slide #9)

Mound Laboratory is a relatively small operation as AEC sites go, but each month we ship out for burial about 200 30-gallon drums of sludge - about 10,000 cubic feet per year.

In round numbers, the cost of packaging, shipping and burying a single drum of sludge breaks down as shown on this slide. And, this does not include the cost of producing the sludge in the first place. Our annual budget for processing 6-7 million gallons of waste water is $330,000 or about $50 per 1,000 gallons.

About two years ago, we decided to take another look at our waste disposal process to see if we couldn't make use of some of the technology developed in the last 20 years to reduce the amount of sludge we were shipping out and at the same time to reduce the cost of producing it.

Plutonium-238 was now the most important single radioisotope in our influent waste stream, while the present and projected processing of polonium-210 was declining. Any new or modified process should be based primarily on the chemistry of the actinides and only incidentally, if at all, on the chemistry of polonium.

All of the actinides can be precipitated as phosphates from weakly acid, neutral or alkaline solutions. However, the introduction of any significant amount of phosphate into the environment is a no-no by present environmental standards. So any phosphate added to precipitate actinides would itself have to be removed before the effluent water could be discharged into the river.

On the other hand, both di- and tribasic calcium phosphates are insoluble in neutral or alkaline water. So it seemed possible that a column of insoluble phosphates could be used for the continuous removal of plutonium and other actinides from the waste stream.

FILTER	FILTRATE (DIS/MIN/ML)	%
NONE	11,362	100
WHEATMAN #4	2,432	21
WHATMAN #1	48	0.4
WHATMAN #42	34	0.3
FINE SAND	24	0.2
DIATOMACEOUS EARTH	20	0.2
$Co_3(PO_4)_2$	1.15	0.01

SLIDE #10

(Slide #10)

A sample of waste water was taken for testing. It contained about 11,000 d/m/ml of alpha and about 90 d/m/ml of beta activity. It also contained some black particles which were probably activated carbon stirred up from the bottom of the influent tank. The pH was about 7. An alpha spectrum showed that it contained both plutonium-238 and polonium-210, but the resolution was poor because of the large amount of solids present, so it was impossible to determine the relative amounts of the two alpha-emitters.

The water was passed through Whatman #4 filter paper (a qualitative fast-flowing grade). This removed most of the visible solids and about 80% of the alpha activity. An alpha spectrum of this filtrate showed plutonium-238 and polonium-210 in a ratio of about 2:1. The filtrate was then passed successively through two finer grades of Whatman filter paper and, finally, through fine sand and diatomaceous earth.

These results showed that a substantial decontamination could be had simply by filtration. But the count rate was still too high for discharge to the river.

FILTER	FILTRATE (DIS/MIN/ML)	%
NONE	15,500	100
WHATMAN #1	150	1
GELMAN 0.45μ	64	0.4
GELMAN 0.1μ	49	0.3

SLIDE #11

On the other hand, when a fresh sample was filtered first through Whatman #1 paper and then through a short column of tribasic calcium phosphate, the alpha activity of the effluent dropped to 1.15 d/m/ml, comfortably below the RCG of 1.5 d/m/ml (assuming that all the alpha activity came from polonium). If the ratio of plutonium to polonium remained constant at 2:1, the actual RCG for this material would have been 7.3 d/m/ml.

Tests with other batches of waste water gave similar results: filtration at a pH around 7 removed 95-99% of the alpha activity and the remainder was taken out by calcium phosphate. The beta activity, after this treatment, was undetectable.

FILTER	FILTRATE (DIS/MIN/ML)	%
NONE	15,500	100
WHATMAN #1	150	1
GELMAN 0.45μ	64	0.4
GELMAN 0.1μ	49	0.3

SLIDE #11

(Slide #11)

An obvious question was whether filtration alone could remove all the alpha activity if the filter were fine enough. To test this possibility, a batch of waste water was filtered by gravity through Whatman #1 paper and then successively through two submicron Gelman filters under mild suction. As this slide shows, there was some additional decontamination, but not enough to meet the RCG.

Another series was run with an ultrafiltration apparatus, using Amicon filter papers with nominal porosities as low as 10,000 molecular weight. These required fairly high pressures and gave very slow flow rates without significantly improving the decontamination over what was obtained with 0.1 μ paper. So it seemed reasonably certain that the calcium phosphate was doing something useful.

pH	pH SUPERNATANT DIS/MIN/ML	%	$PO_4^{\equiv}$ SUPERNATANT DIS/MIN/ML	%
1.4	3.5×10^6	100	–	–
4.1	8.6×10^5	29	–	–
6.0	1.0×10^6	29	6.0×10^5	17
6.6	5.6×10^5	16	3.2×10^5	9
7.0	1.5×10^5	4.3	8.6×10^4	2.5
7.6	2.2×10^4	0.6	1.0×10^4	0.3
8.1	9.6×10^3	0.3	5.0×10^3	0.1
8.6	3.6×10^3	0.1	1.8×10^3	0.05
9.0	6.4×10^3	0.2	1.7×10^3	0.05
10.2	5.5×10^3	0.2	–	–

SLIDE #12

(Slide #12)

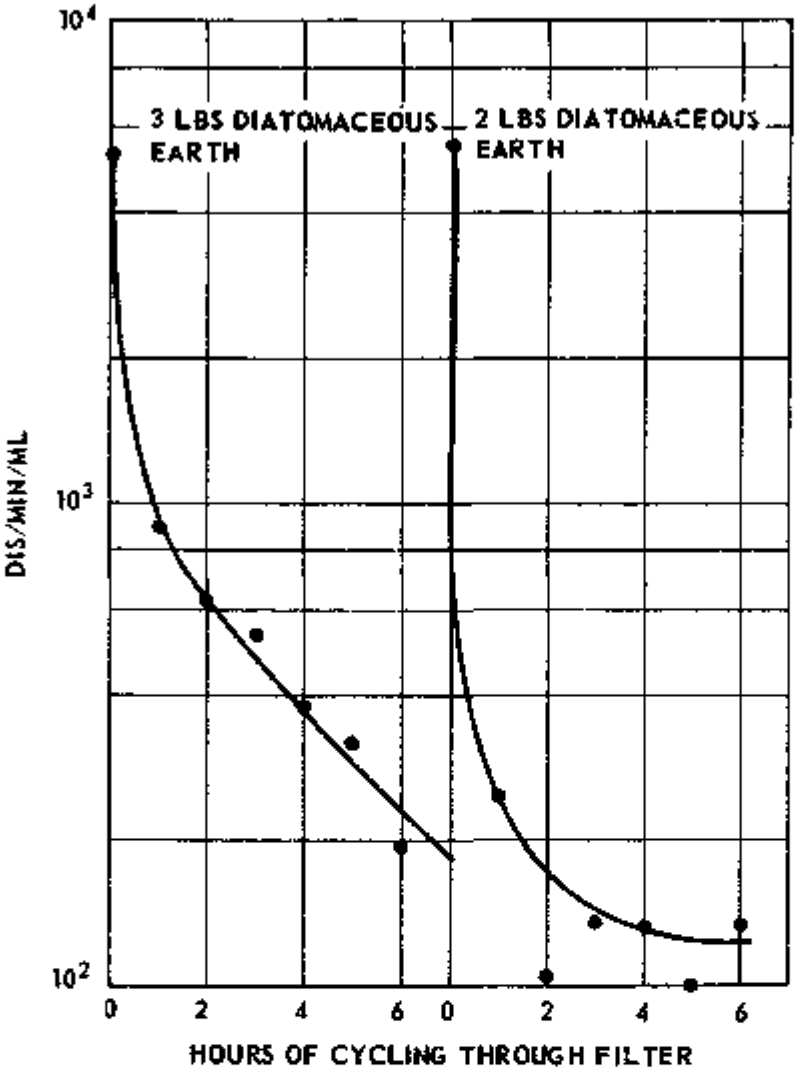
Ordinarily, waste water arrives at the waste disposal building with a pH between 6 and 8. This is due either to the high degree of dilution or to preliminary neutralization at the point of origin or both. However, one batch was received which was unusually high in both radioactivity and acidity.

This gave us a chance to test the effect of pH on the decontamination factor resulting from centrifugation. The pH was adjusted with sodium hydroxide and the solution was centrifuged for five minutes at 2,000 rpm. The supernatant was counted and then mixed with 0.25 mg per ml of $Ca_3(PO_4)_2$ and stirred for 30 minutes, after which it was centrifuged again and counted.

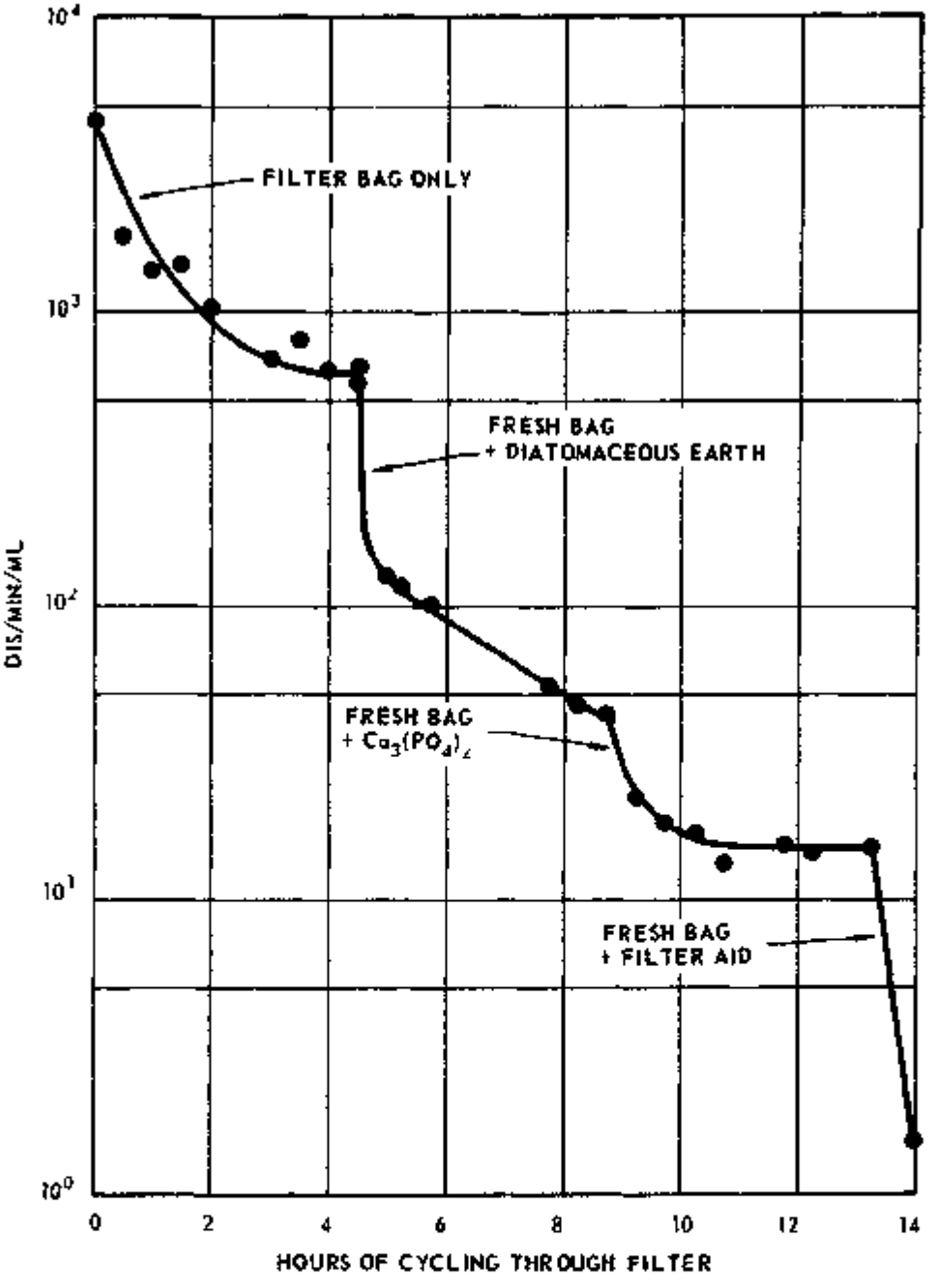
These results show that substantial decontamination begins at about pH 7 and no significant improvement takes place above pH ~8.5. At all concentrations of plutonium, about half of it was removed by stirring with 0.25 mg/ml of tribasic calcium phosphate, indicating that the phosphate has a true distribution coefficient similar to that of an ion exchange resin. It should therefore be possible to calculate the required bed height for complete decontamination when enough data are available.

(Slide #13)

We have made a number of runs on 500-gallon batches of waste water. This slide shows the results of two runs in which we were testing the effectiveness of a GAF Pressure Vessel filter system. In both cases, we added Celite diatomaceous earth as a filter aid and then cycled the water through the filter and back into the tank for several hours. The results essentially confirm what we found in the laboratory - namely, that over 95% of the alpha activity is removed by filtration alone.


10⁴
10³
10²
DIS/MIN/ML
3 LBS DIATOMACEOUS EARTH
2 LBS DIATOMACEOUS EARTH
0
2
4
6
0
2
4
6
HOURS OF CYCLING THROUGH FILTER

SLIDE #13

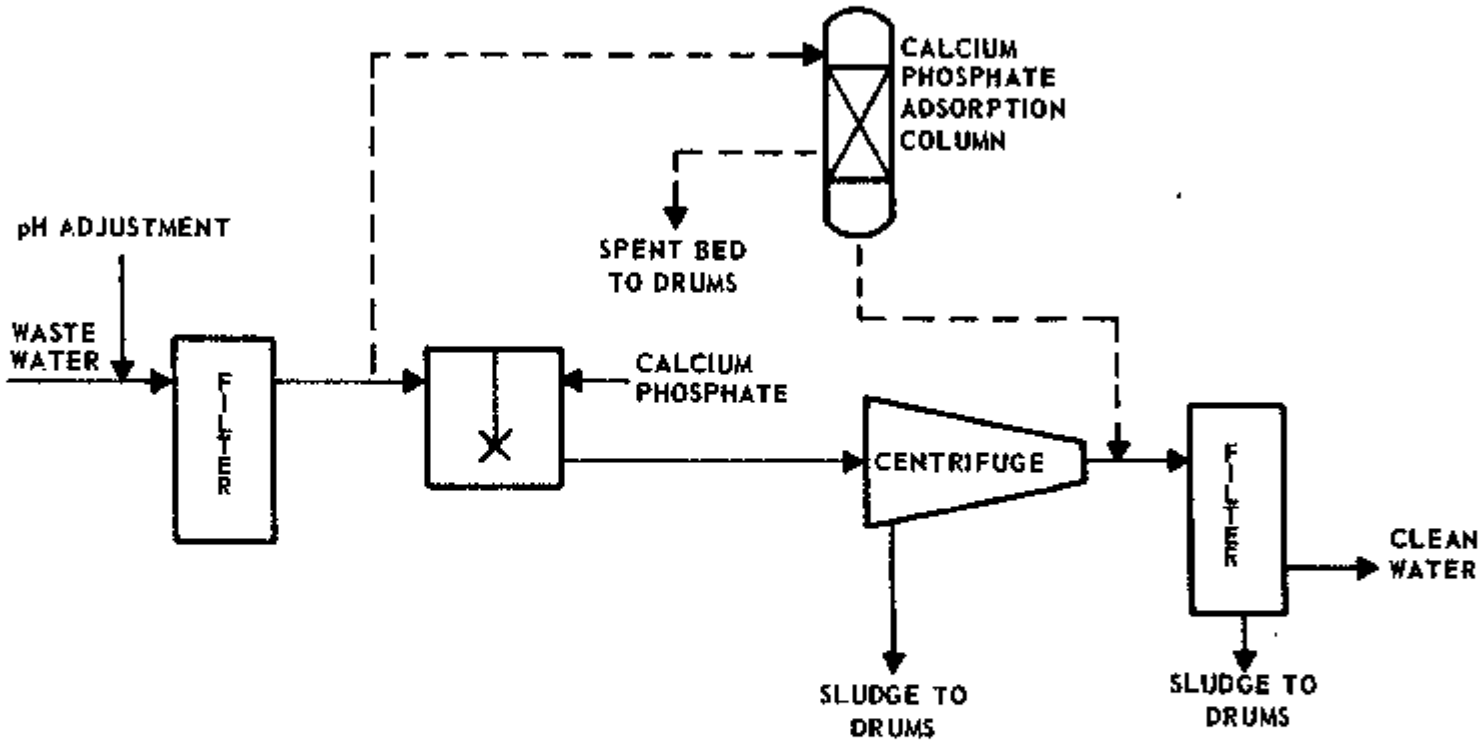

10^4
10^3
10^2
10^1
10^0
DIS/MIN/ML
FILTER BAG ONLY
FRESH BAG
+ DIATOMACEOUS EARTH
FRESH BAG
+ $Ca_3(PO_4)_2$
FRESH BAG
+ FILTER AID
0
2
4
6
8
10
12
14
HOURS OF CYCLING THROUGH FILTER

SLIDE #14

(Slide #14)

This slide shows another 500-gallon batch being decontaminated in four stages. In the first stage, we used the 5-micron filter bag alone. This removed about 87% of the alpha activity. Then we changed filter bags and added diatomaceous earth, bringing the activity down to about 45 d/m/ml or about 1%. The bag was changed and two pounds of tribasic calcium phosphate was added but no filter aid. This brought the activity down to 15 d/m/ml, but clogged the filter. At this point, the bag was changed again, two pounds of filter aid were added and the alpha activity promptly dropped to 1.5 d/m/ml.

SLIDE #15


CALCIUM
PHOSPHATE
ADSORPTION
COLUMN
SPENT BED
TO DRUMS
pH ADJUSTMENT
WASTE
WATER
FILTER
CALCIUM
PHOSPHATE
CENTRIFUGE
FILTER
CLEAN
WATER
SLUDGE TO
DRUMS
SLUDGE TO
DRUMS

(Slide #15)

The results that I have described have given us confidence that we can develop a continuous flow process which will do on a plant scale what we have done repeatedly on a laboratory scale.

We envision a system which will consist essentially of two stages; first, a pH adjustment and filtration to remove as much as possible of the coarser particulate matter, including the larger plutonium polymers, and, second, a calcium phosphate treatment, possibly in the form of a replaceable cartridge, which will do the final decontamination.

The system can probably be engineered as a package which would come in various sizes, so that it may be possible to do away with a centrally located waste disposal plant. Instead, we would install a waste treatment station at each point where liquid radioactive waste is generated.

We already know that our biggest problems are going to be filtration and pressure drop. Tribasic calcium phosphate is sold commercially as a precipitated powder. It is extremely fine, with particle sizes ranging down to two microns. This means that filters will have to be fine and pressures high in order to

have an adequate flow rate. To eliminate part of this problem, we hope to be able to use centrifugation. We have already tested a pilot scale centrifuge which removed upwards of 75% of the calcium phosphate from a water slurry.

As an alternative to precipitated calcium phosphate, we have tested ground phosphate rock. This is much coarser and has better filtering characteristics. It can be obtained in any specified mesh size and is relatively inexpensive. It also appears to do a good job of decontamination if the flow rate is controlled to allow sufficient contact time between the water and the available surface.

We also hope to adapt the process to the removal of radioactive wastes other than the actinides. Phosphate is a relatively unselective anion and there are few metallic cations which do not precipitate as phosphates in neutral or alkaline solution. This includes the alkaline earth and rare earth fission products as well as most of the metallic elements found in the middle of the Periodic Table.

But that is for some time in the future. In the meantime, our problem is plutonium and we are concentrating on that.