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DEVELOPMENT OF A FLUIDIZED BED CALCINATION PROCESS FOR ALUMINUM NITRATE WASTES IN A TWO-FOOT-SQUARE PILOT PLANT CALCINER

PART III: INTERMEDIATE PROCESS STUDIES-RUNS 11 THROUGH 22

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ABSTRACT

Intermediate process studies comprising twelve runs (Runs 11 through 22) were made in a two-foot-square calciner to provide support data for the Waste Calcination Facility (WCF) and to study further the fluidized bed calcination process. For each run, the objectives, conditions, and results are given. Simulated aluminum reactor fuel processing wastes were calcined to a granular free-flowing solid under a variety of operating conditions and with various types of atomizing nozzles. Demonstration of the operability of the feed nozzle selected for use in the large-scale WCF and determination of the factors affecting the intra-particle porosity of alumina product were major results of these studies. The sodium concentration of the feed was shown to have a significant effect on the formation of alpha alumina in the product. Neither the presence nor absence of mercury in the feed had any detectable effect on calciner operation or product properties.

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PART III: INTERMEDIATE PROCESS STUDIES--RUNS 11 THROUGH 22

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I. SUMMARY

Intermediate process studies on calcination of aluminum nitrate waste solutions comprising twelve runs (Runs 11 through 22), made in a two-foot-square calciner, are described. These runs were made to provide support data for the plant-scale Waste Calcining Facility (WCF), and to study further the fluidized bed calcination process. Specific studies were directed toward: (1) demonstration of the operability of the feed nozzle selected for use in the WCF, (2) study of designs of feed nozzle caps to reduce cap erosion, and (3) determination of the factors affecting the intra-particle porosity of calcined alumina product. In addition, other process variables were studied to a lesser extent in the course of this work. Previous process studies in this unit were conducted using four small feed nozzles(10), whereas, in the present studies, a single, larger feed nozzle was tested. Equipment development during the first ten runs in this unit(10) resulted in a trouble-free pilot plant calcination system for this later series of runs.

The performance of the NaK heating system was excellent during these runs. The continued satisfactory operation of this system has demonstrated that a low pressure, high temperature, liquid metal system is a reliable and effective method of supplying heat to a fluidized bed calciner. A satisfactory low rate of corrosion of this system was observed after prolonged use.

Satisfactory operation of a feed nozzle selected for use in the WCF was demonstrated at feed rates up to 120 l/hr at a bed temperature of 400°C. Bed temperature and operating data indicate that no problem should be encountered when operating with a feed rate of 150 l/hr, the maximum design rate per nozzle for the WCF.

Erosion of the feed nozzle caps constructed of titanium and Type 347 stainless steel observed during early process studies was successfully circumvented by the substitution of boron carbide as a material of construction. In a search for methods to reduce cap erosion, several caps of different design were tested, including an extended divergent cap and two types of extended convergent caps. None of the

caps were considered superior, process-wise, to the flat-faced caps normally used. Hardened stainless steel caps appear satisfactory for use in the WCF under normal operating conditions, based on subsequent WCF operating experience.

The results of a single run suggest that a single-fluid atomizing nozzle might be used successfully to introduce feed to a fluidized bed calciner, provided that the problem of severe corrosion or erosion on the internal parts of the nozzle can be solved.

The intra-particle porosity fraction of the alumina generated by fluidized bed calcination was found to lie between 0.05 and 0.60. The factors which had a major effect on the intra-particle porosity of the alumina were bed temperature and aluminum concentration of the feed. Low-porosity alumina is generated by employing a suitable combination of low bed temperature and dilute feed. Details of this study are published in a separate report(15).

The relative amounts of amorphous and alpha alumina in the product greatly affect the product properties and dependent operating variables; high absolute densities and high elutriation rates are associated with high alpha alumina content product. The nitrate content of the product varies both with alpha alumina content and bed temperature; low nitrate values are associated with high alpha alumina values and high bed temperature.

The rate of formation of alpha alumina was shown to be dependent upon the sodium content of the feed. A sodium concentration of 0.25<u>M</u> (with 1.29<u>M</u> aluminum nitrate) in the feed resulted in production of large quantities of alpha alumina while with sodium concentrations of 0.03<u>M</u> or less in the feed, no alpha alumina was formed.

Control of average bed particle size was generally possible by selecting a suitable nozzle air-to-liquid volume ratio (NAR) or by introducing a separate high velocity air stream into the bed.

Collection and quantitative measurement of the fines removed from the off-gas by the primary cyclone was first accomplished in a satisfactory manner during the final run covered by this report.

The fluidized bed calcination process was demonstrated to be operable over wide ranges of operating conditions and feed introduction methods; the efficacy of the control mechanisms and the ability to predict and control effects of upsets of the process were also demonstrated. Additional studies, however, were necessary to determine quantitative relationships among the many variables of the process, and results of these additional studies will be reported in a subsequent report in this series.

II. INTRODUCTION

Extensive studies of methods for the ultimate disposal of radioactive waste solutions produced in processing spent reactor fuel elements are being conducted on an international scale. These efforts have been discussed at AEC Working Meetings on the Fixation of Radioactivity in Solid Media[1,2,3,], at an International Conference on the Peaceful Uses of Atomic Energy[4], and at two IAEA Symposia[5,6]. Current storage of radioactive waste solutions in large underground tanks is temporary and potentially hazardous. It is believed that converting the liquid wastes into suitable solids would minimize long term hazards due to vessel corrosion or rupture and at the same time would reduce considerably the storage volume.

One of the most promising methods of converting aluminum nitrate and other reactor fuel processing wastes into a solid form, and the most advanced technically, is the fluidized bed calcination process. This process was originally conceived by the Argonne National Laboratory Chemical Engineering Division[7]. Since May, 1955, the Technical Branch of the Idaho Chemical Processing Plant has been actively engaged in developing this process. Following initial studies in a six-inch diameter calciner[8,9], a two-foot-square calciner was built and tested[10] to obtain engineering design data for a large-scale Waste Calcination Facility (WCF)[11], to develop further the calcination process, and to test and operate a NaK heat transfer system. The intermediate process studies in the two-foot-square calciner reported herein were conducted primarily to develop support data for the large-scale unit. A nozzle development program was pursued, along with a study of the factors relating to intra-particle porosity and alpha alumina formation in the calciner product.

The four small feed nozzles used for Runs 1 through 10[10] were replaced for these later studies by a single feed nozzle identical to the one specified for the 48-inch diameter calciner in the WCF[11,12]. During the initial portion of these later investigations it appeared that flat-faced nozzle caps of titanium and Type 347 stainless steel might not be suitable for prolonged use in the pilot plant because of excessive erosion. For this reason, a significant amount of the work reported herein was directed to a study of methods to minimize nozzle erosion. However, subsequent testing in the WCF demonstrated the adequacy of both of these materials. Nozzle testing was followed in the pilot plant by a study of other significant process and product variables which had not been studied before. Included among these variables were: (1) the effect of feed concentration and temperature on product intra-particle porosity[13], (2) the effect of feed concentration and operating conditions on the formation of alpha alumina, and (3) the effect of nozzle design characteristics on fluidized bed stability. One result of these studies was that areas requiring additional development efforts were better defined.

III. PROCESS AND EQUIPMENT

1. PROCESS DESCRIPTION

A schematic diagram of the two-foot-square calciner system is shown in Figure 1. A solution of aluminum nitrate is sprayed through an atomizing nozzle into a heated, fluidized bed of suitable granular particles. (During these studies, alumina, sand, or a combination of both was used as starting bed material.) The majority of the spray droplets are deposited and calcined on the granular particles in the bed. Some of the droplets are spray dried and calcined as independent particles, most of which are carried out of the calciner by the off-gas stream, which is composed of the decomposition gases and the fluidizing gas. The alumina product, in the form of free-flowing granular particles, continuously overflows from the bed to a product collection vessel.

Heat is supplied to the fluidized bed by circulating eutectic sodium-potassium alloy (NaK) through heat exchange tubes located in the bed. An oil-fired furnace is used to heat the NaK to the required temperature (between 800 and 1400°F). Off-gas cleanup is effected by means of a cyclone, a venturi-scrubber with its associated cyclone, a York-mesh tower, and a condenser, all arranged in series. Since the pilot plant calciner was designed to operate over wide ranges of off-gas rates, no single off-gas cleaning system could be installed to give maximum efficiency for all operating conditions.

2. EQUIPMENT CHANGES

The equipment comprising the two-foot-square calciner unit was that described previously[10] except that a single feed nozzle was employed in lieu of the two pairs of opposed feed nozzles. Figure 2 is a drawing of the assembled calciner vessel showing the location of the single feed nozzle. A description of the single feed nozzle and changes of the equipment follow.

2.1 York-mesh Tower

A York-mesh tower was installed in the off-gas system following the scrubbing-system cyclone and was used during all of these runs. The tower, added to provide a coalescence surface for fine droplets of liquid from the scrubber cyclone, is a 4.5-ft section of 12-inch diameter Type 347 stainless steel pipe packed with York-mesh. Off-gas entering the bottom of the tower flows countercurrent to wash water which is discharged to the drain.

2.2 Dry Fines Return System

Changes were made in the return of dry fines from the dust discharge of the primary cyclone to the bed as part of these studies. During Runs 13 and 14, dry fines were introduced into the plenum chamber of the

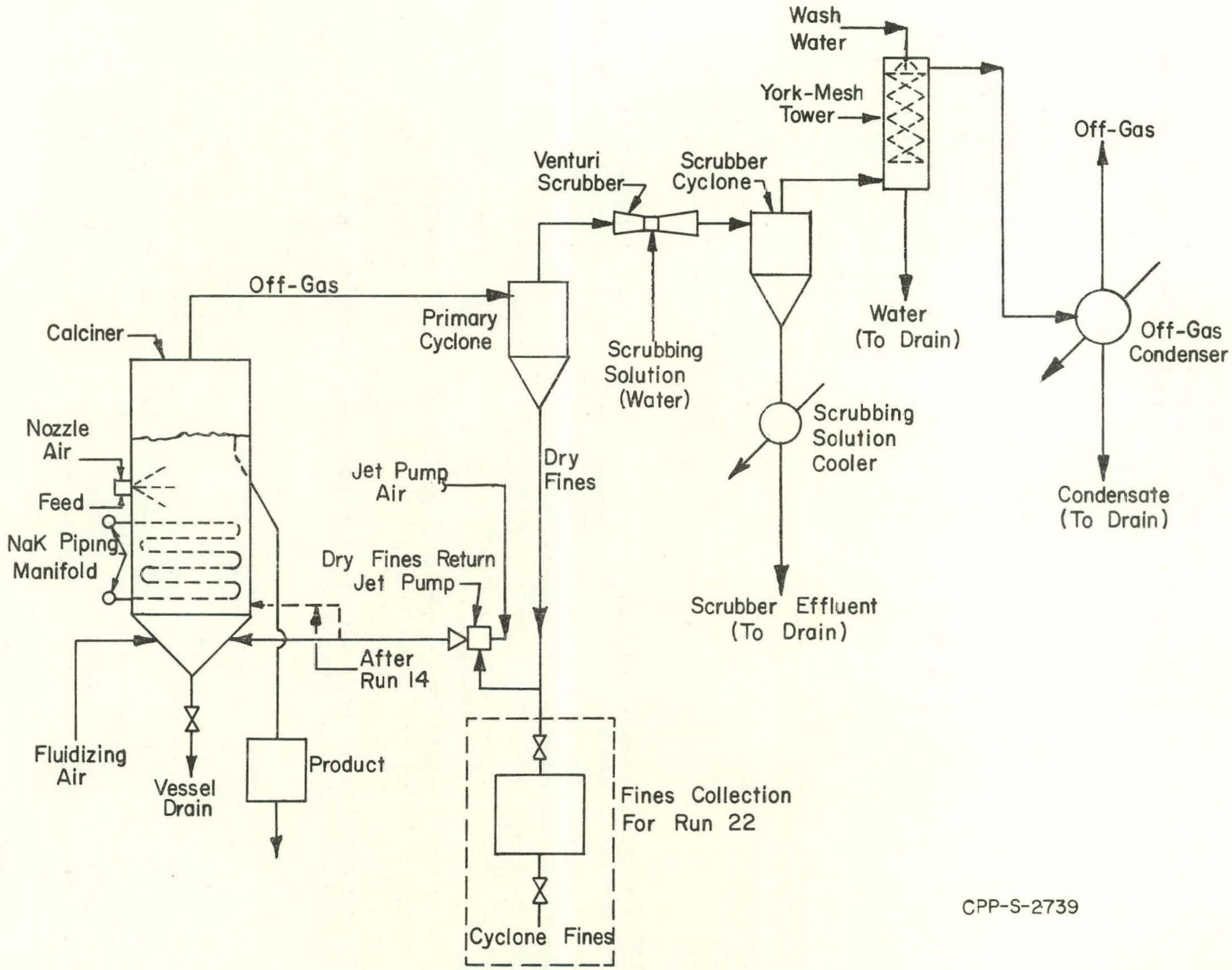


Fig. 1 Schematic diagram of two-foot-square pilot plant fluidized bed calciner system.

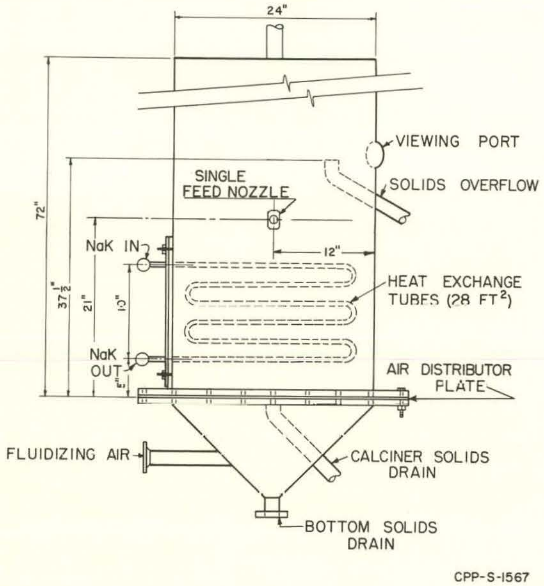


Fig. 2 Calciner vessel details.

calciner where they were mixed with the fluidizing air and forced through the orifices of the air distributor plate into the bed. During Runs 15 through 20, fines were returned to the bed through a three-inch inlet port located on the calciner wall directly below the single feed nozzle and between the air distributor plate and the NaK tube bundle to increase the probability of the returned fines being captured by spray droplets from the feed nozzle. During Runs 11, 12, and 21, fines were not returned to the bed, but were removed from the off-gas downstream of the primary cyclone. During Run 22, the fines removed by the primary cyclone were collected batchwise in a vessel similar to that in which product is collected.

2.3 Test Nozzles for Feed Introduction

2.31 The 1/2 J Pneumatic Atomizing Nozzle. A cross section of the WCF nozzle which was tested during part of these runs is shown on Figure 3. These nozzles are manufactured by Spraying Systems Company and are designated as Type 1/2 J two-fluid, external-mixing, pneumatic atomizing nozzles. Nozzle parts are fabricated of titanium; air and liquid supply connections are of Type 347 stainless steel. Liquid to be atomized issues from a central 0.25-inch diameter orifice which is surrounded by a concentric annular air orifice 0.375-inch I.D. and 0.437-inch O.D. A cleanout plunger is provided for removing plugs from the liquid orifice if necessary. The plunger, however, was not used in pilot plant studies. The 1/2 J nozzle was used during all of these runs except Run 20 in which a single fluid atomizing nozzle was used.

2.32 Feed Nozzle Caps for the 1/2 J Nozzle. The nozzle cap of the 1/2 J nozzle, as shown on Figure 3, is a standard flat-faced cap. Four additional different types of caps for the 1/2 J nozzle were tested; an extended divergent cap was used during Run 13, two types of extended convergent caps were used during Runs 14 and 19, a boron carbide, modified flat-faced cap was used during Runs 21 and 22. Standard flat-faced caps were used during the other runs made with this nozzle. The description and design, materials of construction, and operation and wear rate data of the caps tested are included in Table I in Section V of this report.

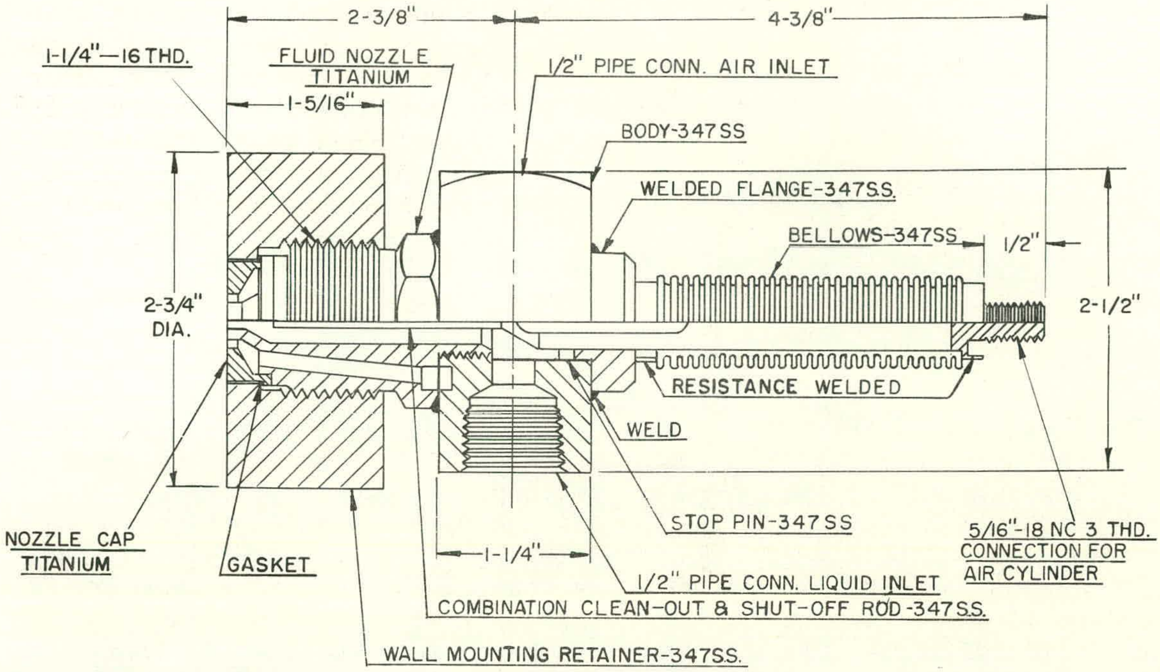


Fig. 3 Cross section of pneumatic atomizing nozzle (Spraying Systems Company, Type 1/2 J, with combination clean-out and shut-off needle.)

2.33 The 1/4 LN Single-Fluid Atomizing Nozzle. A single-fluid atomizing nozzle was used to introduce feed to the calciner during Run 20. The nozzle was manufactured by Spraying Systems Company and is designated as a Type 1/4 LN No. 12, single-fluid atomizing nozzle; the orifice diameter of this Type 316 stainless steel nozzle is 0.076 inch. The original hexagonal nozzle cap was machined to a cylindrical shape and then threaded for use with the existing nozzle mount in the calciner wall. A separate jet grinder was used in conjunction with the nozzle to provide small seed particles by impingement of a high velocity air stream into the bed. The jet grinder consisted of five 1/8-inch diameter orifices in a blind flange which was installed on the calciner vessel between the support plate and the lower NaK tube, opposite the dry fines return port. The air flow rate to each of the orifices was separately controlled.

2.4 Thermocouples

Additional thermocouples, bringing the total to 14, were installed throughout the fluidized bed prior to these studies. It was necessary later to remove two of the thermocouples because of their proximity to the spray zone; cakes built up on the thermocouples, then broke off into the bed. A moveable thermocouple, inserted into the bed through an opening in the calciner wall and sealed with a packing gland, was used for a short time during a special study to obtain temperature profile data in the spray zone.

2.5 Venturi Scrubber and Demister Cyclone

Two different venturi scrubbers were used during these runs. A scrubber with a 5/8-inch diameter throat and a 1-1/2-inch diameter connecting pipe to the scrubber cyclone was used during Runs 11 through 18E. During subsequent runs a larger scrubber was used, 1-3/4-inch diameter throat and a 4-inch connecting pipe, to reduce the high gas-liquid velocity and minimize erosion of the scrubber cyclone. The penalty for using the larger off-gas equipment was less efficient separation of solids from the off-gas; however, this caused no operating problems.

3. EQUIPMENT OPERATION

Equipment and operation were generally satisfactory during these runs, thus verifying that a unit capable of extended trouble-free operation was developed during the initial process studies in the two-foot-square calciner[10]. An exception was difficulty associated with the air-jet pump used to return fines from the bottom of the primary cyclone to the bed; however, this was not of serious consequence to the objectives of these runs. Erosion of the mixing section and sizing of the air jet were troublesome. The erosion can be circumvented by use of ceramic liners for the throat of the jet. Sizing a jet for widely varying and unknown solids loading of the dry fines gas is difficult.

Erosion in pipe bends in the off-gas system was experienced during these runs. Elimination of some of the piping bends and lengthening of the radius of curvature of the remaining bends circumvented this problem.

4. NaK HEATING SYSTEM

The operation of the recirculating NaK heating system was quite satisfactory during these runs. The continued excellent operating performance of this system has demonstrated that a liquid-metal system is a reliable and effective method of supplying heat to a fluidized bed calciner.

4.1 Operation

At the conclusion of the runs reported herein, the system had been heated from room to operating temperature a total of 171 times. Over the same period, the system had been operated a total of 6914 hours with the NaK temperature above 1000°F at the inlet to the calciner and for 2779 hours with this temperature below 1000°F.

Minor problems included leakage of NaK through a faulty valve to a storage vessel, and an electrical short circuit in the NaK electromagnetic pump. In addition, one Carpenter-20 (Cb) tube of the NaK heat exchange bundle in the fluidized bed was eroded to a depth of 53 mils by impingement of air from one orifice of the inappropriately located jet grinder. The original wall thickness of the tube was 83 mils.

Some, but much less, erosion of adjacent tubes in the bundle was also incurred. Three eroded tubes of the bundle were replaced prior to Run 21.

4.2 Service Test Evaluation of Corrosion

The direct-fired Type 316 stainless steel NaK heater bundle in the furnace and the Carpenter-20(Cb) heat exchanger bundle in the calciner were inspected for corrosion during these runs; the results are discussed below for each of the systems. It was generally concluded that these materials were well chosen for the applications[14,15].

4.21 Direct-Fired Liquid Metal Bundle. An inspection of the Type 316 stainless steel tube bundle was made after a total of 6115 hours of operation, 5273 hours with the NaK to the calciner above 1000°F and 842 hours with this temperature below 1000°F, and after a total of 115 startups. During this period, the 500,000 Btu/hr burner was supplied with ASTM D 396-48T Grade No. 2 fuel oil.

Visual examination of the bundle indicated that the tubes had suffered negligible corrosion. All tubes were coated with a porous, rather tenacious, non-uniform scale. Numerous small pits, estimated to be less than 5 mils deep, were found under the scale. Micrometer measurements on one-half of the 35 vertical connecting tubes showed a maximum loss of 17 mils. This value represents about 2.3 mils per month loss during 5273 hours at operating temperatures above 1000°F, or 2.0 mils per month loss during the total period of service. No evidence of preferential corrosion was found on either the top or bottom headers.

A later inspection of this system after a total of 9089 operating hours (6359 hours above 1000°F), indicated a lower overall rate of corrosion for the extended period of only 1.4 mils/month.

4.22 Fluidized Bed Heat Transfer Tubes. A tubular section for examination was cut from the Carpenter-20(Cb) heat exchanger which had been in NaK-fluidized bed heat transfer service for 2206 hours above 1000°F and for 611 hours below 1000°F. Tube dimensions, by micrometer measurement, were 0.750" O.D., 0.574" I. D., and 0.088" wall thickness. These dimensions are well within the tolerance limits for new 3/4-inch O.D. x 14 BWG tubing. Accordingly, during the 2817 hours of operating time, corrosion associated with liquid NaK and the calcination product appears to be negligible.

Spot determination of the outside diameter of the tubes after a total of 6115 hours service showed the diameter was 0.745" ± 0.005". This represents a maximum possible loss of 10 mils; i.e., a corrosion rate of less than 1.2 mils per month.

IV. SCOPE OF CONDITIONS AND VARIABLES STUDIED

Providing support data for operation of the WCF was the major objective of most of these studies. Therefore, operating conditions employed were, where possible, those intended for operation of the WCF. In cases where these conditions were not yet established, efforts were made to identify operable ranges for WCF operation.

1. FEED COMPOSITION

The two feed compositions generally used during these runs are as follows:

	Concentrated	Dilute
Aluminum nitrate, M	1.95	1.29
Nitrate acid, M	1.25	2.84
Sodium nitrate, M	0.089	0.078
Mercuric nitrate, M	0.006	0.015

The concentrated feed, the composition used in previous studies[10], was used in Runs 11, 16, and 17. While this composition does not correspond precisely to that of the liquid in any of the ICPP waste tanks, it is similar to that of the liquid stored in all of them.

The dilute feed represents an early estimate of the composition of the combined raw (fresh) feed and recycled scrubbing solution, based on the assumed insolubility of the alumina in the scrubbing solution. This feed composition was employed in Runs 12, 13, 14, 15, 19, 21, and 22.

The composition of the dilute feed was adjusted during Run 18, which consisted of 14 separate operating periods, by varying the aluminum concentration from 0.8 to 1.95M to study the effect of the feed aluminum concentration on the intra-particle porosity of the alumina product. The sodium concentration of the dilute feed was adjusted to 0.01 M for Run 20 and was varied from 0.03 to 0.25M during Run 22. Mercury was removed from the dilute feed for a portion of Run 21.

2. BED TEMPERATURE

A bed temperature of 400°C was employed in all of these runs except for Runs 11, 17 and 18 and for part of Run 15. A bed temperature of 500°C was employed during Run 11 and for part of Run 15; and a temperature of 425°C was employed during Run 17. During Run 18, which consisted of 14 separate operating periods, the bed temperature was varied from 250 to 550°C to determine the effect of bed temperature on the intra-particle porosity of the alumina product.

3. SUPERFICIAL FLUIDIZING VELOCITY

The superficial fluidizing velocity was not varied extensively for study during this series of runs. A superficial fluidizing velocity of 0.78 ft/sec was used in Run 11, 0.90 ft/sec in Run 12, and 1.0 ft/sec in the remainder of the runs. During a special attrition test, superficial fluidizing velocities between 0.78 and 1.15 ft/sec were employed.

4. FEED NOZZLE AIR RATE

The feed nozzle air rate is generally expressed as the feed nozzle air-to-liquid volume ratio (NAR). This ratio (NAR) has been useful in characterizing, in a general way, the nature of the spray from the feed nozzles. For consistency in applying this ratio, the air volume was determined at the metered temperature and the calciner pressure. A high NAR value produces a spray having a large number of very small droplets; a low NAR produces a spray having fewer but larger droplets. Significant grinding of the bed has occurred with higher NAR values; thus, NAR adjustment provides a means of controlling particle size. During the process studies of the 1/2 J pneumatic nozzle, defining operable ranges of NAR values and determining the response of the bed particle size to NAR changes were part of the testing program. NAR values from 120 to 1100 were employed.

V. PROCESS STUDIES AND RESULTS

Process studies employing a single atomizing nozzle provided data directly applicable to the WCF. These studies included determination of operable feed rates and nozzle air-to-liquid volume ratios, and development of a suitable nozzle cap. A single-fluid feed nozzle was tested in one run as a possible alternate means of introducing feed. Considerable data of process significance were obtained simultaneously with nozzle testing. Included in these studies were a determination of the factors affecting the intra-particle porosity of alumina product, a study of some of the factors affecting the rate of formation of alpha alumina, and the beginning of a study of factors affecting the rate of elutriation of solids from the calciner. Product properties were observed over a wide range of operating conditions.

Detailed data summaries for each of the runs are presented graphically in the Appendix. Included with these summaries are the run objectives, results, operating conditions, and equipment operation. These data may be of interest to investigators of fluidized beds as a guide for expected ranges of some of the variables.

The terms used in this report and the variables studied are defined in the Appendix.

1. TESTING OF 1/2 J PNEUMATIC ATOMIZING NOZZLE

The process design of the WCF specifies a feed rate of 150 l/hr for each of two 1/2 J nozzles, a feed rate about seven times the highest rate per nozzle that had been previously studied. The mass and heat transfer rates in a fluidized bed must be adequate to calcine the feed sprayed into a narrow (18° solid spray angle) zone of the fluidized bed, and bed caking can undoubtedly be brought on by excessively high feed rates to a single nozzle. Although the calibration and atomization testing of the 1/2 J nozzle was satisfactory(12), the need for nozzle testing in actual calcination runs was apparent.

1.1 Operability

The operability of a single 1/2 J feed nozzle with a standard flat-faced cap (Table I) was demonstrated at a feed rate of 80 l/hr during Run 11 and at a feed rate of 120 l/hr during Run 12. Operation during both of these runs was satisfactory. In order to establish the lower operable limit of NAR, during Run 11 the NAR was reduced from the initial 500 value to 120 which was used for a short period before run termination. A subsequent examination of the calciner bed showed no evidence of caking; thus, although a minimum operable limit of NAR was not established, a feed rate of 80 l/hr through a single feed nozzle was calcined satisfactorily without caking, even at the relatively low NAR of 120, for a short period. Bed caking was not observed during Run 12, even with a relatively low NAR of 300 and the 120 l/hr feed rate. Both of these runs were terminated because of large MMPD which resulted in poor heat transfer between the NaK tubes and the bed.

Temperature profiles of the bed at the center line of the spray nozzle showed that normal bed temperatures prevailed beyond 12 to 15 inches in front of the nozzle. Little difference in temperature profile of the spray zone was noted with either water or regular feed at rates between 80 and 120 l/hr. Based on these two satisfactory runs, operability of the 1/2 J nozzle was adjudged satisfactory. Although a feed rate of 150 l/hr, the maximum WCF design feed rate per nozzle, was not achieved during these runs; no problems are expected at the higher feed rate.

1.2 Erosion of Caps

The original standard flat-faced nozzle cap fabricated of titanium and a duplicate cap of Type 347 stainless steel were used during Runs 11 and 12, respectively. Both of these caps suffered excessive erosion. The erosion occurred on the flat face of the nozzle cap near the annular atomizing air orifice. Data on wear of nozzles are given in Table I for all caps tested.

Nozzle cap erosion was caused by the circulation pattern of particles near the 1/2 J nozzle located below the surface of the fluidized bed. It is believed that the atomized feed and nozzle air issuing from the nozzle produce a low pressure region which induces a flow of bed solids to sweep across the nozzle face before they are propelled by the nozzle spray. Nozzle erosion is caused probably by some function of the following factors: (1) design, (2) material of construction, (3) nozzle operating conditions, (4) location in bed, (5) physical properties of bed particles, (6) bed temperature, and (7) characteristics of the feed solution.

Attempts were made to prevent erosion of the nozzle cap by changing the design of the caps -- in effect distributing the circulation pattern of the solids -- and by fabricating the nozzle cap from various materials. The latter method proved to be the most effective. A boron carbide cap only slightly different than the standard flat-faced cap had negligible erosion after 623 hours of operation.

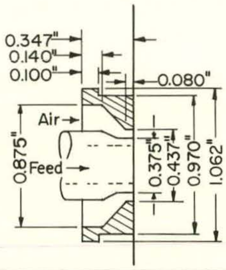
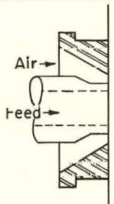
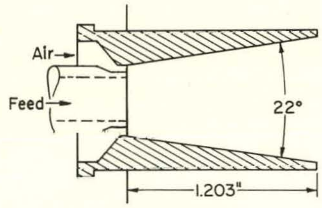
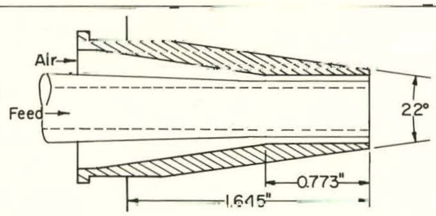
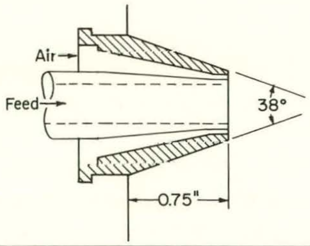
1.3 Testing of Feed Nozzle Caps

The various cap configurations tested are shown in Table I along with operating and wear data. None of the caps, process-wise, was considered superior to the standard flat-faced caps.

1.31 Extended Divergent Nozzle Cap. An extended divergent nozzle cap was tested during Run 13. With this type of cap, the atomizing air and liquid feed streams were mixed internally within the cap, rather than externally in the bed as occurs with use of the flat-faced cap. Although the erosion of this cap was negligible, process-wise, the performance of the cap was unsatisfactory. Adjustment of NAR was not adequate for controlling the mass median particle diameter (MMPD). A NAR value of 1100 at a feed rate of 45 l/hr failed to retard an increase in MMPD, and the run was terminated when the MMPD exceeded 1.1 mm.

TABLE I

DESCRIPTION AND OPERATING DATA FOR FEED NOZZLE CAPS TESTED ON THE 1/2 J FEED NOZZLE

Description	Pertinent Dimensions (Cross Section)	Material of Construction	Run On Which Tested	Operating Time (Hrs.)	Rate of Erosion
Standard Flat-Faced Cap. External Air-Liquid Mixing.		Ti	11	272	2.9 g/yr
			18	29	2.9 g/yr
		347 SS	12	172	4.0 g/yr
			18	99	4.0 g/yr
		440-C SS	15	106	2.6 g/yr
			18	420	0.07 g/yr
		Ti-- Flame Sprayed With Alumina	16	205	0.53 g/yr
			17	388	—*
Boron Carbide, Modified, Flat-Faced Cap. External Air-Liquid Mixing.	 ← Reference Line For Inside Of Vessel Wall. (Typ. all nozzles)	B_4C	21	360	None
			22	263	None
Extended Divergent Cap. Internal Air-Liquid Mixing.		347 SS	13	140	Negligible
Long Extended Convergent Cap. External Air-Liquid Mixing.		347 SS	14	169	0.2 g/yr
Short Extended Convergent Cap. External Air-Liquid Mixing.		440-C SS	19	216	1.0 g/yr

* Penetration of the alumina coating occurred during Run 17; thus a weight loss is not given.
Note: All diametrical dimensions not shown are identical with those of the standard flat-faced cap

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It is possible that, with the addition of an auxiliary means of controlling particle size, the extended divergent nozzle could be used. The formation of numerous large agglomerates of particles, which were removed from the final calciner bed, indicates another significant problem associated with this nozzle cap. Because of the uncontrolled MMPD and agglomerate formation, the extended divergent nozzle cap was not used again.

1.32 Long Extended Convergent Nozzle Cap. A long extended convergent nozzle cap was tested during Run 14. Although the use of this nozzle presented no serious problems during calcination, it appeared to be overly sensitive to changes in the NAR. A relatively small change in the NAR resulted in a large change in the product MMPD. During one part of the run, an increase in the NAR from 275 to 426 was accompanied by a reduction in MMPD from 0.62 to 0.36 mm in only nine hours. Other adjustments in NAR and resultant MMPD values indicated that stability of MMPD might have occurred in a relatively narrow NAR range of 275 to 300. This narrow operable range and the relatively sensitive response to changes make use of this extended convergent nozzle cap undesirable and it was not used again.

1.33 Short Extended Convergent Nozzle Cap. In Run 19, a short extended convergent nozzle cap was tested. Use of this nozzle cap is unattractive because of formation of caked material and production of abnormally large quantities of elutriated fines. At run termination, about 75 per cent of the calciner support plate inlet nozzles were found to be at least partially obstructed by caked or packed alumina. Bed caking was believed to be a direct result of using the short extended convergent nozzle cap and it was not used again.

1.34 Boron Carbide (Modified) Flat-Faced Nozzle Cap. A modified flat-faced nozzle cap, constructed of boron carbide, was tested in Runs 21 and 22. Operation was satisfactory both process- and erosion-wise, although a relatively high NAR was required to produce a stable MMPD in an amorphous bed.

During the first six days of operation of Run 21, changes in the NAR from 400 to 500, and then to 600, failed to retard an increase in the MMPD. The MMPD increased from 0.26 mm (sand starting bed) at startup to 0.99 mm at the time of a shutdown for repair of the air compressor. After the shutdown, a visual inspection revealed that a deposit of caked alumina in the form of an extended divergent nozzle had formed around the feed nozzle. It is possible that this deposit had the same effect on MMPD control as the extended divergent nozzle used in Run 13 when an increasing MMPD could not be retarded with a NAR of 1100. When Run 21 was resumed with a cleaned nozzle cap, the MMPD dropped from 0.98 mm to a relatively stable 0.5 mm within 48 hours at a constant NAR of 600. An inspection of the nozzle after termination of Run 21 revealed no caked alumina around the nozzle. The reason for the initial caking around the nozzle may be that adequate atomization was not obtained at a NAR of 400.

During Run 22, operation with the modified flat-faced cap of boron carbide was similar to that during Run 21. At equivalent operating conditions, the MMPD stabilized at essentially the same value (0.5 mm) in both of these runs. A small cake, 1/2-inch high, was found partly surrounding the cap at the completion of the run.

A visual inspection of the boron carbide cap after a total of 623 hours of operation during Runs 21 and 22, revealed no detectable erosion; machining marks were still evident on the exposed face of the cap. Because of the fragile nature of boron carbide, the cap was left in place for additional testing.

2. TESTING OF SINGLE-FLUID ATOMIZING NOZZLE

A Spraying Systems Company, single-fluid atomizing nozzle, Type 1/4 LN No. 12, was used during Run 20 for feed introduction in conjunction with a jet grinder to control particle size. The results of this run indicate that a single-fluid nozzle might be successfully used to introduce feed into a fluidized bed calciner, provided that the problems of severe corrosion or erosion to the internal parts of the nozzle are solved. At the completion of the nine-day run, the orifice of the single-fluid nozzle had increased from the original diameter of 76 mils to 150 mils. Some corrosion, and perhaps concurrent erosion, occurred. The increase in orifice diameter was accompanied by a gradual decrease in pressure drop across the feed nozzle from 40 psi to 15 psi at a constant feed rate of 40 l/hr.

The jet grinder satisfactorily controlled the MMPD. However, it generated significant quantities of fine solids which were elutriated from the calciner and passed through the primary cyclone. Since other methods of furnishing new particle nuclei are available, such as addition of fine sand, particle size control probably can be accomplished satisfactorily when using a single-fluid feed nozzle.

3. STUDIES OF THE FACTORS AFFECTING THE INTRA-PARTICLE POROSITY FRACTION OF THE PRODUCT

Factors affecting the intra-particle porosity, a measure of the pore space in the alumina particles, were studied to determine means to effect a greater volume reduction of liquid waste to solids during calcination. This study was completed during these process studies and details are published in a separate report(13).

The intra-particle porosity fraction of the alumina generated by fluidized bed calcination was found to vary from 0.6 to 0.05, equivalent to a sevenfold to twentyfold reduction in volume when compared to aqueous waste. Factors having a major effect on the intra-particle porosity of the alumina are bed temperature and feed aluminum concentration. Low-porosity alumina was generated by employing a suitable combination of bed temperature and dilute feed as shown in Figure 4.

Some minor effects were also observed. Use of unusually high concentrations of sodium in the feed appears to cause a slight decrease in the intra-particle porosity of calcined alumina. Alpha alumina, if not created by the addition of large amounts of sodium in the feed, generally causes a slight increase in intra-particle porosity. No other factor was found to have a significant effect on product intra-particle porosity.

Much of the data on intra-particle porosity were obtained in a series of short operating periods of Run 18.

4. CRYSTALLINITY OF THE PRODUCT

Although alumina can exist in a number of crystalline forms and as amorphous, the calcined product has usually been either amorphous alumina or a mixture of amorphous and alpha alumina. On rare occasions, the gamma crystalline form of alumina and crystalline sodium nitrate have been observed in the product, but because of a lack of a suitable standard for the X-ray diffractometer, absolute amounts in the product were not determined. Material not indentifiable as crystalline by X-ray diffraction analysis has been defined as amorphous.

The significant direct effect of the relative amounts of amorphous and alpha alumina in the product on product properties and its indirect effect on many of the variables of the process were detected during the initial process studies[10]. These effects were further defined during these studies.

4.1 Effect of Alumina Crystalline Structure on Product Properties and on the Process

The relationships between product properties and alpha alumina content were obtained from data of these and the first ten runs[10]. These data and certain related process effects are presented in this section.

4.11 Absolute Density of Product. A relationship between the absolute density and alpha alumina content is shown on Figure 5. Absolute densities ranged from 2.6 g/cc for amorphous alumina to 3.8 g/cc for alumina containing 60-80 per cent alpha alumina. Reasons for the difference in absolute densities of the two correlations of Figure 5 are unknown. As would be expected, the absolute density approaches 3.97 g/cc, the reported value[16] for alpha alumina, as the alpha content approaches 100 per cent.

4.12 Bulk Density of Product. The bulk density of the product was a function of total porosity and absolute material density, and hence was indirectly affected by its alpha alumina content. Inter-particle void fraction for as-poured granular alumina product has been exceptionally constant at about 41 per cent. The effect of intra-particle porosity has a significant effect on the bulk density of the product[13]. Product bulk densities from 0.6 to 1.6 g/cc were observed.

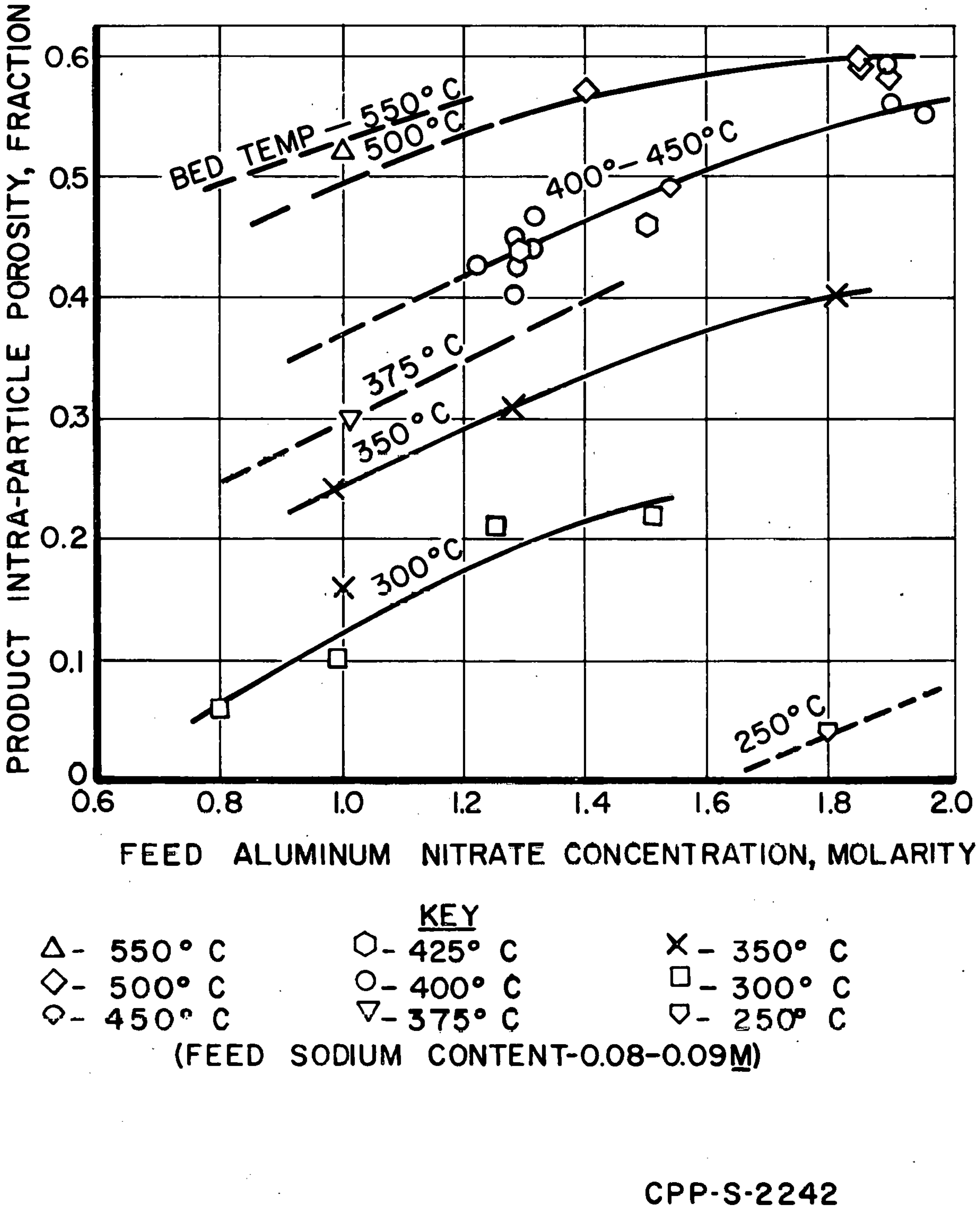

Fig. 4 Effect of aluminum feed concentration and bed temperature on the intra-particle porosity of amorphous alumina produced under a wide variety of other operating conditions.

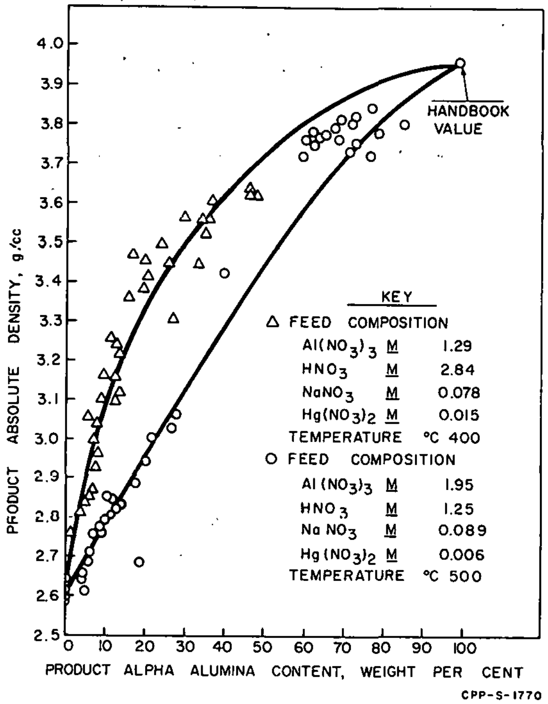

Fig. 5 Effect of alpha alumina content of product on the absolute density of product.

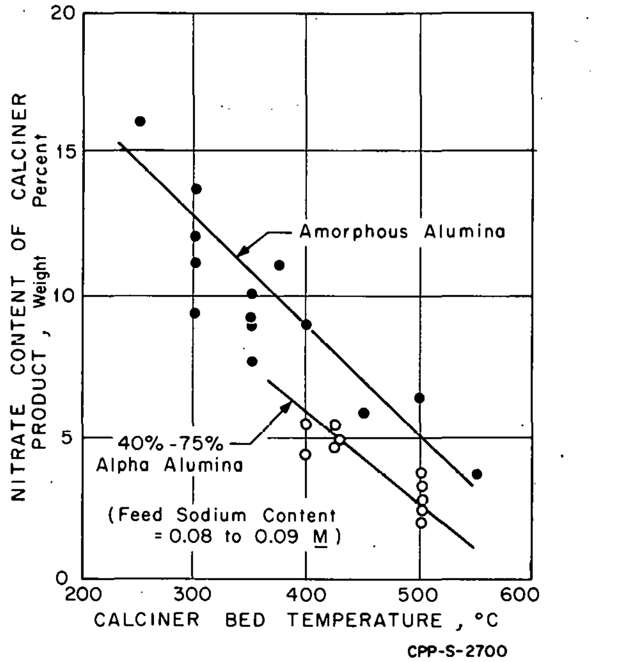

Fig. 6 Effect of alpha alumina content and bed temperature on the nitrate content of alumina product.

4.13 Nitrate Content of Product. The residual nitrate content of alumina product was affected by alpha alumina content and calcination temperature as shown on Figure 6. Temperature has the greatest effect. Nitrate content of product may also be affected by bed residence time.

The nitrate in the alumina is not necessarily in the form of sodium nitrate. The nitrate content of alumina free of sodium is only slightly lower than that of the sodium-containing product obtained under similar calcining conditions. Most of the sodium in the alumina is apparently in the form of an oxide.

4.14 Off-Gas Loadings. Because of the friable nature of the alpha form, the rate of elutriation of solids from the calciner was greatly affected by the alpha alumina content of the product. Highest elutriation rates have been generally observed with product containing significant quantities of alpha alumina, indicating that the alpha form is more friable than amorphous alumina. This was also indicated by results of an attrition index test. When the alpha alumina content of the product has been low, the attrition index has been as high as 90-96 per cent of particles unchanged in size by the standard test, whereas for beds containing significant quantities of alpha alumina this index has been as low as 20-25 per cent particles unchanged in size by the same test.

4.15 Mass Median Particle Diameter. The MMPD of the product was significantly affected by its alpha alumina content. In general, beds containing significant quantities of alpha alumina have had MMPD values smaller than those of beds containing small amounts of alpha alumina. The high rate of attrition of the particles which are predominantly alpha alumina causes them to break before they can increase in size. Moreover, fracturing of bed particles creates a large number of small "seed" particles, which causes the bed to have a smaller average particle diameter.

4.2 Factors Affecting Crystallinity of Alumina Product

The rate and extent of formation of alpha alumina are complex functions of temperature and time factors, of sodium concentration of the feed, and perhaps of other variables.

4.21 Sodium Concentration of the Feed. Promotion and inhibition of the formation of alpha alumina were effected by adjusting the sodium concentration of the feed. For both the concentrated and dilute aluminum feed concentrations, when the sodium concentration of the feed has been below 0.03M, formation of the alpha crystal structure did not occur; with sodium concentration between 0.07 and 0.10M the formation of alpha alumina has been intermittent; and with the sodium concentration of the feed at 0.25M formation of alpha alumina has always occurred.

The effect of the sodium concentration of the feed on the formation of alpha alumina in the product was shown vividly during Run 22. After the initial 66 hours of relatively stable operation with 0.078M sodium in the feed, the product and cyclone fines contained less than 5 per cent alpha alumina. The sodium concentration of the feed was then adjusted to 0.25M, and 24 hours later, detectable amounts of alpha alumina (~ 7 per cent) appeared in the product; during the subsequent 22 hours of operation this percentage increased to 16-17 per cent. To determine if the bed could be restored to its initial amorphous character, the sodium concentration of the feed was then decreased to 0.03M. Following this change, the alpha alumina content remained near the 16-17 per cent level for 23 hours, then decreased gradually to 7 per cent by run termination. The alpha alumina content of the cyclone fines followed closely the alpha content of the product. (Further details are given in the data summaries of Run 22 Appendix B.) The results of Run 22 indicate that if alpha alumina product is desired, it can be obtained by adjusting the sodium concentration of the feed to 0.25M.

Alpha alumina was not detected in the product during Run 20 which was made with only a 0.01M sodium concentration in the feed or during Runs 8 and 9[10] when sodium was not added to the feed. Thus, formation of amorphous alumina beds in the pilot plant was possible by omitting sodium in the feed. However, the first actual process waste scheduled to be calcined by the WCF contains sodium at the 0.04M concentration--a value in the range where the formation of alpha alumina is unpredictable. Thus, control of formation of alpha alumina in the WCF by means of sodium concentration control will not be possible. In subsequent studies, the addition of boric acid inhibited the formation of alpha alumina.

4.22 Operating Conditions. The rate of formation of alpha alumina during several runs appeared to be influenced by the operating conditions employed as described in the following paragraphs.

4.221 Starting Bed. The starting bed material may have influenced the rate of formation of alpha alumina during initial phases of Runs 12, 13, and 14. Unique to these runs (when compared to other runs in the two-foot-square calciner) was a rapid increase in the alpha alumina content of the bed (from 12 per cent to a high of 36 to 48 per cent) during the first 60 to 18 hours of operation, followed by a gradual decline in alpha alumina content (to a value between 4 and 12 per cent) after 100 hours of operation. All of these runs employed material from Run 11 for starting beds. Figure 7 relates the alpha alumina content of the bed for each of these runs to the operating time after the aluminum nitrate feed solution was introduced to the calciner. (Equipment problems necessitated a second startup after 32 hours of operation in Run 14; hence, two distinct sets of data points are shown from this run in Figure 7.)

The similarities in operating conditions on these runs are: starting bed material, bed temperature, and feed composition. Other operating conditions--such as feed rate, nozzle air-to-liquid volume ratio, type of feed nozzle caps, and superficial fluidizing velocity--differed on these runs. Since the behavior with respect to alpha formation was similar in these runs, one or a combination of the similar operating conditions employed must have been the cause of the similar pattern formation of alpha alumina. The subsequent decline of the alpha alumina content after peaking indicated that the operating conditions of these runs were not conducive to continued formation of alpha alumina. In contrast to this phenomenon, during other calcination runs[10] at 500°C, beds having an alpha content slightly above 28 per cent were unstable and transformed rapidly to beds containing over 60 per cent alpha alumina, with no evidence of any retrogression to a lower level content prior to a change in operating conditions. It is postulated that the new alumina generated during Runs 12, 13, and 14 was amorphous, and that the alumina converting to the alpha structure was the starting bed material--material generated during Run 11 in which the alpha alumina content of the product had stablized at 10-15 per cent.

Necessary startup checkouts, lasting from six to sixteen hours and which baked the bed, may have "triggered" the initial rapid increase of alpha alumina during these runs which continued until the "active" amorphous alumina had converted to the alpha structure; then the alpha alumina washed out of the bed as fresh amorphous alumina was generated.

The use of sand as starting bed material for part of the runs eliminated "prior history" effects associated with alumina starting beds such as these.

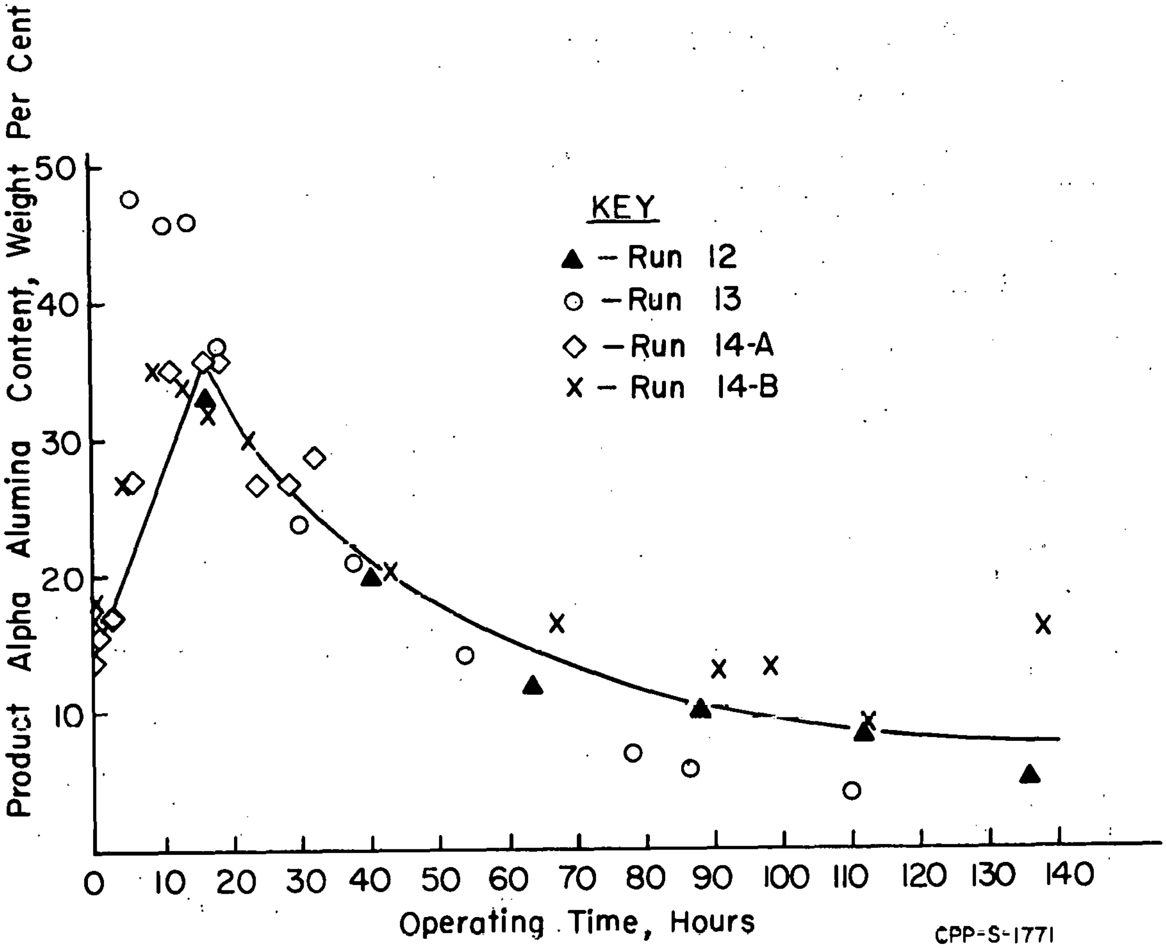

Fig. 7 Variation in alpha alumina content of alumina product during Runs 12, 13, and 14 A and B.

4.222 Bed Temperature. The formation of alpha alumina appeared to be somewhat dependent on bed temperature. The results of Run 15 (bed temperature of 500°C) suggest that higher bed temperatures favor formation of alpha alumina. In direct contrast to the results of Runs 12, 13, and 14 (bed temperature of 400°C), in which the alpha alumina content of the bed peaked at 30 to 48 per cent after about 18 hours and then declined to a value of 4 to 12 per cent, the alpha alumina content of the bed during Run 15 (bed temperature of 500°C) continued to rise above 48 per cent, with no indication of any recession. Common calcining conditions for Run 15 and for the previous runs at a bed temperature of 400°C were the concentration of aluminum in the feed and the alpha alumina content of the starting bed.

An additional study was made during Run 15 to identify the cause of this radical difference in the alpha behavior of alumina from that previously observed at the 400°C bed temperature. To do so, a deliberate attempt was made, at a bed temperature of 400°C, to cause the behavior of the alpha alumina to parallel that of the three previous runs. This time, after the alpha alumina content of the bed had peaked and declined to a value of 13 per cent, the bed temperature was increased to 500°C. Subsequently, the alpha content of the bed increased and reached a value of 23 per cent by the end of the run.

Although the effect of temperature on the alpha alumina behavior during Run 15 was not conclusive in itself, the behavior of the alpha alumina content of the bed during this run compared with that of the other three runs indicates that the higher bed temperature, 500°C, does promote the formation of alpha alumina. At a 400°C bed temperature, the relatively high alpha alumina content of the bed was transient, and declined after a short period of operation; whereas, at a bed temperature of 500°C, there was no indication that the alpha content would recede to lower values.

4.223 Bed Residence Time. The formation of alpha alumina appeared to be related also to bed residence time as suggested by the results of several runs. No alpha alumina was generated during any of the short, 24-hour, operating periods of Run 18. However, after 60 hours of operation of Part J of Run 18 alpha (and gamma) alumina was detected in the product, and after 155 hours of operation on that part of the run the maximum concentration of alpha alumina reached 5-6 per cent. Although the aluminum concentration of the feed relative to the sodium concentration was low during Part J, it was also similarly low during some of the 24-hour operating parts of Run 18. Thus, the formation of alpha (and also some gamma) alumina after 60 hours of operation of Part J lends credence to the hypothesis that newly-generated alumina must be exposed to the elevated bed temperature for some number of hours to promote alpha alumina formation.

Bed residence time may have indirectly caused the cyclic variation observed in the dependent variables during Run 16. Uniform cycling of all product and bed characteristics was evident during most of this run. This cycling is clearly evident in the data summaries for this run presented in the Appendix; the frequency between the cyclic peaks on all data plots was approximately 38 hours (five cycles were completed). In general, the alpha content, the bulk and absolute densities, the solids leaving with the scrubbing solution, and the time required for 90 per cent bed replacement all passed through maxima at approximately the same time that the intra-particle porosity, the nitrate content, the product rate, the product mass median particle diameter, the bed height, and bed weight all passed through minima. A review of operating techniques showed that the cycling was independent of normal variations in operating techniques. Thus, it appears that the cycling was caused by a peculiarity of the process; the operating conditions apparently bordered a region of unstability. Because of the significant effect of alpha alumina on the process, the cycling residence time of the product may have caused the formation rate of alpha alumina to cycle, although this cannot definitely be proved. Run 16 was the only run where this cycling of all product and bed characteristics was observed.

4.224 Atomization Characteristics of Feed. The formation of alpha alumina may be related also to the atomization characteristics of the feed. Figure 8 shows the various NAR values used during a portion or Run 17, together with the alpha alumina concentration in the product and in the off-gas solids. The cycling of alpha alumina in Run 17 appeared to be related to variation in NAR values; no other independent variables were changed.

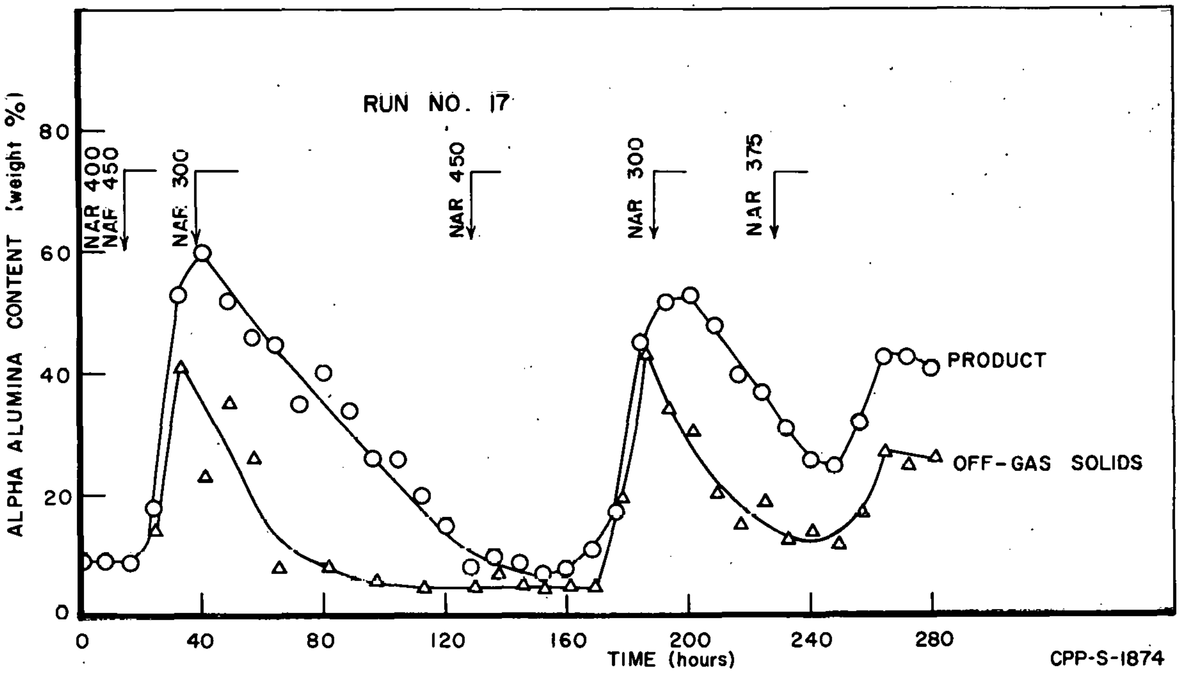

Fig. 8 Influence of nozzle air-to-liquid volume ratio (NAR) on alpha alumina content of calcined solids during Run 17.

5. ELUTRIATED SOLIDS

The rate of elutriation of solids from the calciner, as measured by their rate of removal from the off-gas by the scrubbing solution, has, at times, been excessive. Thus, the factors affecting the generation of elutriated solids, their disposal, and measurement of their physical properties are significant to understanding and controlling the process. Studies of these effects are described below.

5.1 Attrition Effects

The factors affecting particle attrition rate during fluidization were partially isolated by observing the rate of elutriation of solids from the calciner at the various operating conditions given in Table II. These tests were conducted with a predominantly amorphous alumina bed at a bed temperature of 500°C; the data were collected after thermal equilibrium was reached in each case. The results of these tests show that:

a. The rate of input of high-velocity nozzle atomizing air has (apparently through a jet-grinding action) a significant effect on product attrition, which in turn affects the bed depletion rate. For example, when atomizing air (but no liquid) was introduced through the feed nozzle into the fluidized bed, the rate of bed depletion increased tenfold over that with fluidizing action alone, to over 7000 grams per hour. In this case, the atomizing air rate was only about 12 per cent of the fluidizing gas rate, and was equal to that amount required to maintain a NAR of 500 if the liquid rate had been 80 liters per hour instead of zero. A further increase in that atomizing air rate, to the equivalent of NAR of 880, was accompanied by a significant increase in the rate of bed depletion.

b. With a water feed rate of 80 liters per hour at either of these nozzle air rates, there was an almost 100 per cent increase in the rate of bed depletion. This higher weight loss may have been partially caused by the increased space velocity of the total fluidizing gas. (Addition of the water feed increased the superficial velocity of the gas at the top of the calciner from 0.8 ft/sec to 1.35 ft/sec.) A second possible cause of the increased bed depletion rate may be higher product attrition rate caused by thermal shock of the water feed contacting the hot calcine particles.

c. The superficial velocity of the fluidizing gas had a much smaller effect on the rate of bed depletion in the limited area studied than did the nozzle air or the introduction of feed. A change in superficial velocity from 0.81 to 1.15 ft/sec, when operating without feed or nozzle air, caused a 75 per cent increase in the rate of bed depletion, i.e., from 0.8 to 1.4 kg/hr. Both of these depletion rates, however, are significantly less than rates observed when either or both nozzle air or feed were used. This lower rate of elutriation of fines may have been due primarily to increased elutriation rather than increased attrition.

TABLE II

RESULTS OF ATTRITION TEST EVALUATING THE 1/2 J FEED NOZZLE WITH STANDARD FLAT-FACED NOZZLE CAP

Superficial Fluidizing Velocity (ft/sec)	Water Feed Rate (l/hr)	Nozzle Air-To-Liquid Volume Ratio*	Wt. Loss From Bed (kg/hr)***
0.81	None	No Air	0.8
0.80	None	488	7.6
0.78	None	884	36.4
1.15	None	No Air	1.4
1.08	None	495	9.1
1.10	None	810	26.7
0.78	80	500	13.4
1.00	80	463	15.8
0.95	80	761-625**	24.3
0.78	80	763-690**	21.9

* NAR values reported for operation with no liquid are based on an assumed liquid rate of 80 l/hr.

** First number indicates starting value; second number is the final value.

*** Represents average of samples taken at 5-minute intervals over 20-minute periods.

5.2 Disposal of Fines

No effect on the particle size distribution was apparent during operation of the dry fines return system which was described earlier. Thus, it was doubtful that the returned fines were acting, in significant numbers, as nuclei for new particle growth, but rather were possibly building up to an equilibrium concentration in the calciner off-gas with the excess fines passing through the primary cyclone and increasing the loading of solids in the scrub solution.

Operation of the six-inch diameter calciner had shown that return of fines to the bed resulted in a generally small bed particle size [9], thus indicating that the fines were acting as nuclei for new particle growth. However, the six-inch diameter calciner was operated with a superficial fluidizing velocity generally above 2.0 ft/sec and as high as 4.5 ft/sec, whereas, in these runs the superficial fluidizing velocity varied between 0.78 to 1.0 ft/sec. Based on terminal settling velocities, the diameters of particles elutriated from the six-inch calciner would be two to four times as large as particles elutriated from the two-foot-square calciner. It is believed that the elutriated fines returned to the bed in the two-foot-square unit were generally too small to act effectively as nuclei for new particles at the particular conditions of these runs. Some may have agglomerated to form larger particles which may have been effective as nuclei, and some may have been captured by the fresh material deposited on particles.

The two-foot-square calciner was successfully operated without return of fines to the bed. Because of the success of this mode of operation, the primary cyclone was bypassed during Run 21; operation was satisfactory and a stable particle size distribution was achieved by use of a high NAR (600). After Run 21, the primary cyclone was reinstalled in the off-gas system with provisions to collect the fines for study on succeeding runs.

The rate of removal of fines from the off-gas by the primary cyclone during Run 22 (plotted with the general data of Run 22 in the Appendix) varied considerably: about 1 kg/hr for a predominantly amorphous bed; about 4 kg/hr for a bed containing 16-17 per cent alpha alumina which decreased to about 1 kg/hr as the alpha alumina content declined to 7 per cent. Additional data may indicate further effects of operating conditions on the rate of elutriation of solids from the calciner.

5.3 Characteristics of Cyclone Fines

The solids removed from the off-gas by the primary cyclone during Run 22 were analyzed for alpha alumina content, absolute density, nitrate content, and bulk density. These data are presented in the data summary of Run 22 in the Appendix. The absolute density and alpha alumina content followed closely the characteristics of the bed. The nitrate content of the fines was generally higher than that of the product, indicating that the fines contained a relatively large portion of the freshly generated alumina. The bulk density of the fines was lower than that of the product.

6. MERCURY IN FEED

Mercury in the feed was found to have no noticeable effect on the extent or rate of formation of alpha alumina or on any other property of the product during Run 21. This run included periods of operation without mercury and other periods with 0.015M mercury in the feed; these changes of the mercury concentrations of the feed were abrupt and produced no discernable effects in any of the operating variables of the calciner.

VI. EXPERIMENTAL INNOVATIONS

Techniques developed to improve operation and to obtain special information about the process are described.

1. SAND AS A STARTING BED

Sand, used in lieu of alumina as a starting bed in Runs 17 through 21, resulted in several advantages: identifiable trends in alumina properties were established early in a run; consideration of history of the bed was made unnecessary; and particle growth characteristics were easily observed. This use of a different material for a starting bed made it possible to determine the characteristics of newly generated alumina early in a run by eliminating the influence of the starting material on measurements and analysis through suitable calculations. The use of sand for a starting bed for the short operating periods of Run 18, when the factors affecting the intra-particle porosity of the alumina product were studied, reduced the experimental time of this study by 60 to 80 per cent[13] when compared to previous use of alumina starting beds. Prior to Run 17, and for Run 22, alumina generated from previous calciner runs was used as starting beds.

Disadvantages of using sand as a starting bed were the accumulation of insoluble material in quiescent spots of the system and the possibility of greater erosion in parts of the system.

Some of the properties of the sand are compared in Table III with those of calcined alumina.

2. IDENTIFIABLE SHELLS ON PRODUCT BY CHEMICAL TRACER

Identifiable shells on the alumina product were produced during Run 22 by adding nearly saturated solutions of the nitrate salts of chromium, copper, iron, and nickel to the feed stream for 15 minute periods, spaced about four hours apart. Mixing with the aluminum feed, these salts (in mass ratios of chromium to aluminum of 0.5, of copper to aluminum of 2, of iron to aluminum of 0.5, and of nickel to aluminum of 15.) produced colored shells, easily identified as colored rings in sectioned product particles.

Rings produced through use of the chromium spike were bright yellow; however, they were not as sharply defined against the white alumina in sectioned particles as were rings produced by the other three metals. The copper spike produced a sharp dark-green ring; the iron spike produced a very sharp dark-red ring; and a dark, almost black, sharp ring was produced by the nickel spike.

TABLE III

COMPARISON OF VARIOUS PROPERTIES OF SAND AND ALUMINA

	Sand		Alumina	
	Value	Temp.	Value	Temp.
Thermal conductivity Btu/hr(ft^2)(°F/ft)	0.19	20°C	0.08	100°C
			0.17	400°C
			0.198	500°C
Specific heat, Btu/lb	0.19	20°C	0.20	100°C
			0.274	1500°C
Absolute density, g/cc	2.62		2.62-3.95	
Bulk density, g/cc	1.46-1.53		0.7-1.6	
Particle density, g/cc	2.56		1.18-2.0	
Intra-particle porosity, fraction	0.02		0.05-0.60	
Mass median particle diameter, mm	0.26		0.26-1.20	

The formation of identifiable rings in this manner presents many possibilities for practical application as a tracer technique. Basically, the technique provides a method of identifying in each particle the time at which any part of the particle was formed. Thus the effect of various calciner variables on the particle growth rate may be determined with some assurance, and the effect of calciner variables on the statistics of particle movement in the fluidized bed may be evaluated.

VII. CONCLUSIONS

The following conclusions are drawn from information obtained in Runs 11 through 22 in the two-foot-square calciner:

1. EQUIPMENT PERFORMANCE

1.1 Equipment and operating techniques used were satisfactory; the runs were usually terminated by intent rather than because of equipment failure.

1.2 The continued excellent operating performance of the NaK heating system indicates that a high temperature, low pressure liquid metal system is a reliable and effective method of supplying heat to a fluidized bed calciner.

1.3 The feed nozzle intended for use in the WCF was satisfactory in tests at feed rates up to 120 liters per hour through a single nozzle. No problems are expected when calcining waste at a rate of 150 liters per hour through a single nozzle, the upper design value per nozzle for the WCF, provided sufficient heat can be transferred from the NaK tubes to the bed.

1.4 Nozzle caps employing design features or materials of construction to mitigate cap erosion were tested in the WCF type nozzle. In addition to the original flat-faced cap, caps with the following design features were tested: (a) an extended divergent; (b) a long and a short extended convergent; and (c) a modified, boron carbide flat-face. Materials of construction tested were titanium, Types 347 and 440-C stainless steel, boron carbide, and titanium flame-sprayed with alumina. The use of boron carbide reduced cap erosion to an absolute minimum. However, hardened stainless steel caps appear to be satisfactory for WCF use based on subsequent operating experience in the WCF.

1.5 A single-fluid nozzle might be used as a feed nozzle for a fluidized bed calciner, provided that the problem of severe corrosion or erosion to internal parts of the nozzle can be solved.

2. PRODUCT CHARACTERISTICS

2.1 The intra-particle porosity of alumina was affected significantly by bed temperature and by the aluminum concentration of the feed solution being calcined. Alumina with porosities as low as 0.05 may be generated by employing combinations of low bed temperatures and dilute feed solutions.

2.1 Alpha, the predominant crystalline form of alumina found in the calciner product, varied from zero to 80 per cent by weight in the product of these runs. The gamma crystalline form of alumina and crystalline sodium nitrate were occasionally detected. Many of the properties of the product were related to the structure of the alumina.

2.3 The rate of formation of alpha alumina was related to the sodium concentration of the feed. With a sodium concentration of 0.25M, formation of alpha alumina occurred; with a 0.03M concentration, formation of alpha alumina did not occur; and with a 0.078M concentration, alpha alumina formation was unpredictable. Other factors influencing the formation of alpha alumina may include bed temperature, feed atomization characteristics, starting bed material, startup technique, and bed residence time.

2.4 The absolute density of product increased with increasing alpha alumina content. Absolute densities ranging from about 2.6 g/cc for amorphous alumina to 3.8 g/cc for alumina containing 60-80 per cent alpha were observed.

2.5 The nitrate content of product varied with both the alpha alumina content and the bed temperature. For amorphous alumina, calcination at a 250°C bed temperature resulted in a product containing 15 weight per cent nitrate; at 550°C bed temperature the product contained only about three weight per cent nitrate. For product containing 40-70 per cent alpha alumina, the nitrate content was about three weight per cent less than for amorphous alumina generated at similar bed temperatures.

3. PROCESS CHARACTERISTICS

3.1 The rate of elutriation of solids from the calciner varied considerably and the solids appeared to be created as a result of interactions of the feed spray with the bed. High rates of elutriation of solids generally were associated with high nozzle air rates and with increasing alpha alumina content of the product, other significant conditions being equal.

3.2 Control of the particle size of the bed was possible by selecting a suitable nozzle air-to-liquid volume ratio (NAR) or by use of an air jet grinder. High NAR values generally result in product having a small mass median particle diameter (MMPD). However, for any given value of this ratio, low MMPDs are associated with product containing high percentages of alpha alumina. Jet grinding a bed controlled MMPD but resulted in the generation of significant quantities of elutriatable solids.

3.3 Addition to the calciner of feed spiked with various metallic nitrate salts for short periods of time produced sharply defined rings on bed particles which are useful in determining particle growth rates.

3.4 Mercury in the feed was found to have no discernible effect on product properties.

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IX. APPENDIX

1. DEFINITIONS

Absolute density refers to the material portion of solids; the volume associated with this density excludes all voids within and between individual particles. Absolute densities were determined by a displacement method using CCl_4 which is believed to penetrate all voids.

Apparent particle density refers to the density of the individual particles of the product. The volume term in this density expression includes the volume of the material and the intra-particle pores, but excludes the void space between and around individual particles; it was determined by a displacement method employing mercury which at low pressure penetrates voids around particles but forms a protective envelope around individual particles because of the high interfacial tension and does not penetrate internal pores in particles. The cyclone fines material was too fine to employ this method for determining their particle densities.

Intra-particle porosity refers to the void space within individual particles. It was calculated as follows:

$$\text{Intra-particle porosity} = \frac{\rho_A - \rho_P}{\rho_A}$$

where ρ_A = product absolute density

ρ_P = product apparent particle density

Bulk density refers to the poured, unpacked, bulk solids. The volume in this density determination includes the material volume, the intra-particle pore volume, and the inter-particle void volume. The bulk density of alumina generated with a pneumatic nozzle was consistently about 59 per cent of the apparent particle density over the range of particle size distributions encountered in these studies. This correlation did not appear applicable when a jet grinder was utilized to control the particle size of the product during Run 20. Apparently the jet grinder changes the size distribution and shape of the product so that the resultant inter-particle void space was also changed.

Inter-particle void fraction refers to the space between particles. The inter-particle void fractions for typical alumina produced in pilot plant calciners have been remarkably constant at about 0.41, except when the jet grinder was used during Run 20.

Nitrate content of both the product and cyclone fines were determined by a Kjeldahl method.

Alpha alumina content of the product and cyclone fines was determined by X-ray diffraction analysis. Material not identifiable as crystalline by this method was defined as amorphous.

Solids leaving with the scrubbing solution includes both the dissolved and undissolved solids separated from the off-gas by the venturi scrubber. This rate was calculated from the measured flow rate of the scrubbing solution to the drain and from an analysis of the stream for total solids.

The product particle size distribution was determined by use of Tyler screens generally consisting of 14, 20, 28, 35, 65, and 100 mesh; other sizes were used occasionally.

Attempts were made to screen the cyclone fines during Run 22 by the above method. However the fine material agglomerated to an extent that the screens were blinded.

The results reported herein are cumulative weight percentage finer than the screen size shown.

The mass median particle diameter (MMPD) refers to the particle diameter of a sample at that point where 50 per cent of the mass is associated with larger particles and 50 per cent with smaller ones. It can be determined graphically by plotting the cumulative screen analysis vs the particle diameter or from the following empirical equation:

$$\text{MMPD} = d_n - 0.008 \text{ (mm)}$$

$$d_n = \bar{n}_1 \, Dp_1 + \bar{n}_2 \, Dp_2 + \dots = \sum \bar{n} \, Dp$$

where $\bar{n}$ = weight fraction retained between two consecutive screens

Dp = geometric mean size of the openings of the two corresponding consecutive screens (mm)

Product hardness was found from the average force in grams required to crush, individually, 20 particles of a closely sized product. Ordinarily, particles passing through a -28 but retained on a -35 Tyler mesh screen were used for this test. Reproducibility of the test results was poor. Consequently, this test was discontinued after Run 12, and was replaced by an attrition index test.

The product attrition index is the term applied to the weight percentage of a closely sized product unchanged in size after undergoing attrition by a jet grinder for a specified period. Ordinarily, particles passing through a -28 but retained on a -35 Tyler mesh screen were used for this test. The test apparatus used was a 1-inch I.D. glass tube with an air distributor plate drilled with a single, 1/64-inch diameter orifice. A 50-gram sample of the size product was subjected to the grinding action of an air stream issuing from the orifice at sonic velocity for a one-hour period. The sample was again screened and the weight per cent of solids remaining unchanged in size was reported as the attrition index. An attrition index of 100 is, therefore, equivalent to zero attrition during the standard test.

The product rate was an average hourly rate determined from the amount of product accumulated over a four-hour period. Elutriated solids are not included in this rate.

Theoretical production rates shown on the run summary sheets in the Appendix are based on the arbitrary assumption that all of the aluminum, mercury and sodium in the feed are converted to the respective oxides (Al_2O_3, HgO and NaO) and appear as product.

Time required for 90 per cent bed replacement was determined from a "washout" equation, assuming that the bed is perfectly mixed and steady-state conditions exist over the interval involved. The fraction of initial bed material removed at any time during a run can be calculated from the following equation:

$$x = 1-e^{\left(\frac{-pt}{w}\right)}$$

where x = weight fraction of initial bed removed at time t
w = weight of fluidized bed, kg
p = product rate, kg/hr
t = time, hours

Plots in the Appendix show continuous records of the value of t for which x is 0.9.

The fluidized bed weight refers to the weight of the bed supported (fluidized) by the fluidizing gas, and was determined by the pressure differential across the bed.

The fluidized bed height refers to height of the fluidized bed as determined by pressure differentials over the lowest one-foot increment of bed and over the entire bed. Dividing the latter by the former gives the bed height in feet.

The fluidized bed density refers to the fluidized density of the bottom one-foot of the bed and was determined by pressure differential.

Cyclone fines are the material collected from the dust discharge of the primary cyclone. Collection of this process stream was initiated during Run 22. Previously, this stream was usually returned to the bed via the dry fines return system.

The cyclone fines rate was an average hourly rate determined from the amount of fines accumulated from the dust discharge of the primary cyclone over a four-hour period.

The feed nozzle air-to-liquid ratio (NAR) is the term applied to the volumetric ratio of the atomizing air-to-liquid feed rate.

For consistency in applying this ratio, the air volume was determined at the metered temperature and the calciner vessel pressure. A high NAR value produces a spray having a large number of very small droplets; a low NAR produces a spray having fewer and larger droplets. Grinding of the bed may occur with higher NAR values; thus it was a means of controlling particle size.

Superficial fluidizing velocity refers to the velocity of the combined fluidizing gas (fresh air and dry fines return gas) on the basis of the empty cross section of the calciner at the bed temperature and vessel pressure.

2. RUN DATA SUMMARIES

Run 11

Period Covered: July 18, 1960 to July 29, 1960.

Objective: To study the operability and performance of the nozzle selected for use in the Waste Calcining Facility.

Equipment: That used during Run 10 with the exception of the feed nozzles. A single Spraying Systems Company Type 1/2 J feed atomizing nozzle with a standard flat-faced nozzle cap fabricated of titanium was used in lieu of the two pair of opposed smaller feed nozzles used on previous runs.

Cumulative NaK Heating System Operating Data: (including this run)

116 start-ups; 5743 hours above 1000°F; 823 hours below 1000°F.

Run Conditions:

Starting bed	Predominantly amorphous alumina generated during Run 10
Bed temperature, °C	500
Feed rate, l/hr	80
Nozzle air-to-liquid volume ratio	590 → 120
Superficial fluidizing velocity, ft/sec	0.78
Dry fines return to bed	No
Bed pressure, psia	18.5
Operating time, hours	272

Feed Composition:	Aluminum nitrate, M	1.95
	Nitric acid, M	1.25
	Sodium nitrate, M	0.089
	Mercuric nitrate, M	0.006

Results: Satisfactory operation was achieved with a feed rate of 80 liters per hour through a single feed nozzle. A study of factors affecting the bed attrition rate with the 1/2 J nozzle was completed prior to calcination of regular feed; this study showed a pronounced increase in attrition rate with increases in nozzle air rate; also noted was a slight increase in attrition rate with an increased superficial fluidizing velocity and a significant increase upon the initial introduction of water feed. A temperature traverse of the feed spray zone showed that beyond 12 to 15 inches from the nozzle along the axial centerline, normal bed temperature was maintained when using both water and regular feed at an 80-liter-per-hour rate. The feed nozzle cap was eroded at the rate of 2.9 g/yr, a rate considered excessive. Erosion of the off-gas line between the venturi scrubber and the scrubber cyclone occurred during the attrition test.

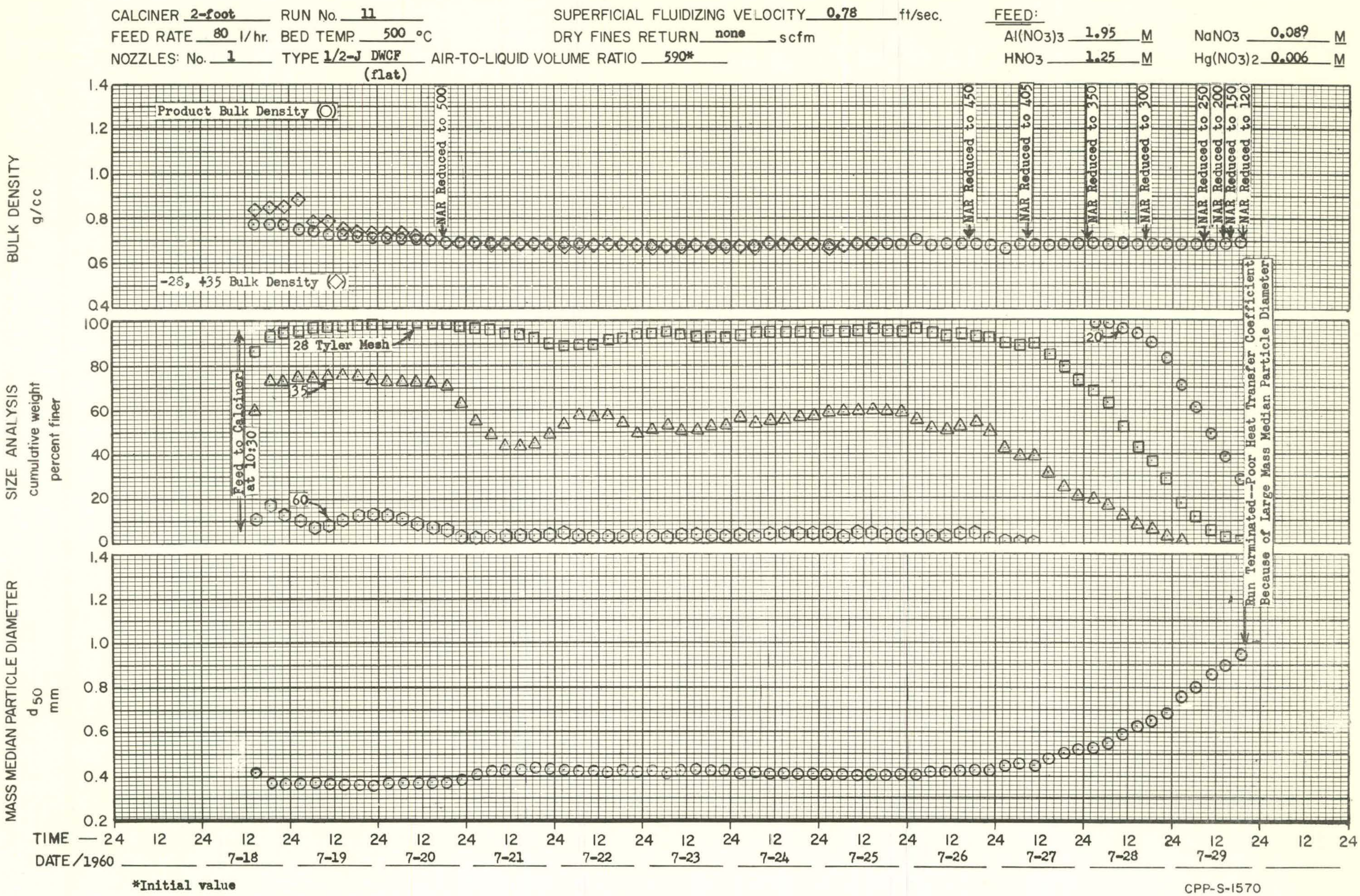


Fig. 9 Product data, Run 11.

CALCINER 2-foot RUN No. 11 SUPERFICIAL FLUIDIZING VELOCITY 0.78 ft/sec

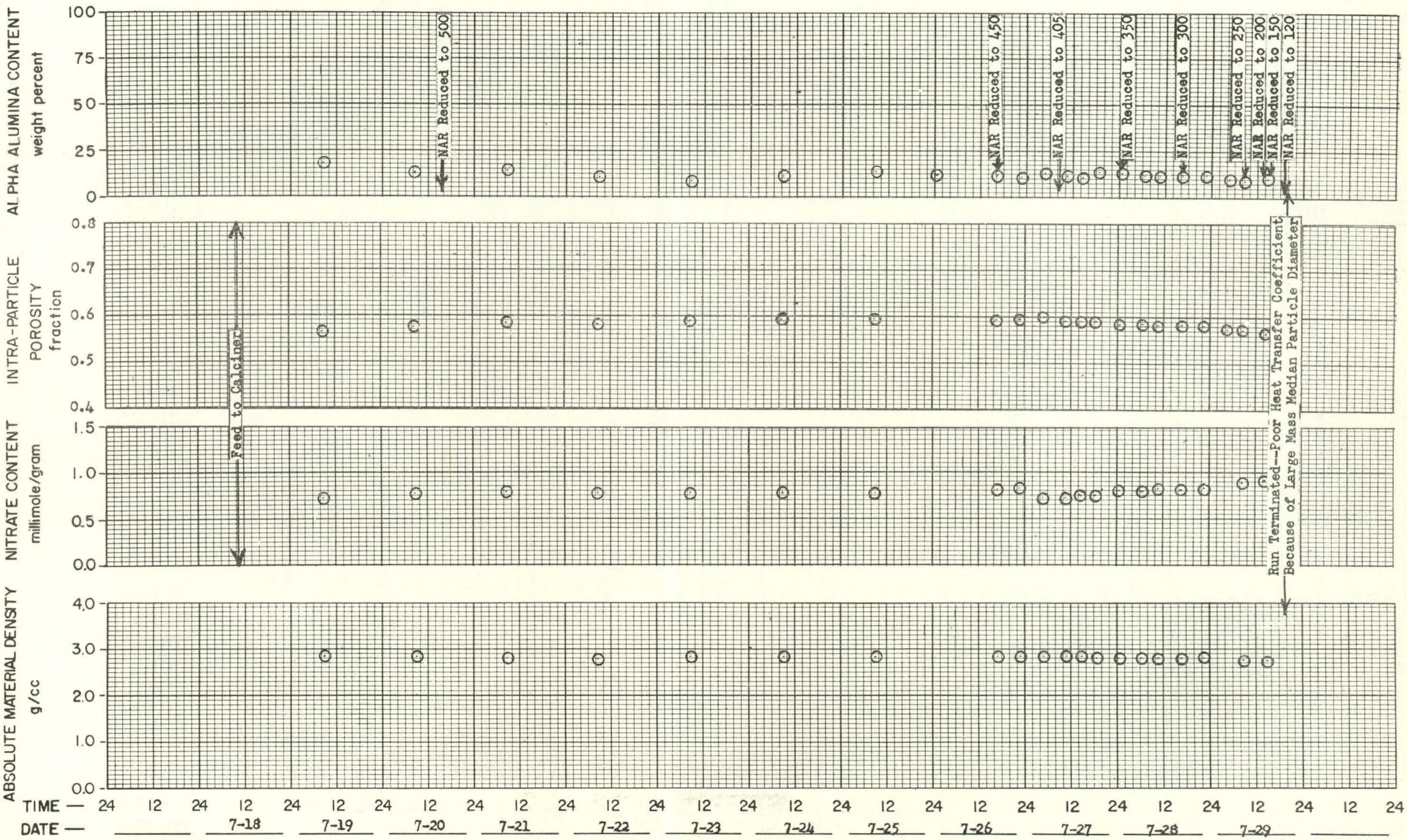
FEED RATE 80 l/hr BED TEMP. 500 °C DRY FINES RETURN none scfm

NOZZLES: No. 1 TYPE 1/2-J DWCF (flat) AIR-TO-LIQUID VOLUME RATIO 590*

FEED:

$Al(NO_3)_3$ 1.95 M $NaNO_3$ 0.089 M

HNO_3 1.25 M $Hg(NO_3)_2$ 0.006 M



*Initial value

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Fig. 10 Additional product data, Run 11.

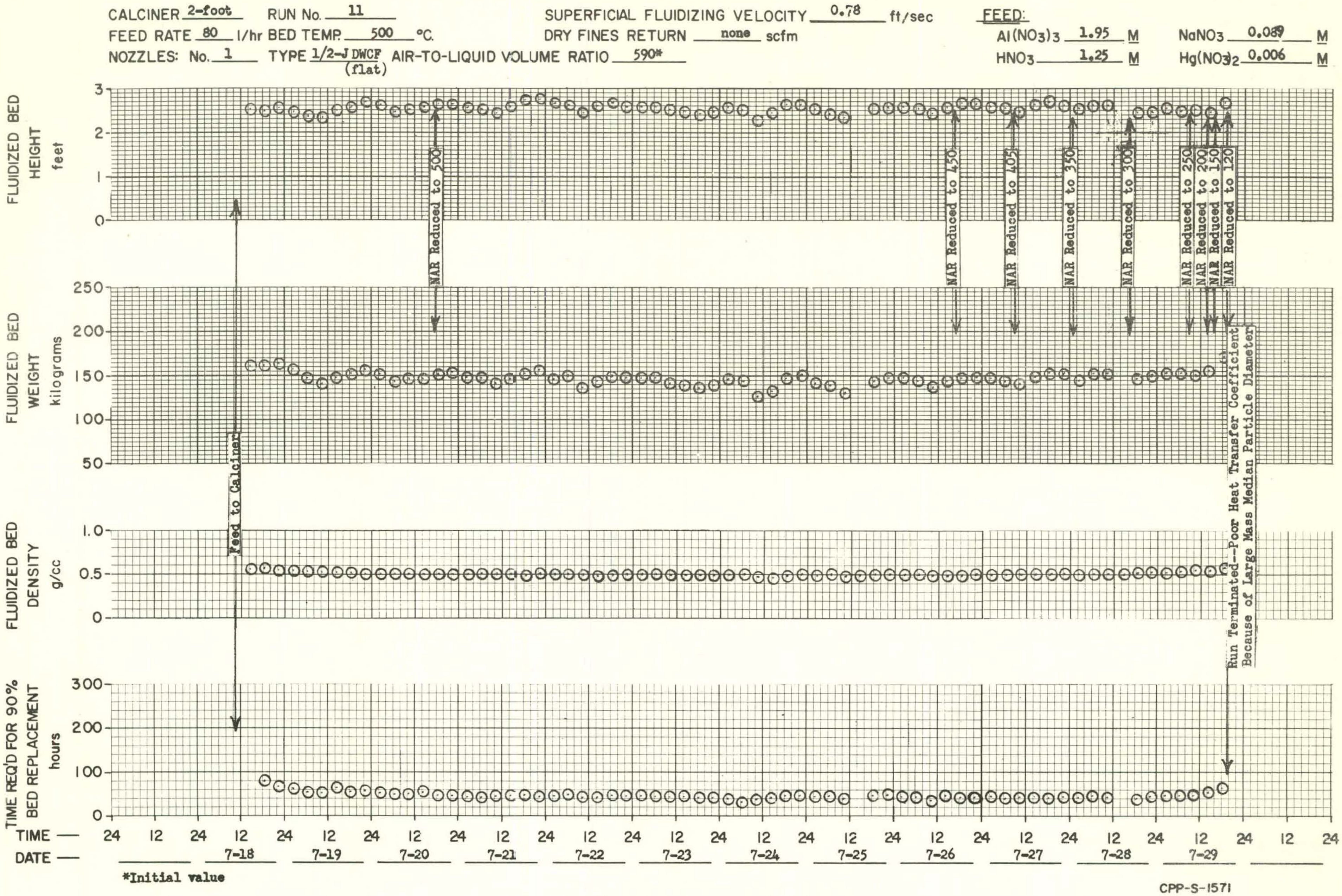


Fig. 11 Calciner bed data, Run 11.

CALCINER 2-foot RUN No. 11 SUPERFICIAL FLUIDIZING VELOCITY 0.78 ft/sec

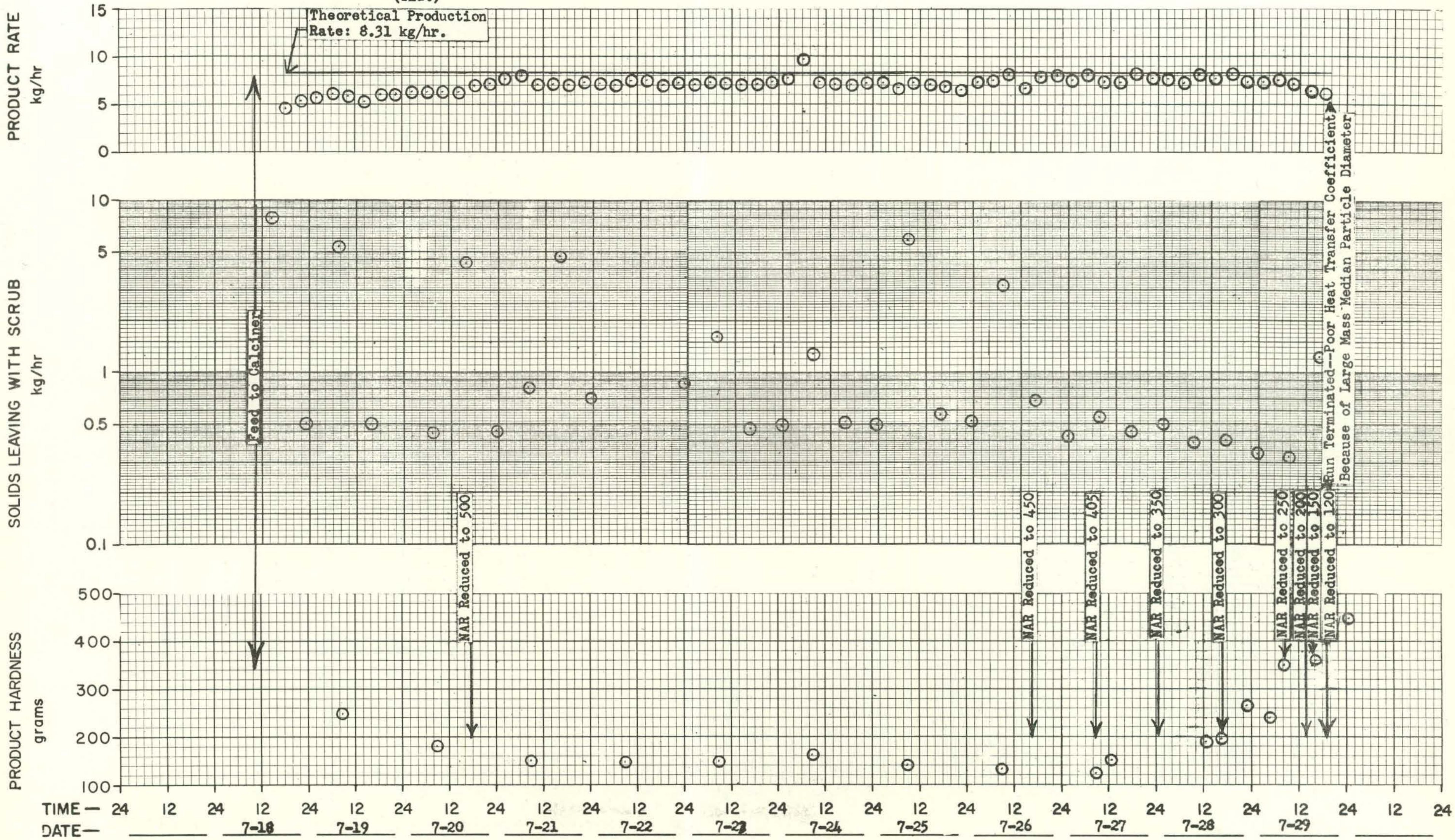
FEED RATE 80 l/hr BED TEMP. 500 °C DRY FINES RETURN none scfm

NOZZLES: No. 1 TYPE 1/2-J DWCF (flat) AIR-TO-LIQUID VOLUME RATIO 590*

FEED:

$Al(NO_3)_3$ 1.95 M $NaNO_3$ 0.089 M

HNO_3 1.25 M $Hg(NO_3)_2$ 0.006 M



*Initial value

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Fig. 12 General data, Run 11.

Run 12

Period Covered: From August 9, 1960 to August 17, 1960.

Objective: To simulate, as closely as possible, operation at the design conditions of the Waste Calcining Facility.

Equipment: That used during Run 11 with the exception of the feed nozzle cap. A standard flat-faced cap of Type 347 stainless steel was used in lieu of the similar cap of titanium used during Run 11.

Cumulative NaK Heating System Operating Data (including this run):

129 startups; 5823 hours above 1000°F; 992 hours below 1000°F.

Run Conditions:

Starting bed	Predominantly amorphous alumina generated during Run 11
Bed temperature, °C	400
Feed rate, l/hr	120 → 112 → 120
Nozzle air-to-liquid volume ratio	300
Superficial fluidizing velocity, ft/sec	0.9
Dry fines return	No
Bed pressure, psia	20.0
Operating time, hours	172

Feed Composition:

Aluminum nitrate, M	1.29
Nitric acid, M	2.84
Sodium nitrate, M	0.078
Mercuric nitrate, M	0.015

Results: A feed rate of 120 liters per hour was successfully maintained through a single nozzle, a value approaching the WCF design basis of 150 l/hr per nozzle. Also observed was the desirable product combination of high bulk density (0.90 g/cc) and low alpha alumina content (2 per cent), indicative of a relatively low intra-particle product porosity.

The feed nozzle cap was eroded at the rate of 4.0 g/yr, a rate considered excessive.

The scrubber cyclone downstream of the venturi scrubber eroded, necessitating a stainless steel patch.

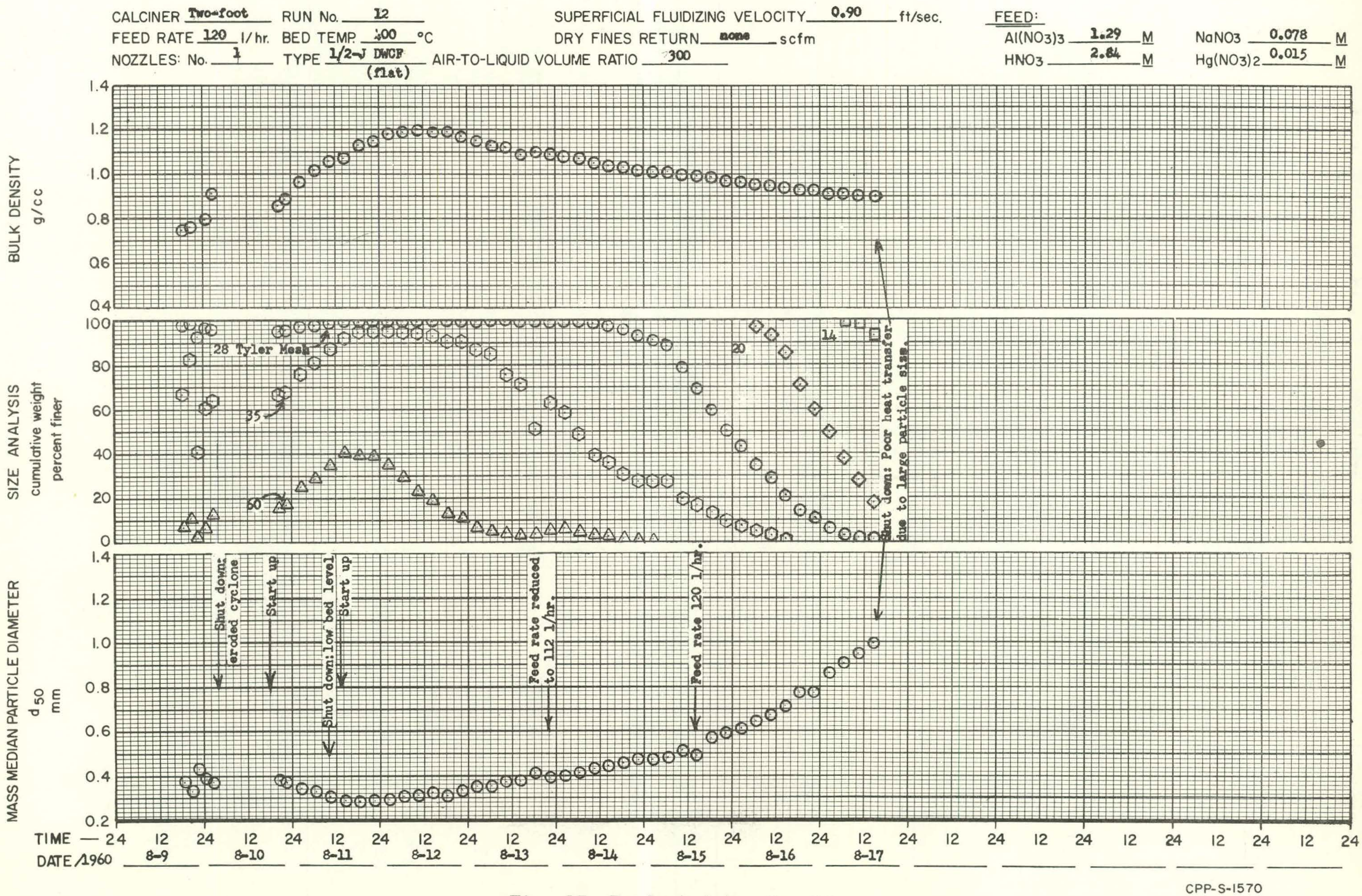

Fig. 13 Product data, Run 12.

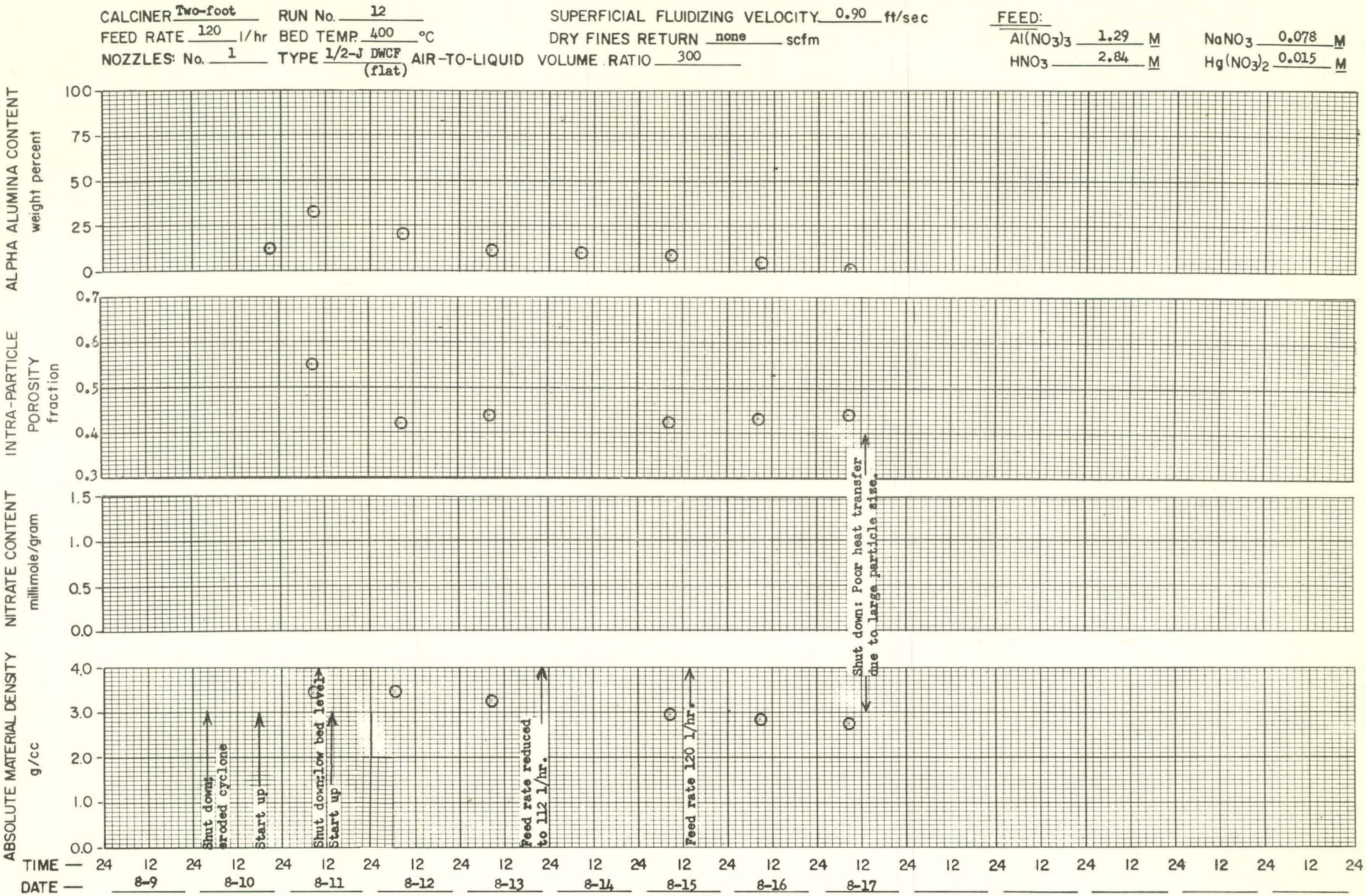

Fig. 14 Additional product data, Run 12.

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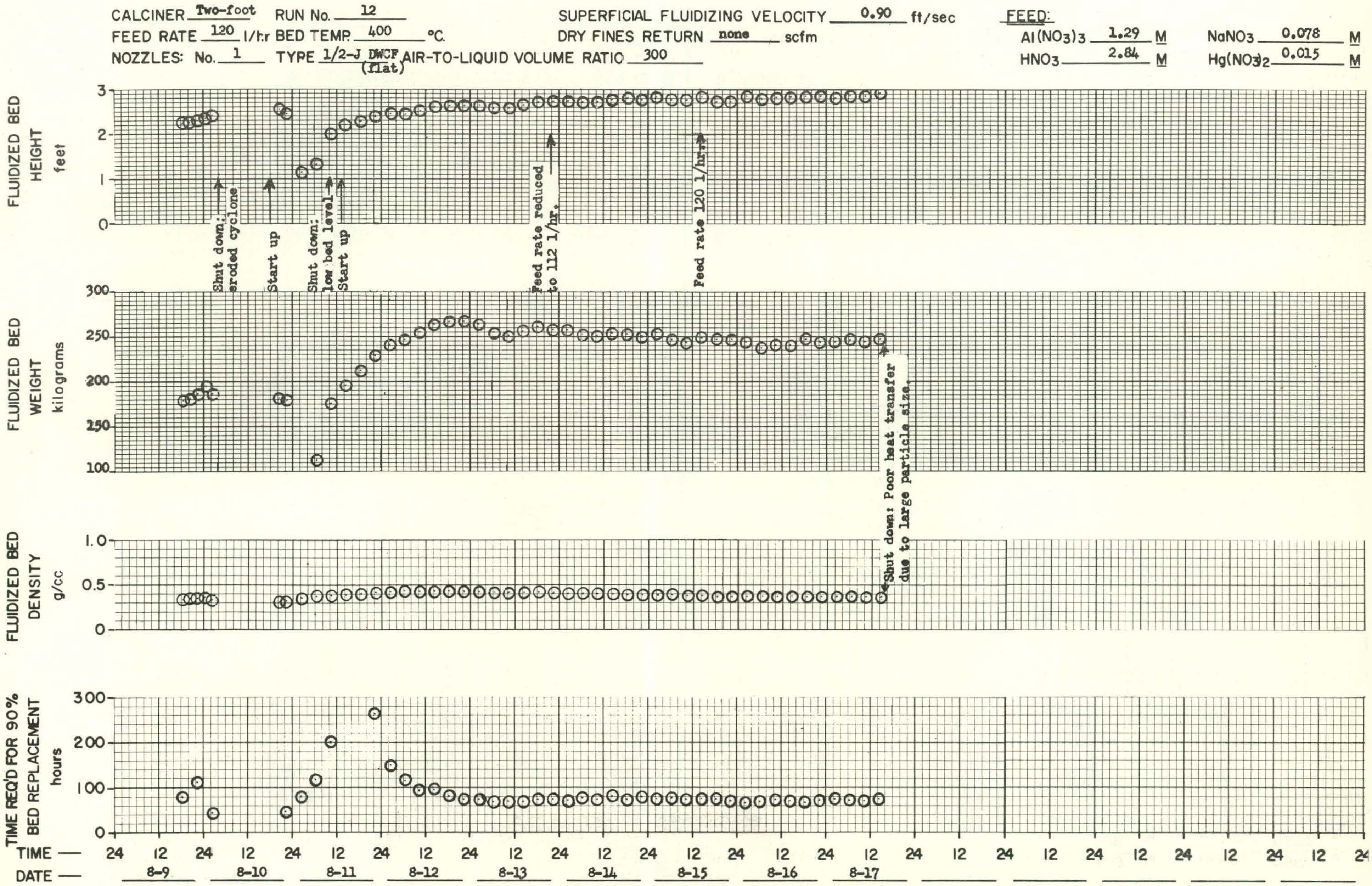

Fig. 15 Calciner bed data, Run 12.

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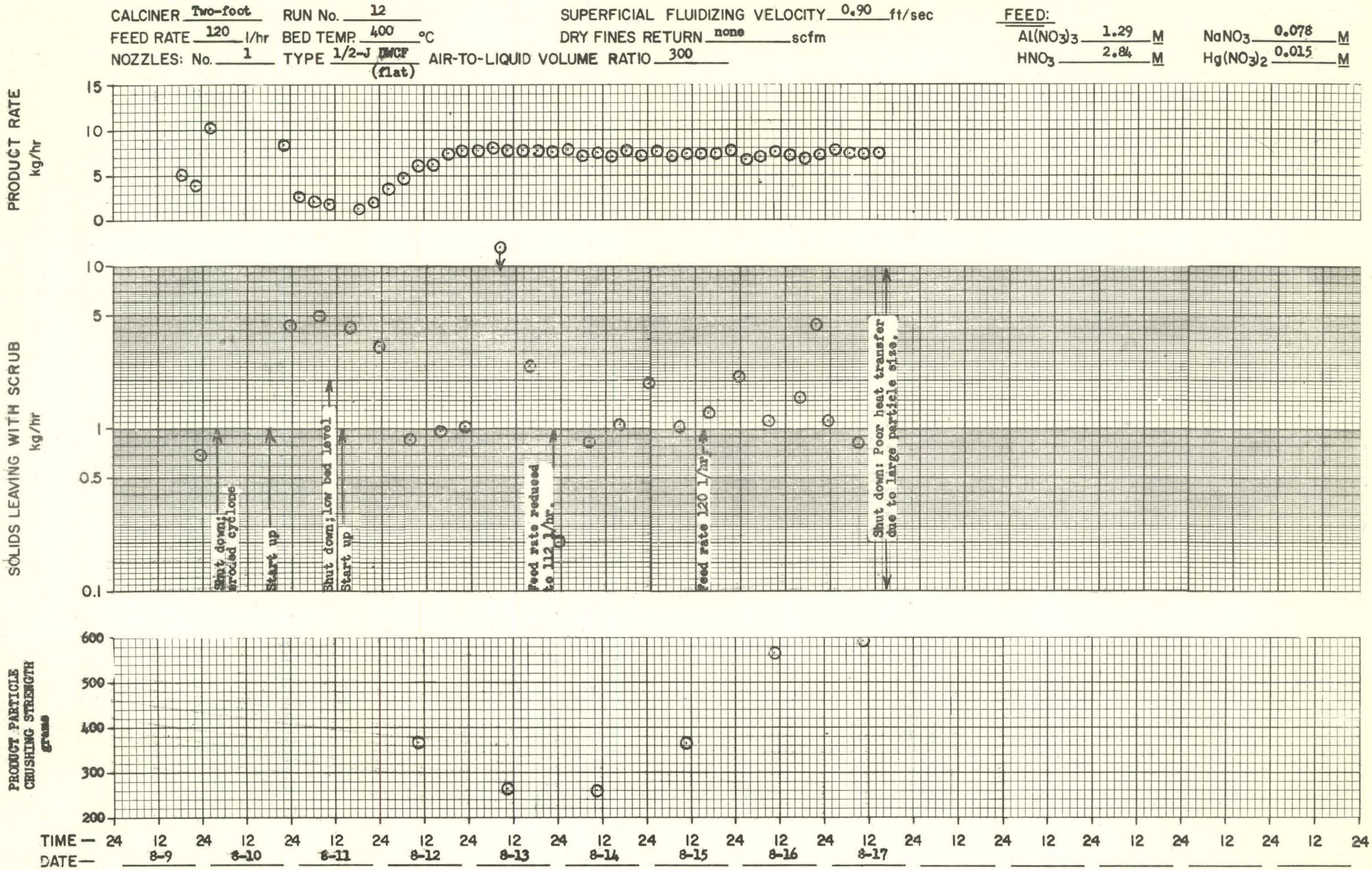

Fig. 16 General data, Run 12

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Run 13

Period Covered: From October 24, 1960 to October 30, 1960.

Objective: To study the performance of a feed nozzle cap of extended divergent design involving internal air-liquid mixing. This design change was made in an effort to minimize nozzle erosion.

Equipment: That used during Run 12 with the exception of the feed nozzle cap. An extended divergent cap of Type 347 stainless steel (two-fluid, internal mixing) was used in place of the standard flat-faced cap used during Run 12.

Cumulative NaK Heating System Operating Data (including this run):

131 startups; 5963 hours above 1000°F; 1014 hours below 1000°F.

Run Conditions:

Starting bed	Predominantly amorphous alumina generated during Run 11
Bed temperature, °C	400
Feed rate, l/hr	100 → 93 → 45
Nozzle air-to-liquid volume ratio	400 → 500 → 1100
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	10-22
Bed pressure, psia	18.7
Operating time, hours	140

Feed Composition:

Aluminum nitrate, $\underline{M}$	1.29
Nitric acid, $\underline{M}$	2.84
Sodium nitrate, $\underline{M}$	0.078
Mercuric nitrate, $\underline{M}$	0.015

Results: Erosion of the extended nozzle cap was negligible. The steady increase in the mass median particle size, however, could not be stemmed even at high nozzle air rates. The alpha alumina content of the product increased from 14 to 48 per cent within six hours then decreased to 4 per cent by run termination. The new product attrition index test, instituted during this run, indicated a correlation between high alpha alumina and high product attrition rate.

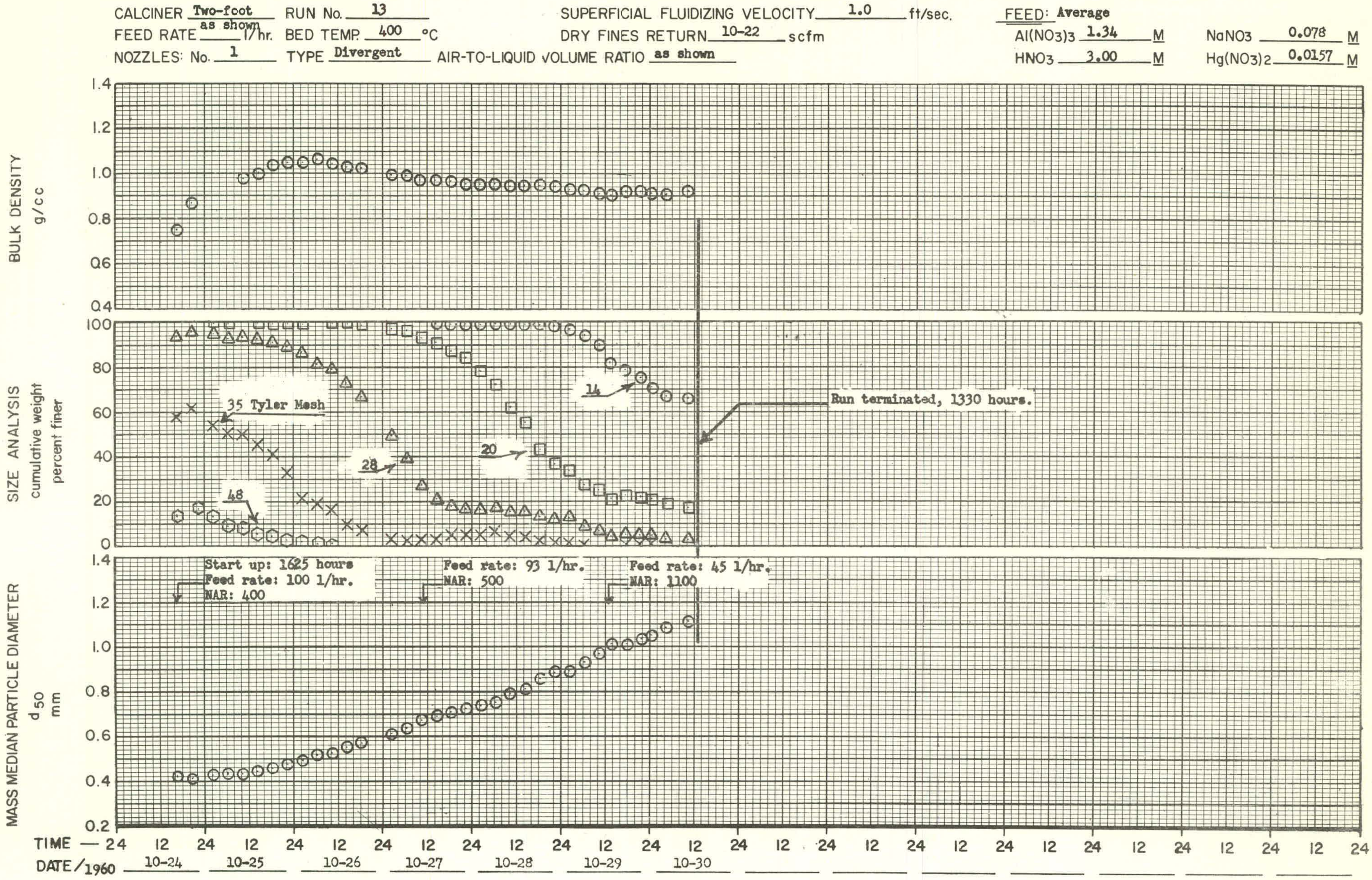

Fig. 17 Product data, Run 13.

CALCINER Two-foot RUN No. 13 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec
FEED RATE as shown l/hr BED TEMP. 400 °C DRY FINES RETURN 10-22 scfm
NOZZLES: No. 1 TYPE Divergent AIR-TO-LIQUID VOLUME RATIO as shown

FEED: $Al(NO_3)_3$ 1.34 M; HNO_3 3.00 M; $NaNO_3$ 0.078 M; $Hg(NO_3)_2$ 0.0157 M

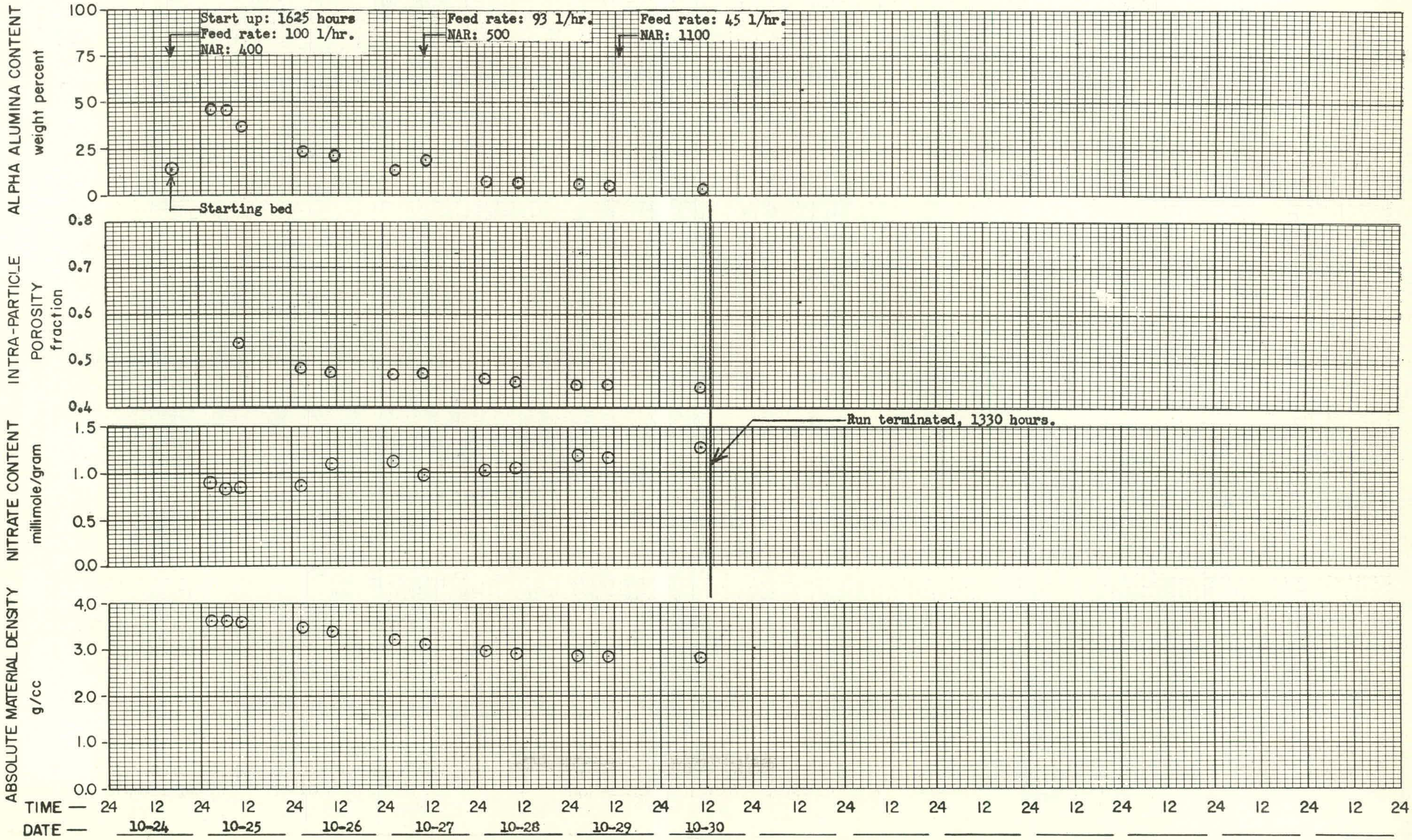

Fig. 18 Additional product data, Run 13.

CPP-S-1572

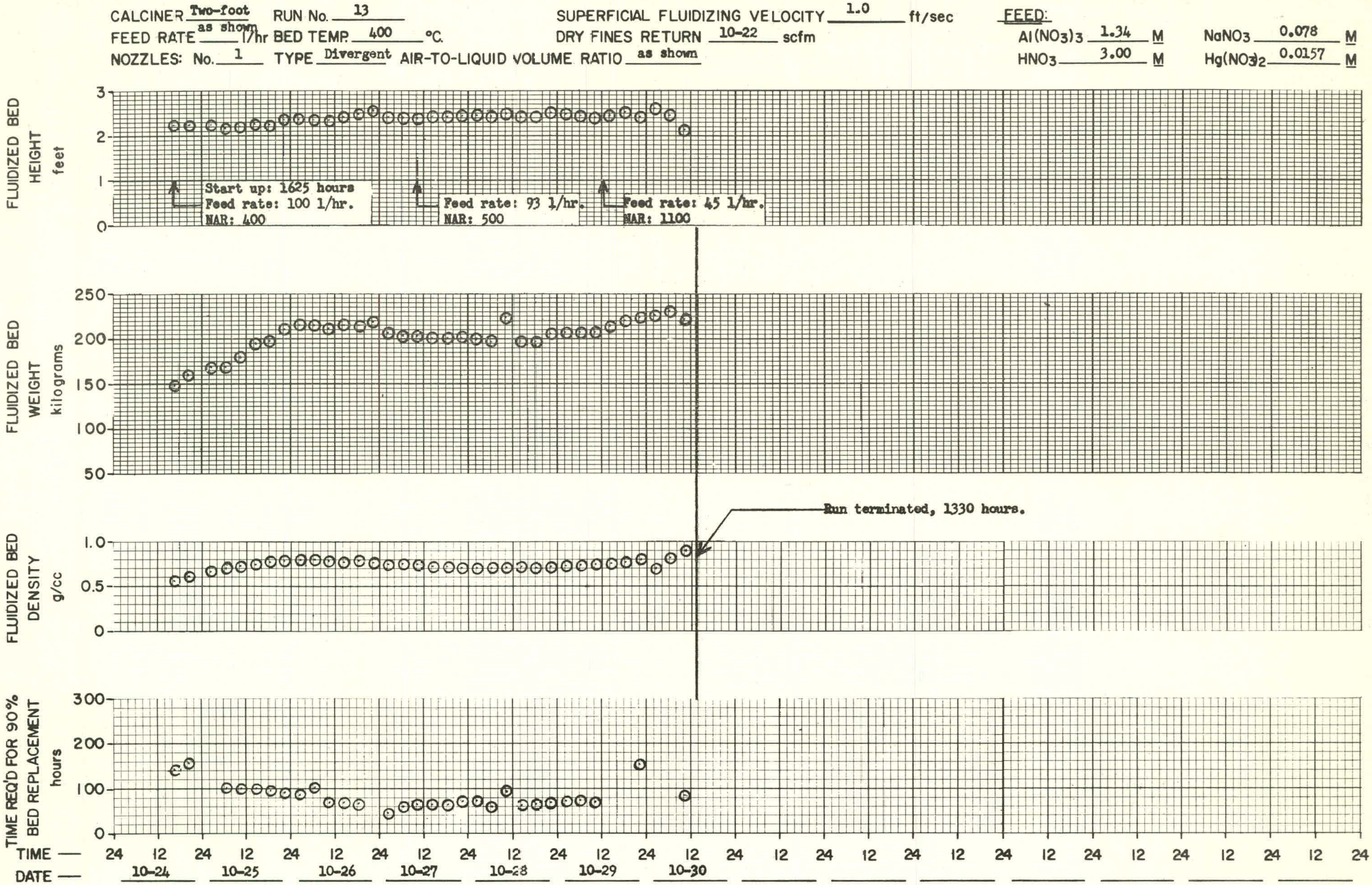

Fig. 19 Calciner bed data, Run 13.

CPP-S-1571

CALCINER Two-foot RUN No. 13 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec FEED:
FEED RATE as shown l/hr BED TEMP. 400 °C DRY FINES RETURN 10-22 scfm $Al(NO_3)_3$ 1.34 M $NaNO_3$ 0.078 M
NOZZLES: No. 1 TYPE Divergent AIR-TO-LIQUID VOLUME RATIO as shown HNO_3 3.00 M $Hg(NO_3)_2$ 0.0157 M

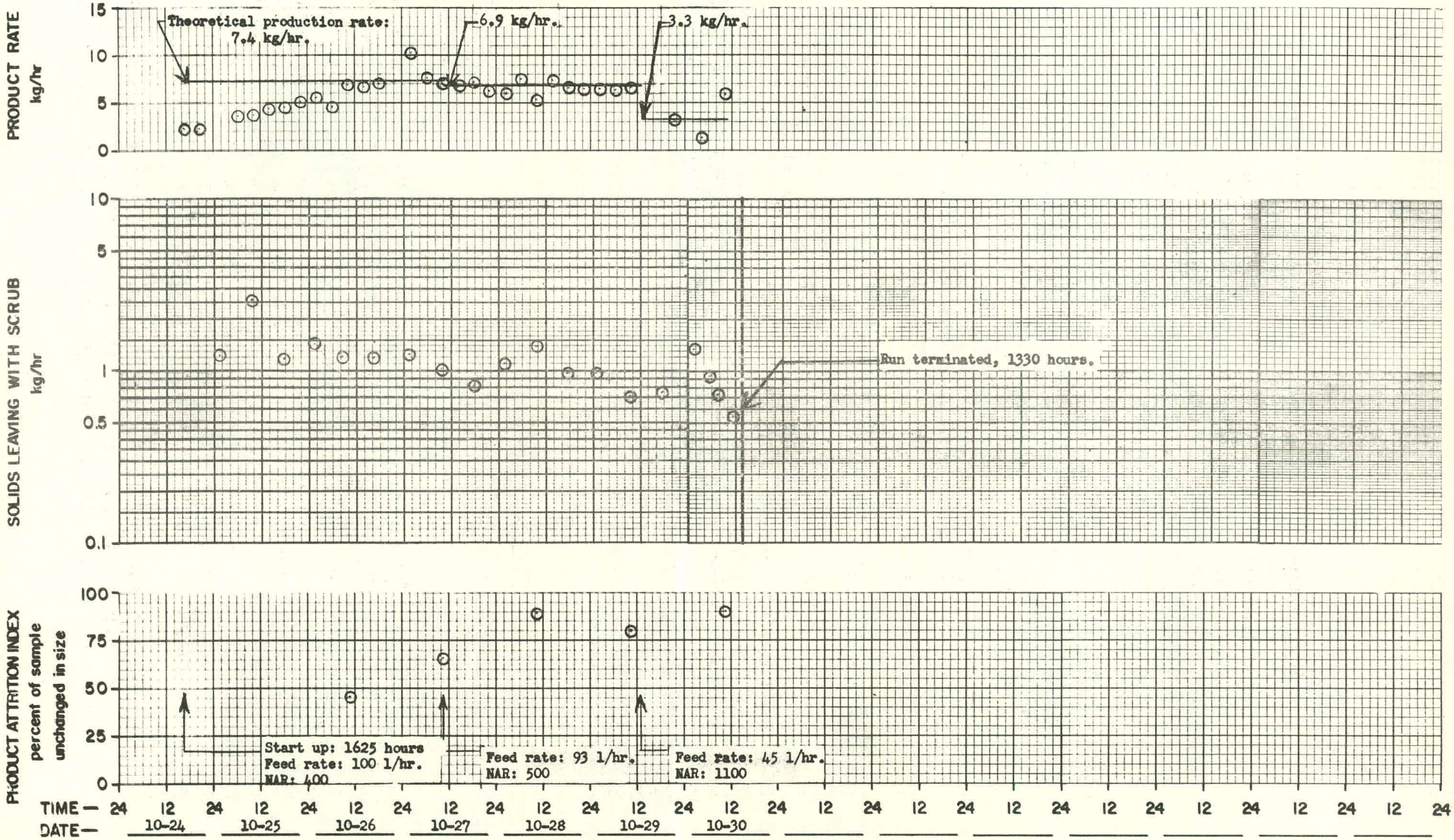

Fig. 20 General data, Run 13.

CPP-S-1573

Run 14

Period Covered: From November 7, 1960 to November 17, 1960.

Objective: To study the performance of a new feed nozzle cap of extended convergent design involving external air-liquid mixing. This design was used in an effort to minimize nozzle erosion. Another objective was to maintain the mass median particle diameter of product between 0.3 and 0.6 mm by adjusting the nozzle air-to-liquid volume ratio (NAR).

Equipment: That used during Run 13 with the exception of the feed nozzle cap. An extended convergent cap of stainless steel Type 347 (two-fluid, external mixing) was used in place of the extended divergent cap used during Run 13.

Cumulative NaK Heating System Operating Data (including this run):

134 startups; 6058 hours above 1000°F; 1208 hours below 1000°F.

Run Conditions:

Starting bed	Predominantly amorphous alumina generated during Run 11
Bed temperature, °C	400
Feed rate, l/hr	100 → 115 → 100
Nozzle air-to-liquid volume ratio	Set at several values between 250 and 426
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	6-16
Bed pressure, psia	20.1-22.4
Operating time, hours	119

Feed Composition:		
	Aluminum nitrate, M	1.31
	Nitric acid, M	2.97
	Sodium nitrate, M	0.081
	Mercuric nitrate, M	0.0156

Results: The erosion incurred by the extended convergent nozzle cap was negligible (0.2 g/yr). This nozzle, however, appeared to be sensitive to changes in NAR, in that relatively small changes produced sweeping changes in the product particle size. The alpha alumina content of the product increased from 14 to 36 per cent within 18 hours, and then decreased to 11 per cent at run termination. The intra-particle porosity (0.42-0.45) of the alumina product was again in the relatively low range which indicates that feed concentration and bed temperature affect the product porosity.

Shutdowns were caused by a leaking calciner flange gasket, by an air compressor failure, and by a leaking flange in the calciner off-gas line. The dry fines return flow was erratic, and

Run 14 (continued)

this system was shut down for the last 72 hours of the run when a hole eroded in the jet pump.

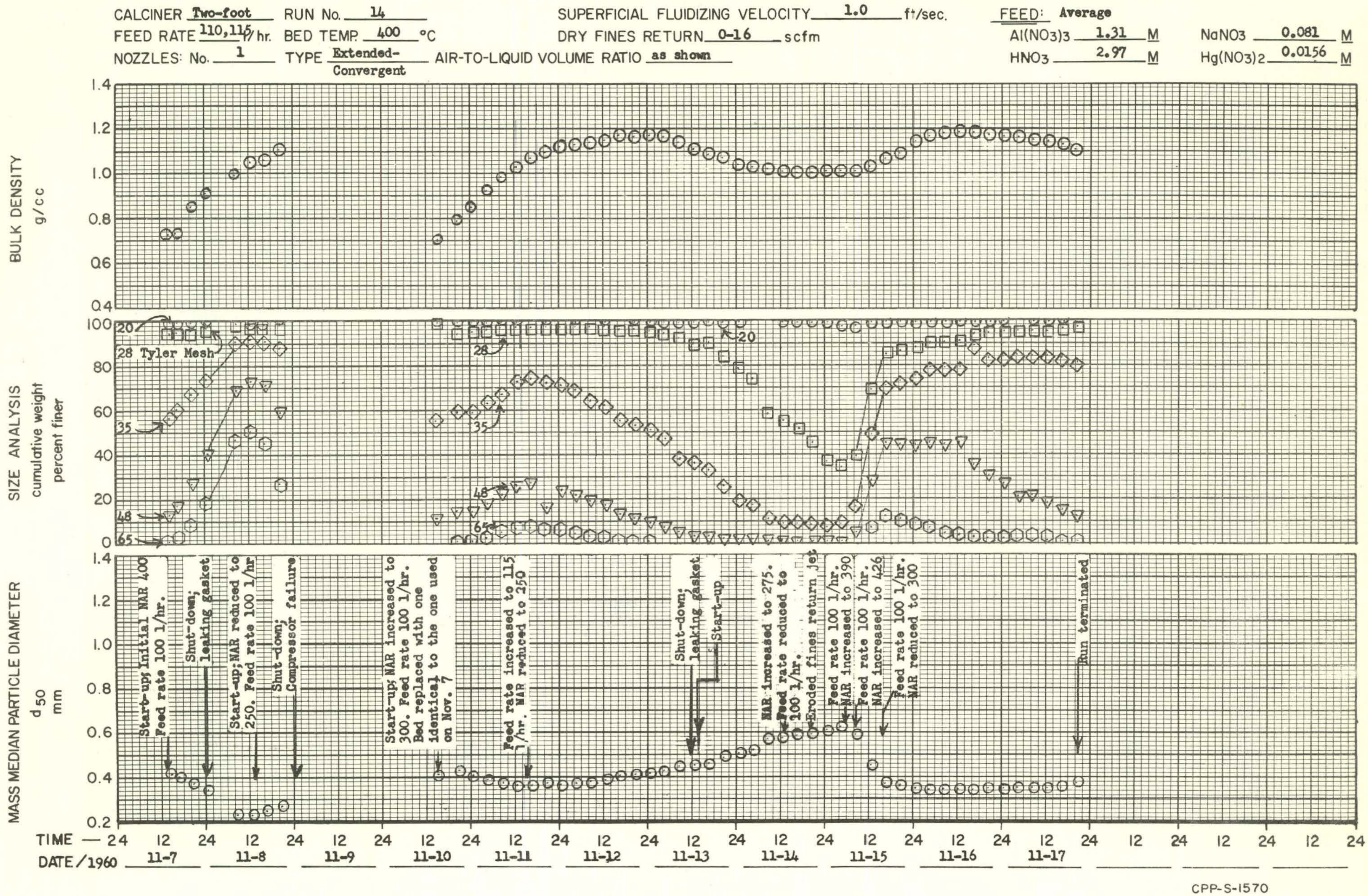

Fig. 21 Product data, Run 14.

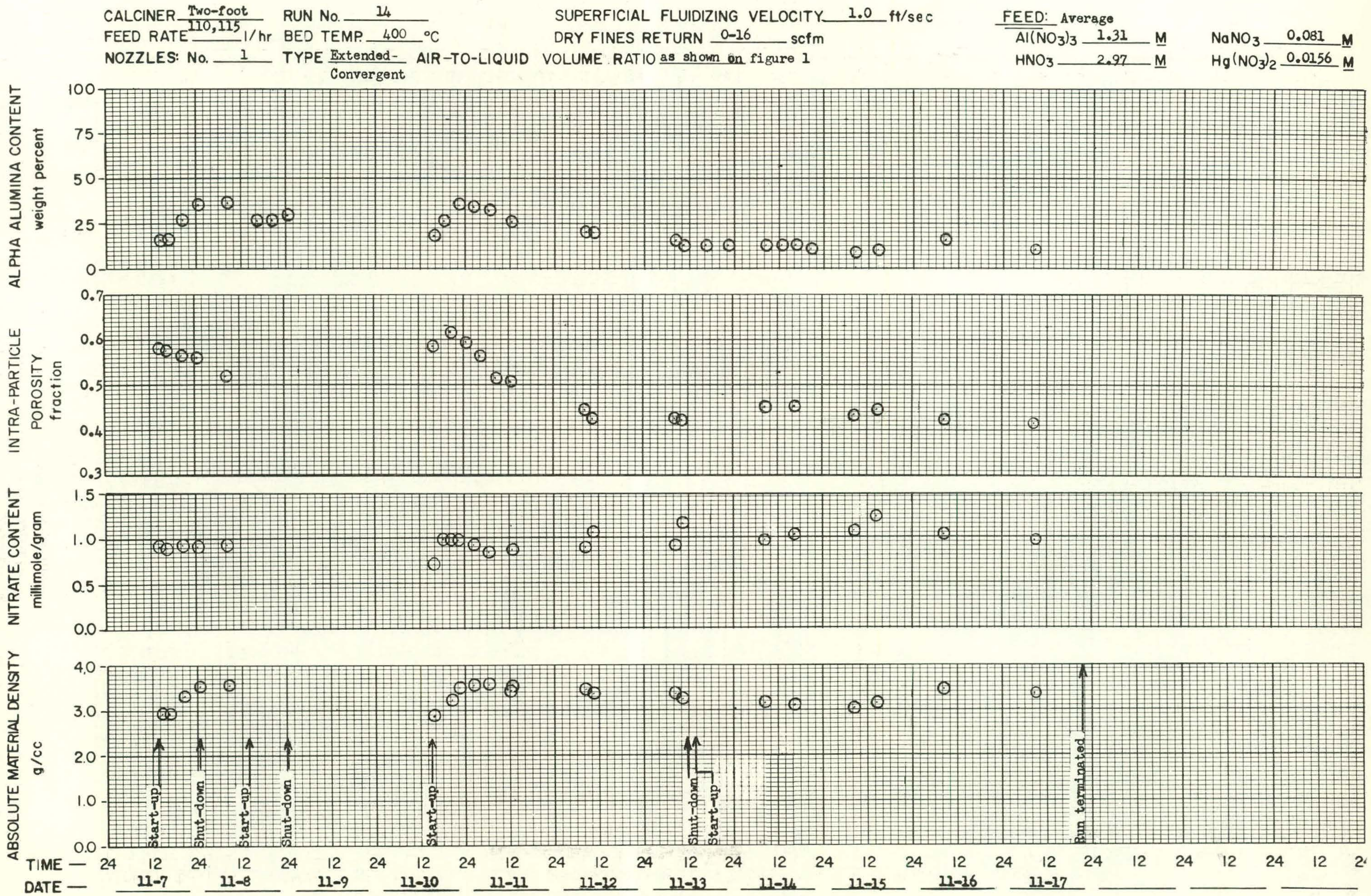

Fig. 22 Additional product data, Run 14.

CPP-S-1572

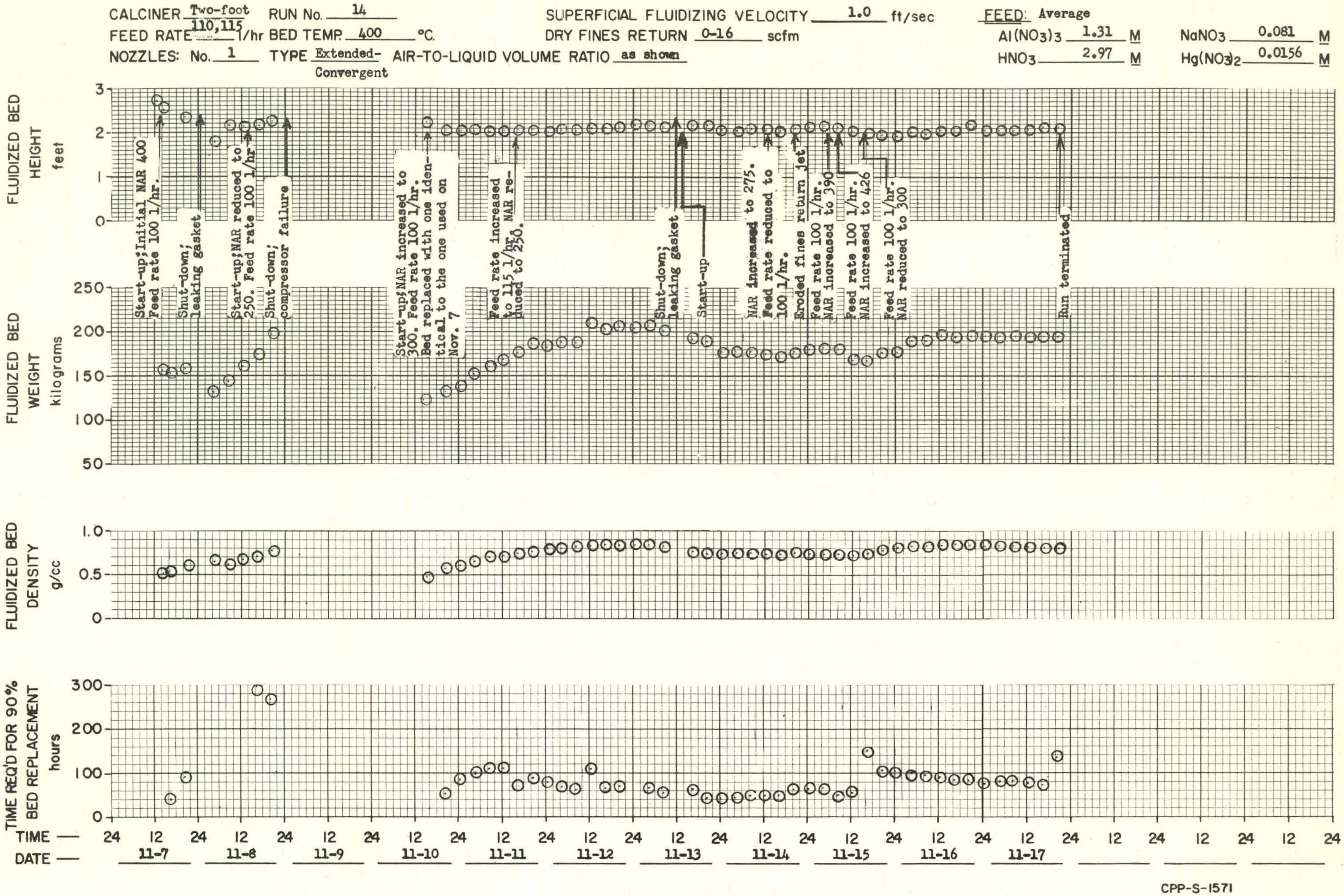

Fig. 23 Calciner bed data, Run 14.

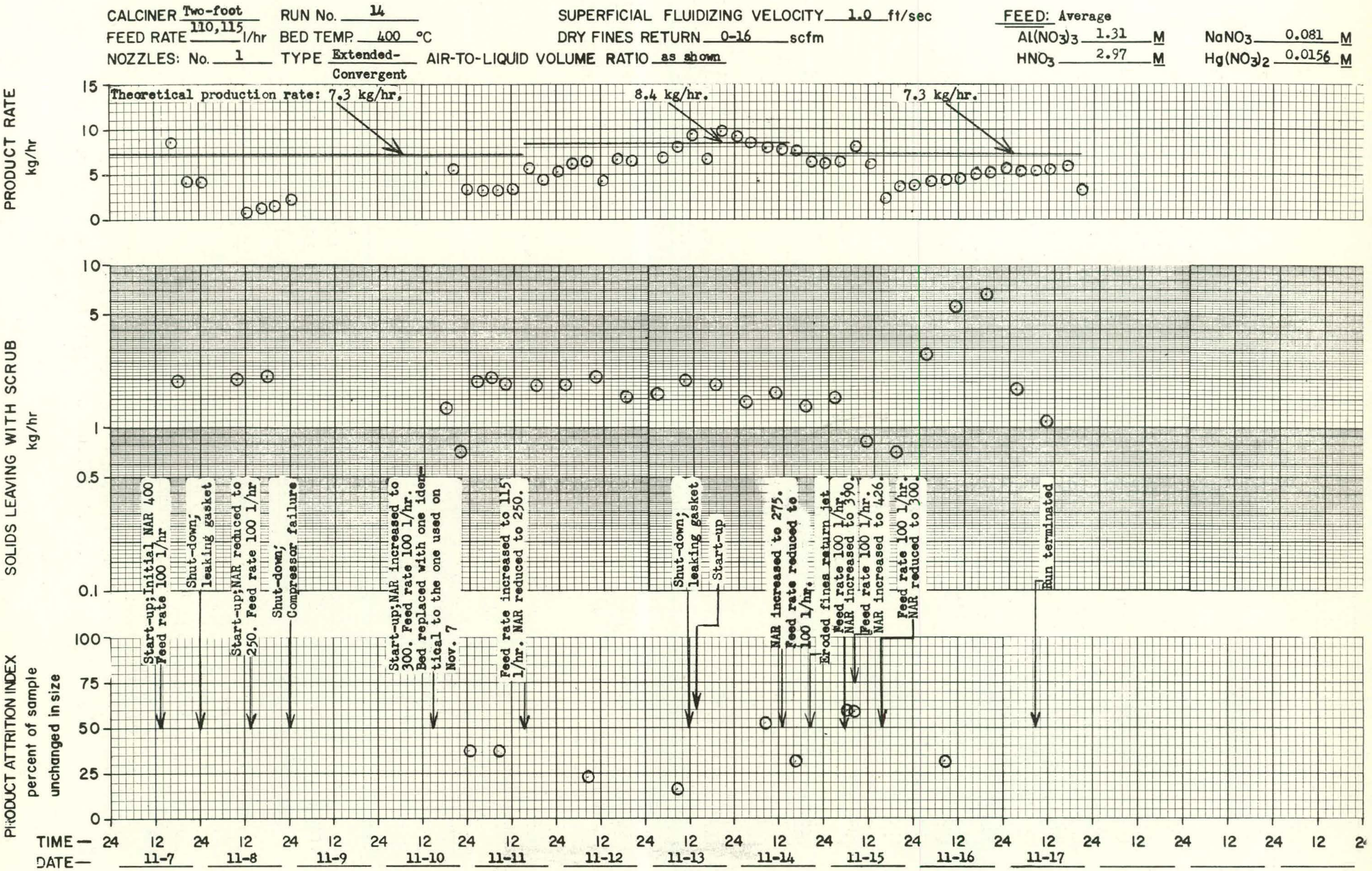

Fig. 24 General data, Run 14.

CPP-S-1573

Run 15

Period Covered: From December 6, 1960 to December 18, 1960.

Objective: To determine the effect of 500°C bed temperature and intermediate aluminum concentration on product porosity, to determine the erosion resistance of a standard flat-faced cap fabricated from Type 440-C stainless steel, and to determine the effect of 500°C bed temperature on alpha alumina behavior.

Equipment: That used during Run 14 with the following exceptions: (1) a standard flat-faced feed nozzle cap fabricated of Type 440-C stainless steel was used in place of the extended cap used during Run 14, and (2) the dry fines return system was modified for this and subsequent runs to return the fines to the bed at a point just above the air distributor plate, directly below the feed nozzle. (Fines had previously been returned to the plenum chamber below the air distributor plate.)

Cumulative NaK Heating System Operating Data (including this run):

140 startups; 6148 hours above 1000°F; 1208 hours below 1000°F.

Run Conditions:

Starting bed	Predominantly amorphous alumina generated during Runs 11 and 14(1)
Bed temperature, °C	500, 400→500(2)
Feed rate, l/hr	90
Nozzle air-to-liquid volume ratio	400
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	14-20
Bed pressure, psia	19.3-20.6
Operating time, hours	141

Feed Composition:	Aluminum nitrate, M	1.40
	Nitric acid, M	2.89
	Sodium nitrate, M	0.086
	Mercuric nitrate, M	0.016

(1) The alumina used for starting beds on December 6 and December 8 was that generated during Run 11. On December 9 the bed was replenished by using 88 kg of alumina from the final bed of Run 14. The starting bed on December 13 was alumina generated during Run 11.

(2) Run 15 consisted of two parts, A and B, differing with respect to bed temperature; during Part A the bed temperature was 500°C; during Part B the bed temperature was initially 400°C and was later increased to 500°C.

Results: A high porosity (0.57) alumina was generated from feed containing an average aluminum concentration of 1.40M calcined at 500°C bed temperature. Product having a porosity of 0.47 resulted

Run 15 (continued)

from calcining the same feed at 400°C bed temperature. The rate of formation of alpha alumina was enhanced at the higher (500°C) bed temperature. The erosion resistance of the regular flat-faced cap made of Type 440-C stainless steel was unsatisfactory (2.6 g/yr), although it was an improvement over that of the similar caps of titanium and Type 347 stainless steel tested during Runs 11 and 12, respectively.

The over-insulated lead gaskets sealing the air distributor plate and air entry plenum to the calciner vessel melted causing a shutdown. Other brief shutdowns were caused by an electrical short circuit of the NaK pump and by a failure of the feed pump.

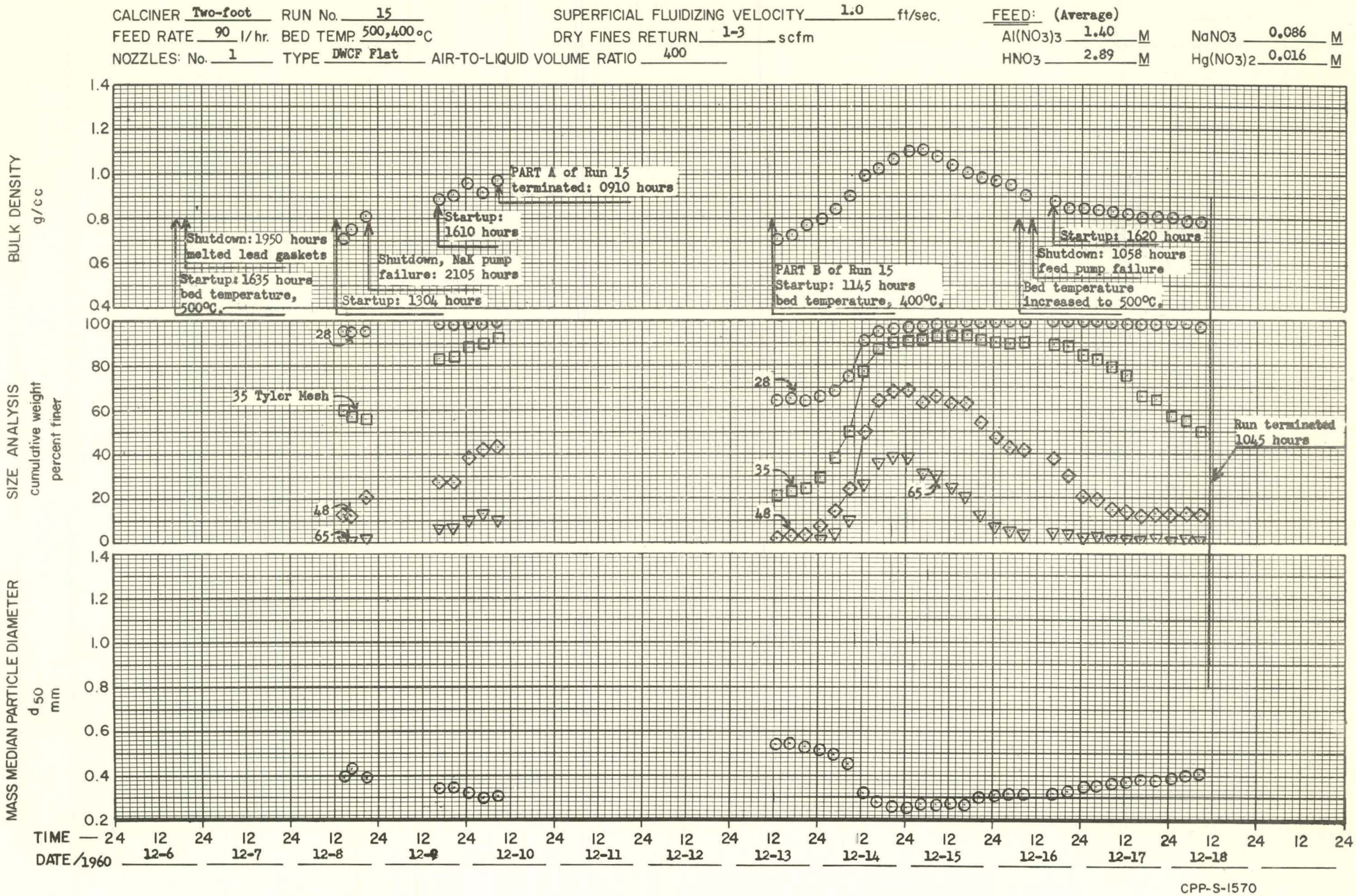

Fig. 25 Product data, Run 15.

CALCINER Two-foot RUN No. 15 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec FEED: Average

FEED RATE 90 l/hr BED TEMP. 500, 400 °C DRY FINES RETURN 1-3 scfm $Al(NO_3)_3$ 1.40 M $NaNO_3$ 0.086 M

NOZZLES: No. 1 TYPE DWCF Flat AIR-TO-LIQUID VOLUME RATIO 400 HNO_3 2.89 M $Hg(NO_3)_2$ 0.016 M

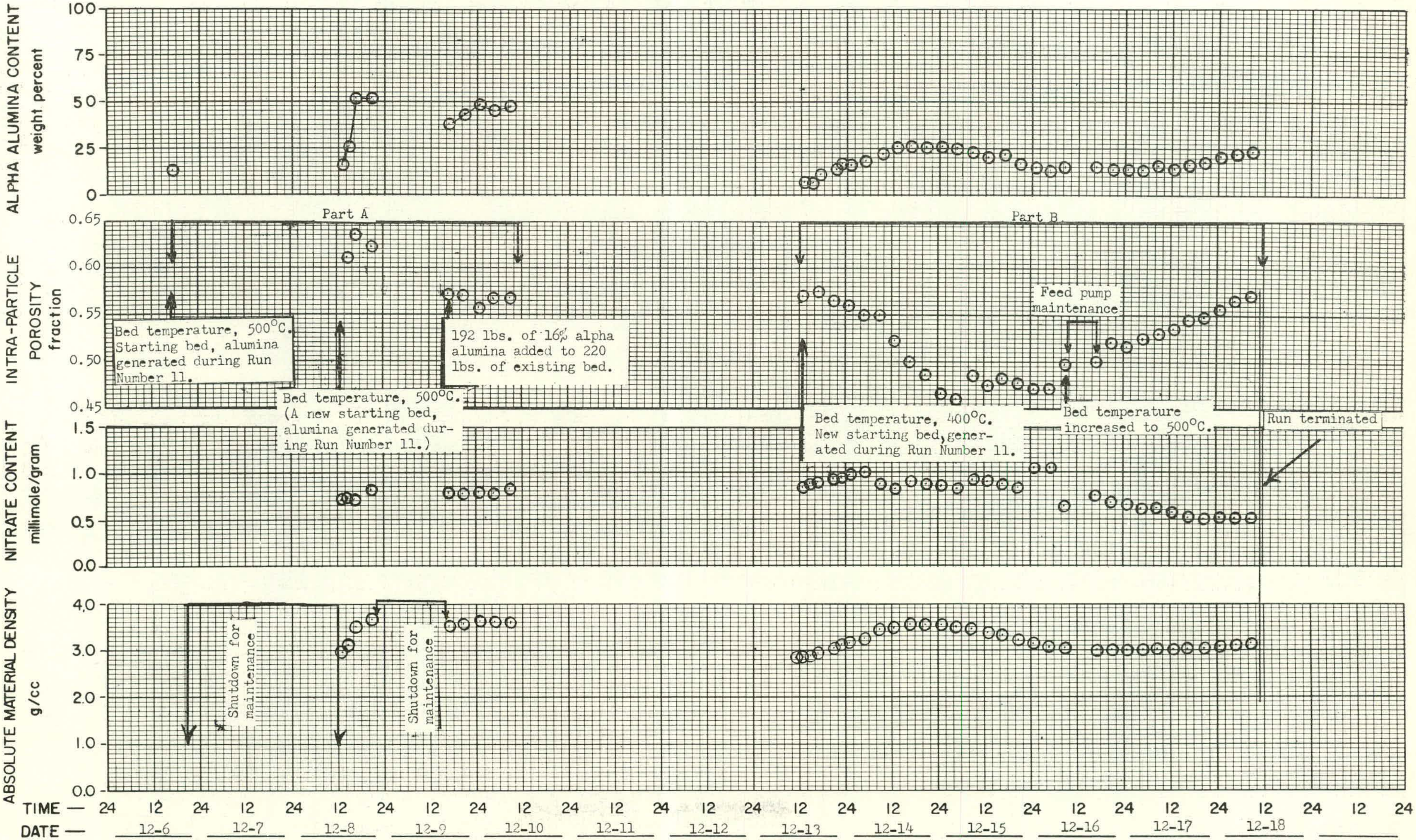

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Fig. 26 Additional product data, Run 15.

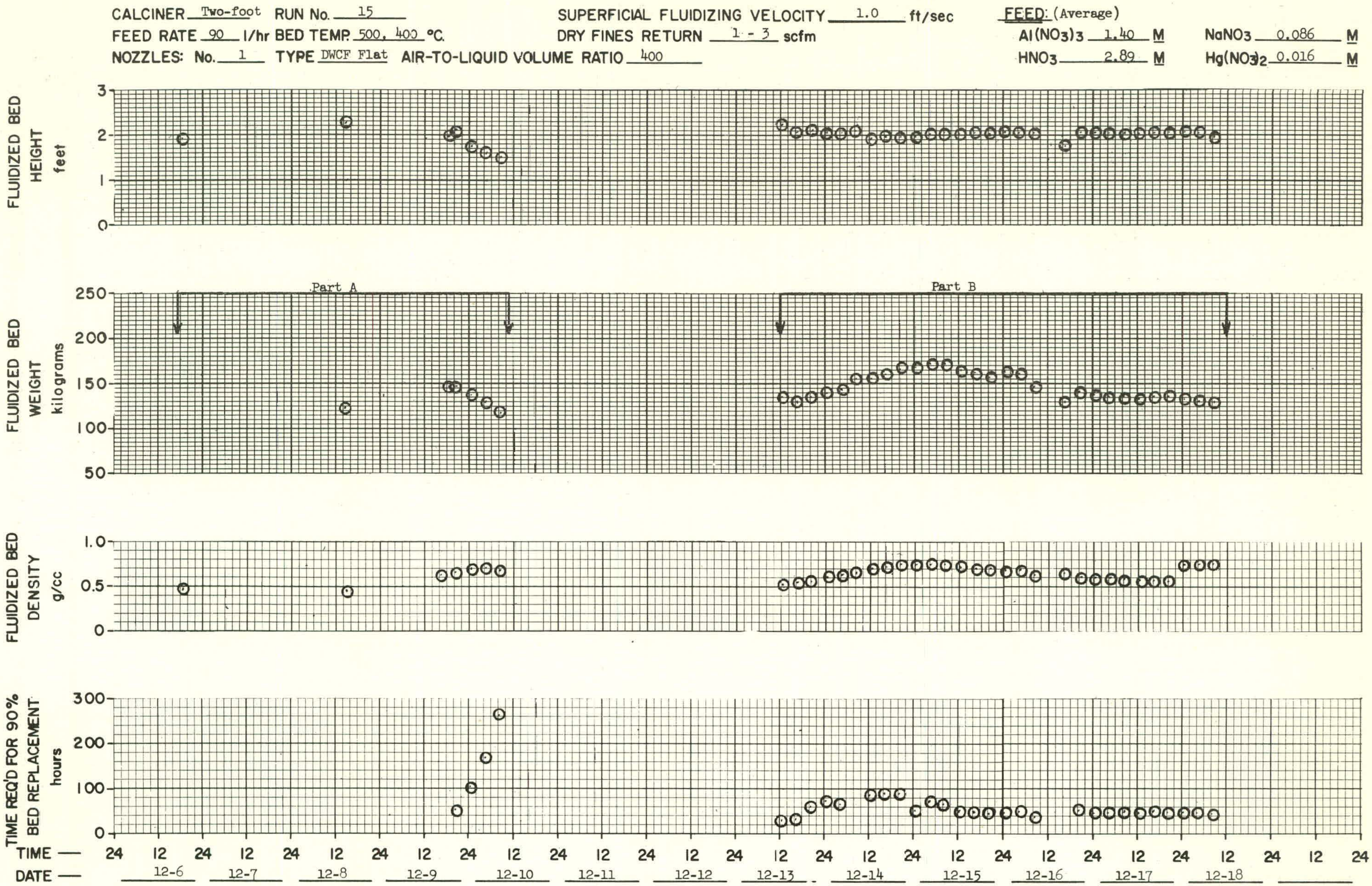

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Fig. 27 Calciner bed data, Run 15.

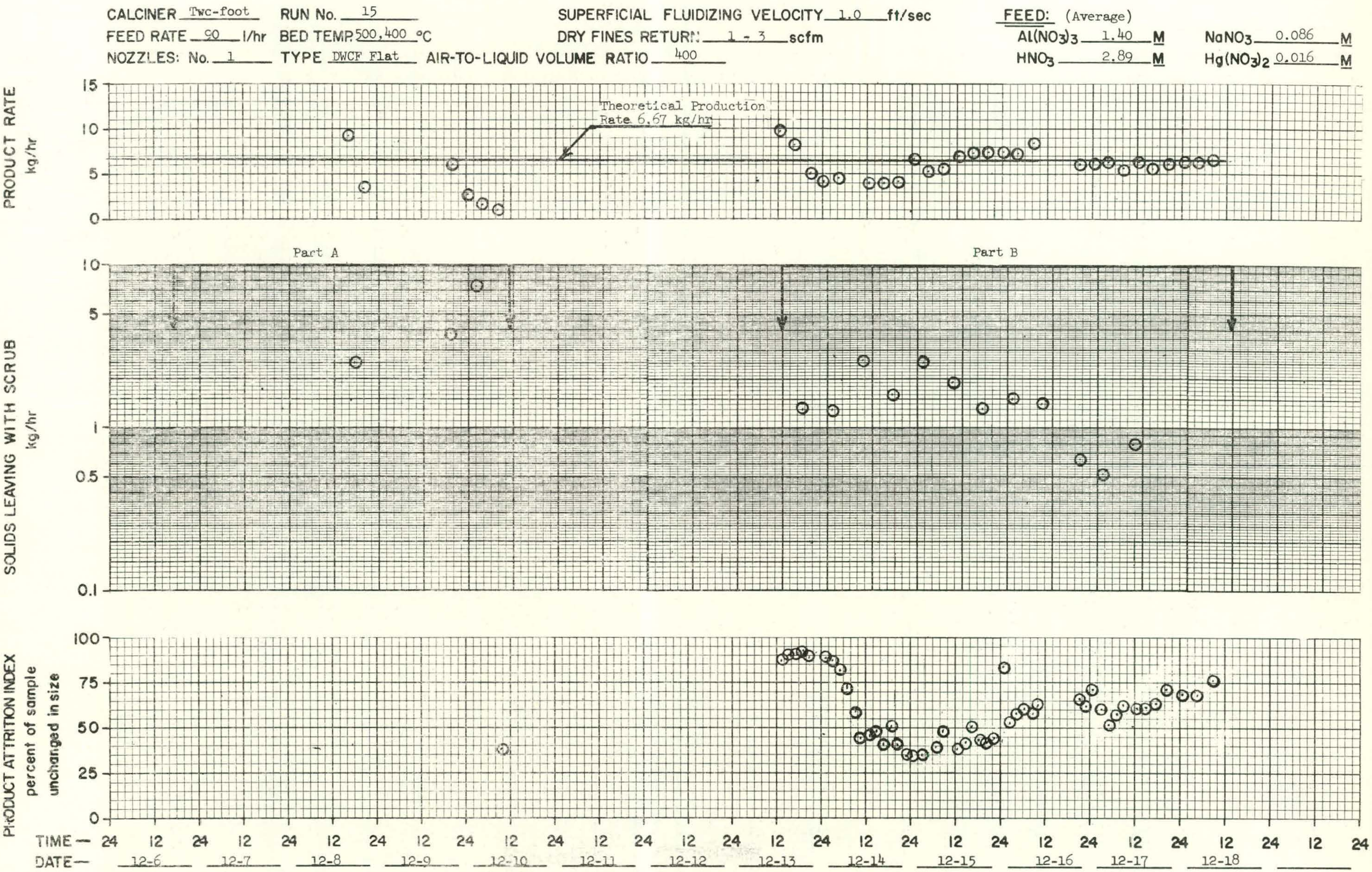

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Fig. 28 General data, Run 15.

Run 16

Period Covered: From December 28, 1960 to January 5, 1961.

Objective: To determine whether feed concentration as well as bed temperature influences intra-particle porosity of alumina product by calcining feed containing 1.95M aluminum nitrate at 400°C. This aluminum feed concentration had previously been calcined at 500°C and had produced a more porous product than 1.29M aluminum feed concentration at 500°C.

Equipment: That used during Run 15 with the exception of the feed nozzle cap. A standard flat-faced cap fabricated of titanium and flame-sprayed with alumina was used in lieu of the similar cap of Type 440-C stainless steel used during Run 15.

Cumulative NaK Heating System Operating Data (including this run):

144 startups; 6150 hours above 1000°F; 1426 hours below 1000°F.

Run Conditions:

Starting bed	Alumina generated during Run 12
Bed temperature, °C	400
Feed rate, l/hr	90
Nozzle air-to-liquid	400
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	15.4-18.4
Bed pressure, psia	20.9-21.3
Operating time, hours	200

Feed Composition:		
	Aluminum nitrate, M	1.95
	Nitric acid, M	1.25
	Sodium nitrate, M	0.089
	Mercuric nitrate, M	0.006

Results: Product of a high intra-particle porosity (0.52-0.58), indicated a direct dependence of this property upon feed aluminum concentration. Uniform cycling of all product and bed characteristics was clearly evident during most of this run. The cause of the cycling was not determined; a review of the operating procedures indicated that the cycling was not caused or disturbed by normal variations in the operating technique. The alpha alumina content of the product appeared to be related to the bed retention time before and during the cycling.

The erosion resistance of the flame-sprayed nozzle cap of the feed nozzle was excellent. An erosion rate of 0.5 g/yr was observed.

CALCINER TWO-FOOT RUN No. 16 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec.
FEED RATE 90 l/hr. BED TEMP. 400 °C DRY FINES RETURN 0.8-2.3 scfm
NOZZLES: No. 1 TYPE DWCF-Flat AIR-TO-LIQUID VOLUME RATIO 400

FEED:
$Al(NO_3)_3$ 1.95 M $NaNO_3$ 0.089 M
HNO_3 1.25 M $Hg(NO_3)_2$ 0.006 M

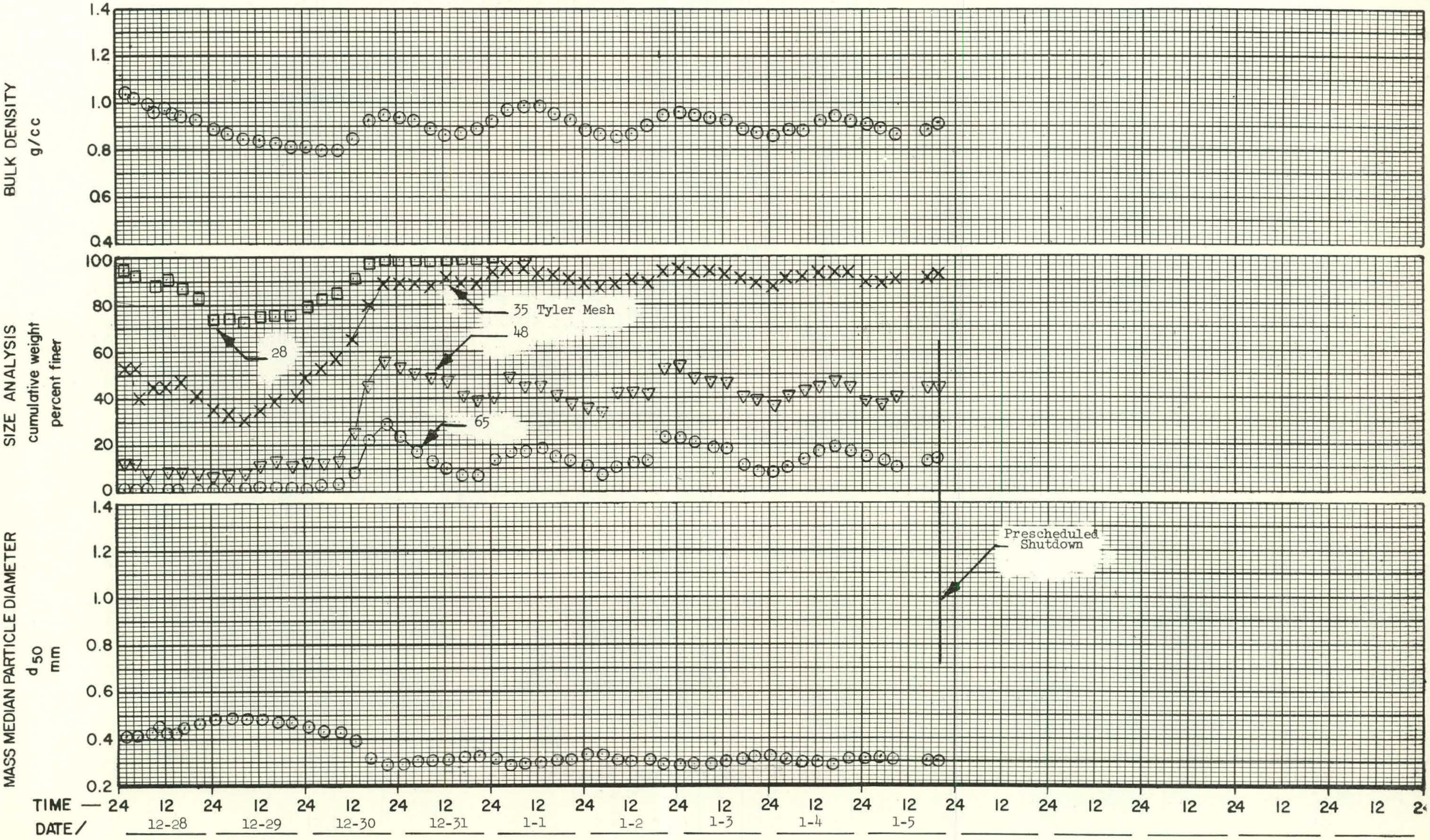

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Fig. 29 Product data, Run 16.

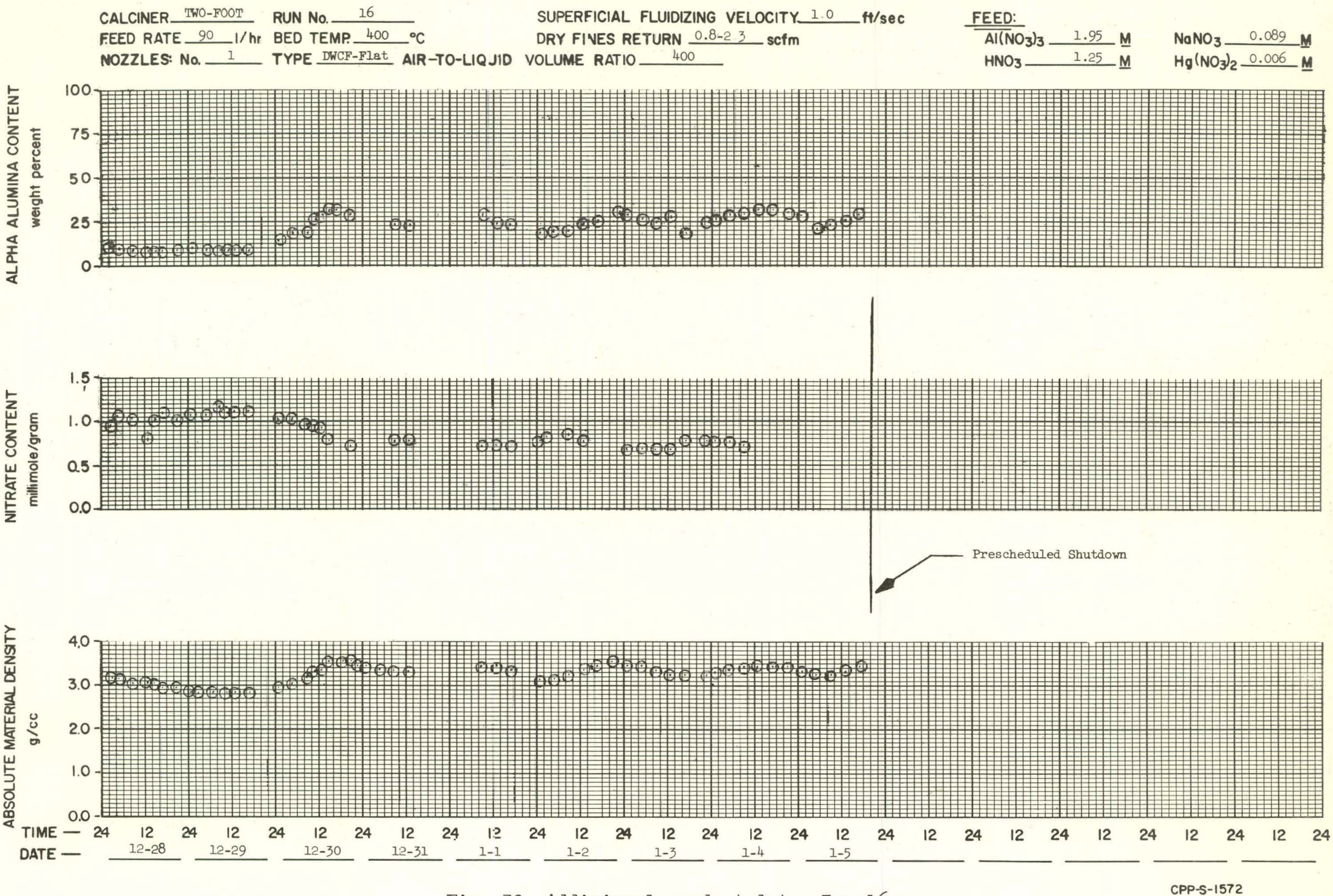

Fig. 30 Additional product data, Run 16.

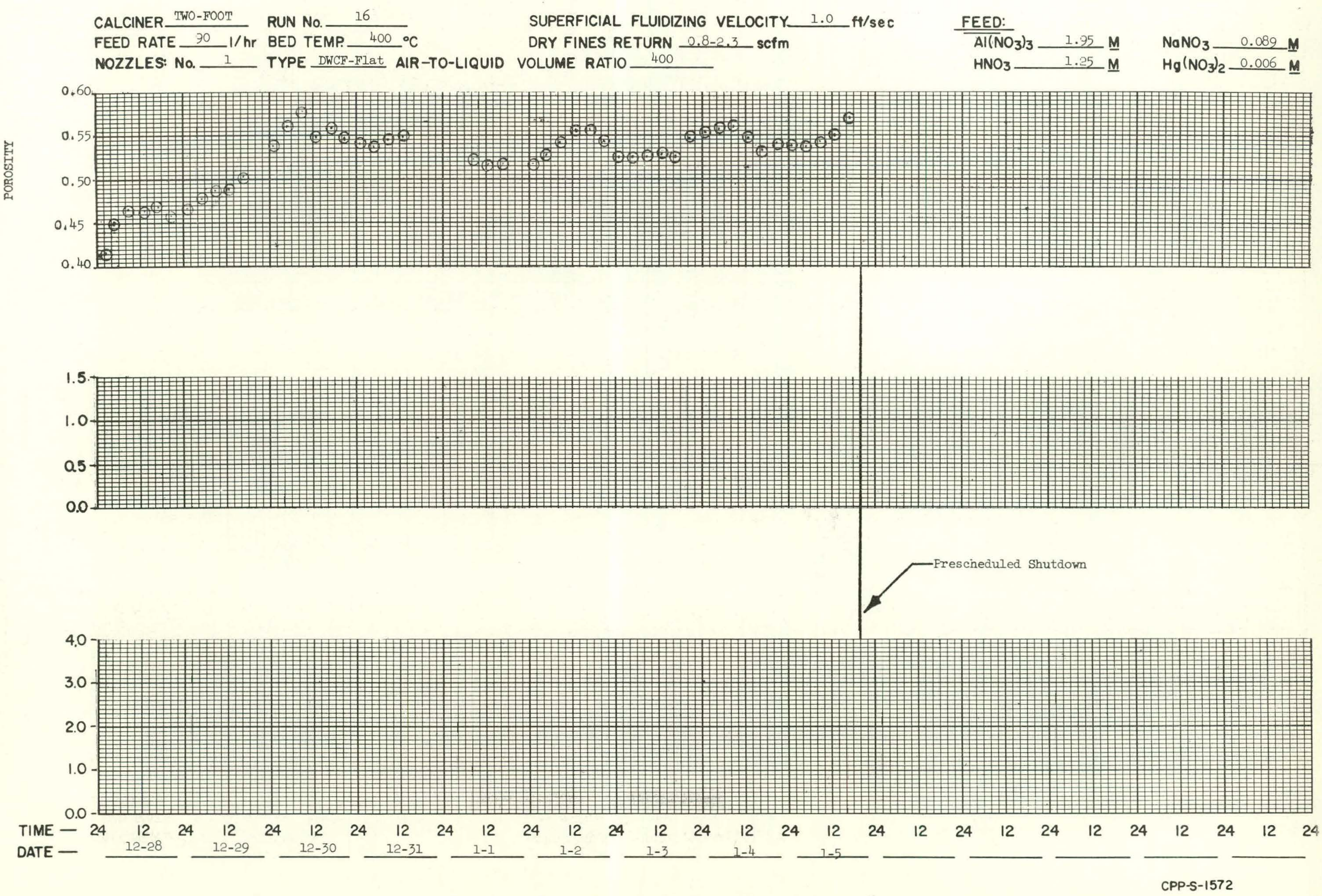

Fig. 31 Additional product data, Run 16.

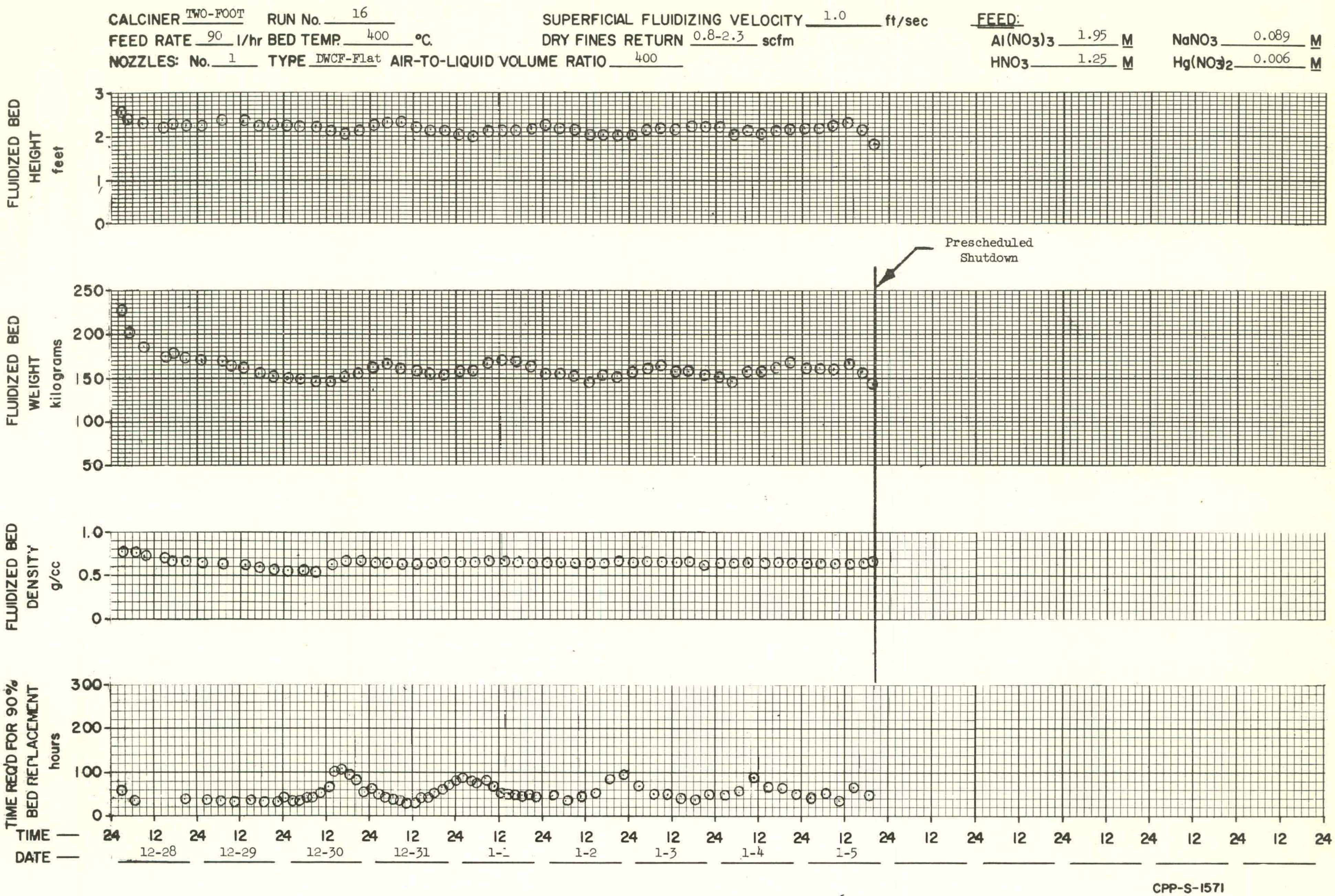

Fig. 32 Calciner bed data, Run 16.

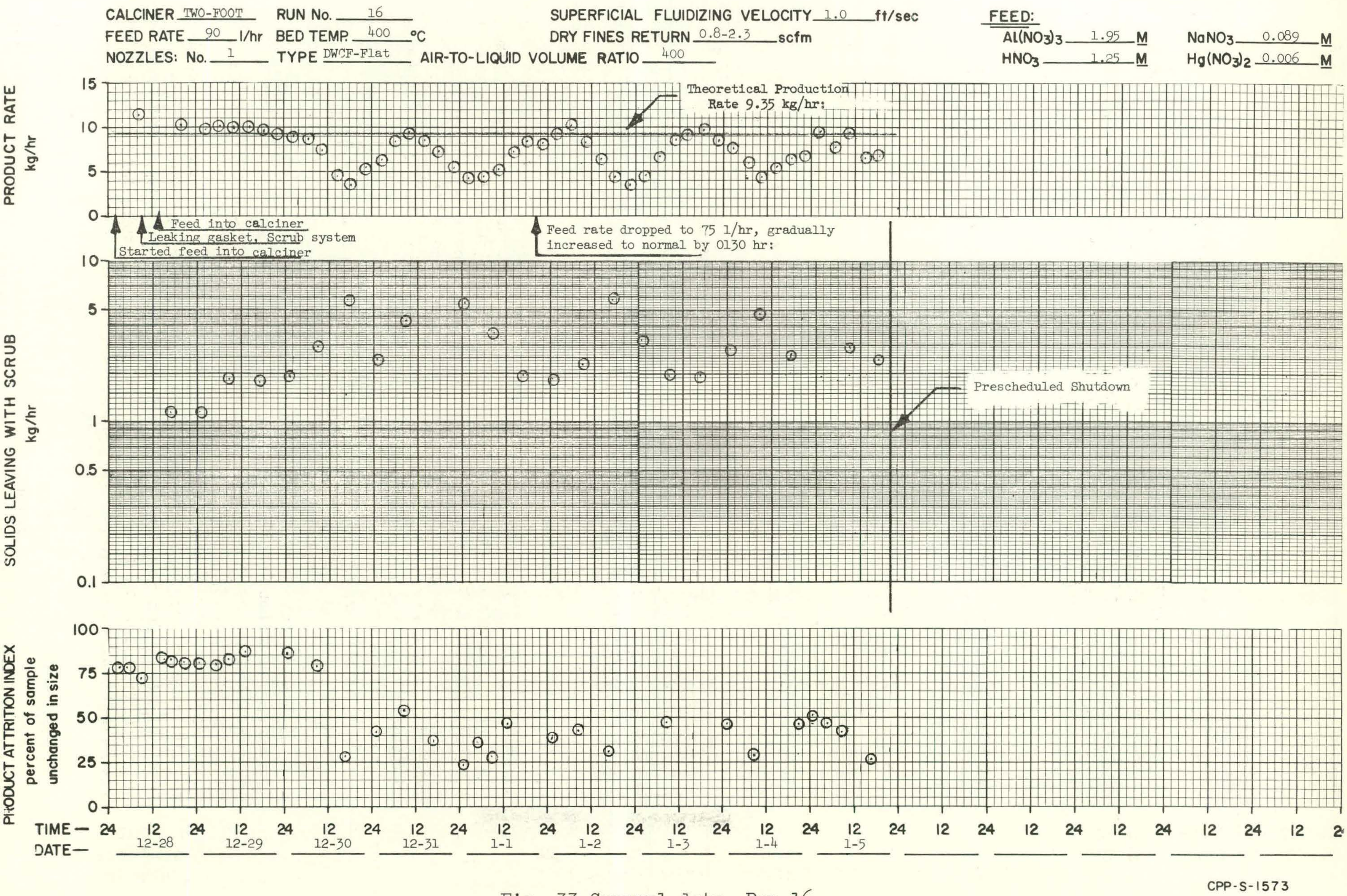

Fig. 33 General data, Run 16

Run 17

Period Covered: From January 24, 1961 to February 9,1961.

Objective: To define further the calcination conditions necessary to generate alumina having a low intra-particle porosity and to check out use of sand starting bed. During this run, 1.50M aluminum nitrate feed solution was calcined at 425°C bed temperature.

Equipment: That used during Run 16.

Cumulative NaK Heating System Operating Data (including this run):

146 startups; 6257 hours above 1000°F; 1707 hours below 1000°F.

Run Conditions:

Starting bed	Ammon sand
Bed temperature, °C	425
Feed rate, l/hr	90
Nozzle air-to-liquid volume ratio	400 → 450 → 300 → 450 → 300
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate	None to variable
Bed pressure, psia	20.4-21.5
Operating time, hours	388

Feed Composition:		
	Aluminum nitrate, M	1.50
	Nitric acid, M	1.25
	Sodium nitrate, M	0.089
	Mercuric nitrate, M	0.006

Results: Alumina having a porosity of about 0.46 was generated from the feed containing 1.50M aluminum nitrate at 425°C bed temperature. A relatively high NAR appeared to enhance the conversion of an amorphous bed into an alpha alumina bed. Sand was effectively utilized as a starting bed, thus eliminating "past history" effects of the starting bed material.

The flame-sprayed alumina on the flat-faced nozzle cap previously used on Run 16 flaked off.

Erosion of an S-shaped pipe between the venturi scrubber and the scrubber cyclone required a calciner shutdown while a patch was welded over the eroded pipe. From the start of the run, the dry fines return air jet and/or line periodically tended to clog; finally after 6-1/2 days of the run, the line became so tightly clogged that no further attempts were made to return fines to the calciner bed. Intermittent clogging of the slurry effluent line from the scrubber cyclone occurred during periods when the off-gas had a high solids loading.

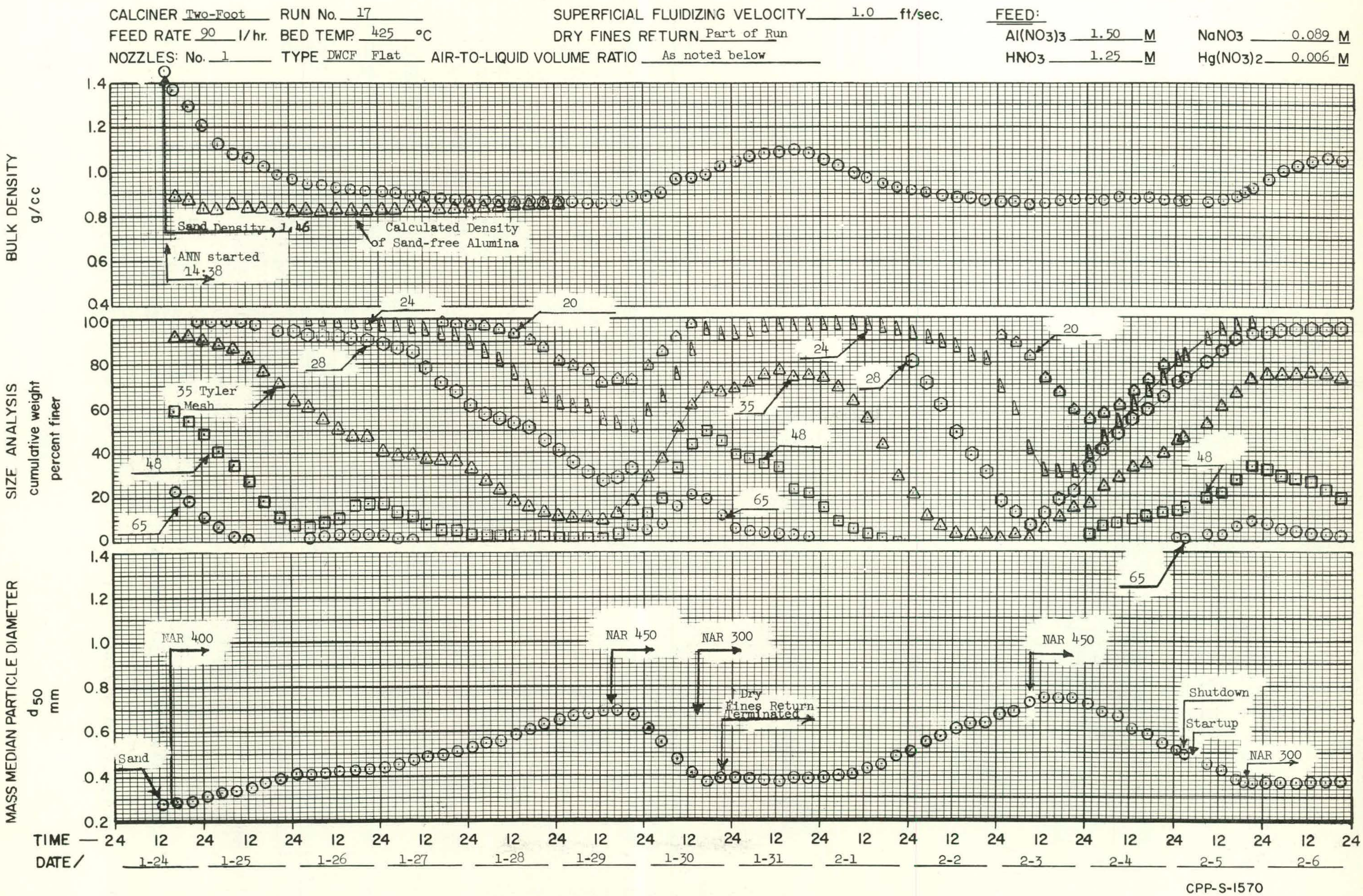

Fig. 34 Product data, Run 17 (sheet 1 of 2).

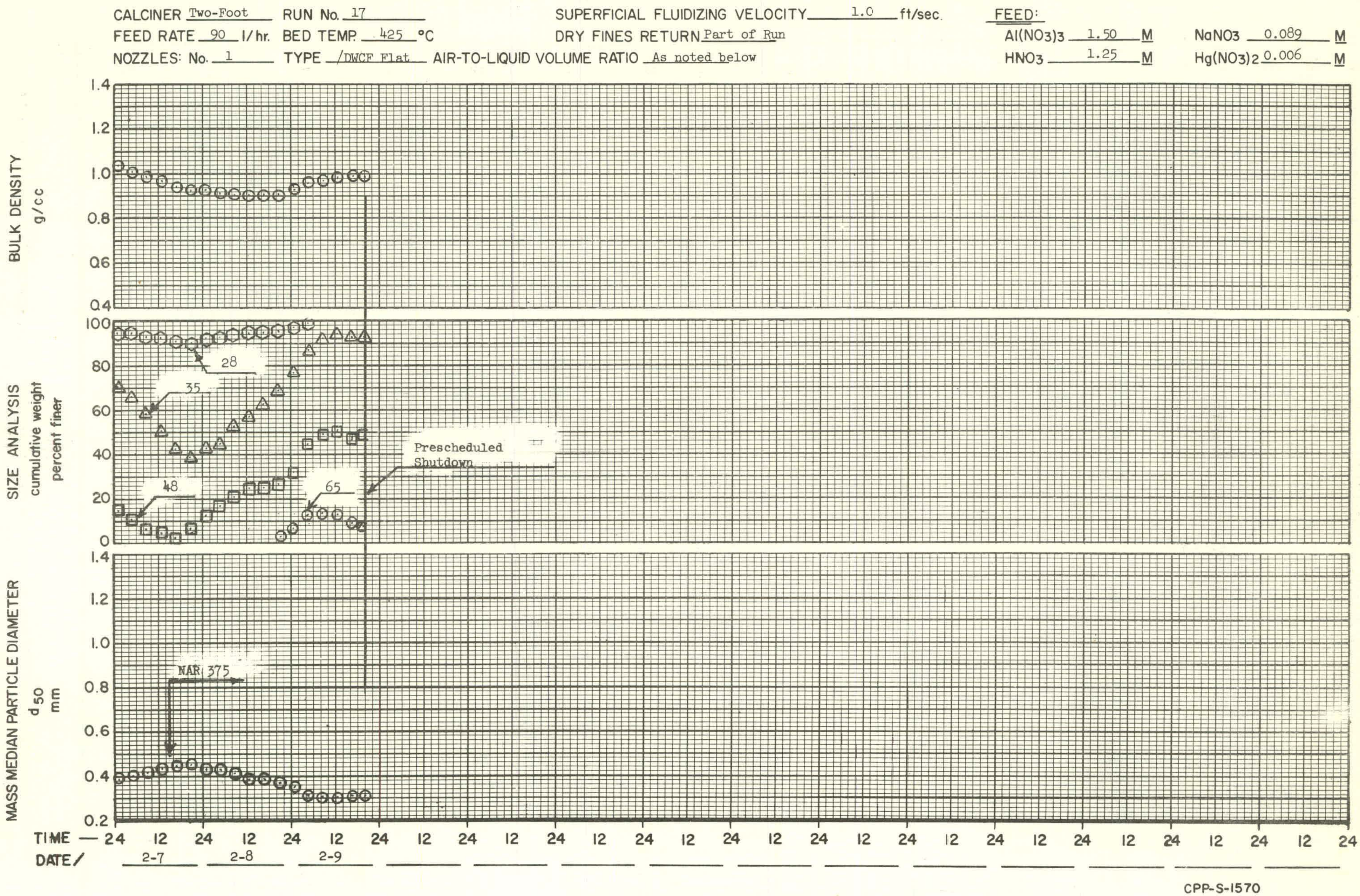

Fig. 34 Product data, Run 17 (sheet 2 of 2).

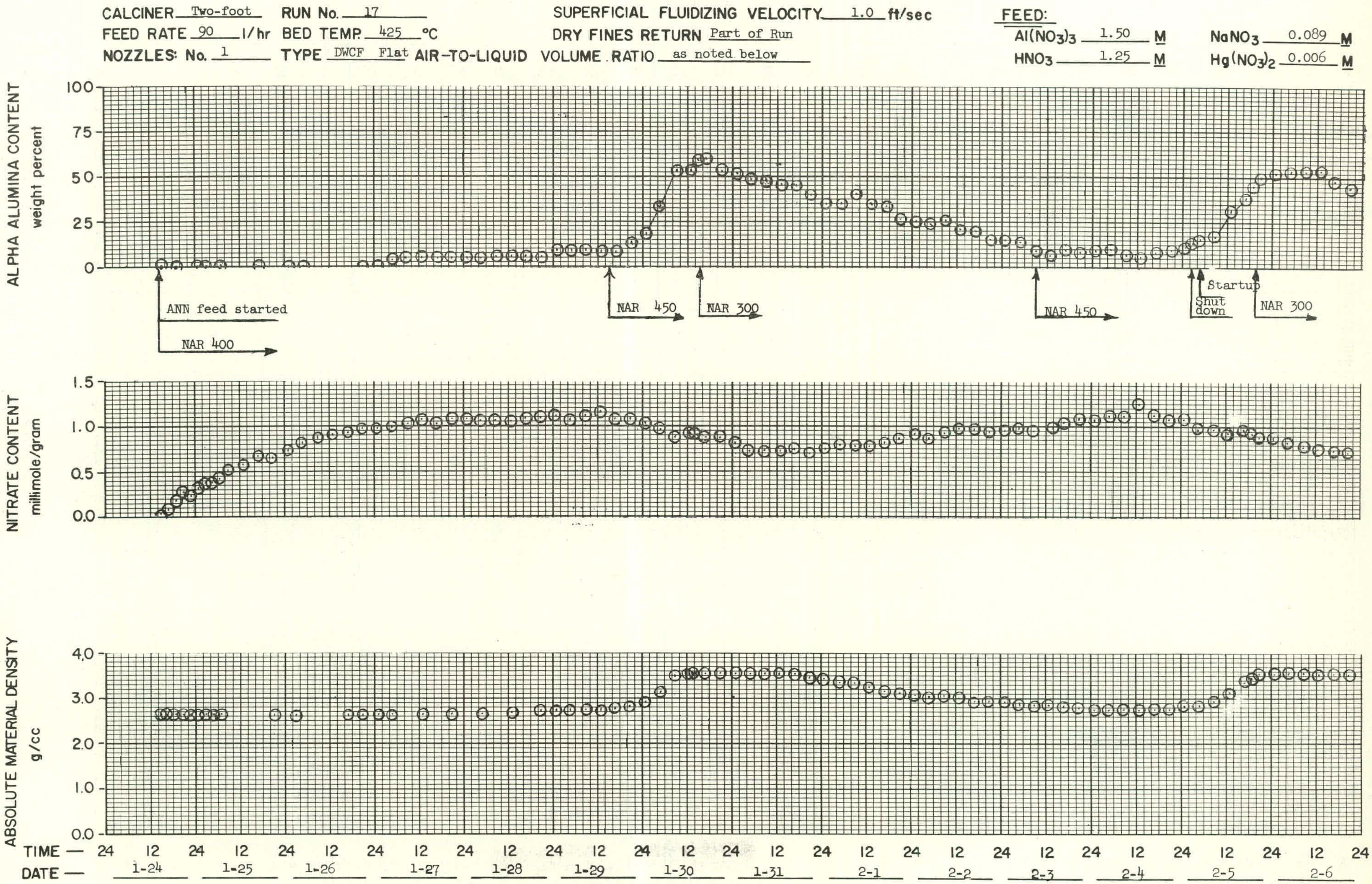

Fig. 35 Additional product data, Run 17 (sheet 1 of 2).

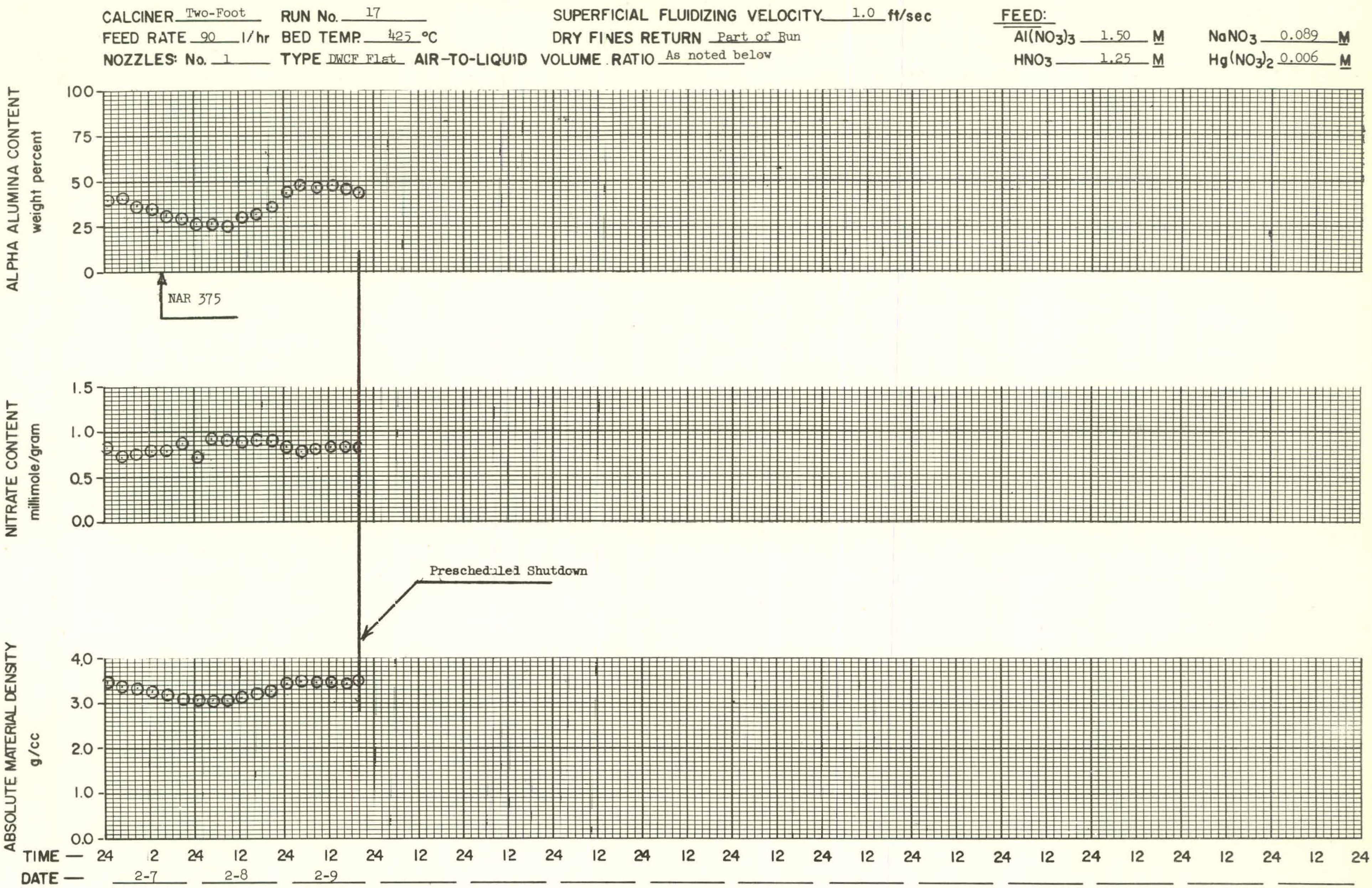

Fig. 35 Additional product data, Run 17 (sheet 2 of 2).

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CALCINER Two-Foot RUN No. 17 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

FEED RATE 90 l/hr BED TEMP. 425 °C DRY FINES RETURN Part of Run

NOZZLES: No. 1 TYPE DWCF Flat AIR-TO-LIQUID VOLUME RATIO As noted on Figure 1

FEED:

$Al(NO_3)_3$ 1.50 M NaNO$_3$ 0.089 M

HNO$_3$ 1.25 M $Hg(NO_3)_2$ 0.006 M

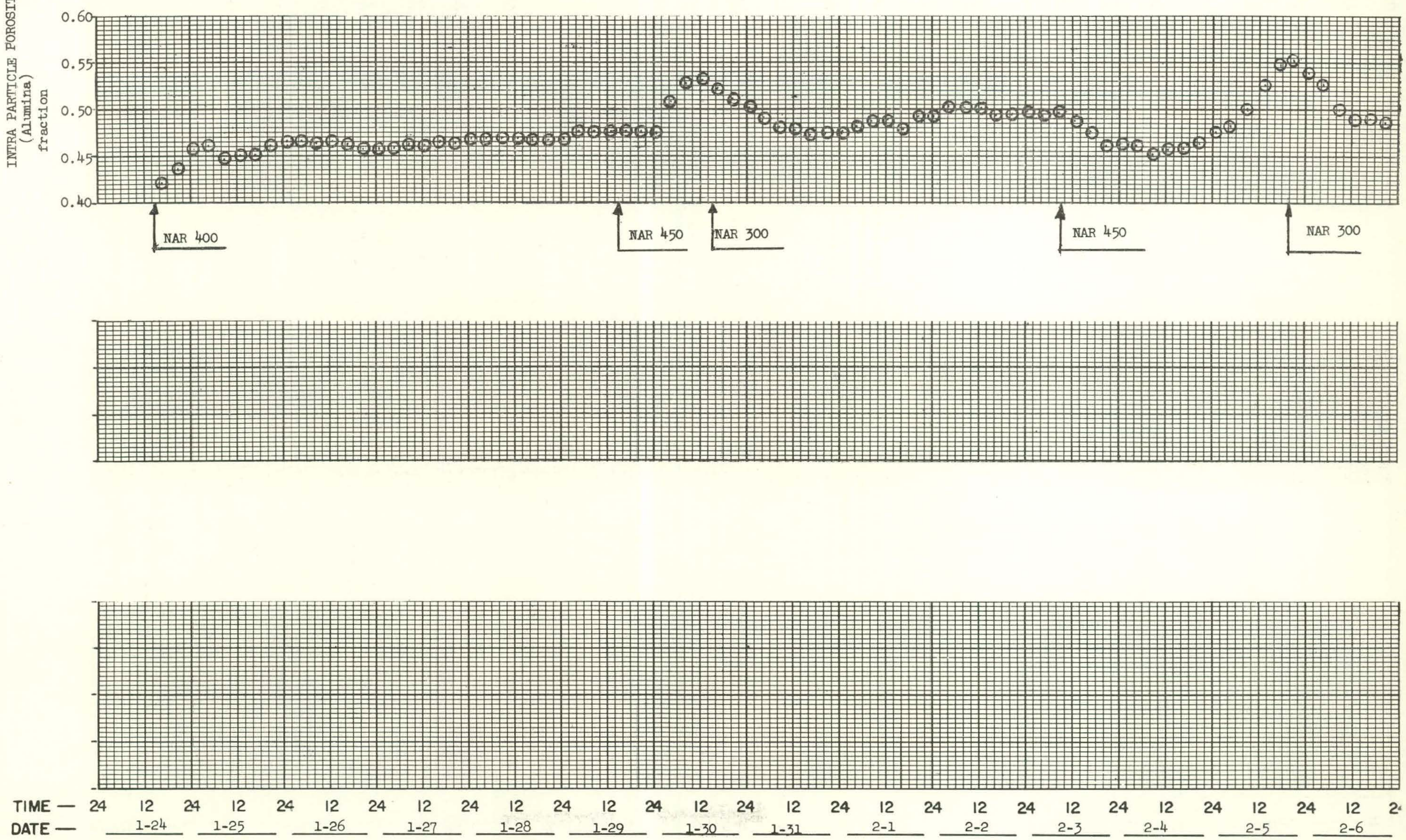

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Fig. 36 Additional product data, Run 17 (sheet 1 of 2).

CALCINER Two-Foot RUN No. 17 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

FEED RATE 90 l/hr BED TEMP. 425 °C DRY FINES RETURN Part of Run

NOZZLES: No. 1 TYPE DWCF Flat AIR-TO-LIQUID VOLUME RATIO As noted on Figure 1

FEED:

$Al(NO_3)_3$ 1.50 M $NaNO_3$ 0.089 M

HNO_3 1.25 M $Hg(NO_3)_2$ 0.006 M

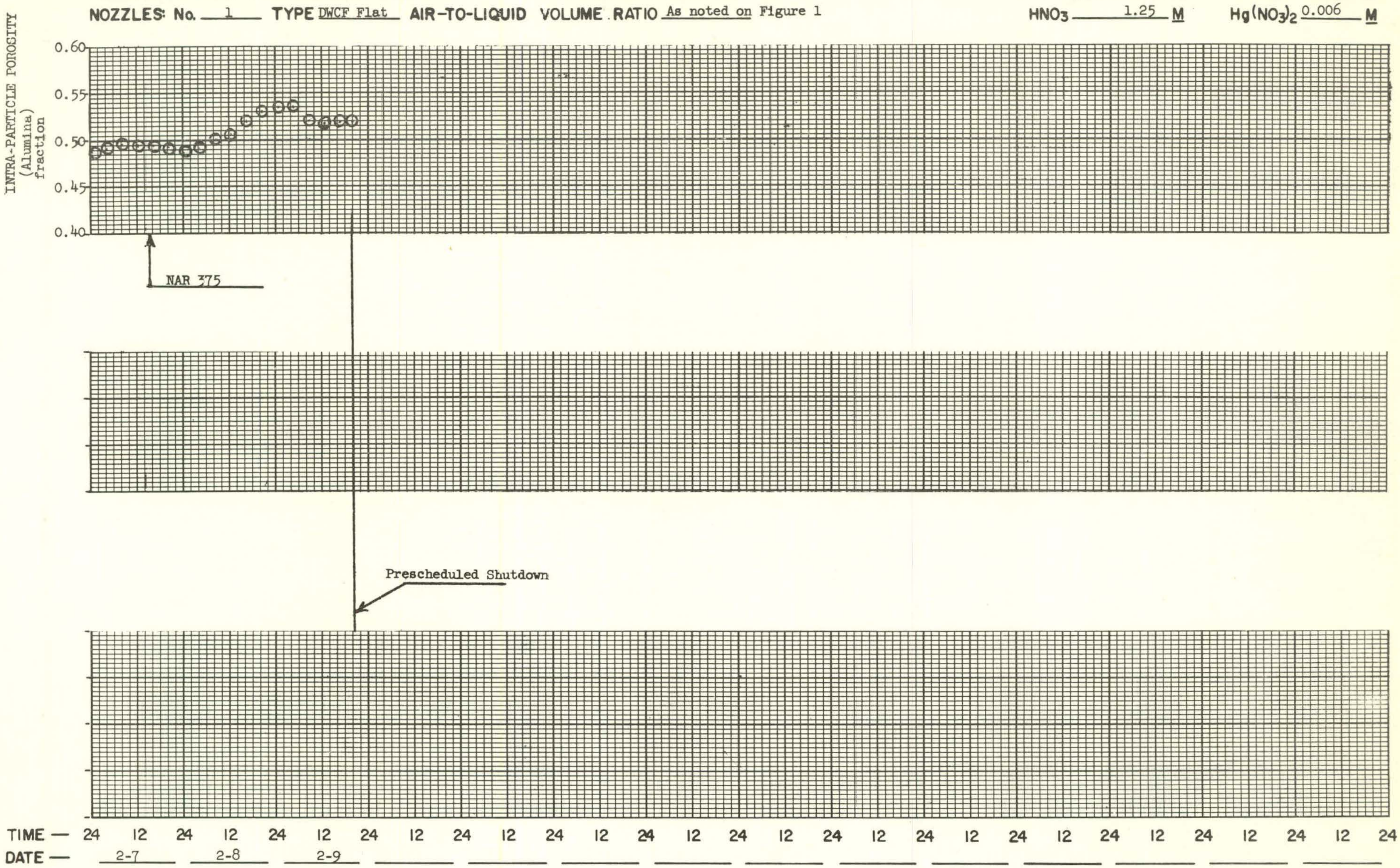

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Fig. 36 Additional product data, Run 17 (sheet 2 of 2).

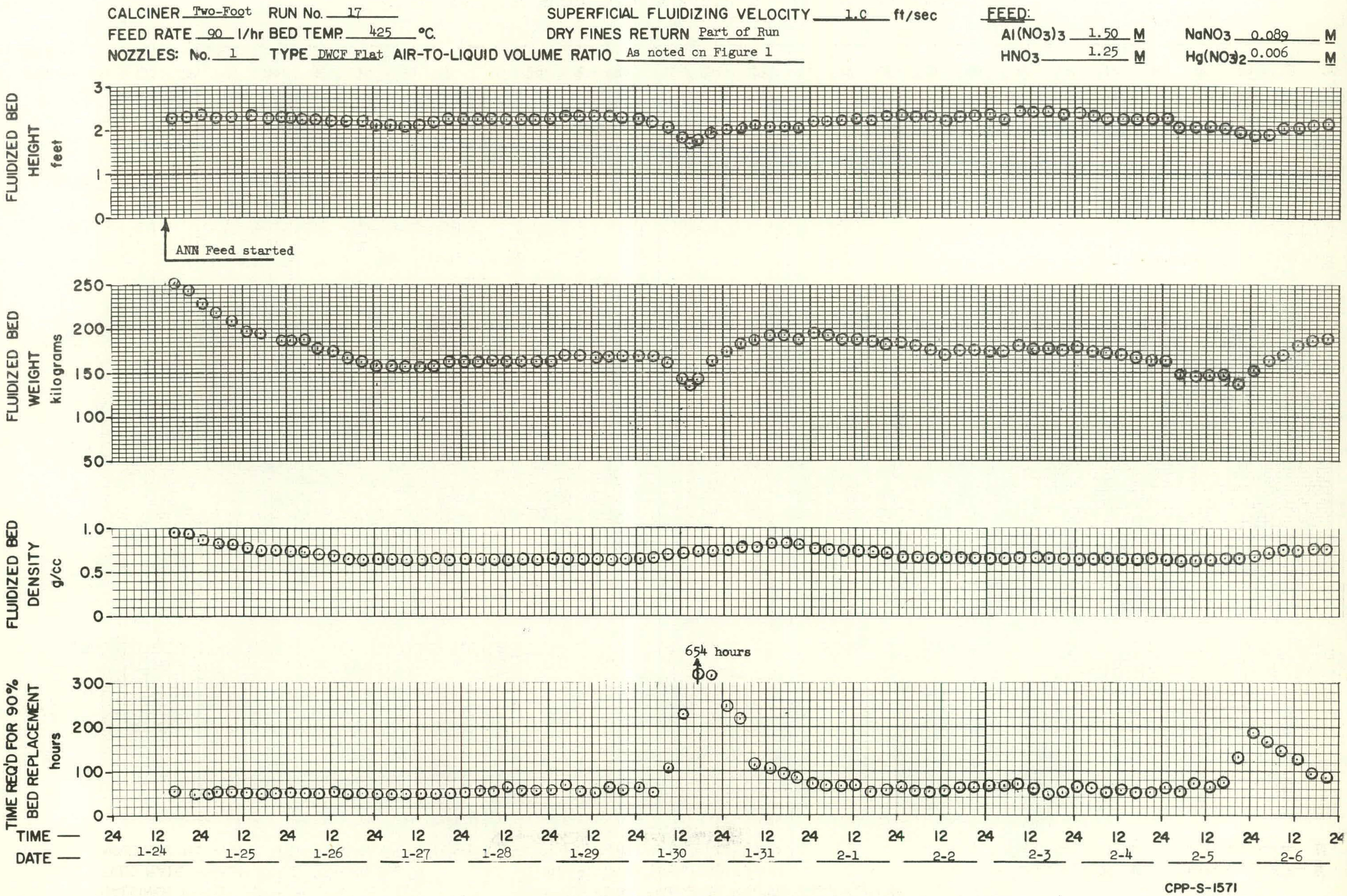


Fig. 37 Calciner bed data, Run 17 (sheet 1 of 2).

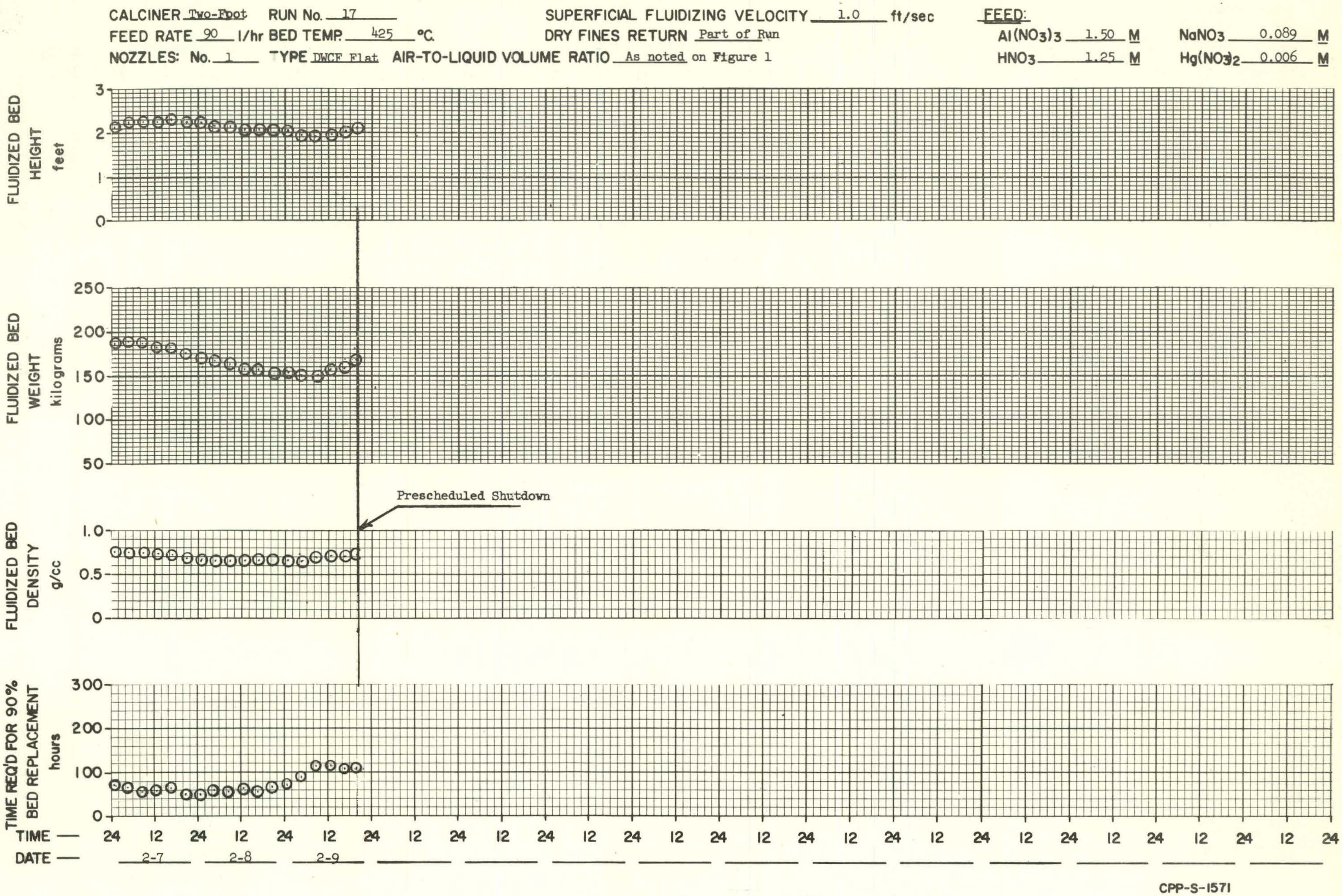
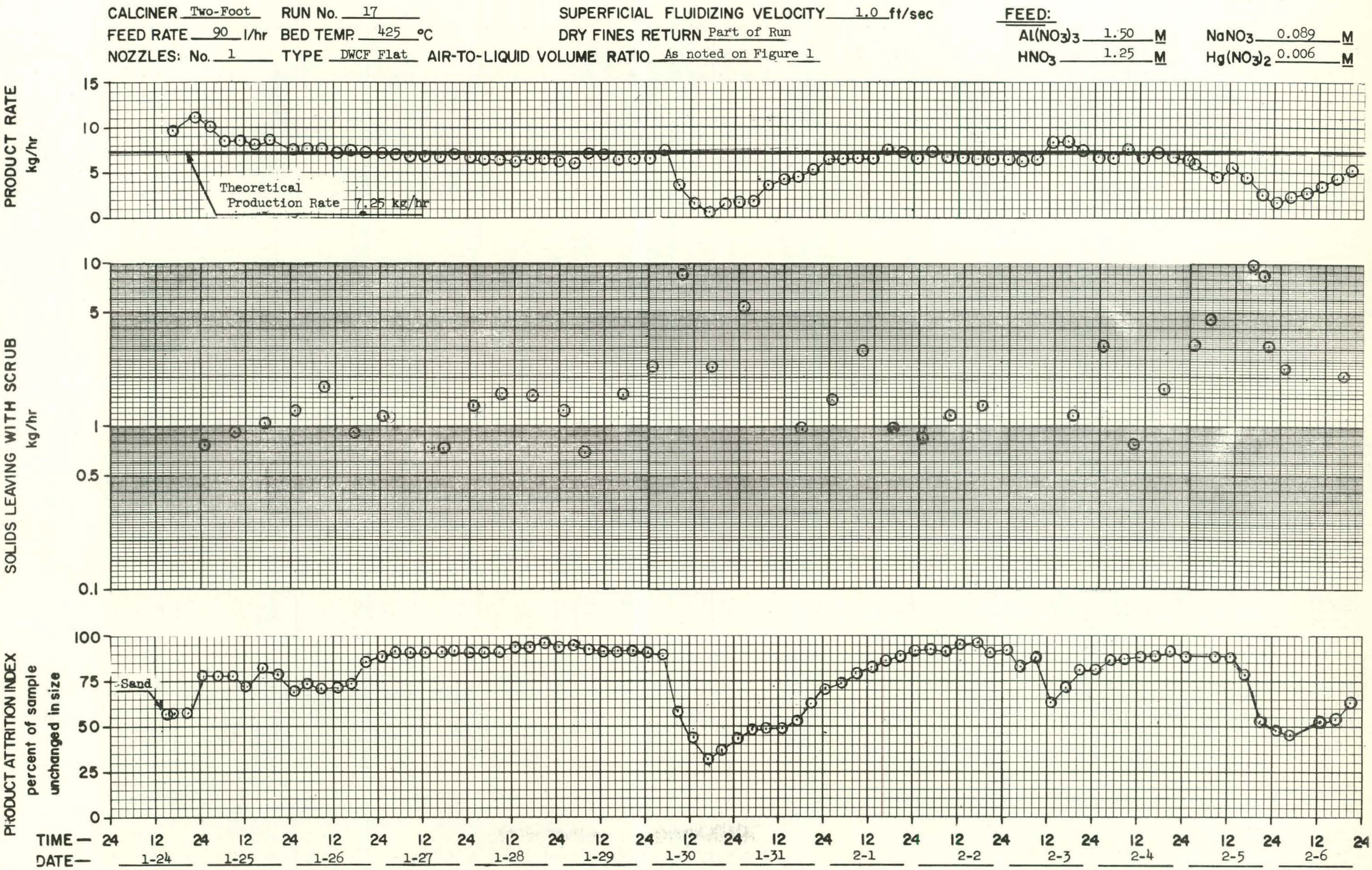


Fig. 37 Calciner bed data, Run 17 (sheet 2 of 2).



CPP-S-1573

Fig. 38 General data, Run 17 (sheet 1 of 2).

CALCINER Two-Foot RUN No. 17 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

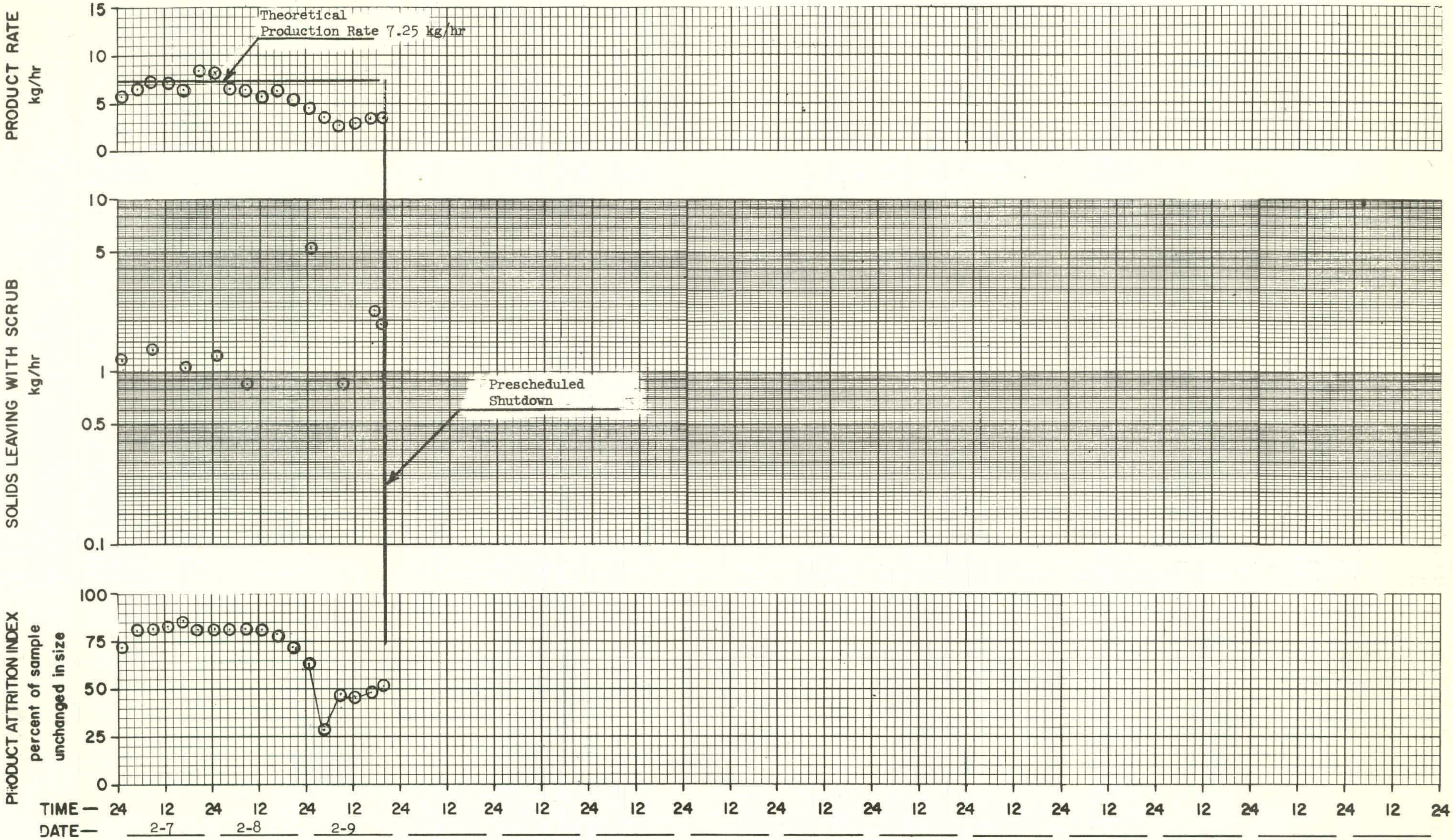
FEED RATE 90 l/hr BED TEMP. 425 °C DRY FINES RETURN Part of Run

NOZZLES: No. 1 TYPE DWCF Flat AIR-TO-LIQUID VOLUME RATIO As noted on Figure 1

FEED:

$Al(NO_3)_3$ 1.50 M $NaNO_3$ 0.089 M

HNO_3 1.25 M $Hg(NO_3)_2$ 0.006 M



CPP-S-1573

Fig. 38 General data, Run 17 (sheet 2 of 2).

Run 18

Period Covered: Intermittent, February 20, 1961 to April 19, 1961; 14 separate operating periods, each at different operating conditions and each starting with a fresh bed of sand.

Objective: To determine quantitatively the effect of bed temperature and aluminum nitrate feed concentration on the intra-particle porosity of calcined alumina.

Equipment: That used during Run 17 with minor exceptions. Standard flat-faced feed nozzle caps fabricated from titanium, Type 347 stainless steel, and Type 440-C stainless steel were tested during parts of this run. Erosion of the scrubber cyclone occurred during this run, necessitating installation of a new venturi scrubber with a 1-3/4-inch diameter throat and cyclone after Part E.

Cumulative NaK Heating System Operating Data (including this run):

159 startups; 6351 hours above 1000°F; 2302 hours below 1000°F.

Run Conditions:

Starting bed	Ammon sand
Feed rate, l/hr	90
Nozzle air-to-liquid volume ratio	400
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	0 to 22
Bed pressure, psia	17.0-19.7 Parts A, B, C,E 13.9-14.8 Remaining parts
Operating time, hours	548

Feed Composition: Nitric acid,	$\underline{M}$	1.25
Sodium nitrate,	$\underline{M}$	0.089
Mercuric nitrate,	$\underline{M}$	0.006

Run 18 (continued)

Bed temperature and aluminum feed concentrations:

Part	Bed Temperature (°C)	Aluminum Nitrate (M)
A	500	1.90
B	400	1.96
C	450	1.54
E	550	1.00
F	350	1.00
J	350	0.98
K	300	1.25
L	300	0.99
M	375	1.01
N	350	1.81
P	250	1.80
Q	350	1.28
R	300	0.80
S	300	1.51

Results: Intra-particle porosities between 0.04 and 0.60 can be obtained by an appropriate selection of bed temperature and feed aluminum concentration. Alumina with a porosity of about 0.04 was generated by calcining 1.80M aluminum nitrate solution at 250°C bed temperature. Increased porosity product results from increases in bed temperature or feed aluminum concentration. An intra-particle porosity of 0.58 was obtained by calcining 1.90M aluminum feed at a bed temperature of 500°C. The nitrate content of the amorphous product was shown to be an inverse function of operating temperature. No alpha alumina was detected in any of the product generated during the 24-hour periods. Small amounts of alpha alumina were produced in the extended portion (Part J) of the run at 350°C bed temperature and 1.0M aluminum nitrate and 0.089M sodium nitrate feed solution, 60 hours after startup. Gamma alumina was also produced on that part of the run, and at termination of Part J the product contained more gamma than alpha alumina.

Nozzle erosion of standard flat-faced feed nozzle caps:

Cap Material	Hours In Operation	Erosion Rate
Titanium	29	2.9 g/yr
SS Type 347	99	4.0 g/yr
SS Type 440-C	420	0.07 g/yr

In addition to the erosion of the scrubber cyclone, the throat insert of the dry fines return air jet pump eroded three times

Run 18 (continued)

during the run requiring new jet throat inserts of Type 440-C stainless steel to replace the eroded inserts.

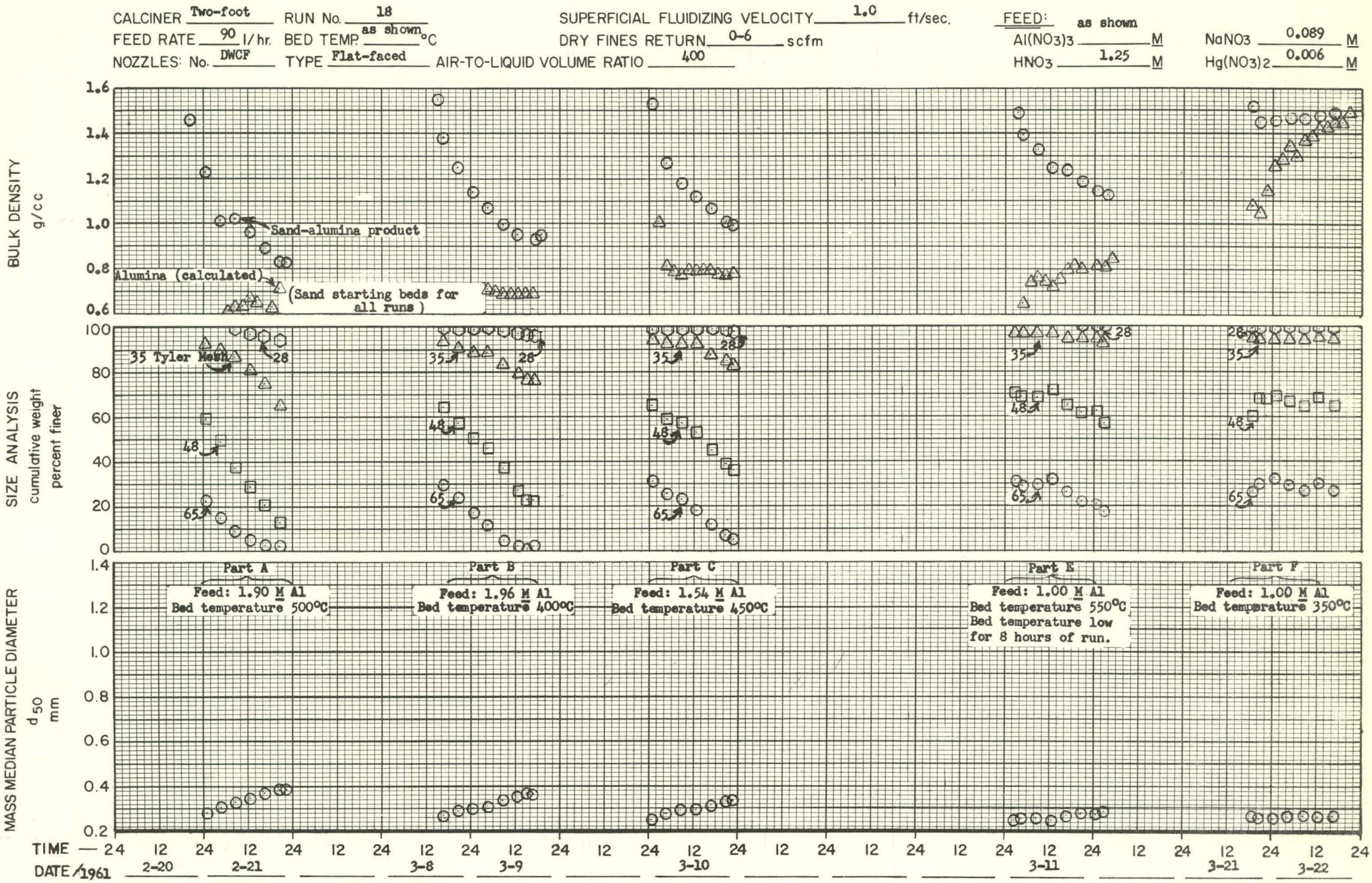


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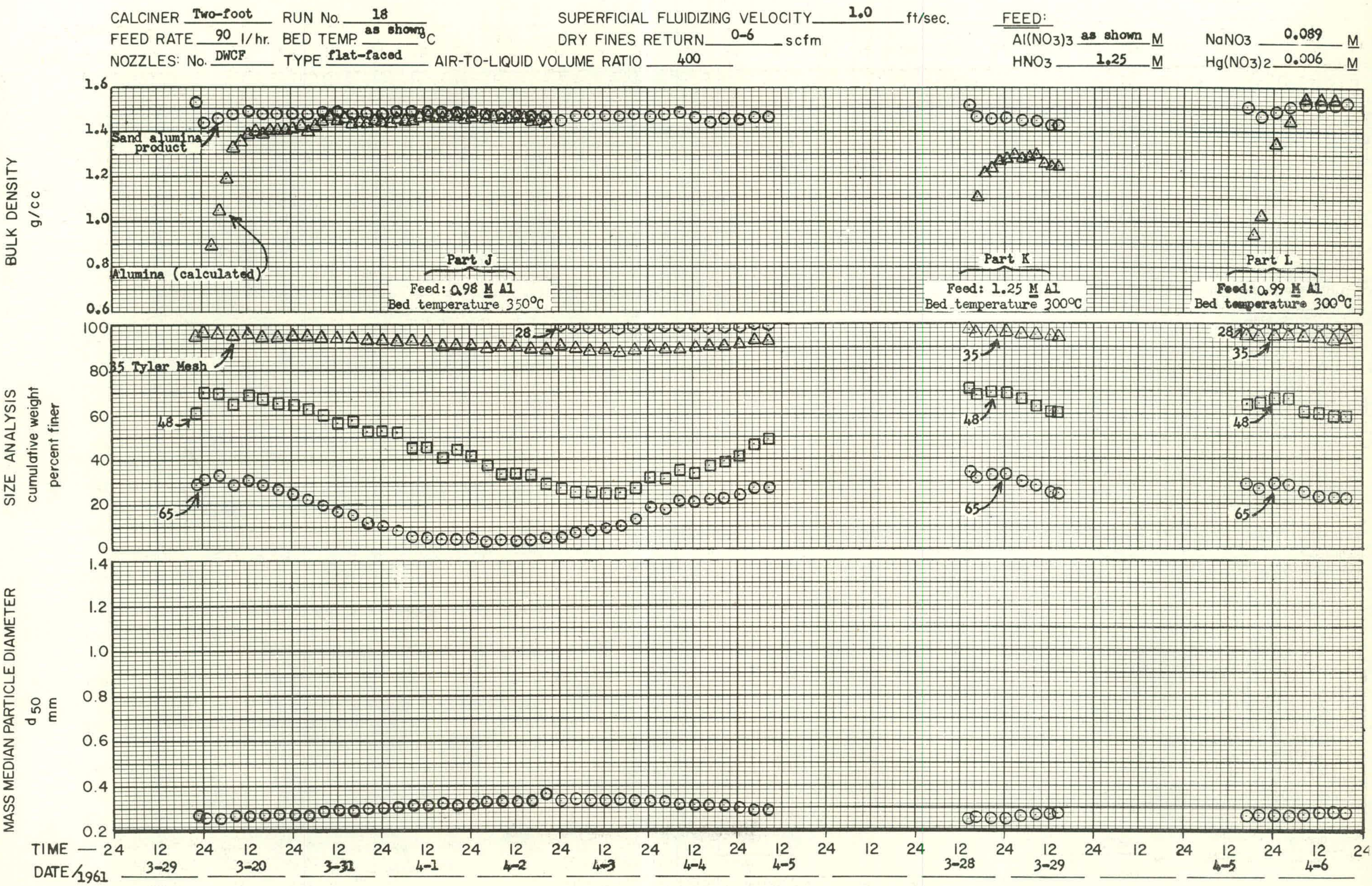
Fig. 39 Product data, Run 18 (sheet 1 of 3).



CPP-S-1570

Fig. 39 Product data, Run 18 (sheet 2 of 3).

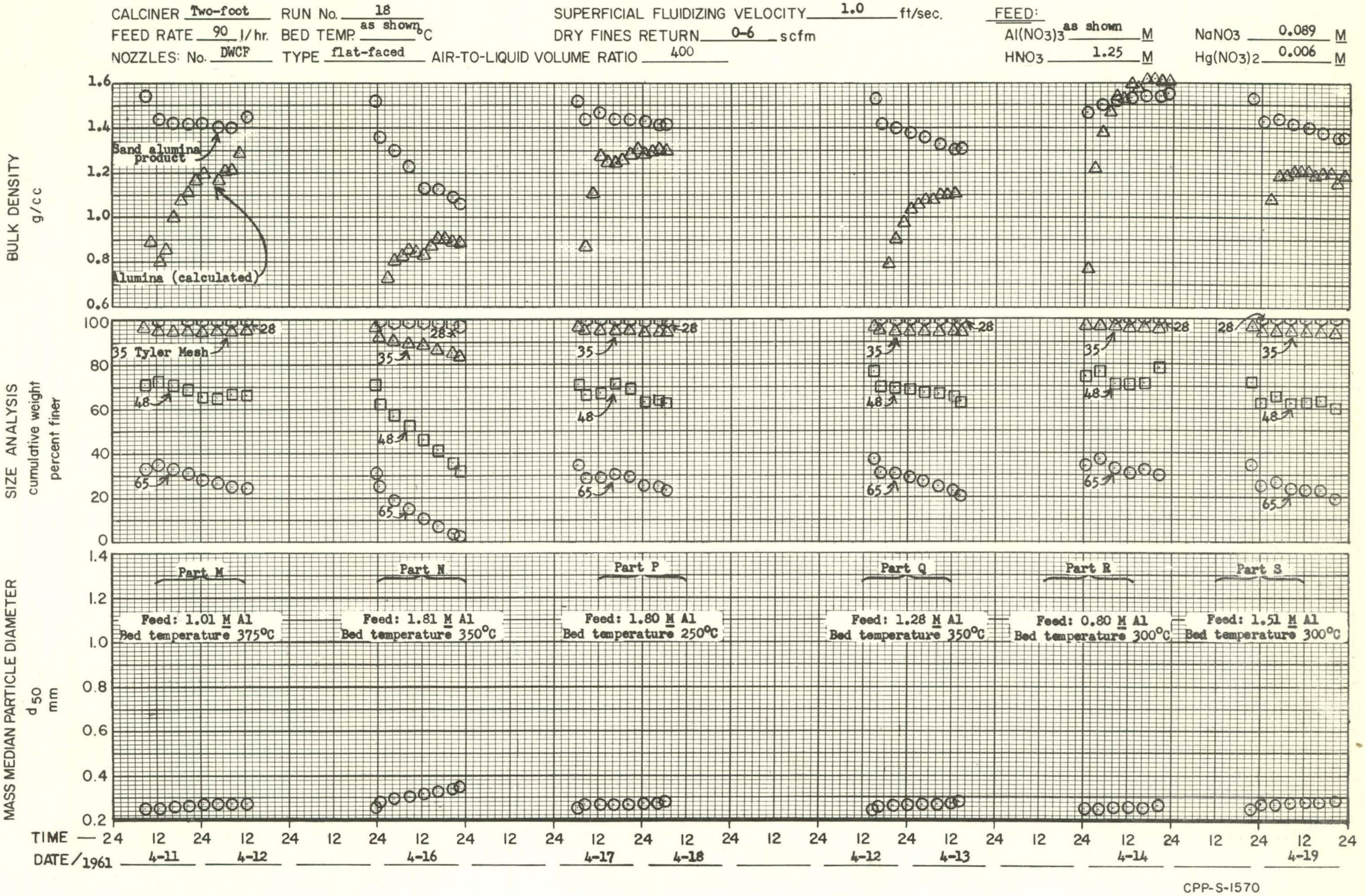


Fig. 39 Product data, Run 18 (sheet 3 of 3).

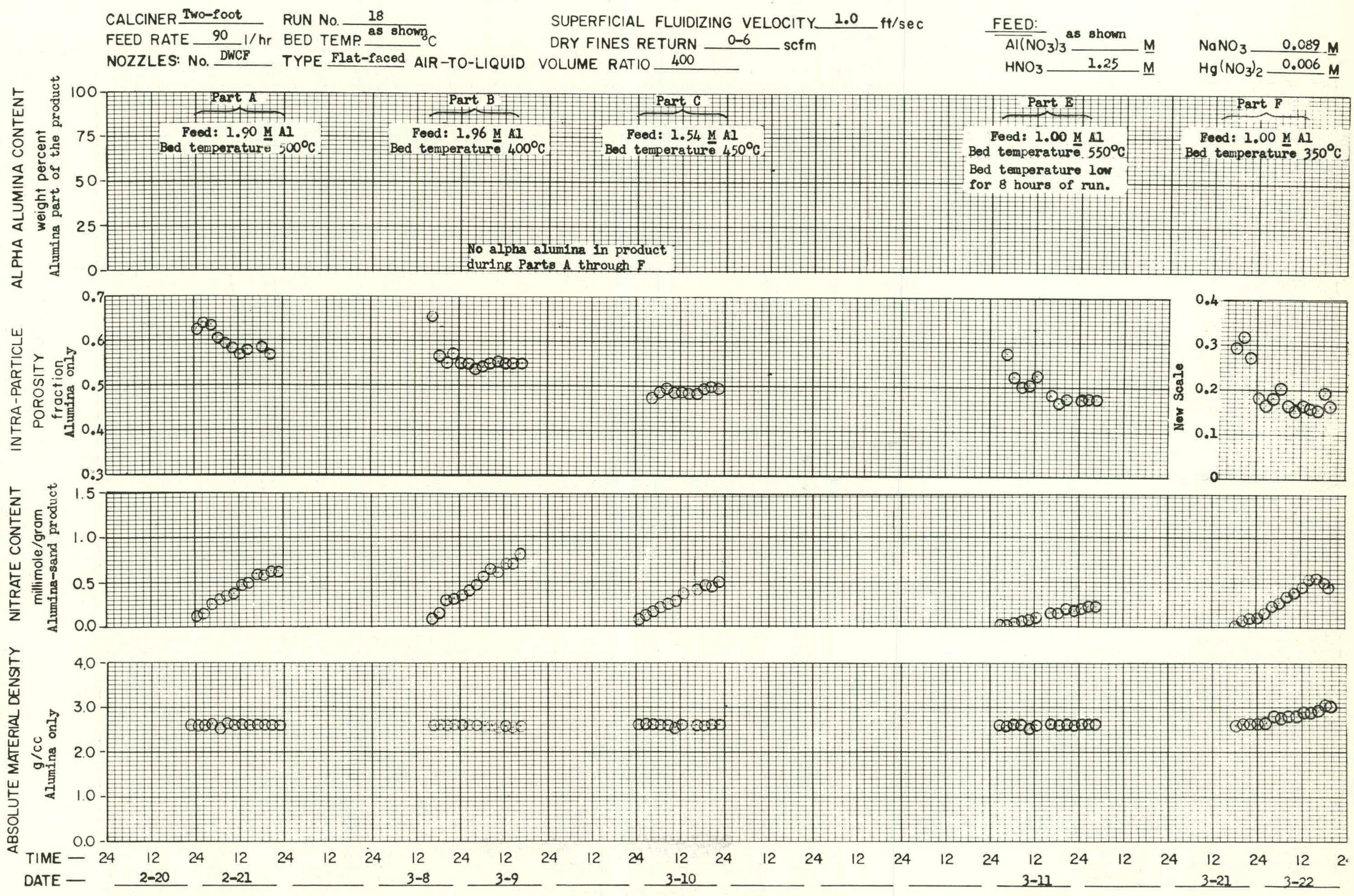


Fig. 40 Additional product data, Run 18 (sheet 1 of 3).

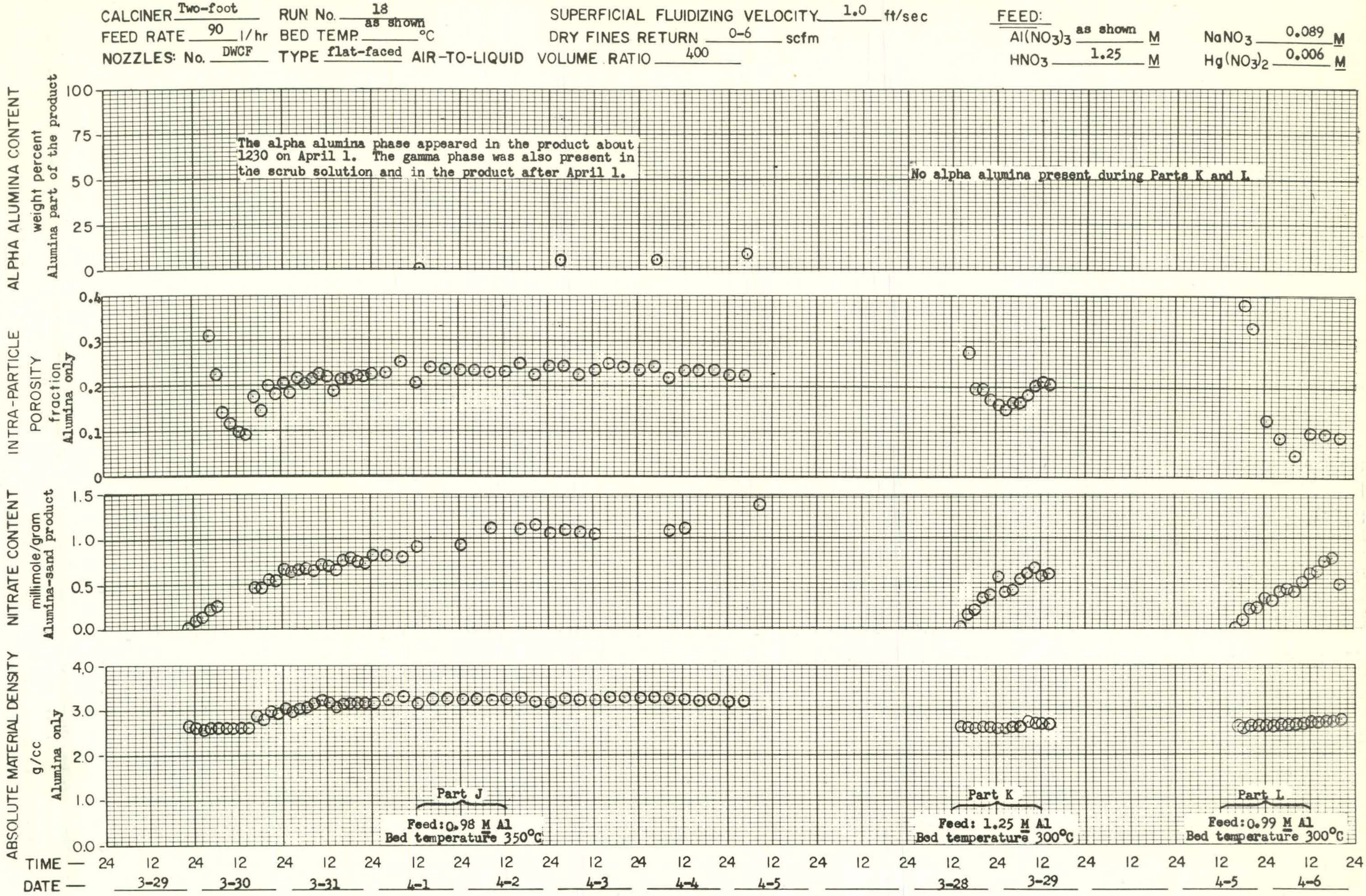


Fig. 40 Additional product data, Run 18 (sheet 2 of 3).

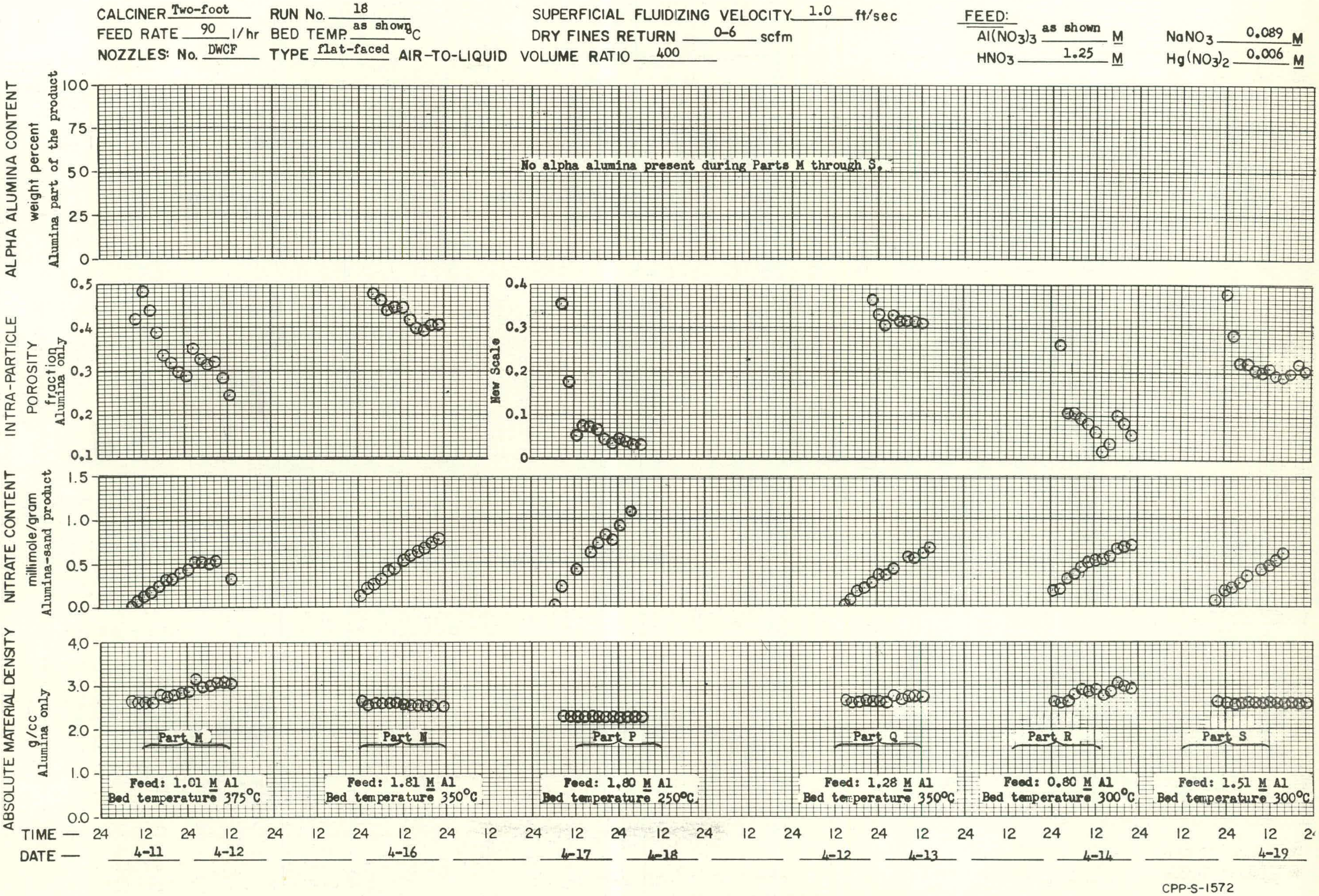


Fig. 40 Additional product data, Run 18 (sheet 3 of 3).

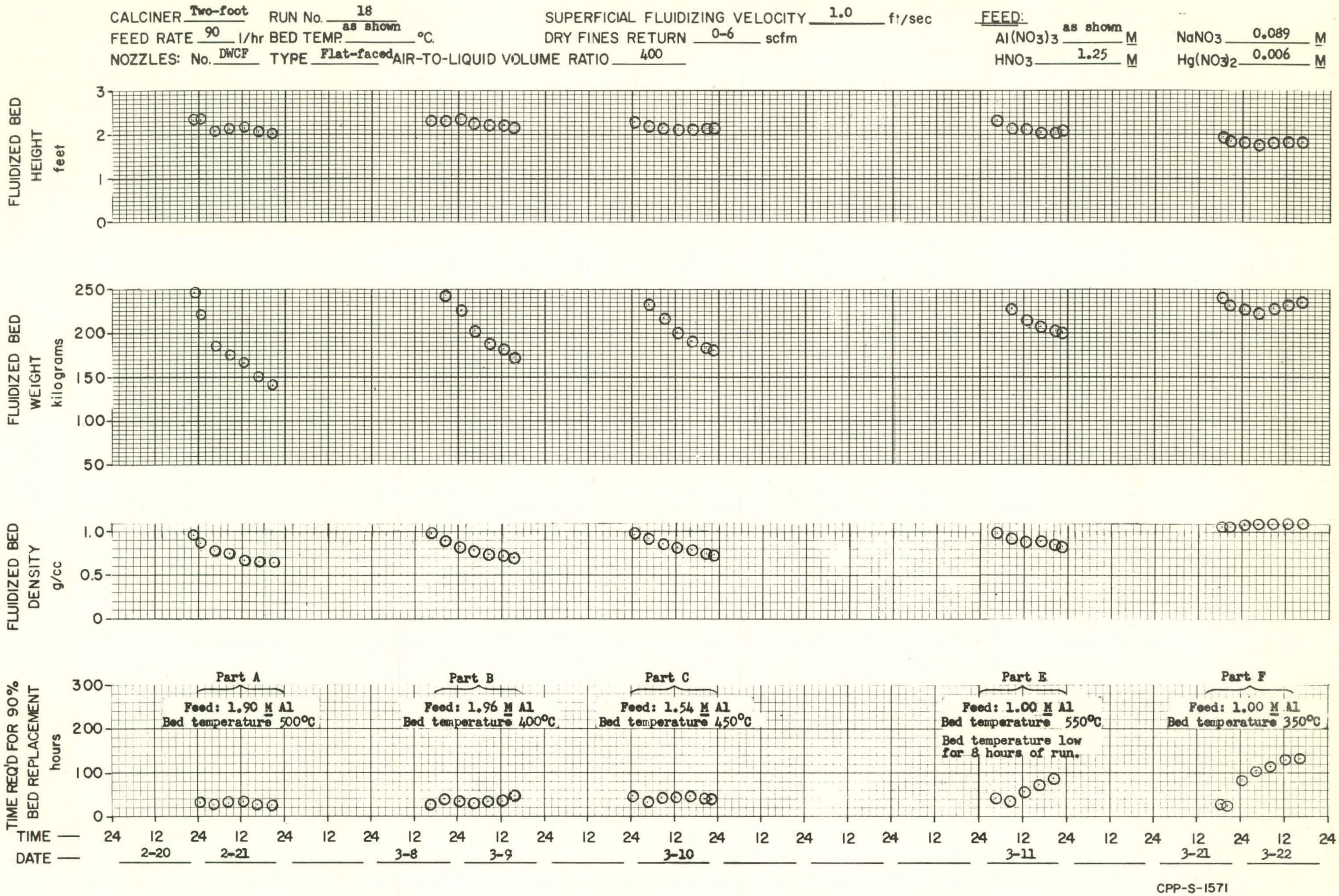


Fig. 41 Calciner bed data, Run 18 (sheet 1 of 3).

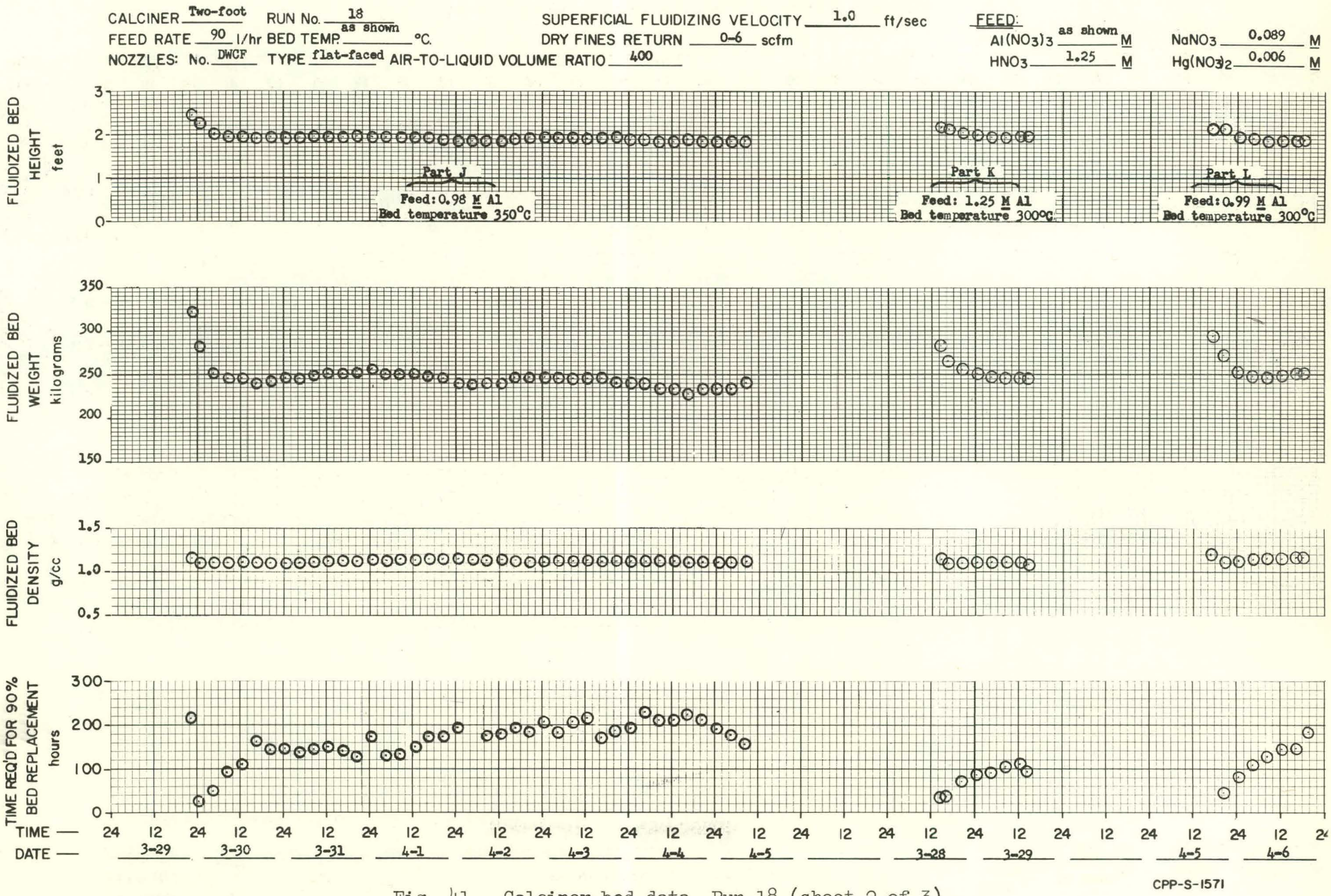


Fig. 41 Calciner bed data, Run 18 (sheet 2 of 3).

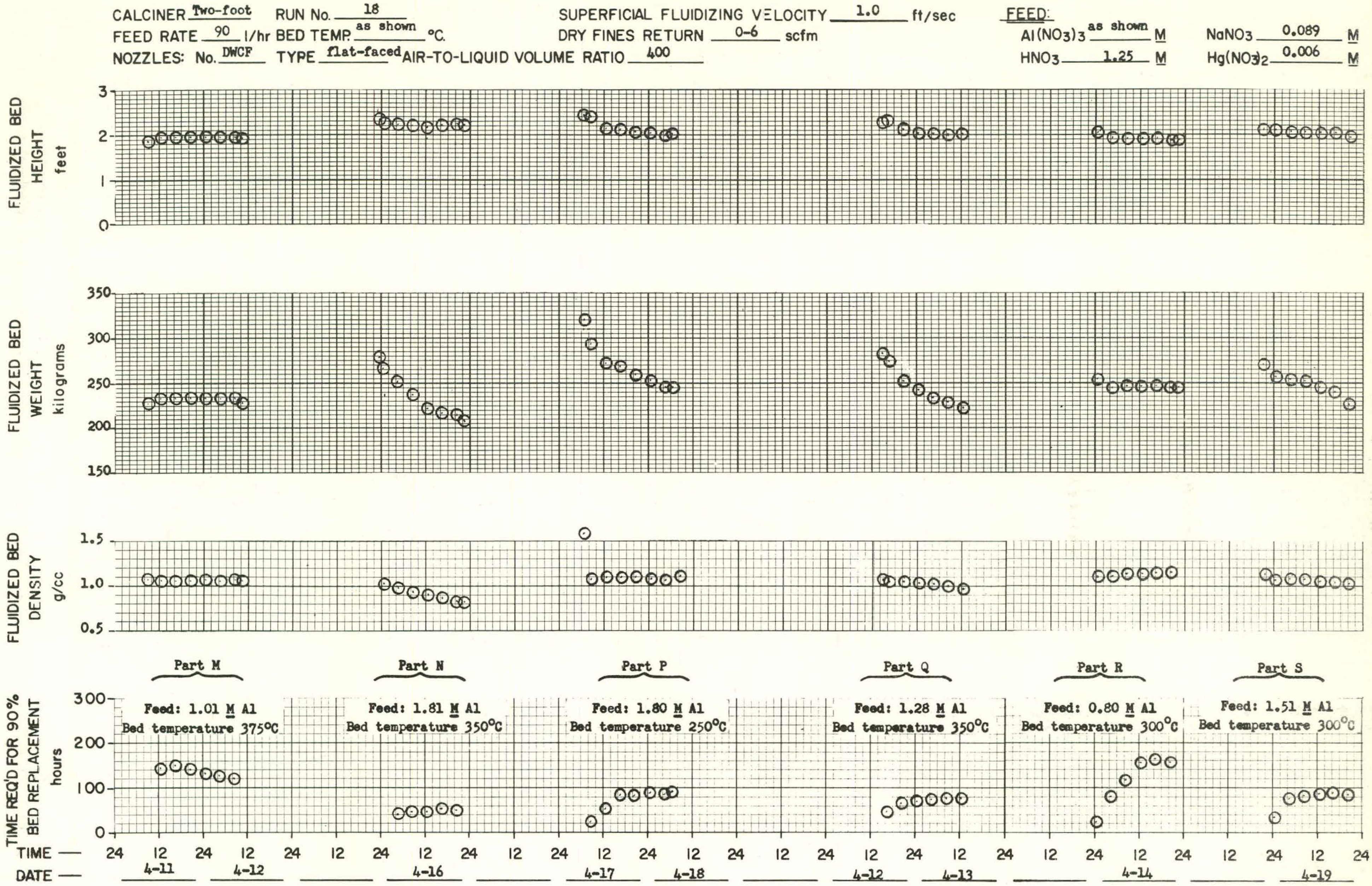


Fig. 41 Calciner bed data, Run 18 (sheet 3 of 3).

CALCINER Two-foot RUN No. 18 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

FEED RATE 90 l/hr BED TEMP. as shown °C DRY FINES RETURN 0-6 scfm

NOZZLES: No. DWCF TYPE Flat-faced AIR-TO-LIQUID VOLUME RATIO 400

FEED: $Al(NO_3)_3$ as shown M; HNO_3 1.25 M; $NaNO_3$ 0.089 M; $Hg(NO_3)_2$ 0.006 M

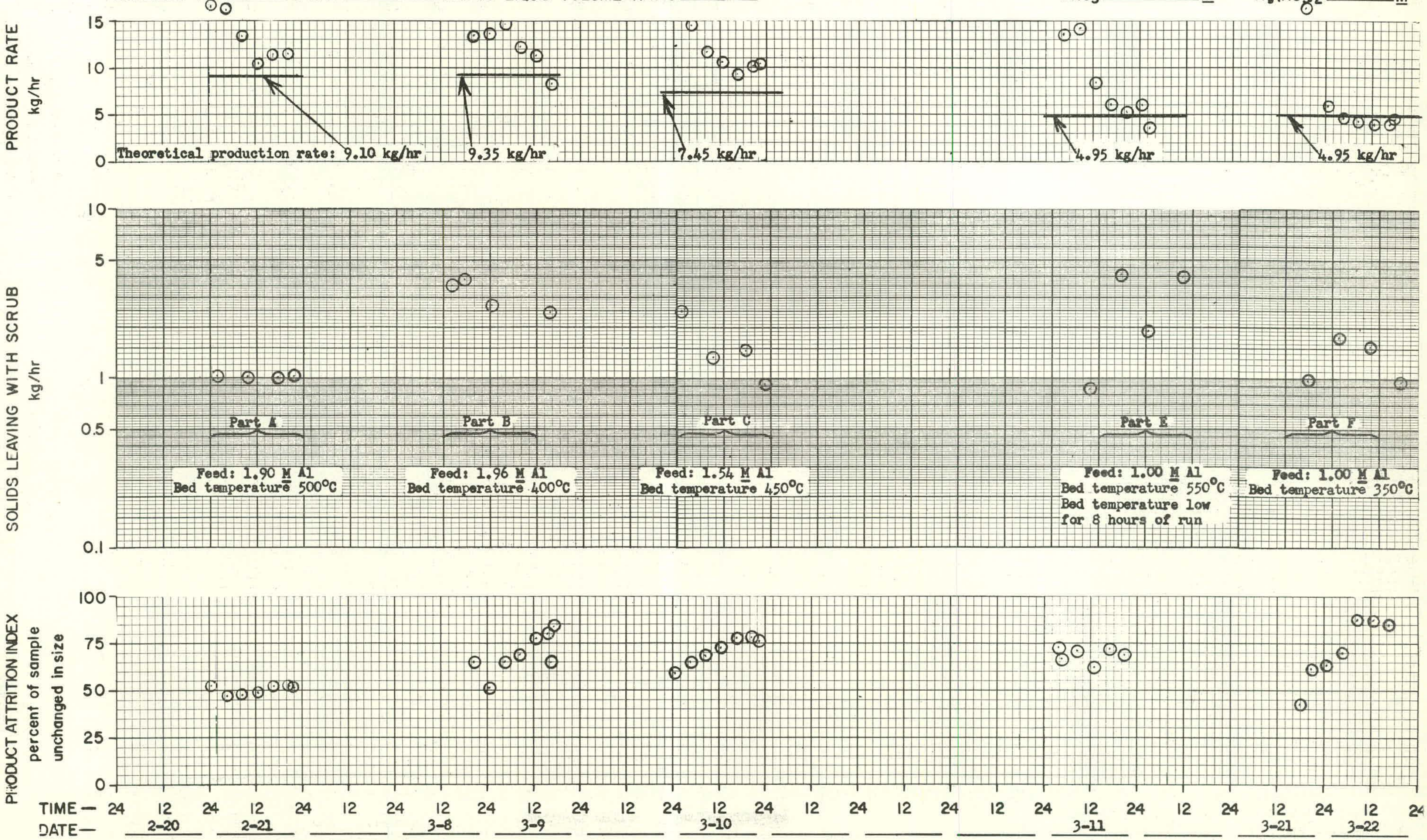


Fig. 42 General data, Run 18 (sheet 1 of 3).

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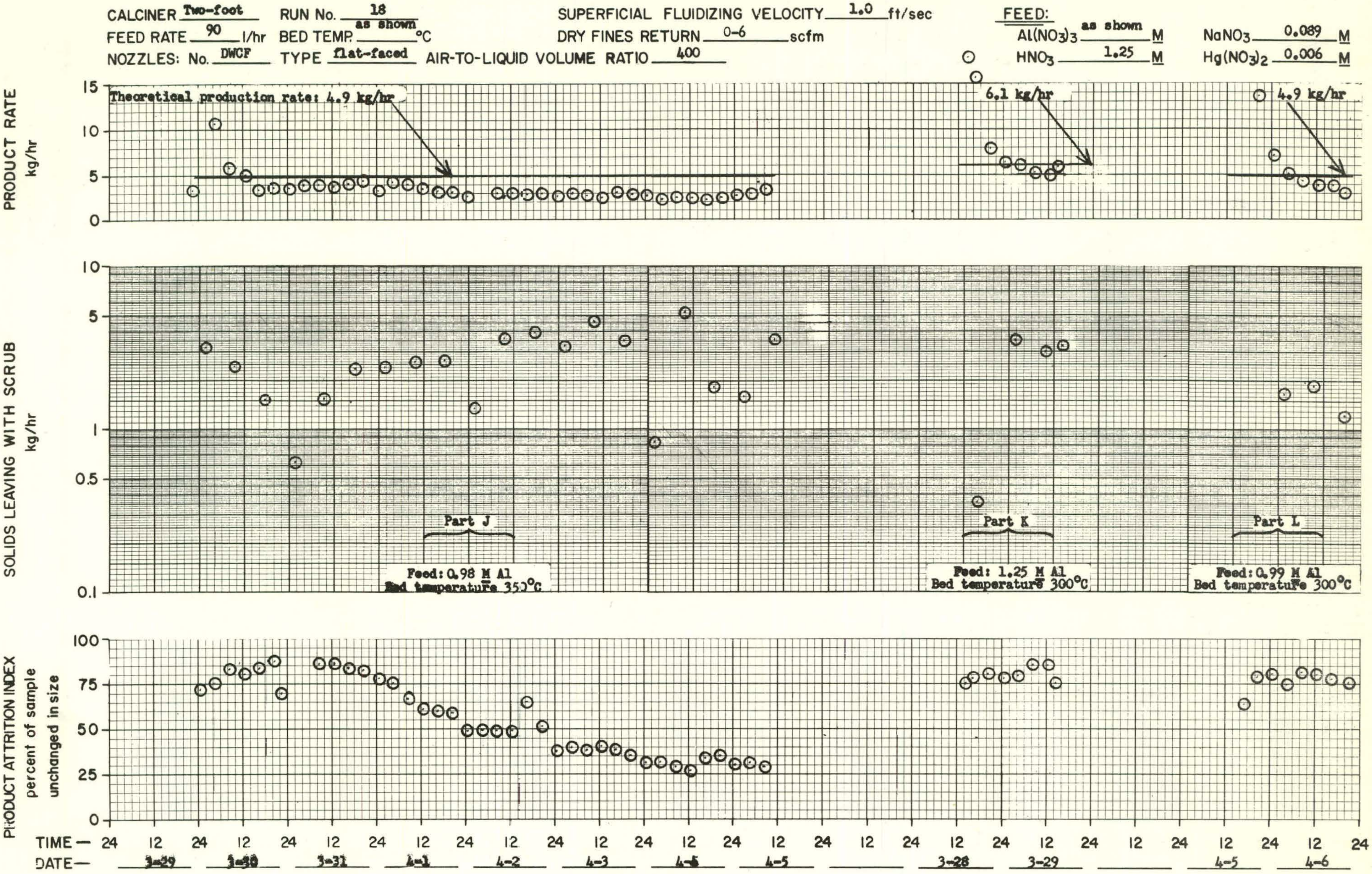

Fig. 42 General data, Run 18 (sheet 2 of 3).

CPP-S-1573

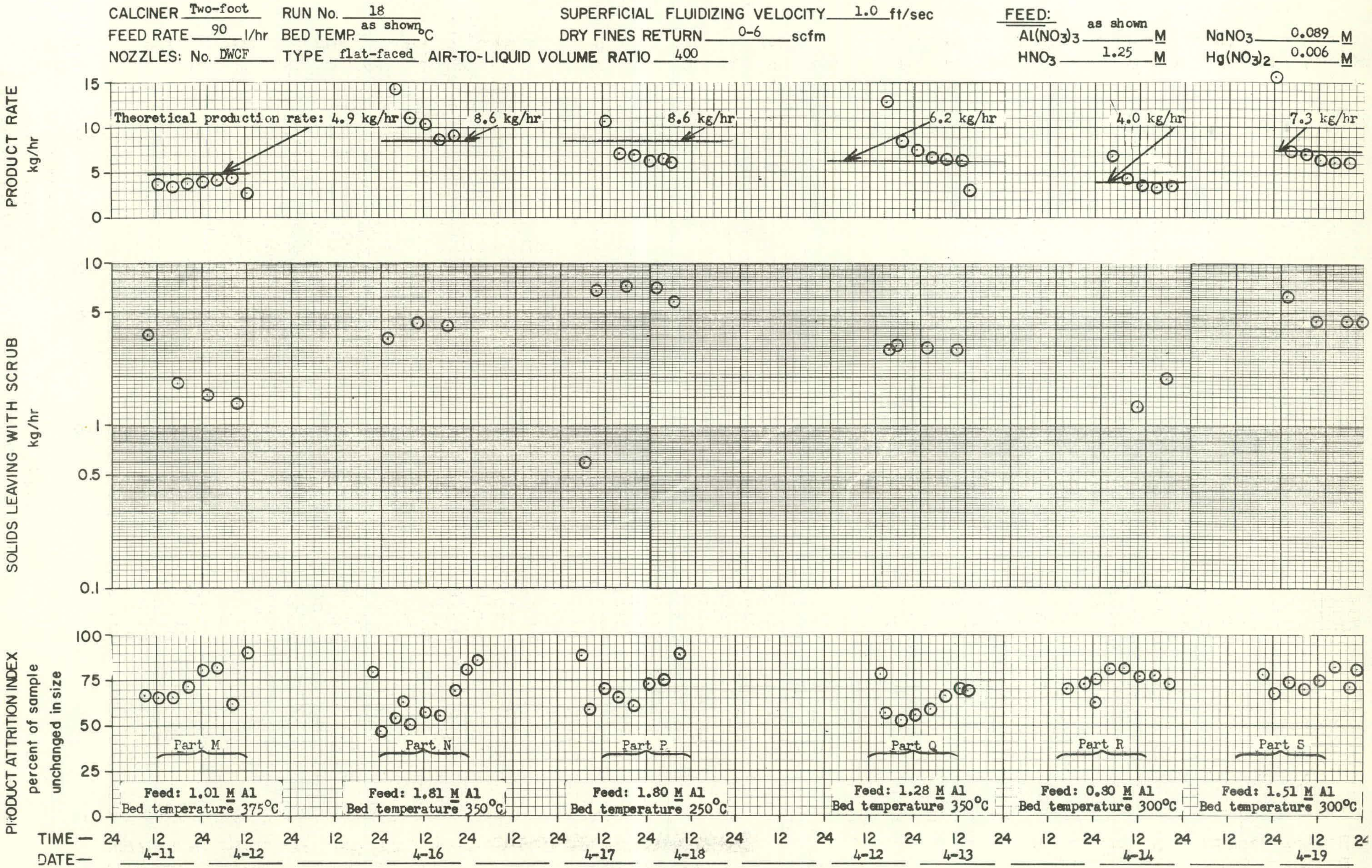

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Fig. 42 General data, Run 18 (sheet 3 of 3).

Run 19

Period Covered: From April 25, 1961 to May 4, 1961.

Objective: To study the performance of a new feed nozzle cap of a short extended convergent design. This design change was made in a further effort to minimize nozzle erosion.

Equipment: That used during Run 18 except for the nozzle cap. A newly designed short extended convergent nozzle cap of Type 347 stainless steel, extending 0.75-inch into the bed, was used in lieu of the standard flat-faced caps used during Run 18.

Cumulative NaK Heating System Operating Data (including this run):

161 startups; 6359 hours above 1000°F; 2522 hours below 1000°F.

Run Conditions:

Starting bed	Ammon sand
Bed temperature, °C	400
Feed rate, l/hr	90 → 80
Nozzle air-to-liquid volume ratio	250 → 500
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	13.7-19.9
Bed pressure, psia	14.4
Operating time, hours	216

Feed Composition:	Aluminum nitrate, M	1.29
	Nitric acid, M	2.84
	Sodium nitrate, M	0.078
	Mercuric nitrate, M	0.015

Results: The erosion rate (1.0 g/yr), formation of caked material, production of an abnormally large quantity of overhead fines removed by the scrubbing solution, and a relatively slow response of particle size to NAR changes are apparent disadvantages of this nozzle cap. Alpha alumina was not produced over the ten-day period of this run.

Frequent clogging of the dry fines return jet was experienced; the jet was shut down for the last 8 hours of the run. Frequent clogging of the scrubber cyclone also occurred. The unit was shut down once to clear a clogged cyclone. Several lumps of calcined material were found in the final bed.

CALCINER Two-foot RUN No. 19 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec.
FEED RATE 90,80 l/hr. BED TEMP. 400 °C DRY FINES RETURN 7.0-7.5 scfm
NOZZLES: No. 1 TYPE DWCF-conical AIR-TO-LIQUID VOLUME RATIO 250,500

FEED:
$Al(NO_3)_3$ 1.29 M $NaNO_3$ 0.078 M
HNO_3 2.84 M $Hg(NO_3)_2$ 0.015 M

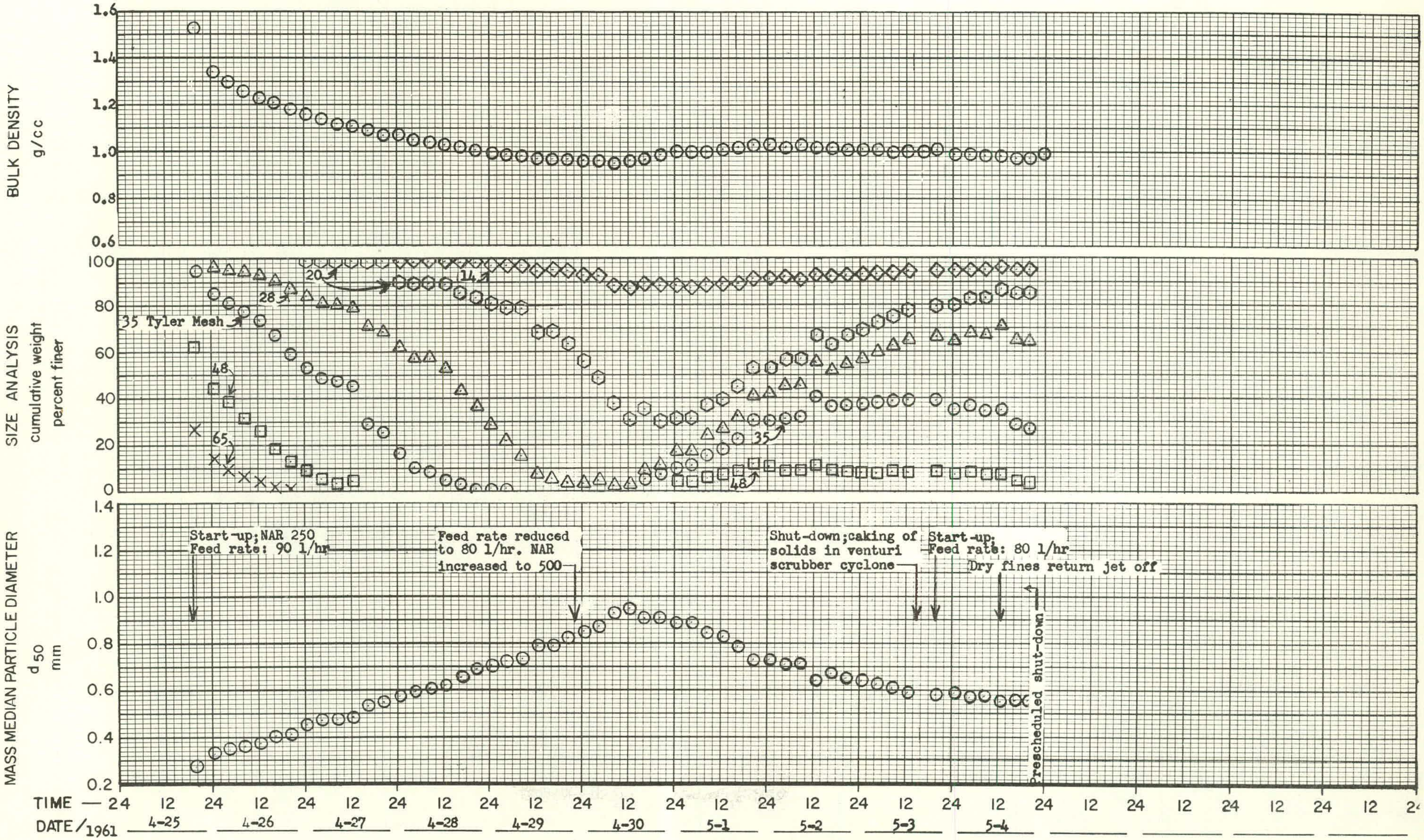

Fig. 43 Product data, Run 19.

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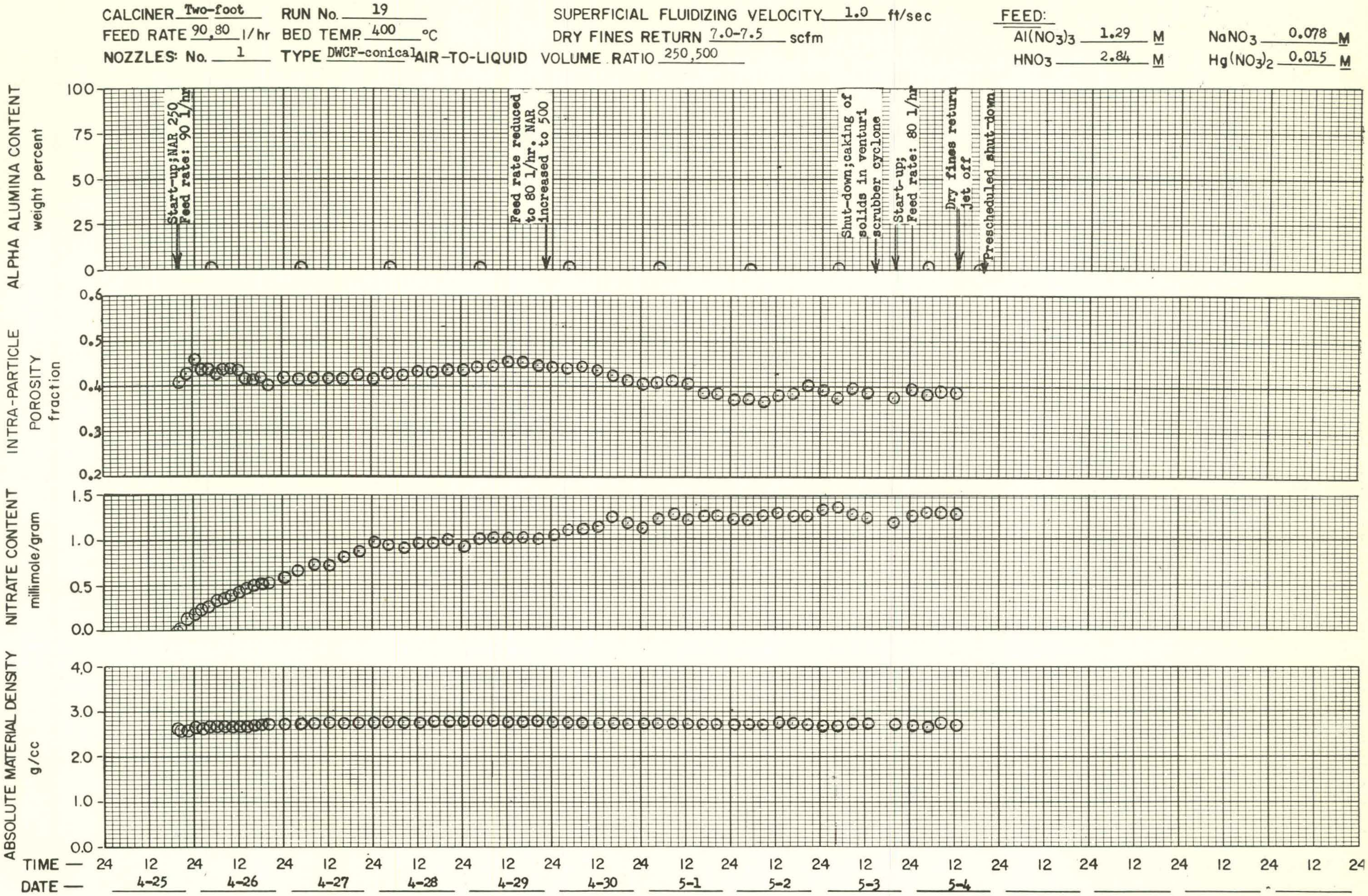

Fig. 44 Additional product data, Run 19.

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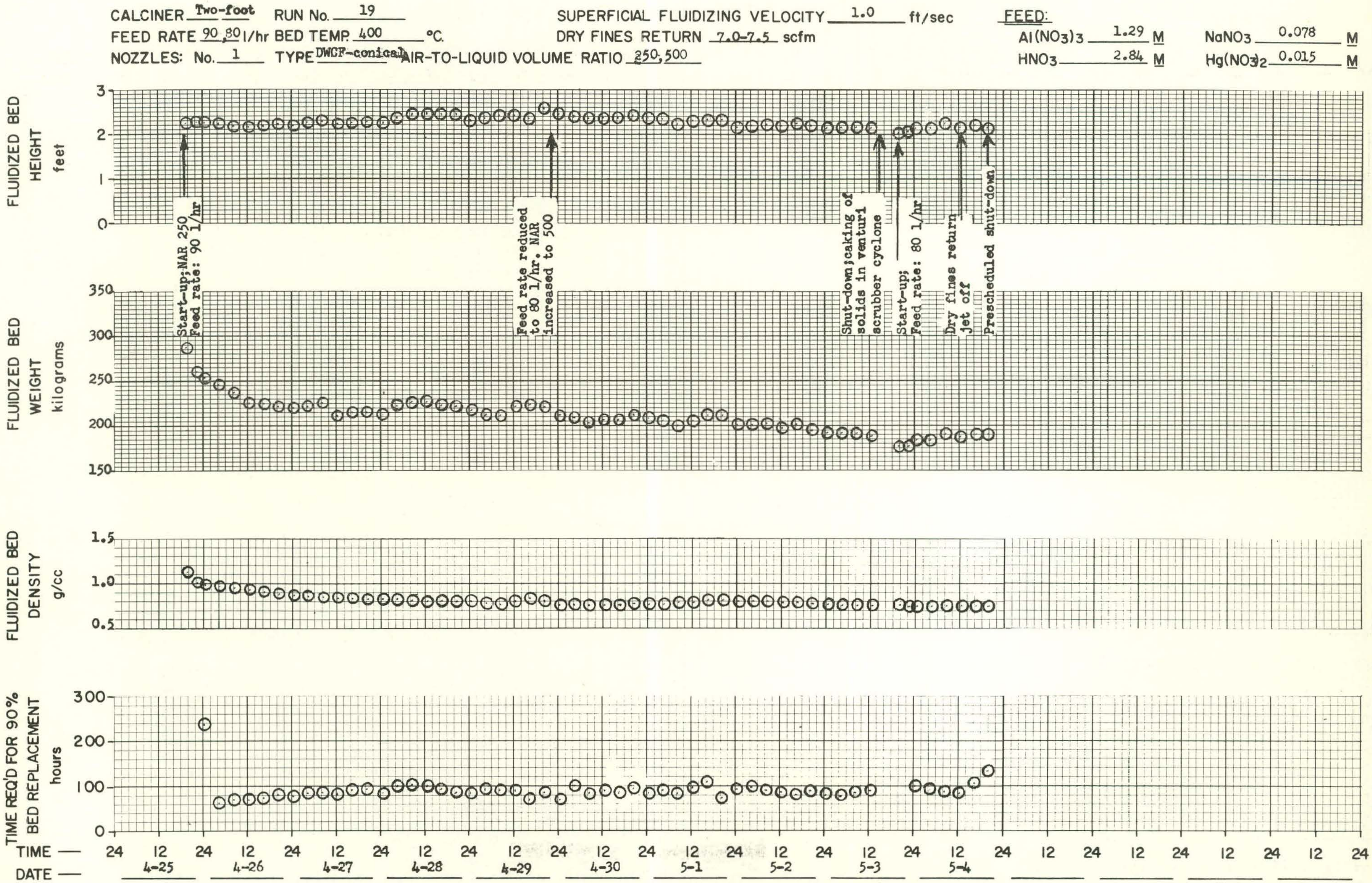

Fig. 45 Calciner bed data, Run 19.

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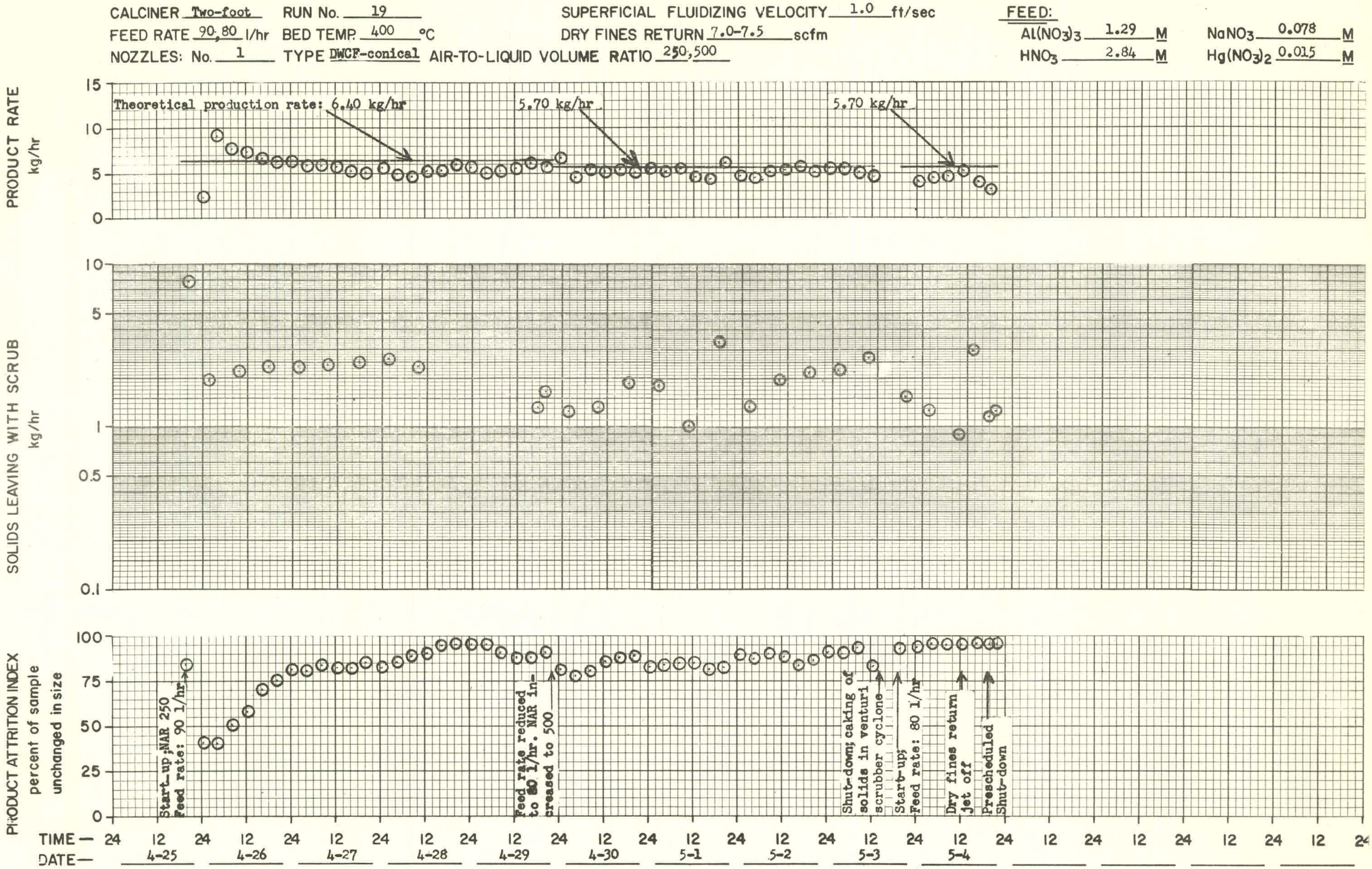

Fig. 46 General data, Run 19.

CPP-S-1573

Run 20

Period Covered: From May 10, 1961 to May 18, 1961.

Objective: To study the performance of a single-fluid feed nozzle used together with a jet grinder to control particle size.

Equipment: That used during Run 19 except that a Spraying Systems Company Type 1/4 LN, No. 12, single-fluid atomizing nozzle was used in lieu of the 1/2 J pneumatic atomizing nozzle used in previous runs. A jet grinder, consisting of five 1/8-inch diameter air orifices discharging horizontally into the fluidized bed just above the support plate, was installed to control the particle size.

Cumulative NaK Heating System Operating Data (including this run):

163 startups; 6359 hours above 1000°F; 2730 hours below 1000°F.

Run Conditions:

Starting bed	Ammon sand
Bed temperature, °C	400
Feed rate, l/hr	40
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return gas rate, scfm	17.9-22.5
Bed pressure, psia	14.0-14.2
Operating time, hours	193

Feed Composition:	Aluminum nitrate, M	1.29
	Nitric acid, M	2.84
	Sodium nitrate, M	0.01
	Mercuric nitrate, M	0.015

Results: A single fluid nozzle might be successfully used to introduce feed into a fluidized bed calciner, provided that the problem of severe corrosion or erosion to the internal parts of the nozzle is solved. The nozzle orifice diameter increased during the run to 150 mils from the original diameter of 76 mils. Inspection of the feed nozzle definitely indicated that corrosion had taken place; co-occurence of erosion is speculative. Numerous alumina cakes were found in the interior of the vessel and in the final bed at run termination. It is believed that most of the bed caking was due to the poorly atomized feed caused by the increasing fluid orifice of the nozzle. As the run progressed, the pressure of the feed at the nozzle decreased from 40 to 15 psig while the feed rate remained constant.

The jet grinder made possible the control of the particle size; proper adjustment of the air flow rate to the grinder could maintain the mass median particle diameter within the desired range 0.5-0.6 mm. A high concentration of fines in the off-gas leaving the calciner was experienced when the grinder was in use, however.

Run 20 (continued)

While the jet grinder was operating, the inter-particle void fraction decreased from 0.41 to 0.35.

Alpha alumina was not detected in the product. This agrees with previous results obtained when sodium nitrate concentration of the feed was extremely low.

One Carpenter-20 tube in the NaK heat exchanger bundle in the fluidized bed was eroded to a depth of 53 mils by impingement from an orifice of the jet grinder; the original wall thickness of the tube was 83 mils. Some, but much less, erosion of adjacent tubes in the bundle was also incurred. Three of the eroded tubes of the bundle were replaced. Frequent clogging of the dry fines return jet occurred when the jet grinder was in operation, presumably because of a high concentration of fines in the off-gas.

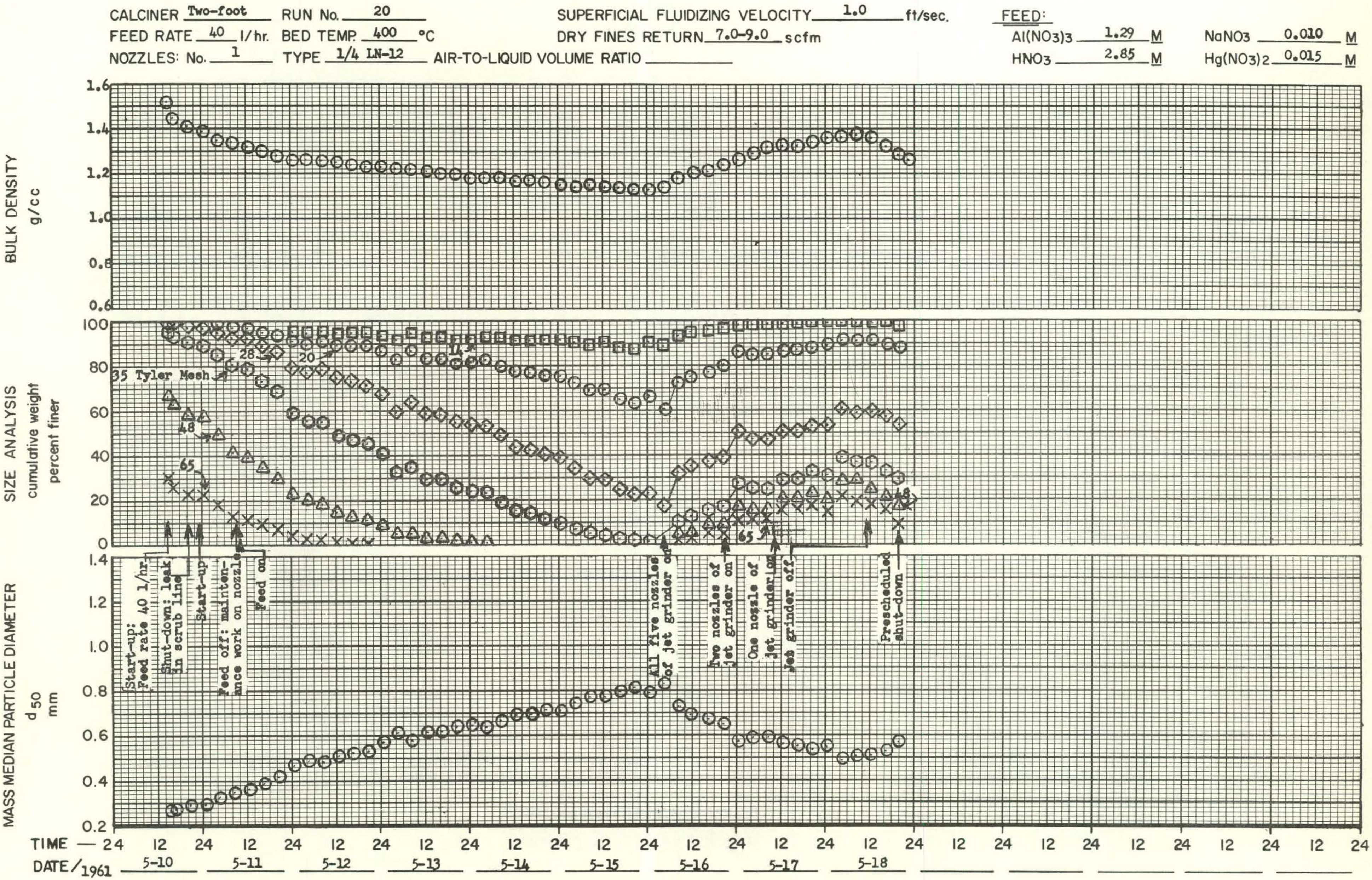

Fig. 47 Product data, Run 20.

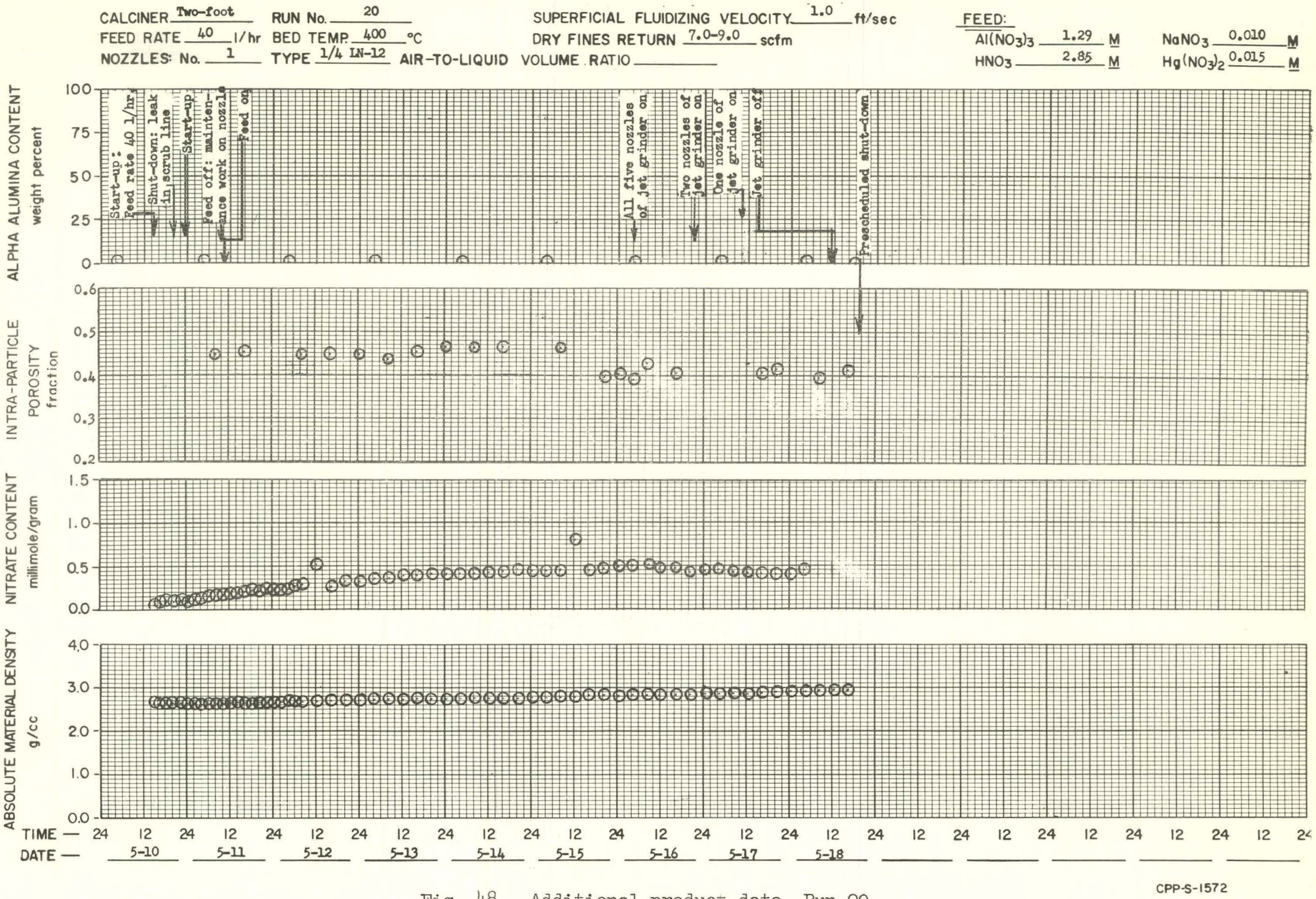

Fig. 48 Additional product data, Run 20.

CALCINER Two-foot RUN No. 20 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec
FEED RATE 40 l/hr BED TEMP. 400 °C. DRY FINES RETURN 7.0-9.0 scfm
NOZZLES: No. 1 TYPE 1/4 LN-12 AIR-TO-LIQUID VOLUME RATIO ______

FEED:
$Al(NO_3)_3$ 1.29 M
HNO_3 2.85 M
$NaNO_3$ 0.010 M
$Hg(NO_3)_2$ 0.015 M

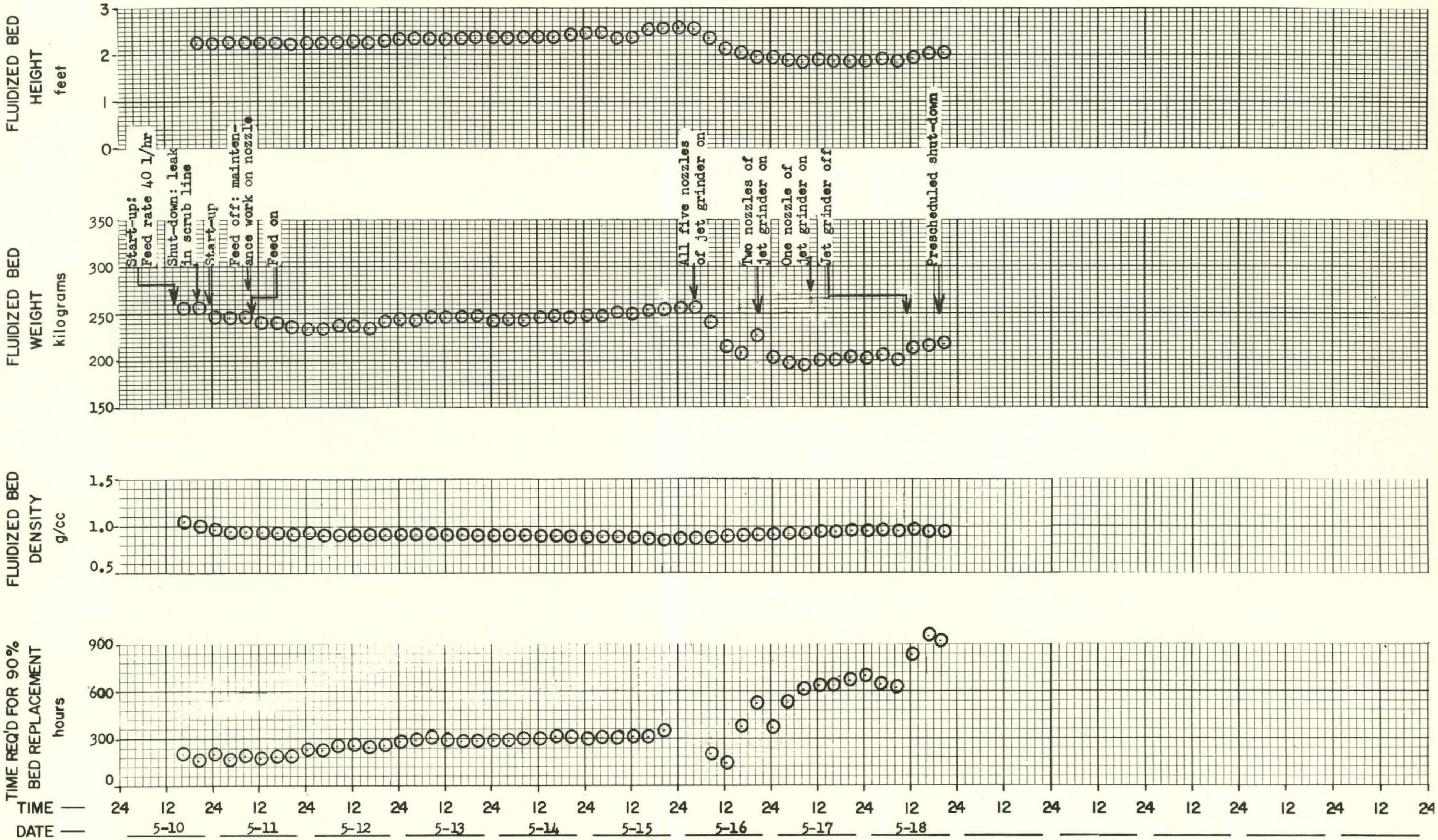

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Fig. 49 Calciner bed data, Run 20.

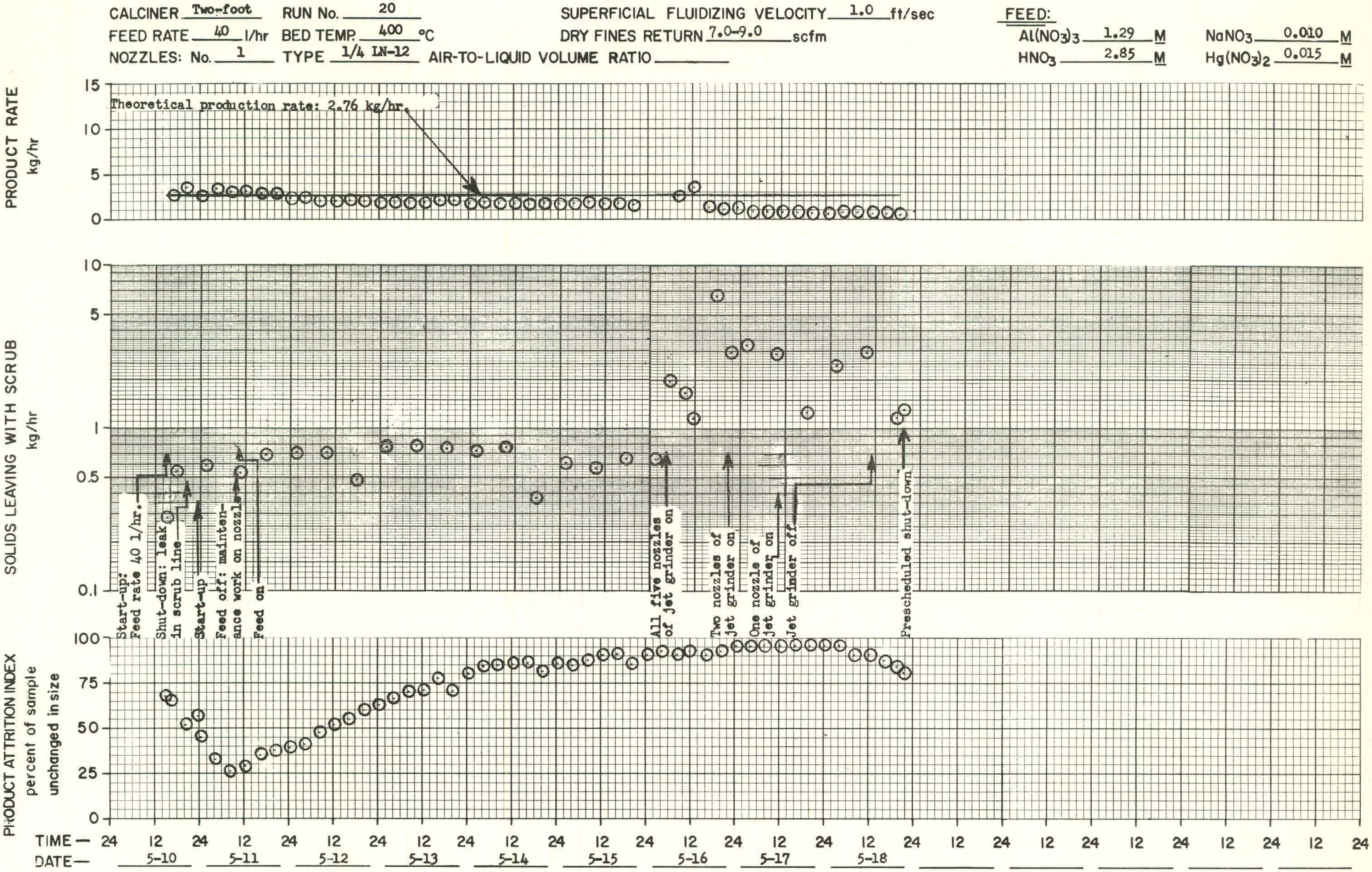

Fig. 50 General data, Run 20.

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Run 21

Period Covered: From August 2, 1961 to August 24, 1961.

Objective: To study the performance of a newly designed boron carbide feed nozzle cap, and to determine the effect of mercury in the feed.

Equipment: That of Run 20 except: (1) the Type 1/2 J pneumatic atomizing nozzle was re-installed in place of the single fluid nozzle used during Run 20, and (2) the primary cyclone was removed from the off-gas system thus allowing nearly all of the fines to be removed by the venturi scrubber. The feed nozzle cap was a newly designed cap of boron carbide.

Cumulative NaK Heating System Operating Data (including this run):

169 startups; 6710 hours above 1000°F; 2774 hours below 1000°F.

Run Conditions:

Starting bed	Ammon sand
Bed temperature, °C	400
Feed rate, l/hr	80
Nozzle air-to-liquid volume ratio	400 → 500 → 600
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return	No
Bed pressure, psia	13.6-14.0
Operating time, hours	360

Feed Composition:		
	Aluminum nitrate, M	1.29
	Nitric acid, M	2.34
	Sodium nitrate, M	0.078
	Mercuric nitrate, M	none → 0.015

Results: The boron carbide feed nozzle cap operated satisfactorily but required a relatively higher NAR than the standard flat-faced cap to maintain satisfactory particle size. A NAR of 600 produced a product with a stable mass median particle diameter of 0.48-0.53 mm. A small cake which had formed around the nozzle was found during a forced shutdown after the particle diameter had increased from 0.26 to 0.99 mm. After resuming the run with a cleaned nozzle the particle size decreased to 0.48-0.53 mm at NAR of 600. The alpha alumina content of the bed was always less than 5 per cent.

Although not measured, the nozzle cap erosion was minor. Because of the fragile nature of boron carbide (one cap fractured during initial installation attempt) the cap was left in place for use in the next run. A visual inspection revealed only minor polishing of the cap face.

The addition of mercury to the feed had no detectable effect on product properties.

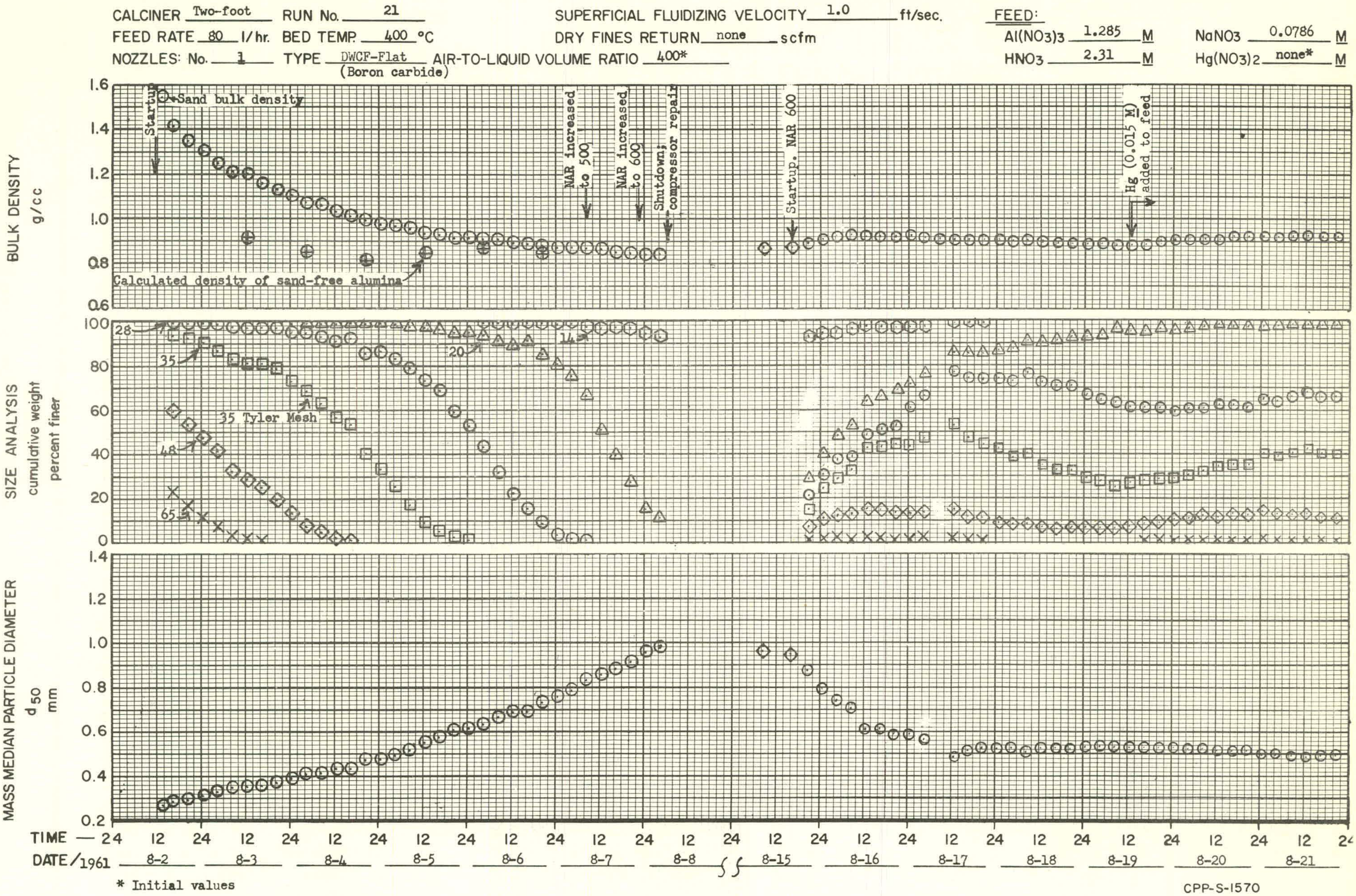


Fig. 51 Product data, Run 21 (sheet 1 of 2).

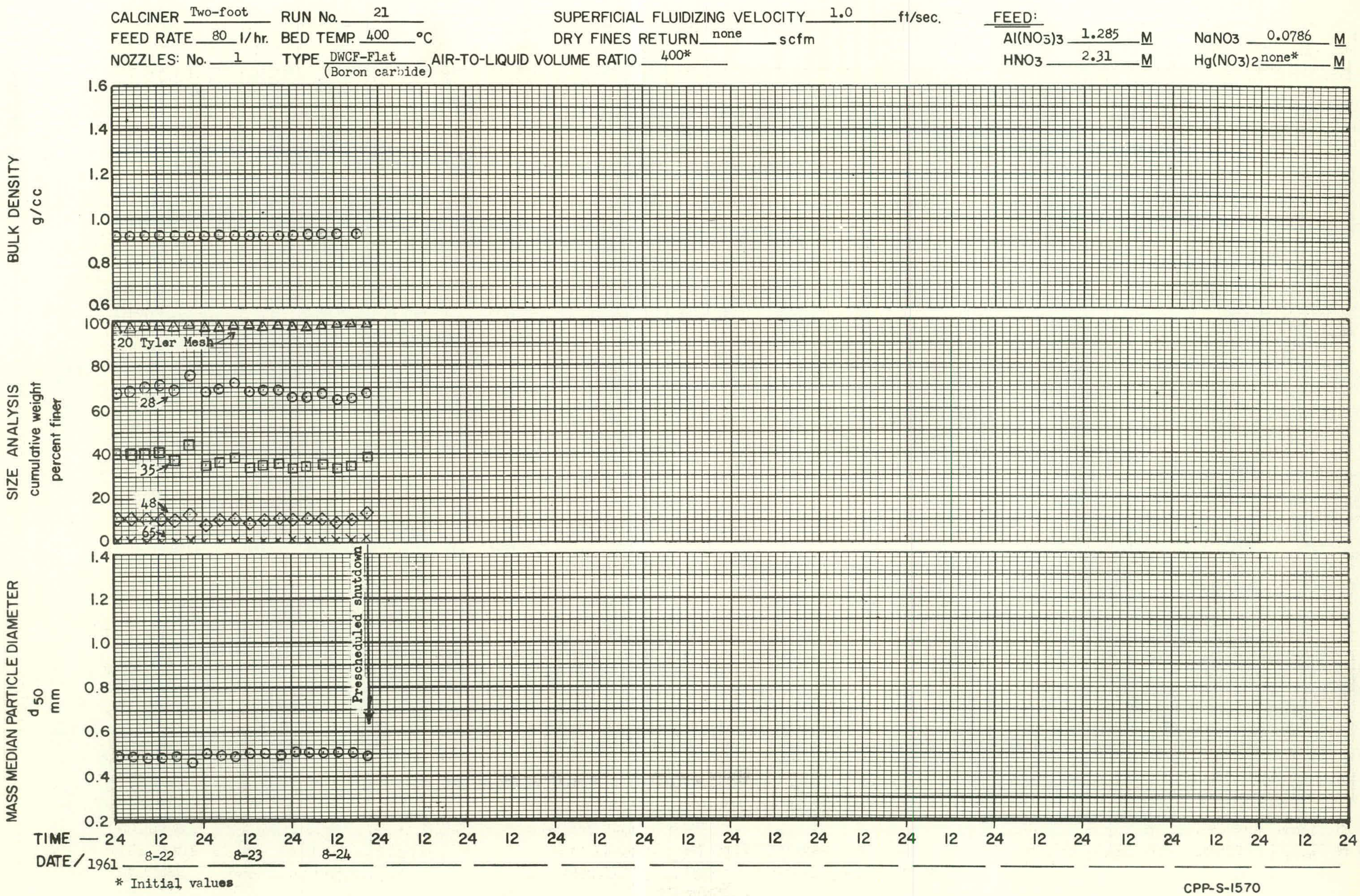


Fig. 51 Product data, Run 21 (sheet 2 of 2).

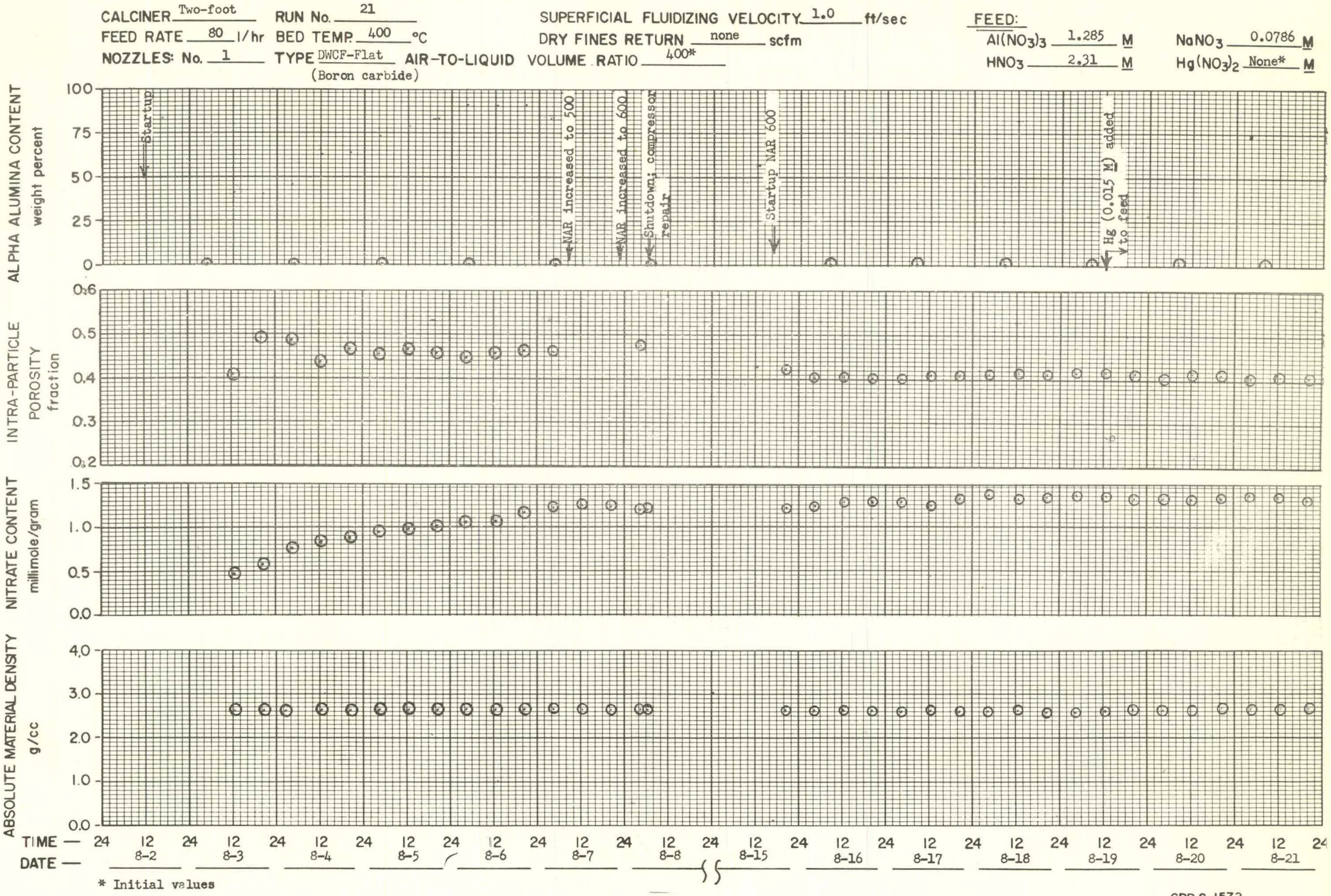


Fig. 52 Additional product data, Run 21 (sheet 1 of 2).

CALCINER Two-foot RUN No. 21 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

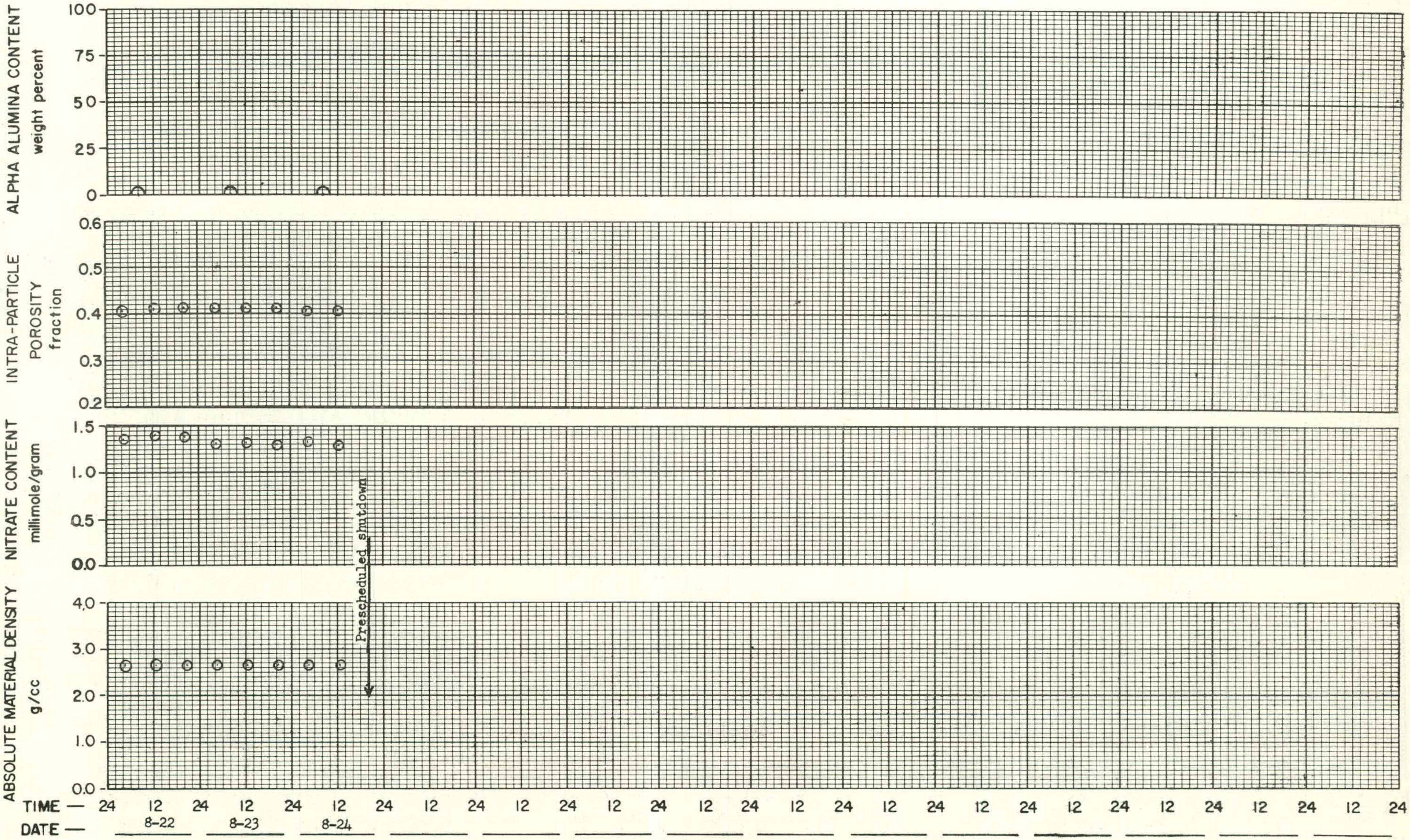
FEED RATE 80 l/hr BED TEMP. 400 °C DRY FINES RETURN none scfm

NOZZLES: No. 1 TYPE DWCF-Flat (Boron carbide) AIR-TO-LIQUID VOLUME RATIO 400*

FEED:

$Al(NO_3)_3$ 1.285 M $NaNO_3$ 0.0786 M

HNO_3 2.31 M $Hg(NO_3)_2$ none* M



* Initial values

Fig. 52 Additional product data, Run 21 (sheet 2 of 2).

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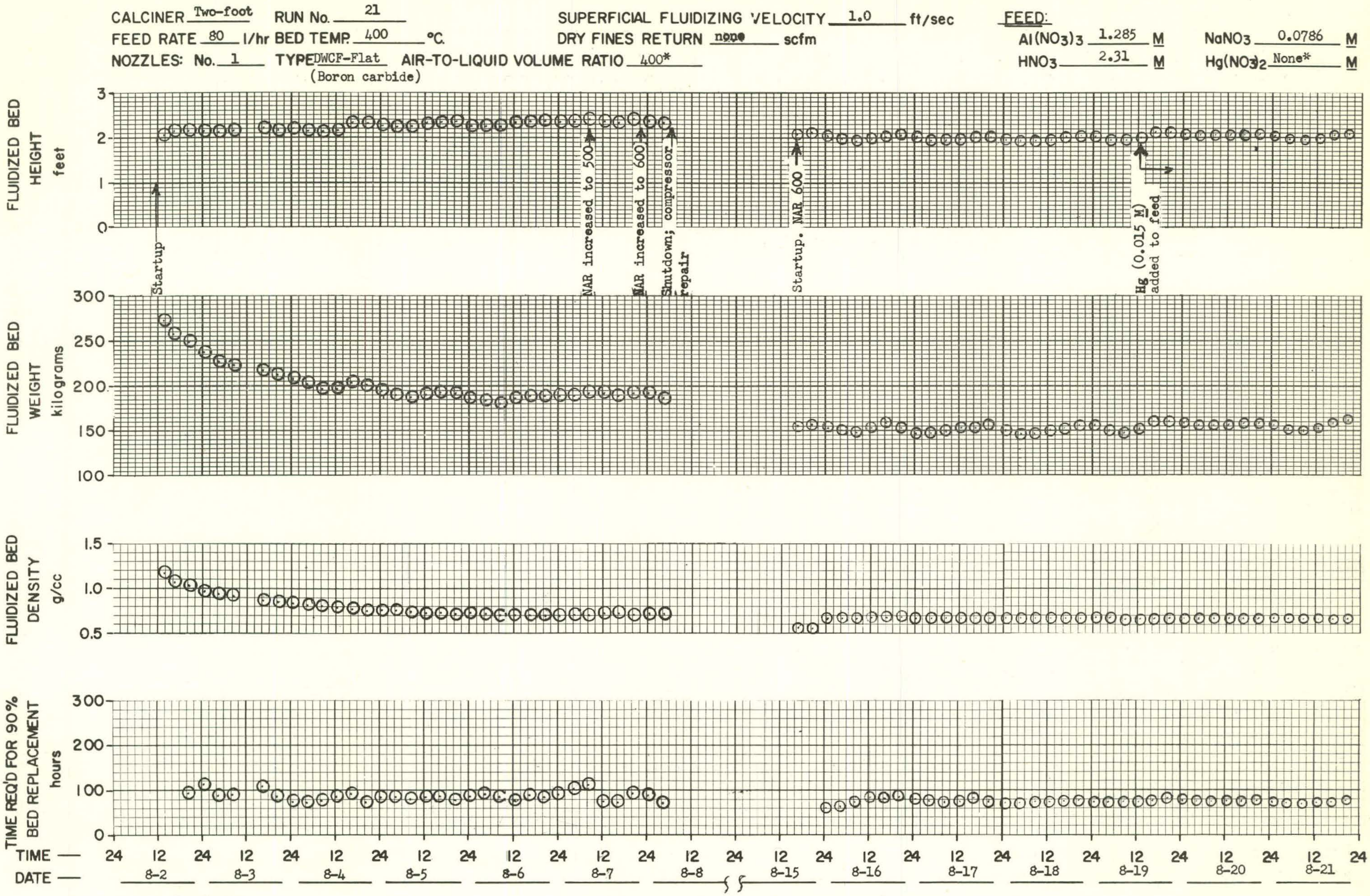


* Initial values

Fig. 53 Calciner bed data, Run 21 (sheet 1 of 2).

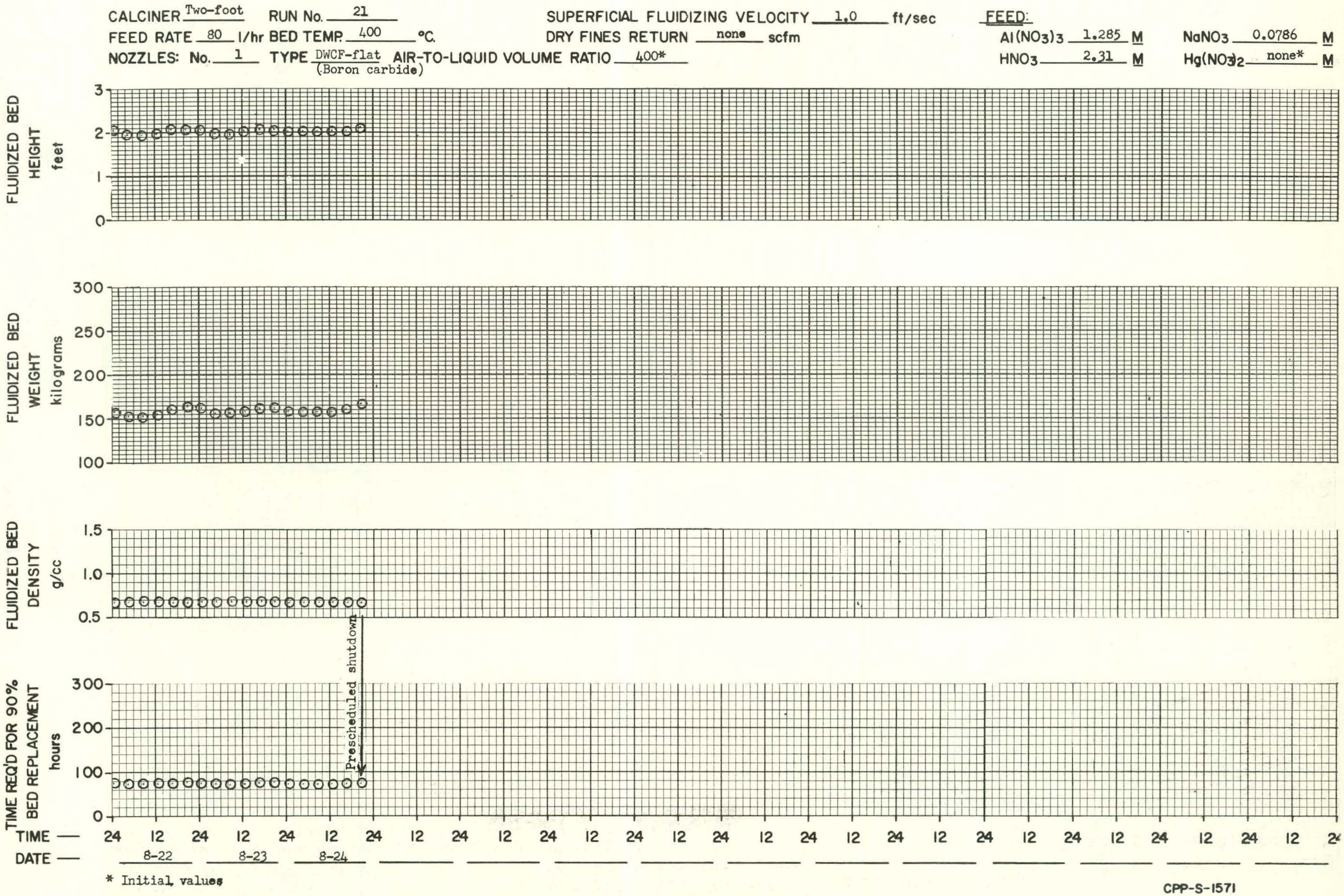


Fig. 53 Calciner bed data, Run 21 (sheet 2 of 2).

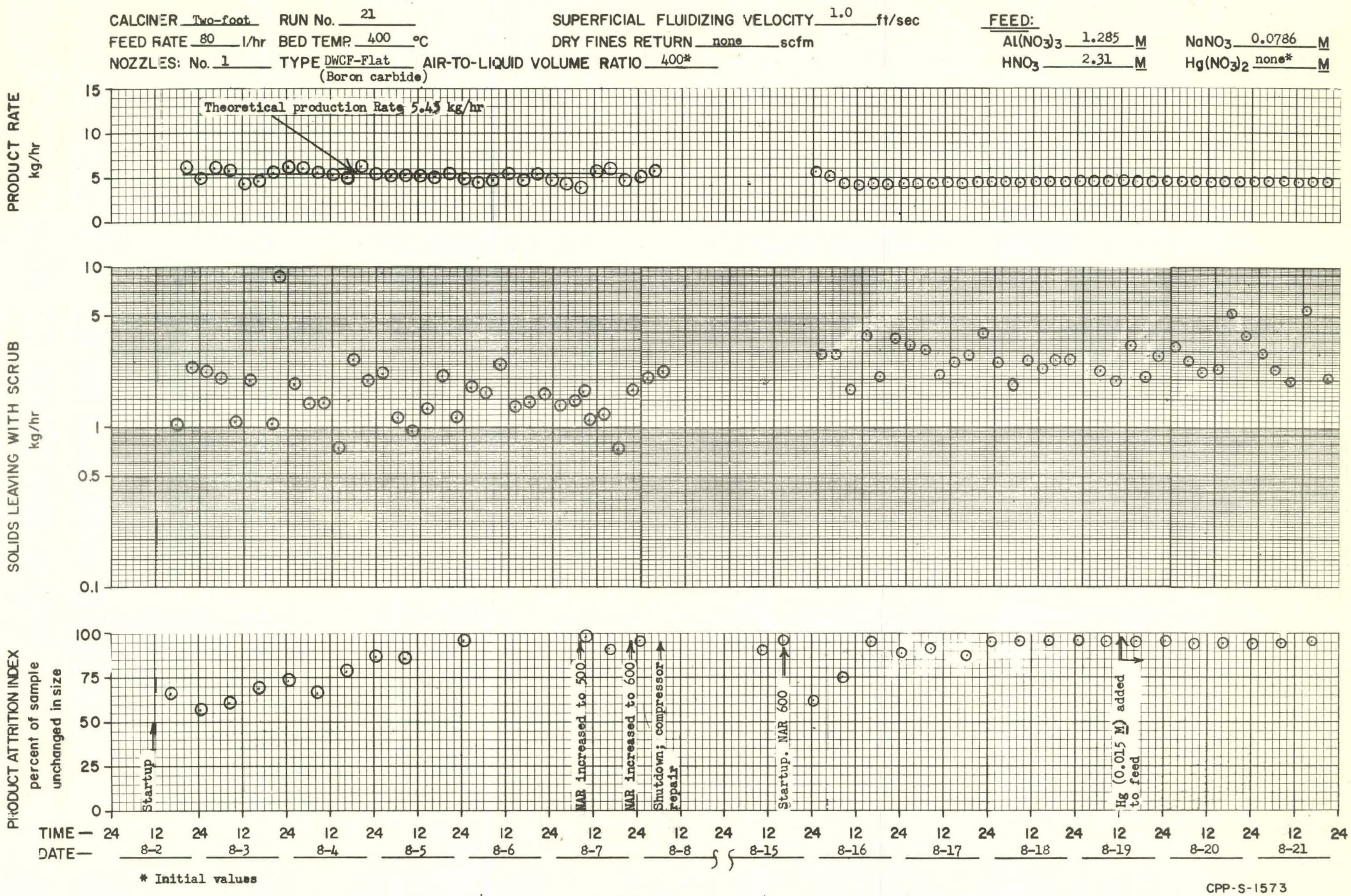


Fig. 54 General data, Run 21 (sheet 1 of 2).

CALCINER Two-foot RUN No. 21 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

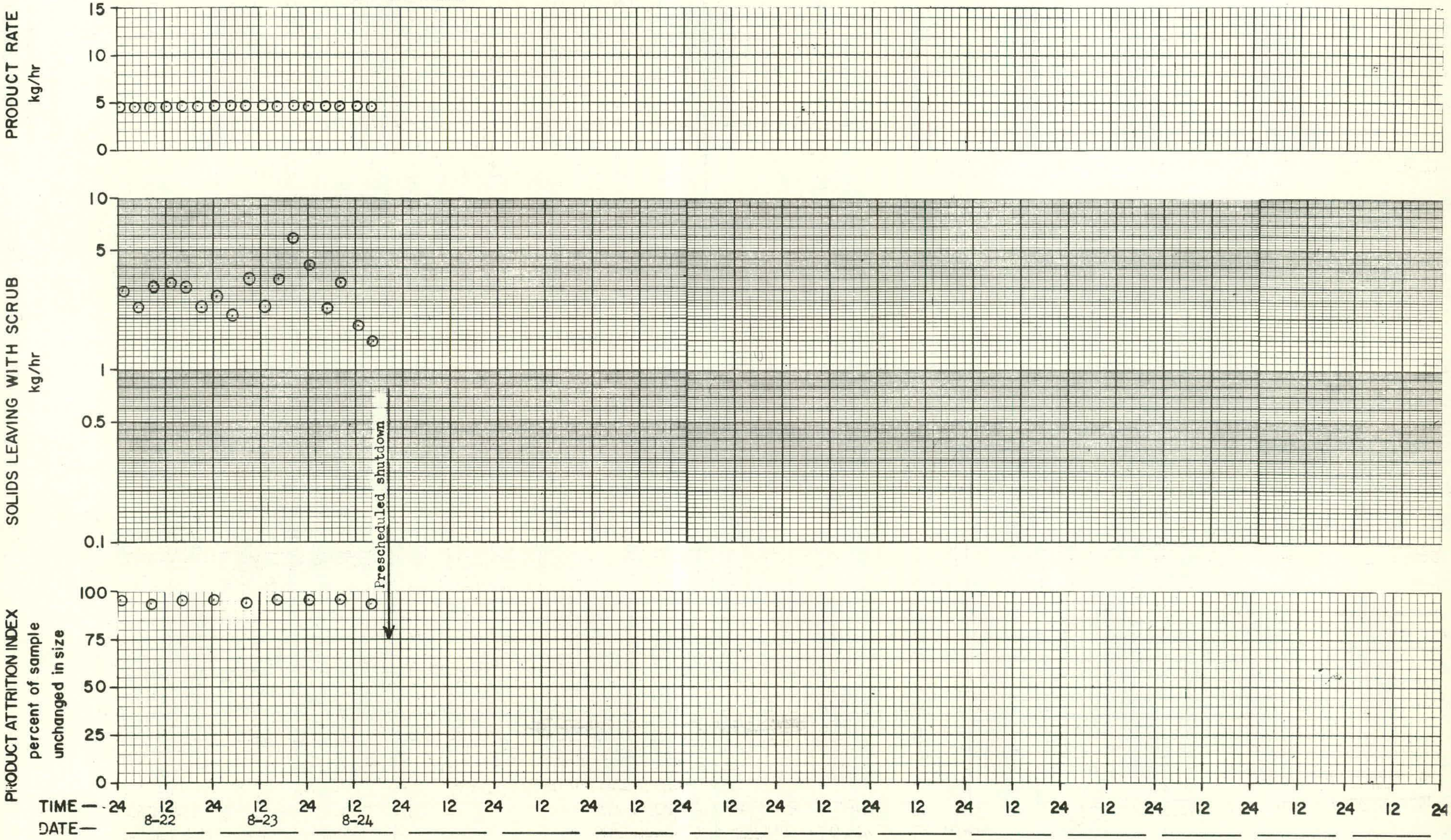
FEED RATE 80 l/hr BED TEMP. 400 °C DRY FINES RETURN none scfm

NOZZLES: No. 1 TYPE DWCF-flat (Boron carbide) AIR-TO-LIQUID VOLUME RATIO 400*

FEED:

$Al(NO_3)_3$ 1.285 M $NaNO_3$ 0.0786 M

HNO_3 2.31 M $Hg(NO_3)_2$ none* M



* Initial values

Fig. 54 General data, Run 21 (sheet 2 of 2).

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Run 22

Period Covered: From September 6, 1961 to September 14, 1961.

Objective: To determine the effect of sodium concentration of the feed on the formation of alpha alumina, to continue testing a boron carbide feed nozzle cap used in Run 21, and to obtain information on the rate of elutriation of solids from the calciner by collecting the solids from the primary cyclone underflow.

Equipment: That used in Run 21 except that the primary cyclone was re-installed in the off-gas system and a sample pot was connected to the underflow (dust discharge) of the primary cyclone for batch collection of the cyclone fines.

Cumulative NaK Heating System Operating Data (including this run):

171 startups; 6914 hours above 1000°F; 2779 hours below 1000°F.

Run Conditions:

Starting bed	Predominantly amorphous alumina generated during Run 21
Bed temperature, °C	400
Feed rate, l/hr	80
Nozzle air-to-liquid volume ratio	600
Superficial fluidizing velocity, ft/sec	1.0
Dry fines return to bed	No
Bed pressure, psia	13.5-15.5
Operating time, hours	203

Feed Composition:	Aluminum nitrate, M	1.295
	Nitric acid, M	2.34
	Sodium nitrate, M	0.078 → 0.25 → 0.03
	Mercuric nitrate, M	0.015

Results: The formation of alpha alumina in the product was affected by the sodium concentration of the feed. Increasing the sodium concentration of the feed to 0.25M from 0.078M resulted in an increase of the alpha alumina content of the product from 5 to 17 per cent; decreasing the sodium concentration to 0.03M from 0.25M resulted in a decrease of the alpha alumina content of the product to 8 per cent during the final 91 hours of operation. The fines collected from the primary cyclone contained approximately the same alpha content as the product. The cyclone fines accumulation rate increased fivefold when the alpha content increased from 5 to 17 per cent, and this rate was greater than the product rate when the alpha alumina content was above 10 per cent. Characteristics of the fines were not significantly different from those of the product except the nitrate content was higher and the bulk density lower. The fines were too small to screen.

Run 22 (continued)

Erosion of the feed nozzle cap was minor as indicated by visual observation which revealed only minor polishing of the cap face; finishing marks on the face were still evident. A small cake of calcined material about 1/2-inch-thick partly surrounded the feed nozzle. No lumps were found in the final bed, however.

A special test near the end of the run demonstrated successfully the capability of forming colored shells on the bed particles by adding various metallic nitrate solutions to the calciner feed.

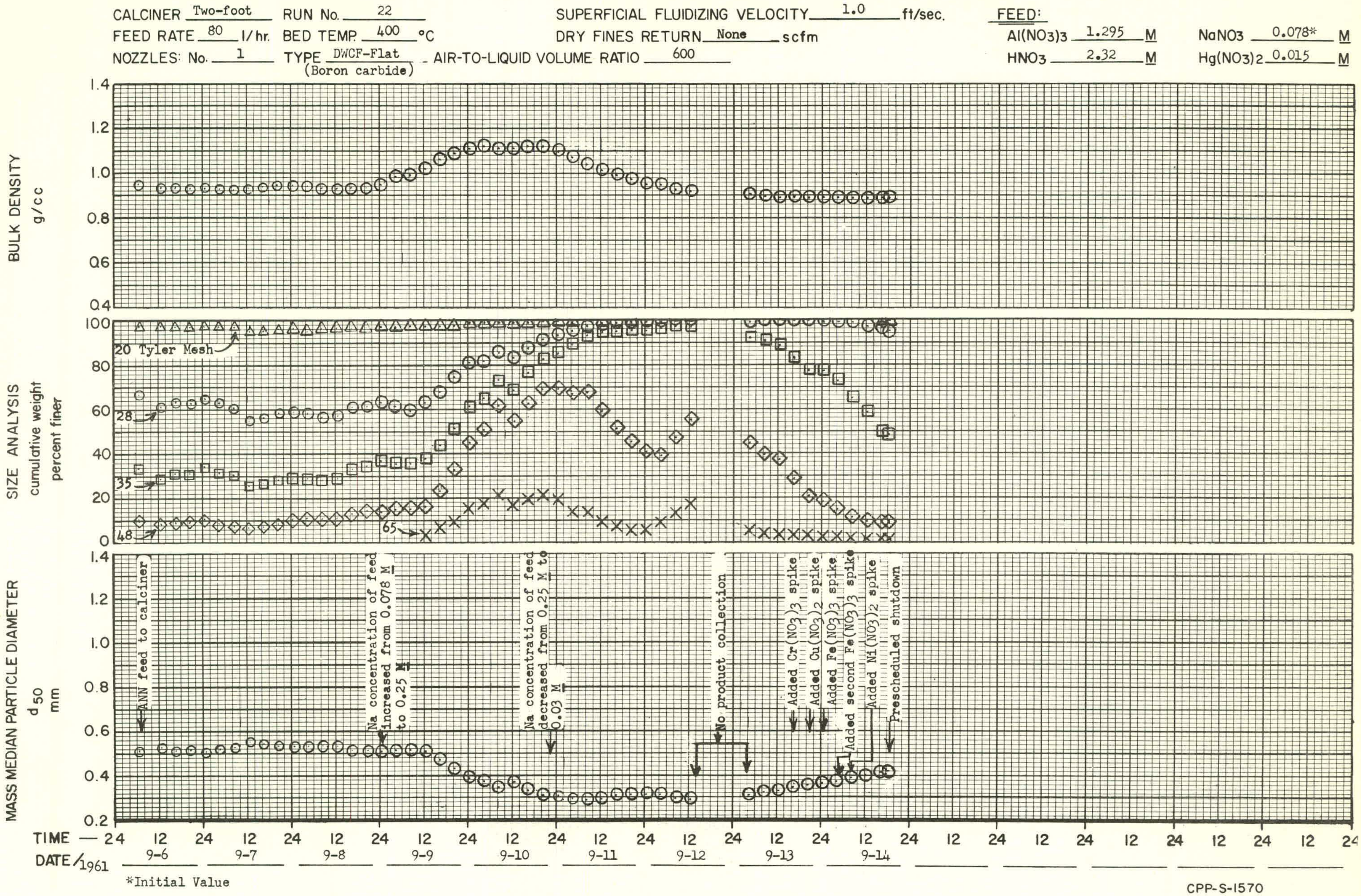


Fig. 55 Product data, Run 22.

CYCLONE FINES DATA

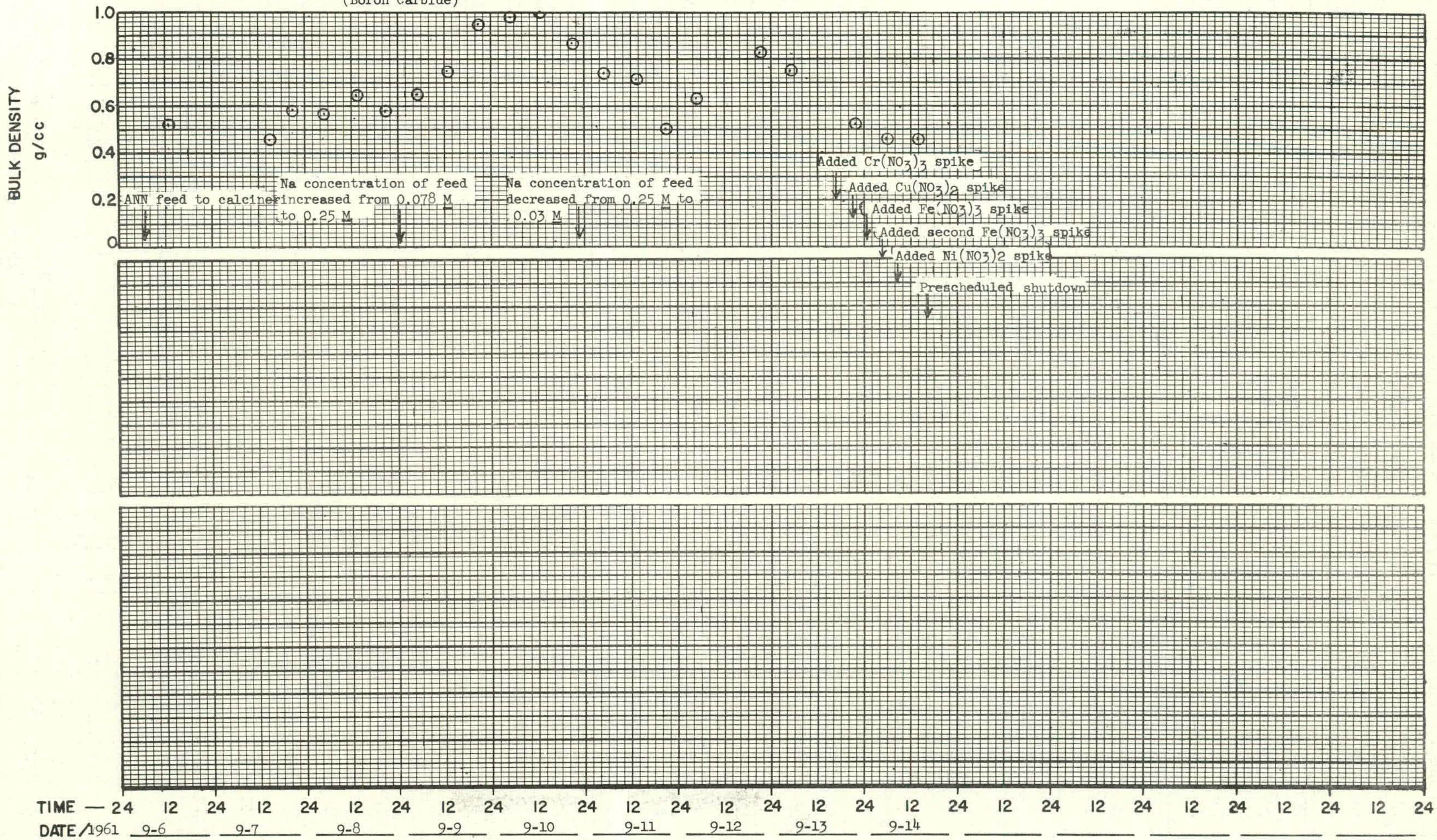
CALCINER Two-foot RUN No. 22 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec.

FEED RATE 80 l/hr. BED TEMP. 400 °C DRY FINES RETURN None scfm

NOZZLES: No. 1 TYPE DWCF - Flat (Boron Carbide) AIR-TO-LIQUID VOLUME RATIO 600

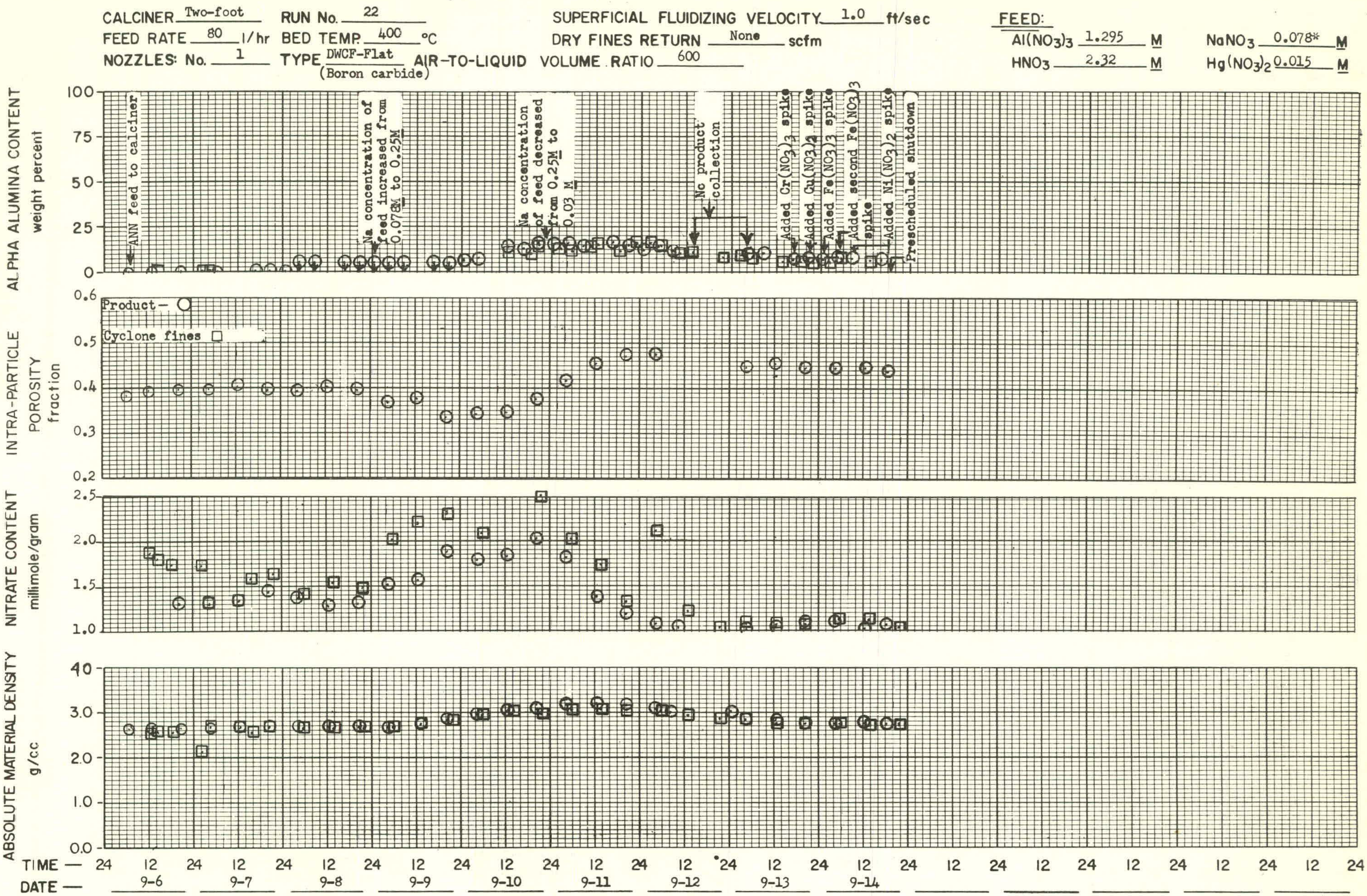
FEED: $Al(NO_3)_3$ 1.295 M NaNO3 0.078* M

HNO_3 2.32 M $Hg(NO_3)_2$ 0.015 M



*Initial Value

Fig. 56 Cyclone fines data, Run 22.



*Initial Value

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Fig. 57 Additional product and cyclone fines data, Run 22.

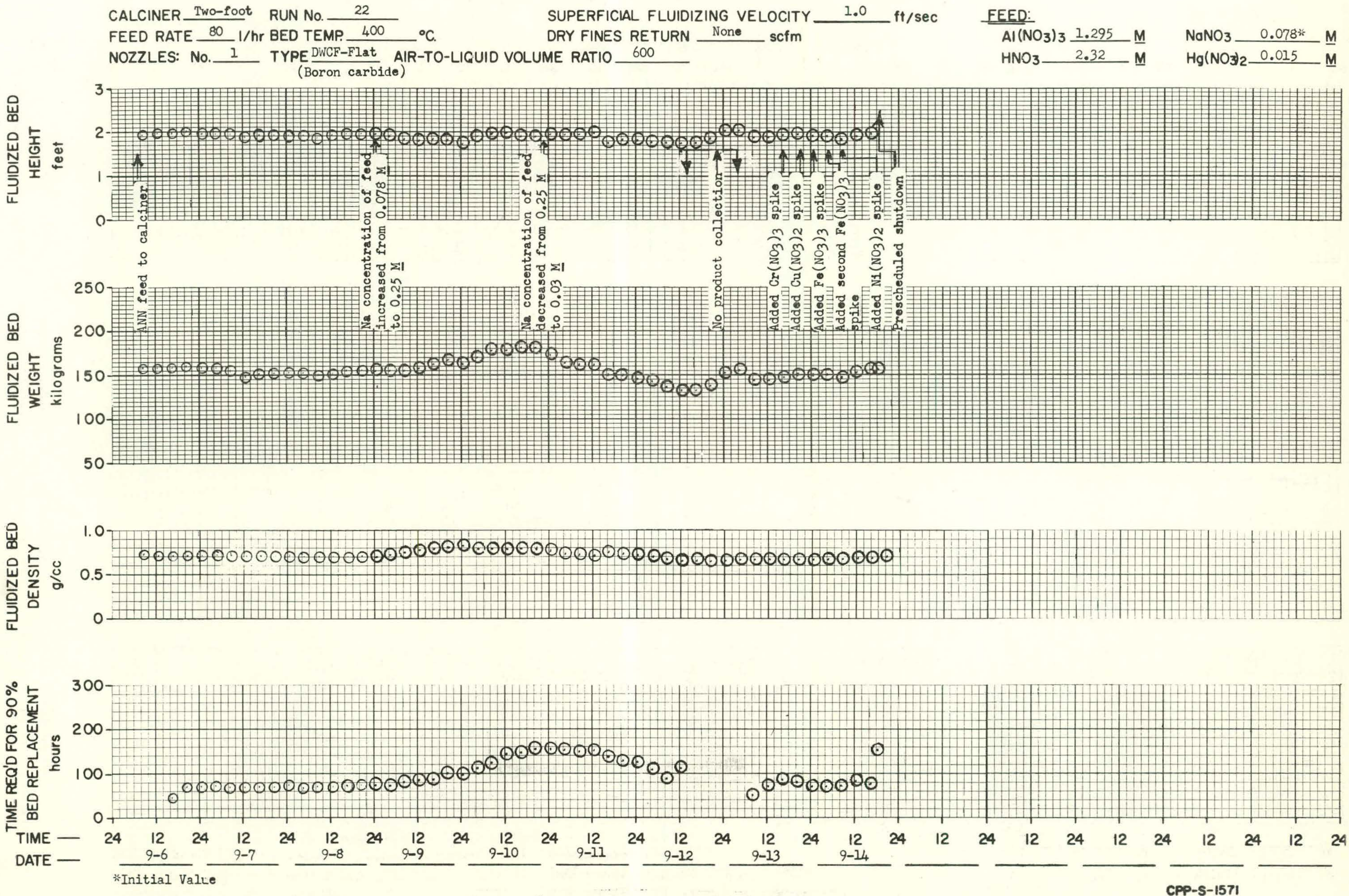


Fig. 58 Calciner bed data, Run 22.

CALCINER Two-foot RUN No. 22 SUPERFICIAL FLUIDIZING VELOCITY 1.0 ft/sec

FEED RATE 80 l/hr BED TEMP. 400 °C DRY FINES RETURN None scfm

NOZZLES: No. 1 TYPE DWCF-Flat (Boron carbide) AIR-TO-LIQUID VOLUME RATIO 600

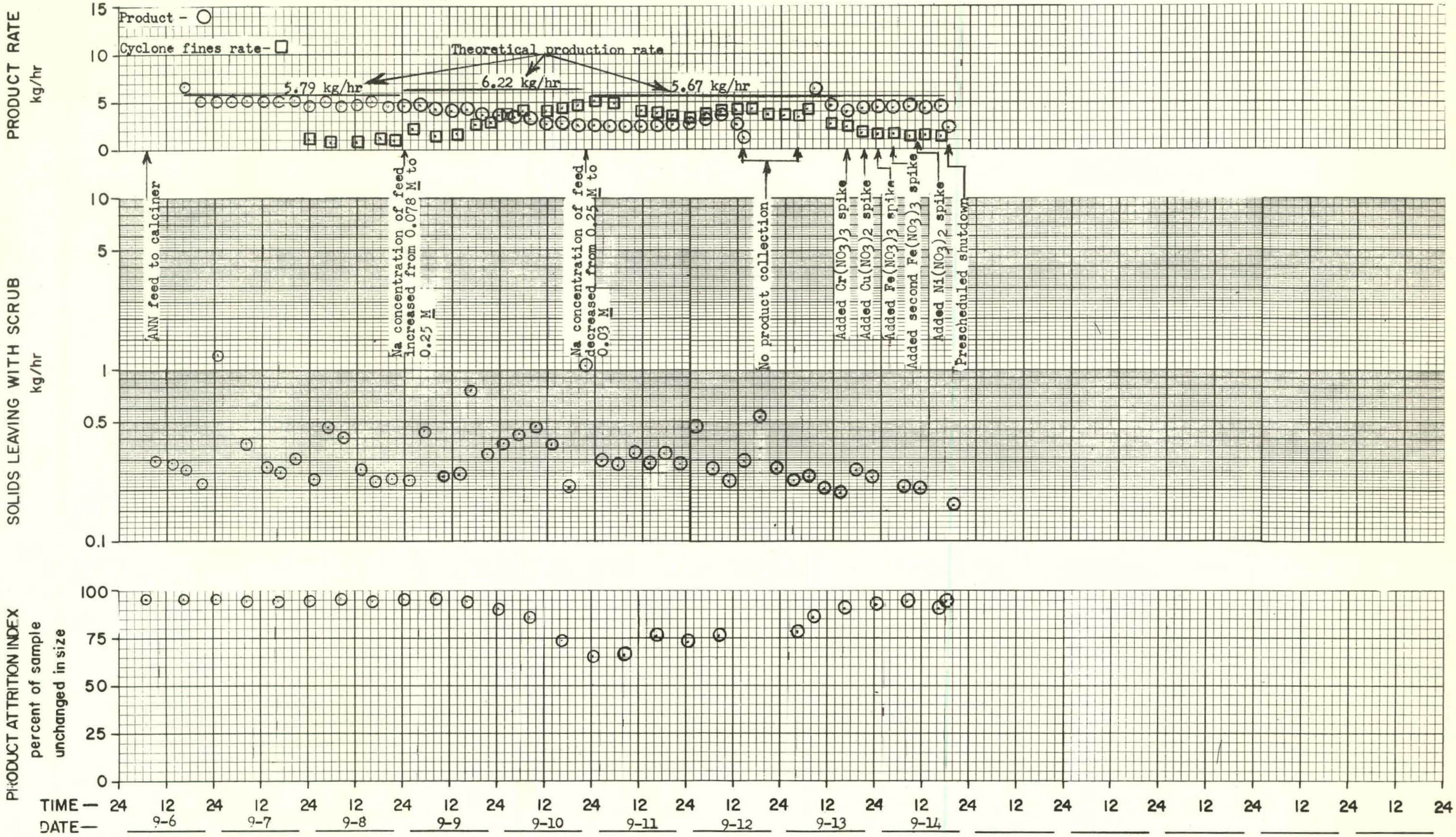
FEED:

$Al(NO_3)_3$ 1.295 M

HNO_3 2.32 M

$NaNO_3$ 0.078* M

$Hg(NO_3)_2$ 0.015 M



*Initial Value

Fig. 59 General data, Run 22.

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