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HEALTH PHYSICS DIVISION

LABORATORY PROGRESS ON THE DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE BY DEEP-WELL INJECTION

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HEALTH PHYSICS DIVISION

LABORATORY PROGRESS ON THE DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE BY DEEP-WELL INJECTION

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ABSTRACT

Results of laboratory studies on the neutralization of Purex-type wastes are reported, including the radiochemical distribution of the fission products in the precipitate and supernate and the effect of sodium and calcium neutralizations on fission-product separation.

The problem of interstitial precipitation encountered when a second incompatible liquid is injected into a formation is discussed. Results indicate a piston-like displacement of the interstitial liquid by the injected waste with only a small zone of precipitation formed along the contacting edge.

Slurry tests were performed to determine the capacity of various geologic materials for sorption of cesium and strontium from a synthetic Purex-type waste containing carriers and tracers. The materials studied include sands, feldspars, shales, clays, and limestone. The amount of cesium sorbed was found to be a function of several variables, among which are (1) concentration of cesium in the waste, (2) concentration of other cations, (3) amount and nature of the clay material, and (4) composition and amounts of other minerals in the disposal formation.

Several types of shales and clay minerals, including illite, bentonite, montmorillonite, kaolinite, halloysite, and Conasauga shale, were slurried with simulated 6 M Purex waste which had been neutralized. Sorption of cesium ranged from 0.6 to 6.0 mg/20 g, respectively, for the various materials tested. Results of slurry tests indicate that if the Purex-type waste were diluted 30-1 with concentrated brine, the amount of cesium sorbed per cubic foot would be about 2.7 curies. This is within

the 2-8 curies/ft^3 estimated to be safe from thermal considerations. Core tests on a Berea sandstone showed similar sorptive capacities.

Sequestering or complexing agents, that is, versenes, did not materially affect the cesium removal, but did result in a decreased sorption of strontium by clays. Strontium sorption in systems studied ranged from less than 0.2 to 2.0 mg of strontium sorbed per 20 g of clay, illite sorbing most and halloysite least.

Slurry results indicated (1) increased H ion concentration decreases sorption; (2) sorption of cesium is a function of the Na/Ca ratio;[6] (3) the Na/Sr ratio is not as important to strontium removal as pH of the solution; and (4) limestone slightly decreases the amount of cesium sorbed per gram of illite.

The results of the sorption studies suggest that undue localized heat production, due to sorption of radioactive materials near the well, can be controlled so that it will not be a serious problem.

1.0 INTRODUCTION

The work completed to date on the injection of radioactive wastes into deep permeable formations can be divided into two main subclasses: (1) characterization of the various types of fuel-reprocessing waste and (2) experiments using various techniques. Experiments have been made using a dynamic system, an equilibrium system, and, finally, a dynamic system of core testing.

Sorption of radionuclides on various minerals within the formation must be considered when disposing of radioactive waste by well injection. This problem can easily be studied using standard laboratory tracer techniques. It is generally known that the amount of radioactive material sorbed will greatly depend on the type and amount of clay within the disposal formation. The sorption of large concentrations of the fission products may result in a problem of heat dissipation. Such thermal problems have been studied by Professor Francis Birch, Harvard University.[1] He has concluded that heat dissipation will have to be carefully considered, but will not impose serious restriction on the disposal method.

The following investigations were made to obtain quantitative values on the sorption of radioisotopes by various formation materials.

2.0 TYPES OF REACTOR WASTES

There are several processes in current use for the various types of fuel elements. Based on the predictions of people in the chemical processing field, the five following types of processing wastes are those likely to be important for several years to come. These wastes are from

the Purex (HNO_3), TBP-25 (Al-HNO_3), STR (Zr-HF-Al), Darex (stainless steel - aqua regia), and SIR (stainless steel - H_2SO_4) processes. A report[2] has been published on the chemical composition of these wastes and the heat output of each; a summary of these characteristics is given in Table 1.

For test purposes Purex-type waste was selected for further study, because it comprises the greatest column of high-level waste available at present. The stored Purex waste is normally neutralized to reduce corrosion of the tanks, and the waste volume is reduced by evaporation to conserve tank space and to recover nitric acid. Therefore, it is desirable to use a neutralized and concentrated waste solution for laboratory work.

Empson[3] has done additional work on the physical characteristics of these five synthetic fuel-reprocessing waste solutions to reduce the volume and make the residue more suitable for storage or for treatment prior to disposal.

The main source of high-level wastes today results from the processing of irradiated fuel elements and are, therefore, evolved primarily at Hanford, Savannah River, and the National Reactor Testing Station. In the future high-level wastes will come from the processes mentioned above and may occur at other AEC installations. Table 2 lists some of the pertinent factors which indicate the magnitude of the high-level liquid waste storage situation. The cost figures cited are felt to be conservative, since the cost of process equipment and facilities in which both wastes and product streams are treated is not included.

At Hanford the present plans call for scavenging cesium and strontium and discharge of the supernates to soil. If this is successful, it

Table 1. A Composite of the Characteristics of Reactor Fuel-Processing From a Multipurpose Plant

Radioactivity	
Gross Beta Activity	1.6×10^{6} to 2.2×10^{10} counts min^{-1} ml^{-1}
Alpha Activity	6.0×10^{3} to 6.0×10^{5} counts min^{-1} ml^{-1}
Radioactivity	100 to 400 curies/gal (neutralized)

Chemical	
Ions	Concentration (moles/liter)
Al^{+3}	0.5 - 2.5
NO_3^-	2.0 - 8.0
H^+	0.5 - 7.0
Na^+	0.1 - 5.0
F^-	2.0 - 3.5
Zr^{+4}	0.3 - 0.6
SO_4^{-2}	0.03 - 0.6

Others

Effective life, about 600 years.

Heat generation, 1.7 to 88 Btu/hr/gal.

Power equivalent, 1 g U^{235} = 24,000 kwhr (100% efficiency).

Waste from processing, 0.11 to 3.0 gal of solution per g U^{235} consumed.

Specific gravity, 1.1 to 1.4.

Table 2. High-Level Liquid Waste Handling Data
Up to January 1, 1957*

	HAPO	SRP	NRTS	Total
Waste in Storage (10^6 gal)	58.2	3.5	0.38	62.08
Total Tank Capacity (10^6 gal)	90	12.2	1.6	103.8
Total Number of Tanks	145	16	9	170
Costs - Tanks and Appurtenances ($\$10^6$)	37.5	16.6	6.6	60.7
Estimated Tank Operating Cost (per year) $50,000				

Future Estimates	HAPO	NRTS
Period of Estimate	to June 1959	to June 1959
Additional Wastes (10^6 gal)	9.1	1.5
Additional Cost ($\$10^6$)	7	6.5

*"Status Report on Handling and Disposal of Radioactive Wastes in the AEC Program," Division of Reactor Development, WASH-749, August 1957.

is likely that the large volume of waste in storage (58.2×10^6 gal) will not increase over present levels, and need for additional tankage may be reduced or eliminated. A calciner is being constructed at NRTS to handle the aluminum-nitrate high-activity waste. The success of the operation of this calciner will dictate their future storage needs; so no long-term estimates are given in Table 2.

3.0 RESULTS OF NEUTRALIZATION STUDY

In the deep-well injection of neutralized waste, it would be necessary to know the identities and approximate concentrations of the fission products. Therefore, the behavior of fission products during neutralization was investigated by using concentrated synthetic Purex waste. Appropriate amounts of carriers of the important high-yield radioactive fission products were added to the waste solution; they include: strontium, yttrium, zirconium-niobium, tellurium, rhodium, cesium, barium, and cerium. Enough radioactive isotope of each important fission product was added to the solution to serve as a tracer. Samples of the solution were neutralized with either a concentrated NaOH solution or a $Ca(OH)_2$ suspension. The original solution, the supernatant liquid, and the precipitate after neutralization were analyzed radiochemically.

When nitric acid waste is neutralized with sodium hydroxide, several precipitates form and tend to scavenge many of the fission products. The concentration of iron, which is present in actual waste from the addition of ferrous sulfamate, is more than adequate to serve as a scavenger on neutralization. In addition, an appreciable concentration of uranyl ions, present from losses in solvent extraction, helps in scavenging the solution.

Solutions containing from 50 to 280 mg per liter of the nonradioactive carrier (the range of fission-product concentration in actual waste) were tested for each radioelement. In the laboratory, the solution was adjusted to pH 7; in production plants, enough caustic is added to raise the pH to above 10.5, at which point the amount of strontium and trivalent rare earths remaining in solution would be reduced by a factor of 2 or 3. The caustic was added very quickly in these tests, and the samples for radiochemical analysis were removed a few hours after the precipitate settled. If the caustic were added more slowly and the precipitate allowed to stand longer, the cesium removal would probably have been reduced, because less cesium would be occluded in the floc. However, the test results from neutralization of the waste do give useful values for fission-product scavenging by ferric hydroxide. The effectiveness of this scavenging diminishes with the age of the waste, because the more easily scavenged fission products generally have short half lives and will have already decayed from the older wastes. The more easily removed fission products with short half lives are zirconium, yttrium, niobium, and cerium. Strontium-90 (28-year, principal beta emitter) and cesium-137 (30-year, principal gamma emitter) have considerably longer half lives.

A gross fission-product decontamination factor (D.F.) of between 2 and 10 was expected from neutralization. Neutralization and filtration removed most of the scavengeable fission products in one step. The volume reduction achieved by repeating the procedure was limited by the volume of the precipitated iron, uranium, and fission products. The nonscavenged fission products (mainly cesium and strontium and detectable quantities of ruthenium) remained in the liquid phase.

The sludge and supernatant liquid from neutralization by sodium hydroxide and by calcium hydroxide were radiochemically analyzed, and the results are shown in Table 3. Both hydroxides gave significant decontamination factors for strontium, zirconium, niobium, and rare earths; but there was very little decontamination of ruthenium and cesium. Sodium neutralization resulted in a higher D. F. than calcium on Purex waste, mainly because the precipitate formed with calcium did not scavenge as much as strontium and zirconium. These results were within the expected range of removal.

4.0 COMPATIBILITY STUDIES

One of the problems in deep-well disposal is plugging of the well (1) by suspended solids, (2) by chemical reaction of the waste solution with the solid matrix of the aquifer, or (3) by chemical interaction between waste and interstitial fluids. The following are typical reactions which might bring about the third type of plugging:

$$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 \downarrow + 2\ NaCl$$

$$4\ Fe(HCO_3)_2 + O_2 + 2\ H_2O \rightarrow 4\ Fe(OH)_3 \downarrow + 8\ CO_2$$

$$FeSO_4 + H_2S \rightarrow FeS \downarrow + H_2SO_4$$

An obvious test would consist of mixing a sample of the interstitial water with the waste solution to see whether a precipitate forms. If a precipitate does form, it might be expected that difficulty would be encountered in injecting the waste solution into a well without plugging the formation.

Table 3. Decontamination of Simulated Purex Waste by Neutralization

Radioelement	Radiation Counted	Simulated Waste		Neutralized by NaOH		Neutralized by $Ca(OH)_2$	
		Activity (counts min^{-1} ml^{-1})	Activity (% of total)	Activity (counts min^{-1} ml^{-1})	D.F.*	Activity (counts min^{-1} ml^{-1})	D.F.*
Strontium	Beta	53.1×10^3	19	12.4×10^3	4	23.7×10^3	2
Zirconium	Gamma	21.5×10^3	7.7	75	290	8.5×10^2	25
Niobium	Gamma	99.5×10^3	35	46	220	15	6.6×10^3
Ruthenium	Gamma	1.1×10^3	0.5	103	11	80	14
Cesium	Gamma	27.7×10^3	10	12.3×10^3	2	17.9×10^3	1.5
Cerium	Beta	2.06×10^3	0.8	24	86	157	13
Trivalent Rare Earths	Beta	74.2×10^3	27	6.6×10^3	11	1.24×10^3	60

*D.F. = Decontamination factor = $\frac{\text{activity in original solution}}{\text{activity remaining in solution}}$.

However, a paper by Bernard[4] reported results contrary to this opinion. Some of Bernard's results have been confirmed in this laboratory. A 0.1 M $SrCl_2$ solution tagged with radioactive Sr^{90} was injected into a column containing 6450 g of clean Ottawa sand, the pore spaces of which were previously filled with 0.1 M Na_2SO_4. The reaction which would occur if these solutions were mixed is:

$$SrCl_2 + Na_2SO_4 \rightarrow SrSO_4 \downarrow + 2\ NaCl$$

A small quantity (2 mg) of indigo carmine dye was added to the injected solution to serve as a visible tracer of the flow pattern. As the strontium chloride solution displaced the sodium sulfate solution, there was no loss in permeability and no plugging of the column, because there was only a small zone of contact between the two solutions. The data shown in Fig. 1 indicate that during injection there is a displacement of the interstitial solution; and because the sand acts to prevent the two liquids from mixing, precipitation and eventual plugging of the column is prevented. This indicates that there is little mixing within the sand bed and very little precipitation under conditions of laminar flow. These salt concentrations are high compared with the concentrations of the interstitial solutions found in most formations.

After about 3500 ml of solution had passed through the 23-in. sand bed, the sand was rinsed with distilled water. The column effluent showed a rapid decrease in counting rate, the counterpart of the rapid increase exhibited by the initial breakthrough of Sr^{89}.

From this it may be concluded that the probability of plugging the formation, by injecting a solution that normally forms a precipitate with

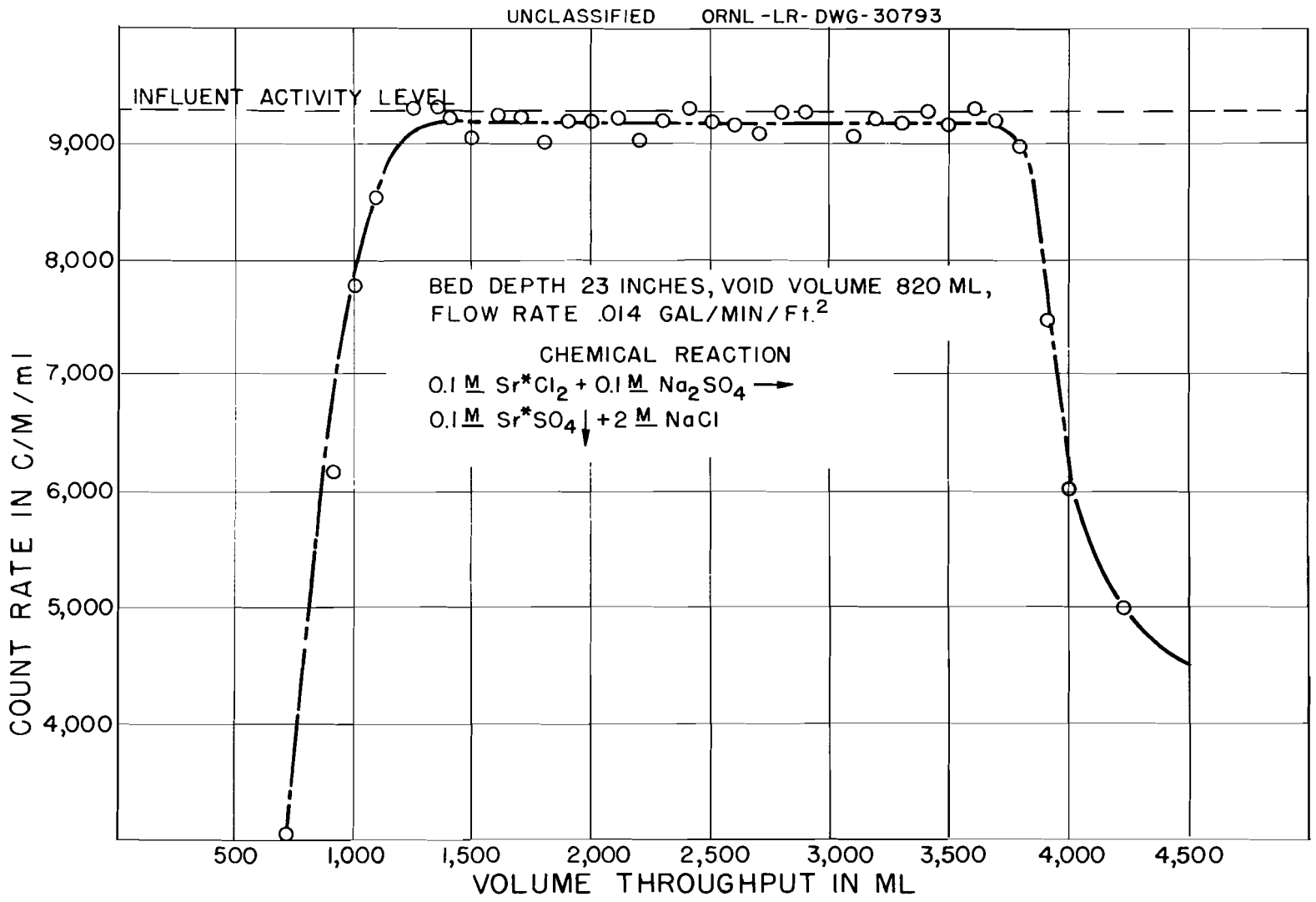

Fig. 1. Interstitial Solution Compatibility Study Using Ottawa Sand and Sr^{89} as the Radioactive Tracer

interstitial solution, is less than expected. Instead of mixing, there is a piston-like displacement of the interstitial liquid by the injected waste and only a small zone of precipitation along the contact edge, which forms a barrier to prevent further mixing. Still to be considered and studied are the other processes; that is, the interaction of the solids within the formation with the injected waste solution.

5.0 SORPTION STUDIES

The sorption of radionuclides, particularly Cs^{137}, by small amounts of clay was investigated. The clay minerals considered to be of greatest importance included illite, kaolinite, halloysite, and montmorillonite. The procedure was to add from 0.3 to 20 g of clay to 300 ml of the Purex waste solution and to stir for 2 hr at 216 rpm, using a laboratory stirring device. After stirring, the solution was filtered through filter paper, and samples were taken for counting. The counting was performed on a well-type gamma scintillation counter using an NaI (Tl) crystal. Three samples were prepared for counting by placing 1-ml aliquots in 10 x 75-mm glass culture tubes and counting the liquid. It was possible to determine the amount of cesium sorbed per 100 g of clay by the removal of Cs^{137} tracer from solution and knowing the ratio of radiocesium to stable cesium. This same procedure was used on all the slurry tests.

5.1 Cesium Sorption

Figure 2 is a graph showing the sorption of radiocesium from a sodium hydroxide neutralized 6 M Purex waste solution by the clay minerals listed above as well as by Conasauga shale. The Conasauga shale contains a mixture

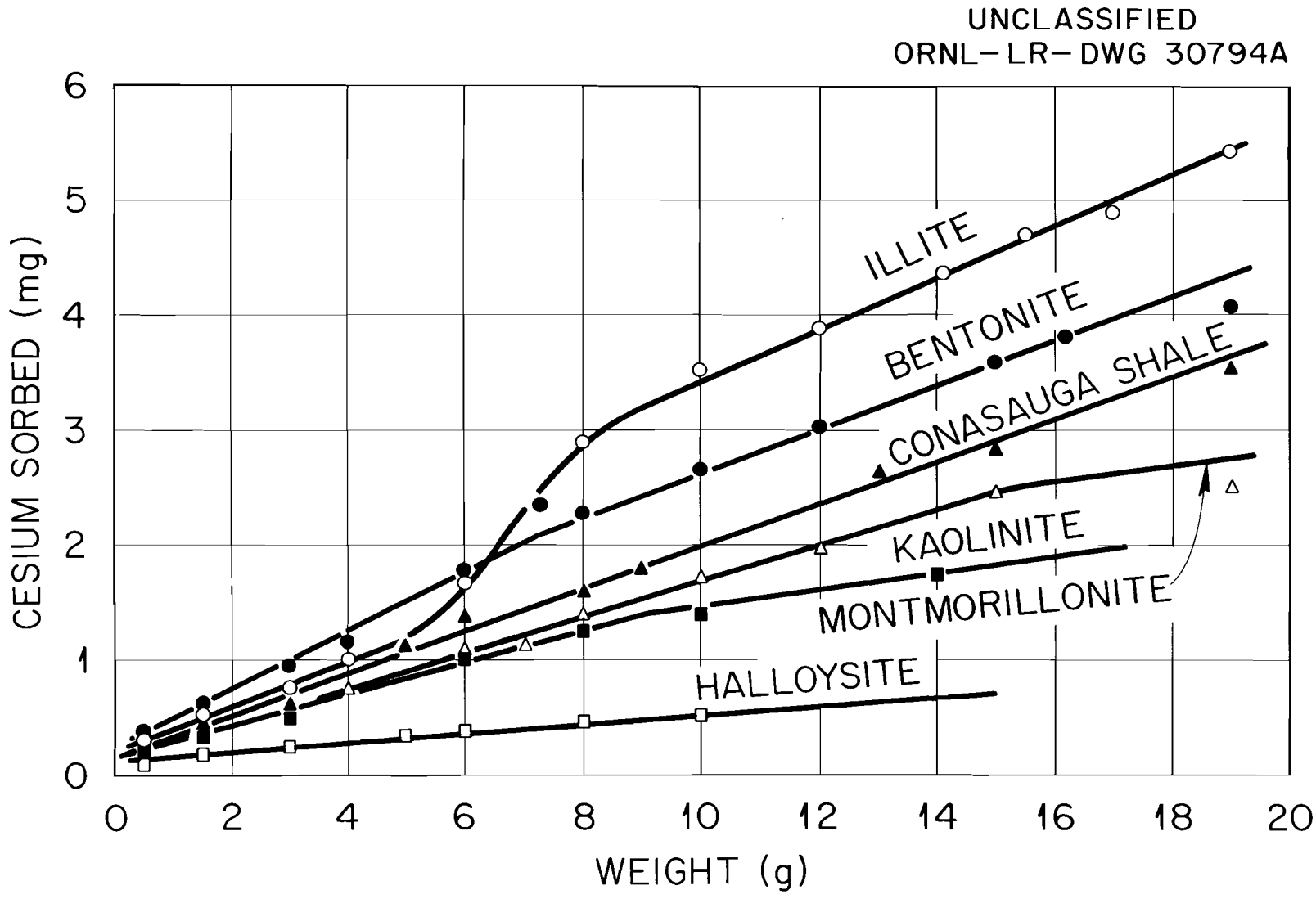

Fig. 2. Efficiency of Various Clay Materials for Removal of Cesium from Neutralized Purex Waste

of clay minerals and quartz. A sample analyzed by Tamura[5] using x-ray, chemical, and base-exchange procedures was found to consist of about 40% illite, 25% montmorillonite, and 25% quartz. Its ability to sorb cesium from the waste solution is large, considering the relatively large content of inert quartz. The bentonite sample is a clay of undetermined composition from Texas.

Studies were made on the sorption of radiocesium by illite from solutions having varying sodium nitrate concentrations. Sodium nitrate results from neutralization of Purex waste (which contains HNO_3) by sodium hydroxide. Concentrations of sodium nitrate ranged from 6 M to 0.5 M; this range of sodium concentrations includes neutralized, evaporated Purex waste, which is about 6 M, and unconcentrated waste, which is 1 M. The results (Fig. 3) show a threefold increase in cesium sorption with a tenfold decrease in sodium ion concentration. Next, the effect of cesium concentration on cesium sorption from 6 M sodium nitrate solution was determined. These concentrations ranged from 10 mg per liter of cesium to 100 mg per liter of cesium. The 10-mg-per-liter cesium concentration level is representative of a diluted 1 N unconcentrated Purex waste, while the 100-mg-per-liter level is slightly more concentrated than the 7.0 M evaporated waste. The results indicate approximately a threefold increase in cesium adsorption with a tenfold increase in cesium concentration, as shown in Fig. 4. The relative effect on the amount of cesium sorbed per gram of clay, by increasing the concentration of sodium ion by the same factor, was the same.

A series of jar tests were made to study the effect of calcium carbonates on the sorption of cesium, as calcium carbonate may be present in

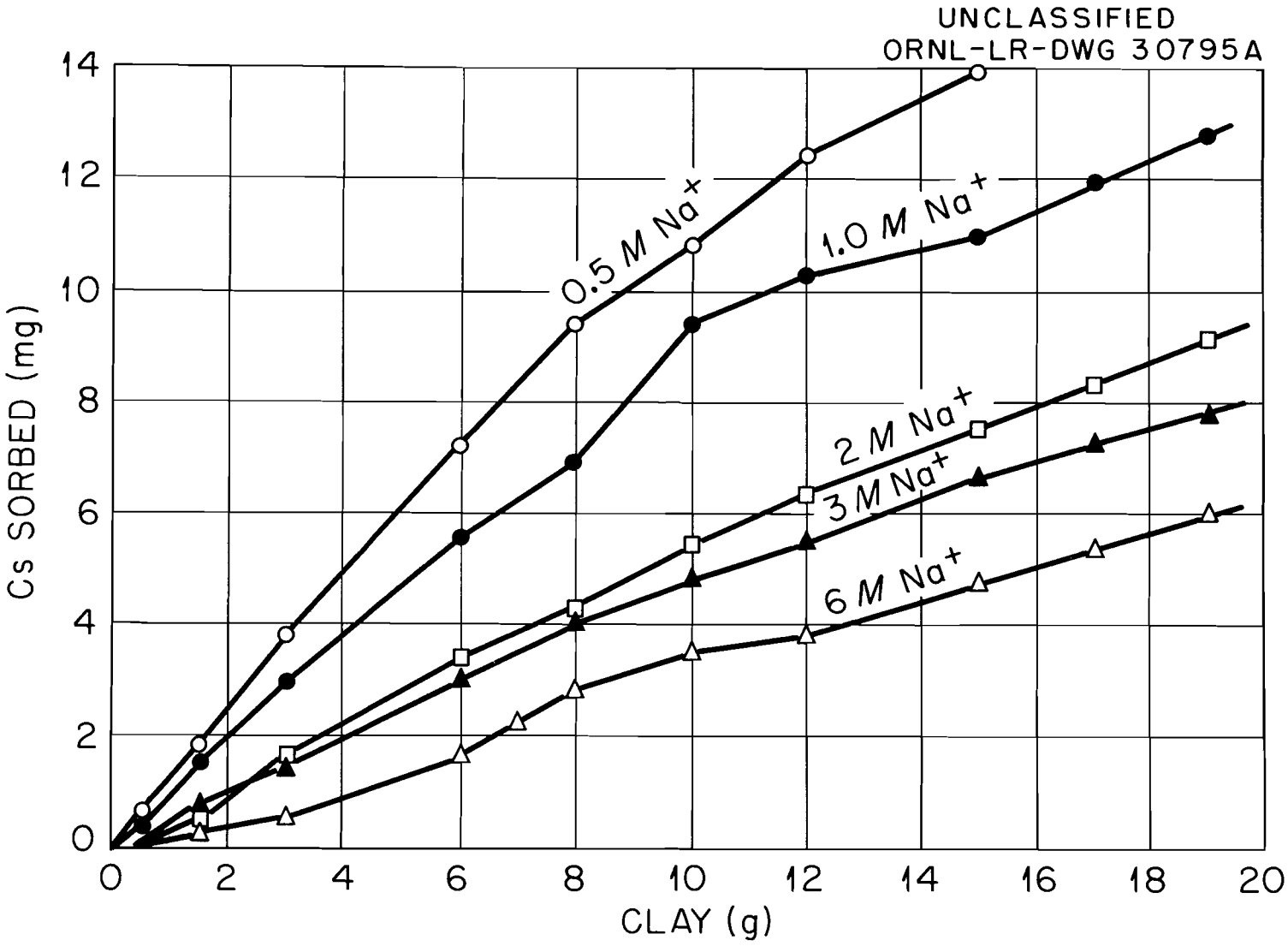

Fig. 3. The Effect of Sodium Ion Concentration on the Adsorption of Cesium by Illite Clay. The Concentration was 100 mg/liter in all Tests.

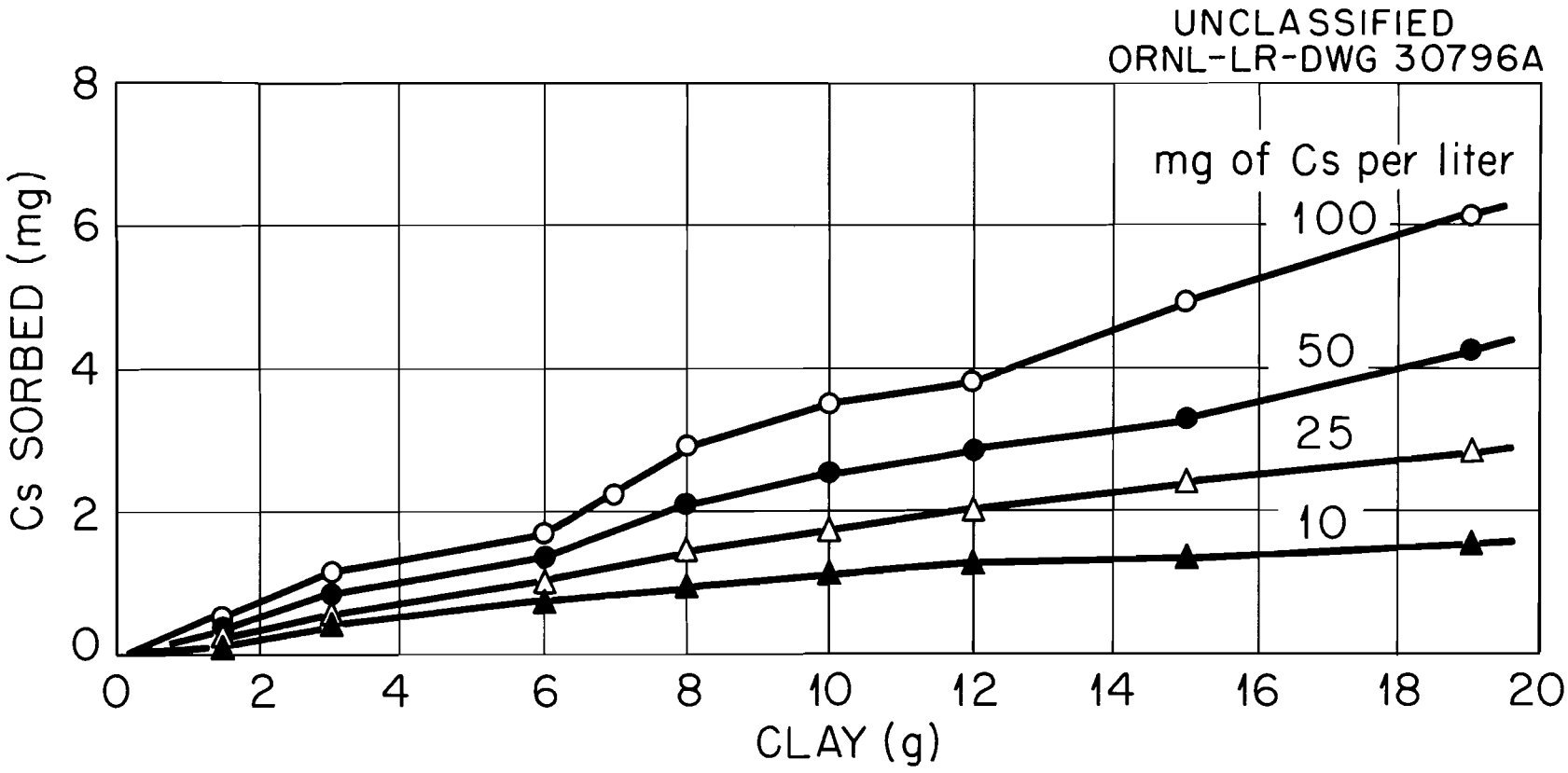

Fig. 4. The Effect of Cesium Concentration on the Desorption of Cesium by Illite from a 6 M $NaNO_3$ Solution

a disposal formation as a limestone. The carbonate used was calcium carbonate ($CaCO_3$), as pulverized limestone.

Three runs were made using 2 to 20 g of material at five different concentrations. The previously described jar-test procedure with tagged carrier solutions was used.

The first run was made using only limestone ($CaCO_3$). This was to determine the amount of cesium sorption obtained on limestone only. Run 2 was to study the sorption of cesium on pure illite, while run 3, which was a 1:1 mixture of illite and limestone, gave experimental values for various weights of the mixed material.

These experimental results are shown on Fig. 5 as solid lines. The 1:1 mixture shows a lower removal of cesium than when illite or limestone are used alone. One might expect greater sorption by the mixture than using the illite alone, because 20 g of limestone removed up to 0.4 mg of cesium from 150 ml of waste solution.

The small difference between the calculated results (dashed line) and the experimental values shown on the two middle curves (solid line) may be due to the hydrolysis of limestone to result in increased ionic competition for the sorption of cesium on the illite. These tests indicate that the presence of calcium carbonate does not increase the sorption of cesium by illite, but rather it slightly decreases the amount sorbed. The slight difference obtained suggests that the presence of limestone within a disposal formation will not affect the amount of cesium sorbed from neutralized Purex-type waste.

A series of four tests were conducted using 1-molar unconcentrated Purex waste to compare the effectiveness of illite and Conasauga shale

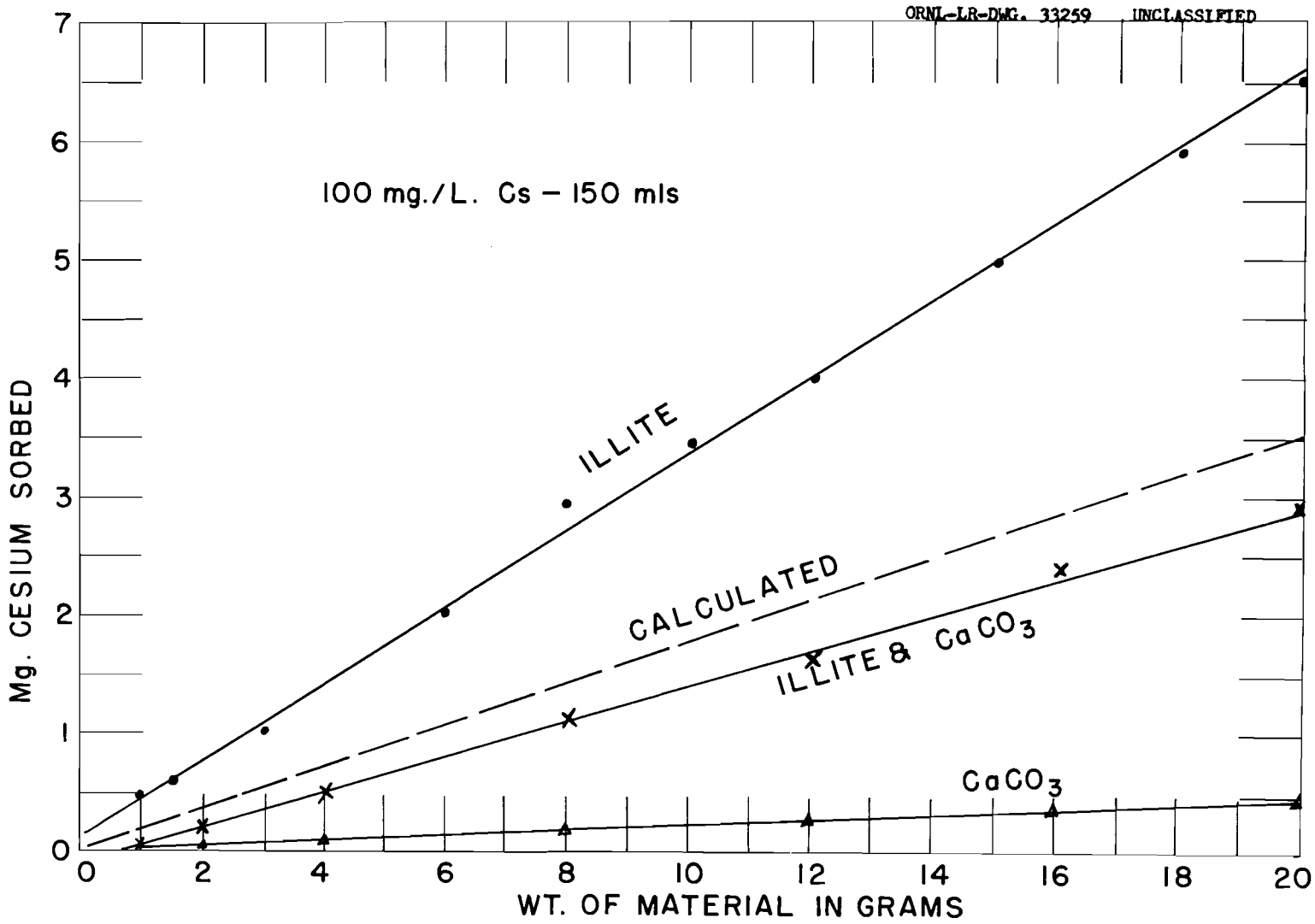

Fig. 5. The Effect of Calcium Carbonate on Cesium Sorption by Illite from 6 M Sodium Neutralized Purex Waste

for the removal of cesium from an acid and a neutralized solution. Five weights of soil material in 150 ml of solution were used in each of the four tests. The beakers were slurried for 2 hr using a laboratory stirring device. Samples of the initial solution and the final supernate were taken, dried, and counted.

The results show good agreement between the tests; that is, with both materials the presence of hydrogen ions decreased sorption (Fig. 6). Sorption from 1 M $NaNO_3$ was higher than the sorption from 1 M HNO_3 solution using both illite and Conasauga shale. The cesium sorption capacity of illite from 1 M HNO_3 is about half the capacity from 1 M $NaNO_3$, while the cesium capacity of Conasauga shale with 1 M $NaNO_3$ is decreased by almost 70% when 1 M HNO_3 was used. The results indicate there would be less cesium sorption on clay material of this type, in a disposal formation, from an acid solution than from a neutralized solution.

To carry this one step further, it has been shown by Jacobs and Tamura[6,7] that sorption or exchange of cesium by the collapsed layer lattice clay minerals is a function of ionic radius of the competing ions. For exchange sites with no steric specificity, the tightness with which an ion is bonded to a charged surface is an inverse function of the hydrated radius of the ion. However, cations must be dehydrated to enter the fixation sites. Cesium has an ionic radius of 1.69 Å and is more easily dehydrated than the lighter alkali metal cations. Thus Na^+ ($r = 0.95$ Å) offers little competition for sorption of small amounts of cesium by illitic clays. Potassium ($r = 1.40$ Å) and rubidium ($r = 1.48$ Å) offer more competition for cesium sorption.

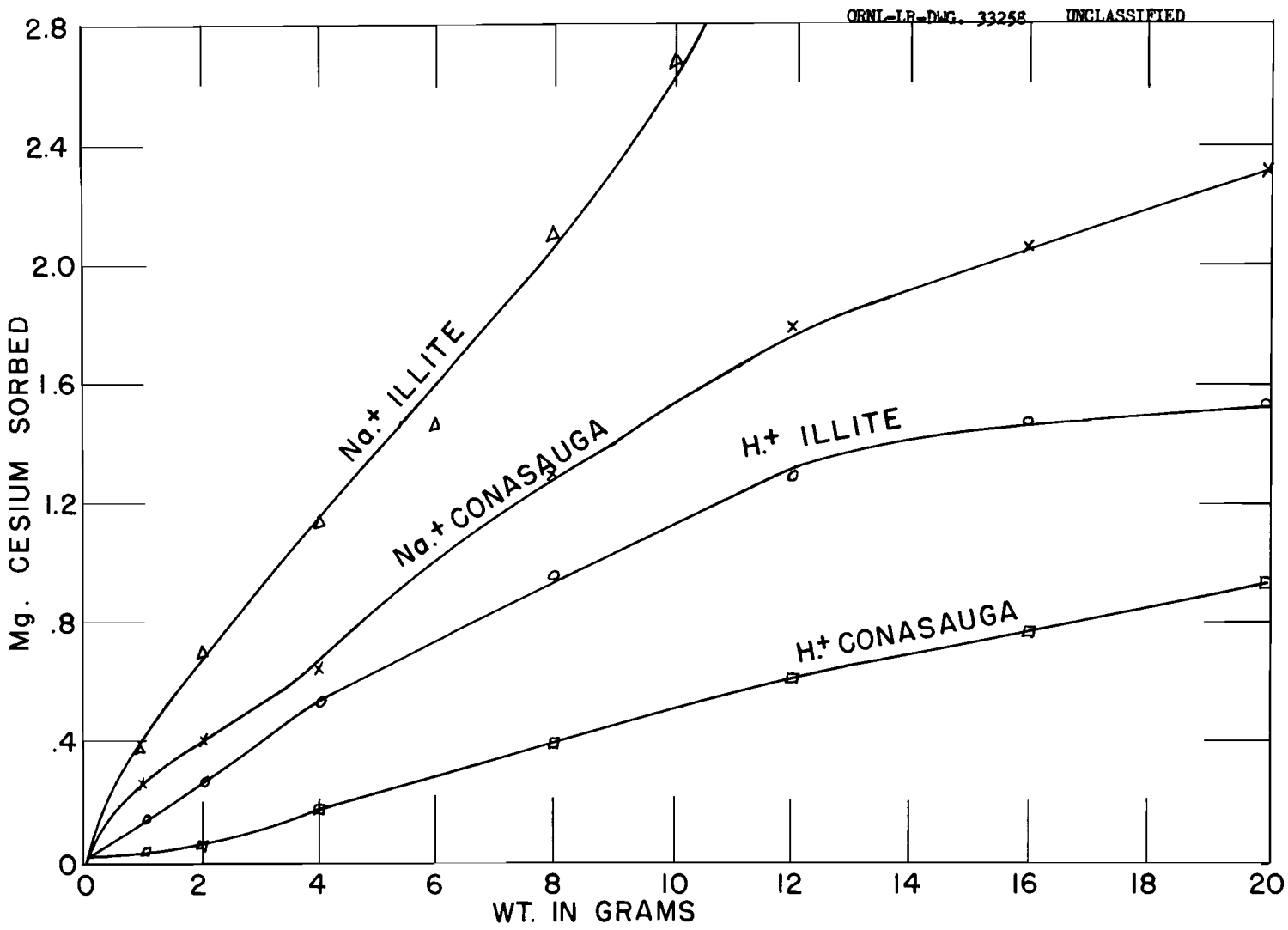

Fig. 6. Sorption of Cesium from 1 M Solutions of $NaNO_3$ and HNO_3 Containing 10 mg/liter Cesium Carrier

A series of five tests were made to determine the equilibrium concentration of cesium sorbed on Conasauga shale from a slurry. The procedure involved using a 6 M $NaNO_3$ solution to which 100 mg per liter of cesium carrier was added and enough Cs^{137} to give a low counting error; 2 to 20 g of air-dried Conasauga shale were slurried for 2 hr at 216 rpm in 150 ml of the solution. The shale was then separated from the solution by centrifugation, and three 1-ml aliquots were taken from each beaker for counting in a well-type scintillation counter.

The amount of cesium adsorbed can be calculated by the following method:

$$\frac{\text{Initial Activity - Final Activity}}{\text{Initial Activity}} \; 15 \text{ mg} = \text{mg Cs sorbed}$$

The solution was discarded; the shale samples were again placed in beakers, and another 150 ml of the solution described above was added to each beaker and the test repeated. This same procedure was repeated a third time.

Results are shown on Fig. 7. About 50% of the saturation value was achieved by a single slurry treatment; the two successive slurry treatments resulted in an additional 60% removal of the cesium present or about 90% of the estimated concentration of cesium remaining solution. Therefore, it can be estimated that approximately 5% of the shale was still unsaturated.

Although more cesium could be sorbed from a fresh solution, one must increase the concentration ratio of cesium to sodium or replenish the cesium already removed from the solution. The equilibrium value was not changed by either increasing the contact time or the rate of stirring.

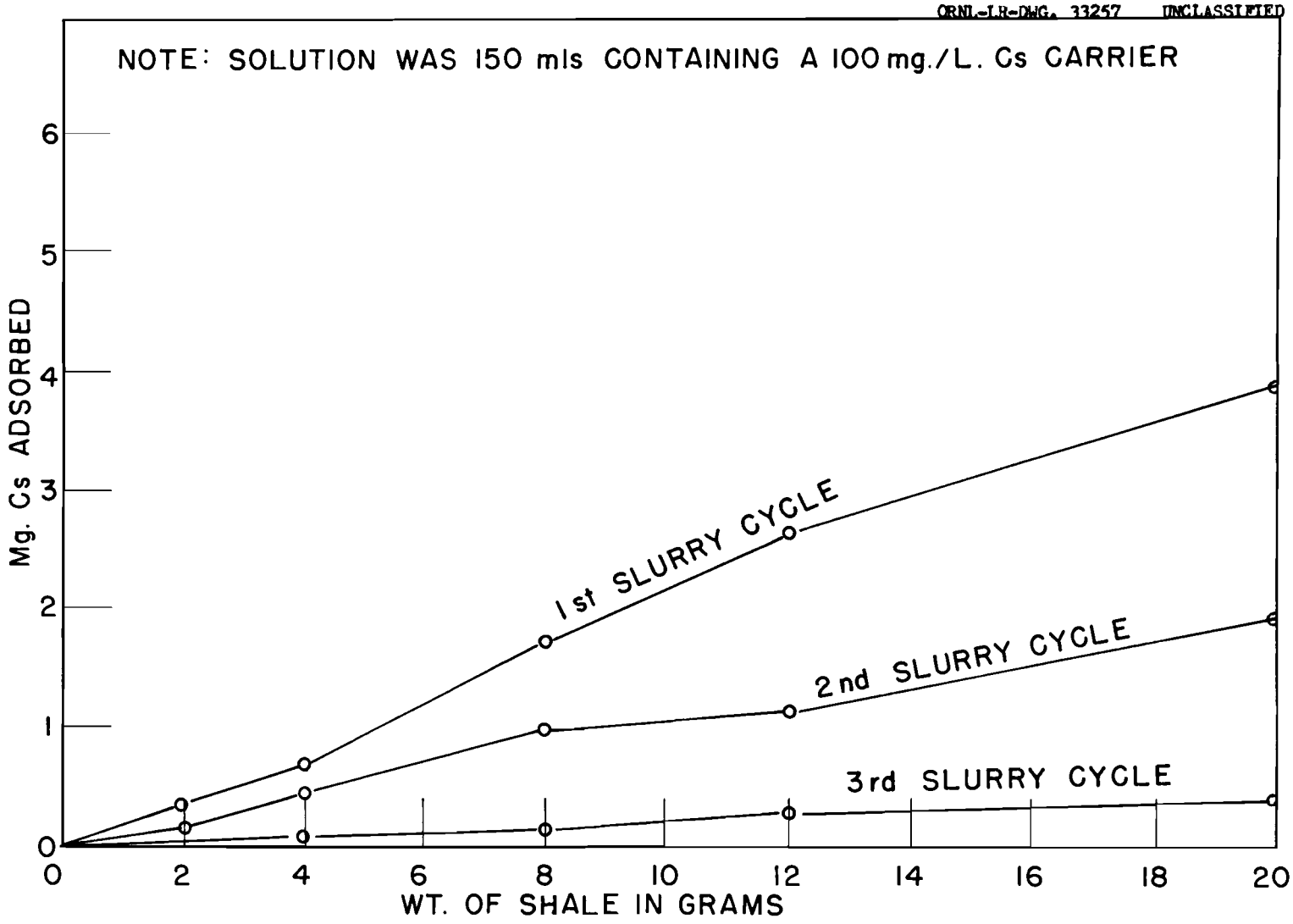

Fig. 7. Cesium Sorption by Conasauga Shale from Successive Slurries with 6 M Neutralized Purex Waste

The results of these tests indicate that in a $NaNO_3$ system the Cs/Na ratio of the solutions determines the capacity of the clay for cesium removal. Jacobs[6] observed the same results in a series of studies on cesium sorption with Conasauga shale.

5.2 Strontium Sorption

The jar-test results covered here indicate the amount of strontium in milligrams removed from a neutral Purex solution by various clay minerals. Results shown on Fig. 9 indicate the sorption of strontium from 150 ml of 6 M $NaNO_3$ solution containing 40 mg per liter of strontium carrier. This is approximately the sodium and the strontium concentrations of Hanford-type neutralized Purex waste.

The clay materials studied included: (1) Conasauga shale, (2) Fithian illite, (3) New Mexico kaolinite, (4) montmorillonite (Wyoming bentonite), (5) North Carolina vermiculite, and (6) Utah halloysite. The effectiveness of the material for strontium sorption is from Conasauga shale, the best, to halloysite, the poorest, in the order listed above.

A comparison of the amount of strontium removed by these materials to the amount of cesium removed under similar test conditions indicates that about one-third as much strontium as cesium is removed by the same weight of clay material. However, the specific activity of Sr^{90} is 1.5 times the specific activity of Cs^{137}. The net result is that for each curie of strontium sorbed there will be 2 curies of cesium sorbed.

In all coagulation studies on the removal of radiostrontium from water, it has been observed that pH, or hydrogen ion concentration, played a major role. Therefore, three series of jar tests, involving at least

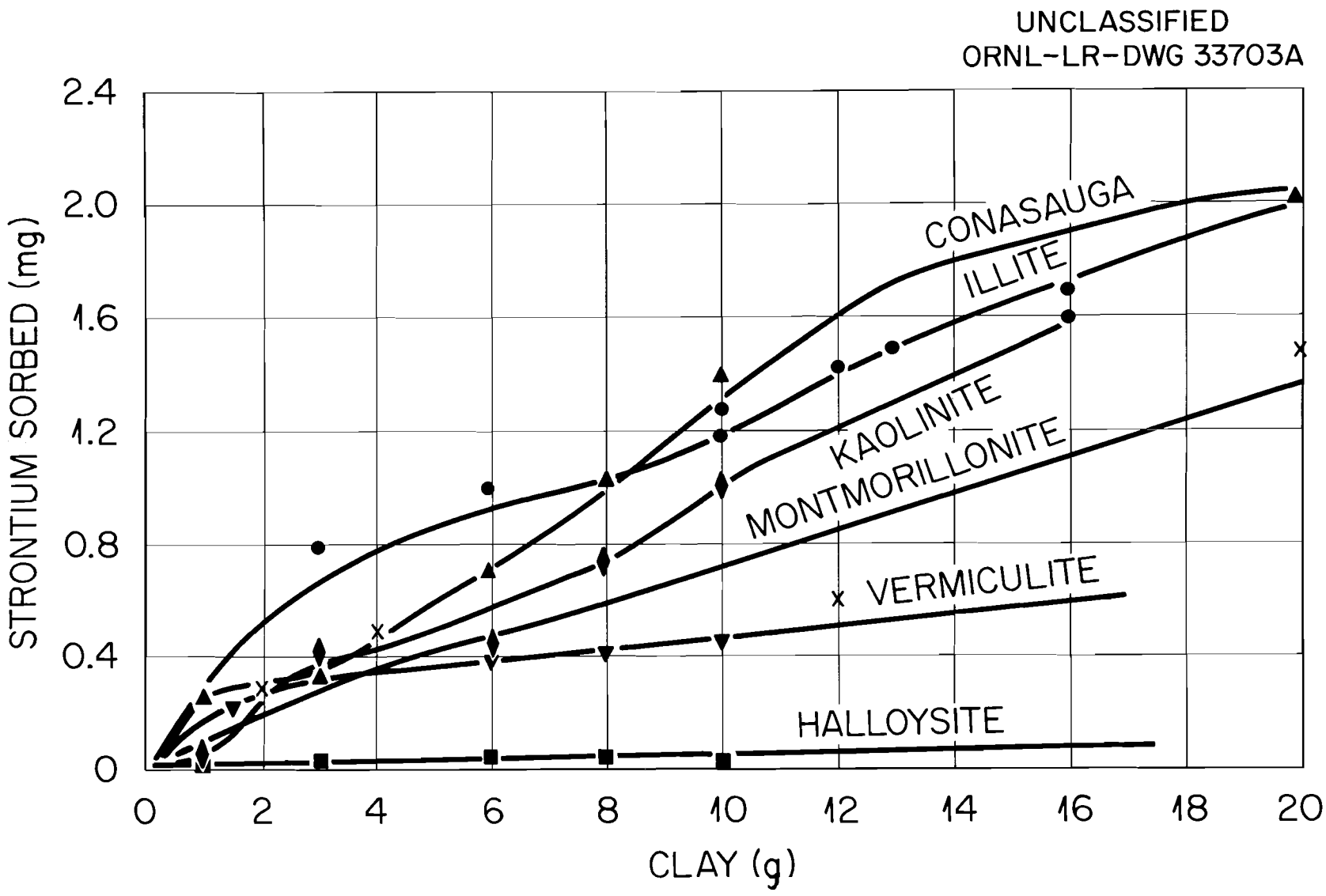

Fig. 8. Sorption of Strontium from 6 M $NaNO_3$ Containing 40 mg Sr/liter

ten beakers per series, was made to determine the effect of pH on the removal of strontium from a 1 M sodium neutralized Purex-type waste using Conasauga shale. The range of pH values studied was from 5.2 to 11.5 using from 1 to 20 g of shale, 150 ml of solution, and a slurry technique.

Results shown on Fig. 9 indicate that the higher the pH the greater the amount of strontium sorbed on the same weight of shale. These results agree with results obtained in water decontamination studies where it was found that pH affected the per cent of strontium removed from solution.[9,10] Increase in pH increased the amount of strontium removed from aqueous solutions. At pH values above 11.5 little effect due to pH was observed. The experimental results indicated (1) increasing weight of shale gave increasing amounts of strontium sorbed but with diminishing returns, and (2) high pH values resulted in proportionately greater amounts of strontium being sorbed.

Other results were obtained on the study of amount of strontium sorbed by various clay minerals from 1 M $NaNO_3$, and the effect of calcium-carbonate-clay mixtures on the amount of strontium sorbed.

In the first test illite sorbed 1.5 to 2.2 mg of strontium over the range of 8 to 20 g of material, while Wyoming bentonite sorbed 1.0 to 1.2 mg of strontium over this same range of material used. When 10% calcium carbonate was added to the clays, 0.4 to 0.9 mg of strontium were sorbed by illite and 0.6 to 1.0 mg of strontium were sorbed by the Wyoming bentonite. The same jar-test procedure using halloysite resulted in no change in the amount of strontium sorbed when calcium carbonate was present. However, it should be mentioned that the amount of strontium sorbed by 20 g of halloysite, from a 1 M Na^+ solution containing 40 mg Sr per liter,

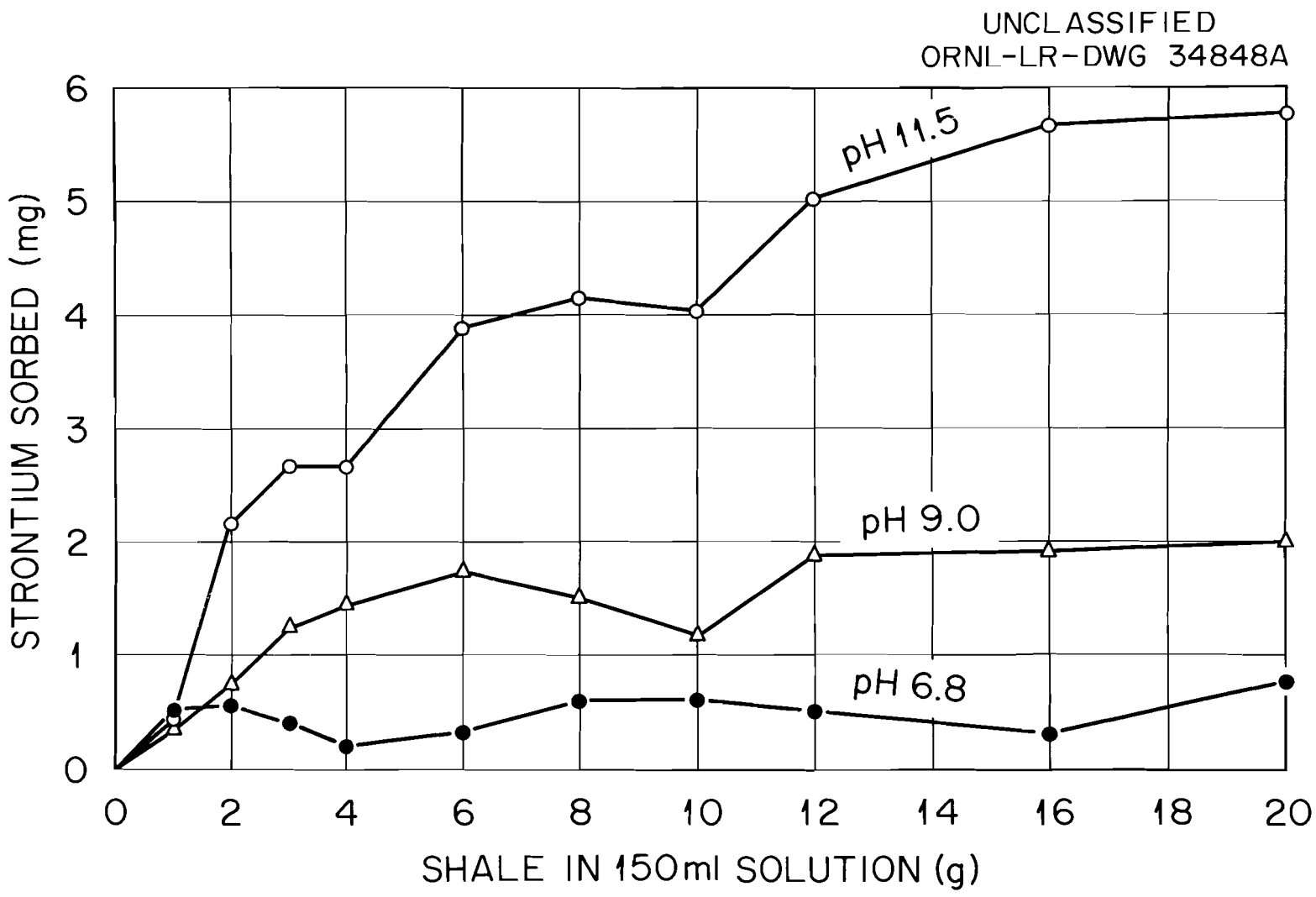

Fig. 9. Effect of pH on the Removal of Strontium from 1 M $NaNO_3$ Containing 6 mg Sr per liter by Conasauga Shale (ORNL LR DWG 34848A)

was 0.9 mg. This is much lower than the amount of cesium sorbed and lower than the amount of strontium sorbed by most clays.

The experimental results shown in Fig. 10 are for the sorption of cesium and strontium on four types of clay materials from a neutralized, complexed, and diluted waste solution. The four types of clay materials used were (1) Wyoming bentonite, (2) illite, (3) illite and limestone, and (4) Conasauga shale. The solution was 1 molar of Purex waste that had been complexed with citric acid, sodium neutralized (pH 7.5), and diluted 1:9 with 1 M sodium chloride solution. The citric acid was added to keep iron in solution.

In this study the cesium sorption was equal to, or slightly less than, the amount of cesium that would be sorbed from this solution if citric acid were not added. However, the amount of strontium sorbed was less by about a factor of 3 when the waste was complexed with citric acid. The results shown on Fig. 9 indicates that under the test conditions citric acid does not noticeabley affect the sorption of cesium, but does depress the sorption of strontium. This observation agrees with the general theory of chelation; that is, the higher the valence the greater the ease of chelation. Therefore, it can be assumed that some of the strontium in the waste solution was chelated by the citric acid and, therefore, not available as a cation for sorption or exchange with the replaceable ions of the clay material. The monovalent cesium and the relatively high concentration of sodium ions, also present in the waste solution, were not complexed by the citric acid, and no change in sorption was found.

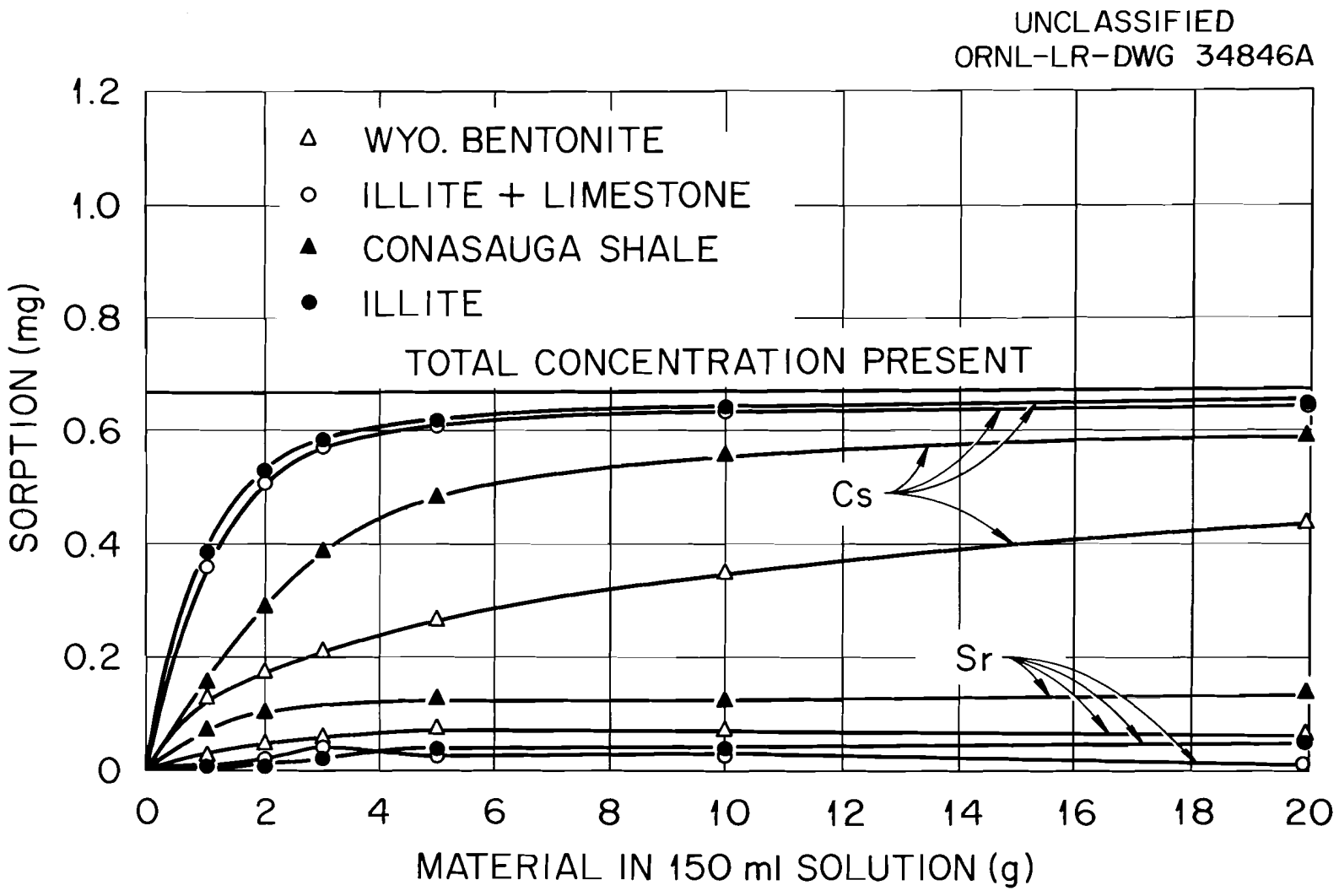

Fig. 10. Sorption of Cesium and Strontium by Various Materials from a Citric Acid Complexed, 1 M Sodium Neutralized Purex Waste Solution that has been Diluted 9:1 with 1 M NaCl

5.3 Column Sorption Studies

The sorption of radiocesium from neutralized Purex waste by quartz sand (SiO_2) and mixtures of quartz, feldspar, mica, and several types of clay was investigated by means of column experiments. The initial column tests were made with clean Ottawa sand, either water rinsed or acid-leached, packed in columns of various sizes. Neutralized Purex waste, 300 to 4000 ml, containing tracer quantities of Cs^{137} (to give a count rate of ~ 9000 counts min^{-1} ml^{-1}), plus 100 mg per liter of cesium carrier, was passed through the sand at a low flow rate. Virtually no sorption of radiocesium by either the normal or the acid-leached Ottawa sand was observed. Visual observations indicated no change in permeability during the run, and no formation of precipitate in the sand; no coating of the sand grains could be detected.

Glass columns, 1 in. in diameter by 10 in. long, were then packed with clean quartz sand and 140-mesh Conasauga shale. These columns were used to check the partial sorptive capacity of the shale for cesium from 6 M $NaNO_3$ containing 100 mg Cs per liter. The results of these tests indicated a partial sorptive capacity of 2.31 mg Cs per 10 g of shale, while slurry equilibrium studies give a partial capacity of 3.3 mg Cs per 10 g of shale. This difference in the lower column value may have been due to less effectiveness in solid-solution contact in the column.

6.0 CORE TESTS

The next phase of the laboratory test program was the testing of cores. The type of data obtained could be generally termed "partial radionuclide capacity analysis" and is to be differentiated from basic

core analysis measurements - porosity, permeability, and residual fluid content. It is also more simple than the specialized and complex tests, such as restored state or capillary pressure, relative permeability, and water-flood susceptibility.

As so many variables are connected with coring operations and the type of information desired, it is difficult to obtain specific recommendations on core handling, sampling, preservation procedures, and methods of analysis. However, the Geochemistry and Petrology Branch of the U. S. Geological Survey agreed to make the basic core analysis needed and to make any specific mineralogic or chemical analysis requested.

6.1 Core Tests on Cesium Sorption

Several cores of Berea sandstone were obtained from the Crystal Lake Laboratories of the Pure Oil Company* for preliminary testing and technique development (See Fig. 11.). The method suggested and adopted for mounting cores for fluid flow and sorption of radioisotopes consisted of coating the outside of the core with an epoxy resin. After allowing the resin to harden, two plexiglass or stainless steel end plates with neoprene gaskets were used to mount the cores. All these components were held together by four brass tie rods threaded at both ends. Other methods of core mounting which may be used include use of Hassler sleeves, Lucite casing, and low melting alloys.

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*Pure Oil Co. obtained the cores from Silica Chemicals, Inc., Amherst, Ohio.

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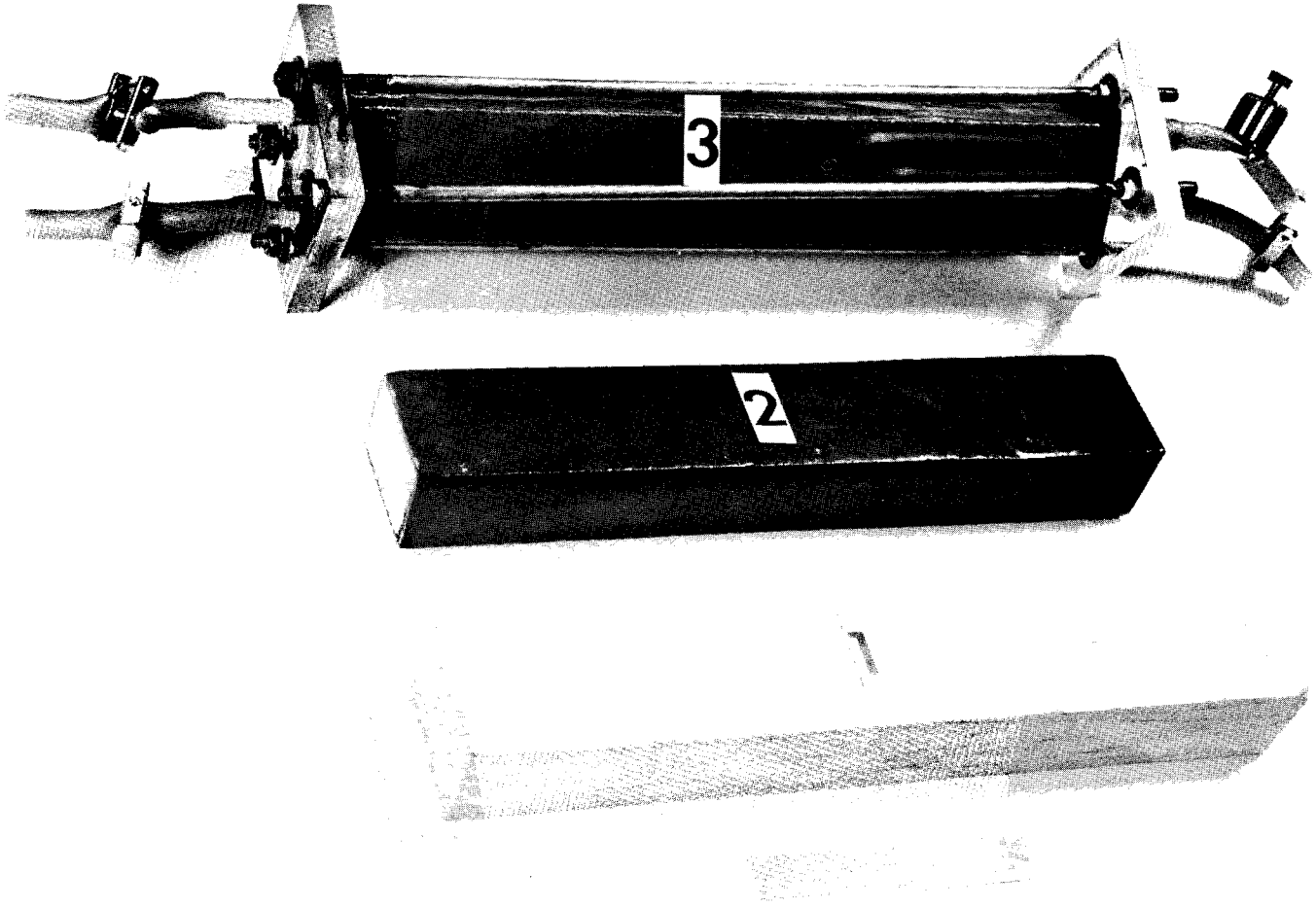

Fig. 11. Mounting of Berea Sandstone Cores

The fluid was pumped through the core using a Lapp pulsafeeder* driven by a 1/20 H.P. electric motor. The influent solution was 1 molar sodium-neutralized, citric acid complexed, Purex waste which had been diluted 1:9 using 1 M NaCl. The solution contained 0.67 mg per liter of stable cesium and sufficient Cs^{137} to give a count rate of ~ 15,000 counts min^{-1} ml^{-1}.

The coated Berea core had an effective volume, the total volume minus the volume occupied by the epoxy resin, of 388 cc. The void volume, determined by filling the interstitial spaces with distilled water, was found to be 87.6 cc, corresponding to a porosity of 22.6%. The results of chemical analysis or two different samples of Berea is shown in Table 4.

A photograph of the experimental setup is shown in Fig. 12. The solution was pumped through the core at a rate of about 25 ml per hr. Samples of the effluent were taken every 50 ml and counted in the well-type scintillation counter and 1024 scaler.

The results are shown on Fig. 13, as a plot of Cs^{137} activity in the effluent versus the cumulative volume of solution passed through the core. The influent solution was made up in two batches of 2 liters each: in the first batch, the count rate of Cs^{137} was 15,000 counts min^{-1} ml^{-1}; in the second, 17,000 counts min^{-1} ml^{-1}. However, this small difference in count rate would have no detectable effect on the estimation of the capacity of the core for cesium. The results show a typical breakthrough curve with the exception of the nightly variations after 2900 ml of

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*Products of Lapp Insulator Co., Inc., Le Roy, New York.

Table 4. Analysis of Berea Sandstone*

Constituent	Per Cent	
	Sample 429	Sample 1931
Ca	1	Trace
Mg	0.4	None
SiO_2	86	88
Al_2O_3	1	1.3
Fe	1.5	4
CO_2	0.71	0.88
Ignition Loss	2	0.95
Clay Content (Approx.)**	5	4

*A nonswelling type.

**Reported by the Crystal Lake Laboratories, Pure Oil Co., Crystal Lake, Illinois.

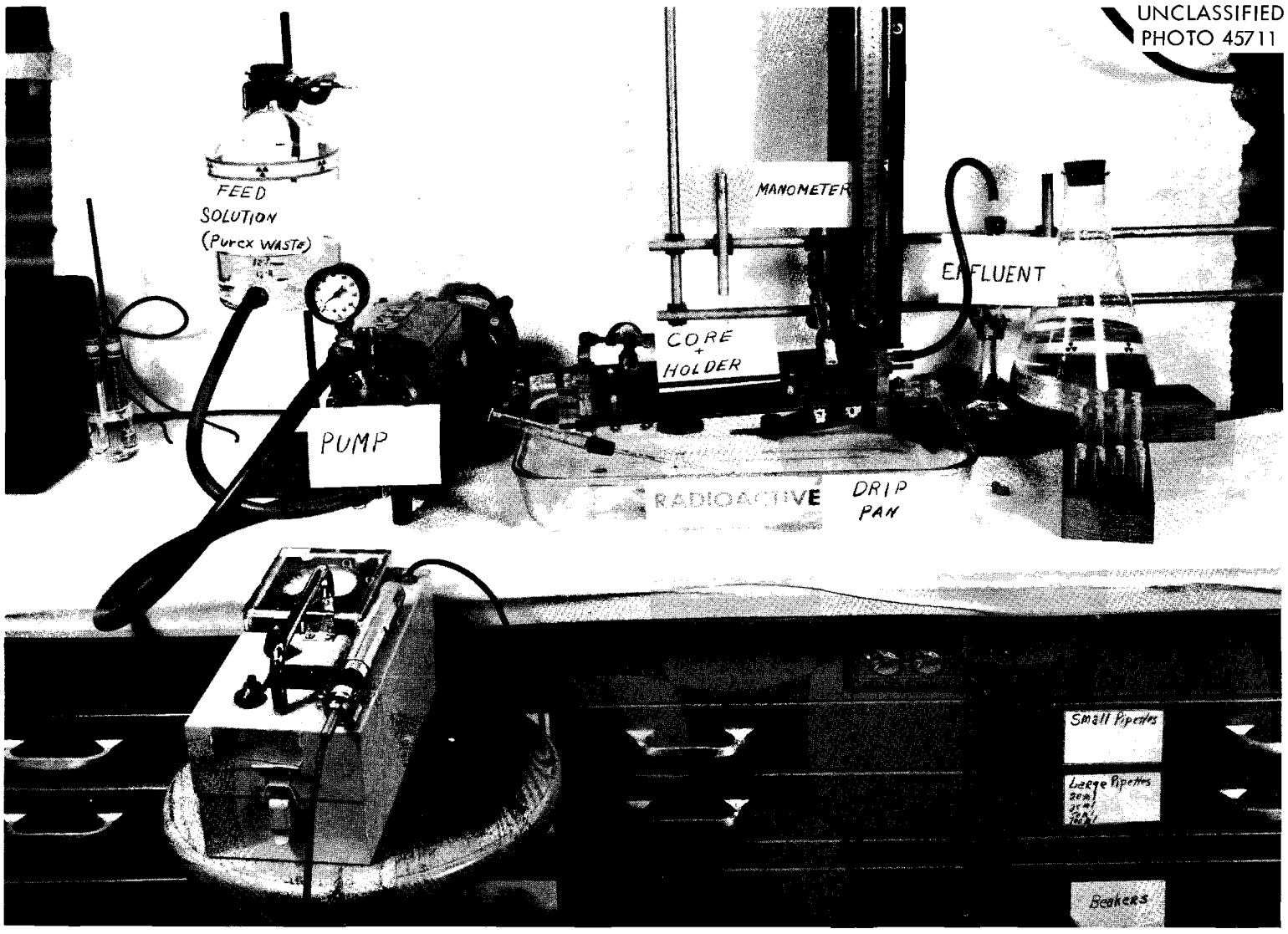

Fig. 12. Experimental Arrangement for Core Testing

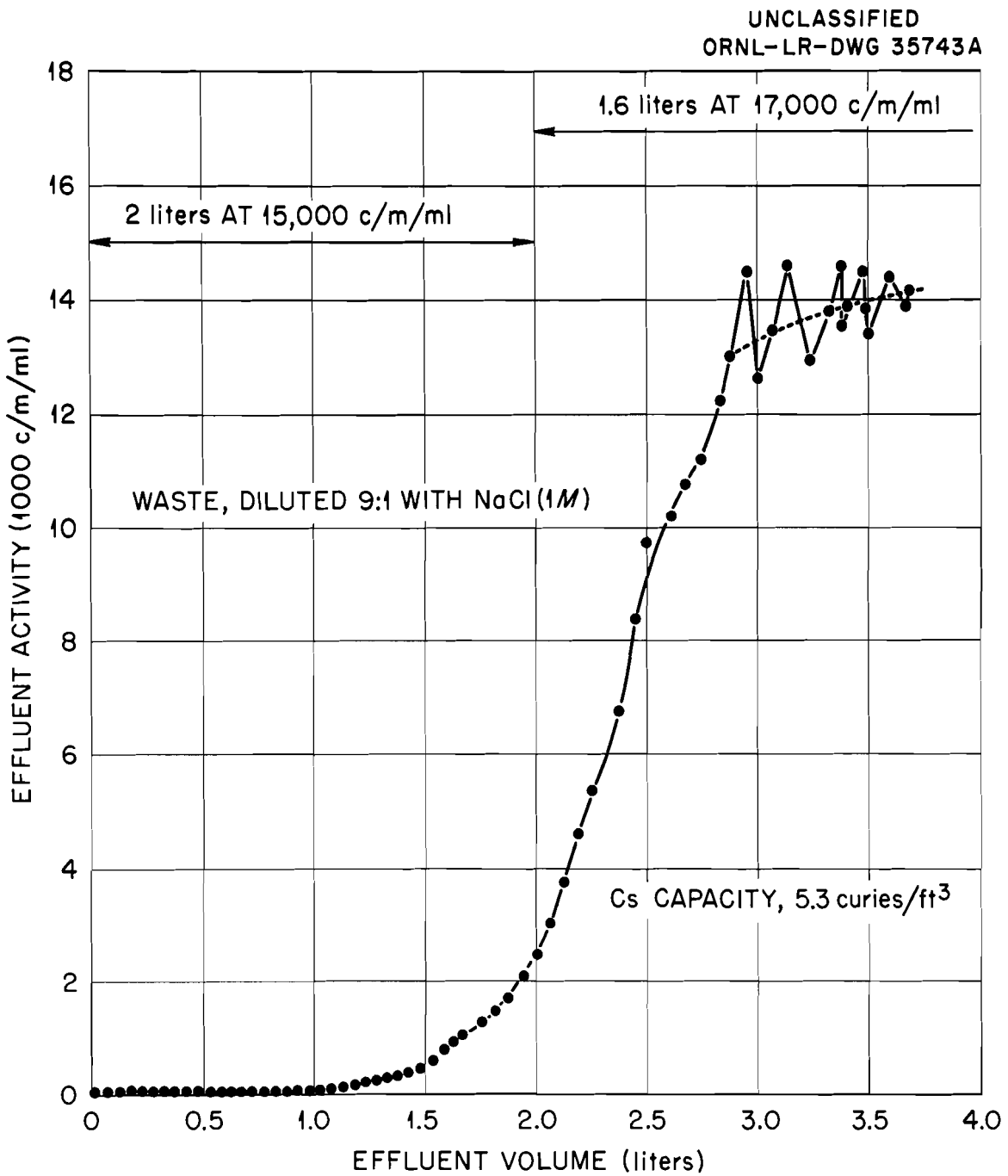

Fig. 13. Effluent Activity Versus the Effluent Volume of Purex Waste (Neutralized, Citrate Complexed) from Sandstone Core No. 1

solution had passed through the core. Throughout the test runs, no increase in head pressure was detected; no plugging of the leading face of either core was found. This column, as well as the second column, worked well at operating pressures of less than 80 psi.

The following is the partial cesium capacity of the core for this influent solution:

(1) Cesium concentration in influent - 0.67 mg/liter.

(2) Cesium sorbed - 1.67 mg.

(3) Core volume - 388 cc.

(4) Cesium sorbed per cubic foot - 122 mg.

If the specific activity of the cesium in Purex waste were 40 curies per gram, then 1 cu ft of Berea sandstone would sorb about 4.9 curies per cubic foot.

A second core test was made using the same material and experimental techniques, except the waste was diluted 30:1 with 1 M NaCl instead of 9:1 as in the first experiment. The results of this test are shown on Fig. 14. Calculations on the amount of cesium sorbed per cubic foot of Berea sandstone from a 30:1 dilution of the waste solutions are as follow:

(1) Cesium concentration in influent - 0.22 mg/liter.

(2) Cesium sorbed - 1.37 mg.

(3) Core volume - 491 cc.

(4) Cesium sorbed per cubic foot - 80 mg.

6.2 Core Tests on Strontium Sorption

Following the core testing of cesium sorption, core experiments were conducted using strontium carrier plus Sr^{89} as a tracer. The concentration

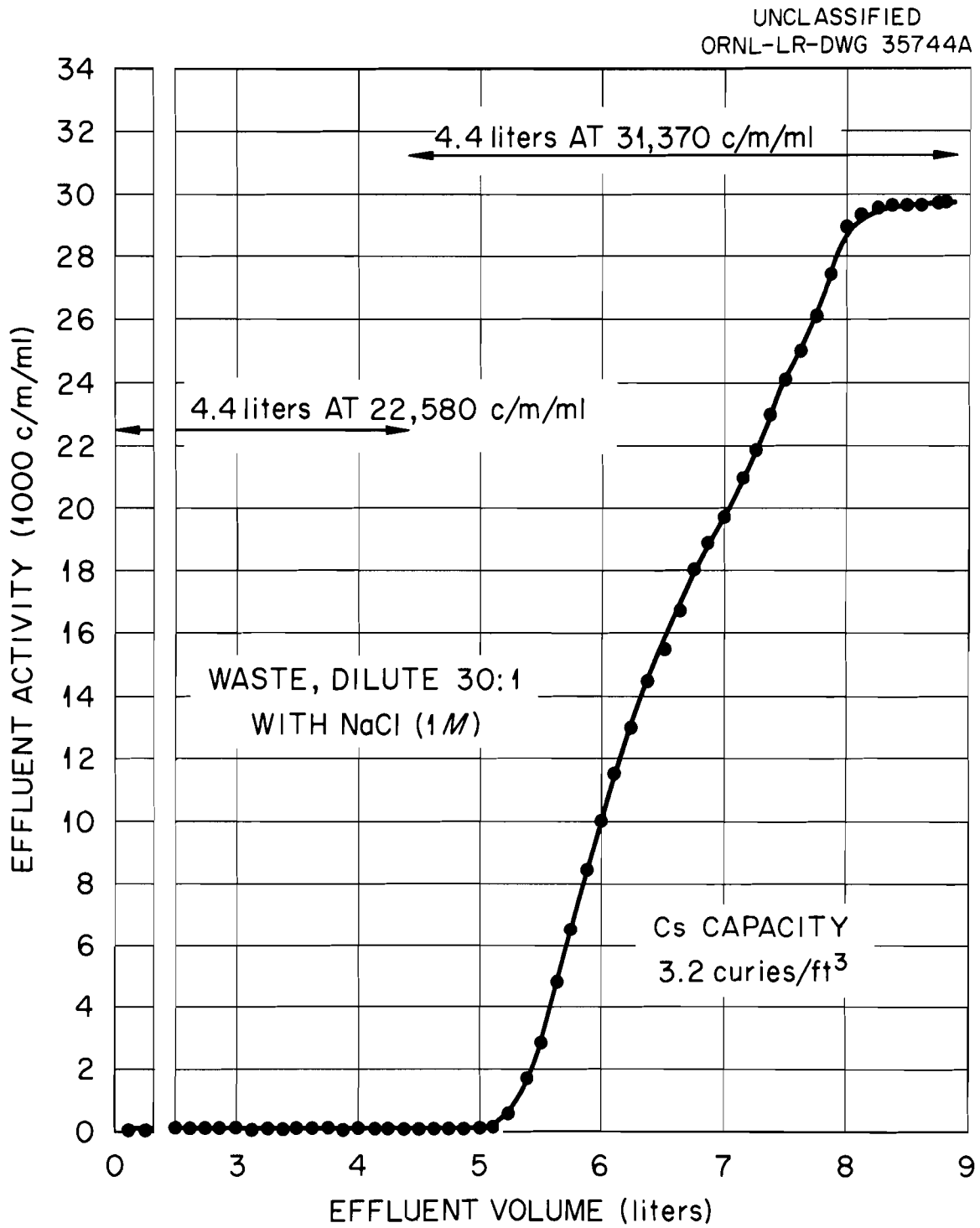

Fig. 14. Effluent Activity Versus the Effluent Volume of Purex Waste (Neutralized, Citrate Complexed) from Sandstone Core No. 2

of carrier used was 1.33 mg of strontium per liter, which is the approximate concentration of fission-product strontium present in unconcentrated Purex waste diluted 30:1.

Calculations are based on both the amount of strontium removed from the influent solution and on the amount of strontium actually sorbed on various samples of the core. The calculations showed that at a 9:1 dilution, 0.33 mg of strontium was sorbed in the core; thus, 1 cu ft of this sandstone would sorb 2.4 curies of strontium (Fig. 15). Similar calculations for the 30:1 dilution showed 0.178 mg of strontium was sorbed. This is equivalent to about 1.9 curies of Sr^{90} per cubic foot of sandstone. These values assume the specific activity of Sr^{90} in the waste to be 80 curies per gram. The results of the 30:1 dilution study are shown on Fig. 16.

While results of cesium sorption showed the amount of cesium sorbed to be dependent on the Na/Cs ratio, the amount of strontium sorbed is only slightly affected by the Na/Sr ratio. It may be noticed on Fig. 16 that due to the length of time required to complete the experiment (9 days) a correction was required for the decay of Sr^{89} ($T_{1/2}$ = 53 days).

The results of these tests and a comparison to the cesium sorption studies, using sandstone cores, shows that a 9:1 dilution sorbs 2.4 curies of strontium per cubic foot and 4.9 curies of cesium per cubic foot, while a 30:1 dilution sorbs 1.9 curies of strontium per cubic foot and 3.2 curies of cesium per cubic foot. In the jar-test slurry studies the results indicated that approximately 2 curies of strontium would be removed by various clays for every 3 curies of cesium removed under similar conditions. The results of the core tests compared very favorably with the values obtained by slurry treatment.

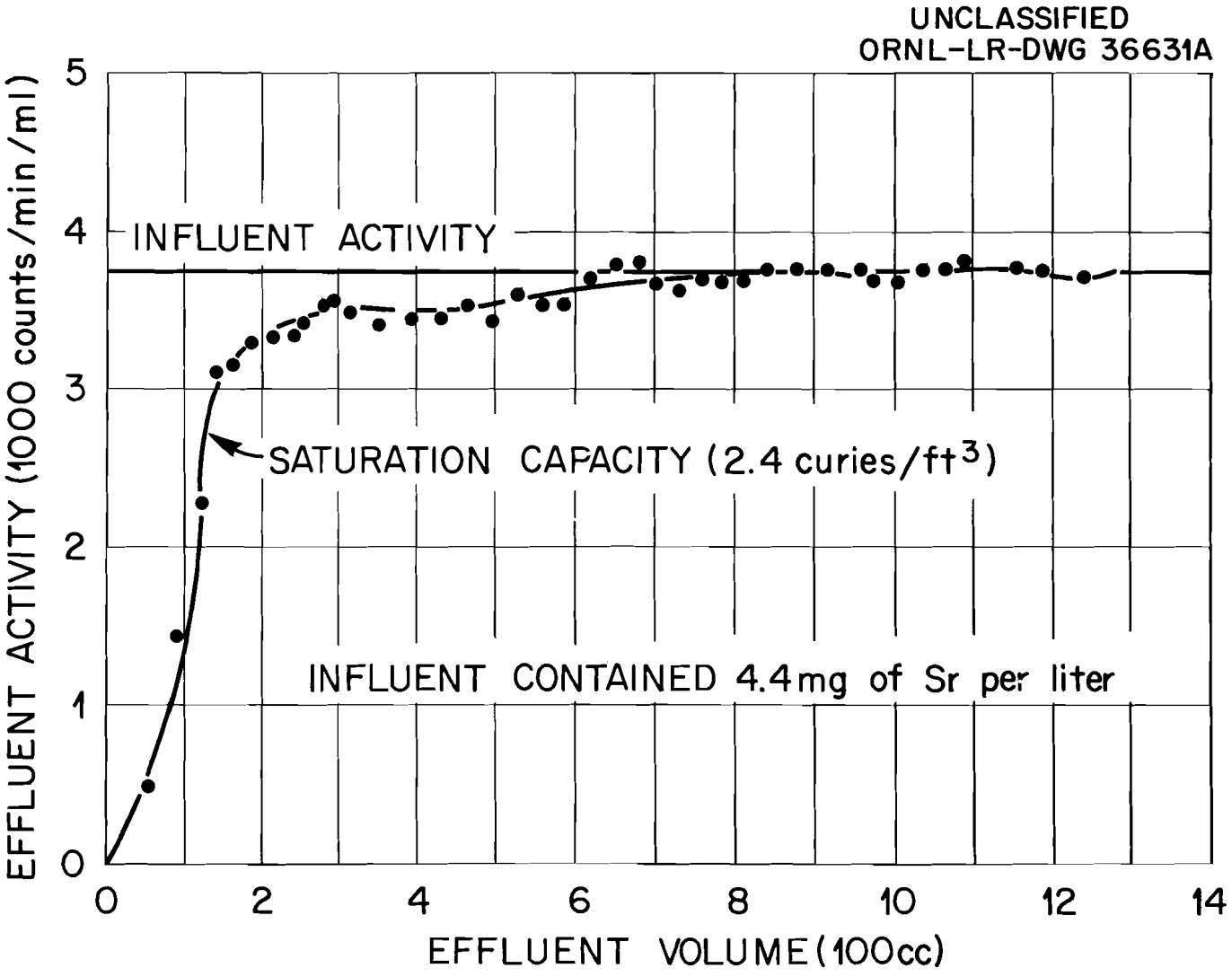

Fig. 15. Strontium Sorption from a 9:1 Dilution of 1 M Purex Waste by Berea Sandstone

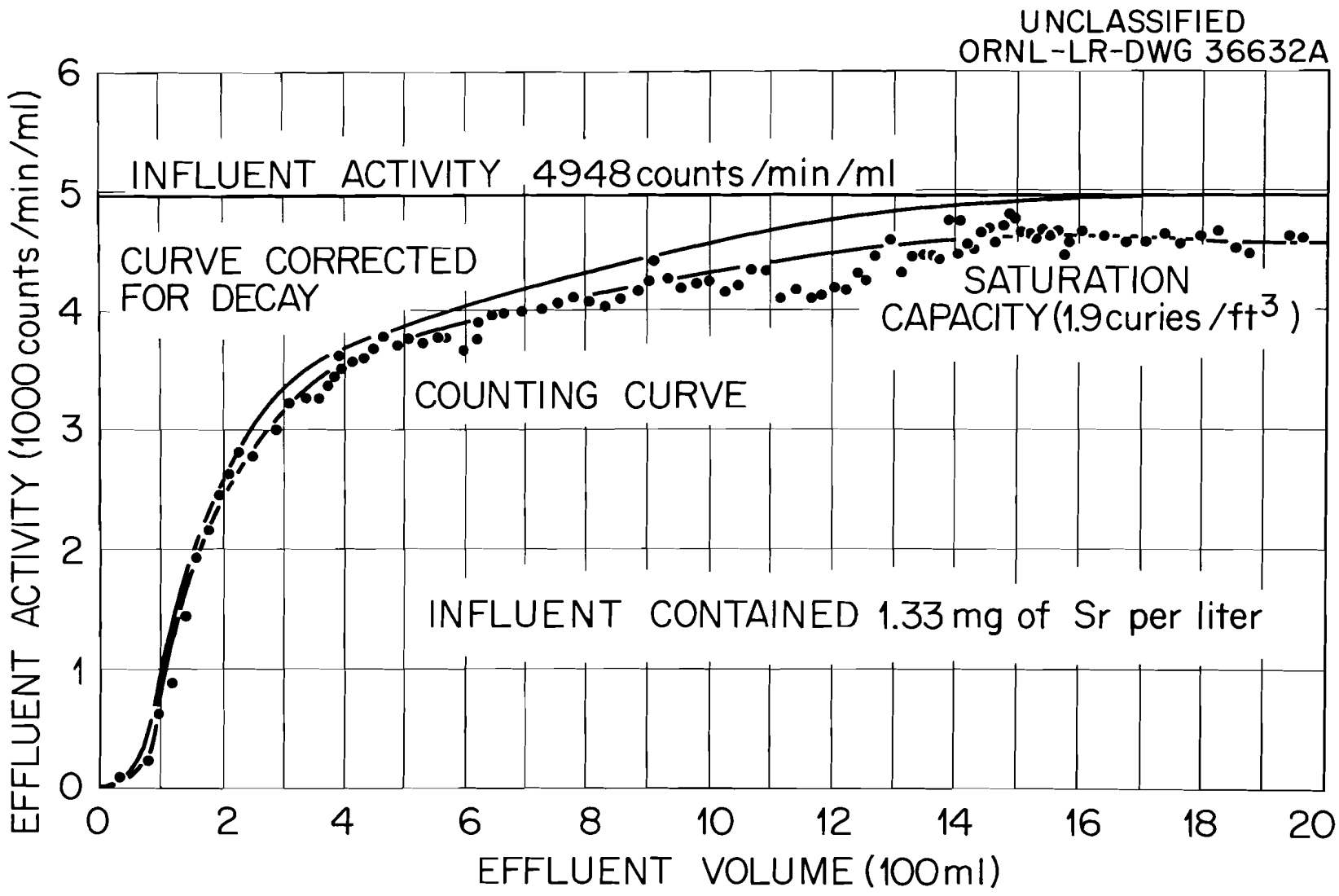

Fig. 16. Strontium Sorption from a 30:1 Dilution of 1 M Purex Waste by Berea Sandstone

7.0 SUMMARY

A study of the results of sodium and calcium neutralization of a Purex-type waste was made. The distribution of fission products in both the solid and liquid phase was determined radiochemically. The laboratory work on the deep-well program so far suggests that plugging of the disposal formation by precipitates, resulting from chemical interaction between the waste and the brines already in the formation, is not likely to be a problem. This conclusion is in agreement with the experience of the petroleum industry. The possibility of plugging due to chemical reaction between the waste and the solid matrix of the formation has yet to be studied. The results of the sorption studies suggest that localized heat production, due to sorption of radioactive materials near the well, can be controlled so that it will not be a serious problem. Laboratory tests, involving the use of cores, help confirm the results of slurry tests, which were used to determine the sorptive capacity of several types of clay minerals, feldspars, and shales. The tests to date have shown good agreement between capacity values obtained using both cores and slurry techniques and demonstrates that the problems connected with heat production, due to fission-product sorption in a porous formation, may be less important than some others that will be confronted.

REFERENCES

[1] F. Birch, Thermal Considerations in Deep Disposal of Radioactive Waste, NAS-NRC, Washington 25, D. C., July 1958.

[2] Status Report on Handling and Disposal of Radioactive Wastes in the AEC Program, WASH-742, August 1957.

[3] F. M. Empson, Physical Characterization of Acidic and Neutralized Synthetic Fuel Reprocessing Waste Solutions on Evaporation and Calcination, ORNL-2566, February 1959.

[4] G. G. Bernard, Ill. State Geol. Survey Bull. 80, p 98-115 (1960).

[5] T. Tamura, Health Physics Division, Oak Ridge National Laboratory, personal communication.

[6] D. G. Jacobs, "Sorption of Cesium by Conasauga Shale," Health Physics 4, 157 (1960).

[7] T. Tamura and D. G. Jacobs, "Structural Implications in Cesium Sorption," Health Physics 2, 391 (1960).

[8] D. G. Jacobs and W. J. Lacy, "Adsorption and Ion Exchange of Radioactive Waste Liquor by Shale," presented at the 135th National Meeting of the American Chemical Society, Boston, Massachusetts (April 5-10, 1959).

[9] C. P. Straub, W. J. Lacy, and R. J. Morton, "Methods for Decontamination of Low-Level Radioactive Liquid Wastes," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, August 8-20, 1955 9, 24-27, United Nations, New York, 1956.

[10] W. J. Lacy, Manual for the Preparation of Simulated Fuel Reprocessing Waste Solution, ORNL CF-58-4-45, June 1958.

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