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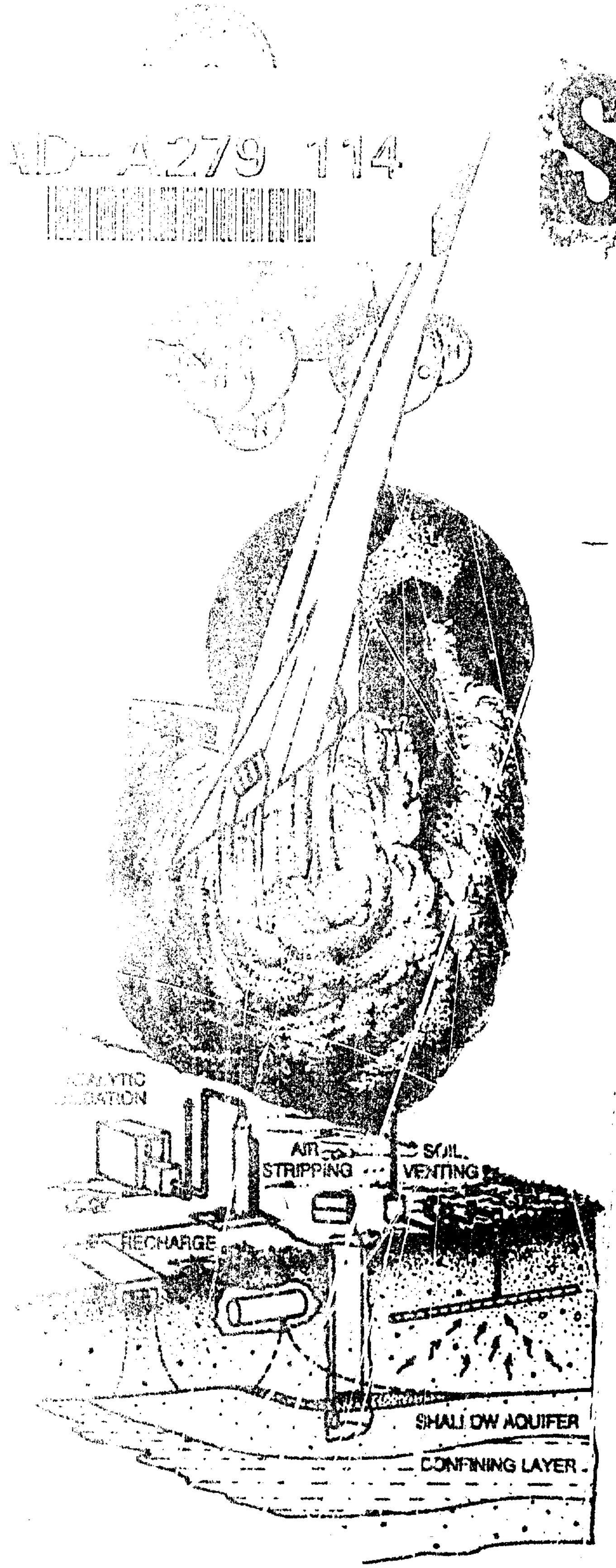
Volume IV

SEPARATION OF DEPLETED URANIUM FRAGMENTS FROM GUN TEST CATCHMENT, VOL IV: BENCH-SCALE TESTS OF SEPARATING DEPLETED URANIUM FROM SAND



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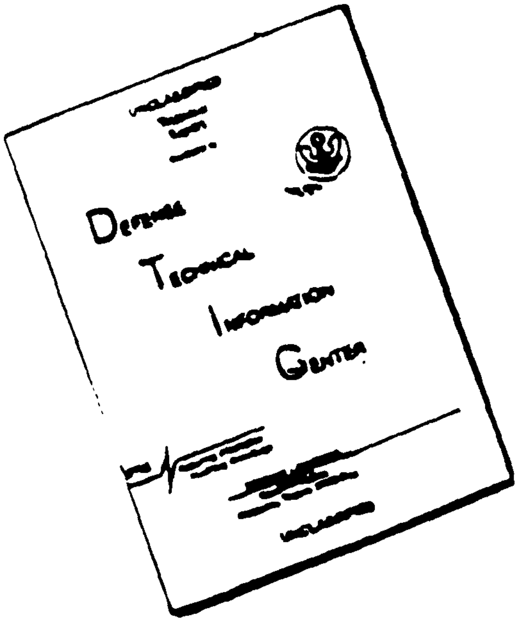

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13. ABSTRACT (Maximum 200 words)

This technical report is divided into four volumes. Volume I presents Summary and Recommendations, Volume II contains Catchment System Evaluation and Separating Methods, Volume III contains an Economic Comparison of Disposal Options, and Volume IV documents Bench-Scale Tests for Separation.

Phase 2 activities are described for a task entitled "Separation of Depleted Uranium Fragments from Gun Test Catchments, Vol. IV, " sponsored by the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida. The purpose of the work is to develop an improved means for separating depleted uranium projectile fragments from target materials, principally sand. The Phase 2 activities included bench-scale tests of separation processes that had the potential to minimize the amount of contaminated sand that must be treated as radioactive waste. The tests reported here achieved a high degree of separation but did not manage to meet the 35-pCi/g requirement for unrestricted disposal. In addition to the separation tests, a series of tests was conducted to determine the likelihood of dissolving sufficient DU in the process water to classify the water as radioactive waste. This was shown to be possible though highly improbable.

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PREFACE

This report was prepared by Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, DE-AC05-84OR21400, for the U.S. Department of Energy (DOE) and the Air Force Civil Engineering Support Agency (AFCESA), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319.

This report presents the results of a series of activities designed to develop an improved method for separating depleted uranium from target materials, principally sand. Recommendations are offered for the most attractive method from both economic and technical perspectives. The search for an improved method considered the environmental, economic, and technical aspects of the problem. The method of choice is to dry, screen,and recycle the intermediate-sized uranium-contaminated sand. This will save the Air Force an estimated several million dollars over the next 20 years and will reduce the volume of low-level waste by about 90 percent.

Much thanks are due E. L. Biddle for the experimental work. Also, the author is grateful to C. S. Daw for helpful discussions and advice, C. Feldman for the analytical chemistry studies with sand-water mixtures, and C. S. Macdougall for expert support work in scanning electron micrography, mass spectrography, and X-ray diffraction.

This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication,

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the work described in this series of reports was to develop and demonstrate an improved means for separating depleted uranium from target sand, the source of the uranium being penetrator projectiles fired into a target building containing sand as the stopping medium. The principle incentive is to reduce the disposal costs of the contaminated sand by providing improved separation methods which diminish the waste volume.

B. BACKGROUND

The engineering and operational test firing of the GAU8 30-mm cannon produces low-level radioactive waste when the depleted uranium projectiles impact the sand contained in the target building. Test hazards and damage to the target building are held to an acceptably low level by periodically removing the large bullets from the sand. Proper operation of the filtration system on the target building roof during firing tests requires periodic elimination of the fine dust generated when bullets impact the sand. A third restriction on the amount of uranium contained in the target building is imposed by the NRC license which limits the amount of depleted uranium on site to 80,000 kgs but this limitation has not been the controlling factor in any of the test operations to date.

The present sand removal and treatment operations are of two types. The first is to remove the sand with a front-end loader and sift it through 1/2 inch opening sieve to remove the projectile fragments. The sand is then returned to the target building. With the second method all of the sand is removed from the building and stored on site in drums pending further treatment prior to shipment for long term storage at an off-site location. The target building is then filled with fresh sand. These methods are effective but, because of the large volumes sent to storage, very expensive.

C. SCOPE

This volume reports the results of a series of bench-scale experimental studies which characterized the DU/sand mixture and examined the feasibility of wet density separation methods. The experiments also determined the solubility of DU in process water over the range of process conditions likely to occur at the Eglin AFB test site, and sought ways to chemically remove uranium contamination from the process water.

D. METHODOLOGY

The sand/DU particle characterization and the DU solubility studies were evaluated in the ORNL analytical chemistry laboratories using conventional laboratory apparatus. The separation studies were conducted in a bench-scale, water-fluidized bed constructed especially for this project.

The characterization studies investigated: (1) the analysis of uranium in heavy particles, (2) the density of individual particles of DU/sand, and (3) the bulk density correlation of the DU/sand mixture with the uranium content of the mixture as a weight fraction. Conventional analytical laboratory methods were used to determine the amount of uranium in individual heavy particles by immersing them in a column of fluid with a known density gradient. Gas displacement density measurements and chemical analysis for total uranium content were used to establish the bulk density correlation.

The solubility studies were conducted over a range of pH values which were adjusted by adding various amounts of calcium carbonate and hydrochloric acid to the process water.

E. RESULTS

The density separation tests achieved a high degree of separation, as much as 14-fold reduction in DU content but still fell short of achieving the 35 pCi/g requirement for unrestricted disposal. The characterization studies yielded information useful in the design of density-driven separations. The uranium solubility studies showed that only in extreme cases (when limestone is present and the solution pH is buffered to 5) will the 40 pCi.mL activity limit be exceeded.

F. CONCLUSIONS

The wet density separation methods examined in this series of experiments are not sufficiently effective to be of use in improving the means of disposal of DU/sand waste.

G. RECOMMENDATIONS

The information developed in this study should be retained for possible future use. The method for improved screening of the target sand with recycle of the intermediate fractions combined with the use of presized sand for make-up should be instituted at the present test facility when funding is available for the procurement and installation of the necessary equipment.

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SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of the work described in this series of reports was to develop and demonstrate an improved means for separating depleted uranium from target sand, the source of the uranium being penetrator projectiles fired into a target building containing sand as the stopping medium. The principle incentive is to reduce the disposal costs of the contaminated sand by providing improved separation methods which diminish the waste volume.

ORNL was tasked to support the United States Air Force Engineering and Services Center (USAFESC) in evaluating and designing alternative means of disposing of this waste more economically.

The purpose of the ORNL bench-scale work was to obtain basic information to help answer key questions about the potential for density separation and solubility of DU in water under a range of possible process conditions at the Eglin test site. The three principal issues were (1) to quantify the level of contamination in process water for a range of possible process conditions, (2) to find ways of chemically removing the radioactive contamination in water, and (3) to estimate the potential separation of DU from sand based on particle density differences.

B. BACKGROUND

The United States Air Force periodically samples and tests ammunition from storage to ensure that it is in field- ready condition. In particular, the test site at Eglin Air Force Base, Florida, test fires 30-mm armor-piercing incendiary (API) ammunition, which is largely constituted of DU. The engineering and operational test firing of the GAU8 30-mm cannon produces low-level radioactive waste when the depleted uranium projectiles impact the sand contained in the target building. Test hazards and damage to the target building are held to an acceptably low level by periodically removing the large bullets from the sand. Proper operation of the filtration system on the target building roof during firing tests requires periodic elimination of the fine dust generated when bullets impact the sand. This sand is currently classified as a low-level radioactive waste since it has an activity >35 pCi/g. A third restriction on the amount of uranium contained in the target building is imposed by the NRC license which limits the amount of depleted uranium on site to 80,000 kgs but this limitation has not been the controlling factor in any of the test operations to date. Current practice is to dispose of the entire catchment inventory by packaging and shipment for burial at approved sites.

This report describes bench-scale experimental studies supporting the overall objective. Additional bench-scale studies were performed by K D Engineering, who tested wet and dry screening systems as well as wet separators such as jigs and spirals. Economic analyses have shown that if the DU-sand fines (<60-mesh) can be derated (i.e., no longer classified as radioactive because they have been purified so that their activity is ≤35 pCi/g), the addition of a separation process may be cost-effective.

C. SCOPE

This volume reports the results of a series of bench-scale experimental studies which characterized the DU/sand mixture and examined the feasibility of wet density separation methods. The experiments also determined the solubility of DU in process water over the range of process conditions likely to occur at the Eglin AFB test site, and sought ways to chemically remove uranium contamination from the process water.

SECTION II
LABORATORY TEST WORK

The sand/DU particle characterizations and the DU particle water solubilities under a simulated range of process conditions were evaluated in the ORNL analytical chemistry laboratory using conventional chemical laboratory apparatus. The fluidization testing was performed using laboratory apparatus designed and fabricated for this program. Chemical analyses supporting the fluidized-bed tests were performed in the Oak Ridge Plant Y-12 analytical chemistry laboratory.

A. CHARACTERIZATION STUDIES

Three properties were investigated: (1) analysis of uranium in heavy particles, (2) density of individual particles of DU/sand, and (3) bulk density correlation of the DU/sand mixture, with the uranium content of the mixture as a weight fraction.

1. Analysis of Uranium on the Heavy Particles

Using a water-fluidized bed that will be described later, the heavier particles in the 16-20-mesh size range were separated easily by simply increasing the flow until only a few particles remained in the bed. The particles that moved the least were easily isolated by using the side ports in the flow tube to remove the lighter (and hence more mobile) ones. The heavy particles, which were dark in color, were collected and sent for (1) scanning electron micrography (SEM), (2) uranium fluorescence analysis, (3) mass spectrometric analysis, (4) X-ray scattering analysis, and (5) chemical uranium analysis.

The SEM of one particle at 50× magnification is shown in Figure 1(a), and a uranium dot map of the same particle is shown in Figure 1(b). The uranium dot map shows the fluorescence of the uranium atoms on the surface (the dark shadows are probably due to the slope of the particle surface). The SEM image of the same particle is shown on a 400 scale in Figure 1(c), with the accompanying uranium dot map in Figure 1(d). The increased magnification minimizes the effect of particle texture and shows that the uranium is relatively evenly spread on the surface of the particle. In Figure 1(e) a SEM image of the particle is shown on a 200 scale.

In the mass spectrogram, elements lower than oxygen in the periodic table could not be analyzed. The results are displayed for one of the particles in Figure 2 and show, as suspected, that uranium is the main constituent, followed by silicon, aluminum, iron, and traces of titanium in order of decreasing concentration levels. The X-ray diffraction pattern

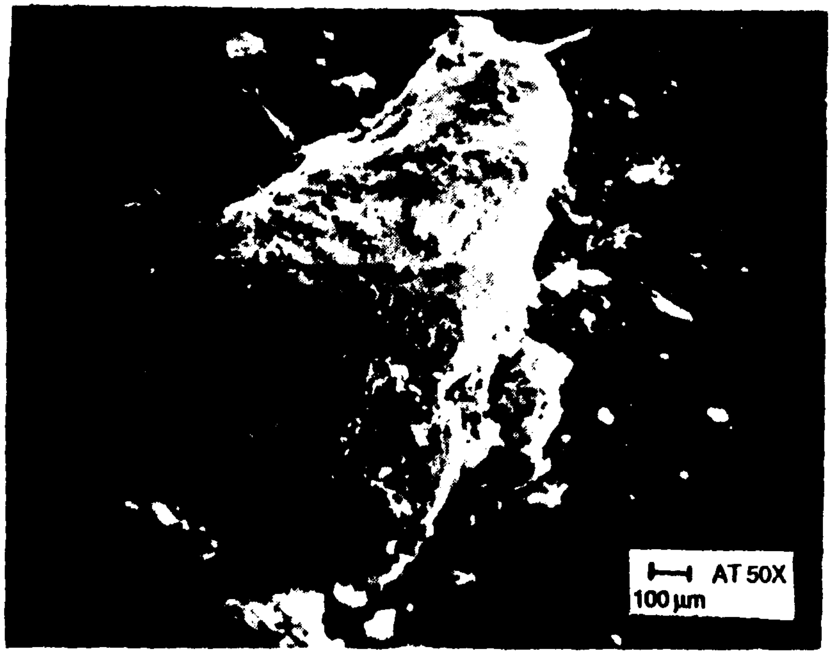

Figure 1(a). Scanning Electronic Micrograph of a Particle (50X Magnification).

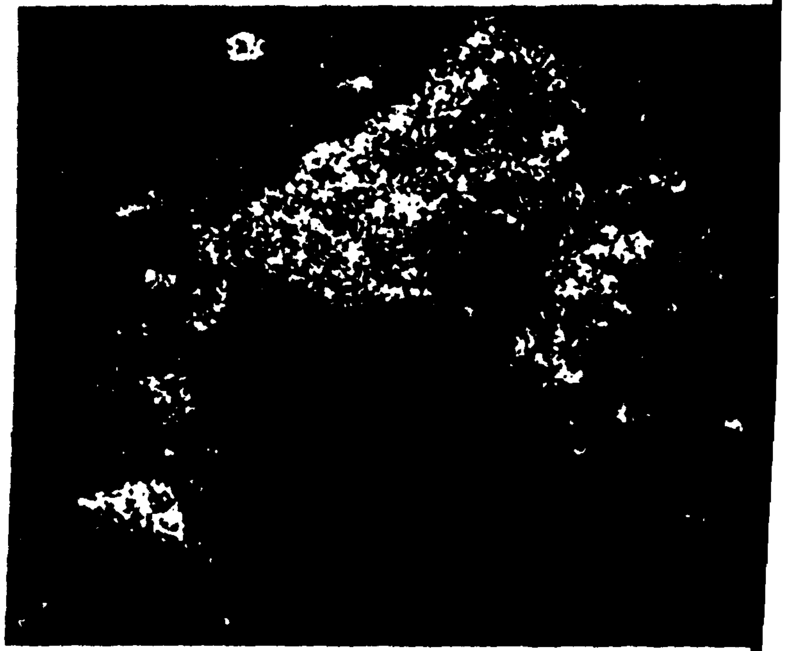

Figure 1(b). Surface Uranium Distribution on a Particle (50X Magnification).

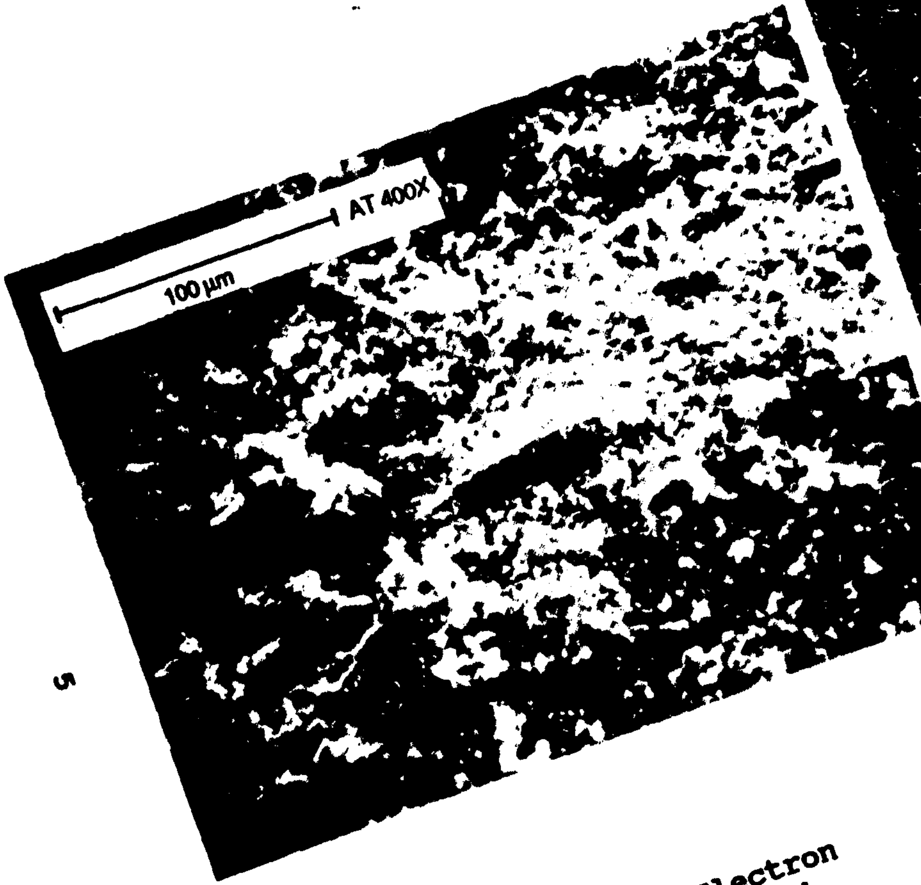

Figure 1(c). Scanning Electron Micrograph of a Particle (400X Magnification).

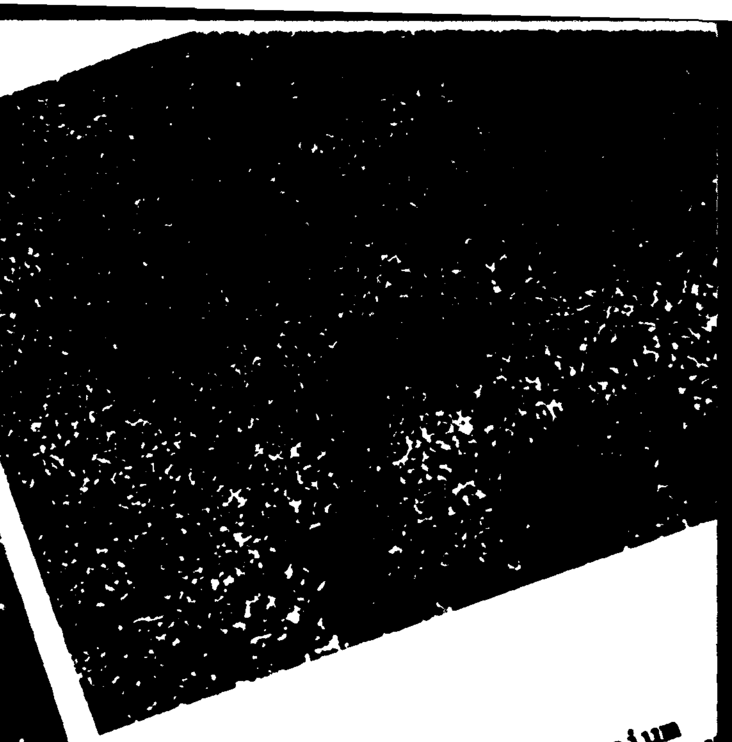

Figure 1(d). Surface Uranium Distribution on a Particle (400X Magnification).

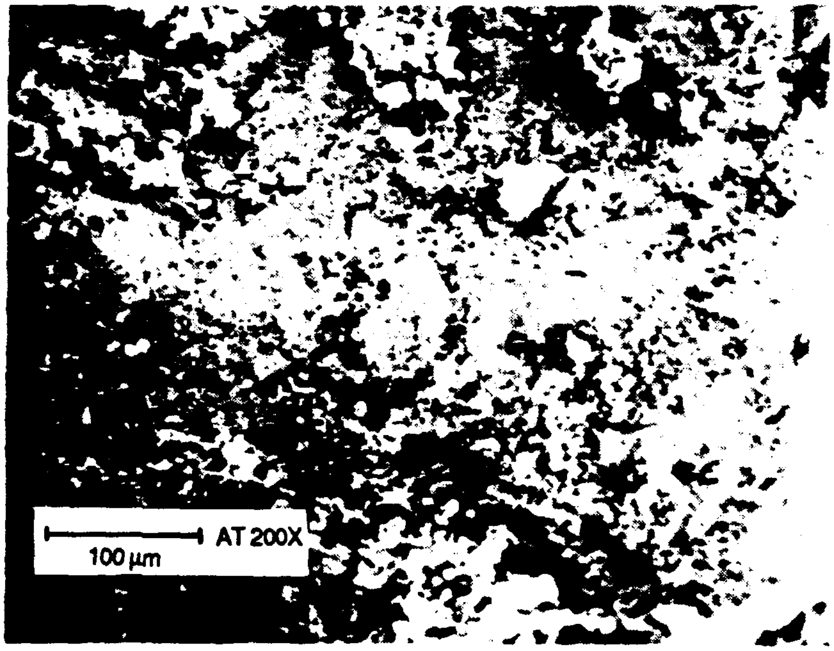

Figure 1(e). Scanning Electron Micrograph of a Particle (200X Magnification).

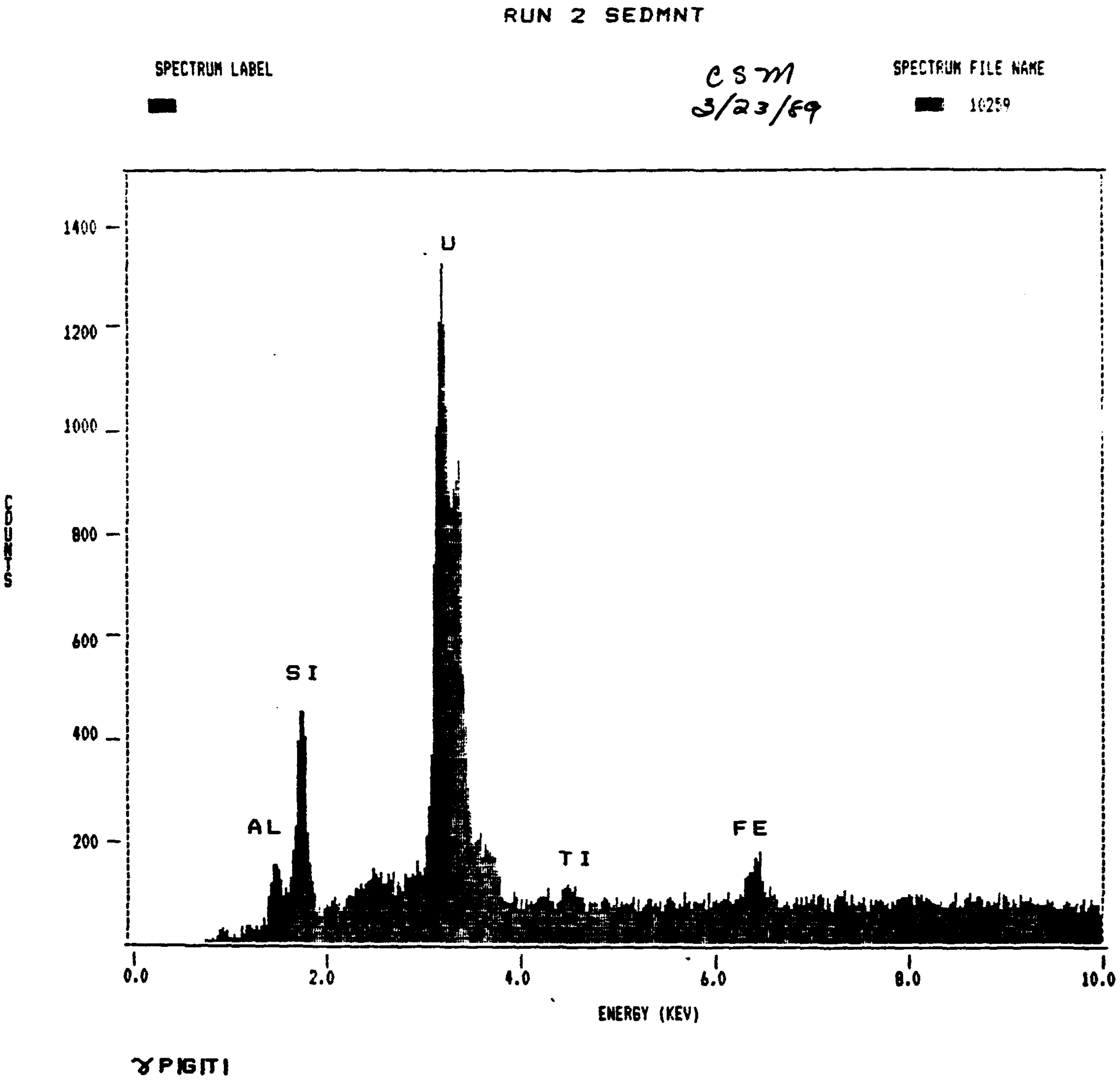

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Figure 2. Mass Spectrograph of Elements in a Heavy Particle.

shown in Figure 3 was compared with a data base of existing uranium compounds. It was found that in the heavy particles the most likely compound is uranium oxide hydrate ($UO_3 \cdot 2H_2O$), with lesser amounts of the uranium oxides of the formula U_8O_{19}, U_3O_7, and UO_2.

The chemical analysis of small samples of the heavy particles indicated that about 76 percent of the enriched stream mass was uranium.

Although much of the single-particle information is qualitative, some of the following observations may be useful for designing processes for physical and chemical separation of DU from sand:

a. The heavy particles contain various types of uranium oxide and perhaps some uranium metal.

b. Uranium is spread relatively homogeneously over the surface of the particle.

c. The uranium is in mixed oxidation state (i.e., exhibits both IV and VI valences, as shown by the nonstoichiometric compounds). To chemically extract the uranium, further oxidation is needed to convert all uranium to a VI state.

Extraction studies by Los Alamos Consultants (Reference 3) showed that it is necessary to completely oxidize the uranium to achieve satisfactory results.

- The heavy particles contain silicon as well as aluminum, iron, and titanium; this suggests that complete separation of the uranium from sand by physical means may not be possible.

2. Densities of Individual Particles

Since the density of the individual particle is important in separation, density tests were performed on 1000 particles randomly selected in two batches of 500 each. One group of 500 was obtained from 10-16-mesh particles by riffling four times and spreading the remaining sample in a circle. The circle was then divided into quarters, from which the particles were selected. The second batch of 500 (in the 16-20-mesh size range) was obtained in a similar manner.

These particles were then put in a tube with a fluid mixture of known density gradient. In both cases, the particles clumped together, as shown in Figure 4(a) for 10-16-mesh and Figure 4(b) for 16-20-mesh. The only quantitative results

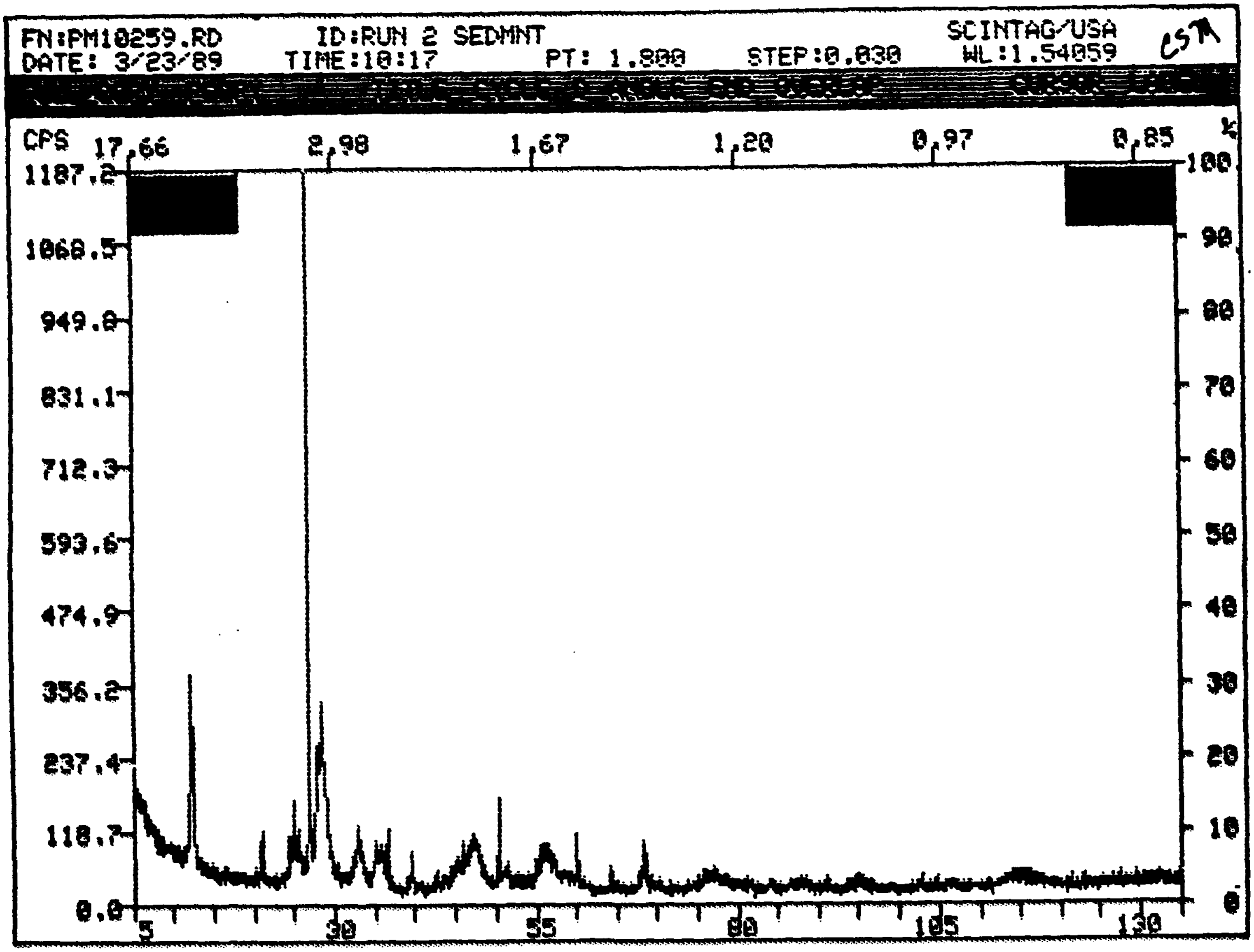

Figure 3. X-Ray Scattering Pattern of a Heavy Particle.

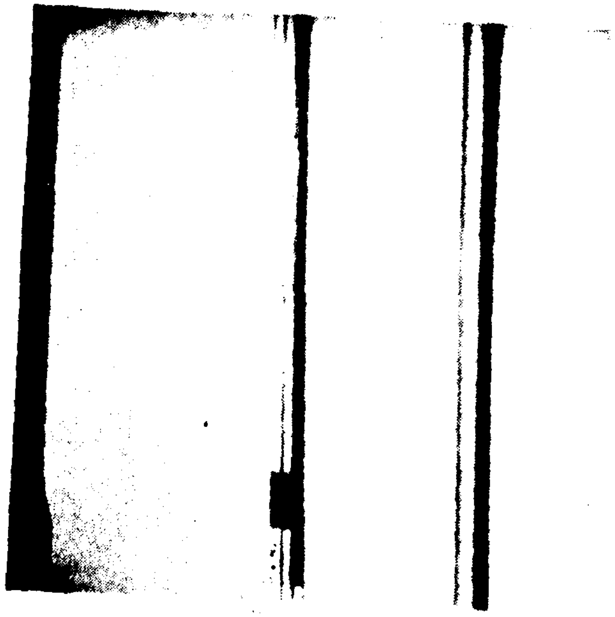

Figure 4(a). Particles in a Tub with a Liquid of Varying Density (10-16-Mesh).

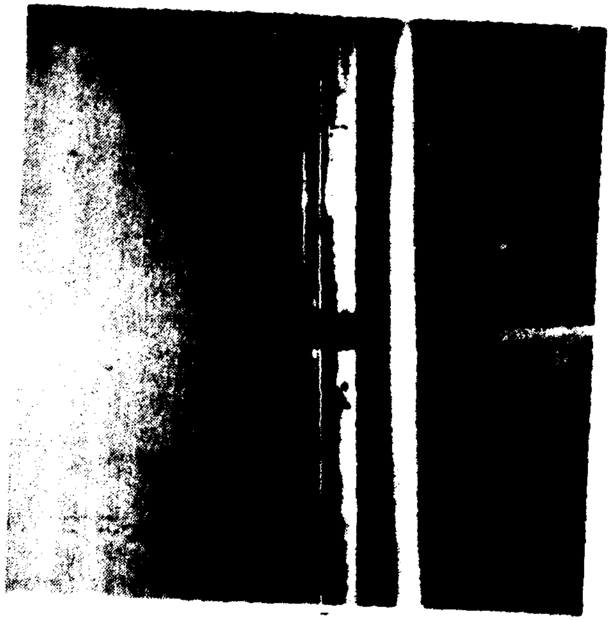

Figure 4(b). Particles in a Tube with a Liquid of Varying Density (16-20-Mesh).

obtained were for high and low densities. For the 10/16-mesh samples, the high density value was 2.71 g/mL, and the low density was 2.58 g/mL. For the 16/20-mesh particles, the high density was 2.78 g/mL, and the low density was 2.37 g/mL.

From separate measurements, the density of pure sand from Eglin AFB was found to be 2.65 g/mL. For each of the above samples, the average is about 2.65 g/mL (i.e., the same as that of pure sand). This suggests that no heavy particles were among the 1000 sampled particles. As described in Section II.C.4, a fraction with a bulk density of 8.7 g/mL was separated from the mixture; therefore, it appears that the heavy particles are present in very low concentration. The conclusion that most of the DU is concentrated on a few particles seems even more credible.

3. Density Correlation of Solids with DU Fractions

A number of 5-gram samples were taken at different levels in a fluidizing test, and different densities were measured. The density of the samples after drying was measured by dividing the mass by the volume. (The volume was accurately measured by a gas displacement method.) Each 5-gram sample was then analyzed for total uranium content. The uranium content was found to correlate approximately to the density as shown in Figure 5. The correlation coefficient is 0.9699. Density measurement thus provides a quick but approximate way of determining uranium content.

B. CONTAMINATION AND REMOVAL OF URANIUM FROM WATER

This section summarizes the bench-scale tests of contamination caused by DU dissolution or fines carryover. Laboratory tests on reduction of DU contamination are also discussed.

1. Background

Theoretical aspects governing the solubility of DU in water are discussed in the report by Mallory (Reference 4). This is an important aspect of contamination since, once DU is dissolved, the only methods of removal are by ion exchange, chemical extraction, or precipitation.

As shown by the analysis of a heavy particle in Section II.A.1, the uranium in the Eglin target sand is probably in the form of an oxide with various oxidation states. One of the ways to leach this uranium, as discussed in the Phase 1 report (Reference 2), is by having all the uranium in a high oxidation state and either exposing it to an acid or a concentration of carbonates. The leaching process is time dependent, as discussed in Reference 5. However, since there are so many

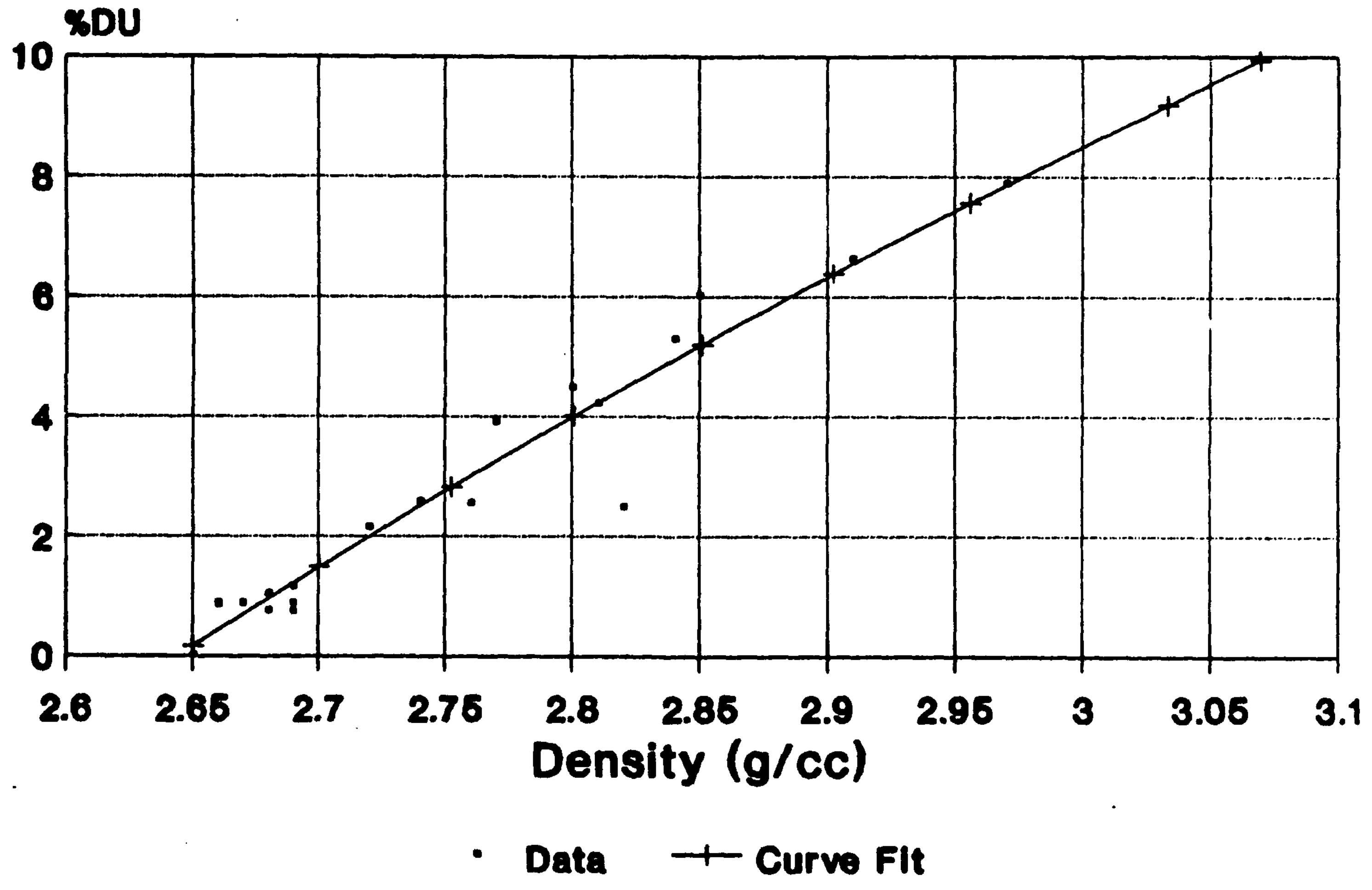

Figure 5. Correlation of Solids Density with Percent DU.

interdependencies, the process is complex, and the concentrations of the various constituents can only be practically calculated using computer programs. Such computer programs are available at ORNL (Reference 2). Since the theoretical aspects of the dissolution phenomena have been well covered in the literature and have been discussed in the Phase 1 report (Reference 2), it will not be presented here.

In addition to solubility, contamination may be present in supernatant water because of fine solids being carried over. Fine particles that contain uranium will always remain in the liquid, provided they are less than a certain size, because of Brownian motion. Under some circumstances, however, these particles can coagulate to form larger equivalent particles and settle out. Traces of either electrolytes or polymeric coagulants may enhance coagulation. The best way to study these phenomena is through controlled experiments on uranium-sand mixtures.

2. Contamination Levels of DU in Various Mixtures

The following procedures were used on DU/sand to test contamination levels under various conditions:

a. Sand/DU and Water Mixture

(1) Fifty grams of sand/DU were added to 500 mL of room temperature tap water in a 1-L beaker.

(2) The mixture was stirred gently for 2 min with a stirring rod and then allowed to stand for 5 min.

(3) One hundred milliliters of the supernatant were decanted, and the following analyses were performed:

(a) pH,
(b) carbonate, bicarbonate ions,
(c) conductivity,
(d) mass of suspended solids, and
(e) total uranium.

(4) The original sand/DU and water mix was stirred with a mechanical mixer, and steps (a) to (e) in item (3) were repeated.

(5) After an additional 24 hours, steps (a) to (e) in item (3) were repeated once more.

(6) Step (5) was repeated after 24 hours.

b. Sand/DU, Water, and Calcium Carbonate Mixture (In some cases, calcium carbonate increases the solubility of uranium.)

(1) Fifty grams of sand/DU and 10 g powdered analytical reagent grade calcium carbonate were added to 500 mL tap water in a 1-L beaker and mixed gently.

(2) Steps a.(2) to a.(6) were performed on this mixture.

c. Sand/DU, Water, Calcium Carbonate, and a Small Amount of Hydrochloric Acid Mixture

The pH increase caused by calcium carbonate addition was cancelled by the addition of hydrochloric acid.

(1) Fifty grams of sand/DU and 10 grams reagent grade calcium carbonate powder mixture were added to 500 mL of water. Enough hydrochloric acid was then added until the pH was the same as measured in I(c)(1).

(2) Steps I(b) to (f) were performed on this mixture.

d. Sand/DU, Water, Calcium Carbonate, and a High Hydrochloric Acid Concentration Mixture

Since higher dissolution of uranium occurs at higher acid concentrations (i.e., low pH), attempts were made to bring the same mixture as in step II to a pH of 5.

(1) A mixture of 50 grams sand/DU, 10 grams reagent grade calcium carbonate, and 500 mL tap water was stirred for 2 min in a 1-L beaker. Next, hydrochloric acid was added until the pH of the solution was 5.

(2) The mixture was allowed to settle, and 50 mL of supernatant liquid were decanted and retained for analysis of total uranium.

(3) The mixture was then stirred for an additional 10 minutes and the decantation repeated.

(4) The mixture was then stirred for 20 hours and the decantation was repeated.

(5) The mixture was stirred for 36 hours and decanted again.

The results of the water mixing experiments are shown in Tables 1 to 4. If a wet process is to be used, we expect to have a mixture of water and sand thoroughly mixed for only a limited amount of time. The processes for which this condition applies are wet screening and separators such as cyclones or jigs which provide thorough mixing. Thus, in Table 1 we see that when tap water is used, the supernatant does not reach levels above 40 pCi/mL. The maximum level reached is 1.27 pCi/mL. We also see that there are suspended solids present in amounts as high as 660 mg/L. These solids would normally contribute to the contamination. If the water is allowed to settle, as was done in the fluidized-bed tests, the contamination would be much less than 0.66 pCi/mL. After settling for a week,

TABLE 1. RESULTS OF MIXING TESTS: DU + WATER

Approx. Time	CO_3^- (mg/L)	HCO_3^- (mg/L)	pH	Conduct (μmho/cm)	Susp. (mg/L)	DU (mg/L)	activity[a] (pCi/mL)
2 min	35	80	7.92	300	420	0.935	0.94
10 min	12.5	40	8.19	273	590	1.847	1.80
24 hrs	25	22	7.93	231	150	0.778	0.78
48 hrs	30	45	7.91	278	660	1.268	1.27

[a] In converting from DU mg/L to a specific activity for safe disposal limits, the guidance in 10 CFR, Part 20, Appendix B, p. 299, may be adopted. For DU, the guidance gives specific activity = 3.6×10^{-7} Ci/g DU. It should be noted that this is less by a factor of ~0.36 as that used in Reference 1. From Reference 2, it seems that this increased specific activity is a consequence of consideration of additional emission of gamma from thorium. Since both References 1 and 2 have adopted more conservative criteria of 1 ppm DU ~1 pCi, this will be used for consistency.

TABLE 2. RESULTS OF MIXING TESTS: DU + SAND + WATER + LIMESTONE

Approx. Time	CO_3^- (mg/L)	HCO_3^- (mg/L)	pH	Conduct (μmho/cm)	Susp. (mg/L)	DU (mg/L)	activity[a] (pCi/mL)
2 min	28	90	8.17	312	1700	0.644	0.64
10 min	32	99	8.08	298	3800	0.749	0.75
24 hrs	30	190	8.06	317	30	1.340	1.34
48 hrs	30	311	8.13	436	670	3.128	3.13

TABLE 3. RESULTS OF MIXING TESTS: DU + SAND + WATER + LIMESTONE + SMALL QUANTITY OF HYDROCHLORIC ACID

Approx. Time	CO_3^- (mg/L)	HCO_3^- (mg/L)	pH	Conduct (μmho/cm)	Susp. (mg/L)	DU (mg/L)	activity* (pCi/mL)
2 min	65	102	7.91	722	1100	0.204	0.2
10 min	35	184	8.13	704	120	0.696	0.7
24 hrs	30	186	7.95	620	77	1.070	1.0
48 hrs	30	274	7.97	803	400	4.152	4.1

TABLE 4. RESULTS OF MIXING TESTS: DU + SAND + WATER + LIMESTONE + HYDROCHLORIC ACID TO PH 5

Time	DU (mg/L)	Approx. activity (pCi/mL)
2 min	394	394
10 min	277	277
24 hrs	445	445
36 hrs	472	472

water from the fluidized-bed tests showed a level of contamination of ~0.17 and 0.19 pCi/mL, far below the 40 pCi/mL limit. The pH was found to be about 8. This may be due to some carbonates and bicarbonates present in concentrations of about 30 and 40 mg/L, respectively.

Tables 2 to 4 deal with extreme cases. In Table 2, the effect of excess limestone is illustrated. The data in Table 2 show that the maximum amount of uranium contamination in the supernatant increases to a maximum of 3.13 pCi/mL after limestone addition, still much less than 40 pCi/mL. The effect of adding enough acid to neutralize the additional alkalinity introduced by limestone is shown in Table 3. The contamination level is a little higher (i.e., ~4.1 pCi/mL). In Table 4, the effect of the addition of enough acid to bring the pH level to 5 is presented. The surface uranium is dissolved, and activity levels of about 472 pCi/mL (much higher than the 40-pCi/mL limit) result. Although the exact conditions under which such high solution will occur may vary somewhat, the indication is that the acidity level should be monitored and kept low (i.e., pH >5).

3. Reduction of Aqueous Waste Contamination Levels

Methods have been developed for reduction of the uranium solids and salts in water to <40 pCi/mL. ORNL has developed methods especially suited for removal of hazardous and radioactive wastes from beneficiation of pitchblende ores.[1] It was found that after the addition of limestone and then alkali, such as sodium hydroxide, to a pH of 11.5, a precipitate is formed which removes the uranium from the supernatant. Furthermore, it was found that additional removal takes place when a small amount of ferric ions from ferric chloride are added after the addition of limestone. When the pH is brought to 11.5, the ferric hydroxide precipitate gel removes additional uranium ions by ion exchange and additional coagulation.

In scouting experiments, a mixture of 50 grams sand, 10 grams precipitated $CaCO_3$, and 500 mL tap water was stirred for 2 minutes in a 1 liter beaker. The mixture was allowed to settle, and 50 mL of supernatant liquid were decanted and retained. The remaining mixture was then stirred for an additional 10 minutes, and the decantation step was repeated. Again, the remaining mixture was then stirred for 36 hours and the decantation repeated.

Each sample of the supernatant liquid was divided into three aliquots. One [as (a) in Table 5] was analyzed for uranium as decanted. The second aliquot was treated with NaOH until it reached pH 11.55 and was then centrifuged to remove the resultant precipitate. The supernatant liquid [as (b) in Table 5] was analyzed for uranium. The third aliquot was treated with 10 mg of ferric chloride brought to pH 11.55 with NaOH and centrifuged. The supernatant liquid [as (c) in Table 5] was analyzed for uranium.

TABLE 5. RESULTS OF REMOVAL OF URANIUM FROM SUPERNATANT

	Original supernatant (a)		Precipitation with pH 11.55 (b)		Precipitation with $Fe(OH)_3$ and pH 11.5 (c)	
Time stirred	Conc. of DU (mg/L)	Approx. activity (pCi/mL)	Conc. of DU (mg/L)	Approx. activity (pCi/mL)	Conc. of DU (mg/L)	Approx. activity (pCi/mL)
2 min	32.00	32	10.02	10.0	0.38	0.4
10 min	29.00	29	2.16	2.2	0.57	0.6
36 hrs	23.00	23	4.30	4.3	1.86	1.9

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[1] Cyrus Feldman, Analytical Chemistry Division, Oak Ridge Natl. Lab., personal communication, 1988.

The results of the ORNL removal tests are shown in Table 5. These results indicate that a contamination level of ~32 pCi/mL is attained with calcium carbonate and sand/water after stirring for 2 min. Even though this is below the 40-pCi/mL limit, this level can be further reduced by increasing the pH to 11.55 with NaOH. In the scouting experiments, this caused the activity level to drop to 4.3 pCi/mL after stirring for 36 h. Further reduction in the activity was obtained by adding a trace of ferric chloride and again bringing the pH to 11.55. This drop presumably is caused by the ion-exchange reaction of the $Fe(OH)_3$ gel in addition to the precipitation of DU, in solution. The gel may also capture additional fine particles containing DU, which would result in further purification.

The overall conclusion is that the two chemical methods tested can reduce the aqueous contamination levels. However, the pH of the resultant liquid is 11.55 and would need to be neutralized before discharge.

C. SEPARATION OF DU FROM SAND IN WATER FLUIDIZED BEDS

Water-fluidized beds were used to measure the segregation characteristics of particles that contain DU from those particles that do not.

1. Background

It has been demonstrated (Reference 6) that when a binary mixture of particles is fluidized by water and when the particles are of different size or density, segregation will take place under selected operating conditions. Related work with gas-fluidized beds investigated the separation of particles in gas-fluidized beds of low gas velocity (Reference 7). These observations showed that segregation is particularly sensitive to density difference but less sensitive to size difference. In addition, a thorough investigation was made of gas fluidization as a means of ore separation (Reference 8). The main study in this work was concerned with narrow cuts (20/45-mesh) of germanium ore, consisting of coarse sandstone dispersed with carbonaceous material. The experiments revealed a segregation tendency based on density differences, and the tests showed that optimum segregation occurred near (just above) the minimum fluidization velocity, with a minimum at a higher velocity.

2. Theory of Mixing and Segregation in Water Fluidized Beds

This section is limited to a discussion of a binary system of particles of the same size but different densities (those of pure sand at 2.65 g/mL and the heaviest density found in the bed, 8.7 g/mL). Complete theory can be bought only at a price of extensive interaction between theory and experiment.

However, it is still valuable to review the essential theoretical components because they provide a qualitative perspective of the governing physical parameters. The following development is a modification of work described in Reference 9.

If sufficient particles are dispersed in a tube, they may be suspended by a vertical flux velocity V (m/s) of water flowing upward. Such a fluidized bed can only exist over a range of liquid fluxes (V) if it is to maintain its integrity. For the binary system of same particle size but different densities, the V values must be equal to or greater than the minimum fluidization velocity of the heavy particles and less than the terminal velocity of the lighter particles. If the velocity is less than these values, the heavy particles will settle to the bottom; if it is higher, the bed will lose the lighter material by elutriation. The bed may be designed with velocities outside these limits, so that either the heavy particles settle out or the lighter particles are elutriated. However, since we are considering the fluidized bed at steady state, only the particles that remain in the bed will be accounted for in the model.

The correlation developed in Reference 10 was used to calculate the minimum fluidization velocities. For two particle sizes, 984.8 μm (geometrical mean of 16-20-mesh) and 207.3 μm (geometric mean of 60-80-mesh), the minimum fluidization velocities have been calculated and plotted for different solid densities ranging from 2.65 to 8.7 g/mL. The results are shown in Figure 6, and the numerical values for the two densities are presented in Table 6. Thus, for 16-20-mesh particles of the two densities, the superficial velocity of the fluid has to be greater than the minimum fluidization velocity of the heavy fraction of density 8.7 g/mL, which is 0.0325 m/s (from Table 6).

TABLE 6. MINIMUM FLUIDIZATION VELOCITIES FOR WATER/SOLID PARTICLES AT 25°C

Particle size (μm)	Velocity (m/s) at a density (g/mL) 2.65	8.7
985	0.0093	0.0325
207	0.0047	0.0022

For 16-20-mesh particles, the upper limit for the superficial velocity is found by calculating the terminal velocity for particles of density 2.65 g/mL for single particles. We approximate the particles as spheres and use the correlation developed in Reference 11 to estimate the terminal velocity of single particles of density 2.65 g/mL as 0.145 m/s.

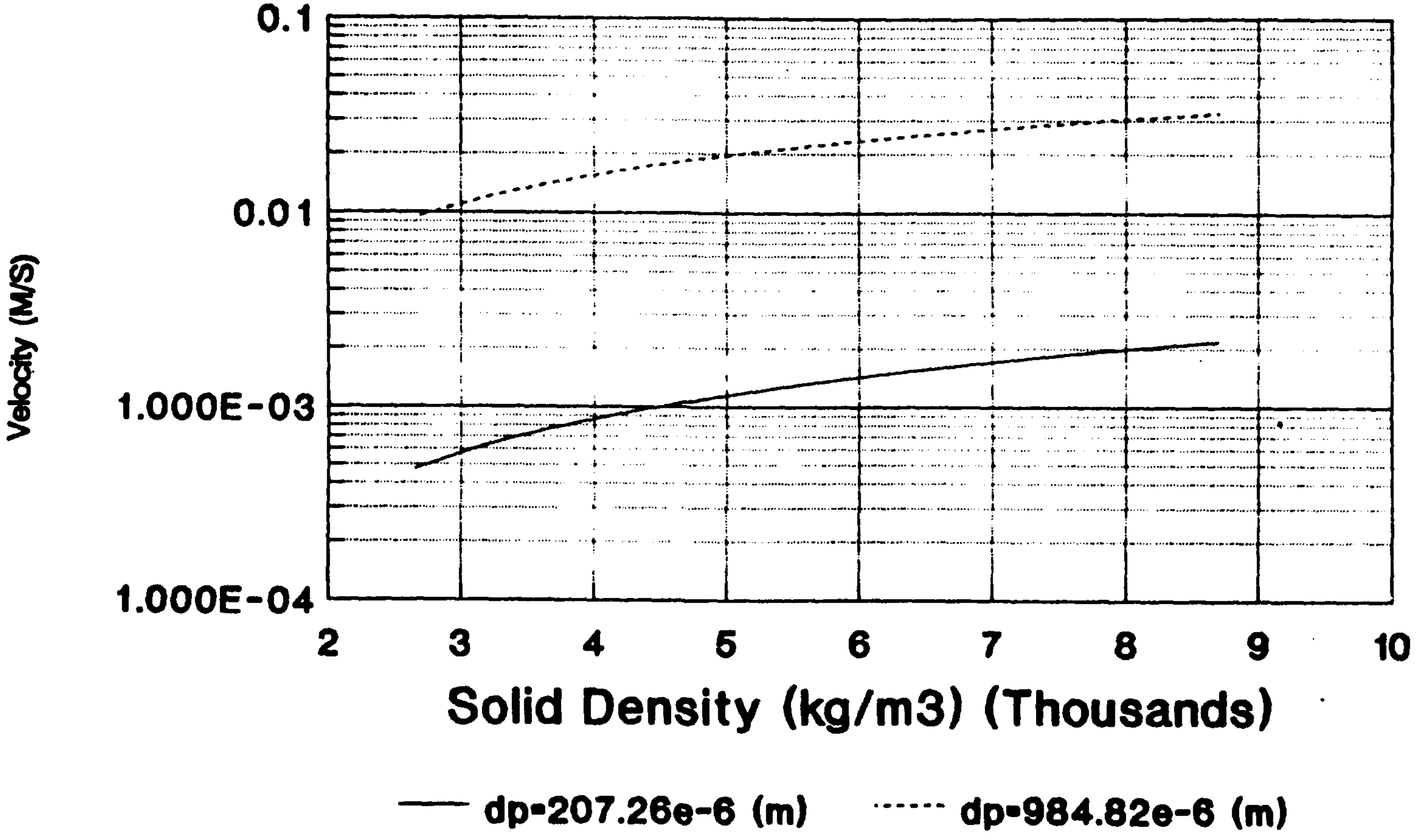

Figure 6. Minimum Fluidization Velocity from Wen and Yu's Correlation.

Thus, to retain the bed integrity of the fluidized bed for the 16-20-mesh particles of densities 2.65 and 8.7 g/mL, the superficial velocity of water has to be between 0.0325 and 0.145 m/s, respectively.

When a water-fluidized bed containing two sets of particles with the same diameter and different density is maintained in steady state, a dynamic equilibrium occurs between the layers of the fluidized bed. An interchange of mass between layers takes place at an equal rate. There are two phenomena that occur. These are

a. Classification: A heavy particle surrounded by lighter ones fall and lighter ones surrounded by heavier ones rise. This is depicted for the heavy particles in Figure 7(a).

b. Dispersion: An irregular motion akin to Brownian motion jostles the heavier particles to rise among the lighter particles and conversely causes the lighter ones to sink among the heavier particles. This is depicted for the heavy particles in Figure 7(b).

The terminal velocity of a particle within a swarm of other particles (hindered settling) is needed for the development of the model. From the expression developed in Reference 11, a normalized terminal velocity (i.e., divided by terminal velocity of a single particle) is evaluated as a function of the bed void fraction for the 16/20-mesh particles of densities of 2.65 and 8.7 g/mL, as shown in Figure 8.

3. Equipment Description

The basic fluidization equipment is shown in the schematic diagram in Figure 9 and in photographs in Figures 10 and 11. The shorter column of about 60 cm (24 inches) height and 2.5 cm (1 inch) diameter was used for larger sized particles. The longer column of about 120 cm (48 inches) height and 2.5 cm (1 inch) diameter was used for finer particles. The longer column was required to accommodate the greater expansion of the beds containing the smaller particles. In addition, a grid made of fine gauze was used to contain the smaller particles.

The tests were conducted in a batch mode in which the fluidized particles were poured into the column and then samples taken at different heights. The fluidizing water flowed up the column and was recirculated by a centrifugal pump. Samples were obtained by withdrawing water and particles through ports located at different levels on the column.

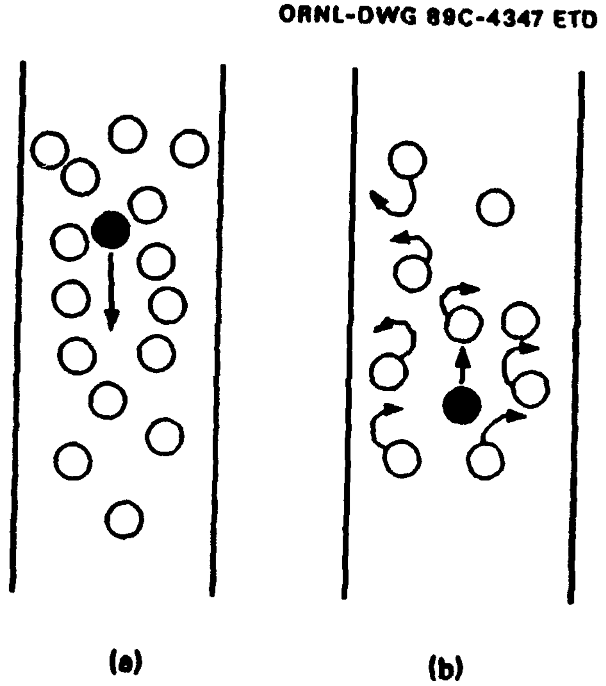

Figure 7(a). Classification of Heavy Particles in Fluidized Bed.

Figure 7(b). Dispersion of Heavy Particles in Fluidized Bed.

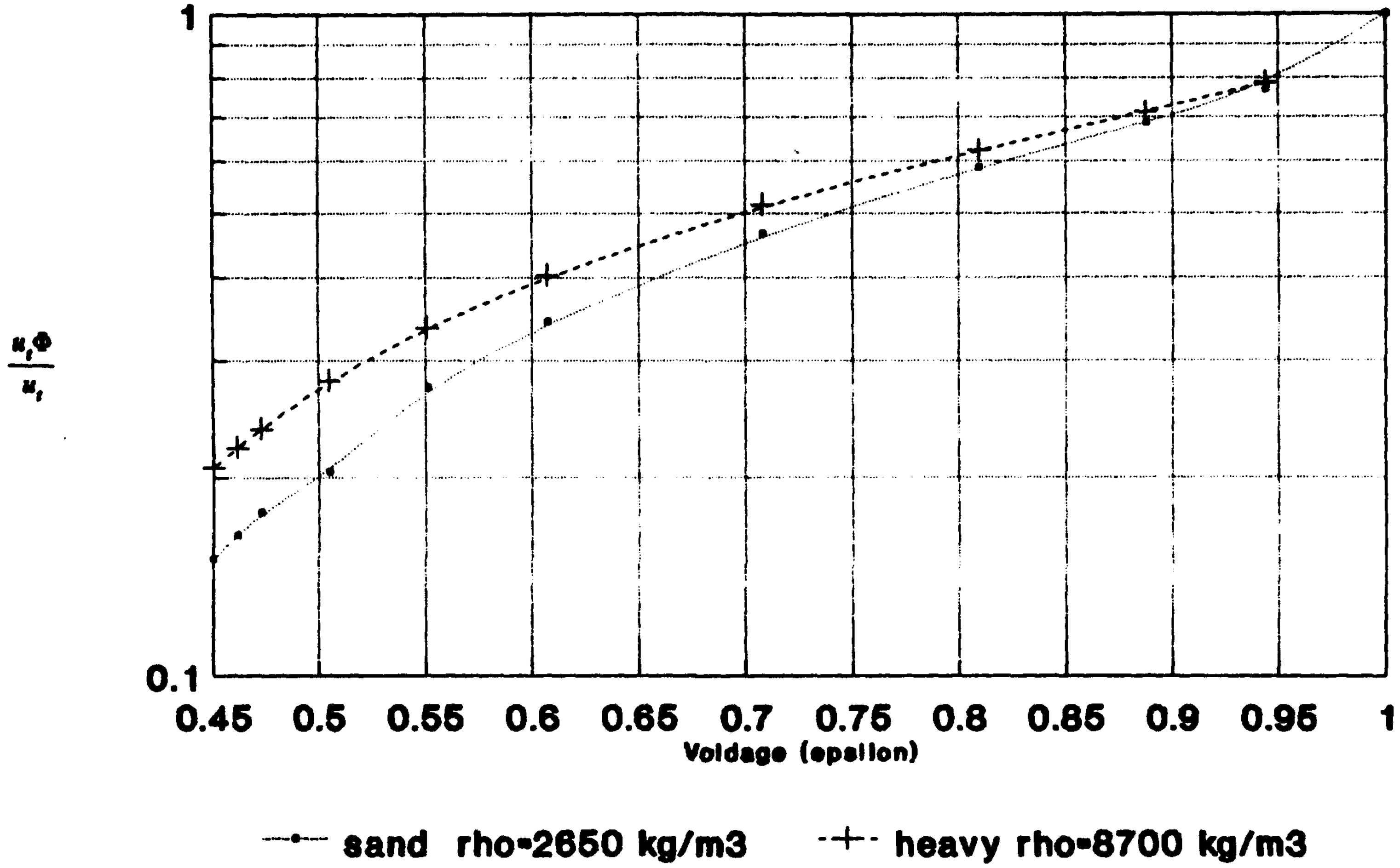

Figure 8. Terminal Velocity of a Particle in Hindered Settling (Two Densities).

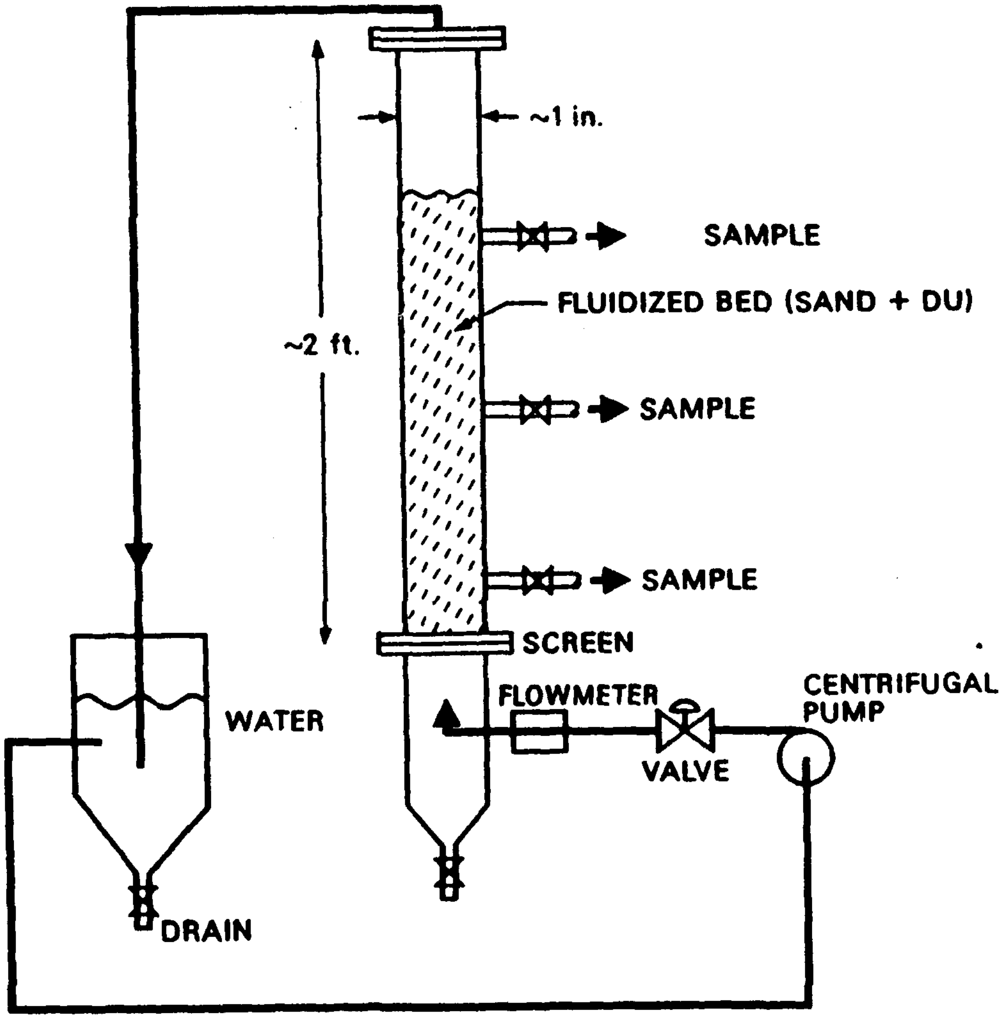

Figure 9. Schematic of Equipment for Fluidized Bed Tests.

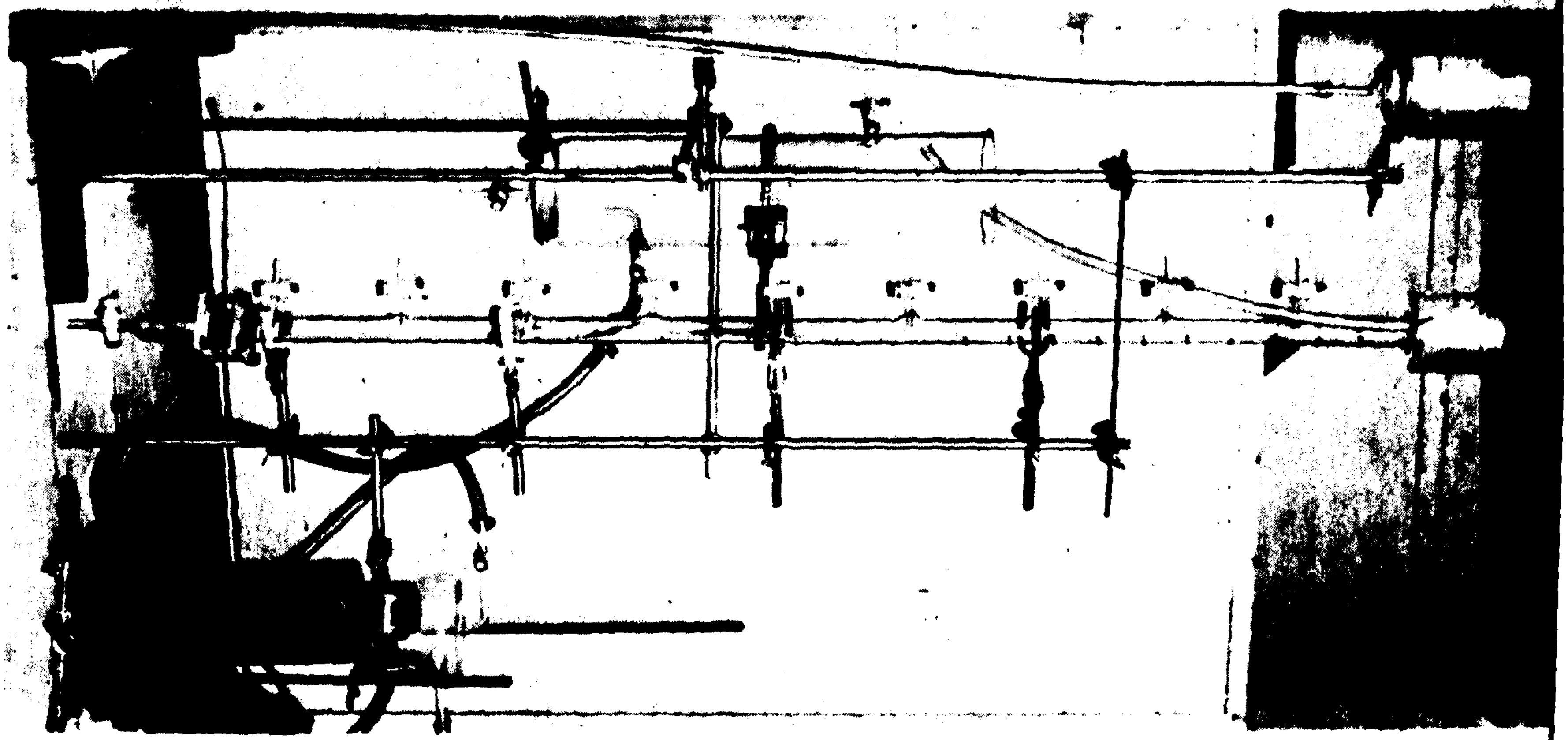

Figure 10. Overall Equipment for the 4-ft Fluidized Bed (for 60-80-Mesh Particles).

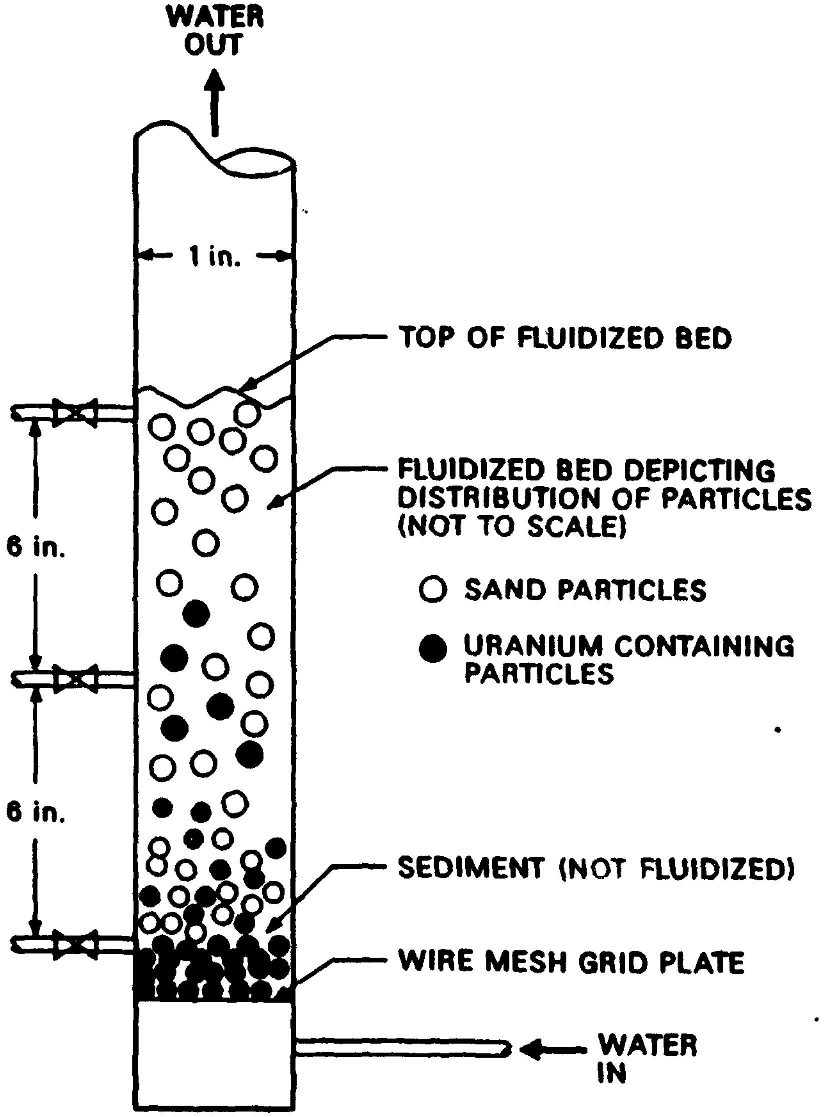

Figure 11. Schematic of Column and Sample Ports.

4. Experimental Procedure and Observations

Three basic experiments were done with the uranium-contaminated sand. The first two involved closely sized particles of 16-20-mesh and 60-80-mesh size, respectively. The third experiment used a mixture of fines of 80-mesh and below mixed with a batch of 60-80-mesh particles. Only the tests with 16/20-mesh particles are reported here.

- **Tests with 16-20-mesh DU/sand particles**

The 16-20-mesh particles were washed with water to remove the fines smaller than 20-mesh. Then the sand was air-dried under a hood. The material was then riffled twice and divided for laboratory samples (3- and 10-gram increments) and the remainder divided into halves for the runs.

The bulk density of the loose sand feed determined by pouring it into a 100-mL cylinder and measuring the mass was found to be 1.56 g/mL. Once the density of the particles was measured, the void volume in the column could be estimated. The density of the feed as measured by the laboratory gas displacement method was found to be 2.777 and 2.774 g/mL, respectively, for two 10-gram feed samples.

a. Fluidization Experiments with 16/20-mesh DU/Sand Particles.

Sand was poured into the column so that it barely covered the third sample port [the ports were 15 cm (6 inches) apart]. The top of the sand in the column was 33 cm (13 inches) above the grid plate. The total mass of the sand in the column was 208.1 grams. The column was then covered to contain the dust and then connected to the rest of the flow system, as shown in Figure 11. Water flow was started slowly, and it was found that the minimum fluidization velocity was too low to be accurately measured with the equipment that was available; however, it could be estimated using existing correlations (Reference 10). As soon as there was enough water flow to move all the particles, it was observed that the greenish yellow and black, heavy sediment immediately sank to the bottom. In contrast, the sand at the top of the column maintained its original cream color. Figures 12 and 13 show the top and bottom sections of the column, respectively.

When the water flow was increased, the bed expanded immediately in particulate fluidization (i.e., without bubbles, which is typical of solid-liquid systems). Upon further flow increase, a fraction of the dark particles at the bottom was stirred up enough to rise and mix with the other particles. However, there was still a fraction of the particles that were so heavy (apparently) that they remained at the bottom, barely moving. It was also noted that when the bed height was lowered

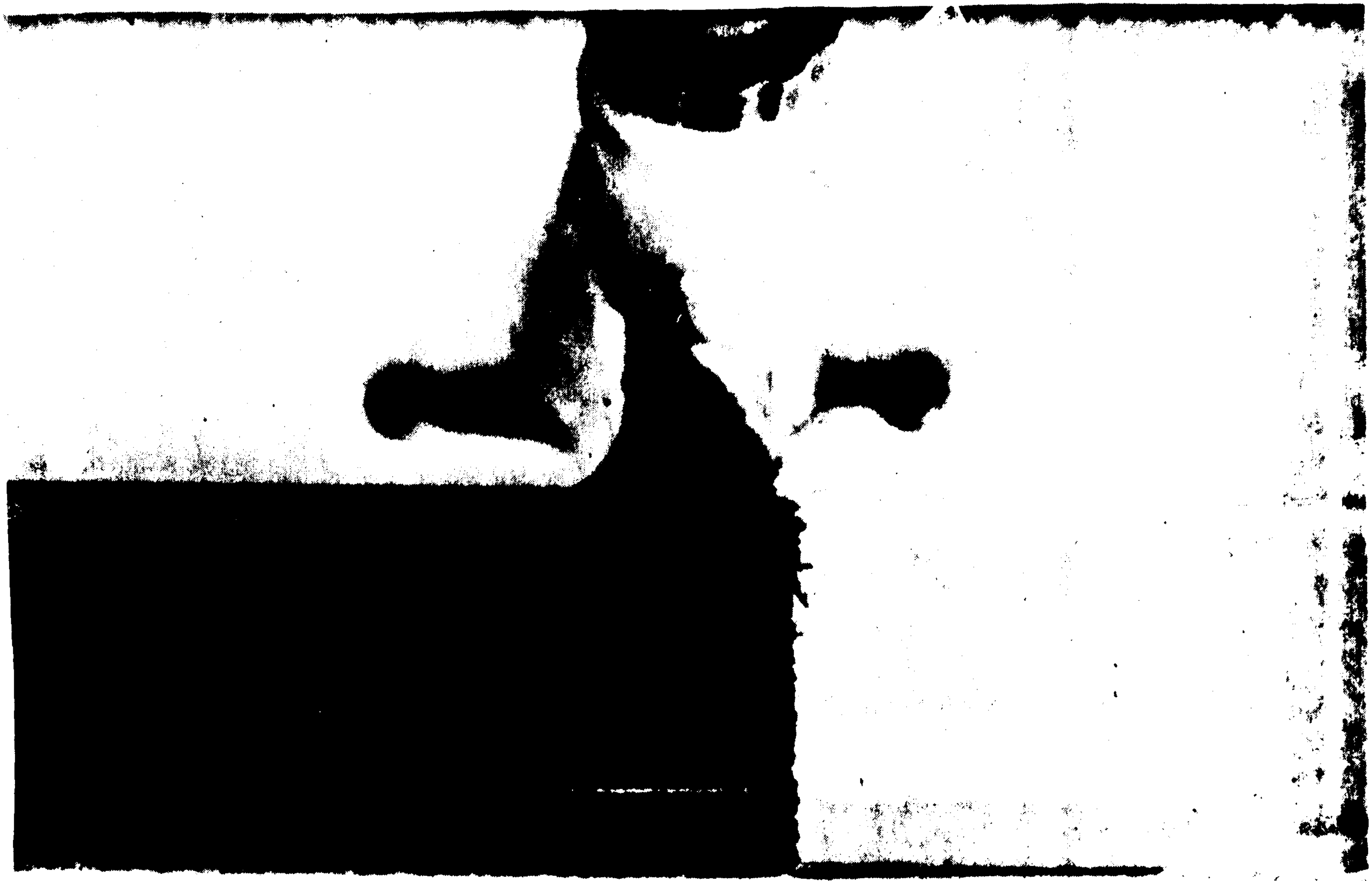

Figure 12. Top Section of the Fluidized Bed After Segregation with 16-20-Mesh Particles.

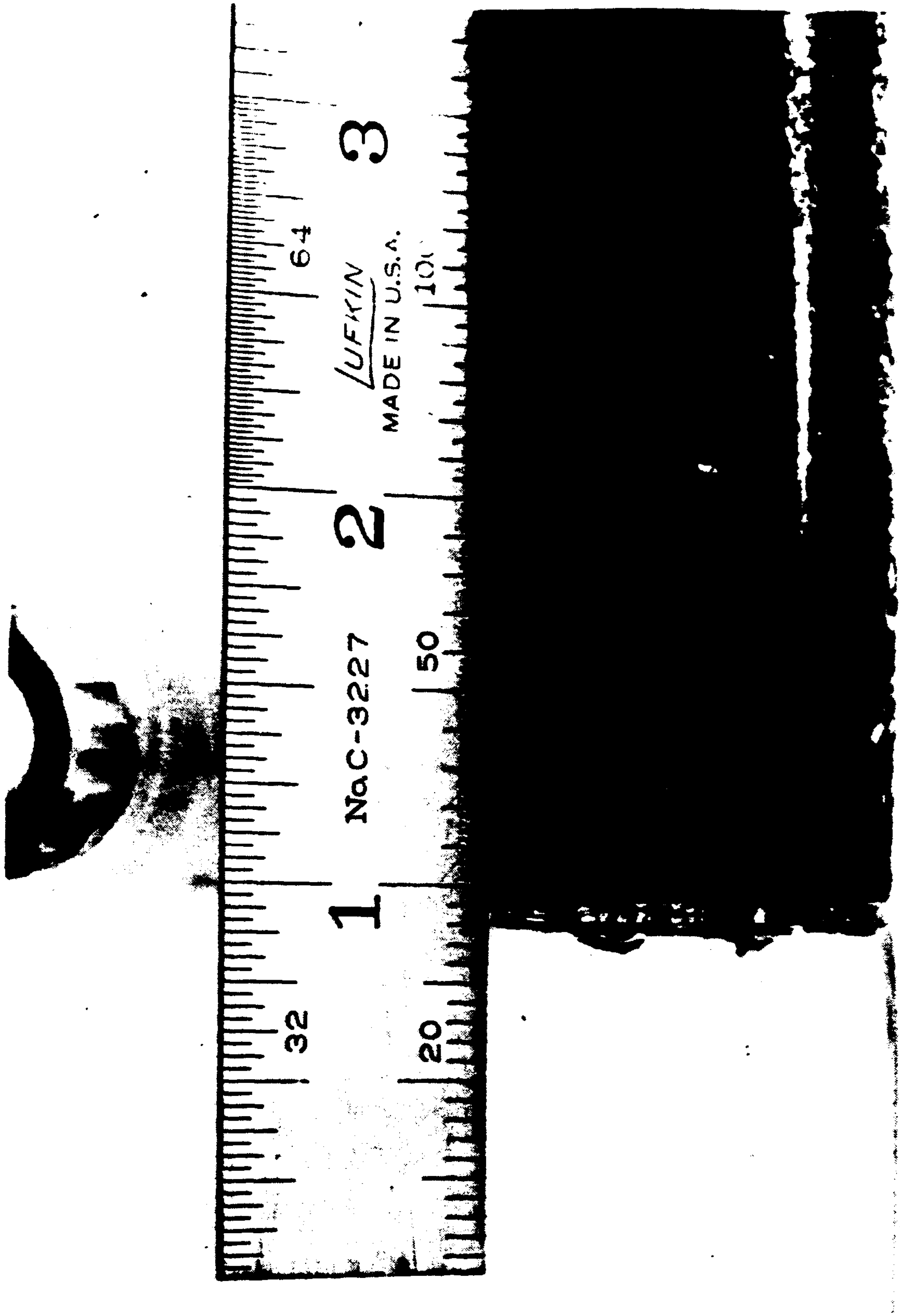

Figure 13. Bottom Section of the Fluidized Bed after Segregation with 16-20-Mesh Particles

by reducing the water flow, the black particles in the bed slowly sank to the bottom after being jostled by the others in a random fashion. If the flow was lowered rapidly, however, these heavy particles did not have time to make their way down and thus were "frozen" in place. After increasing the flow rate to a level such that the system was in its apparent maximum mixed state, the flow was lowered to a rate where the particles were barely moving. This was assumed to be the stage at which maximum segregation could be possible. This condition was maintained for about 2 hours to permit separation to occur.

The water flow was stopped, and the particles in the bed were "frozen" in place so they could be carefully sampled through the ports with minimal disturbance to the others. It was found that the sand readily followed the water once the valves on the sample ports were opened. First, a sample from the top port was taken; then a sample from the middle port was taken, followed by a sample from the bottom port. To isolate the heavy material (sediment) at the grid, it was decided to restart the flow and empty the remaining material (remainder) from the top and middle ports from the column. The sediment remaining on the grid was readily sampled by increasing the flow rate and withdrawing the material through the bottom port.

The samples from the feed, top, middle, bottom, and sediment were analyzed for density and fractional weight of uranium. Black-and-white photographs were also taken of the top sample and the sediment (Figures 14 and 15, respectively). The top samples contained a few uranium-rich dark particles, while the sediment had a larger number of dark, angular particles that contained uranium.

This run was repeated with 256.6 grams of sand in the column. Color photographs were taken of the feed material, the top sample, and the sediment. These are shown in Figures 16, 17, and 18, respectively, which are reproduced in black and white. The sediment displayed the distinct yellow-black color of uranium-bearing particles; no such particles were visible in the top sample. For this run, only the feed, top, and sediment samples were analyzed for fractional uranium content.

b. Experiments with Overflow Separation with 16-20-Mesh Sand.

Increasing the fluidized-bed water flow until the solids just flowed over the top of the column (56.12 mL/s) caused the lighter particles to become separated from the others. This is illustrated in Figure 19. To do this, a small amount of material was placed inside the column (28.34 grams) to minimize the particle-particle interactions. If uniform plug flow could be established in the test column, particles with different terminal velocities could be separated by varying the flow rate.

Figure 14. Top Samples in the Fluidized Bed Run with 16-20-Mesh Particles

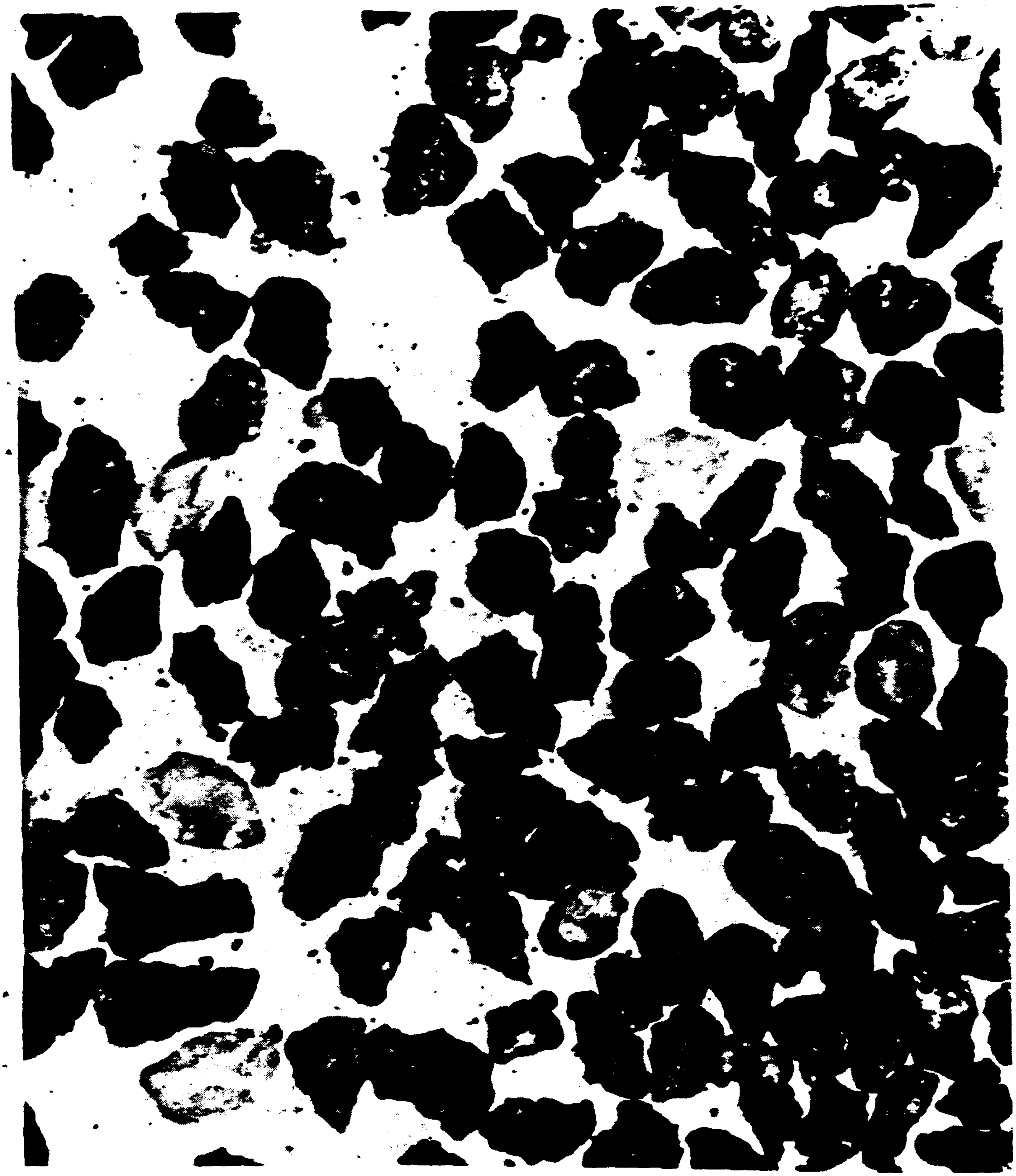

Figure 15. Bottom Sediment Sample in the Fluidized Bed Run with 16-20-Mesh Particles

Figure 16. Feed Sample from the Fluidized Bed Run with 16-20-Mesh Particles

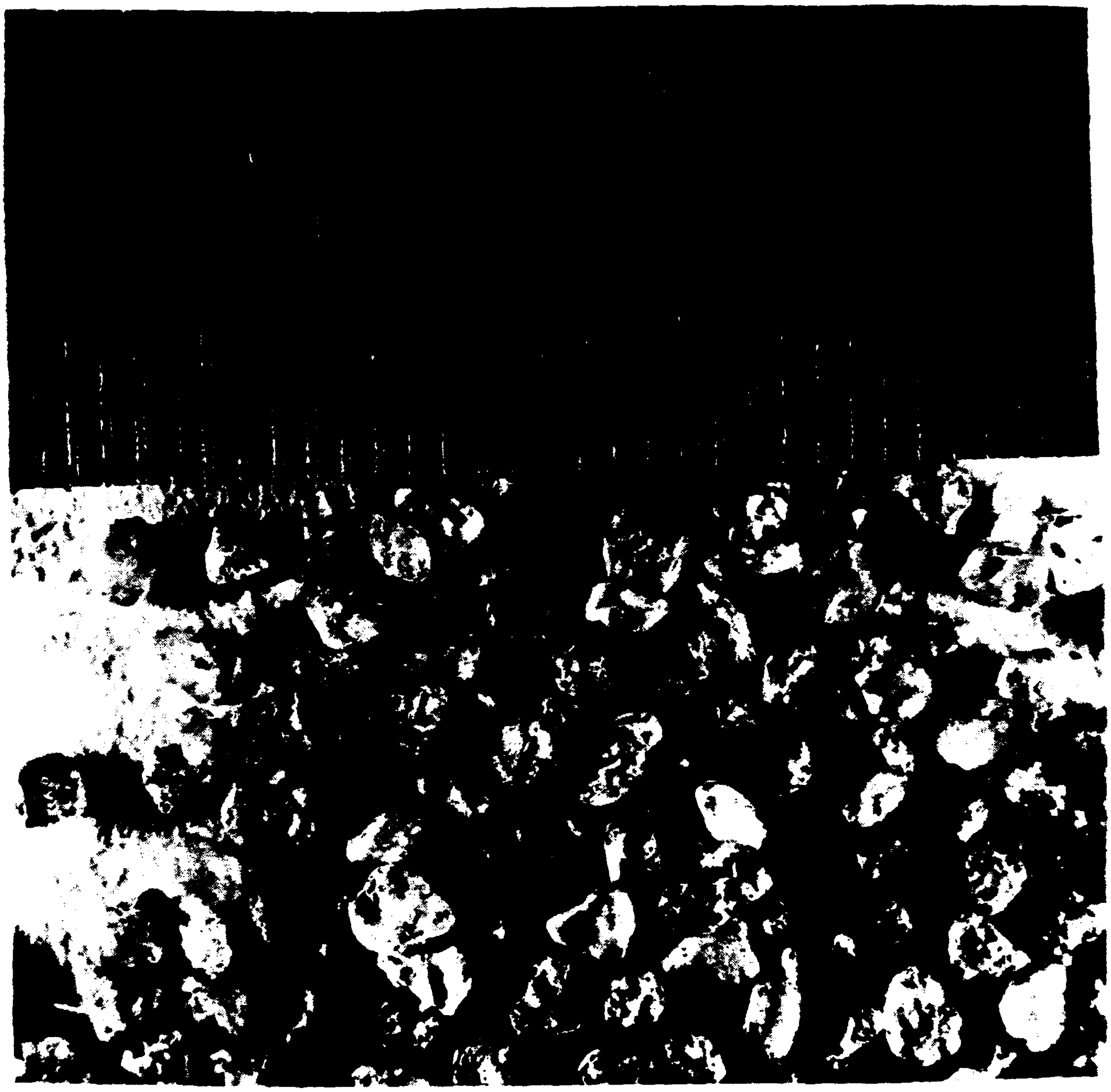

Figure 17. Top Sample from the Fluidized Bed Run with 16-20-Mesh Particles

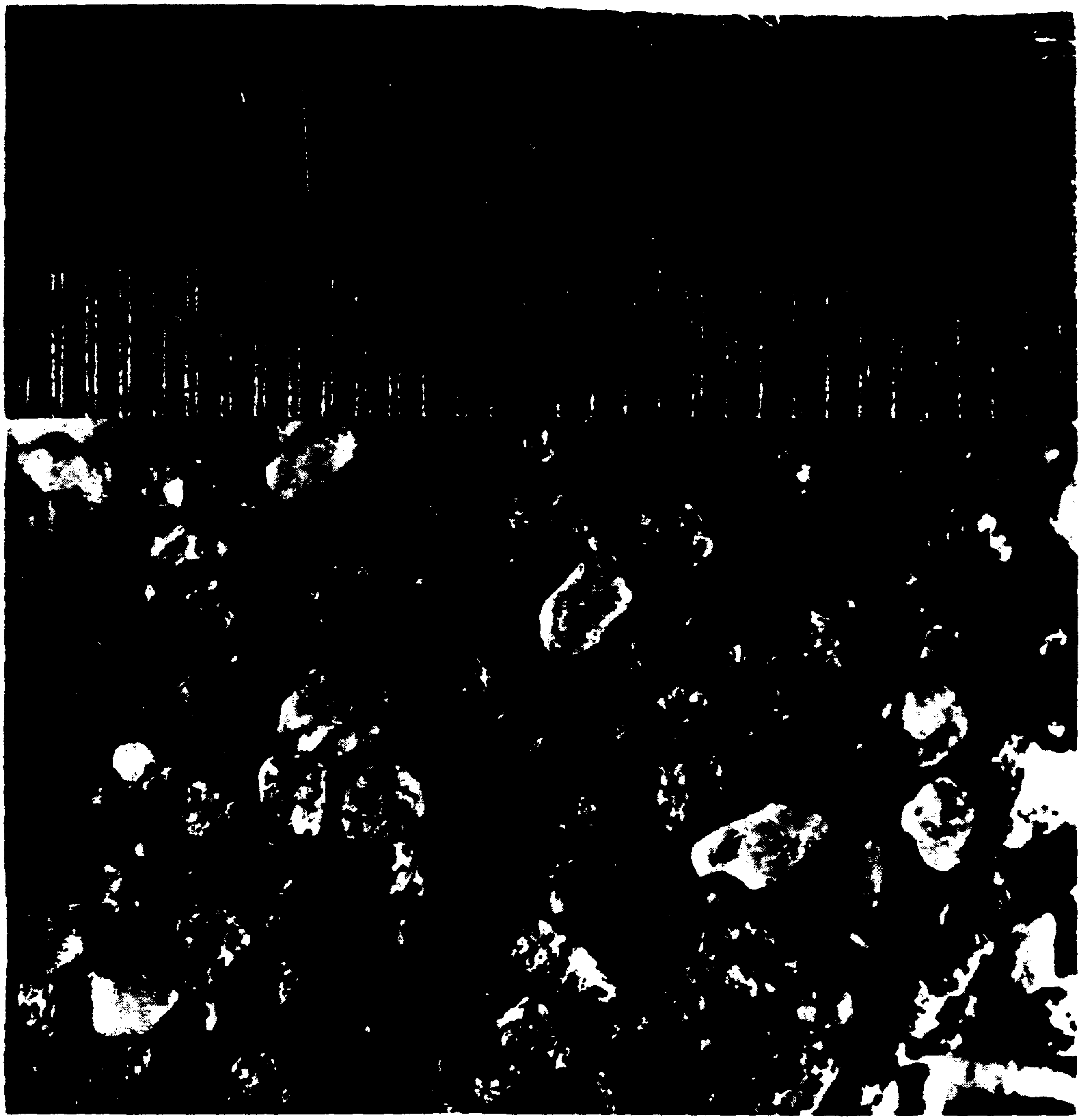

Figure 18. Bottom Sediment Sample from the Fluidized Bed Run with 16-20-Mesh Particles

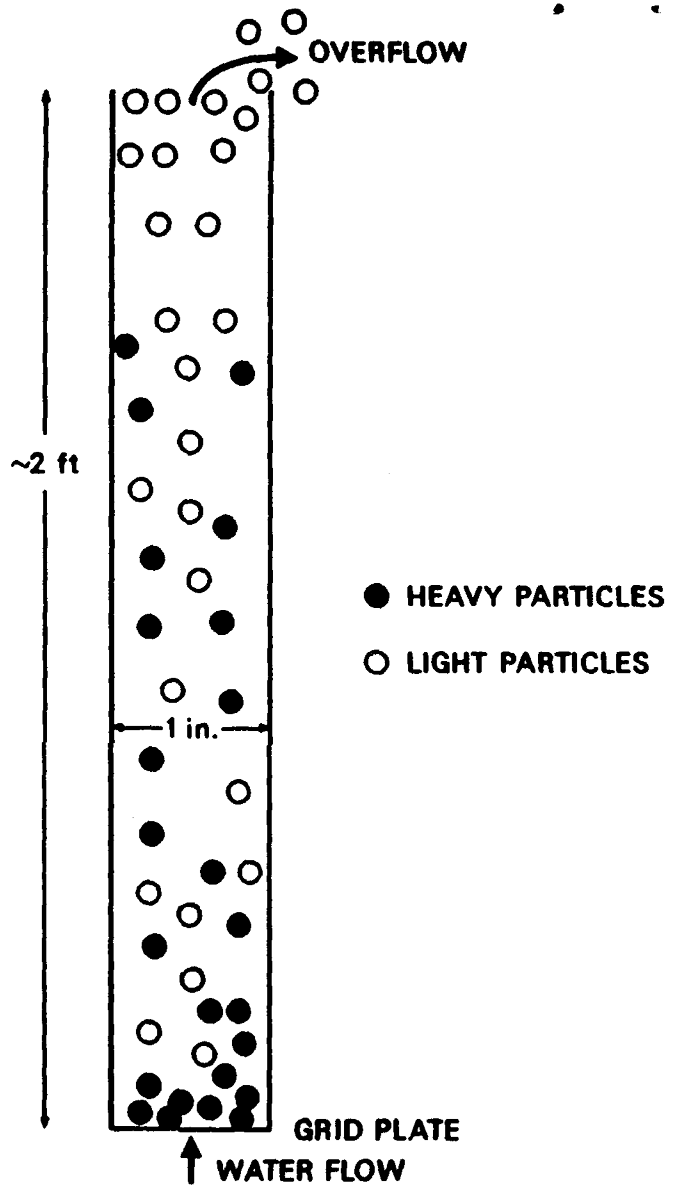

Figure 19. Schematic Showing Separation and Mixing of Heavy Particles with 16-20-Mesh Particles in the Overflow Run

The experimental apparatus used in this test failed to achieve this type of flow, and the resulting turbulence caused some of the darker, heavier particles to be carried up and out of the column. Another sample was tested at a flow rate high enough (88.25 mL/s) to cause all of the lighter particles to leave the separation column. The sediment was removed through the bottom port. All three samples (i.e., the two overflows and the sediment) were weighed and analyzed for fractional uranium content.

c. Results and Discussion for the 16-20-Mesh DU/Sand Separations.

If we look at the results in the two fluidization runs using these particles in Tables 7 and 8, we see that the mass fraction of uranium of the top sample in each case is much reduced from that of the feed. The feed contained a fraction of 0.0263 and 0.0225, and the top fractions contained 0.00164 and 0.00432, respectively. Although the reduction is an order of magnitude, it still leaves an activity of 1636 pCi/g (for the 0.00164 fraction concentration), which is above the 35 pCi/g

TABLE 7. FLUIDIZATION TEST RESULTS FOR 16-20-MESH PARTICLES (FIRST RUN)

Sample	Mass (g)	Density (g/cm^3)	Fraction DU (g/g)	Approx. activity (pCi/g)
Feed[a]	10.00	2.777	0.026310	26,310
Top	18.75	2.660	0.001636	1,636
Middle	13.60	2.668	0.002151	2,151
Bottom	24.55	3.234	0.048340	48,340
Sediment	6.10	8.700	0.667500	667,500
Remainder 1[a]	10.00	2.704	0.011440	114,400
Remainder 2[a]	10.00	2.710	0.011860	11,860

[a] Total feed was 208.1 grams, and the total remainder was 145.1 grams. The masses recorded are the amount sent for analysis.

TABLE 8. FLUIDIZATION TEST RESULTS FOR 16-20-MESH PARTICLES (SECOND RUN)

Sample	Mass (g)	Fraction DU (g/g)	Approx. activity (pCi/g)
Feed	4.136	0.022470	22,470
Top	4.096	0.004317	4,317
Sediment	9.714	0.797300	797,300

criterion for unrestricted disposal. The results also indicate that the sediment has different properties than the feed. It is more dense (i.e., 8.7 g/cm^3) than the feed, which is 2.77 g/cm^3 and also contains a much higher concentration of uranium (i.e., for the first run, it contained 0.668 as compared to 0.0263 weight fraction for the feed; for the second run, it contained 0.797 compared with 0.0225 fraction for the feed). Due to the differences in handling techniques and the experimental uncertainties involved, the variation between the two runs is considered small.

Additional grinding of large particles might enhance DU separation if the sized particles are heterogeneous and if they fragment into DU-lean and DU-rich fractions. Conversely, if the particles are too small, then, as already mentioned in the Phase 1 report (Reference 2), the best methods are (1) flotation and (2) magnetic separation. If the surface forces become predominant at very small sizes (less than 1 mm), the flotation processes may succeed if the surfactants are chosen with care.

The results for the overflow separation for the 16/20-mesh particles are shown in Table 9. Surprisingly, the results show a reduction of uranium fraction from 0.026 in the feed to 0.0017 in the overflow sand at low flow. This separation is comparable to that obtained at lower velocities in the minimum fluidization runs. However, when we examine the concentration of the sediment for the overflow runs, it is 0.0949 as compared to 0.667 and 0.797 in the minimum fluidization runs. Thus, at higher velocities, the greater mixing caused by increased turbulence does not affect the quantity of lighter components at the top. However, it does lower the concentration of uranium in the sediment, as expected.

TABLE 9. RESULTS FOR 16-20-MESH PARTICLE OVERFLOW RUNS

Sample	Mass (g)	Fraction DU (g/g)	Approx. activity (pCi/g)
Low flow	2.93	0.0017	1700
Top	19.17	0.0057	5700
Sediment	6.24	0.0949	95000

The results of these tests show that the lowest concentration of uranium cannot be made to approach an activity of 35 pCi/g by hydrodynamic density separation in a single stage. Multistaging may yield some improvement, but attainment of the objective uranium concentration is not likely.

SECTION
CONCLUSIONS

This report describes a portion of the activities conducted by Oak Ridge National Laboratory (ORNL) as part of an ongoing task entitled "Separation of Depleted Uranium Fragments from Gun Test Catchments." ORNL is performing this task for the U.S. Air Force Engineering and Services Center, Tyndall Air Force Base (AFB), Florida. Phase 2 of the task reported here deals with bench-scale tests of separation processes potentially applicable to minimizing land disposal of sand contaminated with depleted uranium (DU). Included in Phase 2 were wet, density-driven separation tests described in this report and other separation tests (predominantly screening) performed under subcontract and reported separately (Reference 1).

The economic analysis, performed as a separate phase of this task, determined that separation of DU from contaminated sand has practical value for waste disposal only if the activity level of the DU content can be reduced to <35 pCi/g (the level at which the sand can be disposed of on-site). The criterion of 35 pCi/g of waste has proven to be extremely difficult to attain by any physical separation process. Although excellent sand cleansing was achieved in the separations tests reported here, it was not sufficient to meet this criterion. However, this technology may prove useful for decreasing uranium content for safety purposes and possible reclamation of uranium concentrates in the future. This method may also be useful for other solid/solid separations such as removal of plastic wastes from metals.

The particle characterization tests reported in Section II. A provide guidance for determining the chemical form of uranium compounds. In addition, physical characterizations such as density distributions and average bulk density yield parameters useful for the design of density-driven separations. Such information is important when considering future sand-cleaning options. Characterizations were made for both individual particles and mixtures of particles. In the latter case, liquid fluidized- bed separation tests were conducted to estimate the degree of decontamination achievable by this method. The tests and results are described in Section II.C. The feed consisted of contaminated sand containing 2.26 weight percent DU and sized between American Society for Testing and Materials (ASTM) meshes 16 and 20. In general, the fluidized-bed separator achieved a high degree of separation, up to a maximum 14-fold reduction in DU content. However, this still falls short of the 35 pCi/g requirement for the sand to be disposed of on-site.

Contamination of process water with DU is a major concern when considering wet processing techniques. The tests reported in Section II.B deal with the likelihood of dissolving sufficient DU in process water to classify the water as radioactive waste.

This would occur for water exceeding 40 pCi/mL (Reference 2). Although normally unlikely, the possibility needs to be considered for cases where limestone is present in the sand and acidic process water is used. In such case, DU in a highly oxidized state (hexavalent uranium) may tend to dissolve in excess of the 40-pCi/mL limit. Tests, however, showed that in no case was the 40-pCi/mL activity limit reached, except with limestone present and with the pH buffered to 5. This indicated that, in general, the waste water, after settling the solids out, would be safe to dispose of on-site.

The wet density separation methods examined in this series of experiments are not sufficiently effective to be of use in improving the means of disposal of DU/sand waste. If DU contaminant levels in process water are found to exceed the 40-pCi/mL limit for unregulated disposal, measures reported in Section II.B.3 could be used to reduce the dissolved uranium.

The information developed in this study should be retained for possible future use. The method for improved screening of the target sand with recycle of the intermediate fractions combined with the use of presized sand for make-up should be instituted at the present test facility when funding is available for the procurement and installation of the necessary equipment.

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