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APPLICATIONS OF ULTRASONIC ENERGY

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APPLICATIONS OF ULTRASONIC ENERGYProgress Report No. 9
For April-May 1958

by

Aeroprojects Incorporated

ABSTRACT

Studies in aqueous precipitation of thorium oxalate under ultrasonic influence were continued. The smallest and most uniform oxalate particles, many of which were in the submicron region, were produced by fast addition of solid oxalic acid to thorium nitrate solution at a temperature of about 20°C followed immediately by 5 minutes of ultrasonic treatment, or by fast addition of oxalic acid solution to thorium nitrate solution at 20°C followed by 30 minutes of ultrasonic agitation. The shorter treatment time favors the former method.

Further studies in dissolution of fuel-element materials in mercury under ultrasonic influence, carried out with a DBL-2 tool steel coupler which appeared to be resistant to attack by mercury, showed a dissolution rate for thorium (at 180°C) of 0.22 mg/cm²/min. Type 304 stainless steel appeared to dissolve more rapidly at 90°C than at higher temperatures. Exposure of the mercury surface to air appeared to accelerate ultrasonic dissolution of both thorium and stainless steel.

Ultrasonic leaching of a simulated cesium-bearing alumina waste with 0.01 N nitric acid solution was most effectively accomplished in a "fixed-bed" treatment vessel. Extrapolation of experimental data suggested that close to 100% of the radioactive material could be removed from 5 grams of waste in 24 hours by uninterrupted batch-type ultrasonic treatment, using 300 milliliters of nitric acid solution, or in 10-12 hours by continuous-flow treatment using 9-10 liters of leaching liquid.

With the view of applying vibratory energy to accelerate magnesium extraction of plutonium from uranium, preliminary experiments indicated tantalum to be a potentially satisfactory container material for the molten metal system; the tantalum resisted attack, under ultrasonic influence, by molten uranium-chromium alloy at temperatures up to 950°C. Design and construction of a treatment array incorporating a tantalum vessel were initiated.

Agglomeration of a dilute aerosol of solid submicron KCl particles (simulating a highly radioactive aerosol waste stream) in an ultrasonic standing-wave field, using an additive liquid aerosol to promote coalescence, indicated that close to 100% of the aerosol could be trapped by this method, although optimum conditions have not yet been established. Ultrasonic agglomeration in liquid systems using an annular standing-wave treatment vessel appeared promising.

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SECTION I
ULTRASONIC CONTROL OF CRYSTAL SIZE
DURING AQUEOUS PRECIPITATION

PURPOSE AND SCOPE

Submicron particles of thorium oxide may improve HRT blanket slurries by alleviating plugging in regions of low-velocity flow, and slurries with narrow particle size range may decrease erosive action in the loops. However, the desired thorium oxide particle sizes and shapes are difficult to achieve by current methods, which involve precipitation of thorium oxalate, followed by calcination.

This study involves the investigation of ultrasonic energy application during the precipitation reaction in an effort to achieve control over particle size and shape. Such application can produce intense local agitation and possibly nucleation through bulk cavitation accompanied by a scrubbing or hammering action on the precipitated particles.

Initial work with a simulant system of calcium nitrate and oxalic acid showed positive ultrasonic effects in producing smaller particles. This effect has been confirmed in subsequent studies with thorium nitrate and oxalic acid, and current efforts are concerned with establishing specific effects of reagent concentration, temperature, ultrasonic treatment time, rate of addition of the precipitant, etc. in the ultrasonic precipitation process.

HIGHLIGHT DEVELOPMENTS

The previous report (Ref. 1) described experiments in ultrasonic precipitation of thorium oxalate using three different combinations of starting components:

1. Addition of solid oxalic acid to thorium nitrate solution. In this case, the smallest and most uniform particle sizes were obtained with fast addition at low temperature and with short ultrasonic treatment time.
2. Mixing of solutions of oxalic acid and thorium nitrate. Most effective results were achieved when the oxalic acid solution was added at a fast rate to the thorium nitrate solution.

3. Premixing of solid thorium nitrate and solid oxalic acid and subsequent addition of water.

Experiments on Items 2 and 3 were continued, the general procedures being the same as those previously described.

Addition of Oxalic Acid Solution to Thorium Nitrate Solution

Precipitations under ultrasonic influence were carried out with variables of reagent concentration, ultrasonic treatment time, and solution temperature. Since fast addition had been established as more effective than slow addition with ultrasonic treatment, 120 milliliters of oxalic acid was poured rapidly into 60 milliliters of the thorium nitrate solution in the treatment vessel for each test.

In addition, two control runs were made, using a motor-driven stirrer with a draft tube mounted in a beaker containing the thorium nitrate solution. The beaker and contents were cooled with an ice-water bath to a temperature below 10°C, and the oxalic acid solution was added slowly inside the draft tube over a period of 30 minutes, violent agitation being maintained during the addition and for 5 minutes thereafter. The contents of the beaker were then diluted with an equal volume of distilled water and allowed to stand with occasional shaking for 8-12 hours. The precipitated thorium oxalate was removed using a fritted glass filter, washed with distilled water until free of acid, and dried on the filter at 105°-110°C.

Specific conditions for each test are summarized below:

Test No.	Solution Concentration		Rate of Addition	U S Treatment Time (min)	U S Power (watt)	Solution Temperature (°C)		Mech. Agit.
	Th(NO ₃) ₄	H ₂ C ₂ O ₄				Start	End	
50	1 M	1 M	Fast	5	1900	15	22	No
58	1 M	1 M	Fast	30	1850	12	25	No
60	1 M	1 M	4 ml/min 30 min		Control	10	5	Yes
51	0.1 M	0.2 M	Fast	5	1850	12	17	No
59	0.1 M	0.2 M	3 ml/min 30 min		Control	10	8	Yes

The effect of ultrasonic treatment in reducing particle sizes using 1 M solutions of the reagents is apparent from comparison of the ultrasonic and

control samples in the photomicrographs of Figure 1. Control Test No. 60 shows essentially the same results as were previously obtained with Test No. 27 (Ref. 2), even though the temperature was lower and the degree of mechanical agitation was significantly greater for Test 60. Comparison of the ultrasonic samples from Tests 50 and 58 indicate that a 30-minute ultrasonic treatment period produces smaller particles than a 5-minute treatment.

Reduction of the reagent concentration to 0.1 M thorium nitrate and 0.2 M oxalic acid resulted in substantially larger particle sizes, in both ultrasonic and control runs, than were obtained with 1 M solutions. The difference is illustrated by a comparison of ultrasonic Test 50 in Figure 1 with Test 51 in Figure 2 and also by comparison of the control runs, Test 60 in Figure 1 and Test 59 in Figure 2. In view of the results in Figure 1, increasing the ultrasonic treatment time from 5 to 30 minutes may cause a slight decrease in particle size of the thorium oxalate precipitated from the more dilute solutions.

The results of these tests as well as those previously reported indicate that the most favorable conditions for the precipitation of small thorium oxalate particles from oxalic acid and thorium nitrate solutions are as follows: high concentration (1 molar) of solutions, fast addition of the precipitant, solution temperature of about 20°C, and ultrasonic application for approximately 30 minutes. Mechanical agitation superimposed on the ultrasonic treatment appears to have no effect.

The thorium oxalate particles obtained with this combination of reagents appear of approximately the same size as those prepared under optimum conditions from the addition of solid oxalic acid to thorium nitrate solution. Use of the solid acid, however, requires only 5 minutes ultrasonic treatment time, whereas 30 minutes are required when using a solution of oxalic acid.

Solid Thorium Nitrate and Solid Oxalic Acid Premixed and Added to Water

For these experiments, dried solid oxalic acid and dried thorium nitrate were intimately mixed in the calculated amounts for complete reaction and then added to water contained in the ultrasonic treatment vessel. Three tests were made with varying concentrations of the reagents, the mixture of solids being added rapidly to the water and ultrasonic energy being applied during the addition and for 5 minutes thereafter. Actual test conditions are tabulated below:

Test No.	Volume of Water in Vessel (ml)	Solid Reagent Concentrations	Rate of Addition	U S Treatment Time (min)	U S Power (watt)	Solution Temperature (°C)		Mech. Agit.
						Start	End	
52	160	0.1 M acid 0.05 M nitrate	Fast	5	1900	11	18	No
53	150	0.22 M acid 0.11 M nitrate	Fast	5	1900	12	18	No
55	100	0.4 M acid 0.2 M nitrate	Fast	5	1800	13	23	No

Test 52 duplicated the conditions for a previous run, Test 25 (Ref. 3). Comparison of photomicrographs for these two experiments reveals considerably smaller particle sizes for No. 52 (Figure 3). The reason for this is not presently known. Subsequent tests appear to be more reproducible.

Examination of the representative photomicrographs for the above three runs (Figure 3) indicates little apparent difference in thorium oxalate particle size for the three different concentrations, although those prepared at the lowest concentration may be slightly smaller. Comparison of the results of Test 53 with those of the previously reported Test 41 (Ref. 4), prepared in the same manner and with the same reagent concentrations but with 30 minutes ultrasonic treatment, indicates that in this method of combining the reagents, shorter treatment time produces smaller particles. On the basis of these data, the most favorable conditions for precipitation of small thorium oxalate particles from the addition of mixed solid reagents added to water involve fast addition of the solids, short ultrasonic treatment time, low concentration of reagents, low temperature, and no mechanical agitation.

Presently Best Method of Preparing Small Thorium Oxalate Particles

Considering not only the particle sizes obtained but also the required ultrasonic treatment time, the best method for precipitation of fairly uniform, small, rounded particles of thorium oxalate appears to be the fast addition of solid oxalic acid to a 1 M solution of thorium nitrate at a temperature below 20° C with a 5-minute ultrasonic treatment period. Some thorium oxalate particles in the desired submicron range have been produced by this method, and it is evident that the particles are significantly smaller and the size range narrower than similar characteristics of comparable non-ultrasonic precipitates.

Examination with an optical microscope has not permitted more precise evaluation. Therefore, samples selected from various tests have been sent to Oak Ridge National Laboratory for examination and evaluation by sedimentation techniques.

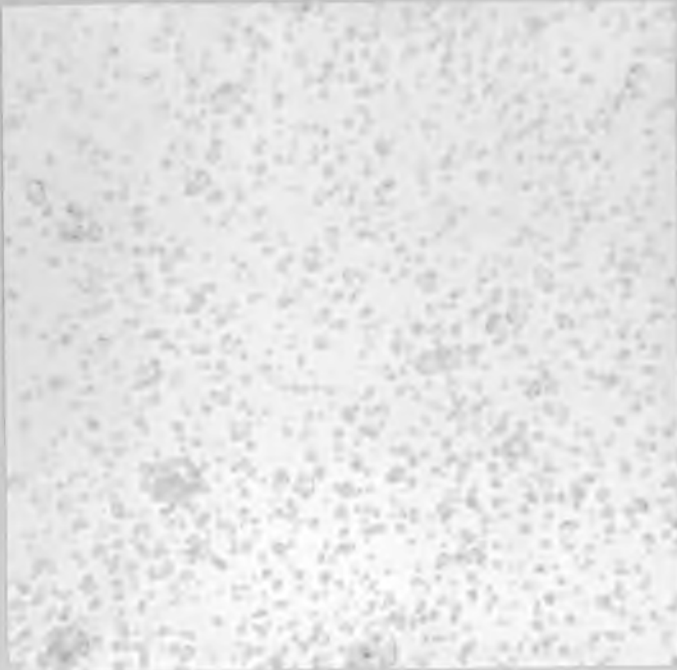
Jet Precipitation of Thorium Oxalate

This technique, as used at ORNL, involves two opposing fine jet streams, one of thorium nitrate solution and the other of oxalic acid solution, introduced into opposite ends of the top of a "T". The resulting precipitate of thorium oxalate with its mother liquor is removed through the bottom leg of the "T". This method has produced oxalate particles of approximately 1 micron size. Using a small-volume ultrasonic treatment vessel with opposing jets for feeding the nitrate and acid solutions, it is expected that further reduction of the precipitated thorium oxalate particles may be achieved. An existent ultrasonic treatment vessel has been modified for this purpose.

FUTURE WORK

Experiments will be conducted on the jet precipitation of thorium oxalate in the presence of ultrasonics. The reagents will be treated on a continuous-flow basis, and the effects of flow rate, temperature, and reagent concentrations will be evaluated.

A converging-coupler vessel of small volume (10-15 milliliters) has been constructed and will be used for both batch and continuous-flow precipitation studies.



Test No. 50

Ultrasonic Treatment Time: 5 min.



Test No. 58

Ultrasonic Treatment Time: 30 min.



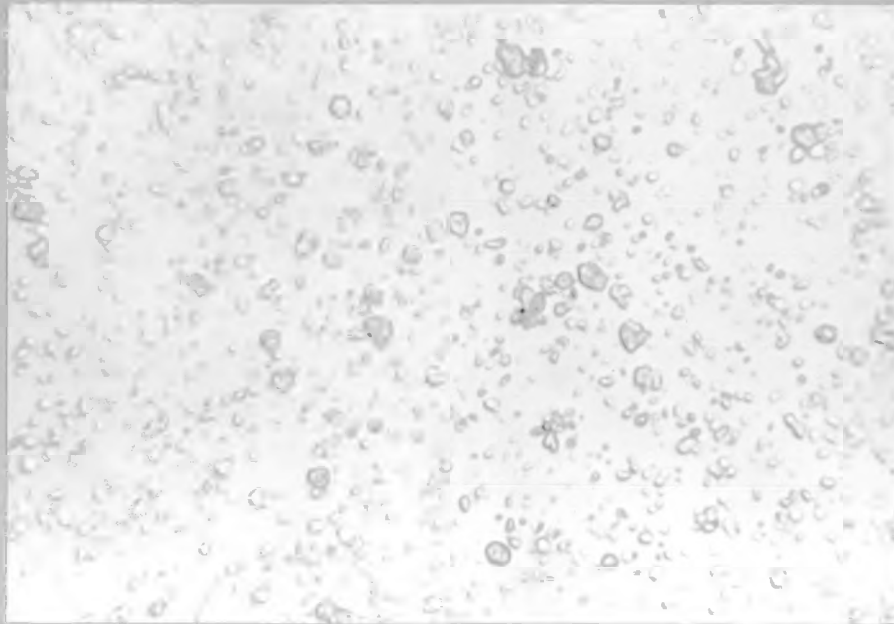
Test No. 60

Control - No Ultrasonics
Mechanical Agitation

Figure 1

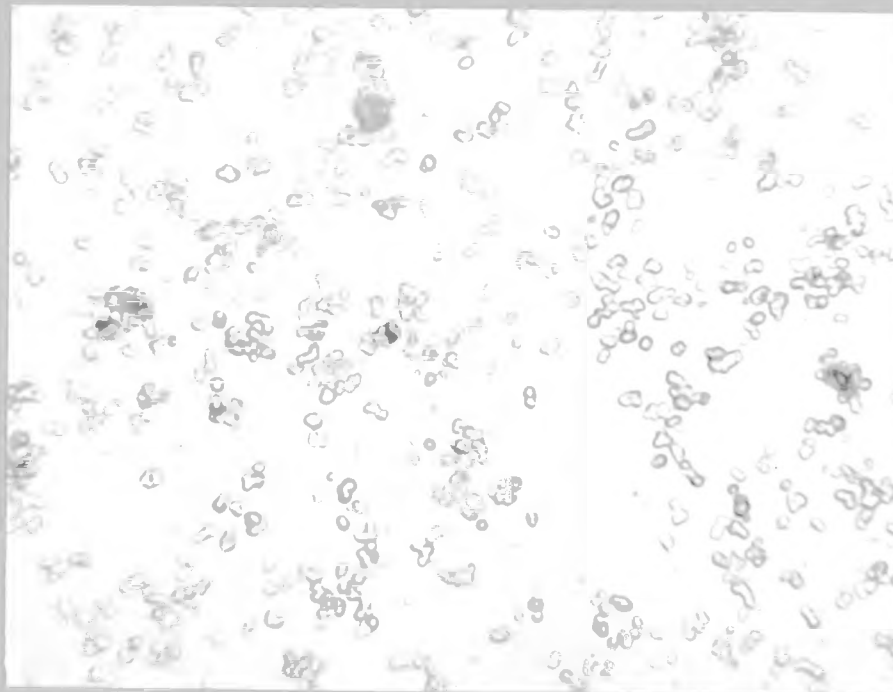
EFFECT OF ULTRASONIC TREATMENT ON THORIUM OXALATE PARTICLES PRECIPITATED
FROM 1 M OXALIC ACID SOLUTION ADDED TO 1 M THORIUM NITRATE SOLUTION
(Magnification: 1120X)

401 013



Test No. 51

Ultrasonic Treatment Time: 5 min.



Test No. 59

Control - No Ultrasonics
Mechanical Agitation

Figure 2

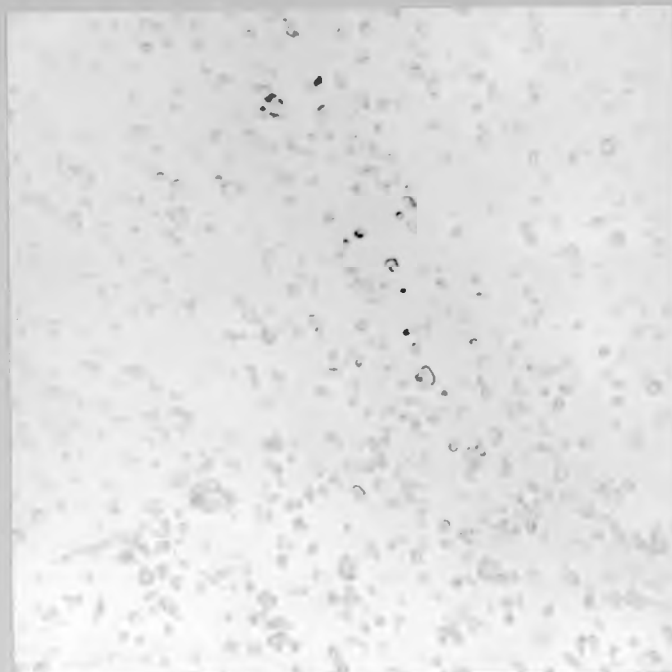
EFFECT OF ULTRASONIC TREATMENT ON THORIUM OXALATE PARTICLES PRECIPITATED
FROM 0.2 M OXALIC ACID SOLUTION ADDED TO 0.1 M THORIUM NITRATE SOLUTION
(Magnification: 1120X)

401 914



Test No. 52

0.1 M Oxalic Acid
0.05 M Thorium Nitrate



Test No. 53

0.22 M Oxalic Acid
0.11 M Thorium Nitrate



Test No. 55

0.4 M Oxalic Acid
0.2 M Thorium Nitrate

Figure 3

EFFECT OF CONCENTRATION OF SOLID OXALIC ACID AND THORIUM NITRATE
PREMIXED AND ADDED TO WATER WITH ULTRASONIC APPLICATION

Ultrasonic Treatment Time: 5 minutes

Rate of Addition: Fast

(Magnification: 1120X)

SECTION II

ULTRASONIC PROCESSING INVOLVING MERCURY

PURPOSE AND SCOPE

Mercury is a relatively good solvent for fissile materials such as thorium and uranium and its use to dissolve spent reactor fuel elements offers advantages over aqueous dissolution techniques, particularly the avoidance of extended cooling periods for the fuel elements prior to treatment, and economy of solvent since the mercury is easily regenerated by distillation.

It would be desirable to develop a process whereby not only the fissile material but also cladding and matrix materials could be dissolved in mercury to avoid the necessity for mechanical stripping or aqueous chemical dissolution. Under ordinary conditions, the usual cladding materials are essentially insoluble in mercury even at high temperatures. However, accelerated erosion of metals has been found to occur under the influence of ultrasonic cavitation (Ref. 5) and the current investigation was undertaken to study methods of introducing vibratory energy into mercury systems, as well as to determine the feasibility of accelerating dissolution and disintegration of fuel-element matrices and claddings by this means.

HIGHLIGHT DEVELOPMENTS

Earlier studies directed toward finding a suitable ultrasonic coupler material for transmission of vibratory energy into mercury (Ref. 6, 7) indicated Allegheny-Ludlum DBL-2 tool steel to be essentially resistant to attack by the mercury within the temperature range of 20°-180°C. This coupler was used for additional tests on representative fuel and cladding materials.

Using the technique previously described (Ref. 7), a thorium cylinder 1 inch in diameter and 1 inch high was supported between the face of the coupler and the bottom of the beaker containing mercury at a temperature of 180°C and was ultrasonically treated at a power level of 500-700 watts in pulses of 30 seconds on and 30 seconds off. After 30 hours, the observed rate of attack was 0.22 mg/cm²/min. As the thorium dissolved, it was observed to oxidize rapidly from exposure to the atmosphere, preventing buildup of solution concentration in the mercury and simulating a condition under which the thorium would be constantly exposed to fresh mercury.

Additional tests were made with cold-rolled Type 304 stainless steel sheet material, using the close-proximity ultrasonic treatment method. Specimens were exposed at temperatures of 90°C and 180°C for periods varying from 2 to 12 hours at an ultrasonic power level of 500 watts in pulses of 30 seconds on and 30 seconds off. When the surface of the mercury was exposed to air, the eroded steel particles oxidized rapidly. To determine the effect of such oxidation on the rate of erosion, some of the tests, particularly at the higher temperature, were carried out with the mercury surface covered with a layer of mineral oil approximately 1 inch thick.

The test results are presented graphically in Figure 4. Although considerable scatter is apparent in the data, in general the rates of attack were higher with the lower temperature and with an exposed mercury surface.

The DBL-2 tool steel coupler was used for all of the above tests, without visible evidence of attack by the ultrasonically activated mercury.

FUTURE WORK

Additional tests on thorium dissolution have been initiated and results will be summarized in the next report. Work has been started on determination of the erosion rate of another cladding material, Zircaloy-2. Establishment of a rigorous procedure and effective treatment has reduced to a minimum the effort required for these lengthy experimental programs.

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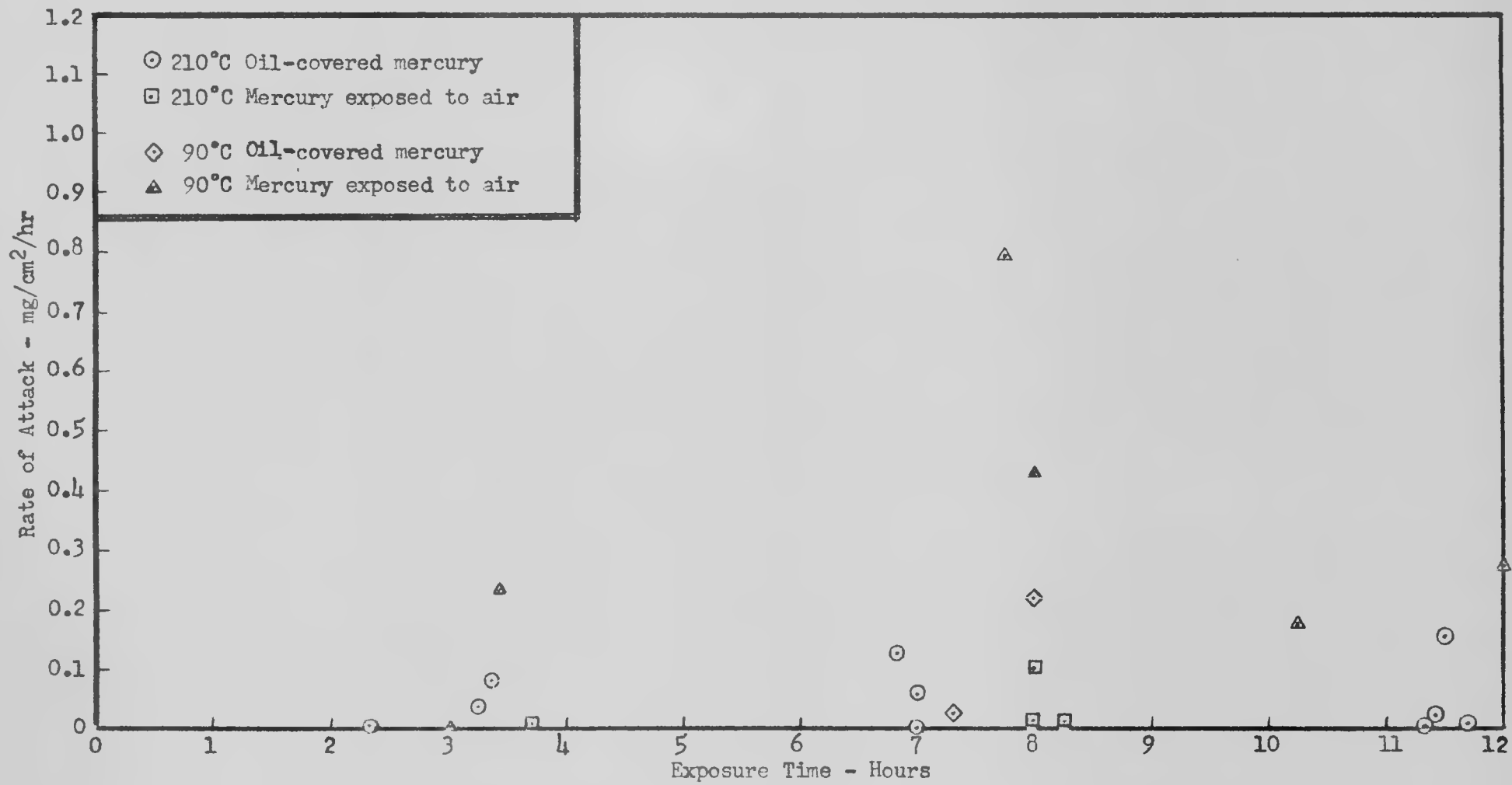


Figure 4

ULTRASONIC EROSION OF TYPE 304 STAINLESS STEEL IN MERCURY

870 304

SECTION III

ULTRASONIC LEACHING IN AQUEOUS SOLUTIONS

PURPOSE AND SCOPE

The residual nitric acid solutions after dissolution and extraction of fuel-element materials contain considerable amounts of fission products as well as aluminum or zirconium. Separation of the leachable fission products, particularly cesium and strontium, from the calcined wastes obtained from these solutions would alleviate cooling and storage problems, and permit disposal of the oxide wastes by simple burial. Present leaching methods can remove 80-90% of cesium-137 and 30-70% of strontium-90 after several days exposure time. Removal of a greater percentage is desirable for safe storage.

This work has been undertaken to evaluate the effectiveness and feasibility of ultrasonic application to the leaching process. It has been established (Ref. 8) that vibratory treatment during leaching of a simulated alumina (from aluminum nitrate) waste containing cesium effects approximately 90 percent removal of the cesium in 8 hours exposure time. Work is continuing using various frequencies and types of ultrasonic treatment vessels on both a batch and continuous basis to establish the best conditions for accelerated aqueous leaching to occur.

HIGHLIGHT DEVELOPMENTS

The application of ultrasonic energy to aqueous leaching of a simulated alumina waste containing cold cesium with a small amount of cesium-137 has been continued, using the three types of ultrasonic vessels previously described (Ref. 9): the resonant-cylinder, "fixed-bed," and converging-coupler vessels. Leaching in the converging-coupler vessel was carried out on a batch basis only; both batch and continuous-flow treatment were carried out in the "fixed-bed" vessel; and continuous flow alone was used with the resonant cylinder. Several control runs were also made in the resonant cylinder as well as in a flask using mechanical agitation.

The results of each test were evaluated by taking 10-milliliter aliquots of the leaching liquor, centrifuging and evaporating the supernatant on a stainless steel planchet, and then counting for beta activity. The total activity in the simulated waste before leaching was determined by dissolving 0.1 gram in 100 milliliters of concentrated nitric acid,

evaporating to a small volume, diluting to 100 milliliters with distilled water, then taking a 10-milliliter aliquot, evaporating to dryness, and counting. Several determinations gave an average value of 4300 counts per minute for the total activity in 1 gram of solid waste. This is somewhat higher than the base value of 3000 counts previously reported.

Batch Treatment in Converging-Coupler Vessel

Three test runs were made in which 1-3 grams of cesium waste were added to 180-200 milliliters of 0.01 N nitric acid solution contained in the treatment vessel. Ultrasonic energy was applied for 1-3 hours at a power level of 500-1000 watts. Ten-milliliter aliquots were taken at predetermined intervals, and the original volume was maintained by the addition of fresh 0.01 N nitric acid solution.

In the first test, 3 grams of cesium waste were treated with 180 milliliters of the leaching liquid for 2 hours at 500 watts power, the liquid temperature being held at 21°C by means of a cooling coil immersed in the liquid. The beta activity counts on the samples taken every 15 minutes are plotted as curve A of Figure 5. At the end of 2 hours, a total of 51.6 percent of the cesium had been removed from the waste.

The second test involved the treatment of 3 grams of waste with two successive 200-milliliter portions of leaching liquid for 1 hour each at 1000 watts power and a temperature of 57°C. In addition to the samples taken every 15 minutes, one additional 10-milliliter sample was taken 15 minutes after the ultrasonic treatment had been discontinued in each case. As indicated in curve B of Figure 5, 47 percent of the cesium was removed. It is of interest to note the increase in leaching during the 15-minute interval without ultrasonic treatment corresponding to results previously obtained with "fixed-bed" treatment (Ref. 8).

The third test involved treatment at 1000 watts of 1 gram of calcined waste with 200 milliliters of the nitric acid solution at 40°-55°C. At the end of 3 hours, the ultrasonic treatment was discontinued, and analysis of a 10-milliliter sample showed the removal of approximately 64 percent of the cesium. After an additional 30 minutes of contact between the solid and the leaching liquid without ultrasonics, another 10-milliliter sample showed the removal of approximately 10 percent more of the cesium. These results are shown in curve C of Figure 5.

Ultrasonic Leaching in "Fixed-Bed" Cylindrical Vessel

1. Batch Treatment

Two additional batch-treatment tests were made with the "fixed-bed" vessel, each using 5 grams of cesium waste and 300 milliliters of nitric acid solution at 38°C. In each test, ultrasonic energy at 50 watts power was applied for 8 hours. In one instance 10-milliliter samples were removed every 30 minutes and replaced with equivalent amounts of fresh nitric acid solution. In the second test, aliquots were removed only at the end of 3 hours and 8 hours. In both tests, the leach liquor was allowed to remain in contact with the treated waste for 3 days without vibratory treatment. As noted in the curves of Figure 6, 80-95 percent of the cesium activity was found in the leaching liquor at the conclusion of this period.

Experiments have not yet been run providing continuous ultrasonic treatment for more than 8 hours. However, on the basis of data accumulated during these tests, it appears that close to 100 percent of the activity might be removed in 24 hours with uninterrupted ultrasonic treatment of a single batch.

2. Continuous-Flow Treatment

Two additional trials in the "fixed-bed" vessel involved continuous flow of 0.01 N nitric acid solution at approximately 40°C through 5 grams of solid waste contained in the chamber adjacent to the ultrasonic coupler, which was activated at a power level of 50 watts.

The flow rate for the first run was 5 milliliters per minute. When the flow of liquid and the ultrasonic treatment were discontinued after 100 minutes, analysis showed the removal of 23 percent of the activity from the waste. Approximately 300 milliliters of leaching liquid which remained in the treatment vessel was left in contact with the treated waste for several days without applied ultrasonic energy. After 65 hours, approximately 36 percent of the total activity had been removed (see curve A of Figure 7), and after 165 hours this had increased to 78 percent.

The second test was run under essentially the same conditions except that the flow rate was increased to 15 milliliters per minute and the vibratory treatment was continued for 6 hours. During this period, 75 percent of the total activity was leached from the waste material. Sixty-eight hours later, the 300 milliliters of nitric acid remaining in contact with the cesium had removed an additional 8 percent (curve B Figure 7). After 10 days, analysis indicated that approximately 100 percent of the total calculated activity had been removed.

These results were checked by analysis of the waste itself. The solid waste was separated from the leach liquor, washed several times with water, and allowed to stand with 200 milliliters of water in a flask for 2 weeks with occasional shaking. Analysis of this water gave a beta count slightly above background, indicating less than 1 percent of the total activity left in the cesium waste.

Extrapolation of these results suggests that essentially complete removal of cesium from 5 grams of calcined waste may be accomplished by continuous-flow treatment in this vessel using 9-10 liters of 0.01 N nitric acid solution and with an ultrasonic treatment time of 10-12 hours, or approximately half the time required with batch-type treatment.

Continuous-Flow Leaching in Resonant-Cylinder Vessel

The difficulties previously experienced with the continuous-flow resonant-cylinder ultrasonic treatment vessel were eliminated, and several leaching tests were made to evaluate the effectiveness of this apparatus, using two different methods of treatment.

In the first method, the vessel was filled with 0.01 N nitric acid solution, and both the solid waste and the nitric acid were fed into the inlet tube at the top of the annulus (Ref. 10) at a predetermined rate for the duration of the test. The treated waste and the leaching liquor were removed through the bottom tube, samples were taken, and the liquor was analyzed for beta activity. These runs were made at an ultrasonic power level of 300 watts and the liquid flow rates of 5, 10, and 20 milliliters per minute, using both 5 and 10 grams of solid waste; the solid-to-liquid flow rate ratio ranged from 1:100 to 1:200.

Results of these tests showed a total activity of 5-12 percent leached from the waste, the lowest flow rate being the most effective. Several control tests at various flow rates run in the same manner but without applied vibratory energy removed only 2-5 percent.

In the second method of treatment, the flow was reversed and all of the solid waste was fed into the bottom tube at the start of the test. Samples were taken as before, and at the end of the test the solid waste was flushed out with the liquid remaining in the annulus. When 5 grams of solid were treated with 1 liter of liquid at a flow rate of 10 milliliters per minute, 16 percent of the total activity was removed. At 5 milliliters per minute, 25 percent of the total activity was removed using only 500 milliliters of nitric acid solution.

None of these results approached the values obtained with the other types of treatment vessel, and no further leaching tests are contemplated with the resonant-cylinder array.

FUTURE WORK

Further work will be carried out along the following lines:

1. Exploration of the use of ultrasonic frequencies in the range of 300-800 kc with a "fixed-bed" type treatment vessel.
2. Continued investigation of the "fixed-bed" and converging-coupler vessels to evaluate the effect of ultrasonic treatment times in excess of 8 hours.
3. Evaluation of intermittent ultrasonic treatment over a 24-hour period in both the above types of vessels.

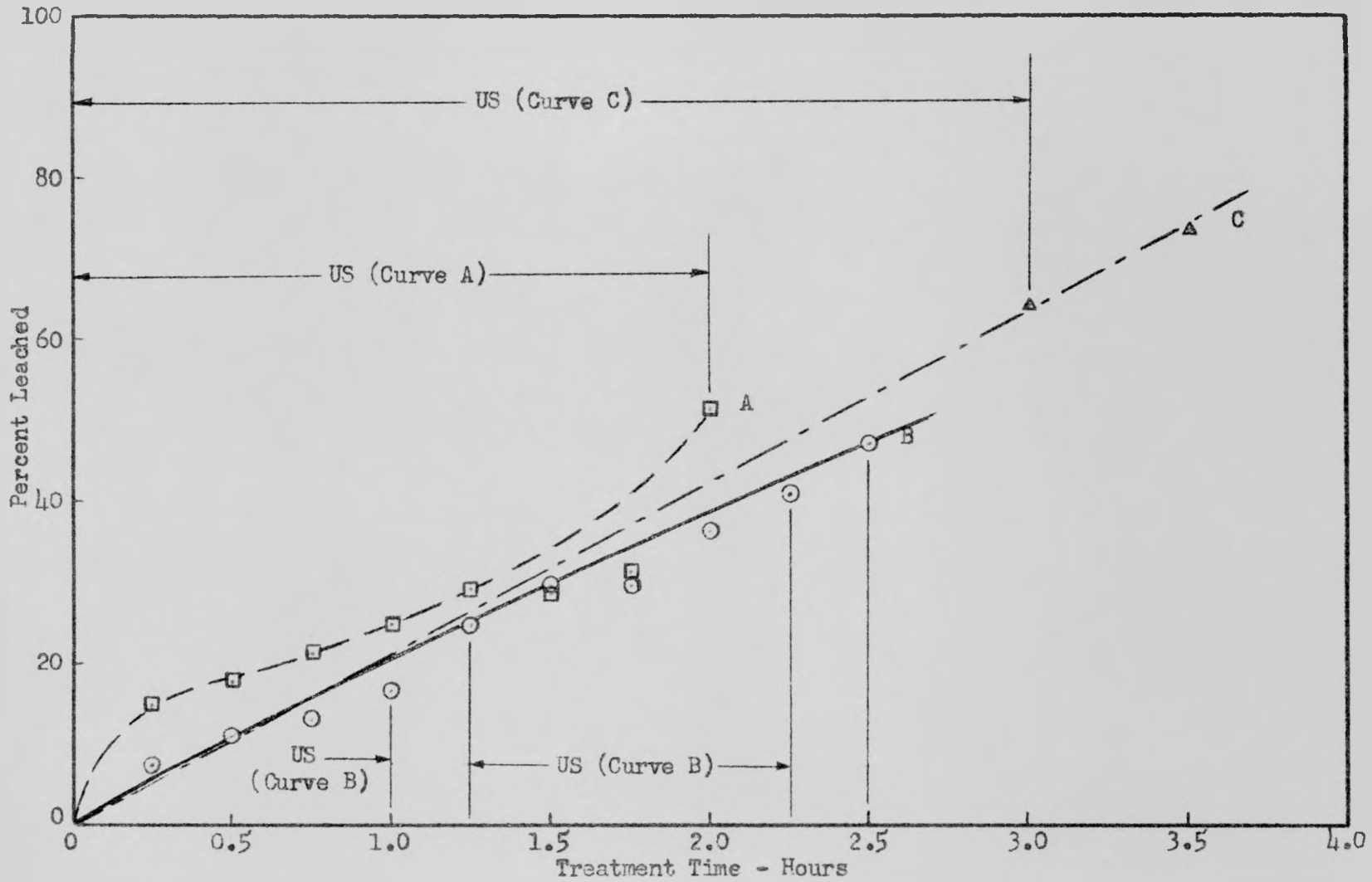


Figure 5

ACCELERATION OF LEACHING OF CESIUM WASTE WITH 0.1 N NITRIC ACID BY BATCH TREATMENT IN ULTRASONIC CONVERGING-COUPLER VESSEL

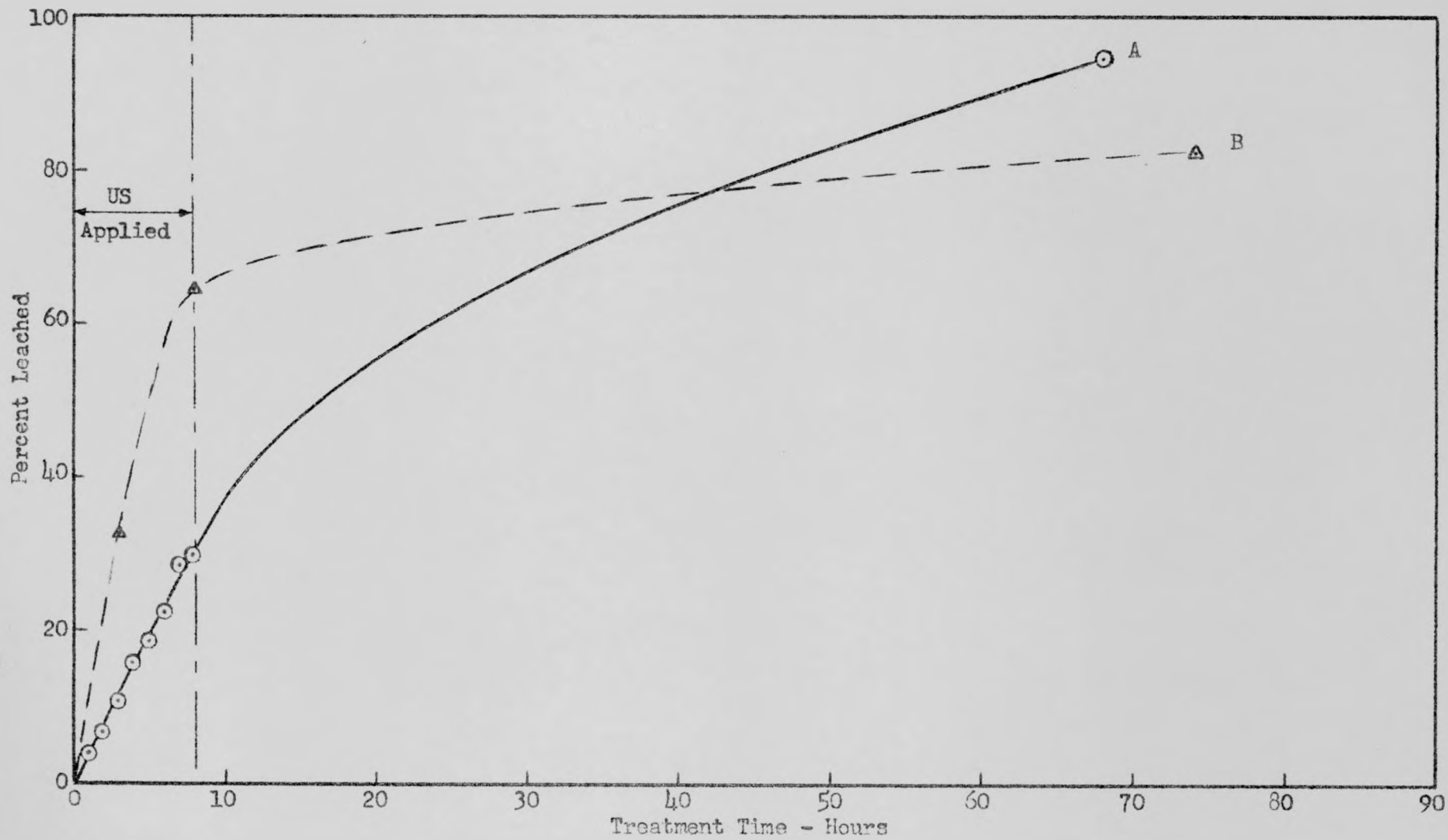


Figure 6

ACCELERATION OF LEACHING OF CESIUM WASTE WITH 0.1 N NITRIC ACID
 BY BATCH TREATMENT IN ULTRASONIC "FIXED-BED" VESSEL

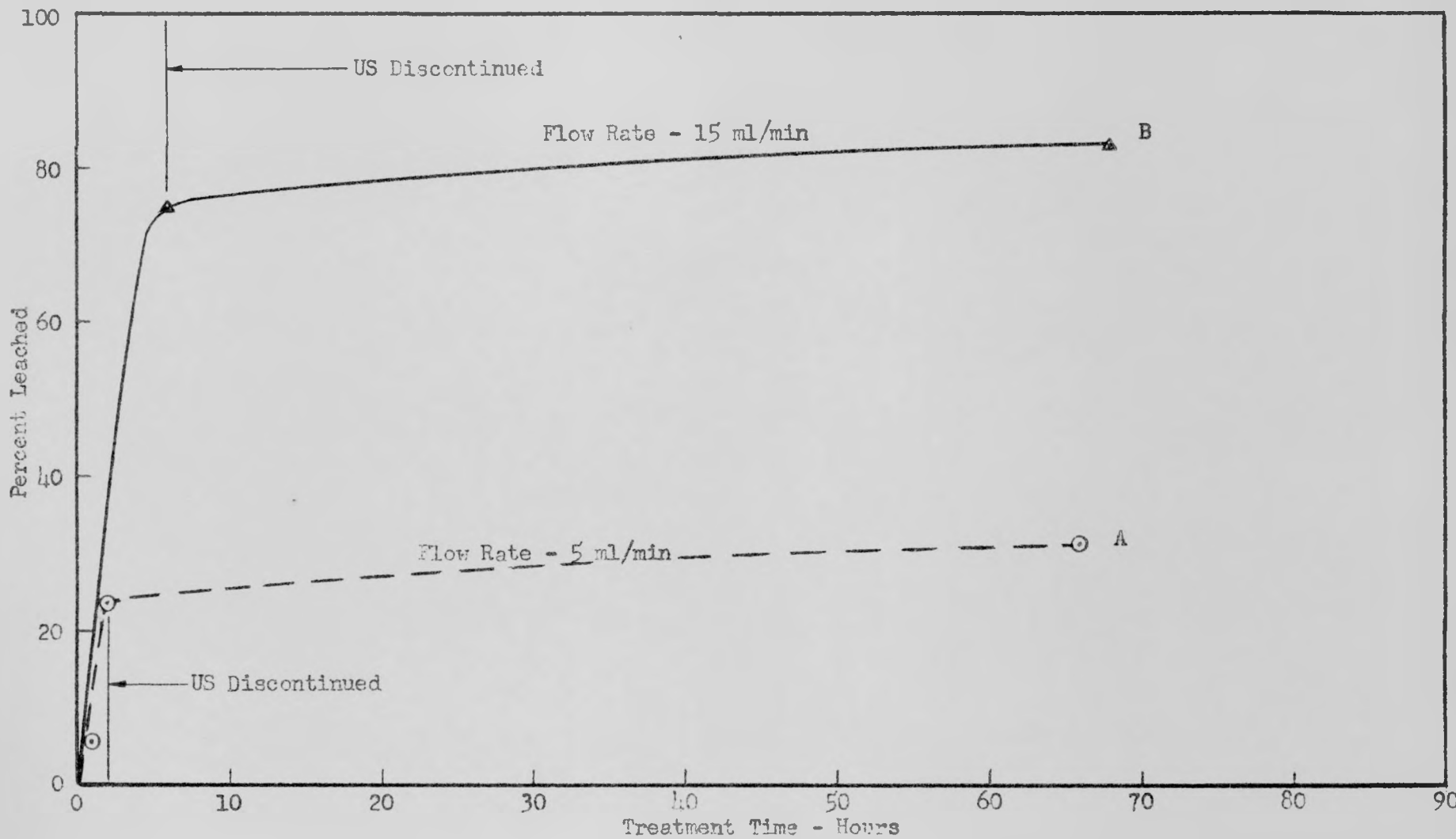


Figure 7

ACCELERATION OF LEACHING OF CESIUM WASTE WITH 0.1 N NITRIC ACID
BY CONTINUOUS TREATMENT IN "FIXED-BED" VESSEL

SECTION IV

HIGH-TEMPERATURE MIXER-SETTLER

(ULTRASONIC EXTRACTION OF LIQUID-METAL SYSTEMS)

PURPOSE AND SCOPE

The use of vibratory energy to accelerate the attainment of heterogeneous equilibria has been found effective in ambient-temperature operations and offers even greater promise for conditions of extreme temperature and corrosiveness, since it eliminates the need for moving parts, stuffing boxes, etc. normally required for such operations. One such potential application of ultrasonic agitation is molten-metal or molten-salt extraction of radioactive materials from fuels and breeder blankets.

The particular process under investigation is the magnesium extraction of plutonium from a uranium-5 weight percent chromium alloy, a process originally developed at Argonne National Laboratory (ref. 11). The use of a reciprocating stirrer has been found to aid in the transfer of plutonium to the magnesium phase. However, stage equilibrium is not attained within reasonable time limits.

It appears likely that the transfer process could be accomplished more efficiently and rapidly with ultrasonic application in a suitable mixer vessel. Because of the low volume of material projected for treatment (approximately 10 kilograms per day), this operation is ideally suited for evaluation with furnace equipment existing at ANL, and the feasibility of adding an ultrasonic mixing unit for this operation is being investigated.

HIGHLIGHT DEVELOPMENTS

Evaluation of Tantalum as Container Material

Prior studies (Ref. 11) had indicated tantalum to be the only metallic material of potential suitability as a container for the molten magnesium-molten uranium (chromium) system. However, since vibratory energy is known to accelerate erosion of materials in molten metals, it was necessary to establish the behavior of ultrasonically activated tantalum in this molten metal system at approximately 900°C.

An experiment was conducted in which uranium--5 percent chromium alloy was heated in a graphite crucible to a temperature of 925°C, the alloy being protected from the atmosphere with an argon blanket. A tantalum rod of 3/4-inch diameter was immersed in the melt, and ultrasonic energy at a frequency of 20 kc and a power input of 200 watts was applied through the rod. This power level, which amounted to approximately 40 acoustic watts per square centimeter of rod face area, had previously been found to cause severe cavitation erosion of various materials in mercury (Ref. 12). However, the tantalum showed no indication of attack after 2 hours of ultrasonic exposure in the molten uranium-chromium alloy.

A second experiment was conducted to evaluate the effect of longer exposure time. In this case, the uranium alloy was heated under argon to 950°C and overlaid with a small quantity of magnesium. The tantalum rod was immersed in the melt and ultrasonically activated for 6 hours at the same frequency and power level. After cooling, both the tantalum rod and the Mg-U(Cr) ingot were examined. The ingot was clean and showed no evidence of oxidation (the physical arrangement of the system had not been designed to promote mixing of the phases, and brief examination of the magnesium phase indicated no uranium to be present). The tantalum rod again showed no evidence of attack by the molten metal, and it appeared that this metal could be successfully used in the extraction equipment.

Design of Ultrasonic Mixer-Settler Array

Because of the difficulties of obtaining large, sound castings or forgings of tantalum, it was decided that the use of this metal would be restricted, as far as possible, to the surfaces actually in contact with the molten metal and that commonly available materials would be used for the balance of the array. The basic design therefore consisted of a tantalum cup attached to a stainless steel bar through which the vibratory energy was introduced. The cup configuration and dimensions were dictated partially by the acoustical properties of tantalum.

Brief analysis indicated that the cup could not be welded or brazed to the steel bar; the coefficient of thermal expansion of tantalum is so low compared with that of any type of stainless steel that stresses induced in such a joint at 900°-1000°C would exceed the tensile strength of steel. A mechanical joint was therefore indicated. The eventual design involved a screw joint between the tantalum and the stainless steel (Type 304), as shown in Figure 8, which is a modification of a design by Winsch and Burris (Ref. 11). The screw joint itself will be cold, so the stainless steel will retain its strength, and the tantalum has good tensile strength at the projected operating temperature. The platinum shim between the cup and the

cylindrical rod has a thermal expansion midway between those of tantalum and steel and will serve to counteract imperfections on adjacent surfaces and prevent serious galling during operation. Furthermore, the design permits tightening of the screw joint after the temperature has been raised to about 800°C; additional heating will result in firm contact between the tantalum and the steel without inducing excessive stresses in the steel rod. The tantalum cup is currently being fabricated.

FUTURE WORK

Pending fabrication and delivery of the tantalum container, the detail design for the remainder of the induction-heated mixer-settler array will be completed. All other necessary components will be fabricated and assembled, and preliminary operational tests will be made, special emphasis being placed on heating and temperature control.

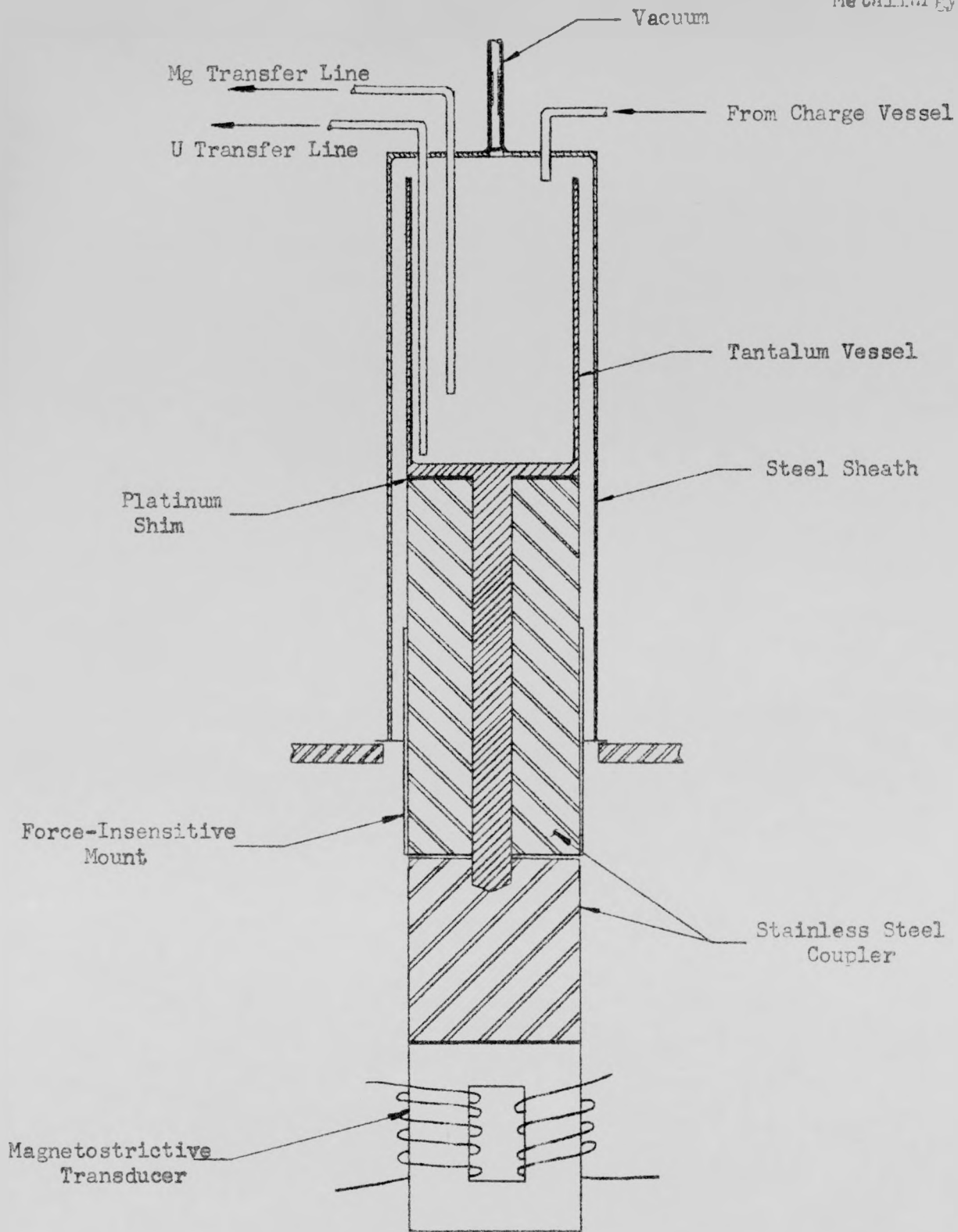


Figure 8

SKETCH OF ULTRASONIC TANTALUM MIXER-SETTLER
TO REPLACE EXTRACTION VESSEL OF BURRIS AND WINSCH (Ref. 11)

SECTION V

ULTRASONIC COALESCENCE IN GASEOUS AND LIQUID SYSTEMS

PURPOSE AND SCOPE

Inasmuch as the equations which describe the motion of fluids in sonic or ultrasonic fields are essentially the same for both liquids and gases, the earlier program (Ref. 13) on coalescence of particulate matter in gas streams has been expanded to include study of coalescence of liquid or solid particulates in liquid systems.

Coalescence in Gaseous Systems

Certain reprocessing steps performed in conjunction with aqueous reprocessing of spent fuel elements lead to production of a dilute, polydisperse aerosol of highly radioactive solids. Because of the small particle size (<1 micron diameter) and low concentrations (approximately 10^{10} particles per cubic foot), the aerosol is exceedingly difficult to collect in conventional equipment. However, if the particles could be agglomerated to larger sizes, devices such as cyclone collectors and bag filters would be satisfactory.

A potential means of achieving agglomeration is by passing the aerosol through a high-intensity ultrasonic standing-wave field, but even this process alone may not be sufficient to achieve the required level of decontamination of the radioactive dust stream, particularly since the particles are solid and probably do not coalesce readily. The use of an additive collecting aerosol should accelerate ultrasonic coagulation by increasing aerosol concentration and promoting coalescence.

This investigation was therefore designed to examine the feasibility of using ultrasonic energy together with an additive aerosol to induce coagulation in low-density aerosols of submicron particles, to evaluate certain physical and acoustical configurations for ultrasonic agglomeration systems, and to establish practical methods whereby the coagulation and subsequent collection can be accomplished.

Agglomeration in Liquid Systems

Agglomeration of dispersed phases in liquids is of particular interest for such processes as extraction and leaching. The rate of attainment of equilibrium in such an operation is at least partially dependent upon the interfacial area between the two phases, and the creation of fine emulsion or a fine solid suspension would be beneficial. However, the resulting system may be so stable that subsequent separation of phases is difficult to achieve.

The use of ultrasonic standing-wave fields for separation of phases in an emulsion (Ref. 14) and to agglomerate solids in liquid suspensions (Ref. 15, 16, 17) has been demonstrated, but practical equipment configurations capable of treating reasonably large volumes on a continuous basis have not yet been developed. It is the purpose of this phase of the work to establish feasibility of agglomeration in liquid systems on a continuous basis and to investigate critical operating parameters, so that applicability to large-scale operation can be established.

HIGHLIGHT DEVELOPMENTS

Coalescence in Gaseous Systems

The solid aerosol agglomeration tests previously reported (Ref. 13) indicated a significant and useful effect obtainable from the use of high-concentration additive liquid aerosols and simultaneous application of well-formed ultrasonic standing-wave fields. On the basis of these preliminary tests, a definitive, replicated experiment was designed to establish quantitatively the effect of such variables as additive aerosol volume, method of formation of standing waves, and ultrasonic frequency on the rate of removal of a potassium chloride aerosol from moving air streams. The experiment is being carried out in the aerosol laboratory which is described in some detail in Appendix A, using the test cells as well as the associated particle-size-determination apparatus and techniques also described in the appendix.

Two ultrasonic agglomerating tubes were connected to the aerosol test cell: a metal tube 5 inches in diameter by 8 feet long, and a Plexiglas tube 2-1/2 inches in diameter by 51 inches long. It has been established that standing waves could be produced in both tubes, in the former through the use of an ultrasonic generator at one end and a reflector at the opposite end, and in the latter with a generator at each end of the tube. Aerosol from the test cell could be drawn through these tubes by means of vacuum pumps, and an all-glas impinger attached to the

end of each tube provided a means for collecting any unagglomerated aerosol that passed through the tube. The air flows could be adjusted so that the total flow rate through the larger tube is four times that through the smaller one, thus providing the same linear velocity in both tubes.

The basic experimental technique in these tests, only a part of which have been completed, involves the generation of a solid potassium chloride aerosol from a 1-weight-percent aqueous solution into the test cell, in order to produce solid potassium chloride particles in the size range of 1 micron and less, followed immediately by the generation of the additive aerosol, which consists of an essentially non-evaporating glycerine-water solution colored with water-soluble blue dye for convenient colorimetric analysis. The latter solution is atomized at a rate of 47 milliliters per minute for a period of 6 to 60 minutes, depending on the volume of additive aerosol desired. The aerosol in the test cell is sampled by means of all-glass impingers at intervals for a total of 60 minutes and the samples analyzed by means of flame photometry in order to monitor the airborne potassium chloride concentration, develop aerosol decay curves, and estimate particle-size distributions by Feather analysis (see Appendix A).

As soon as the potassium chloride aerosol is generated, aerosol flow through one or the other of the agglomeration tubes is initiated and continued for 60 minutes. The all-glass impinger attached to the tube is replaced every 10 minutes. At the conclusion of each test, the impinger samples and the deposits in the tube are analyzed to determine the percentage of solid aerosol and additive aerosol in each. The potassium chloride content is determined with a flame photometer, and analysis of the glycerine-water-blue dye solution is accomplished by colorimetric methods.

The variables involved in the tests, in addition to tube diameter and aerosol treatment rate, include volume of additive aerosol, ultrasonic vs. non-ultrasonic agglomeration, and ultrasonic frequency. Sufficient replication at all experimental conditions is being carried out to permit reliable estimation of precision. Tests are conducted in random order.

The data obtained to date for each of the agglomeration tubes are presented in Tables I and II in terms of potassium ion content collected in the tubes and in the impingers (AGI). Ideally, under a given set of conditions with or without ultrasonics, the total collected in tube and impinger should be constant. For the 5-inch-diameter tube, the mean "total" potassium for those cases in which 3000 milliliters of additive aerosol were used was 20 milligrams with a 95% confidence interval of ± 2 milligrams. In the case of the 2-1/2-inch tube, smaller quantities were analyzed and the precision is not so great.

The data show a substantial increase in ultrasonic over non-ultrasonic agglomeration in both tubes, the increase being greater with the low volume of additive aerosol. However, over-all agglomeration with or without ultrasonics is more effective with the high volume than low volume of additive. The frequency variation investigated with the 2-1/2-inch tube appears to indicate a superiority of 20 kc over 25 kc, although further effort is necessary to establish a frequency effect.

These results indicate that within limits of analytical techniques essentially 100 percent of the solid potassium chloride aerosol can be trapped by the use of an additive liquid aerosol in an ultrasonic standing-wave field. It should be mentioned that some of the material which passed through the tube and was collected in the impinger bottles could probably be collected by standard devices such as cyclone separators. This aspect will be investigated as a part of next month's experimental program.

Agglomeration in Liquid Systems

For a study of coalescence in liquid systems, an annular standing-wave vessel was assembled. This array, shown in Figures 9 and 10, was constructed around a 3-inch-diameter cylindrical barium titanate transducing element which transmitted radial vibration at a nominal frequency of 350 kc into an annular liquid vessel surrounding the transducer. The dimensions of the vessel were selected so that the outer wall reflected the vibratory energy and induced concentric standing-waves in the liquid. Visual observation indicated a good standing-wave pattern with little evidence of bulk circulation.

Means were provided for continuous introduction of fresh emulsified liquid at mid-center of one side of the vessel and for take-off of the separated heavier phase at the bottom of the opposite side. The inflow and outflow could be adjusted to maintain a constant liquid level in the vessel.

Preliminary tests were conducted to determine the effectiveness of this treatment vessel in breaking a gelatine-stabilized kerosene-water emulsion containing approximately 2.4 volume percent kerosene. The vessel was filled with the emulsion and additional emulsion was introduced at flow rates approximating 50 and 100 milliliters per minute. The liquid from the take-off tube, presumably deficient in the kerosene phase, was analyzed for kerosene content by destroying the emulsion with dilute nitric acid and measuring the volume of kerosene in a known volume sample. The results, presented in Table III, show promise of a practical method of inducing coalescence in liquid media by ultrasonic treatment.

FUTURE WORK

The experiment involving coalescence of potassium chloride aerosols in ultrasonic standing-wave fields will be continued and further data, especially relating to effects of aerosol flow rate through the agglomeration tube, will be obtained during the next bi-monthly period. Investigation of various types of sound sources for gaseous systems will continue.

Liquid agglomeration tests in the annular standing-wave vessel will be continued with evaluation of the effects of reflector diameter and liquid flow rate. Larger transducers will be assembled, and tests to establish the influence of the continuous and dispersed phases are contemplated.

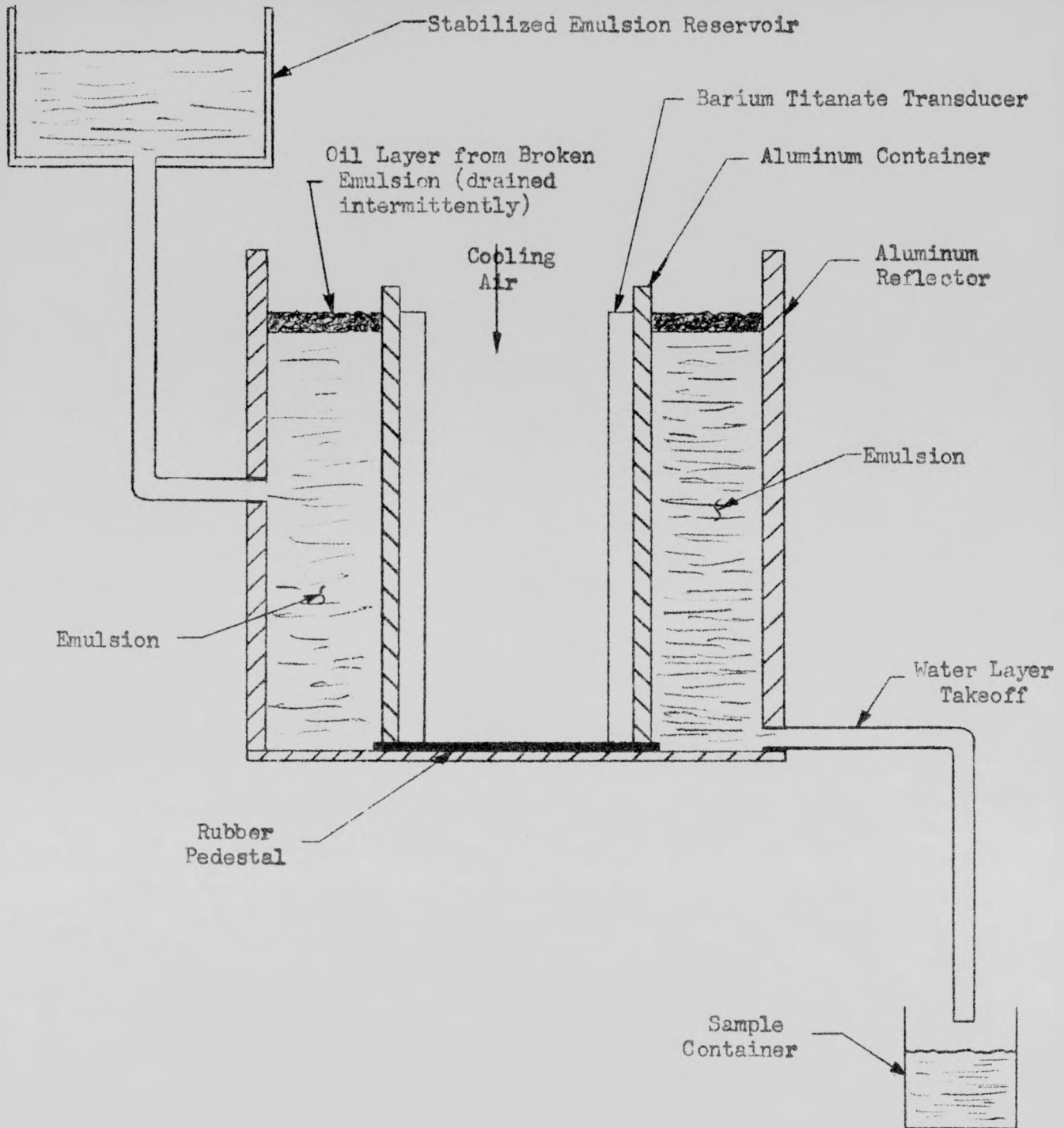


Figure 9

SCHEMATIC DIAGRAM OF ANNULAR STANDING-WAVE VESSEL
FOR EMULSION BREAKING



Figure 10

ANNULAR STANDING-WAVE VESSEL FOR EMULSION BREAKING

Note the two barium titanate ceramic cylinders cemented into the inner aluminum cylinder. The outer cylinder is the 6.22-inch I.D. reflector.

Table I

ULTRASONIC AGGLOMERATION OF POTASSIUM CHLORIDE SOLID AEROSOL

Tube diameter: 5 inches

Aerosol treatment rate: 0.4 cubic foot per minute

Volume Glycerine-Water Solution Dispersed (ml)	Weight of Potassium (mg) in			Ultrasonics	Frequency (kc)	Ratio $K_{\text{Tube}}/K_{\text{Total}}$
	AGI	Tube	Total			
300	10	7.6	17.6	No		0.43
300	9.3	10.1	19.4	No		0.52
300	11.3	9.8	21.1	No		0.46
300	11.2	7.6	18.8	No		0.40
300	3.2	11.0	14.2	Yes	20	0.77
300	3.3	15	18.3	Yes	20	0.82
300	4.1	17.2	21.3	Yes	20	0.81
300	2.0	19.9	21.9	Yes	20	0.91
3000	6.2	11.1	17.3	No		0.64
3000	6.2	14.2	20.4	No		0.70
3000	6.5	17	23.5	No		0.72
3000	7.0	18.2	25.2	No		0.72
3000	6.5	12.2	18.7	No		0.65
3000	6.0	14.0	20.0	No		0.70
3000	6.6	8.6	15.2	No		0.57
3000	0.8	17.0	17.8	Yes	24.5	0.96
3000	0.8	16.4	17.2	Yes	20	0.96
3000	0.6	18.2	18.8	Yes	20	0.97
3000	1.6	20.0	21.6	Yes	20	0.93
3000	1.5	13.2	14.7	Yes	20	0.90
3000	0.9	18.0	18.9	Yes	20	0.95
3000	0.9	23.0	23.9	Yes	20	0.96
3000	1.5	26.0	27.5	Yes	20	0.95

Table II

ULTRASONIC AGGLOMERATION OF POTASSIUM CHLORIDE SOLID AEROSOL

Tube diameter: 2-1/2 inches

Aerosol treatment rate: 0.1 cubic foot per minute

Volume Glycerine-Water Solution Dispersed (ml)	Weight of Potassium (mg) in			Ultrasonics	Frequency (kc)	Ratio $K_{\text{Tube}}/K_{\text{Total}}$
	AGI	Tube	Total			
300	2.2	2.2	4.4	No		0.50
300	2.1	2.6	4.7	No		0.55
300	2.3	2.2	4.5	No		0.49
300	0.5	2.5	3.0	Yes	25	0.83
300	0.9	4.5	5.4	Yes	25	0.83
300	0.2	4.1	4.3	Yes	20	0.96
300	0.3	4.2	4.5	Yes	20	0.93
300	0.2	3.9	4.1	Yes	20	0.96
3000	1.1	2.0	3.1	No		0.65
3000	1.1	2.0	3.1	No		0.65
3000	1.3	1.2	2.5	No		0.48
3000	1.5	1.5	3.0	No		0.50
3000	1.0	1.3	2.3	No		0.57
3000	1.5	1.6	3.1	No		0.52
3000	0.3	2.0	2.3	Yes	25	0.87
3000	0.3	2.4	2.7	Yes	25	0.89
3000	0.1	1.9	2.0	Yes	20	0.95
3000	0.1	2.8	2.9	Yes	20	0.97
3000	nil	3.2	3.2+	Yes	20	0.99
3000	0.2	1.8	2.0	Yes	20	0.90
3000	0.1	2.1	2.2	Yes	20	0.95
3000	0.2	4.0	4.2	Yes	20	0.95

Table III

ULTRASONIC AGGLOMERATION OF WATER--2.4% KEROSENE EMULSION
IN ANNULAR STANDING-WAVE VESSEL

Ultrasonic frequency: 355 kc
Diameter of inner vessel wall: 3.5 inches
Diameter of outer vessel wall: 5.06 inches

Emulsion Flow Rate (ml/min)	R* at time (minutes)					
	0	2	4	6	8	10
55	1	1.0	2.8	3.1	3.6	4.2
57	1	4.8	6.0	6.0	8.0	8.0
90	1	2.7	2.7	3	---	---

* R = $\frac{\text{Volume \% Kerosene in Original}}{\text{Volume \% Kerosene in Take-Off}}$

LIST OF REFERENCES

1. Aeroprojects Incorporated, "Applications of Ultrasonic Energy." NYO-7928, Contract No. AT(30-1)-1836, Progress Report No. 8, April 1958, pp. 8-15.
2. Ibid., p. 41, Figure 9.
3. Idem., NYO-7927, Progress Report No. 7, February 1958, p. 37, Figure 4.
4. NYO-7928, op. cit., p. 42, Figure 10.
5. Strachan, J. F. and N. L. Harris, "The Attack of Unstressed Metals by Liquid Mercury." Journal of the Institute of Metals, Vol. 85 (1956), pp. 17-24.
6. NYO-7927, op.cit., pp. 11-13.
7. NYO-7928, op. cit., pp. 16-20.
8. Ibid., pp. 21-23.
9. NYO-7927, op.cit., p. 15.
10. Ibid., p. 41.
11. Winsch, I. O. and L. Burris, Jr., "Magnesium Extraction Process for Plutonium Separation from Uranium." Chemical Engineering Progress, Vol. 53 (May 1957), pp. 237-242.
12. NYO-7927, op. cit., p. 48.
13. NYO-7927, op. cit., pp. 22-30; NYO-7928, op. cit., pp. 24-30.
14. Straughn, J. L. and W. B. Tarpley, "Investigations to Determine the Feasibility of Ultrasonic Liquid-Liquid Extraction." NYO-7936, Aeroprojects Incorporated, AEC Contract No. (30-1)-1798, February 1957.
15. Marinresco, N., "Action du piezo-quartz oscillant sur les sols et les suspensions." Comptes rendus hebdomadaires des séances de l'académie des sciences, Vol. 194 (1932), p. 1824.

LIST OF REFERENCES (Continued)

16. Lyon, W. A., "The Effect of Ultrasonics on Suspended Material in Waste Water." Sewage and Industrial Wastes, Vol. 23 (1951), p. 1084.
17. Thompson, D. and F. C. Vilbrandt, "Effect of Ultrasonic Energy on Settling of Solids in Phosphate Tailing." Industrial and Engineering Chemistry, Vol. 46 (1954), pp. 1172-1180.
18. Boyd, C. A., "The Theory of Sedimentation and Decay of Aerosols." Report BLIR-7, Chemical Corps Biological Laboratories, Camp Detrick, Frederick, Maryland, July 18, 1952.
19. Green, H. L. and W. R. Lane, Particulate Clouds: Dusts, Smokes and Mists, D. Van Nostrand Co., Inc., New York, 1957, pp. 235-237.
20. May, K. R. and H. A. Druett, "The Pre-Impinger--A Selective Aerosol Sampler." British Journal of Industrial Medicine, Vol. 10 (1953), pp. 142-151.
21. May, K. R., "The Cascade Impactor: An Instrument for Sampling Coarse Aerosols." Journal of Scientific Instruments, Vol. 22, (1954), pp. 187-195.

APPENDIX A

AEROSOL TECHNIQUES
RELATED TO FINE-PARTICLE PRODUCTION,
EVALUATION, AND COALESCENCE

APPENDIX A

AEROSOL TECHNIQUES RELATED TO FINE-PARTICLE
PRODUCTION, EVALUATION, AND COALESCENCE

Introduction

Preliminary work under Contract No. AT(30-1)-1836 has indicated that coalescence of fine particulate matter in gas streams is enhanced by the use of high-frequency sound waves, together with the use of an inert additive aerosol in the most effective size range. Development of such a coalescing principle into a practical system for chemical engineering uses requires a thorough knowledge of the mechanics of producing simulated aerosol clouds and the means for their efficient collection, as well as techniques for the accurate evaluation of the aerosols and the subsequent coalescence promoted by such additive aerosols.

For nearly 8 years Aeroprojects has been involved in aerosol research, evaluation, and device development, chiefly for the Department of Defense, for whom research work has been carried on continuously since September 1950, from the initial contract, No. DA-18-064-CML-447, to the present contract, No. DA-18-064-404-CML-259. Additional experience has been gained in collateral industrial applications. During these investigations, which have been concerned primarily with the design, development, and testing of aerosol generating devices, a well-equipped aerosol laboratory has been designed and built. Extensive study of the dynamics of aerosol behavior has led to the development and construction of identical, adequately stirred, humidity- and temperature-controlled test cells each having a volume of 750 cubic feet. Also during the course of the above work Aeroprojects has developed unique devices for atomizing both liquid and solid materials* in the particle-size range of 1-10 microns. Predictable precision has been achieved through statistically sound experimental design. Precision metering and feeding devices for both liquids and solids have also been developed.

Reliable techniques have been established for sampling aerosols and for evaluating fallout rates and aerosol recovery. Samples collected at all-glass impinger stations incorporated in the cell design can be analyzed by any of several methods, including colorimetry, turbidimetry, and ultraviolet and flame photometry. In addition, precise gating of aerosols into

* Typical liquid and meltable solid materials atomized at Aeroprojects are summarized on page 53.

Cascade impactors has been achieved, and subsequent analysis by both wash-off and optical particle count techniques has been standardized.

The substantial experience in particle-size determination obtained in this work has been reduced to routine laboratory operation with 95 percent confidence limits of the order of ± 3 percent. For the most part, particle-size distributions have been obtained through the application of stirred sedimentation theory and "Feather" analysis (Ref. 18), and these techniques appear to be applicable to the present work. Theoretically calculated aerosol size distributions as a function of time have been checked experimentally.

Ultrafine Particles Laboratory

The laboratory, illustrated in Figure 11, includes facilities for producing ultrafine particles in the 1-10 micron size range from liquids, slurries, and meltable solids (such as water, wax, mercury, glycerine, silicone oils, plasticizers, and surface-active agents), either on an experimental or a prepilot-plant production basis. A variety of special nozzles and precision metering devices have been developed to handle such atomization. A test unit is available for producing 5-10 pound samples of microspheres from meltable materials, and a prepilot plant permits the production of tonnage quantities of such materials. Equipment is also available for deposition of such atomized materials on a variety of surfaces and on granular materials.

The laboratory also contains a comprehensive complement of test and evaluation equipment, including humidity- and temperature-controlled test cells, a dry box for handling hygroscopic materials, various types of sampling and analytical equipment, and testing and measuring instruments for accurate determination of particle sizes.

The aerosol test cells, which have the configuration shown in Figure 12, were designed to provide a convenient, efficient means for the evaluation of aerosols produced from liquid or powdered solid materials. The octagonal design and the absence of sharp-angled corners minimize impingement on the cell walls and facilitate the mixing of the aerosol induced by rotation of the propeller. The cells are suitably instrumented to provide control over the major variables in the aerosolization and aerosol-settling processes. A door is provided in one panel for access to the interior of the cell and glass panels in the cell walls for visual observation of tests in process. Each cell has a total useful volume of 751.6 cubic feet, or 21,285 liters.

The air in the cell is stirred by means of a large, slow-turning propeller and associated driving system. Means are provided for humidification and dehumidification of the cell atmosphere and for measuring temperatures at various locations within the cell. A scavenging system permits expeditious replacement of the cell air between experiments.

Stirring of the aerosol contained in the cell is desirable for several reasons: The aerosol is completely mixed in a short time interval; stratification is eliminated and sampling made reliable; thermal gradients within the aerosol are eliminated and temperature variations on the inside cell surfaces minimized; and assessment of cell content according to Boyd's "Theory of the Sedimentation and Decay of Aerosols" (Ref. 18) becomes possible. Extensive fan speed and directional tests have been made to establish the effects of air currents on the aerosol clouds produced. Visual air flow studies indicated the best over-all arrangement to be fan rotation at 56 rpm with the fan blowing upwards to lift the central core of air, which results in good mixing with minimum impingement of aerosol particles on the propeller blades. Subsequent testing at sampling locations high in the cell, at mid level, and near the base have confirmed that statistically valid homogeneity is achieved in the cell within less than 1-1/2 minutes under these operating conditions.

Aerosol Evaluation

1. Sampling Techniques

At least two sampling systems may be employed for evaluating aerosols produced in the test cell. One involves the use of all-glass impinger bottles and the second employs a specially instrumented Casella Cascade impactor.

The all-glass impinger (AGI), illustrated in Figure 13, is essentially an impaction device which uses a suitable liquid as the collecting medium for the aerosol. In operation, the unit is attached to a suitable port in the wall of the test cell and air is drawn through the system at a controlled rate of approximately 13 liters per minute for intervals of time ranging from between 1/2 and 1 minute. Under operating conditions, the AGI will trap essentially 100 percent of all the aerosol which passes through it. The theory of operation of this type of sampler has been described (Ref. 19).

A modification of the AGI is the combination of a pre-impinger (BP) (Ref. 20) and the all-glass impinger, which in this case is called ABP; this combination is shown in Figure 13. The BP has the function of acting

as a selective trap for all particles larger than 5 microns, so that only those smaller than 5 microns are collected in the ABP. The selection of the AGI system or BP-ABP system is determined by the particle-size measurements that are required.

A specially instrumented Casella Cascade impactor (Ref. 21) is available for determining particle size distributions of aerosols in the test cell. The impactor has been modified in the following manner: A solenoid-operated gate placed in front of the inlet provides means for opening and closing the inlet. A large-diameter plastic tube conducts clean air from outside the test cell through the impactor for vacuum adjustment. When the solenoid is energized, the gate lifts away from the opening, and cell air is drawn through the impactor for the prescribed length of time. An impactor modified in this manner is shown in Figure 14.

2. Evaluation of Atomized Droplet Size Distribution

AGI samples are analyzed by colorimetric, turbidimetric, or other methods to determine the percent of the original mass of material which is airborne at any given time period after atomization. A series of such samples taken at intervals during 60 minutes, for example, after atomization are then used to develop the aerosol decay curve such as that illustrated in Figure 15, in which the percent of the original mass remaining airborne is plotted as a function of time after atomization.

Since aerosol fallout is a function of particle size, the cloud decay curve is routinely used for determination of particle size distribution by means of Feather analysis in accordance with theoretical treatment developed by Dr. Boyd (Ref. 18). Essentially the several slopes of the decay curve are a measure of the size distribution. The value of the ordinate intercept obtained by projection of a selected slope on the curve back to zero time is a measure of the percentage of the initial liquid mass which was atomized into particle sizes below the size corresponding to the slope. For example, Figure 15 includes slope lines calculated for droplet sizes of 4, 5, and 8 microns diameter. The intercepts indicate that 71 percent of the original mass of material passed through the nozzle was in droplets below 8 microns in diameter, 52 percent was in droplets less than 5 microns diameter, and 44 percent was in droplets of less than 4 microns diameter. Experience has shown that this method of determining particle-size distributions is reliable provided the atomized liquid does not evaporate.

In the past, glass slides from the Cascade impactor, onto which aerosol cloud samples have impacted their contained droplets, have been subjected to microscopic examination wherein the impacted droplets have been sized and counted. Data so obtained have confirmed the Boyd Feather

analysis as being a conservative method for appraisal of particle-size distribution.

Typical Atomization of Liquids with Aerojects' Type Nozzles

During the course of the last 8 years, Aerojects has developed a number of specialized atomization nozzles and through this activity has made accessible, for the first time, the production of particles in the "fog" size range, i.e., 1-10 microns. These particles are produced in the form of tiny microspheres discharged from the nozzle in an essentially flat, pancake-shaped plume, as illustrated in Figure 16. Particles in this size range are produced without recourse to evaporation of dilute solutions, and hence there is no solvent evaporation problem in utilizing such fogs.

In contrast, commercially available atomizing nozzles which are driven by compressed gas, as in the case of paint-spraying nozzles, generally produce a very wide particle-size spectrum with very few particles smaller than 40 microns. Smaller particles may be produced only by atomizing large quantities of dilute solution and permitting the 40-micron-and-above droplets to evaporate into the desired size range.

A photomicrograph of a typical as-produced fog (in this case a waxy material which was melted and atomized in the molten state) is shown in Figure 17. Obviously it is possible to produce even finer particles with the Aerojects' type nozzles by utilizing an evaporative technique, where the 1-10 micron particles are allowed to evaporate to submicron particle size.

Driving air pressure for the several nozzles ranges from 35-200 psig, and flow rates of the material being atomized range from 1/2 pound per hour for the smaller nozzles to approximately 200 pounds per hour for the nozzle shown operating in Figure 16. Further details on nozzle performance are discussed below.

Aerosols are generated and appraised in the Aerojects laboratory by delivering metered quantities of compressed air or nitrogen to the atomization nozzle under controlled conditions of pressure and temperature. For aerosolization of liquid materials, liquids may be supplied to the nozzle at precise feed rates by means of a precision liquids metering device (shown in Figure 18) developed at Aerojects.

This precision metering device may be placed outside the cell with appropriate feed lines to the aerosol nozzle, which is then mounted on top of the base cone inside the cell. Alternatively, the metering device

may be installed within the cell by replacing the existing base cone with an alternate cone designed and built to house the metering device.

General Correlations

As the result of a large number of experiments involving many liquids, aerosol properties as a function of operating conditions and liquid properties have been qualitatively related.

All data reported below were obtained with non-evaporating liquids or moltable solids in order that further size change due to evaporation might not confound particle size studies. Particle sizes discussed hereafter are those "as produced" by the nozzles.

1. Effect of Nozzle Pressure

Increasing the rate of flow of air through the nozzle decreases the mass median diameter of the as-generated particles at constant liquid flow rate. A typical example of this effect is shown in Figure 19, which illustrates the particle-size distribution obtained during atomization of polyoxyethylene sorbitan monolaurate*. The behavior illustrated here is generally typical of that found for a great many materials. From these data, it appears that the percentage of the liquid broken down into droplets of 8 microns diameter and smaller continues to increase with increasing pressure at a fairly rapid rate, while the effect on the smaller droplet size is not as marked.

2. Effect of Liquid Flow Rate

Increasing the liquid flow rate through the nozzle tends to reduce the percentage of small particles. A typical result is shown in Figure 20, which illustrates the aerosolization of sorbitan mono-oleate ** in the Aeroprojects nozzle at constant nozzle air pressure but varying liquid flow rate. It will again be noted that the effect on the 8-micron particles is greater than the effect on the smaller particles, although at very low flow rates the rate of increase of production of the smaller particles is much more rapid than those of the larger.

* Tween 20, product of Atlas Powder Co., Wilmington, Delaware

** Span 80, product of Atlas Powder Co., Wilmington, Delaware

3. Liquid Viscosity Effects

Tests were made using essentially non-evaporating glycerine-water solutions containing 21-67 weight percent glycerine and having viscosities ranging from 1.53 to 13.3 centipoises. The results of tests at a nozzle pressure of 35 psi and feed rate of 65 milliliters per minute showed a progressive decrease in the percentage of fine particles and increase in mean particle size with increasing viscosity. Similar tests were made under the same experimental conditions, using sucrose solutions in the viscosity range of 15 to 214 centipoises. At comparable viscosities, the 60-minute recoveries (percentage of original mass airborne after 60 minutes) for the two types of solutions fell within the same scatter band. In both cases, the mean particle size increased with increasing viscosity.

Because surface tension effects were found to be significant, direct comparison of viscosity effects could be made only with liquids having similar surface tensions. Aerosolization tests were made with a group of Dow-Corning 200 Series silicone fluids in the viscosity range of 9.4-50.3 centipoises and having surface tensions in the range of 19-21 dynes per centimeter; with glycerine-water solutions having viscosities of 4.5-13 centipoises and surface tensions of 51-55 dynes per centimeter; with phthalates having viscosities of 16 and 46 centipoises and surface tensions of 33-37 dynes per centimeter; and with polyoxyethylene sorbitan monolaurate atomized at varied temperatures so that viscosities ranged from approximately 25 to 375 centipoises.

The results of these tests with the several liquids show the viscosity effect to be greatest in the lower viscosity range. For example, at a feed rate of 50 milliliters per minute and a nozzle pressure of 105 psi, both the silicone liquids and the phthalates, in the viscosity range of about 10-50 centipoises, show a decrease in fine-particle recovery of about 0.15 percent per centipoise. With the glycerine solutions in the viscosity range of 5-13 centipoises, at the same feed rate and pressure, the decrease in fine-particle recovery is about 1.3 percent per centipoise. In general this viscosity effect is less pronounced at lower pressures and higher feed rates. These observations were confirmed with the test on polyoxyethylene sorbitan monolaurate over a much wider viscosity range.

4. Effect of Surface Tension

In reviewing the viscosity data from the above tests, it was noted that under identical test conditions and at comparable viscosities the silicone liquids showed smaller mean particle sizes than any of the other liquids tested (exclusive of polyoxyethylene sorbitan monolaurate), while the glycerine solutions showed the largest mean particle sizes.

A major variable among the several types of liquids was the surface tension, and the data were analyzed in terms of this characteristic. Surface tensions of the silicone liquids all fell in the range of 19-21 dynes per centimeter; the glycerol solutions, 51-55 dynes per centimeter; and for the phthalates, 33-37 dynes per centimeter.

It was observed that the mean particle size increased with increasing surface tension. As with the viscosity effect, the decrease in fine-particle recovery was greatest at the lower surface tension values. High nozzle pressures showed a more pronounced effect on recovery as surface tension increased than did low pressures. In general, it appeared that increase in surface tension from 20 to 50 dynes per centimeter showed a greater effect than increase in viscosity from 10 to 50 centipoises. This observation was confirmed by the analysis presented below.

5. Correlation of Viscosity and Surface Tension Effects

In view of the indicated effects of viscosity and surface tension, an effort was made to correlate nozzle performance with these physical properties of the liquids used. The resulting relationship, given below, appears to be valid for a wide variety of liquids over the practical range of liquid flow rates and nozzle pressures.

$$\text{Log}_{10} R_{60} = 1.165 - 0.010 \mu^{0.3} \sigma^{0.8},$$

where μ = viscosity in centipoises,
 σ = surface tension in dynes per centimeter, and
 R_{60} = percent recovery at 60 minutes.

This equation is plotted in Figure 21, together with experimental data for each of the liquids investigated. The significance of viscosity in fluid breakup by the nozzle is demonstrated to be subsidiary to that of surface tension.

Representative Materials Atomized by Aerojects' Nozzles

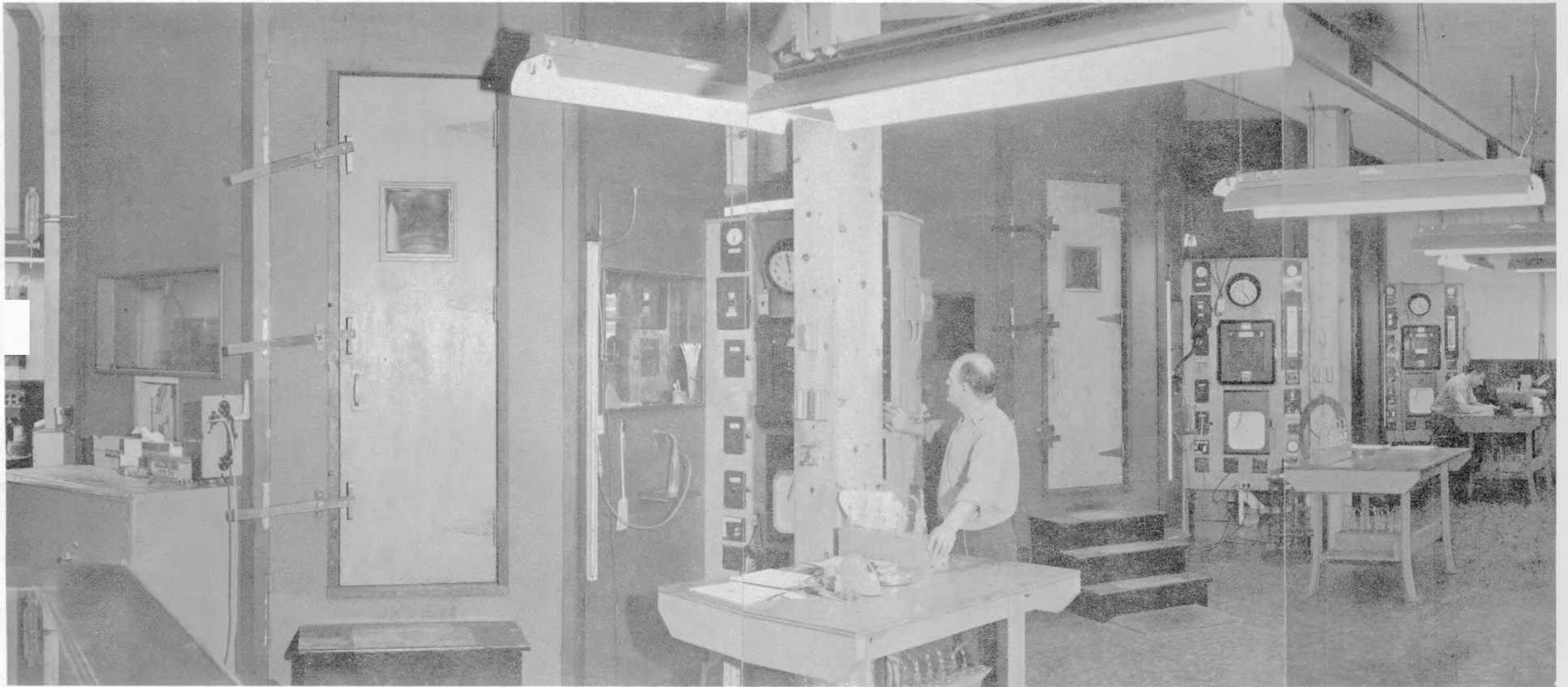
A wide variety of liquids and meltable solids have been aerosolized into the Aerojects test cells and studied by quantitative techniques. These include silicone oils of a wide viscosity range, liquid surfactants, natural and synthetic waxes of low molecular weight, molten metals, molten inorganic compounds, and slurries. Some of the specific materials are listed below.

1. Typical Liquid Materials Atomized

N-cetyl N-ethyl morpholinium ethosulfate
sorbitan mono-oleate
polyoxyethylene sorbitan tri-oleate
polyoxyethylene sorbitan monolaurate
polyoxyethylene alkyl aryl ether
tricresyl phosphate
dibutyl phthalate
butyl benzyl phthalate
5% solution of cellulose acetate in ethylene dichloride-
methylene chloride
70% sorbitol solution in water
phenol formaldehyde resin-water solution and slurry
"Carbowax 300" (polyethylene glycol - Union Carbide)
200 Series silicone oils (Dow-Corning)
Fuel oil No. 2
Fuel oil No. 5
Bunker C No. 6 fuel oil

2. Typical Meltable Solid Materials Atomized

sulfur
bismuth alloy (38.4 Bi, 30.8 Pb, 15.4 Sn, 15.4 Cd)
potassium hydroxide (technical grade)
stearic acid
dichlorodiphenyl trichloroethane (DDT)
yellow beeswax
polyethylene wax
carnauba wax
"Carbowax-4000" (polyethylene glycol - Union Carbide)
"Cardis One" (emulsifiable oxidized microcrystalline
petroleum wax - Warwick Wax Co.)
pentaerythritol
glycerol monostearate
sorbitan monostearate
lactated monoglyceride
distilled monoglyceride
mixture of glycerol monostearate, sorbitan monostearate,
and polyoxyethylene sorbitan monostearate
mixture of "hard" and "plastic" glycerol monostearate
"Crisco" hydrogenated shortening (mostly triglycerides of
fatty acids)



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Figure 11

AEROPROJECTS' ULTRAFINE PARTICLES LABORATORY

401 053

AEROPROJECTS INCORPORATED

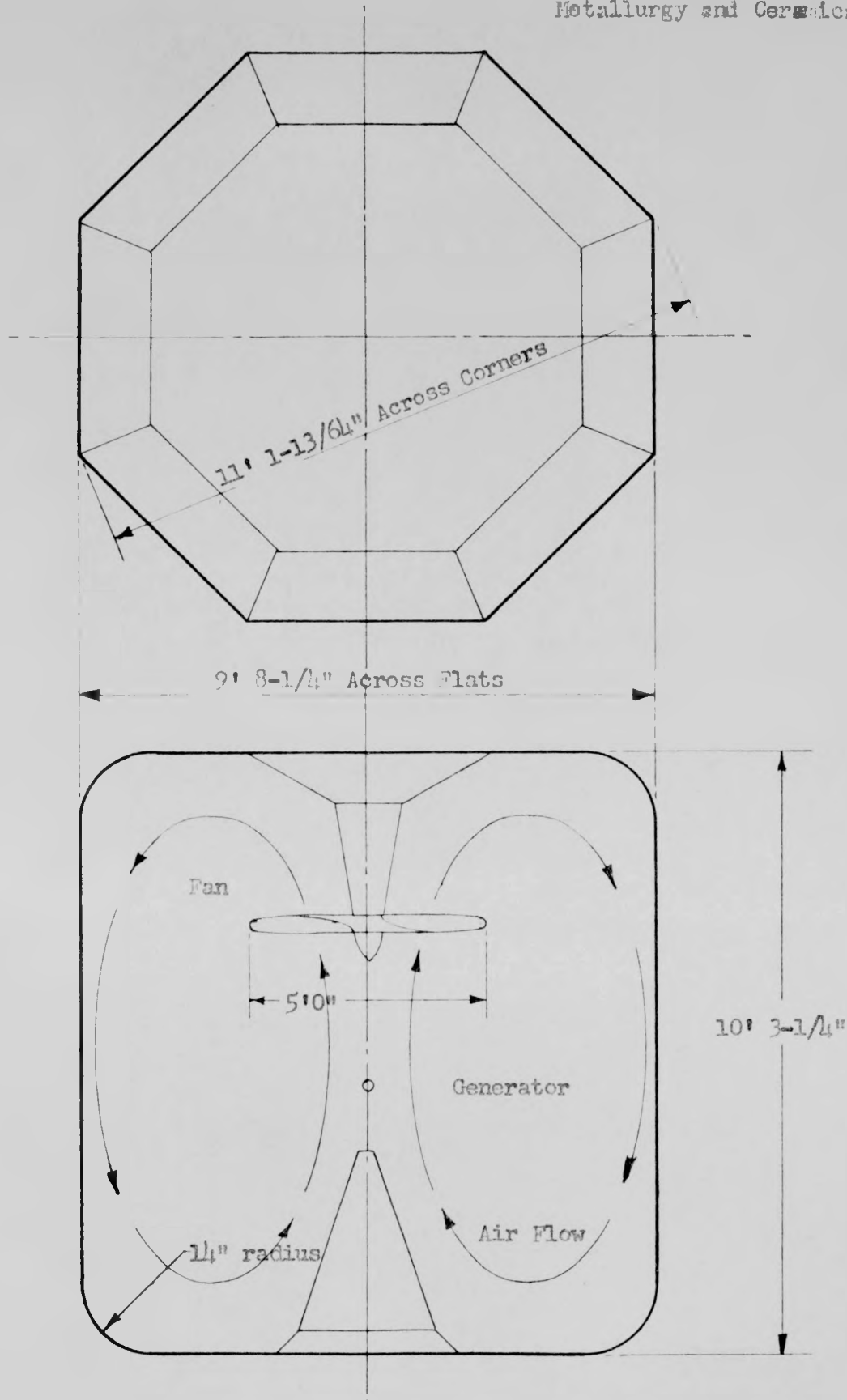


Figure 12
BASIC INSIDE DIMENSIONS
AND AIR FLOW DIRECTION OF TEST CELL

Pre-impinger

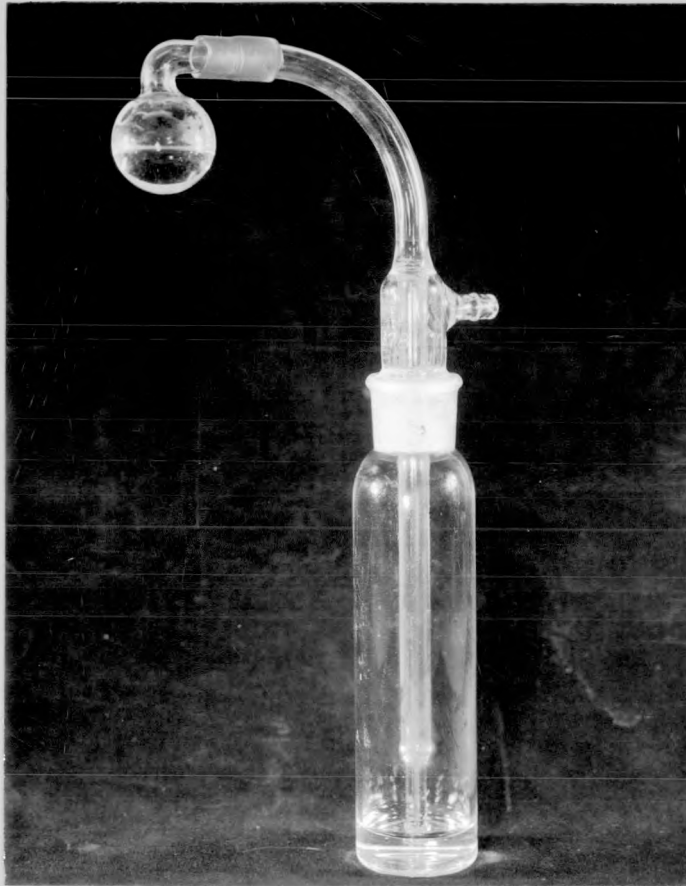


Figure 13

PRE-IMPINGER AND ALL-GLASS IMPINGER (BP-APB) ASSEMBLY
USED FOR SAMPLING AEROSOLS

Alternatively, the all-glass impinger (AGI) may be used
alone without the pre-impinger.

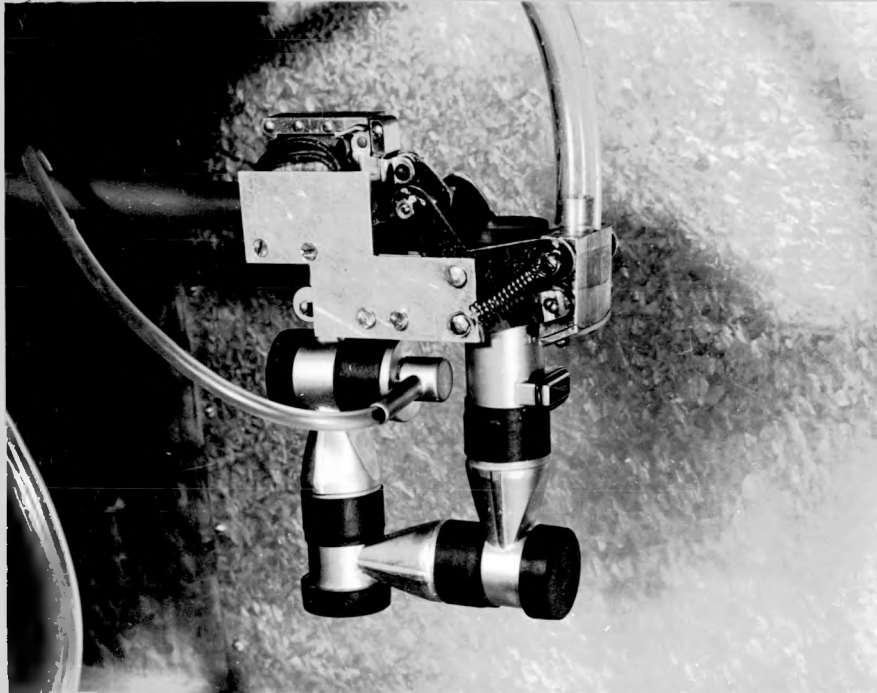


Figure 14
CASELLA CASCADE IMPACTOR
WITH SOLENOID-OPERATED GATE

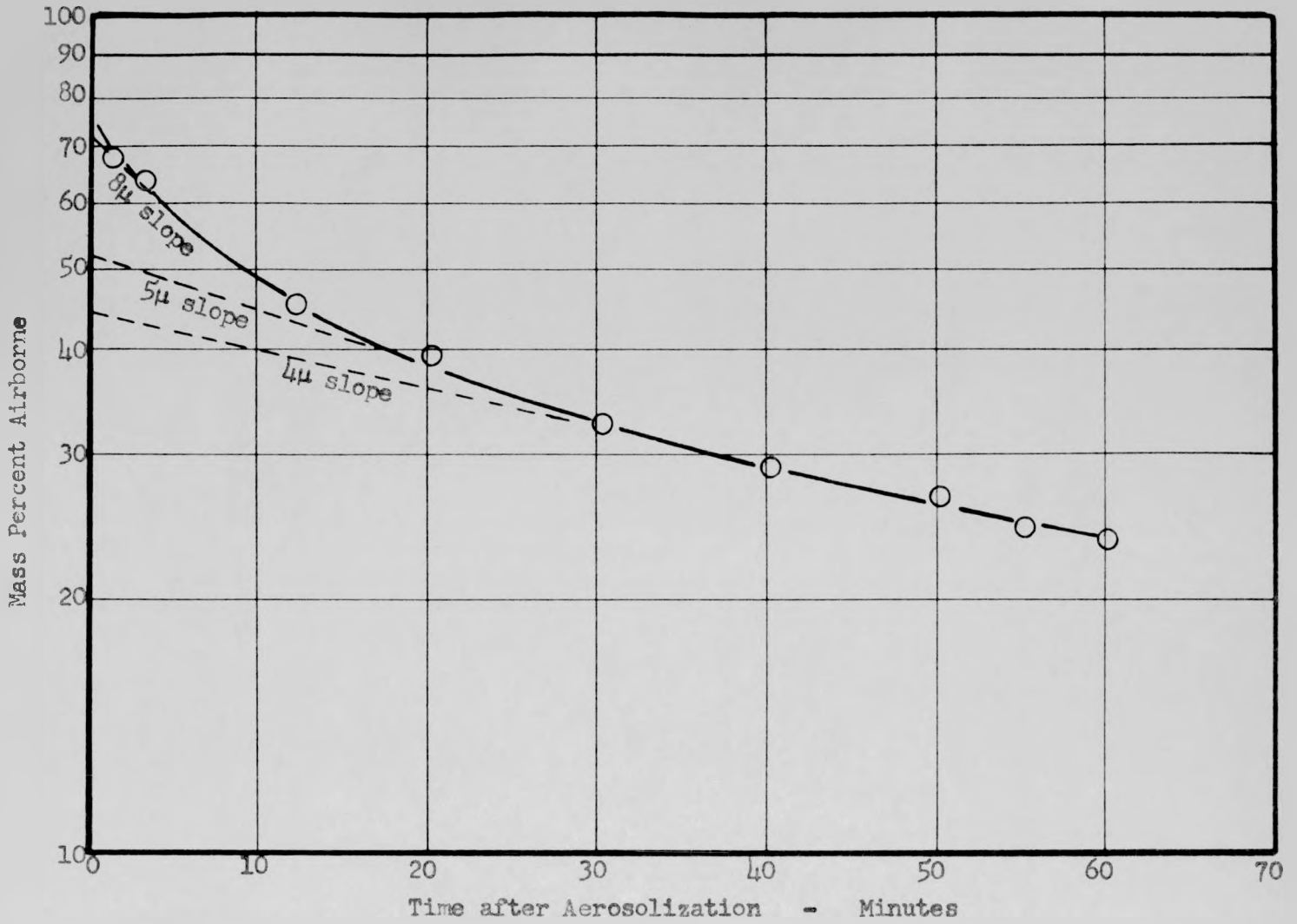


Figure 15

TYPICAL AEROSOL DECAY CURVE FOR
POLYOXYETHYLENE SORBITAN MONOLAUATE
SHOWING DROPLET SIZE SLOPE LINES
DETERMINED BY FEATHER ANALYSIS
(aerosolized at 180°F)

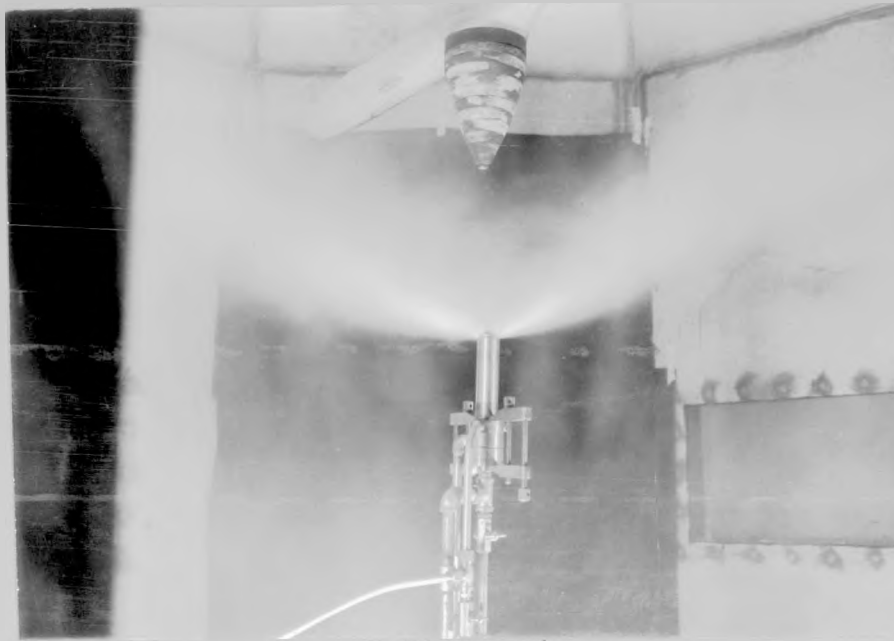


Figure 16

AN AEROPROJECTS LIQUID NOZZLE
PRODUCING AEROSOL CLOUD IN TEST CELL
(Photo taken at beginning of Atomization)

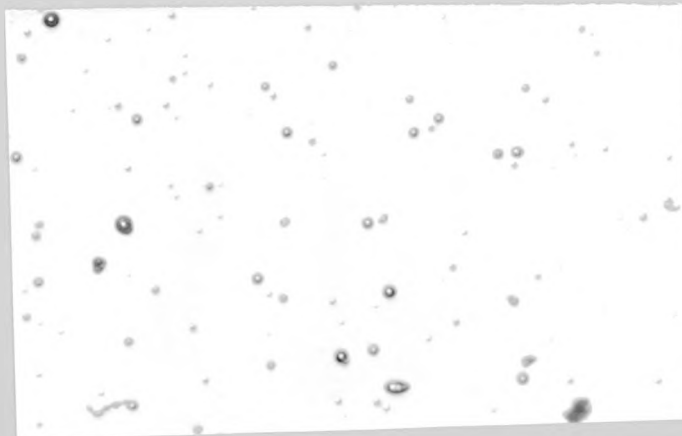


Figure 17

PHOTOMICROGRAPH OF PARTICLES OF WAX-LIKE MATERIAL
ATOMIZED IN MOLTEN STATE BY AEROPROJECTS' NOZZLE.
(Magnification: 285 X)

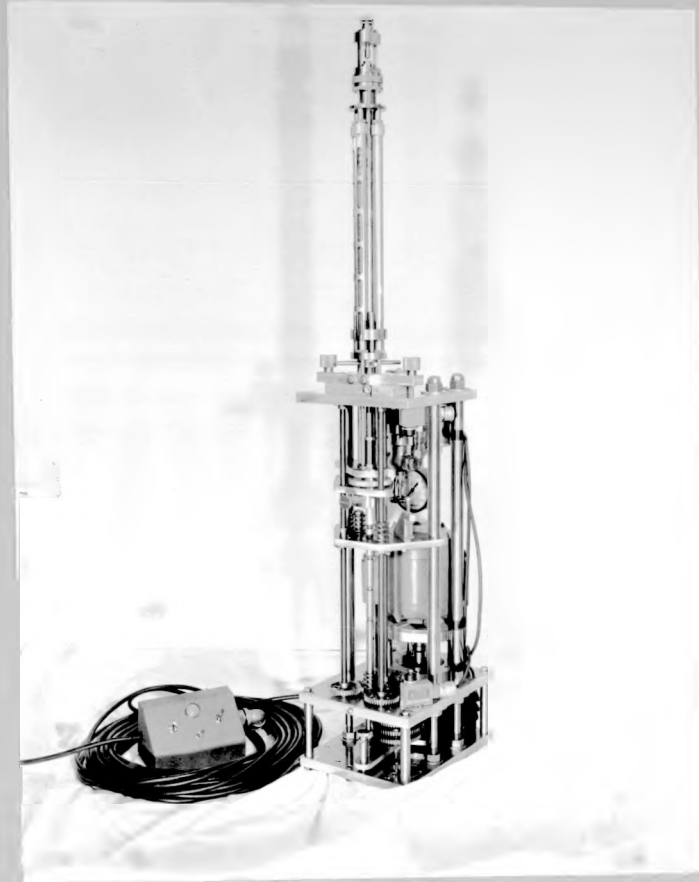


Figure 18
PRECISION LIQUIDS METERING DEVICE
WITH AEROSOL NOZZLE MOUNTED AT TOP

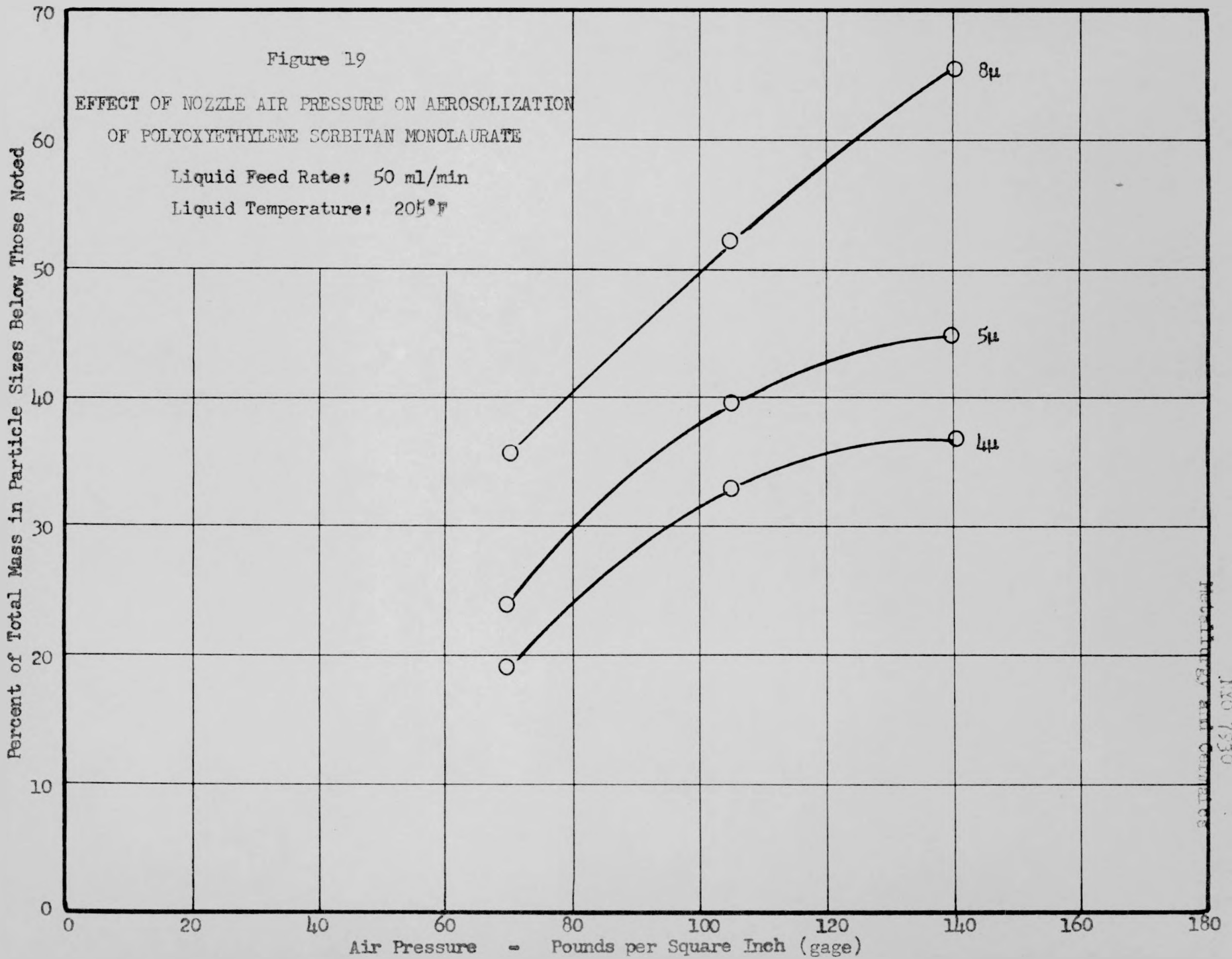
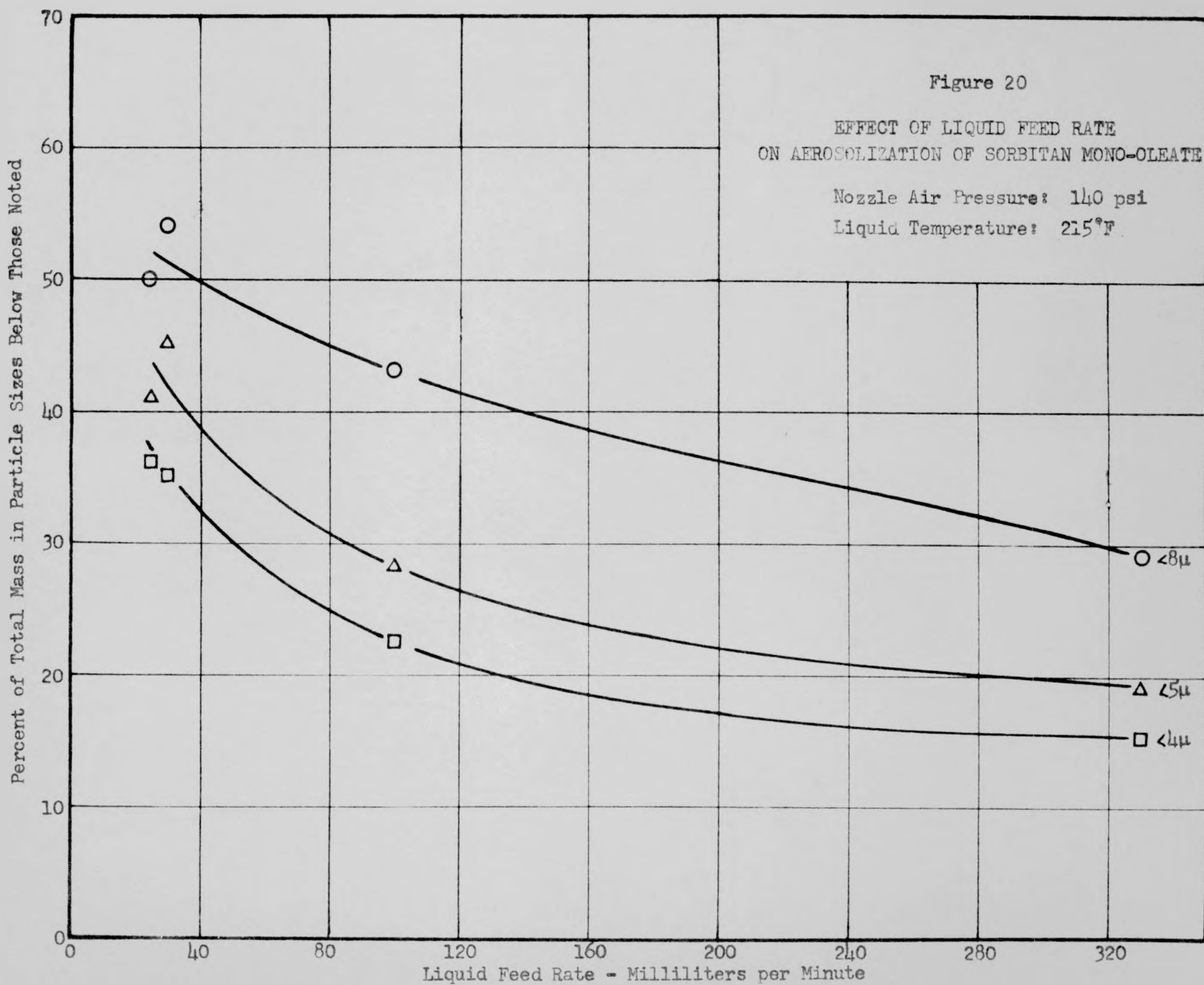


Figure 20
EFFECT OF LIQUID FEED RATE
ON AEROSOLIZATION OF SORBITAN MONO-OLEATE

Nozzle Air Pressure: 140 psi

Liquid Temperature: 215°F



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