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LOS ALAMOS REPORT

John F. Newell (1/10/50)

0708 TA-21

1. ORGANIZATION AND RESPONSIBILITY

The radioactive waste treatment study group at Los Alamos was organized by directive of the Manager, Santa Fe Operations Office in November 1948. The group, organized under the direction and supervision of the sanitary engineer, is a cooperative enterprise to draw upon the experience and knowledge of the following organization:

Los Alamos Scientific Laboratories
United States Public Health Service
United States Geological Survey
SFOO Sanitary Engineer Office

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In general, the contributions of these organizations are as follows:

(a) Cooperation of the Los Alamos Scientific Laboratories is through the CMR Division, Health Division and Department of Engineering. These organizations provide consultation service, instrumentation, monitoring, maintenance and design assistance.

(b) The United States Geological Survey provides technical aid in evaluation of the local geology with respect to environmental considerations.

(c) The United States Public Health Service provides staff assistance with the services of two men. In addition, Dr. C. C. Ruchhoft, Sanitary Engineer Director of the Public Health Service Chemistry and Physics Laboratory at the Environmental Health Center in Cincinnati, Ohio, serves as consultant to the program.

(d) The Sanitary Engineers Office SFOO provides a technical staff of qualified bacteriologist, chemists, and engineers. The Sanitary Engineer is held responsible for coordinating the program and conducting the work

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2. SCOPE OF WORK - LIQUID WASTES

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The scope of the work which has been developed at Los Alamos can be described in three parts:

a. Research on and development of adequate methods of treating and rendering innocuous the liquid wastes containing the plutonium and other chemicals which may be dangerous if discharged to nature.

b. Operation of liquid waste treatment plants.

c. Study of the environmental effects of the present and past discharges to nature of these waste liquids.

The working group described in paragraph 2 attacked the problem of treating these wastes on the basis of using or adapting the use of known methods of waste treatment. Consideration was first given to utilizing the organisms present in activated sludge for concentrating and removing the plutonium from the waste liquids. Laboratory experiments proved that this method of treatment could be applied but would require from two to three stages of treatment before the desirable degree of plutonium removal could be obtained on the particular wastes at Los Alamos. The activated sludge would remove an average of at least 90% of the plutonium from the waste solution. The percentage of removal appeared to be about constant regardless of the plutonium concentration. One objection to the use of activated sludge is the deleterious effect of certain ions (for example copper) on the working organisms. Spectrographic analyses of composited waste effluents, performed by the Los Alamos Scientific Laboratory did not show the presence of any substances in sufficient concentration to be harmful to the organisms. This was no assurance, however, that substances would not be discharged in sufficient concentration to be harmful to the organisms. Experimental work indicated that plutonium had no harmful effects on the sludges.

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It was also learned that supplementary food should be added to the liquid wastes to provide a diet favorable to the development of the organisms. Experiments proved that sludges developed using a sanitary sewage feed were no more efficient than sludges developed using a synthetic feed.

Exploratory screening work also conducted to study the adsorptive characteristics of various inert materials using different types of carbons, fullers earth, pumice and volcanic tuff. Of these materials the finer grained carbons and volcanic tuff appeared more promising. It was found that the plutonium removal ability of the carbon and tuff was dependent upon pH, concentration of adsorptive material and the time of contact. The pH was very critical. More work is under way on these studies as a follow up of the screening explorations.

The most promising and seemingly most foolproof treatment method to date for Los Alamos laboratory wastes consists of co-precipitation with ferric hydroxide at a high pH followed by mechanical filtration with sand filters. Results of experimental work indicates a preponderance of removal values exceeding 99.9%. A pilot treatment plant to accommodate the present tech area wastes has been designed and is now under construction. Upon completion of the plant actual operation experience will furnish more complete data and will allow better evaluation of the method. The sludge obtained from co-precipitation will be dewatered to around 85% moisture content by means of an Eimco Filter. Further treatment of the sludge is being held in abeyance until studies can be made to determine the type of treatment that may be most applicable.

Fluorine, a non-radioactive element of great concern from the environmental standpoint, was found to be present in concentrations up to 200 ppm. Since most fluoride compounds are highly soluble it is improbable that their concentration will be diminished by percolation through the earth. Therefore, the strong

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probability exists for contamination of ground water supplies with untolerable concentrations of this element. Since the recommended optimum concentration of the fluoride ion in drinking water is only 1.5 ppm the removal of fluorides is indeed no less acute than the removal of radioactivity. Laboratory studies indicate that our proposed pilot plant will remove most of the fluorides present in the wastes by the use of excess calcium in the treatment procedure. The solubility of calcium fluoride in normal pH ranges is about 17 ppm. Experimental laboratory work indicates that the fluoride concentration in the final effluent from the pilot plant can be reduced to about that figure. Further studies are in progress on fluoride removal.

Consideration of the laundry effluent, which contains relatively low concentrations of plutonium indicates that biological treatment of these wastes by means of a trickling filter would be desirable. Experimental work is under way to study the feasibility of this method; not only from the standpoint of plutonium removal but also from the standpoint of BOD removal. It is thought that since trickling filters have been successful in treating commercial laundry wastes that the application of this method would be apropos.

3. ENVIRONMENTAL SURVEY

A study of the environmental aspects to determine the effects of the present and past discharges of dangerous wastes was initiated in January 1949. Previous surveys conducted by the Los Alamos Scientific Laboratory Health Division indicated that most of the radioactivity contained in the liquid wastes remained in the upper reaches of the dry canyon to which they were discharged. However, since the wastes eventually disappear below the ground surface and the natural gradient of the area it was deemed mandatory that an investigation should be made to determine these environmental aspects. This study is being conducted with the cooperation of the SFOO, AEC through the Sanitary Engineer, U. S. Geological survey and the Los Alamos Scientific Laboratory Health Division.

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Source of Waste	Daily Flow gpd Max.	Min.	Ave.	Present Disposal	Per C/M/L Max.	Min.	Ave.	pH Max.	Min	Ave.	F ppm Max	Min	Ave	Total Solids ppm Max	Min	Ave
Tech Area	35,000	5,000	20,000	To Canyon	40,000	2,000	3,000	12.0	2.0	3.0	200	0	100	10,000	300	800
Areas T and U DP Area	10,000	1,500	5,000	Subsurface leaching	500,000	20,000	100,000	12.0	2.0	2.8	200	0	100	10,000	300	700
Area V Laundry	20,000	10,000	16,000	Open gravel	20,000	500	1,500	9.0	6.0	7.7	0	0	0	1,200	500	800

The above table shows the sources, volumes, present disposal methods and some of the general characteristics of the liquid wastes at Los Alamos. The present methods of disposal have been in use since the establishments were constructed.

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NOTES

The following was presented at Waste Processing Meeting in Knolls Atomic Power Laboratory on July 1950 by Everett R. Mathews, Industrial Waste Branch, Los Alamos, New Mexico.

NOTES

Pilot Plant Experiences With Chemical Precipitation

As Mr. Christenson has already mentioned, on the two main industrial wastes at Los Alamos the coagulant found to be the most promising in the laboratory jar tests was ferric chloride. In conjunction with this coagulant it was found that sodium hydroxide and calcium chloride or in some instances simply lime, were quite beneficial and necessary.

These laboratory studies had indicated that optimum results could usually be obtained at quite a high pH range--much of the time at pH 12. In order to reach this high range it was necessary to feed sodium hydroxide in place of the usual lime dosage. When necessary to introduce the calcium ion this could be added in the form of calcium chloride. The water supply at Los Alamos is naturally quite soft so very little calcium is available from this source.

For pilot plant operation caustic soda and calcium chloride also have advantages over lime since they form true solutions and can be fed through constant head siphons in ordinary glass carboys whereas the milk of lime is a suspension and requires a much more elaborate feeding device. Consequently, when the first pilot plant was set up provisions were made for

feeding ferric chloride, sodium hydroxide and calcium chloride. Later on experiments were carried out using milk of lime.

Description of Pilot Plant: Tech Area wastes were chosen for the first pilot plant studies on chemical precipitation. The principal reason for setting up a pilot plant was to familiarize ourselves with the treatment characteristics of the Tech Area wastes before the main plant was built. In this way we would be able to meet the various problems that are likely to occur with prompt and correct treatment changes and therefore have a minimum number of plant upsets. Because of the rapidly changing characteristics of this waste it was to be expected that treatment changes and adjustments would be necessary at rather frequent intervals. These wastes are moderately radioactive - having average counts per minute per liter of about 4,000. The pH value fluctuates over a wide range and total solids likewise change rapidly. Furthermore high concentrations of fluorides are present. The average daily flow is 14,900 gallons with a maximum of 22,100 gallons and a minimum of 3,126 gallons.

For pilot plant study a capacity of 1 liter per minute was selected as the most practical rate. It was necessary to haul the waste to the pilot plant building by truck so the volume had to be kept quite small. The plant as set up consisted of a storage reservoir for raw waste, a flocculation basin together with chamical feeders, a settling tank and one rapid sand filter. Later a "fluorex" filter for defluorination was added. Flow through the plant is by

gravity and a constant flow is obtained by means of a constant head float chamber with regulating valve located above the flocculation unit.

(show sketch) The storage tank consists of three 55 gallon steel drums connected together with suitable piping so as to form one reservoir. The flocculation unit consists of a cylindrical steel container with capacity for a 20 minute detention period at the design flow. Vertical paddles revolving from a central vertical shaft mix chemicals and condition the floc so that it has good settling characteristics. Three carboys with constant head siphons are located so that they feed chemicals into the influent line to the flocculation basin which enters at the bottom. In passing through this line the chemicals are thoroughly mixed with the waste. The flocculated waste is then taken off at the top.

The settling tank is a 22 inch steel drum with an overflow collection weir trough across the center. The inlet is at the center and is submerged. The bottom of the drum has been fitted with a hopper bottom for collection of the sludge. The detention time in the basin is $3\frac{1}{2}$ hours.

A rapid sand filter similar to a conventional water treatment filter follows the settling basin. This filter consists of a $2\frac{1}{2}$ inch lucite tube with 24 inches of 0.5 mm sand supported on graded gravel. Provisions for backwashing are available. Recently a filter for fluoride removal has been added to the plant. A specially

prepared calcium phosphate or more accurately described as hydroxy apatite, sold under the trade name "Fluorex" is being used for filter medium. At present the depth of fluorex in the filter is 12 inches and the rate of flow is one gallon per square foot per minute. The filter is operated similar to a zeolite water softener filter except that it is regenerated with caustic solution and then rinsed with water containing a small amount of acid and then finally rinsed with straight water.

A second pilot plant for treating DP Area wastes has also been placed into operation. Since the DP wastes were small in volume it was believed that a batch process could be successfully used and would be the most practical. The volume was expected to be less than 5,000 G.P.D. Consequently, a steel drum for combined mixing and sedimentation was set up. A 24-hour composite of the waste is pumped into the tank, chemicals are added, the contents are stirred for 1 hour and then allowed to settle. Sedimentation is rapid and is normally complete within an hour. This waste has a much higher plutonium content than the Tech Area waste.

Recently the flow in DP Area has increased from 5,000 G.P.D. to an average of about 15,000 G.P.D. with peak figures of 26,000 gallons. Of course batch treatment on this quantity is not economical and a continuous flow set-up is believed more desirable. With this in mind a 2-gallon per minute Accelator plant unit as manufactured by Infilco, Inc. of Chicago, for water clarification and softening has been installed. A number of these units are now in use on other

(Show Accelator sketch)

industrial waste problems. In this unit, chemical precipitation takes place on previously precipitated sludge so that a large surface area is exposed and the chemical reactions are therefore speeded up. This precipitated sludge or slurry is constantly recirculated in a central compartment or hood where the fresh wastes together with the chemicals are added. Separation of the solids and liquid portion takes place in an outer compartment where the flow is vertical and where velocities are decreased. The clear liquid is taken off at the top by means of a weir trough extending entirely around the unit. This plant has only been in operation for a few days and consequently results on it are not yet available. However the installation does appear promising.

Results of Pilot Plant Studies: The following table summarizes these results:

TABLE 1

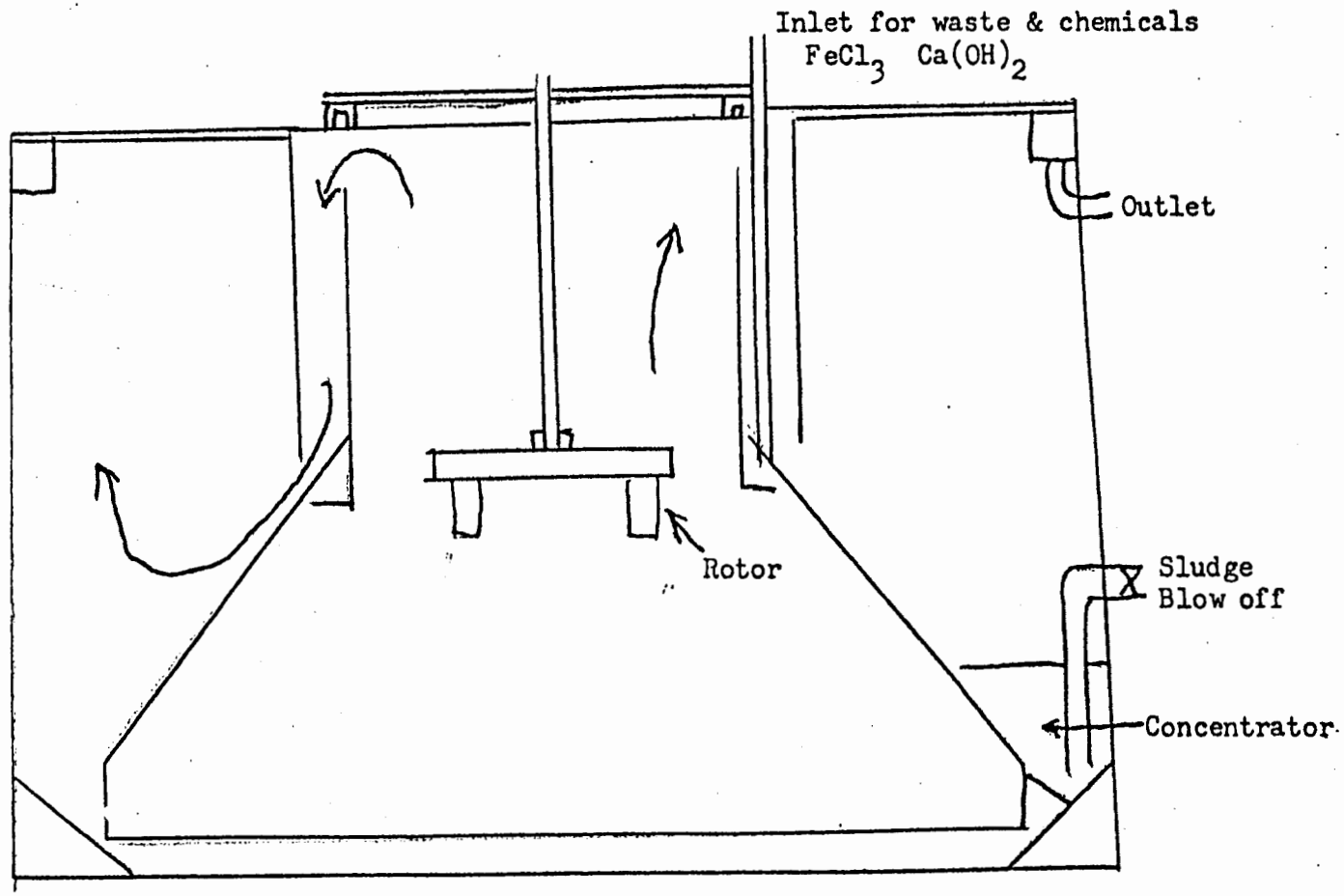
Results of Pilot Plant Studies (PPM)

Source of Waste	Chemicals App. $FeCl_3$ as Fe	$CaCl_2$ as Ca	NaOH as NaOH	Floc ml/L	Sludge Ltrs.	%solids	Flow L/Day	Fluoride Raw	Fluoride Final	Susp. Solids Raw	Susp. Solids Set.	Susp. Solids Filt.	pH Raw	pH Set	Pu C/M/L Raw	Pu C/M/L Set	Pu C/M/L Final
Tech Area	33.7	30.8	440.	183	12.4	1.02	362.	46.	41.	248	1	0	6.3	10.4	4126	31.	11
D.P.Area	36.	$Ca(OH)_2$ 229.		30	6.1	2.49	180	12	9	59	2	0	7.6	9.6	970	355	262

Area T

Note: Tech area results cover period June 1-16, 1950
DP area results cover period May 16 - June 13, 1950

It is noted that a large percentage of the radioactive material has been removed from each of these wastes. These figures are: 99.7% from the Tech Area and 97.3% from DP Area wastes. The process offers a practical means for treatment in a full scale plant. However, data extending over a much longer period of time would be desirable. These pilot plants have only been in operation about 6 weeks. The matter of sludge disposal which offers many problems has not yet been given an intensive study. It is apparent that the water content will need to be further decreased in order to bring the volume down to practical amounts. The fluorex defluorination filter was found to remove fluoride from an average concentration of 47.5 ppm down to 1.25 ppm. One cubic foot of fluorex effected this removal from 400 gallons before regeneration was necessary. Data on this unit are too incomplete to draw definite conclusions. Likewise the Accelator plant has not been operated long enough to draw reliable conclusions.


Inlet for waste & chemicals
$FeCl_3$ $Ca(OH)_2$
Outlet
Rotor
Sludge
Blow off
Concentrator

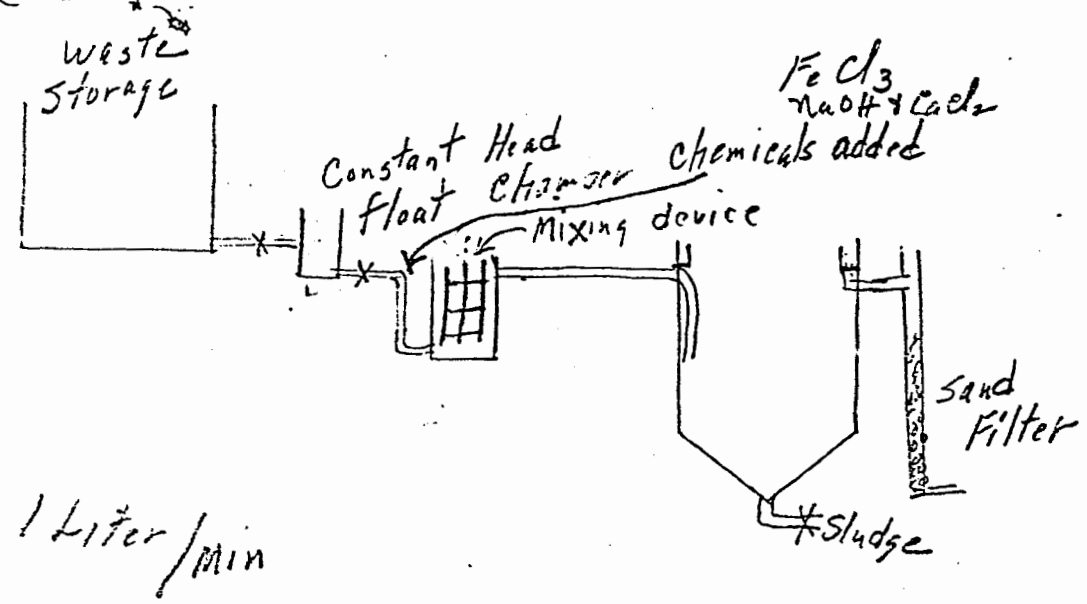
2 g/min

"OF A ECOGNIZED HOTELS"

The Van Curler

Schenectady, N. Y.

THE GATEWAY TO THE WEST



The following was presented by C. W. Christenson, Acting Chief, Industrial Waste Branch, Los Alamos, New Mexico, at the Waste Processing Meeting held at Knolls Atomic Power Laboratory July 1950.

NOTES

The nature of the wastes from the Los Alamos Technical Area has been described before, but to refresh your memories I will summarize it briefly. The pH is in the neighborhood of 3, the solids vary from a low of 200 ppm on weekends to a high of 8,000 ppm, fluorides average about 100 ppm and the activity is about 3,000 C/M/L. The waste has been observed quite closely now for a period of nearly two years and since it comes from a research laboratory it could be expected to contain everything under the sun and it does. I can't think of a thing that can be carried by water that hasn't shown up in the outfall: oils, paints, paper, fragrant organics, not-so-fragrant fecal matter, coffee grounds which clog sampling pumps, dirt, soaps, detergents, and anything else you can name. The goal set for our treated effluents was 70 C/M/L of plutonium. As you all know these tolerance numbers can go up and down considerably from time to time but we based all of our work on this figure and we consider a method of treatment satisfactory only when it will consistently produce an effluent containing less than 70 C/M/L.

The first attempts at carrier precipitation were modeled after ordinary water purification practices. That is, flocculation with iron and lime. In this method, a solution of iron (usually the chloride or sulfate) is added to the water and the

~~pH adjusted to about 9 with lime. The resultant precipitate of ferric hydroxide is then stirred for about 15 - 30 minutes and is allowed to settle. This is usually, though not always followed by filtration through a bed of sand.~~

The results of this treatment were not so good when ordinary water practice dosages were used but on increasing the iron dosage to about 20 ppm the plutonium was nearly all removed. This method of treatment was then tried on several samples of the waste and in nearly every case the sample, after filtration, contained less than our goal of 70 C/M/L.

Since this method showed a great deal of promise the next step was to make an evaluation of the various coagulants and alkalies available. Alum, iron salts, sodium hydroxide, lime, and ammonia were all tried in various combinations and different dosages. They all appeared to be equally effective in plutonium removals. As was expected there was a smaller amount of sludge formed when sodium or ammonium hydroxides were used.

I mentioned that the waste contains a fairly large quantity of fluorides and this must be removed because the ground water in our area contains about 2 ppm of fluoride and any increase would necessitate a very expensive treatment process to reduce the amount of drinking water tolerances. It was felt that the fluoride could be removed as the calcium salt which is soluble to the extent of about 20 ppm and for this reason it was decided to use lime as the alkali since it would provide the calcium ion. The coagulant then chosen was iron since it works best at higher pH values where the calcium fluoride could be expected to be the least soluble. For these reasons subsequent work was confined to the use of iron and lime and the results in treating the Tech Area wastes continued to be quite satisfactory.

Another source of waste at Los Alamos is from the DP or production area. This waste is quite often more concentrated than the Tech Area wastes and seems to have greater variations. The activity is in the neighborhood of 100,000 C/M/L, but this has dropped in the past few months to about 20,000 C/M/L. This type of treatment was then tried on wastes from this area and the results were most disappointing. It was impossible to obtain a floc and hence no plutonium removals. The trouble was soon traced to the presence of fairly large quantities of citric acid which were used in decontamination operations. Since this could be expected to occur, sooner or later, in the Tech Area waste also it was decided to investigate methods of treatment of wastes containing this material and a considerable amount of work was done in trying to obtain a floc in the presence of citric acid. The first attempts were directed towards destroying the stuff by oxidation with chlorine, permanganates, etc. Chlorine did not work at all and the use of permanganate in acid solution showed some promise, but it would be very difficult of application in a plant scale operation. The next step was biological destruction by activated sludge and this worked out quite well. After 24 hours aeration with a well-established activated sludge the citric acid was nearly all used up in the metabolism of the organisms and the solution could then be treated satisfactorily with iron and lime. This method presented many problems in operation but it would be possible. Other coagulants were tried and, I guess we used up most of the periodic table in an attempt to find something

that would form a satisfactory floc. Lead, bismuth, titanium, molybdenum and many others failed miserably.

Meanwhile work was continued on the use of iron and lime. Dosages, pH and other factors were varied and finally a procedure involving the use of excess lime and a pH of 12 produced very good results. Sludge volumes were considerably larger (up to 4% of the volume of waste treated) but the dry solids produced represented only about 1/4 of the total solids originally in the waste. Mr. Mathews will give more data on this later.

Since the citrates presented such a nasty problem it was decided to investigate other complexing agents which might be present in the laboratory wastes. In the operation of the laboratory, as well as the production area, a considerable amount of the waste comes from cleaning up and decontamination operations. The materials used for this operation are chosen for their ability to complex plutonium. Unfortunately for us any material that complexes plutonium does a much better job of complexing all of the coagulants we have tried. As a matter of fact, it got to a point where the men in charge would ask us what would give us the most trouble and then they would go ahead and start using it.

For these reasons we started an investigation of the effect of various phosphates which could be used singly and in combination and with or without citric acid. The effect of fluorides was studied as well as various soaps and detergents. These materials almost all prevented the formation of a floc but on the addition of

fairly large quantities of calcium and on increasing the pH to about 12 a good floc usually resulted and it would carry down the plutonium. Apparently the calcium has a preferential attraction for these materials and the iron can then be converted to the hydroxide to carry down the Pu. In some cases, notably with pyrophosphate, the calcium forms an insoluble salt which masks the iron but it acts as a very good carrier. It appears that if an insoluble salt can be formed in a solution containing plutonium, in most cases, the plutonium will be carried with it. Subsequent work on treatment of the DP wastes and Tech Area wastes have all followed the above procedure and, to date, it has been effective in all cases. The only failure has been in attempts to treat the waste from the contaminated laundry. Here the combination of soap, sour detergents and citric acid has given us a considerable amount of trouble.

Area V

The type of treatment I have described results in a considerable amount of hot sludge which must be disposed of. Understand, of course, that the extra treatment described above does not always have to be used and will be resorted to only when the need arises. By using sodium hydroxide as the alkali and smaller dosages of iron the sludge volume can be reduced considerably and should not amount to over 1% of the volume of waste treated. The use of caustic has been given more attention recently because we are about to come to the conclusion that the above treatment is not at all effective in removing fluorides.

Why this is so remains a deep dark mystery to our group but apparently this compound can be complexed too and it remains in solution in quantities much larger than the 16 ppm the handbook claims. The first laboratory tests confirmed what the literature indicated but it has been proven to be not so. For this reason the use of lime is questionable and we will probably be able to use caustic. An additional advantage of the caustic is that the production area has several barrels of a 25% solution containing about 1 microgram per liter of Pu and they are most anxious to get rid of it. This appears to be an excellent opportunity to accommodate them and save us some money. Of course, we will have to figure out a way to get rid of the fluorides but the use of fluorex appears to be quite effective in this. Mr. Mathews will describe this.

The sludge produced by the operation of the plant has been the cause of a great deal of worry on our part. This sludge will contain all of the plutonium, all of the suspended solids in the original waste, as well as the ferric hydroxide floc and the insoluble hydroxides and other salts of any other metals present in the waste. It will probably contain about 400,000 C/M/L of Pu and about 0.2 gram of iron per liter. We have been unable to do much work in the laboratory on this problem because we didn't have any sludge in quantity to work with. Until such time as a suitable method of disposal is devised we will probably

do as everyone else--take it out to the burial grounds. This, of course, gets the monkey off our back but the authorities frown on such a procedure since ultimately we will run out of space.

The operation of the pilot plant has given us a little material to work on and we have tried out a few things in the laboratory. What we hope to be able to do is to dissolve the sludge, remove the plutonium with the least possible foreign matter and then use the iron again in the plant as a coagulant. In time, of course, we will get a build-up of other metals in the sludge and will have to dispose of it.

There are several ways that appear to be open to us, none of them very simple. Hydrochloric acid will probably be used as the solvent, and we will attempt to get the plutonium out of this solution with another carrier. The possible carriers are: thorium, bismuth, zirconium, lanthanum and, perhaps, calcium. Of these, bismuth phosphate seem the most promising since it is used in this manner at Hanford. Unfortunately in laboratory tests it has not proved very satisfactory. The precipitation should be accomplished at a pH of no less than 3 and at this pH the iron will generally come out of solution. Then too the large quantities of iron tend to complex the phosphate and holds it in solution. Further studies will be made on this carrier, however. One of the analytical procedures uses calcium oxalate as a carrier

for plutonium at pH values of less than 1 and this was tried out but so far the results have not been good. This will be investigated further too. The other salts mentioned have not been given any tests in the laboratory.

Our group has done a considerable amount of work on the adsorption of plutonium by activated carbon and it has proved quite successful in a number of cases. One of the optimum points of Pu removals appears to be at pH 2 in solutions containing plutonium and citric acid. This has been tried on solutions of the sludge produced above and preliminary investigations indicate that about 75% of the activity can be concentrated in the carbon by this method. If this can be improved upon it will be possible to ignite the carbon after treating the sludge and then the plutonium will be left with very little extraneous material.