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MASTER

THORIA POWDER PROCESS DEVELOPMENT

(LWBR Development Program)

OCTOBER 1979

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BETTIS ATOMIC POWER LABORATORY
WEST MIFFLIN, PENNSYLVANIA

Operated for the U. S. Department of Energy by
WESTINGHOUSE ELECTRIC CORPORATION

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C.R. Hutchison
R. Lloyd

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BETTIS ATOMIC POWER LABORATORY WEST MIFFLIN, PENNSYLVANIA 15122

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FOREWORD

The Shippingport Atomic Power Station located in Shippingport, Pennsylvania was the first large-scale, central-station nuclear power plant in the United States and the first plant of such size in the world operated solely to produce electric power. This program was started in 1953 to confirm the practical application of nuclear power for large-scale electric power generation. It has provided much of the technology being used for design and operation of the commercial, central-station nuclear power plants now in use.

Subsequent to development and successful operation of the Pressurized Water Reactor in the Department of Energy (DOE) owned reactor plant at the Shippingport Atomic Power Station, the Atomic Energy Commission in 1965 undertook a research and development program to design and build a Light Water Breeder Reactor core for operation in the Shippingport Station.

The objective of the Light Water Breeder Reactor (LWBR) program has been to develop a technology that would significantly improve the utilization of the nation's nuclear fuel resources employing the well-established water reactor technology. To achieve this objective, work has been directed toward analysis, design, component tests, and fabrication of a water-cooled, thorium oxide-uranium oxide fuel cycle breeder reactor for installation and operation at the Shippingport Station. The LWBR core started operation in the Shippingport Station in the Fall of 1977 and is expected to be operated for about 4 to 5 years. At the end of this period, the core will be removed and the spent fuel shipped to the Naval Reactors Expended Core Facility for a detailed examination to verify core performance including an evaluation of breeding characteristics.

In 1976, with fabrication of the Shippingport LWBR core nearing completion, the Energy Research and Development Administration, now DOE, established the Advanced Water Breeder Applications (AWBA) program to develop and disseminate technical information which would assist U.S. industry in evaluating the LWBR concept for commercial-scale applications. The program is exploring some of the problems that would be faced by industry in adapting technology confirmed in the LWBR program. Information being developed includes concepts for commercial-scale prebreeder cores which would produce uranium-233 for light water breeder cores while producing electric power, improvements for breeder cores based on the technology developed to fabricate and operate the Shippingport LWBR core, and other information and technology to aid in evaluating commercial-scale application of the LWBR concept.

All three development programs (Pressurized Water Reactor, Light Water Breeder Reactor, and Advanced Water Breeder Applications) are under the technical direction of the Division of Naval Reactors of DOE. They have the goal of developing practical improvements in the utilization of nuclear fuel resources for generation of electrical energy using water-cooled nuclear reactors.

Technical information developed under the Shippingport, LWBR, and AWBA programs has been and will continue to be published in technical memoranda, one of which is this present report.

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The development program to identify the critical parameters for the process of converting thorium nitrate solution into thoria powder is described. Thorium oxalate hexahydrate is precipitated from the reaction of thorium nitrate solution with oxalic acid. The resulting thorium oxalate hexahydrate slurry is filter pressed into a cake which is air calcined to form thoria powder. Changes in the critical processing parameters such as free nitric acid content of the thorium nitrate solution, precipitation temperature, and calcining temperature altered the thoria powder charcteristics, and thus its capability for being fabricated into fuel pellets. The objective of the powder preparation effort was to obtain thoria powders which could be formed by conventional ceramic fabrication techniques into thoria and thoria-urania pellets of high density and high integrity having a nearly uniform large grain structure. Parameters in the manufacturing process critical to meeting these objectives were identified and closely controlled to ensure satisfactory process performance. The thoria powders thus produced were successfully used for the manufacture of fuel pellets for the LWBR core.

THORIA POWDER PROCESS DEVELOPMENT

(LWBR Development Program)

C.R. Hutchison
R. Lloyd

I. INTRODUCTION

The thoria powder process development program described in this report was conducted in support of the Light Water Breeder Reactor (LWBR) Program. Thoria serves as the fertile fuel in LWBR and is the base oxide for all of the binary fuel (ThO_2-$U^{233}O_2$) pellets.

The LWBR Program is developing the technology to breed fissile material in a light water thermal reactor and thereby to use available stores of nuclear fuel more efficiently. To achieve this objective, a breeder reactor core has been designed, fabricated, and installed in the existing pressurized water reactor plant at Shippingport, Pennsylvania.

The LWBR design and the fabrication of the reactor core were accomplished by the Bettis Atomic Power Laboratory under the technical direction of the Division of Naval Reactors, DOE. The operation of the LWBR core in the Shippingport Atomic Power Station is expected to confirm that breeding of fissile material can be achieved in a pressurized light water thermal reactor using a thoria (ThO_2) and thoria/urania (ThO_2-UO_2) binary fuel system. This core represents the first large scale fabrication of a thoria-base binary fuel of high density and the first use of uranium-233 fabricated into ceramic fuel in a power reactor.

The LWBR core is a seed-blanket configuration consisting of an inner region containing 12 movable seed assemblies, each surrounded by a blanket assembly. This inner region is surrounded by an outer reflector region containing 15 reflector modules. The mechanical design and operating environments of this core are described in more detail in reference (1).

The purpose of the development program was the production of a thoria powder with physical characteristics compatible with the manufacturing processes for both binary fuel pellets and thoria fuel pellets. The basic fabrication process for the production of thoria base fuel pellets was the cold press and single fire process. There are five basic steps in this process: (1) comminution, (2) press feed preparation, (3) compaction, (4) pretreatment and sintering, and (5) pellet finishing (grinding).

A. Background

Prior to the production of thoria powder and fuel pellets for the LWBR core, several small campaigns of fuel production were performed by a commecial vendor for use in physics and irradiation tests. In these small campaigns, difficulties were encountered in consistently achieving a uniform internal pellet quality, specifically with respect to high density, uranium homogeneity, and grain structure. These difficulties were traced (in part) both to the variability in the thoria powder characteristics which reflected the variability of the powder manufacturing process and to the pellet manufacturing process.

It was known from the literature, References 2 through 5, that thoria powder physical characteristics such as particle size, particle size distribution, and surface area are a function of the powder process parameters and that these parameters are optimized for a particular intended use of the powder. The physical characteristics of a powder which is used for the fabrication of fuel pellets by one production process are not necessarily the optimum characteristics for a different fuel pellet fabrication process. Consequently, as a result of the two pellet types (Thoria and Thoria-Urania) used for LWBR, each requiring a unique pellet manufacturing process, a basic powder process with readily adjustable process parameters was required. Adjustment of the process parameters was made to change the powder properties to fit the given pellet manufacturing process.

The thoria fuel pellet manufacturing process required a higher surface area thoria powder (i.e., one that is more active) than that used in binary fuel pellet fabrication. In the latter case, the UO_2 present in the binary fuel helped to promote densification.

This report describes the development effort associated with defining the basic suitable process for thoria powder. A brief description of the thoria powder process is presented below.

B. Thoria Powder Process

In their review, Reference 2 of technology of dense thoria ceramics, Hepworth and Rutherford noted that the density of sintered thoria depended on the method of powder preparation, precipitation temperature, and calcining temperature. Thoria powder can be prepared from nitrate, oxycarbonate, chloride, and oxalate salts and from the hydroxide. Harada, Baskin, and Handwerk (Reference 3) found that, of the thorium salts investigated, thorium oxalate produced the purest thoria (99.9%). In contrast, thoria derived from either oxycarbonate or thorium nitrate was contaminated with 0.5% silica and 0.2% alkali salts, respectively. LWBR design criteria required fuel with few impurities to minimize parasitic neutron capture. Investigators, References 3-6, have demonstrated that considerable control can be exercised over the physical character of the thoria powder prepared by the oxalate salt process.

The basic process used in the conversion of thorium nitrate to thoria powder by the oxalate salt process is described below.

1. Preparation of Thorium Nitrate Solution. Government Services Administration (GSA) inventory was the source of the thorium for the LWBR core. National Lead Company of Ohio* (NLO) under contract to the Bettis Atomic Power Laboratory prepared the thorium nitrate solution by dissolving thorium nitrate tetrahydrate crystals contaminated with rare earths, e.g., Dy, Eu, Gd, Sm, and transition metals in nitric acid. The solution was purified by a solvent extraction process in which diamyl amyl phosphonate (DAAP) in a kerosene diluent served as the extracting medium. The NLO solvent extraction process is described in Reference 7. Purified thorium nitrate solution for both the development program and core powder production was required to meet the chemistry requirements listed in Table I. The concentrated thorium nitrate solution (450 ± 50 g Th/liter) was adjusted to a concentration of 220 ± 30 g Th/liter by the addition of deionized water. To enchance the growth of the crystallites during precipitation, nitric acid was added to increase the acidity of the thorium nitrate solution to a concentration of 1.1 ± .1 Normality (see References 8 and 9). This addition of nitric acid is referred to as free nitric acid.

2. Preparation of Oxalic Acid Solution. To prevent contamination of the powder during the precipitation step, technical grade oxalic acid dihydrate crystals with impurity

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Box 39158, Cincinnati, Ohio 45239

level compatible with the purity requirements of the thoria powder were obtained. The oxalic acid dihydrate crystals were dissolved in deionized water at a temperature of 57 ± 3°C (135 ± 5°F). The oxalic acid solution was held at this temperature to prevent recrystallization.

3. Precipitation of Thorium Oxalate Hexahydrate Slurry. The oxalic acid $(COOH)_2 \cdot 2H_2O$ solution was sprayed into the purified thorium nitrate, $Th(NO_3)_4$, solution under controlled conditions (e.g. free nitric acid, precipitation temperature, and precipitation rate) to precipitate thorium oxalate hexahydrate, $Th(C_2O_4)_2 \cdot 6H_2O$ according to the following equation:

   $$Th(NO_3)_4 + 2H_2C_2O_4 + 6H_2O \longrightarrow Th(C_2O_4)_2 \cdot 6H_2O + 4\ HNO_3.$$

   Precipitation temperature was the temperature of the thorium nitrate solution during the precipitation of thorium oxalate hexahydrate. Precipitation rate was a function of the addition rate of oxalic acid to the thorium nitrate during precipitation. These parameters are discussed in Section II.

4. Filtration of the Slurry Followed by Washing and Drying of the Thorium Oxalate Hexahydrate Cake. The slurry was filtered in a plate-and-frame-filter press to separate the thorium oxalate from the mother liquor. The resulting cake in the press was washed with deionized water until a pH of 3.0 minimum was obtained in the wash water. Next, the cake was dewatered by blowing filtered air at ambient temperature through the filter cake in the press.

5. Calcination of Thorium Oxalate Hexahydrate to Thoria. Dehydration and decomposition of the thorium oxalate hexahydrate into thoria powder was found to occur in stages giving off water of hydration in the early stages of heating and finally decomposing into ThO_2 powder (References 4 and

6). In general, the thorium oxalate hexahydrate lost water at 100 to 150°C to give the dihydrate which yields the anhydrous oxalate at 200-300°C, and then decomposed to the oxide at 300 to 400°C. These reactions are illustrated below:

Calcining Temperature	Reaction
100 - 150°C	$Th(C_2O_4)_2 \cdot 6H_2O \longrightarrow Th(C_2O_4)_2 \cdot 2H_2O + H_2O$
200 - 300°C	$Th(C_2O_4)_2 \cdot 2H_2O \longrightarrow Th(C_2O_4)_2 + 2H_2O$
300 - 400°C	$Th(C_2O_4)_2 \longrightarrow ThO_2 + 2CO_2 + 2CO$

As the calcining temperature increases above 400°C, the crystallites within the powder particles grow and the particles themselves shrink as discussed by Kinoshita, et al (Reference 4). Electron microscope studies showed that the as-calcined powder consisted of square plate-like particles similar to the precursor oxalate (References 4, 5 and 8). These square plate like particles consisted of aggregates of crystallites. With increasing calcining temperature, for example from 500°C (932°F) to 1100°C (2012°F) the crystallite size increases from 100 to 2100 angstroms and the particle size decreased from 10 to 4 microns.

Parameters for the precipitation and calcination processing steps control the characteristics and sinterability of the powder. A wide range of powders, each with its own characteristics and sinterability properties can be formulated by adjustment of these parameters (References 2-6).

II. OXALATE SALT PROCESS DEVELOPMENT PROGRAM

The purpose of the development program was twofold: (1) to determine those process parameters which consistently produced thoria powder of uniform quality, and (2) to evaluate the powder characteristics compatible with a fuel pellet fabrication process which would yield fuel pellets meeting the LWBR design requirements. As discussed in the literature, References 2 through 6, the precipitation of thorium oxalate and the calcination of thorium oxalate into ThO_2 powder are the primary steps in the powder process. For the former, the development program focused on those parameters, namely, precipitation temperature, precipitation rate, and free nitric acid, which affect the rate of nucleation and the rate of crystal growth of the thorium oxalate. These rate processes, in turn, have a strong influence on the final powder physical characteristics. For the calcination step the development program examined the effects of temperature on surface area, average particle size, and bulk density of the calcined powder.

Under the direction of Bettis, the powder development program was conducted at the DOE Fernald Facility, which is operated by NLO. NLO as prime contractor was responsible for the powder processing steps starting with dissolution of the thorium nitrate tetrahydrate crystals and ending with the packaging of the thorium oxalate hexahydrate cake in transfer cans. General Electric Company* (GE), as subcontractor to NLO, was responsible for the remaining powder processing steps, which included calcination, blending, and packaging of the powder.

To minimize production problems associated with scaling up from either bench or pilot run size powder batches, full size (130 ± 10 kg) production batches were manufactured in the development program. A description of the processing equipment is presented in Appendix A, along with a process equipment and material flow diagram.

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* The General Electric Company's Nuclear Systems Programs facility located in Evendale, Ohio was the site for this phase of the program.

1. Chemical Analyses

Standard emission spectrographic techniques with an estimated precision of ± 30% were used to determine metallic impurities and rare earths.

Carbon and sulfur analyses were determined by chemical combustion procedures.

2. Powder Physical Characteristics

Crystallite shape and size on selected powder samples were determined using scanning electron microscopy (SEM). Characterization of the agglomerates of the discrete crystallites was made by the following methods: (1) average particle diameter was measured by the Fisher sub-sieve sizer; (2) surface area of powders was measured by Brunauer, Emmett, and Teller (BET) nitrogen gas absorption technique using the Numec/AFA-4 instrument; and (3) bulk density was measured by the Scott Volumeter.

3. Sinterability Test

A Sinterability Test program, conducted at Bettis, was performed to evaluate the various powder batches for producing thoria pellets of high density, high quality, and uniform coarse grain sizes. A flow diagram of this test program is shown in Figure 1.

At Bettis the calcined thoria powder was milled by a fluid energy micronizer mill. Comminution of the powder particles, agglomerates of crystallites, occurred by self-attrition. One pass micronize milling using the parameters listed in Figure 1, increased the as-calcined powder surface area by approximately 1 to 2 m^2/gm.

The finely divided milled powder was agglomerated into granules by liquid/solids agglomeration. The binder-solvent (1-2 w/o Carbowax 6000 organic binder - Oxylene solvent) solution was introduced as a spray during the tumbling of the powder in the twin shell blender. Agglomerates ranging in size from approximately 0.004 to 0.25 inch diameter were formed. These agglomerates were granulated through a U.S. Standard 25 mesh screen to produce a size range from approximately 0.004 to .030 inch diameter. Sterotex (0.2 w/o) die lubricant was dry blended into the granules.

Pellets were pressed at each of 6 green density points at 2% intervals in the range of 54 through 64 theoretical density(TD). This green density range was found to be the optimum range to compact pellets free of defects, i.e. cracks, and laminations. The green pellet diameter was 0.886 inch with a length to diameter ratio of 1.0.

Green pellets were pretreated in a CO_2 atmosphere for 4 ± 1 hours at a temperature of 425 ± 25°C to remove the organic binder and lubricant. Next the pellets were sintered at temperatures ranging from 1675 to 1725°C for 12 hours in a dry hydrogen atmosphere (inlet dewpoint of approximately 45°C).

Completed pellets were evaluated for visual integrity (chips and cracks), geometric density and metallographic attributes of grain structure, internal cracks, and granule segregation which is narrow regions of high porosity tracing the outline of the press feed granules. These high porosity regions represented undersirable zones of mechanical weakness and reduced thermal conductivity. Examples of acceptable and unacceptable granule segregation are shown in Figure 2. The pellet requirements, summarized below, reflected the mechanical design requirements described in Reference 1.

Attribute	Limit
1. Geometric Density	
a. Individual Minimum	93% of theoretical density (10.0 gm/cc)
b. Batch* or Blend Average	97 ± 1.5% of theoretical density
2. Metallography	
a. Grain Size	ASTM 3 to 13, (125 to 4 microns)
b. Granule Segregation[1]	Reject if views worse than rating 3 (see Figure 2).
c. Internal Cracks	Maximum crack or series of cracks shall not exceed an area equivalent to 1/3 times nominal pellet diameter times .005 inch.
3. Surface Cracks	
a. Single Crack	No single crack shall exceed either a length exceeding 50% of the circumference or a width exceeding 0.010 inch.
b. Multiple Cracks	The combined total external surface cracking shall not exceed an area equal to 100% of the circumference times 0.010 inch.

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* Batch refers to the pellets (4 to 10) pressed at each green density point as part of the sinterability test.

[1] Granule segregation refers to a type of porosity distribution that consists of narrow regions of high porosity tracing the outline of the press feed granules. A subjective method was developed to evaluate and determine the acceptability of the thoria pellets with respect to granule segregation attribute. The as-polished microstructure view at 50X was compared to a set of photographic standards with ratings of 1 through 7 in order of increasing severity. These standards represented various degrees of granule delineation by the intergranular porosity, ranging from acceptable to unacceptabe conditions. Examples of ratings 1, 2, 3 and 7 are shown in Figure 2.

A. Precipitation of Thorium Oxalate Hexahydrate

Two precipitation parameters were investigated: (1) free nitric acid content in the thorium nitrate solution, and (2) precipitation temperature. A third parameter, precipitation rate, was controlled by the spray rate of the oxalic acid into the thorium nitrate solution and was empirically established at 2.5 ± 0.1 gallons per minute (gpm) based on earlier unreported work. This spray rate was used for all development and production batches.

1. Background

Precipitation temperature affects both the particle size and particle distribution of the thorium oxalate. Kinoshta, et al (Reference 4) reported that, for a low precipitation temperature of 6°C, the thorium oxalate cake consists of fine particles of a narrow distribution: (1) distribution maxima of approximately 0.8 microns and (2) approximately 5% of the particles greater than 2.5 microns. In contrast, for a higher precipitation temperature of 50°C, the thorium oxalate cake is made up of larger particles with a wide distribution: (1) distribution maxima of approximately 2.0 microns, and (2) approximately 25% greater than 2.5 microns.

Free nitric acid influences the growth of larger crystals according to Reference 8 and 9. The greater the acidity, the denser the precipitate; a given amount of thorium oxalate precipitated from 1.5N acid is about half as voluminous as the same amount precipitated from a 0.5N acid solution where the volume of the precipitate reflects the crystal size. The free nitric acid in the thorium nitrate solution affects the crystallite size by controlling the concentration of oxalate ions available to react with the thorium ions to form the thorium oxalate crystallites. Reducing the concentration of oxalate ions available by increasing the free acid level favors the growth of these crystallites, thereby reducing the surface area of the powder.

2. Experimental Procedure

Fifteen thorium oxalate hexahydrate batches (Nos. 27 through 32, 35 through 40, 42, 43, and 44) were precipitated at temperature rangig from 35 to 55°C (see Table II). The calcining temperature was held constant but the filter feed pump pressure was varied. For batches 27 through 32 the thorium oxalate hexahydrate slurry was pumped into the plate-and-frame filter press at a pressure of 45 pounds per square inch (psi). For batches 35, 36, 40, 42, and 43 the slurry was pumped into the plate-and-frame press at a pressure of 175 psi. The pump pressure was increased to eliminate the wet thorium oxalate cake problem discussed below in section II.A.3. Following calcination at 900°C for 8 hours in air the powders were characterized and evaluated by the sinterability test.

Three thorium oxalate hexahydrate batches 34, 40, and 41A were prepared under similar precipitation conditions except that the free nitric acid content of the thorium nitrate solution was varied. The free nitric acid content for batches 34, 40, and 41A was 1.49, 1.17, and 2.0 Normal (N), respectively (Table II). The thorium oxalate cakes were all calcined at 900°C for 8 hours in air. The resulting powders were evaluated for their physical characteristics and sinterability.

3. Results and Discussion

(a) Precipitation Temperature

(i) Thorium Oxalate Hexahydrate: The increase in the rate of settling of the thorium oxalate particles demonstrated that their average particle size increased with increasing precipitation temperature. In Figure 3 the settling rate curves* are presented for 5 batches precipitated over a temperature range of 36 to 53°C. In comparing the settling rate curves, note that thorium oxalate batch 40, which was precipitated at 36°C, continued to settle after 60 minutes. This behavior was indicative of a material with fine particle size. In contrast, thorium oxalate batch 43, which was precipitated at 53°C, reached an equilibrium condition of settling after 30 minutes as the result of its relative coarse particle size.

Examination of the thorium oxalate hexahydrate cake removed from the plate-and-frame filter press revealed that batches 27 through 32 were wet and soupy which presented two problems:

1. The cake was difficult to load in either transfer cans or Inconel calcine boats.

2. Powder characteristics were liable to be altered during calcination. Temperature of the preheat zone of the calcining furnace and the wet and soupy cake were favorable conditions for the redissolution of the original crystallites followed by recrystallization. Through this mechanism both the powder charactersitics and powder sinterability were potentially uncontrollable.

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* The NLO technical staff devised a semiquantitative settling rate test whereby the gravitational settling of the thorium oxalate precipitate was measured as a function of time up to 60 minutes. The settling rate curve was plotted from the observed volume of settled precipitate at given time intervals. The initial volume was 250 ml of thorium oxalate slurry.

Varying the precipitation temperature over a range of 35 to 44°C for batches 27 through 32 did not produce a dry cake condition. Therefore, a mechanical solution was employed.

The existing filter press pump was replaced with a pump capable of delivering a discharge maximum pressure to 180 pounds per square inch gage (psig) from 45 psig. The pump pressure of 45 psig resulted in the non-uniform filling of the plate-and-frame filter press with the thorium oxalate slurry. The slurry was dewatered by blowing air through the press at 50 to 80 psig for a minimum of 2 hours. The applied air pressure disturbed the structure of the thorium particles and forced them into a more open structure of higher free surface energy. The open structure with more space between the particles was able to accomodate and retain additional water. When dewatering of the slurry was completed and the applied force removed, the open structure reverted back to the closed structure of lower free surface energy and released the retained water. This behavior of the thorium oxalate particles under an applied force is known as dilatancy as described by Waye (Reference 10). The cake was observed to be wet and soupy when removed from the press. Batches 27 through 32 were filter pressed under the above conditions.

Pumping the slurry into the press at a maximum pressure of 175 psig resulted in the uniform packing of the press. During the dewatering of the slurry, the structure of the thorium oxalate particles was undisturbed by the dewatering air pressure and thereby permitted the slurry to be dewatered to a dry cake. The pump pressure of 125 to 180 psig was used for the remaining 31 batches of the program (see Table II). The dry cake condition eliminated the potential for uncontrolled dissolution and recrystallization of the thorium oxalate crystallites during the early stages of calcination.

The minimum precipitation temperature for a filterable thorium oxalate precipitate was found to be approximately 36°C. As observed in Figure 3, low precipitation temperatures favored very fine precipitates and therefore led to dilatancy. Seventy-five percent of batch 40, precipitated at 36°C, became wet and soupy when removed from the filter press. Precipitation of thorium oxalate hexahydrate above 36°C resulted in a dry cake when the precipitate slurry was pumped into the plate-and-frame filter press under a pressure of 175 psig.

(ii) Thoria Powder: The physical characterization data, Table III, from the powder batches (nos. 27 through 32, 35, 36, 40, 42, 43, and 44 were fitted to straight line curves by the method of linear regression analysis. The best fit curves for surface area, average particle size, and bulk density as a function of precipitation temperature are shown in Figures 4, 5, and 6 respectively. These curves confirmed the trends reported in the literature, namely, surface area decreased with increasing precipitation temperature and average particle size and bulk density increased with increasing precipitation temperature. The wet and soupy condition observed for batches 27 through 32 did not adversely affect the powder characteristics. Also, the addition of calcia (CaO) by coprecipitation of calcium oxalate (see Section II-C) did not alter the powder characteristics.

Powders derived from a low precipitation temperature had small crystallites and thus a higher surface area. For example, batch 35 precipitated at 41°C had a calcined powder surface area of 9.78 m^2/gm. The higher surface area powder had more surface energy available to act as the driving force for densification during sintering. In contrast, the higher precipitation temperature produced larger crystallites and consequently a powder with a lower surface area and less surface energy for densification. For example, batch 43 precipitated at 53°C had a calcined powder surface area of 7.51 m^2/gm. The relationship of the sinterability of the powder to surface area is illustrated in Figure 7A for batches 35 and 43. For each green density point the sintered density (percent of theoretical) for powder batch 35 was approximately 2% greater than that for powder batch 43 with the lower surface area. The sinterability test results for powder batches 27, 35, 36, 40, 42, and 43 are summaried in Table IV, items 1 through 6, respectively.

Photomicrographs in Figures 8 and 9 illustrated the microstructure observed in the sinterability test pellets fabricated from 2 of the 6 powder batches. The granule segregation over the 10% green density range met the photographic standard rating limit of 3 (see Figure 2) for thoria pellets. However, as can be seen from Figures 8 and 9 for batches 35 and 43, respectively, the grain structure was very fine (<ASTM No. 13 (4.0 microns)) and not discernible at the low green density points (54-58%). Secondary recrystallization was also observed in batch 35 in the form of idomorphic grains (see Figure 8, 64% green density photomicrograph). Nonuniform grain growth was also observed in powder batch 42, item 5 of Table IV.

Undesirable pellet defects appeared at green densities above 60%; these included internal cracks resulting from over compaction of the compact and bloating resulting from the entrapment of gases (CO, CO_2) derived from residual carbon in the pellet.

(b) Free Nitric Acid

(i) Thorium Oxalate Hexahydrate: Free nitric acid influenced the precipitated crystallite size and size distribution as inferred from the settling rate curves. Comparison of the two settling rate curves in Figure 10 for thorium oxalate batches 40 and 41A illustrated the effect on crystallite size of an increase in the free nitric acid from 1.17N to 2.0N. From the difference in the settling rates, it can be inferred that batch 40 had a finer crystallite size than batch 41A. Batch 40 was still approaching an equilibrium condition after 60 minutes in contrast to batch 41A, which reached an equilibrium condition in 30 minutes. Since the 2 batches were precipitated at the same temperature, 36-37°C, the free nitric acid content of 2.0N promoted the growth of the crystallites in contrast to the low free acid level of1.17N which inhibited the growth of crystallites.

(ii) Thoria Powder: The characteristics of three powder batches, 34, 40, and 41A, reflected the change in free nitric acid content. The increase in crystallite size of the thorium oxalate precipitate with increase in free acid level resulted in a decrease in the thoria powder surface area (see Figure 11) and in a corresponding increase in both average particle size and bulk density (see Figure 12).

Despite the effect of free nitric acid content on powder surface area there was little effect on the response of the powders to sinterability. The three powder batches with surface areas of 8.34, 9.10, and 13.79 m^2/gm for batches 34, 41A, and 40, respectively, had nearly identical sinterability curves (see Figure 7-B and items 4, 7, and 8 of Table IV). For example, the high surface area (13.79 m^2/gm) of batch 40 did not effect the expected increase in density at the low end (54 through 60%) of the green density range.

(c) Summary

From the precipitation temperature range (35 to 55°C) investigated, a unique precipitation temperature was selected for each of the two thoria powders produced for the LWBR program. The precipitation temperature selected was based on two criteria: (1) the precipitated thorium oxalate hexahydrate had to be compatible with the subsequent oxalate salt processing steps; and (2) the resulting thoria powders had to be compatible with either the thoria pellet process or the binary (ThO_2-UO_2) pellet process. The precipitation temperature was set at 43 ± 2°C for the powder made for the thoria pellet process while the precipitation temperture was set at 45 ± 2°C for the powder made for the binary pellet process.

Precipitation temperatures below 36°C produced a nonfilterable thorium oxalate precipitate. The thorium oxalate cake when removed from the plate-and-frame filter press was wet and not readily transferable. In addition, the powder physical character was subject to change during calcining through the mechanism of redissolution and recrystallization of the original crystallites. Precipitation temperatures above 53°C resulted in a powder that was too inactive to be compatible with the two pellet processes.

The free nitric acid content was fixed at 1.1 ± .1N; this level of free acid was compatible with the above selected precipitation temperature. The sensitivity of the crystallite size to free acid change emphasized the importance of closely controlling the free acid concentration in the thorium nitrate solution. Therefore, the free nitric acid addition was controlled to ± 0.1N.

B. Calcination of Thorium Oxalate Hexahydrate

Calcination of the thorium oxalate to ThO_2 powder sets the powder characteristics, which in turn control the powder fabricability and sinterability. The focus of this phase of the development program was to identify the calcine temperature range over which thoria powders suitable for the two pellet processes could be made.

1. Background

Previous investigators (References 3, 4, and 5) reported an increase in the average crystallite size with increasing calcine temperature over a range of 400 to 1300°C based on X-ray broadening measurement techniques. Similar changes in crystallite size were measured in electron micrographs in the work of Warren and Elyard (Reference 6).

Electron microscope (TEM and SEM) studies reported in References 4, 5, and 6 show that the thoria particle retained a shape similar to that of the thorium oxalate particle precursor. Warren and Elyard reported a decrease in average particle size (10 to 4 microns) with increasing calcining temperature (500 to 1100°C), from evaluation of electron micrographs (Reference 6). In contrast, Kinoshita, et al and Allred, et al reported no change in average particle size with increasing calcine temperature (References 4 and 5). All investigators, however, were in agreement that the surface area of the powder decreased with increasing calcine temperature. The change in powder character with increasing temperature was interpreted by the investigators to indicate that a sintering process was taking place between the crystallites that make up the particles. This resulted in a decrease in the surface area.

A similar behavior in the change of thoria powder character with increasing time at a given calcine temperature was reported by Warren and Elyard in Reference 6. However, the increase in crystallite size and reduction in powder surface area occurred at a slower rate than that observed for increasing calcine temperature.

2. Experimental Procedure

Two thorium oxalate batches (41 and 44) were prepared to the parameters identified in Table II. During the precipitation of the 2 batches the free nitric acid level and precipitation temperature were 2.0N and 36-37°C for batch 41 and 1.15N and 43-44°C for batch 44. The thorium oxalate cake from each precipitation batch was divided into thirds for calcining at different temperatures: a) one third designated as "A" was calcined at 900°C, b) one third designated as "B" was calcined at 969°C, and c) one third designated as "C" was calcined at 1039°C. Time at temperature was 8 hours. The resulting powders were characterized and evaluated by sinterability tests.

Twenty batches, which evaluated the reproducibility of the oxalate salt process, were prepared according to the process parameters identified in Table II. The precipitation conditions of free nitric acid (1.1 ± .1N) and precipitation temperature (43 ± 2°C) were equivalent to precipitation conditions for the above batch 44. The 20 thorium oxalate hexahydrate batches (Nos. 46 thru 65) were calcined at 941 ± 17°C. As the precipitation conditions are equivalent to these for batch No. 44, the physical character data in terms of average values are included as part of the results and discussion below.

3. Results and Discussion

(a) Calcining Temperature

Calcine temperature influenced the physical character of the thoria powder. Over the temperature range investigated the surface area of thoria powder was reduced by about 43% as the calcine temperature increased from 900 to 1039°C (see Figure 13). The average surface area (7.84 m^2/g) determined from the data for the 20 reproducibility batches agreed with the fitted surface area curve for thoria powders prepared under similar precipitation conditions and calcined at 941 ± 17°C. The decrease in powder surface area reflected the intrasintering of the crystallites within the particle, thereby reducing the intercrystalline porosity. Electron micrographs of powder batch 44, (see Figure 14) show that the powder particles are aggregates of plate-like crystallites and that a rounding of the crystallites developed as the calcined temperature increased from 900 to 1039°C.

As noted earlier, the effect of a higher free nitric acid level (2.0N) was greater than the low precipitation temperature (36°C). Thus, the 2.0N level for batch 41 promoted the growth of the thorium oxalate crystallites to an extent nearly equivalent to the crystallites of batch 44, which was precipitated at 44°C with a free nitric acid level of 1.1N. The resulting surface areas, at a given calcine temperature, differ by only 1 m^2/g.

The average particle size(1) showed a slight increase with increasing calcine temperature (see Figure 15). The average particle size for batch 41 reached a maximum at about 969°C and then decreased. This decrease in average particle size suggested that a change in the particle surface morphology occurred. The surface was becoming smoother as suggested by the electron micrographs (see Figure 14). The bulk density of the powders remained relatively constant with increasing calcine temperature (see Figure 15).

The sinterability data in terms of the relationship between the green density, sintered density, and surface area are shown in Figures 7-C and 7-D. The increasing calcine temperature reduced the powder surface area and thereby affected sinterability of the powder. In general, the sintered density of the pellets increased with increasing green density for each of the powder batches, items 8 thru 13 of Table IV.

Note: (1) The measurement of average particle size with the Fisher Sub-sieve is marginal with fine powders; the analyzer is a simplified air permeameter designed for coarse particle measurement.

Powder batches 44A and 44B, with surface areas of 9.82 and 5.89 m^2/gm, respectively, exceeded the minimum average sintered density of 95.5% over a 10% green density range, Figure 7-D; however, the grain structure development was marginal. Grain size ranged from finer than ASTM 13 to ASTM 5.5. Batch 44C with a surface area of 5.71 m^2/gm exceeded the minimum average density over a 6% green density range. Grain size and granule segregation were marginal. The change in pellet microstructure with decreasing surface areas is shown in Figures 16, 17, and 18 for powder batch 44. A similar behavior was observed for powder batches 41A, 41B, and 41C, Figure 7-C.

The propensity for black coring of the pellet interior was observed in pellets made from the powder (batch 44A), Figure 16. Powder batch 44A in terms of its as calcined surface area (9.82 m^2/gm) plus the increase in surface area (approximately 1.7 m^2/gm) through micronizing was the most active powder. In contrast, powder batches 44B and 44C with lower as-calcined surface areas were less active powders, and therefore had less tendency for black coring.

The highly active powder sinters more rapidly than the lower active powder. This results in densification of the pellet surface with sealing of the surface pores before the residual carbon can be eliminated by the hydrogen atmosphere. The entrapped carbon, unable to escape during sintering, either forms a black core (Figure 16) or in the form of a gas bloats the pellet interior.

The tendencies for pellet black coring and pellet bloating were minimized through control of the powder activity. As shown in Figure 13, increasing the calcine temperature reduced the powder activity, and thereby reduced the rate of densification of the pellet surface and consequently black coring and bloating. The twenty powder batches (46 thru 65) prepared to evaluate the reproducibility of the oxalate salt process were calcined at 941 ± 17°C which was an intermediate temperature between 900° (batch 41A and 44A) and 969°C (batch 41B and 44B). As noted earlier, the average surface area of 7.84 m^2/gm for the twenty batches agreed well with the fitted surface area curve (Figure 13). Evaluation of test pellets fabricated from these powders revealed that the problem of pellet black coring and bloating was not completely eliminated for the thoria pellet process.

The pellet black coring and bloating problem in thoria pellets was eliminated by: (1) controlling the sintering parameters, i.e., furnace atmosphere, and heating rate, and (2) powder activity. The furnace atmosphere was changed to wet from dry hydrogen; and the heating rate limited to 115°C/hr maximum. The powder activity was further deadened by increasing the nominal calcine temperature to 983°C from 941°C. On the basis of the best fit surface area vs calcine temperature curve for batch 44 presented in Figure 13, the surface area of 6.3 m^2/gm was predicted for the calcine temperature of 983°C. The average surface area for the 124 production powder lots was 6.9 m^2/gm which was within 10% of the predicted value of 6.3 m^2/gm.

However, the reduction in powder activity to reduce the problem of pellet coring and bloating had the concomitant effect of reducing the sintered density of the thoria pellets and uniform grain structure development throughout the pellet. The relationships between sintered density and calcine temperature, is illustrated in Figure 19. For a constant green density of 58%, the as-sintered density decreased with increasing calcine temperature; the sintered density for batch 41 was equal to or below the minimum average sintered density of 95.5%. Also, with increasing calcine temperature a degradation in the pellet microstructure was observed, items 8 through 12 of Table IV. For example, the granule segregation deteriorated and the grain structure was extremely fine, less than ASTM 13 (4 microns).

By increasing the green density from 58 to 62%, the density curve was shifted upward; now all of the average sintered values were greater than the 95.5% limit. Grain structure showed a slight improvement but was still considered marginal. To compensate for the reduced powder activity, calcium was added as a densification aid and the sintering temperature was increased to promote uniform grain growth as discussed in the following section.

The nominal calcine temperature of 1039°C was established for the thoria powder used in the binary pellet process. The physical properties of the resulting powder produced acceptable binary fuel meeting the high density and uniform grain structure requirements.

(b) Summary

The powder characteristics and sinterability were controlled by the calcine temperature. The character of the thoria powder changed rapidly with small changes in calcine temperature. This rapid change in powder character illustrated the importance of closely controlling the calcine temperature. Powder surface area, and consequently the sinterability of the powder, decreased with increasing calcine temperature. A highly sinterable powder led to black coring or bloating of the pellet interior. An optimum calcine temperature was selected to meet the criterion that the powder should be sufficiently active to produce the desired density and microstructure throughout the pellet without leading to coring or bloating.

C. Densification and Grain Growth Development

As was described in the previous sections both the density and grain structure were marginally acceptable. Sintered density was acceptable at green densities above 60% of theoretical density but the high frequency of cracked pellets and evidence of bloating in the microstructure made higher green densities unacceptable for pellet production. Below a green density of 60%, the as-sintered density was 1% TD below the density requirements and the grain structure was unacceptable.

The grain structure had two major failings; it was either discontinuous or nonuniform grain growth. The former structure occurs when some small fraction of the grains grow to a large size consuming the uniform grain size matrix. The latter structure occurs when the grains at the periphery of the pellet (to a depth of 50 to 100 mils) grow uniformly while the interior of the pellet has a very fine grain size (<ASTM 13 (4 microns)) as illustrated by thoria batch 35 (see item 2, of Table IV). The results of kinetic studies reported by Smid (Reference 11) demonstrated that the grain growth characteristics of the pellet surface were normal and controlled by uninhibited grain boundary surface tension forces and that the grain growth characteristics of the pellet interior were nonuniform as a result of the presence of an impurity acting as a grain growth inhibitor. The trace impurities which inhibited continuous grain growth at the pellet interior were removed by vaporization at the pellet exterior. The investigation on the kinetics of grain growth in ThO_2-base sintered compacts is reported in Reference 11.

The coprecipitation of calcium oxalate with thorium oxalate was investigated to ascertain if low levels (<150 ppm) of calcium could be successfully added as a densification aid. During calcination the calcium oxalate decomposed into calcia (CaO).

1. Background

Investigators reported in Reference 12 that the dry blending of from 0.5 to 3.0 w/o calcia into thoria powder increased the sintered density up to 96.5% from 80.2% for thoria without the calcia addition. These investigators suggested that the increase in sintering rate was due to the rapid diffusion of Ca^{2+}, Th^{4+}, and O^{2-} through the vacancy structure which was created by the substitution of the divalent calcium ion for the quadrivalent thorium.

Jorgensen and Schmidt (Reference 13) suggested that the addition of calcia allows the sintering of thoria to proceed to theoretical density by inhibiting discontinuous grain growth and permitting a high diffusion flux of vacancies from pores to the grain boundaries. Discontinuous grain growth is inhibited when the solid solubility limit (2.0 mol % for CaO in ThO_2) is exceeded and the second phase particles segregate to the grain boundary. The calcia particles reduce the rate of grain boundary migration by exerting a drag on the grain boundary motion. However, for the low levels of CaO (210 ppm) added to the thoria, Smid (Reference 11) postulated that CaO would not result in significant grain boundary drag and would therefore have no detectable influence on grain boundary migration. However, he did propose a mechanism whereby these small levels of CaO could possibly promote densification through accelerated diffusions resulting from defect structures formed at the grain boundary.

Calcia was selected as a sintering aid because of its relatively low neutron absorption cross-section of calcium. The level of calcium was limited to $\leq$ 150 ppm ($\leq$ 210 ppm CaO) to minimize neutron absorption in the core.

2. Experimental Procedure

The amount of CaO added to the thoria was specified in terms of Ca. Three powder batches 37, 38, and 39 were prepared with levels of 50, 100, and 150 ppm of Ca which was co-precipitated as calcium oxalate with the thorium oxalate. For these batches the free nitric acid content and precipitation temperature were 1.15 ± .02N and 41-42°C, respectively, Table II. The thorium oxalate was calcined at 900°C for 8 hours. The resulting powders were evaluaed for physical characteristics, and sinterability.

3. Results and Discussion

(a) Calcia As a Densification Aid

Coprecipitation of calcium oxalate with thorium oxalate did not change the powder character. Comparison of non-calcia thoria powder batches 35 and 36 with the calcia bearing batches 37 thru 39, Table IV, showed that the surface area of the powders were within the range of 9.8 to 10.8 m^2/gm average particle sizes were within the range of 1.4 to 1.6 microns; and bulk densities were within the range of 1.38 ± .05 gm/cc.

From the 1675°C sinterability tests, the increasing levels of CaO in terms of Ca from 50 to 150 ppm improved the densification of the powder (see Figure 7-E) and items 14, 15, and 16 of Table IV). From a green density of 56 thru 64%, the as sintered densities of powder batches 38 and 39 were nearly equivalent. Comparison of the 1675°C sinterability test curves, Figure 7-F for thoria powder without calcia (batch 35) with thoria powder with calcia (batch 38) illustrated the improvement in sintered density.

(b) Grain Growth Development

Examination of the microstructures (Figures 20, 21, and 22) suggested that there was an improvement in grain structure especially at the low end of the green density range as a result of the improved densification. The black or white core observed in the microstructures pressed at 62 and 64% of theoretical density suggested that gases such as CO and CO_2 were entrapped as the consequence of incomplete binder removal, and retarded the grain growth as noted by a reduction in grain size.

Uniform grain growth throughout the pellet was achieved by increasing the sintering temperature to 1725°C from 1675°C. The effect of the 1725°C sintering temperature is illustrated by batch 38 (see Figure 23 and item 17 of Table IV). Over the entire 10% green density range the grain structure was uniform with no discontinuous grain growth. In contrast, non-uniform grain structure was observed in the pellets from powder batch 38 sintered at 1675°C (item 15 of Table IV).

During thoria pellet production the grain structure was continually improved by systematically increasing the sintering temperature to 1750°C and finally to 1790°C. The improvement in grain structure suggested that the higher sintering temperature enhanced the diffusion rate of impurities that had previously inhibited uniform grain growth (Reference 11) and that the higher sintering temperature provided more energy for grain growth.

(c) Summary

The addition of small quantities (<210 ppm) of calcia by coprecipitation enhanced the densification of the thoria pellets. The calcia addition did not affect the powder physical characteristics. The increase in sintering temperature to 1790°C from 1675°C produced the desired increase in grain size and uniformity desired for the LWBR core.

D. Impurities

Conversion of thorium nitrate solution into ThO_2 powder by the oxalate salt process did not contaminate the finished product. Each batch was sampled and analyzed for impurities. Representative analyses are listed in Table V for the various process parameter conditions. Neither the range of precipitation temperatures (35 through 53°C) evaluated nor the coprecipitation of calcium affected the purity of the thoria. The increase in boron level (from ≤ 1 to > 3.0 ppm) correlated with the increase in calcine temperature from 900 to 1039°C. Limit for boron was 1.0 ppm.

An intensive investigation showed that the increase in boron level came from the Inconel calcine boats. Analysis of thorium oxalate prior to calcination revealed the boron content to be less than 0.2 ppm. Analysis of thoria powder after calcining revealed boron levels of 2.4 to < 10 ppm. This supported the hypothesis that boron contamination occurred in the calcine step. In addition, boron uptake appeared to correlate with the increase in corrosion product (Fe, Ni, and Cr) pickup. The interaction of the acidic thorium oxalate cake with the Inconel plus the calcine temperature of 1039°C resulted in an increase in corrosion product. With repeated cycling of the Inconel boats through the furnace and boron level was reduced below the specification level of 1 ppm. Also, the cleaning of Inconel boats by ThO_2 grit blasting removed the undesirable corrosion product.

III. THORIUM OXALATE SALT PRODUCTION PROCESS

Selection of the thorium oxalate salt process parameters was predicated on the resulting thoria powder being compatible with the given LWBR pellet process. As a result of the need to have the powder characteristics of the thoria and urania powders similar and the pellet process differences (degree of powder comminution), the powder properties required to achieve the same high density and uniform grain structure were different. The optimum calcined surface areas for the thoria pellet process and the binary pellet process were 6 ± 2 m^2/gm and 4.5 ± 1.5 m^2/gm, respectively. The key thorium oxalate salt process parameters were defined as follows:

Process Parameter	Thoria Pellet Process	Binary (ThO_2-UO_2) Pellet Process
Free Nitric Acid	1.1 ± .1N	1.1 ± .1N
Precipitation Temperature	43 ± 2°C	45 ± 2°C
Calcine Temperature	983 ± 17°C (1800 ± 30°F)	1039 ± 17°C (1900 ± 30°F)

The entire production process parameters are summarized in Table VI.

As a remedial method of improving the sintering rate of thoria pellets, calcia was added to the thoria by coprecipitation as calcium oxalate. The quantity of calcium added was 125 ± 25 ppm. Calcia was not required as a densification aid for thoria prepared for the binary (UO_2-ThO_2) pellet process.

The process delineated in Table VI was employed throughout powder production to manufacture powder for thoria pellets. The tolerances placed on the parameters were small to minimize variability in powder character and fabricability.

The maximum filter press pump pressure was increased to 150 psig from 125 psig to reduce the frequency of the wet cakes condition described earlier in the report and observed in early production. Approximately 8% of the earlier thorium oxalate cakes were wet. The rate of wet cakes was reduced to less than 0.5% following the increase in the maximum filter press pump pressure.

Production of thoria powder was maintained at a rate of 1360 to 2050 kilograms per week. The powder was blended into lots of 800 ± 25 kilograms, and each lot was evaluated and certified as meeting the chemical and physical property requirements of the powder specification, Tables V and VII, respectively.

Powder characteristics for powder production are summarized in Table VII. The data demonstrated that the powder process parameters were both properly defined and controlled throughout production. The powder characteristics of the 2 types of powder met the Total Order Quantity (TOQ) statistical requirements, with the exception of 95/99 upper limits for bulk density and average particle size for the first 62 lots of binary ThO_2 powder. The bulk density deviation of 1.62 versus 1.60 gm/cc and average particle size deviation of 2.38 versus 2.30 were insignificant and did not affect pellet manufacturing.

IV. SUMMARY OF RESULTS

Through a series of experimental batches the oxalate salt process parameters for converting thorium nitrate solution into thoria powder were investigated to determine the relation between the process parameters and the physical character of the powder. The results of these experiments revealed that small changes in precipitation temperature (Figure 4), free nitric acid (Figure 11), and calcine temperature (Figure 13) altered the physical character of the powder. The data demonstrated the importance of controlling the selected process parameters to tight tolerances. The specific lessons learned in the development effort are summarized as follows:

a. Free nitric acid influenced the precipitated crystallite size and size distribution. As the free nitric acid content of the thorium nitrate solution increased, an environment resulted that enhanced the growth of thorium oxalate crystallites. Therefore, the free Nitric acid content of the thorium nitrate solution was controlled to ± 0.1N.

b. Precipitation temperature affects both the particle size and particle size distribution of the precipitated thorium oxalate. When the particle size is too fine, the thorium oxalate cannot be readily filtered pressed. The wet soupy thorium oxalate cake is difficult to handle and has the potential to undergo particle size change by recrystallization early in the calcine cycle. A coarse particle size precipitate can result in an inactive powder. The development effort demonstrated that with increasing precipitation temperature, the particle size increased. The precipitation temperature selected was based on two criteria: (1) the precipitated thorium oxalate had to be compatible with the subsequent oxalate salt processing steps; and (2) the resulting thoria powders had to be compatible with either the thoria pellet process or the binary (ThO_2-UO_2) pellet process.

c. Addition of small quantities (< 210 ppm) of calcia by coprecipitation improved the densification of thoria pellets during sintering. Crack free pellets prepared from thoria powder without the calcia addition sintered to densities that were 1% TD below the 96.5% limit. Sintered pellet densities of 98.1% TD were achieved using thoria powder with calcia addition. The physical properties of thoria powder were not altered by the calcia addition.

d. Early development thorium oxalate hexahydrate cakes removed from the plate-and-frame filter press were found to be soupy and consequently difficult to transfer to either transfer containers or Inconel calcine boats. In addition, both the powder characteristics and powder sinterability were potentially uncontrollable through the mechanism of redissolution of the original crystallites followed by recrystallization during the early stages of calcining.

Application of various precipitation temperatures ranging from 35 to 44°C failed to eliminate the wet and soupy cake condition. The problem was resolved by replacing the filter press pump. The new pump had the capability of delivering a discharge pressure of approximately 180 psig in contrast to the replaced pump's discharge pressure of 45 psig.

Pumping the slurry into the press at the higher pump pressures (125 to 180 psig) resulted in uniform packing of the press. The uniform structure of the thorium oxalate particles was undisturbed by the dewatering air pressure and thereby permitted the slurry to be dewatered to a dry cake.

The dry cake was more suitable for in process handling and eliminated the potential for uncontrolled dissolution and recrystallization of the thorium oxalate crystallites during the early stages of calcination.

e. Calcining was done in two stages: (1) low temperature stage and (2) high temperature stage. The low temperature stage converted the thorium oxalate hexahydrate into ThO_2 powder and the high temperature stage established the physical properties of the powder.

The decomposition of the thorium oxalate during the low temperature stage reduced the volume of the cake by approximately 30 to 50%. Following the low temperature calcine stage, the powder from two calcine boats was combined into one calcine boat. However, incomplete conversion of the thorium oxalate to ThO_2 powder results in a bulky cake which is difficult to consolidate from two boats into one boat.

Three methods of obtaining complete decomposition of the thorium oxalate were considered; these were the following:

1) Reducing the bed depth of the thorium oxalate in the calcine boat from 6 inches to approximately 3 to 4 inches.

2) Stirring of the thorium oxalate during calcining.

3) Alter the temperature profile of the low temperature calcine furnace.

The first two items were impractical to implement as the methods resulted in a reduction in production rate.

To optimize the low temperature clacining temperature profile, thorium oxalate material was processed through the furnace under the conditions summarized below:

Test	Furnace	Furnace Control Temperature Settings			Thorium Oxalate
No.	Stoking Speed	Zone 1	Zone 2	Zone 3 and 4	Time Above 300°C
1	2 ft./hr.	540°C	700°C	700°C	3 hrs. minimum
2	2	540	540	700	1 hr.
3	4	540	700	700	0

A thermocouple buried in the thorium oxalate cake measured the temperature of the cake as it proceeded through the furnace.

Thorium oxalate starts to decompose into ThO_2 powder at 300°C. The temperature profile defined by test No. 1, as noted above, resulted in the thorium oxalate cake being above 300°C for a minimum of 3 hours. This provided the conditions for decomposition of the thorium oxalate into ThO_2 powder. During powder production, the temperature profile of the low temperature furnace was controlled to the conditions of test 1.

Final powder physical properties were established during the high temperature stage. Control of the as-received thoria powder surface area and particle size is important to ensure proper micronization in terms of surface area increase and mixing of UO_2 and ThO_2 powders in order to sinter to densities greater than 96.5% blend average, to achieve grain growth during sintering and to ensure a satisfactory homogenization of urania mixed with the thoria. The calcine temperature was controlled to a temperature tolerance of ± 30°F (± 17°C) to achieve a powder of consistent physical properties.

The process parameters were established to produce two different thoria powders; each powder was designed to be compatible with one of the two pellet manufacturing processes. The free acid was 1.1 ± .1N for the two powder processes. The precipitation temperature was 43 ± 2°C for powder made for the thoria pellet process while the precipitation temperature was 45 ± 2°C for powder made for the binary pellet process. The calcine temperatures were 983 ± 17°C for thoria pellet process powder and 1039 ± 17°C for binary pellet process powder.

With the understanding of how to alter the physical character of the thoria powder through control of the oxalate salt process parameters, a thoria powder was produced to be compatible with the developed pellet fabrication processes. A sinterability test program was performed to evaluate the various powder batches for producing thoria pellets of high density, high quality, and uniform grain size. The flow diagram of this test program is shown in Figure 1. Sinterability test program test pellets were compacted to a size of 0.896 in. diameter and .890 in. length. This size pellet was selected as it was considered to be the most difficult pellet to make with respect to handling the pellet in the green state and achieving a high density pellet with uniform grain size in contrast to the blanket and seed size pellets.

Many of the process development problems are summaried above. The problems of contamination of the powder either by the starting materials or by the process have not been discussed. The lessons learned in resolving the powder contamination are summarized as follows:

a. To minimize contamination of the ThO_2 powder from starting materials, specification requirements were imposed on the vendor supplying the materials such as oxalic acid crystals. The chemistry requirements for oxalic acid crystals were as follows:

1.	$H_2C_2O\ 2H_2O$ (oxalic acid)	99.5% min.
2.	Ca	125 ppm max.
3.	Sulfate	1000 ppm max.
4.	Individual Cations	80 ppm max.
5.	Total Impurities	1000 ppm max.

a. During the first production period (1970 - 1973) the sulfate level in the oxalic acid crystals was within the specification requirements. The sulfate limit was relaxed to 1500 ppm to accommodate schedular considerations in the second production period (1974-1975).

Metallographic evaluation of sintered pellets made from ThO_2 powder precipitated from oxalic acid of high sulfate levels (1000-1500 ppm) revealed second phase at the grain boundaries. Scanning electron microscope examination identified the presence of transition metal sulfides. The transition metal sulfides second phase was not observed in pellets produced from ThO_2 powders precipitated from oxalic acid with sulfate levels of $\leq$ 1000 ppm.

Oxalic acid with sulfate levels exceeding 1000 ppm was not permitted to be used in the precipitation step of the process.

b. Thorium oxalate cake periodically was observed to exhibit yellow discoloration. The yellow discoloration of the cake was attributed to iron contamination of both the oxalic acid solution and deionized water.

Stainless steel corrosion product resulting from the interaction of the oxalic acid with the stainless steel storage tanks was the source of the high iron levels in the acid solution. The iron level in the acid solution was controlled by maintaining the temperature of the acid solution below 140°F and discarding the acid solution if the Fe level exceeded 500 ppm.

Iron contamination of deionized water was visually identifiable by a discoloration of the water. Process controls were established to ensure that water from the deionizers was free of discoloration before being placed in storage tanks. These controls were the following:

1. Maintaining a flow of water through the piping leading to the deionizers at all times.
2. Examination of this flow of water (item 1.) above, for color periodically.
3. Starting a flow of water from the deionizers and examining this flow for color before diverting the flow to storage tanks.
4. Verifying and taging the water in the storage tanks as free of color prior to use.
5. Changing the in-line filters after preparation of each batch of oxalic acid solution.

c. Foreign black particles observed in both the thorium oxalate precipitate and the thoria powder were considered as a possible cause of blowholes observed on the surface of thoria pellets and binary pellets. To eliminate these unacceptable foreign particles the following actions were performed:

1. The graphite packing in the packing gland on the precipitation tank agitator was replaced with a nylon bushing.

2. Three old plug cocks in the heel (residue thorium oxalate slurry) were replaced with teflon lined stainless steel plug cocks.

3. The existing stem packing in the needle valve controlling the flow of oxalic acid solution was replaced with teflon packing.

d. Increasing the calcine temperature to 1039°C from 983°C resulted in a contamination of the powder with nickel. The level of nickel increased from typically 10 to 25 ppm to levels of 40 to 90 ppm versus the specification limit of 50 ppm.

Source of the nickel contamination was traced to Inconel corrosion product found in the thoria powder following the high temperature calcining. The interaction of the acidic thorium oxalate with the calcine boat during calcining promoted the spalling of the Inconel boat into the powder.

Thoria grit blasting of the interior and exterior Inconel boats after each calcine run effectively removed nearly all of the Inconel corrosion scale. In addition, the specification limit for nickel was raised to 100 ppm from 50 ppm for binary thoria powder. The level of nickel contamination was reduced to acceptable levels.

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TABLE I

IMPURITY REQUIREMENTS FOR THORIUM NITRATE SOLUTION

Impurity	Specification Limit
Al	50 ppm
B	1
Ca	40
Cl + Br	10
Co	10
Cr	35
Cu	10
F	10
Fe	75
Hg	10
Mg	25
Mn	5
Mo	25
Ni	50
Si	50
P	150
Ti	10
U	20
V	5
Rare Earths	
Dy	1.6
Eu	.71
Gd	3.1
Sm	2.4

TABLE II
PROCESS CONVERSION PARAMETERS

Batch No.	27	28	29	30	31	32	34	35	36
Thorium Nitrate Sol'n.									
Concentration (gm/l)	196	200	200	199	198	198	196	193	198
Free Acid (N)	1.09	1.12	1.13	1.14	1.13	1.10	1.49	1.13	1.15
Ca Addition (ppm) (ppm added/ppm analyzed)	None	None	None	None	None	None	None	None	None
Oxalic Acid Sol'n.									
Concentration (w/o)	20.13	20.8	20.5	20.5	20.6	20.6	20.74	20.24	20.40
Temperature (°C)	62	57	57	57	57	57	56	58	58
Precipitation									
Temperature (°C) Actual	43-44	39-40	38-39	35-38	35-36	38-39	38-39	41-42	41-42
Addition Rate (Gal./Min.)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.4
Digestion Time (Min.)	15	15	15	15	15	15	15	16	15
Filtration									
Filter Feed Pump Press (psig)	45	45	45	45	45	45	175	175	175
Wash Time (Min.)	90	90	90	95	136	93	154	114	110
Air Time (Min.)	125	125	125	125	125	130	128	125	125
pH Wash Water	4.2	3.4	3.6	3.2	3.0	3.3	3.2	3.2	3.2
Cake Condition	Wet	Wet	Wet	Wet	Wet	Wet	Dry	Dry	Dry
Calcining									
Max. Temperature (°C)	900	900	900	900	900	900	900	900	900
Time (Hours)	8	8	8	8	8	8	8	8	8

TABLE II (continued)
PROCESS CONVERSION PARAMETERS

Batch No.	37	38	39	40	41	42	43	44	Reproducibility Phrase 46 thru 65
Concentration (gm/l)	198	198	200	198	198	198	195	198	199 ± 3
Free Acid (N)	1.14	1.17	1.15	1.17	2.0	1.1	1.06	1.15	1.07 to 1.18
Ca Addition (ppm)	50/61	100/120	150/170	None	None	None	None	None	125 ± 25
Oxalic Acid Sol'n.									
Concentration (w/o)	20.30	20.35	20.42	20.40	20.36	20.40	20.30	20.32	20.35
Temperature (°C)	58	57	58	58	58	57	58	57	57
Precipitation									
Temperature (°C) Actual	41	42	42	36	36-37	43-48	53	43-44	42 to 45
Addition Rate (Gal./Min.)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5 ± 1
Digestion Time (Min.)	15	17	17	17	15	17	21	16	15
Filtration									
Filter Feed Pump Press (psig)	175	175	175	175	175	175	175	175	125 to 180
Wash Time (Min.)	100	215	170	153	94	100	98	328	90 to 186
Air Time (Min.)	125	125	130	125	125	126	125	130	125 to 130
pH Wash Water	3.3	3.1	3.1	3.15	3.1	3.3	3.3	3.4	3.2 ± .2
Cake Condition	Dry	Dry	Dry	Wet	Dry	Dry	Dry	Dry	Dry
Calcining									
Max. Temperature (°C)	900	900	900	900	A-900 B-969 C-1039	900	900	A-900 B-969 C-1039	941 ± 17
Time Hours	8	8	8	8	8	8	8	8	

TABLE III
THORIA POWDER CHARACTERISTICS - NLO DEVELOPMENT PROGRAM

Batch No.	27	28	29	30	31	32	34	35
Avg. Particle Size (microns)	1.63	1.54	1.16	1.10	.75	1.14	1.44	1.59
Surface Area (m^2/gm)	9.26	11.19	12.25	12.26	11.92	11.50	8.34	9.78
Bulk Density (gm/cc)	1.42	1.39	1.24	1.24	1.05	1.25	1.59	1.36

Batch No.	36	37	38	39	40	41A	41B	41C	42
Avg. Particle Size (microns)	1.50	1.47	1.42	1.58	1.00	1.97	3.48	3.09	1.99
Surface Area (m^2/gm)	10.07	10.77	10.10	10.49	13.79	9.10	6.35	4.94	9.04
Bulk Density (gm/cc)	1.34	1.38	1.43	1.42	1.26	1.88	1.89	1.92	1.46

					Reproducibility Phase 46 thru 65	
Batch No.	43	44A	44B	44C	Average	Range
Avg. Particle Size (microns)	2.08	1.69	1.52	2.31	1.53	1.08 to 1.78
Surface Area (m^2/gm)	7.51	9.82	5.89	5.71	7.84	6.60 to 8.89
Bulk Density (gm/cc)	1.53	1.40	1.44	1.58	1.45	1.32 to 1.52

TABLE IV
SINTERABILITY TESTS: EVALUATION OF ThO_2 POWDERS

	ThO_2 Batch No.	Sintering Temp °C	% Green Density	% Sintered Density	Cracks		Granule Segregation	Grain Size (ASTM No.)	
					Internal	External		Edge	Mid Pt. + Center
1	27	1675	54	94.2	3/3	0/7	1-5	N.D.	N.D.
			56	94.3	3/3	0/7	1-5	N.D.	N.D
			58	94.7	3/3	0/7	2-5	12.3	13-N.D.
			60	95.2	3/3	0/7	2-5	N.D.-D	N.D.
			62	96.2	2/3	0/7	2-7	9.7-N.D.	N.D.
2	35	1675	54	95.4	0/3	0/7	1-1	N.D.	N.D
			56	95.6	2/3	0/7	1-2	8.7-N.D.	9.9-N.D.
			58	96.0	0/3	0/7	1-3	N.D.	N.D.
			60	96.9	0/3	0/7	1-2	10.7-N.D.	8.7-N.D.
			62	97.3	2/3	5/7	1-1	9.1	11.1-N.D.
			64	97.8	1/3	5/7	1-1	9.8	10.8-N.D.
3	36	1675	54	95.4	2/3	6/7	1-1	N.D.	N.D.
			56	96.4	1/3	1/7	1-4	N.D.	N.D.
			58	96.5	2/3	0/7	1-2	N.D.	N.D.
			60	97.1	1/3	0/7	1-1	10.4-N.D.	N.D.
			62	98.3	0/3	0/7	1-1	9.9-N.D.	10.5-N.D.
			64	98.9	0/3	0/7	1-2	9.9	9.9-N.D.

N.D. - Grain Structure not discernible at a magnification of 250X.

D - Discernible grain structure that is finer than ASTM 13.

* - The ratio (a/b) refers to the number of metallographic samples (a) rejected out of the number of metallographic samples (b) inspected.

TABLE IV (continued)

	ThO_2 Batch No.	Sintering Temp °C	% Green Density	% Sintered Density	Cracks		Granule Segregation	Grain Size (ASTM No.)	
					Internal	External		Edge	Mid Pt. + Center
4	40	1675	54	94.7	0/3	0/7	1-1	N.D.	N.D.
			56	94.6	0/3	0/7	1-1	N.D.	N.D.
			58	95.7	1/3	7/7	1-1	N.D.	N.D.
			60	97.0	2/3	7/7	1-1	7.0-N.D.	7.0-N.D.
			62	97.5	-	7/7	-	-	-
5	42	1675	54	94.1	0/3	0/7	2-3	N.D.	N.D.
			56	95.1	1/3	0/7	1-2	N.D.	N.D.
			58	95.2	1/3	0/7	1-2	N.D.	N.D.
			60	96.1	3/3	0/7	1-1	12.2-N.D.	N.D.
			62	97.7	0/3	0/7	1-1	8.7	5.3
			64	96.9	0/3	0/7	1-1	8.6	5.4
6	43	1675	54	92.1	0/3	0/7	1-1	N.D.	N.D.
			56	93.4	0/3	0/7	1-1	N.D.	N.D.
			58	94.1	0/3	0/7	1-1	N.D.	N.D.
			60	95.0	0/3	0/7	1-2	N.D.	N.D.
			62	95.7	0/3	0/7	1-2	N.D.	N.D.
			64	96.4	1/3	0/7	1-1	N.D.	N.D.
7	34	1675	54	95.5	0/3	0/7	1-2	N.D.	N.D.
			56	95.3	0/3	0/7	2-2	N.D.	N.D.
			58	96.6	0/3	0/7	1-2	11.0	N.D.
			60	97.6	0/3	0/7	1-2	10.2	9.8
			62	98.9	1/3	0/7	1-1	9.3	9.6
			64	97.8	1/3	3/7	1-1	9/7	9.9-N.D.
8	41A (Calcine Temp of 900°C	1675	54	93.7	0/3	0/7	1-1	N.D.	N.D.
			56	94.5	0/3	0/7	1-1	N.D.	N.D.
			58	95.5	0/3	0/7	1-1	N.D.	N.D.
			60	96.7	0/3	0/7	1-1	N.D.	D-N.D.
			62	97.9	1/3	0/7	1-1	7.8-N.D.	9.4
			64	98.5	0/3	0/7	1-1	D-N.D.	10.7

TABLE IV (continued)

	ThO$_2$ Batch No.	Sintering Temp °C	% Green Density	% Sintered Density	Cracks		Granule Segregation	Grain Size (ASTM No.)	
					Internal	External		Edge	Mid Pt. + Center
9	41B (Calcine Temp of 969°C)	1675	54	93.3	0/3	0/7	5-7	N.D.	N.D.
			56	95.0	0/3	0/7	1-4	N.D.	N.D.
			58	95.6	0/3	0/7	1-6	N.D.	N.D.
			60	96.7	0/3	0/7	1-4	11.7	11.9
			62	96.5	0/3	1/7	1-3	10.4	11.5
			64	97.7	0/3	0/7	1-3	9.9	11.7
10	41C (Calcine Temp of 1039°C)	1675	54	92.4	0/3	0/5	7-7	N.D.	N.D.
			56	92.8	0/3	1/5	7-7	N.D.	N.D.
			58	94.4	0/3	2/5	2-7	N.D.	N.D.
			60	95.2	1/3	0/5	1-3	10.2-D	10.2-N.D.
			62	96.7	0/3	1/5	2-3	10.5	11.0
			64	97.3	0/3	0/5	1-1	9.9-D	10.6
11	44A (Calcine Temp of 900°C)	1675	54	96.7	0/3	0/7	1-3	D.	D.
			56	96.9	0/3	0/7	1-2	D.	11.9
			58	97.8	0/3	0/7	1-2	11.3-D	5.5
			60	97.8	0/3	2/7	1-2	10.3	6.8
			62	97.6	1/3	4/7	1-2	5.5-D	6.9-D
			64	97.3	1/3	4/7	1-5	6.0-D	6.0-D
12	44B (Calcine Temp of 969°C)	1675	54	95.9	0/3	0/5	1-1	10.5-D	D.
			56	96.4	0/3	0/5	1-1	10.5-D	D.
			58	97.0	0/3	0/5	1-1	9.9-D	10.5-D
			60	98.2	0/3	0/5	1-1	9.6	9.0
			62	98.2	0/3	0/5	1-1	9.5-D.	6.8
			64	97.1	1/3	0/5	1-1	8.2	7.9-D
13	44C (Calcine Temp of 1039°C)	1675	54	93.2	0/3	0/5	2-5	D.	D.
			56	94.8	0/3	0/5	2-7	D.	D.
			58	95.7	0/3	0/5	2-5	D.	D.
			60	96.7	0/3	0/5	1-3	D.	10.7
			62	97.8	1/3	0/5	1-5	9.0-D.	10.3
			64	98.8	0/3	0/5	1-3	9.2	10.1

TABLE IV (continued)

	ThO_2 Batch No.	Sintering Temp °C	% Green Density	% Sintered Density	Cracks		Granule Segregation	Grain Size (ASTM No.)	
					Internal	External		Edge	Mid Pt. + Center
14	37 (Ca-61 ppm)	1675	54	95.1	1/3	0/7	1-2	N.D.	13.5-N.D.
			56	96.0	1/3	0/7	1-5	N.D.	N.D.
			58	95.9	0/3	0/7	1-2	N.D.	12.6-N.D.
			60	98.2	0/3	0/7	1-1	9.2	10.8-N.D.
			62	97.9	0/3	0/7	1-1	5.3	8.2-N.D.
			64	97.8	2/3	6/7	1-2	8.9	11.3-N.D.
15	38 (Ca-120 ppm)	1675	54	95.7	1/3	0/7	1-2	N.D.	10.1
			56	97.1	1/3	0/7	1-3	11.2-N.D.	8.6-N.D.
			58	98.4	0/3	0/7	1-1	10.6-N.D.	7.6
			60	98.5	1/3	0/7	1-1	9.1	6.7
			62	98.4	1/3	2/7	1-1	9.3	7.4
			64	98.4	0/3	4/7	1-2	10.2	9.5
16	39 (Ca-170 ppm	1675	54	97.0	0/3	0/7	1-2	10.1	N.D.
			56	97.4	1/3	0/7	1-1	10.3	12.5-N.D.
			58	98.0	0/3	0/7	1-1	9.8	11.5
			60	98.4	0/3	0/7	1-1	10.1	11.4
			62	98.7	1/3	2/7	1-1	11.0	11.1-N.D.
			64	98.7	2/3	7/7	1-1	9.7	10.7-N.D.
17	38	1725	54	97.4	0/3	0/7	1-2	8.5	7.1
			56	97.7	0/3	0/7	1-3	7.8	6.3
			58	98.0	0/3	0/5	1-1	8.4	6.7
			60	97.9	2/3	0/5	1-1	9.6	7.5
			62	98.5	0/3	0/5	1-1	9.2	8.6
			64	97.7	2/3	4/6	1-1	9.8	10.4

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(1) Samples were too severely cracked for geometric density determination.

TABLE V
REPRESENTATIVE IMPURITY ANALYSES OF DEVELOPMENT POWDER BATCHES

Batch No. Impurity	Maximum Allowable Limit (ppm)		Development Program			
		3C	43	44A	44C	38
Al	100	<1	<1	1	<2	3
B	1	.46	.11	.20	3.04	.32
C	500	389	122	155	111	127
Ca	150	<20	<20	<20	<20	155
Cl + Br	15	<2.0	<2.0	<3.4	<2.0	<2.0
Co	10	<1	<1	<1	<1	<1
Cr	80	7	6	9	15	9
Cu	10	<1	<2	<2	<2	<2
F	20	6.3	4.7	3.7	4.7	5.0
Fe	75	10	<5	9	5	7
Hg	2	<1	<1	<1	<1	<1
Mg	50	<1	<13	<1	<1	<13
Mn	5	<1	<1	<1	<1	<1
Mo	25	<1	<1	<1	<1	<1
N	40	<5	<5	<5	<5	<5
Ni	50	14	11	14	11	12
Si	100	<10	<10	<5	12	<10
Ti	15	<3	<1	<3	<1	<1
U	10	<5	<5	<5	<5	<5
V	10	<1	<1	<1	<1	<1
Dy	1.6	.25	.20	.21	<.20	<.20
Eu	.71	<.10	<.10	<.10	<.10	<.10
Gd	3.1	.20	.28	<.20	<.30	.26
Sm	2.4	1.04	.52	.96	.44	.48
%Th	87.0% min.	87.71	87.75	87.76	87.77	87.71
Comments		Ppt. temp =35-33°C	Ppt. Temp = 53°C	Calcine Temp. = 900°C	Calcine Temp. = 1039°C	Calcine level = 155 ppm

TABLE VI
PRODUCTION THORIUM OXALATE CONVERSION PROCESS PARAMETERS

Process Step	Thoria with Ca Addition
1. Purification of Thorium Nitrate	a. Process parameters described in Reference (7)
2. Preparation of Thorium Nitrate Solution	a. Thorium Concentration: 220 ± 30 gm. Th/liter b. Free HNO_3: 1.1 ± 0.1N c. Batch size: 285 ± 25 lb. Th
3. Addition of Calcium in the Form of Calcium Nitrate Crystals to Thorium Nitrate Solution (Applies to thoria powder with calcium addition).	a. Quantity: 46.8 ± 0.1 gm. calcium nitrate/100 lb. equivalent ThO_2 to yield 125 ± 25 ppm b. Mixing time: Minimum of 5 minutes
4. Preparation of Oxalic Acid Solution	a. Concentration: 20.45 ± 0.60 w/o oxalic acid b. Mixing time: Minimum of 5 minutes c. Temperature: 135 ± 5°F (5 ± 3°C)
5. Precipitation of Thorium Oxalate	a. Temperature of thorium nitrate: 1. Thoria with calcium addition: 110 ± 3°F (43° ± 2°C) 2. Thoria without calcium addition: 113 ± 3°F(45° ± 2°C) b. Temperature of oxalic acid: 135 ± 5°F (57 ± 3°C) c. Spray rate of oxalic acid: 2.5 ± 0.1 gpm d. Quantity: 5 ± 2 w/o excess of the stoichiometric quantity of oxalic acid e. Digestion period: Minimum of 15 minutes at temperature of 110 ± 3°F (43 ± 2°C)
6. Filtration and Drying by Plate-and-Frame Press	a. Pump pressure: 100 to 150 psig b. Filter cloth: Polypropylene felt of 0.070" thick by 25" wide c. Wash cake with deionized H_2O until pH 3.0 and a minimum wash time of 90 minutes using flow rate of 5-12 gpm d. Air dry for a minimum of 120 minutes

TABLE VI (continued)

Process Step	Thoria with Ca Addition
7. Packaging and Shipment	a. Thorium oxalate cake removed from the press and packaged in polyethylene bags (2) inside of 5-gallon steel can or packaged in 5-gallon polyethylene containers. Then the containers are shipped to the vendor (GE) for calcination and blend steps of the process.
8. Air Calcination of Thorium Oxalate to ThO_2 Powder by a 2-stage Thermal Cycle	a. Low temperature stage (1) Bed depth: 6" maximum (2) Temperature: 1300 + 30 -75°F (705 + 16 - 42°C) (3) Atmosphere: Air b. High temperature stage (1) Bed depth: 6" maximum (2) Temperature: a. Thoria with calcium additions: 1800° ± 30°F (983° ± 17°C) b. Thoria without calcium additions: 190° ± 30°F (1039 ± 17°C) (3) Time at temperature: 8 ± 0.25 hr. (4) Atmosphere: Air
9. Blending and Packaging	a. Blend six powder batches in a 20 cu ft stainless steel twin shell blender for 30 ± 5 minutes. Nominal powder lot size of 700 kgs. b. Sample lot for chemistry and physical property characterization. c. Powder (12.5 kg) packaged inside polyethylene bags (2) inside of 3.5 gallon steel can.

TABLE VII
PRODUCTION ThO_2 POWDER CHARACTERISTICS SUMMARY

		Surface Area** (m^2/g)	Maximum Particle Size (microns)	Bulk Density (gm/cc)	Average Particle Size (microns)	Porosity (v/o)
A. ThO_2 Powder with Calcium Addition						
No. of Lots		124	124	124	124	124
Mean		7.435	45.6	1.48	1.78	.776
Standard Deviation		0.459	3.64	0.04	0.14	.005
95/95	LL	6.42	--	1.40	1.47	.77
Limits	UL	8.44	52.5	1.56	2.09	.79
TOQ Spec.Limits		4.0-8.0	≤55	1.2-1.7	1.4-2.3	.60-.80
B. ThO_2 Powder without Calcium Addition						
No. of Lots		62	62	62	62	62
Mean		5.65	34.2	1.51	1.94	.769
Standfard Deviation		.318	1.6	.046	.188	.006
95/95	LL	4.92		1.40	1.51	.753
Limits	UL	6.39	37.4**	1.62	2.38	.785
No. of Lots		23	23	23	23	23
Mean		5.53	34.1	1.46	1.75	.774
Standard Deviation		.244	0.8	0.04	0.14	.004
95/95	LL	4.88		1.32	1.40	.762
Limits	UL	6.19	36.0	1.59	2.10	.787
TOQ Spec. Limits		3.0-6.0	≤36	1.4-1.6	1.4-2.3	.72-.80

* Out of specification condition that was accepted.

** Bias corrected based on overinspection data, for ThO_2 with Ca addition K = 1.075 and for ThO_2 without Ca addition K=1.175.

FIGURE 1

SINTERABILITY TEST FLOW DIAGRAM

RECEIVE ThO_2 POWDER.

1 PASS MICRONIZE
FEED RATE: 150 ±25 GM/MIN.
FEED PRESSURE: 95 ±5 PSI
GRINDING PRESSURE: 50 ±5 PSI

LIQUID/SOLID AGGLOMERATION
1.0 W/O CARBOWAX
OXYLENE MIXING VEHICLE
25 KG. BATCH SIZE

GRANULATE
16 MESH SCREEN

AIR DRY GRANULES
TEMPERATURE: 50 +0 -5°C
TIME: 2 HRS. -0 +15 MIN.

PRESSING LUBRICANT ADDITION
0.2 W/O STEROTEX
BLEND TIME: 10 ±1 MINUTES

PRESSING
COMPACT 4 TO 15 PELLETS AT EACH OF 6 GREEN DENSITY POINTS.
PELLET DIAMETER: .896"

PRETREATMENT
TEMPERATURE: 425 ± 25°C
TIME: 4 ±1 HRS.
ATMOSPHERE: 100 CFH OF CO_2

SINTERING
TEMPERATURE: 1675 ± 25°C FOR DEVELOPMENT BATCHES UNLESS OTHERWISE SPECIFIED AND 1725 ± 25°C FOR REPRODUCIBILITY POWDER
TIME: 12 HRS. MINIMUM
ATMOSPHERE: 150 ±25 CFH DRY H_2

EVALUATION

1. VISUAL EXAMINATION FOR SURFACE CRACKS.
2. GEOMETRIC DENSITY
3. METALLOGRAPHY
   - A. GRANULE SEGREGATION
   - B. GRAIN STRUCTURE
   - C. INTERNAL CRACKS

FIGURE 2
AS-POLISHED METALLOGRAPHIC PELLET CROSS SECTIONS OF GRANULE SEGREGATION

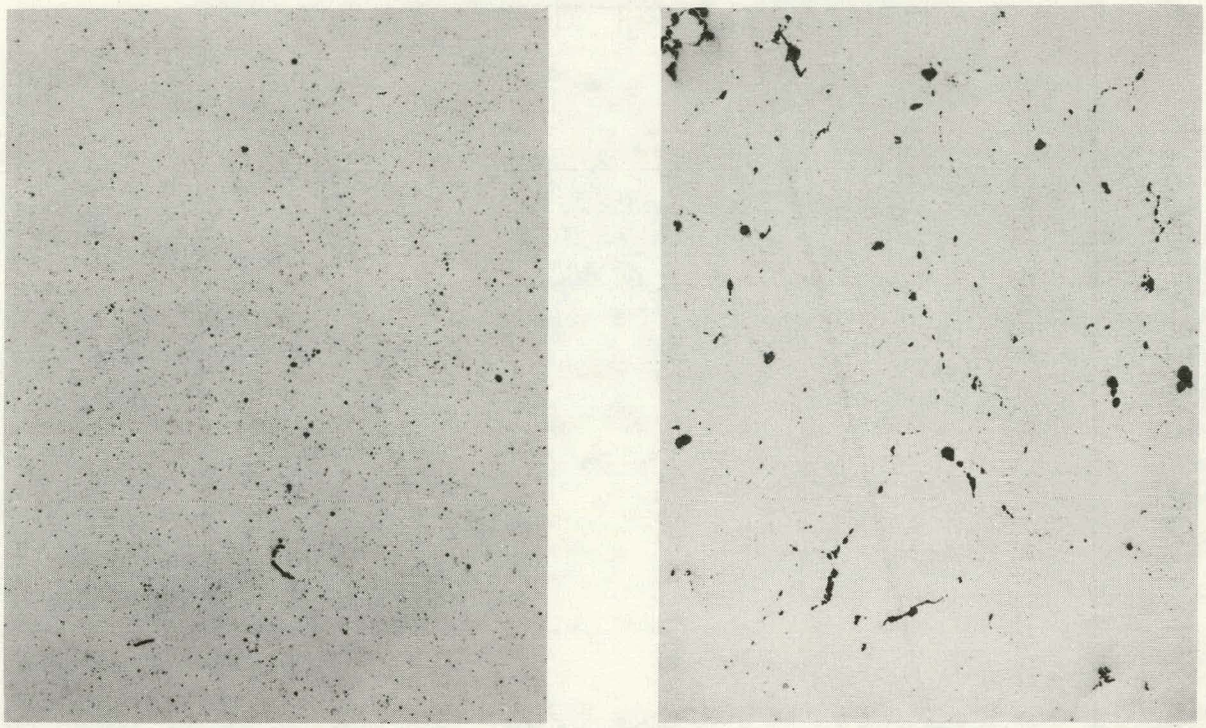


FIG. 2-A ACCEPTABLE GRANULE SEGREGATION-RATING NO. 1 (50X)

FIG. 2-B ACCEPTABLE GRANULE SEGREGATION-RATING NO. 2 (50X)

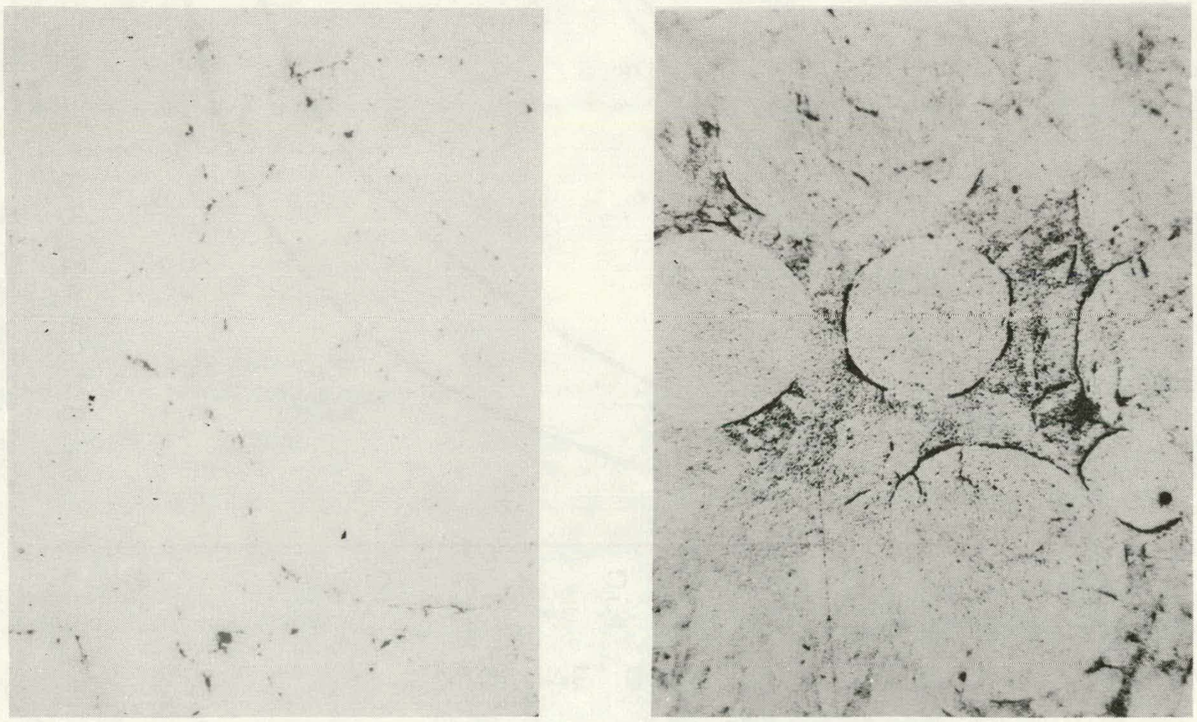


FIG. 2-C ACCEPTABLE GRANULE SEGREGATION-RATING NO. 3 (50X)

FIG. 2-D UNACCEPTABLE GRANULE SEGREGATION-RATING NO. 7 (50X)

FIGURE 3
SETTLING RATE CURVES FOR THORIUM OXALATE BATCHES
PREPARED AT VARIOUS PRECIPITATION TEMPERATURES

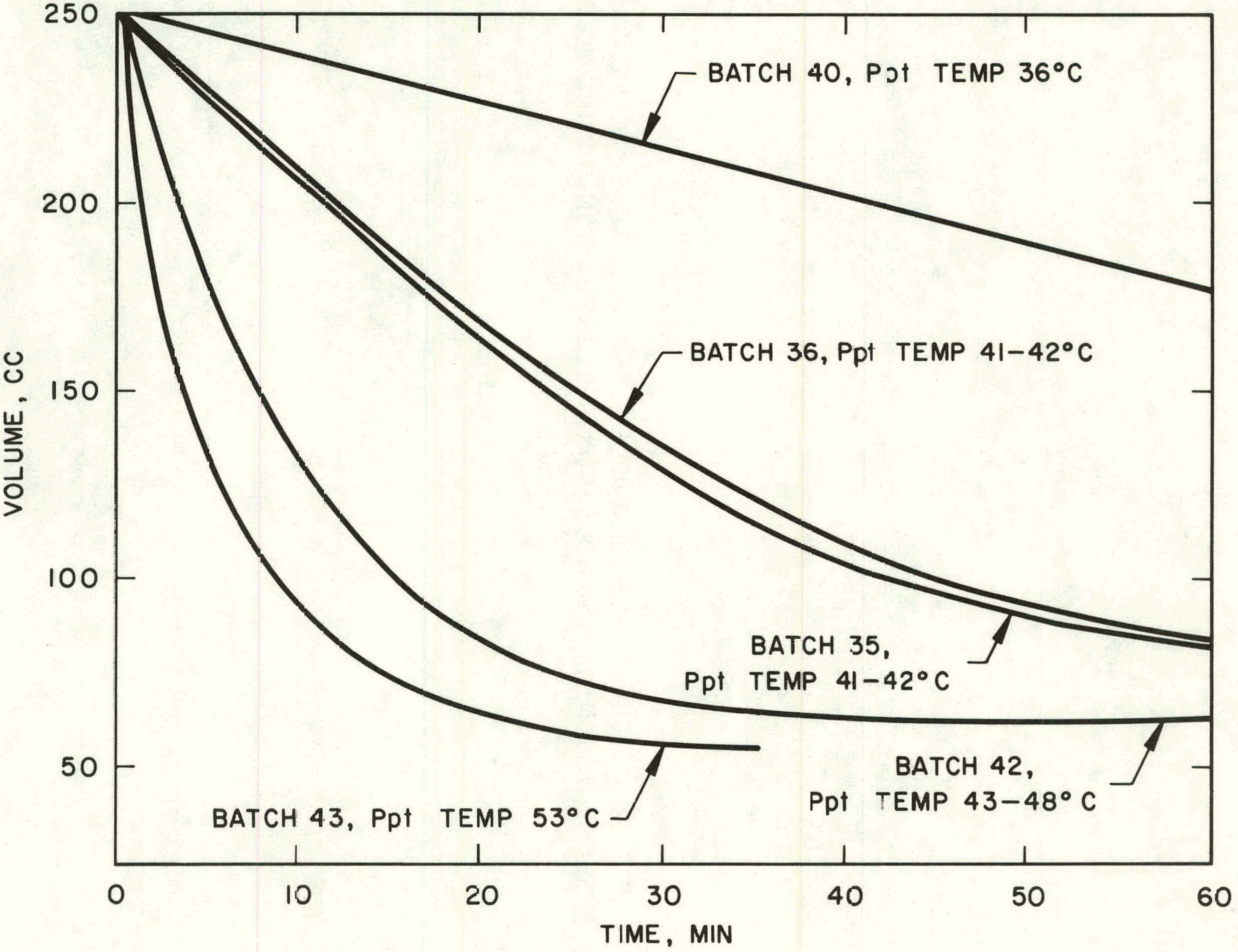


FIGURE 4

SURFACE AREA AS A FUNCTION OF PRECIPITATION TEMPERATURE

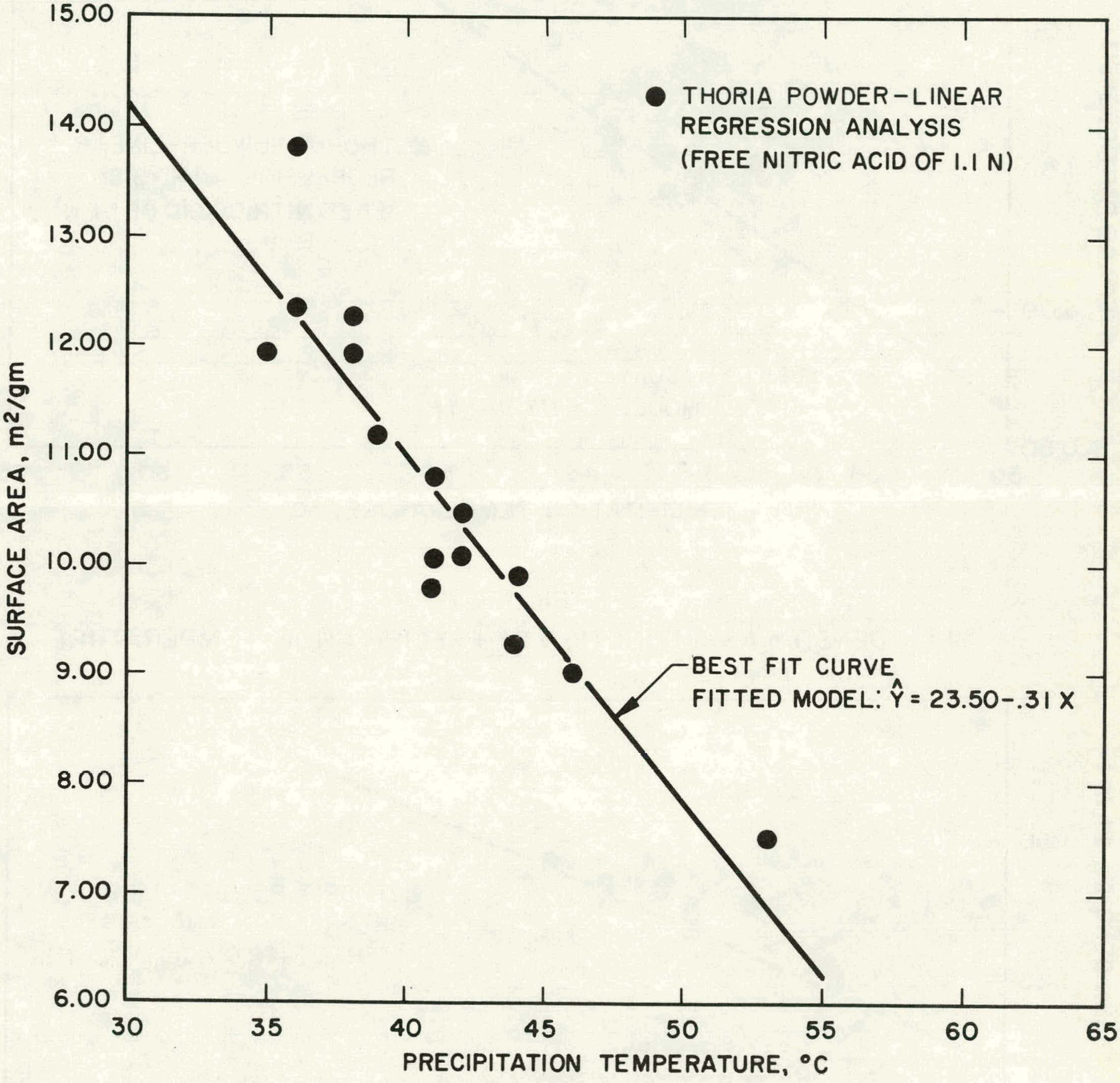


FIGURE 5
AVERAGE PARTICLE SIZE AS A FUNCTION OF PRECIPITATION TEMPERATURE

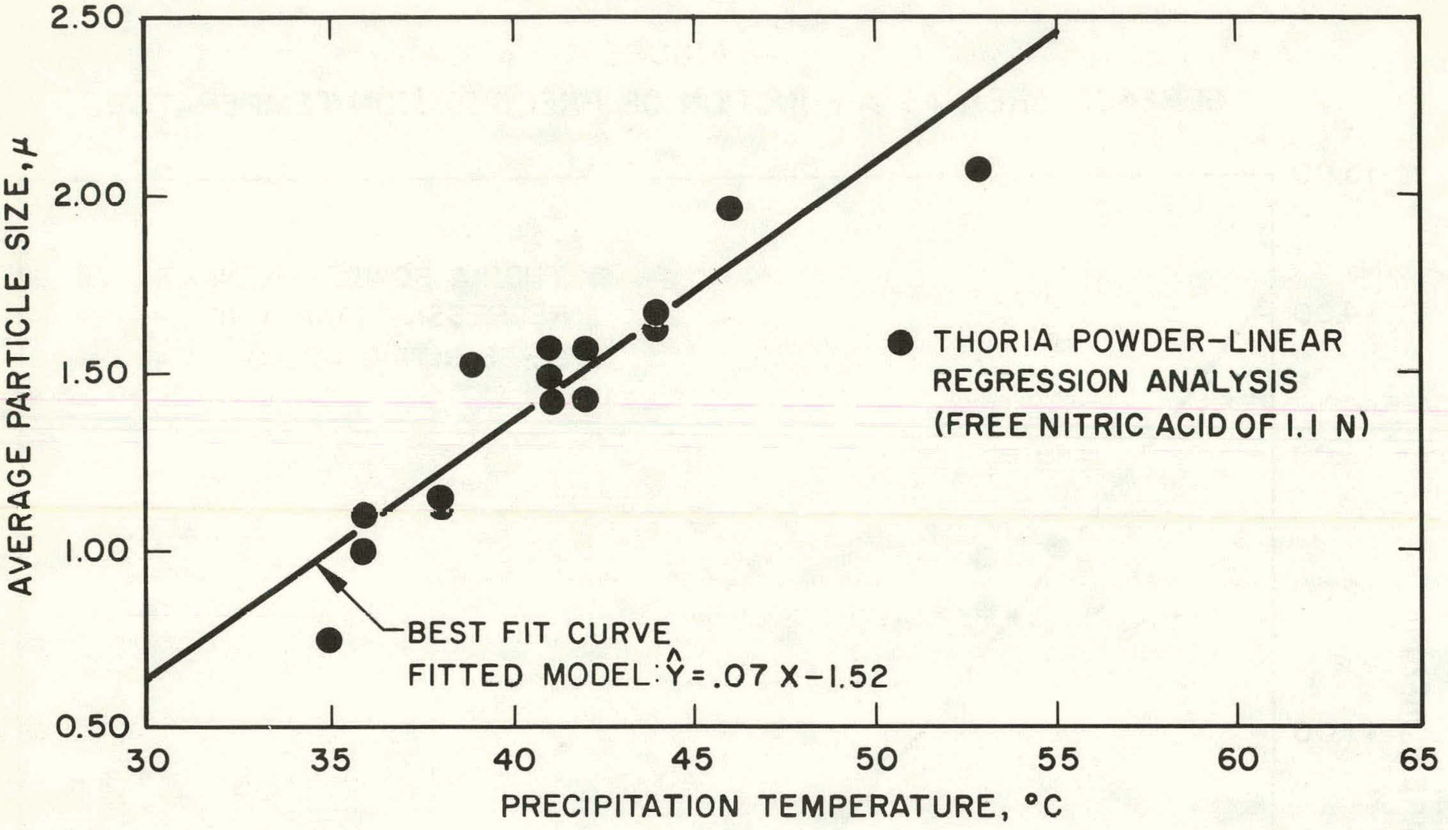


FIGURE 6
BULK DENSITY AS A FUNCTION OF PRECIPITATION TEMPERATURE

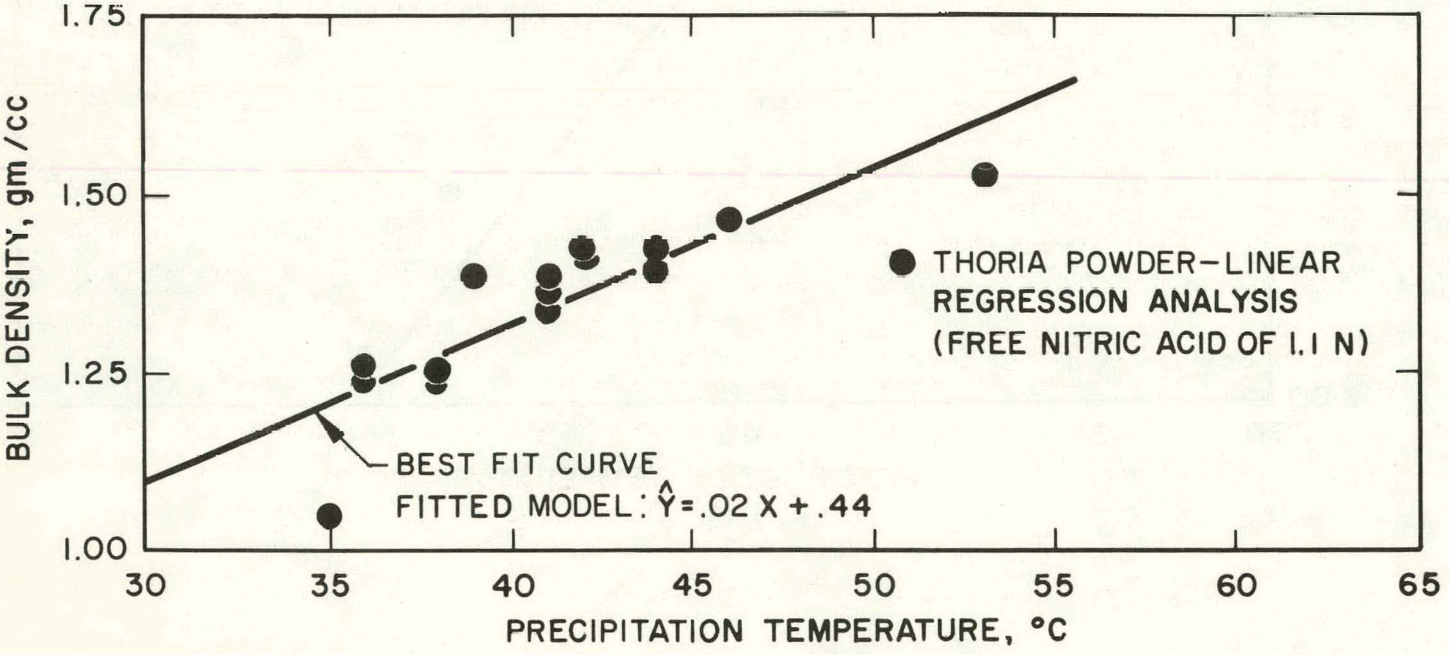


FIGURE 7

SINTERABILITY TEST EVALUATION OF ThO_2 POWDERS

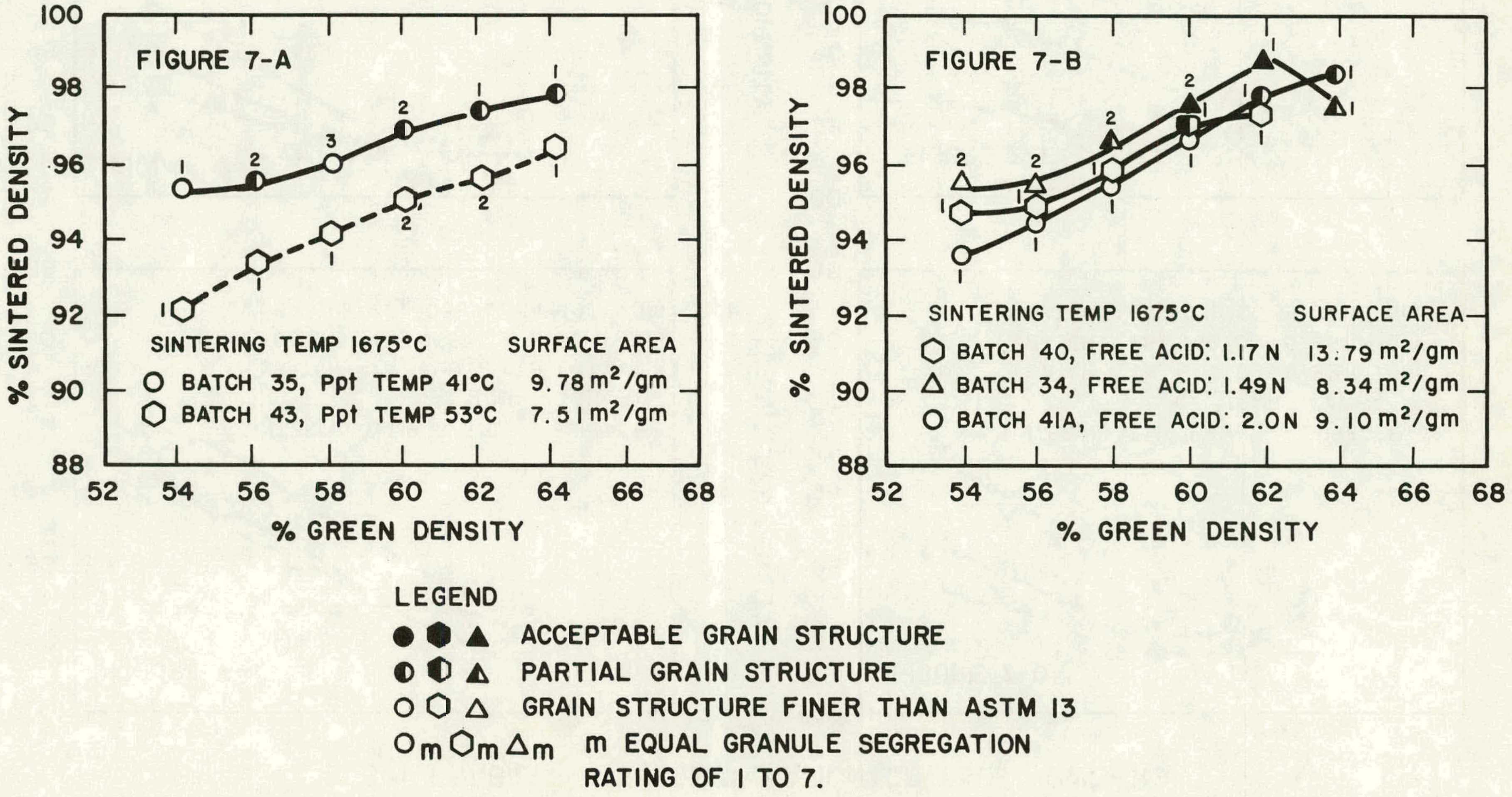


FIGURE 7 (CONT)

SINTERABILITY TEST EVALUATION OF ThO_2 POWDERS

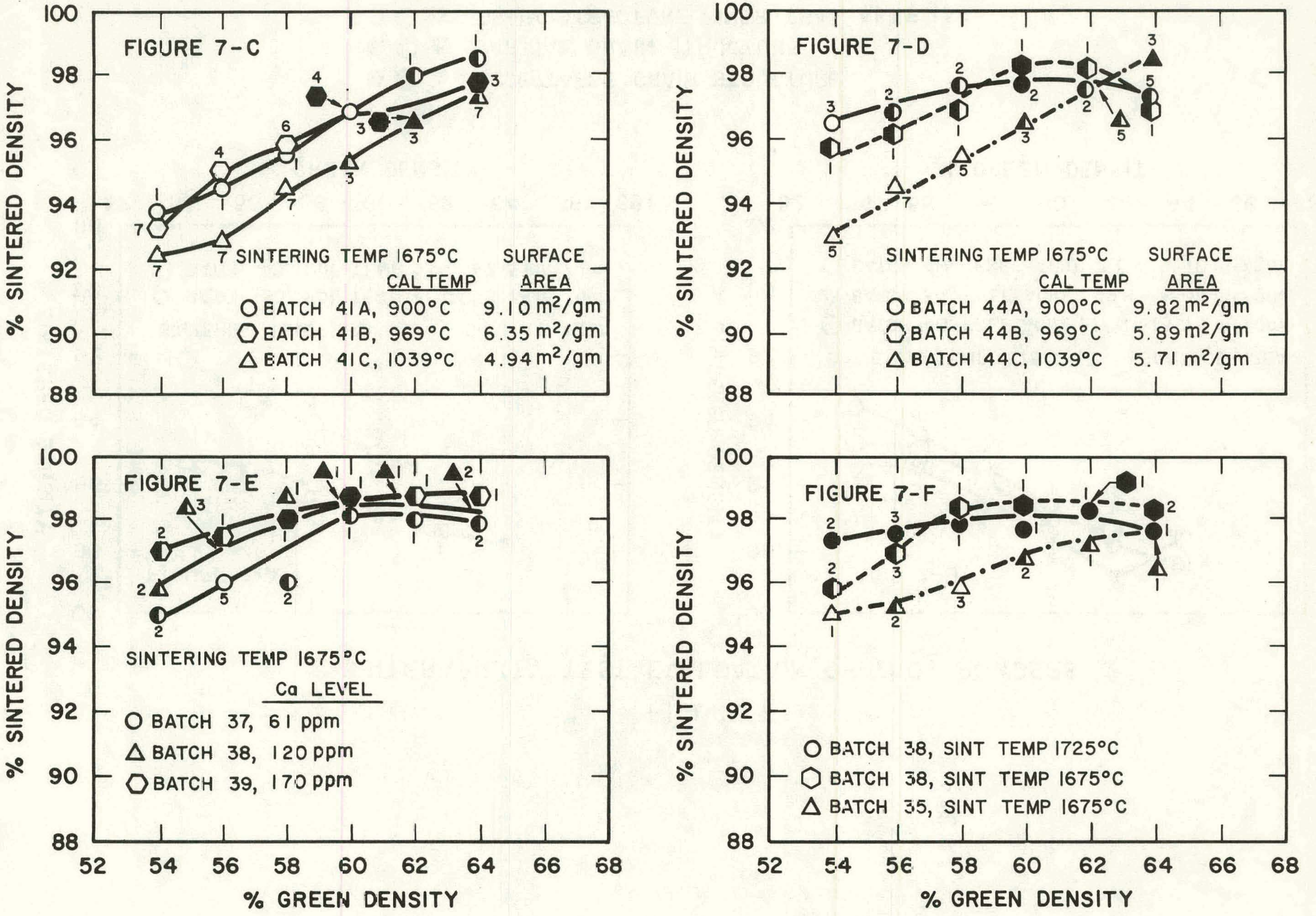
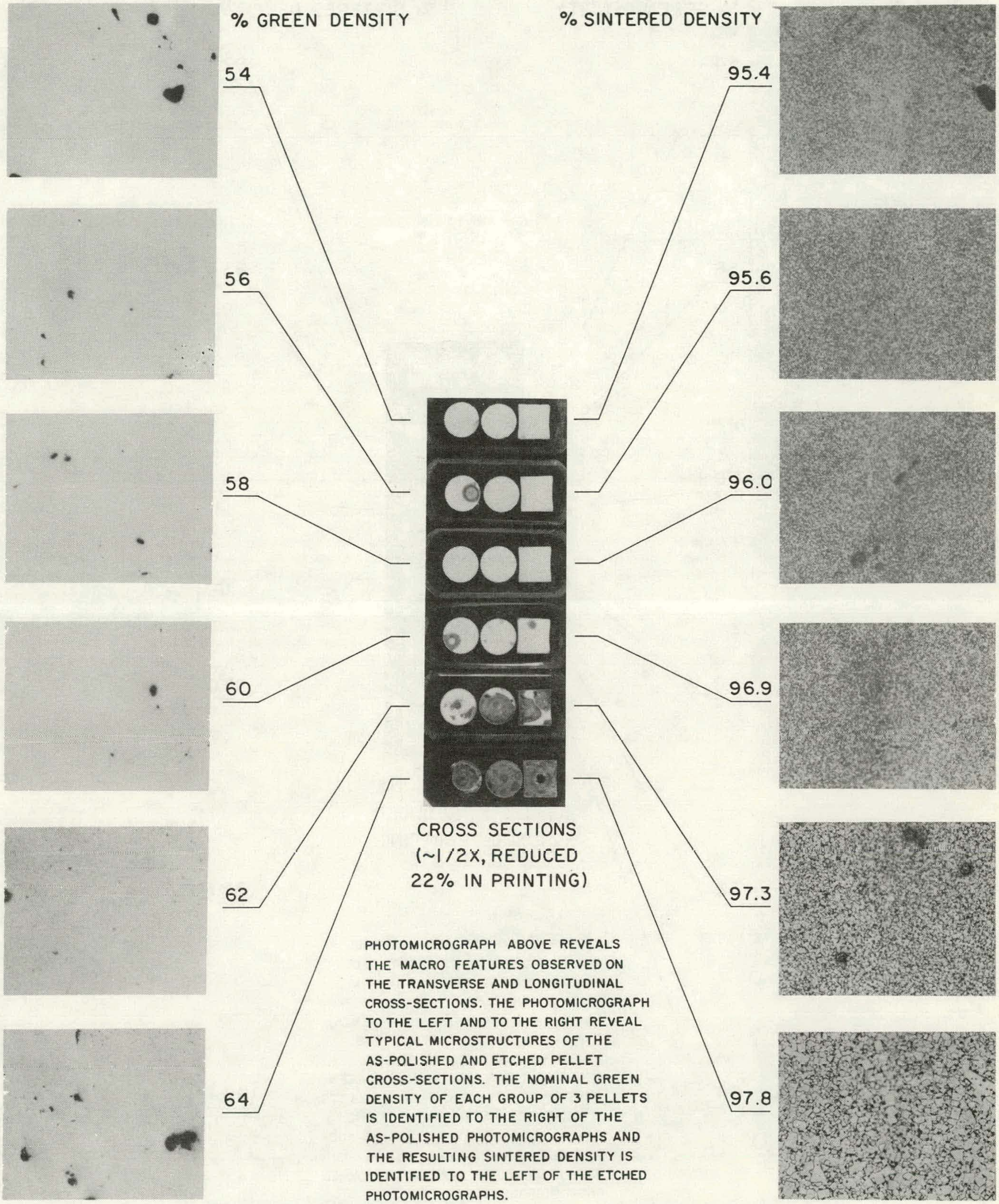


FIGURE 8
PHOTOMICROGRAPHS OF BATCH 35 SINTERABILITY TEST
SAMPLES SINTERED AT 1675 °C



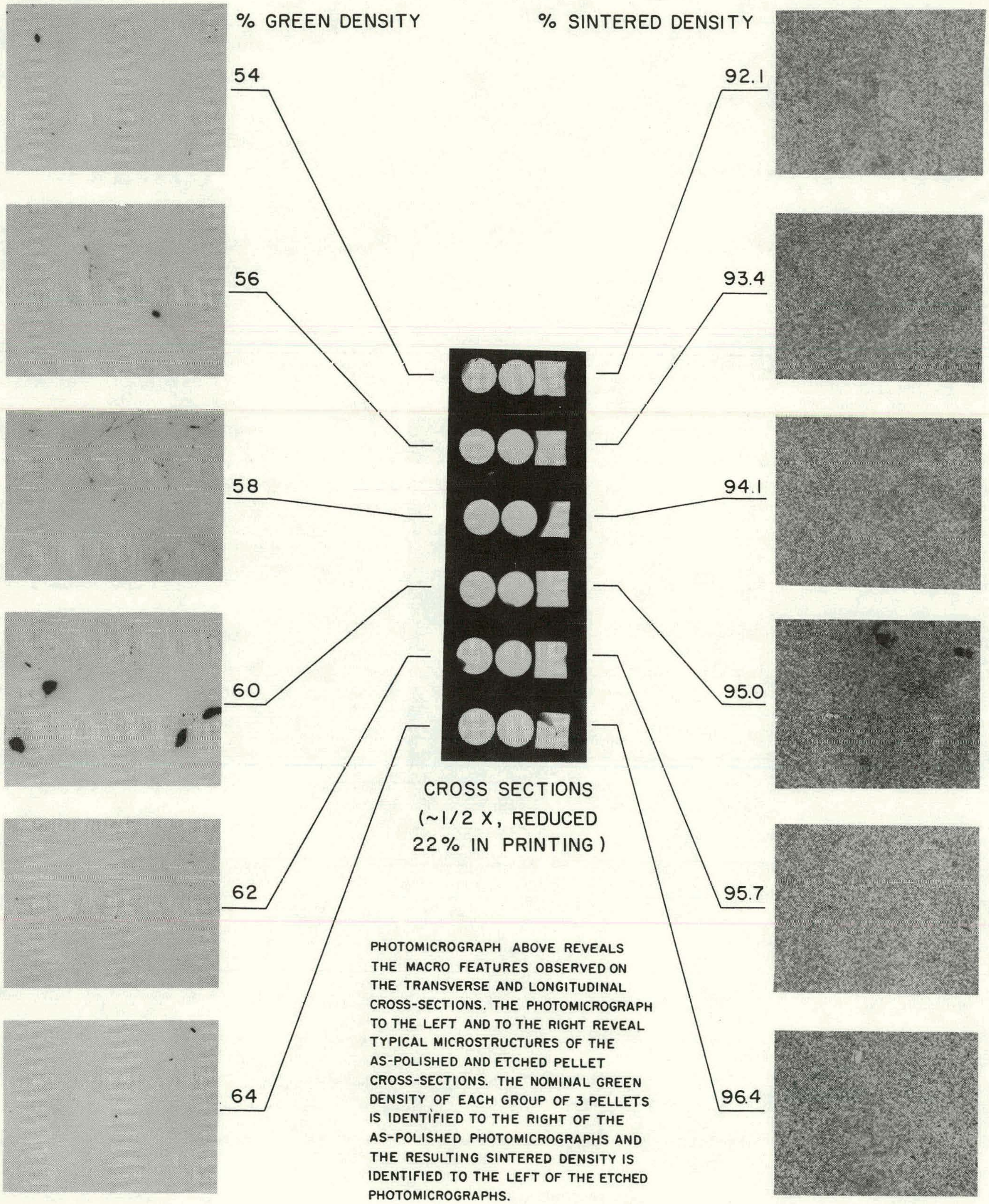
CROSS SECTIONS
(~1/2X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250X, REDUCED
22% IN PRINTING)

FIGURE 9
PHOTOMICROGRAPHS OF BATCH 43 SINTERABILITY TEST SAMPLES SINTERED AT 1675°C



CROSS SECTIONS
(~1/2 X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50 X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250 X, REDUCED
22% IN PRINTING)

FIGURE 10
SETTLING RATE CURVES FOR THORIUM OXALATE BATCHES AS A FUNCTION OF FREE NITRIC ACID

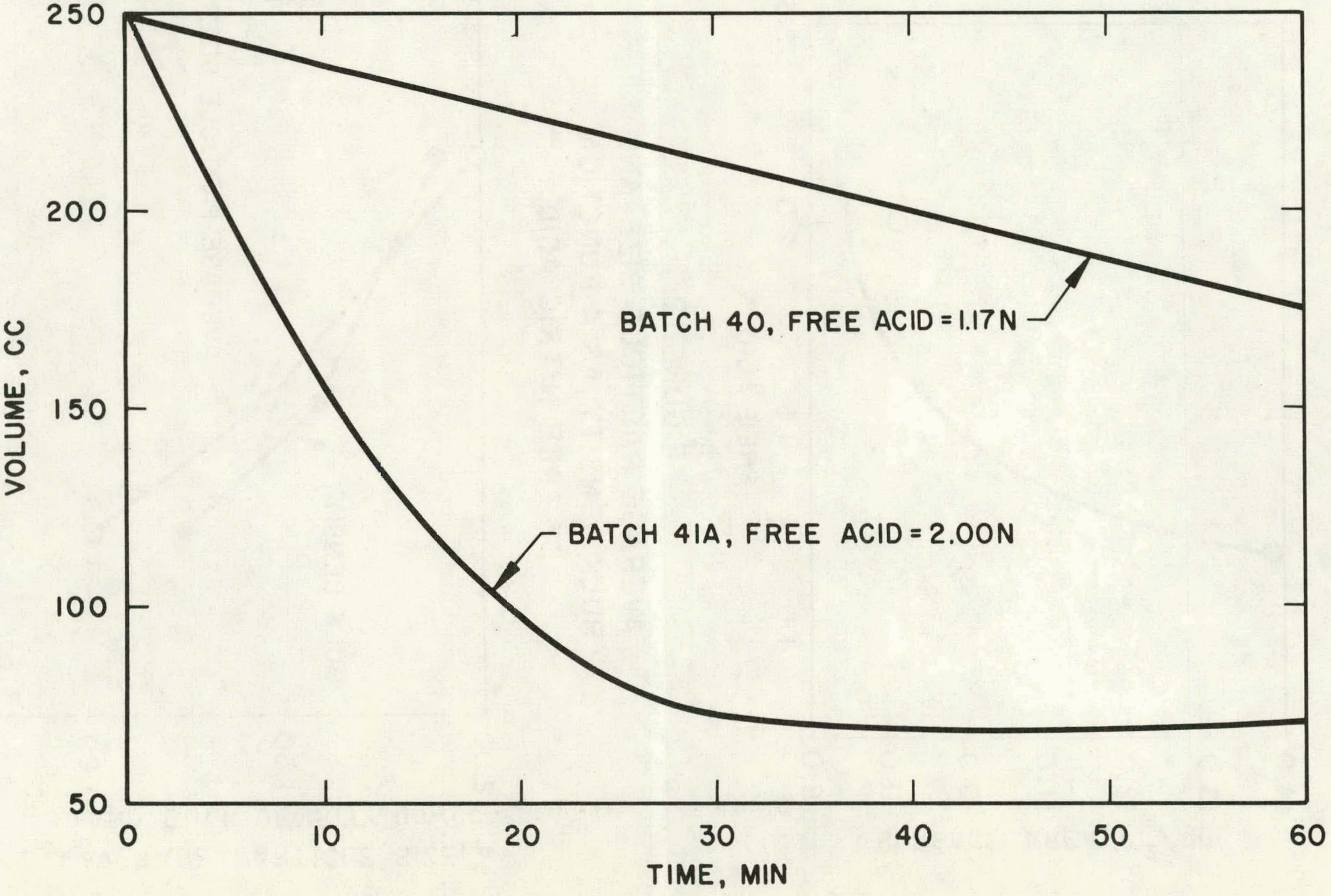


FIGURE 11

SURFACE AREA AS A FUNCTION OF FREE NITRIC ACID

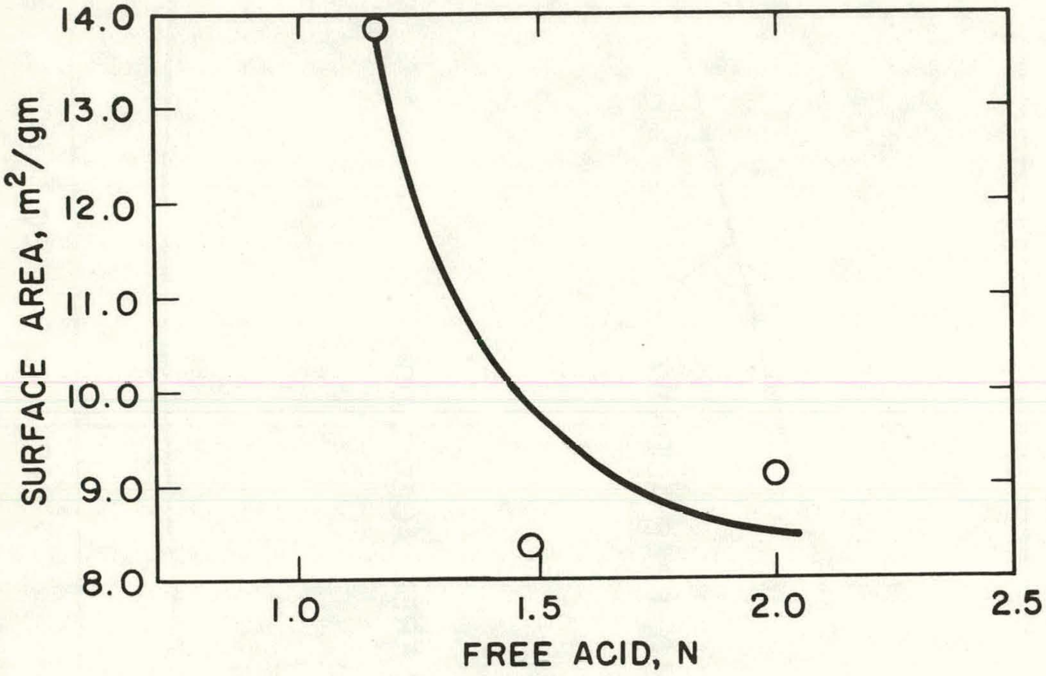


FIGURE 12

AVERAGE PARTICLE SIZE AND BULK DENSITY AS A FUNCTION OF FREE NITRIC ACID

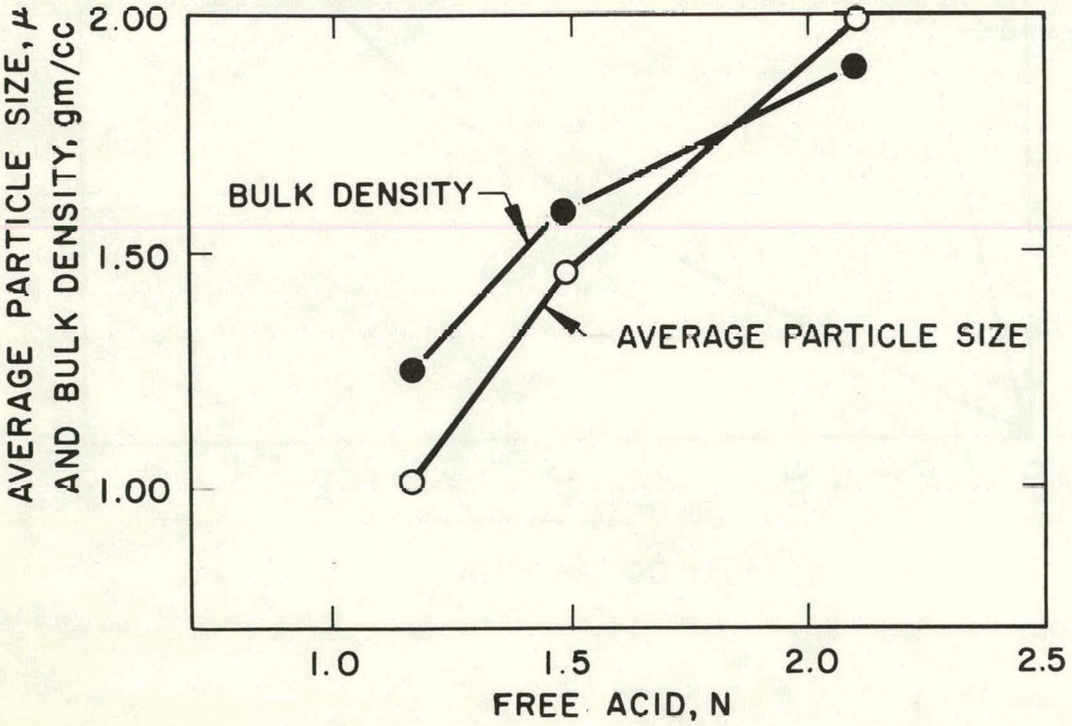


FIGURE 13
SURFACE AREA AS A FUNCTION OF CALCINATION TEMPERATURE

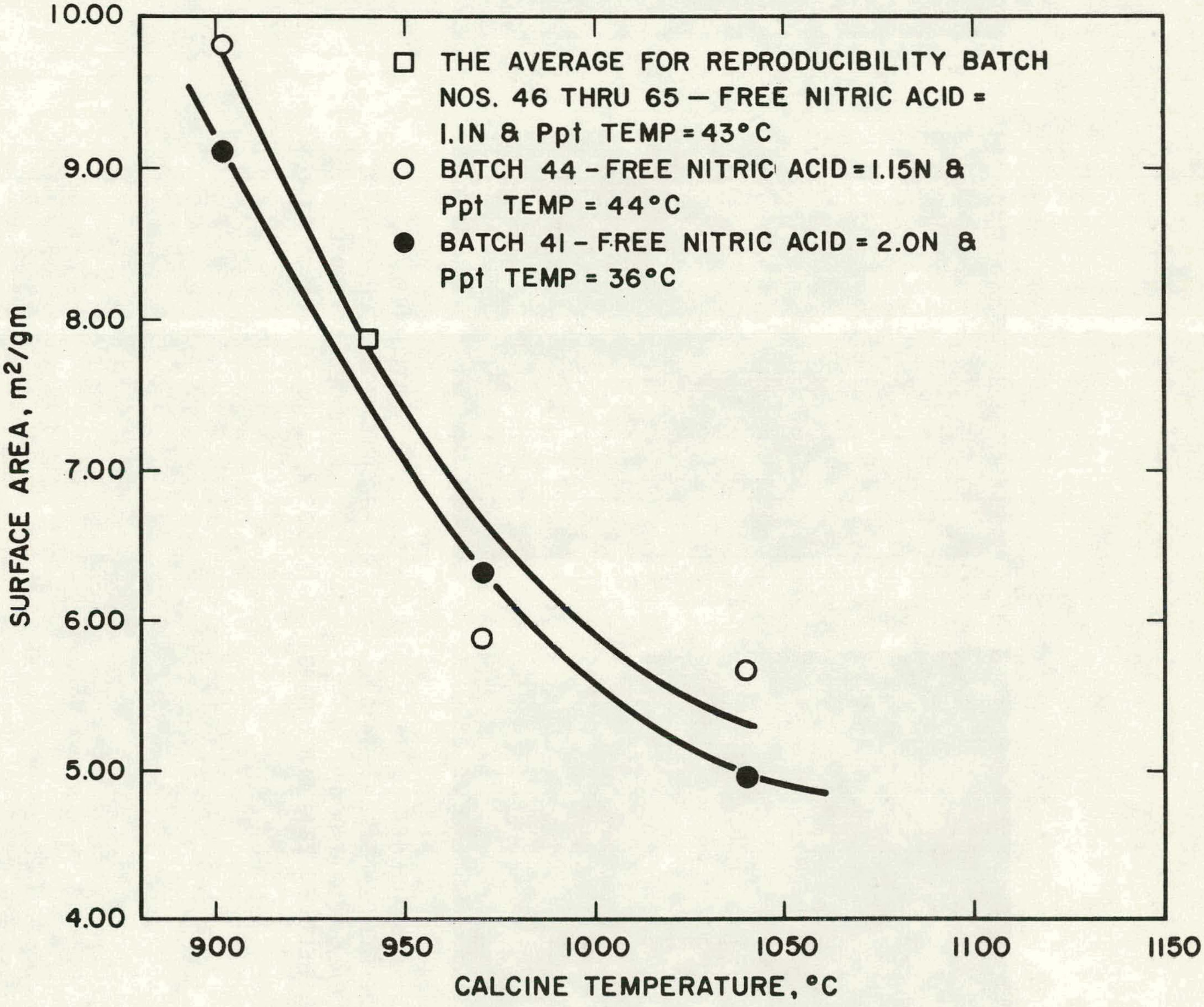
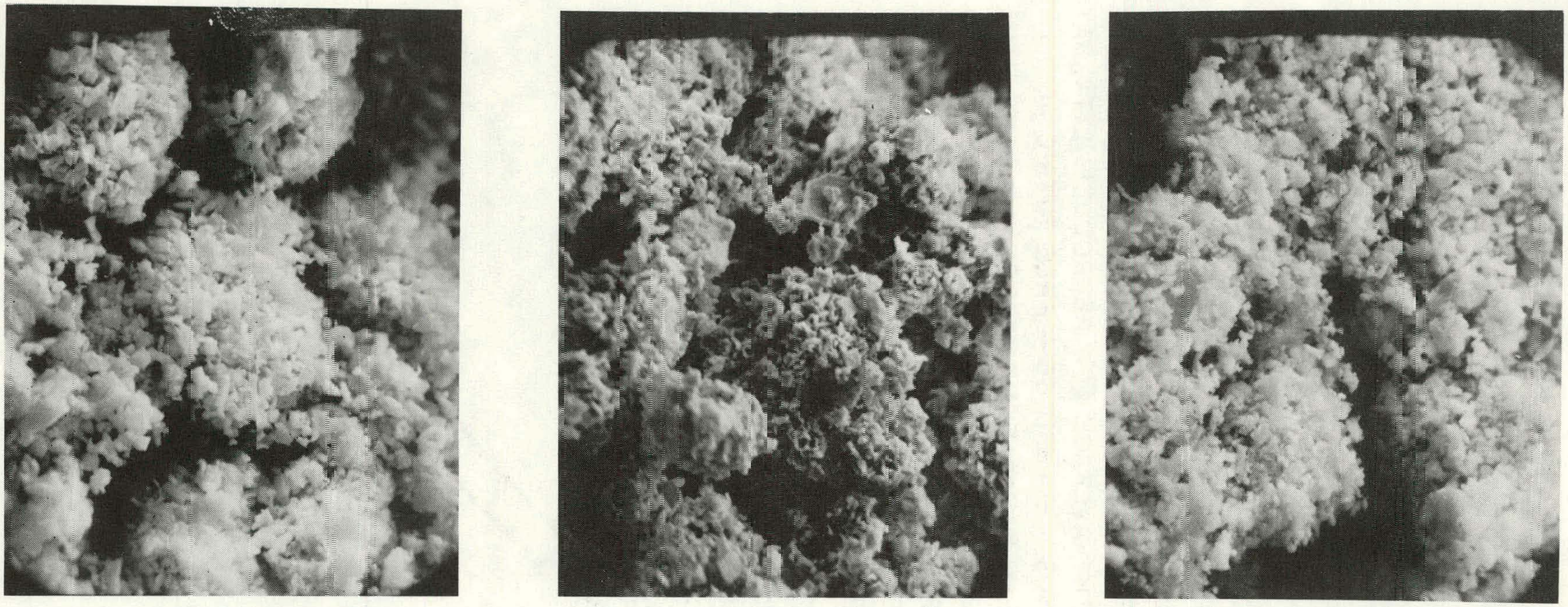


FIGURE 14
ELECTRON MICROSCOPE PHOTOMICROGRAPHS OF THORIA POWDER
AS A FUNCTION OF CALCINE TEMPERATURE



BATCH 44A
PRECIPITATION TEMP: 43-44°C
CALCINED AT 900°C
(3500 X, REDUCED 22% IN PRINTING)

BATCH 44B
PRECIPITATION TEMP: 43-44°C
CALCINED AT 969°C
(3500 X, REDUCED 22% IN PRINTING)

BATCH 44C
PRECIPITATION TEMP: 43-44°C
CALCINED AT 1039°C
(3500 X, REDUCED 22% IN PRINTING)

FIGURE 15
AVERAGE PARTICLE SIZE AND BULK DENSITY AS A FUNCTION OF CALCINE TEMPERATURE

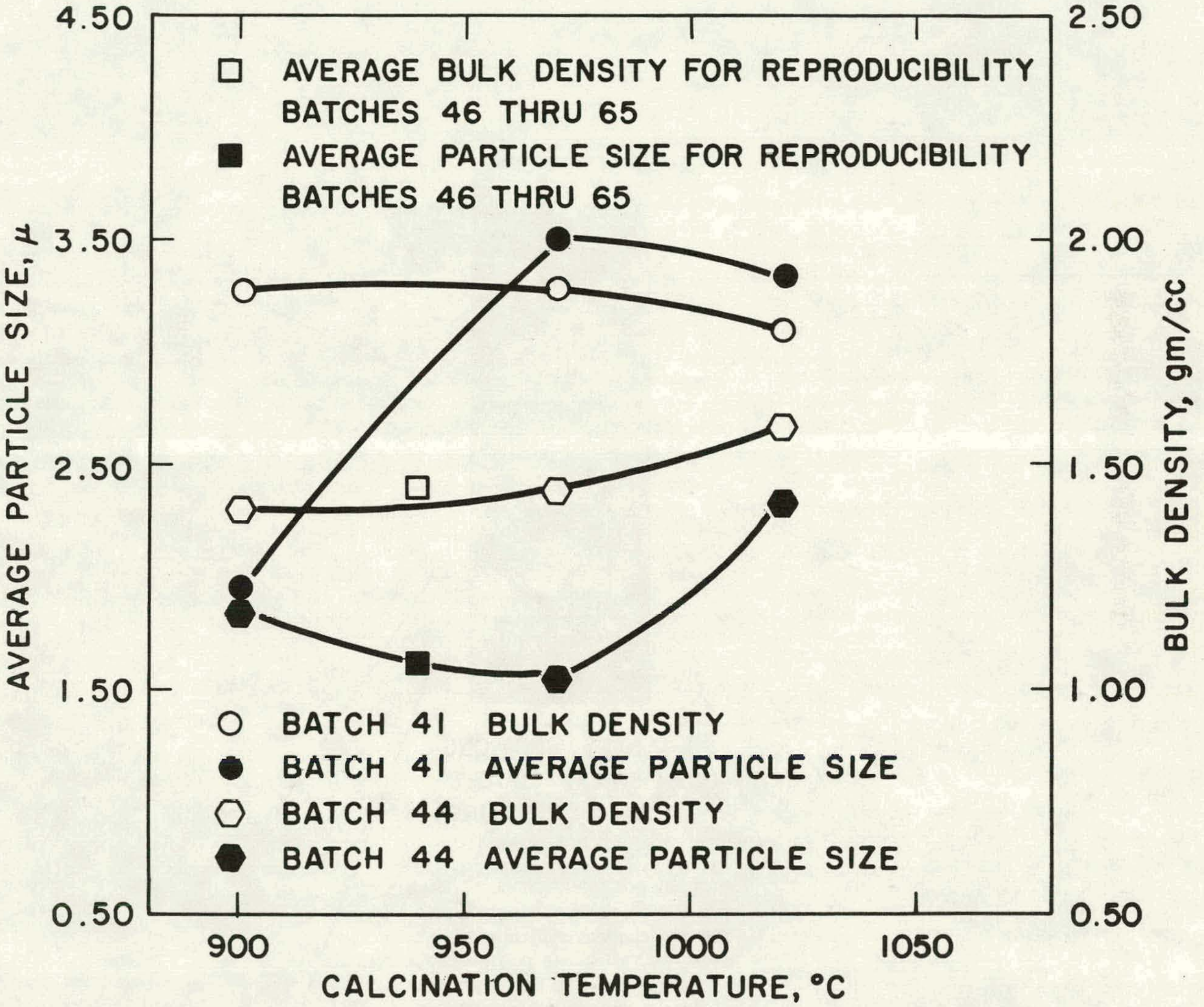
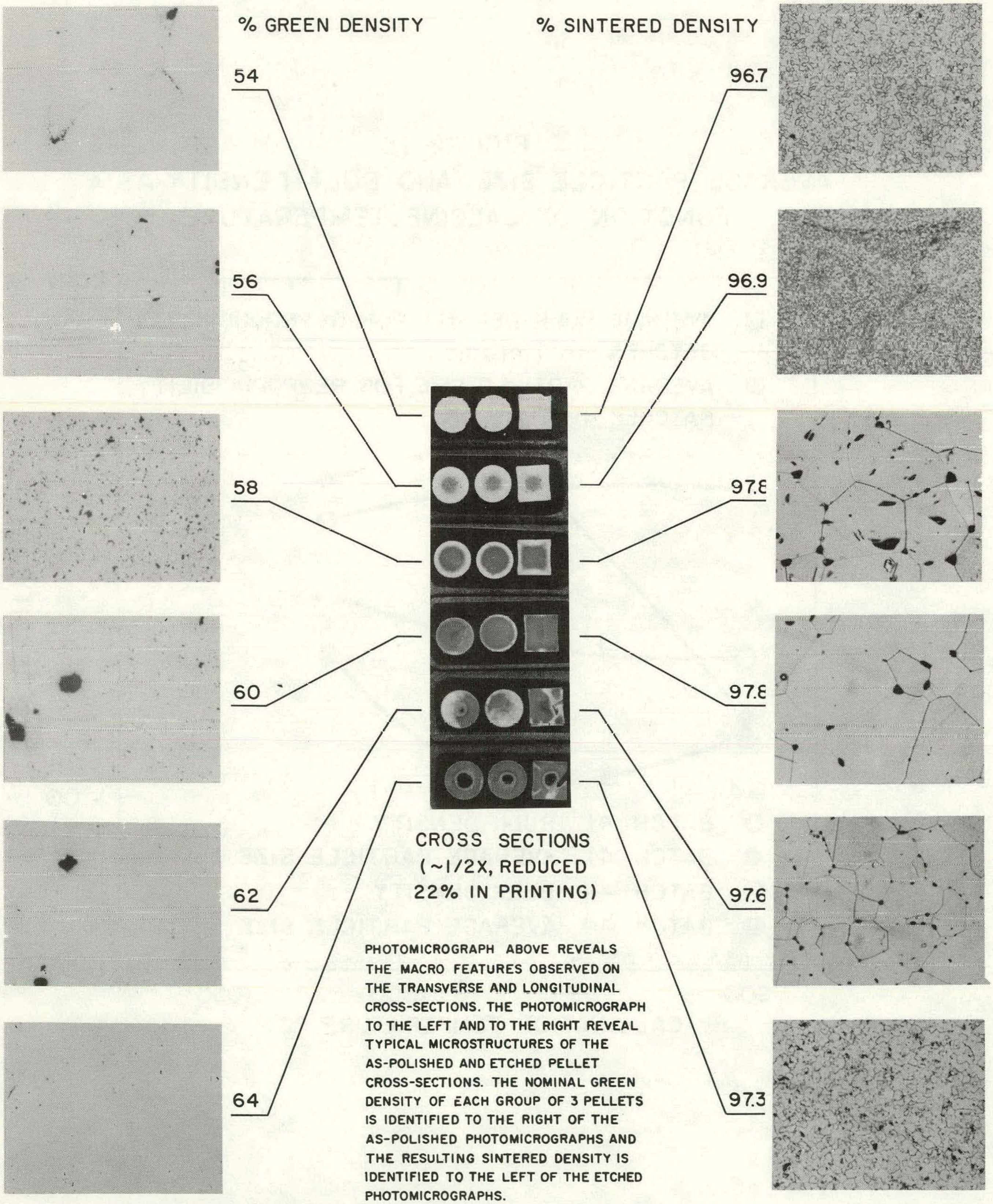


FIGURE 16

PHOTOMICROGRAPHS OF BATCH 44A SINTERABILITY TEST SAMPLES SINTERED AT 1675°C



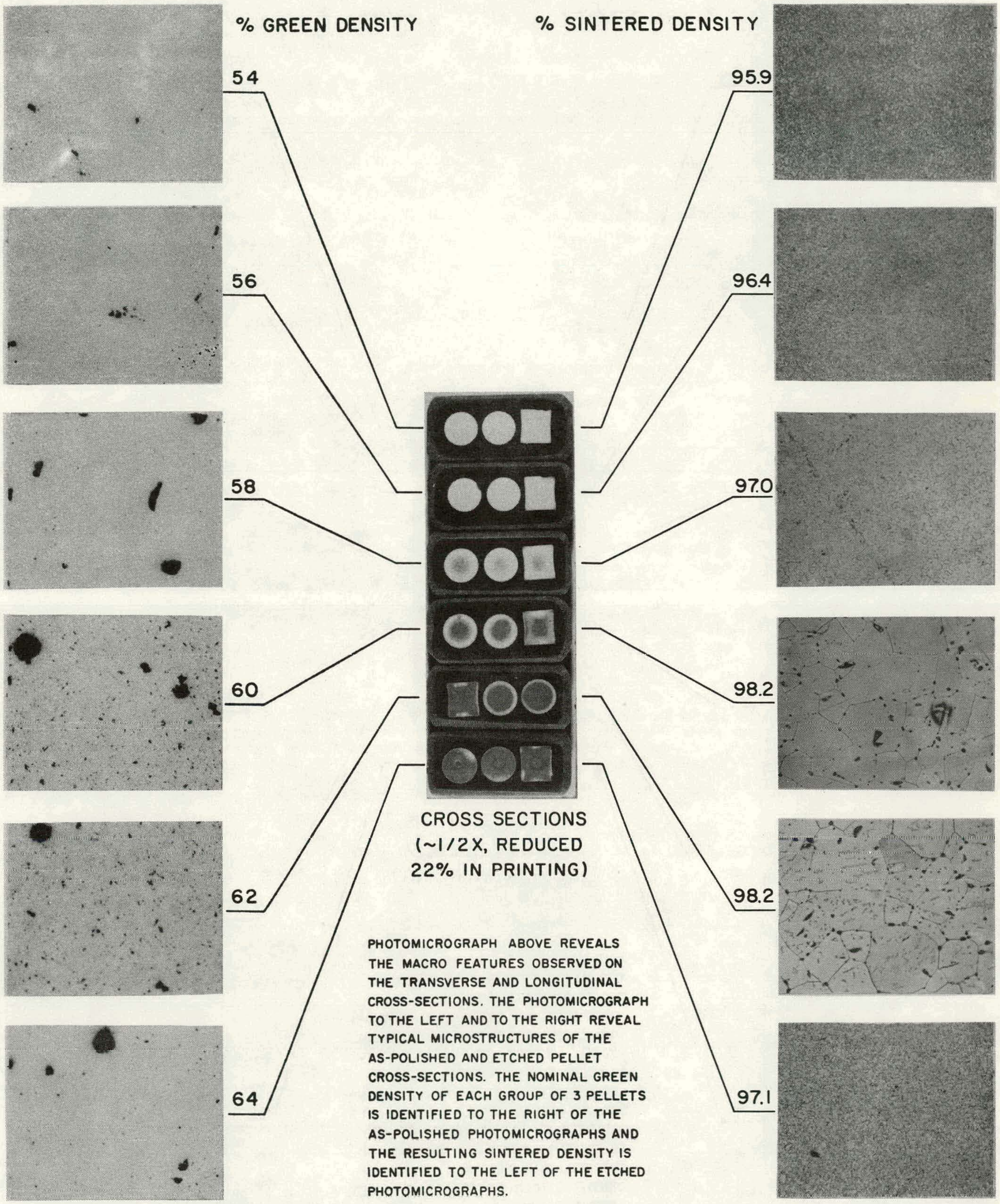
CROSS SECTIONS
(~1/2X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250X, REDUCED
22% IN PRINTING)

FIGURE 17
PHOTOMICROGRAPHS OF BATCH 44B SINTERABILITY TEST
SAMPLES SINTERED AT 1675°C



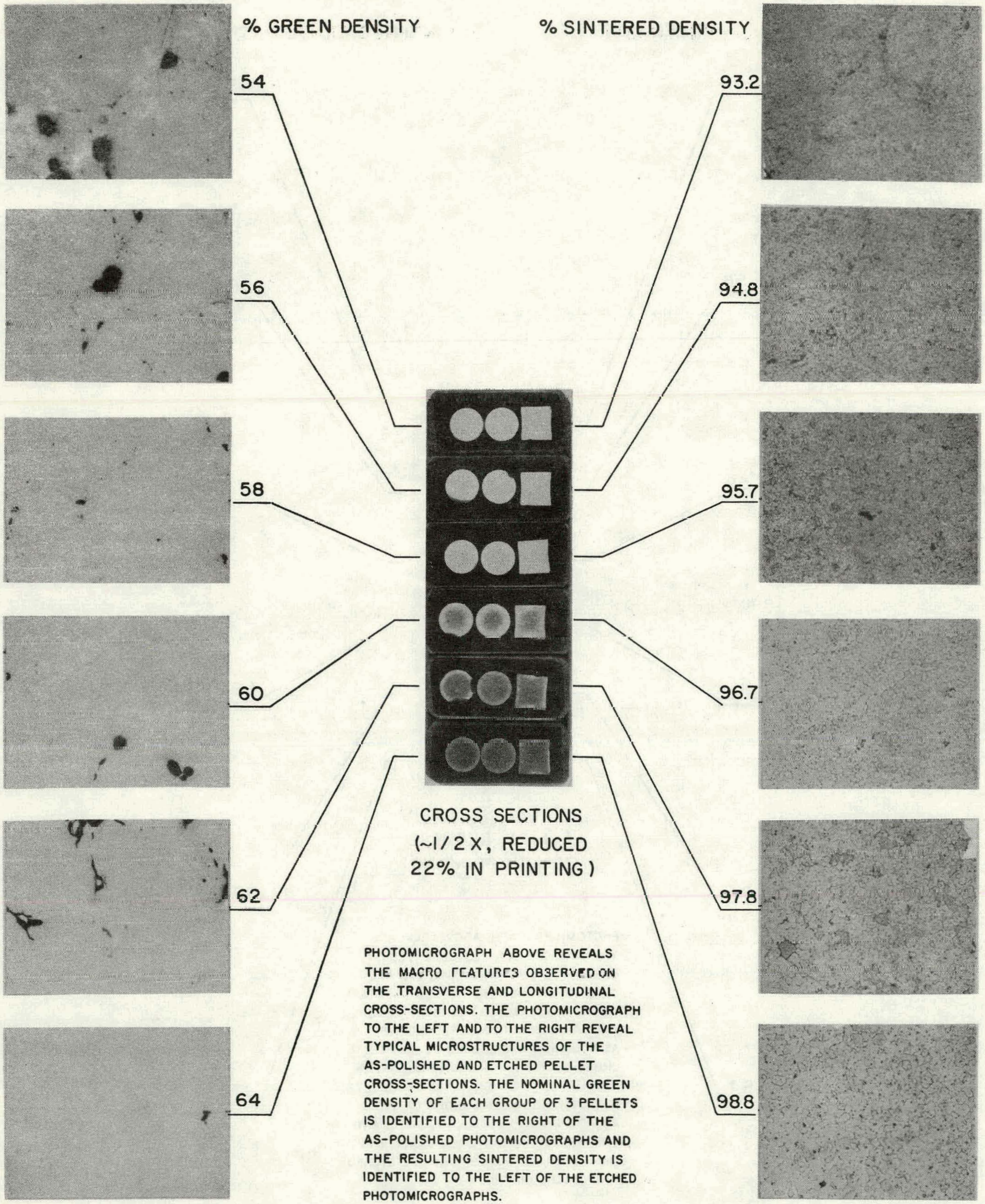
CROSS SECTIONS
(~1/2X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250X, REDUCED
22% IN PRINTING)

FIGURE 18
PHOTOMICROGRAPHS OF BATCH 44C SINTERABILITY TEST
SAMPLES SINTERED AT 1675°C



CROSS SECTIONS
(~1/2 X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50 X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250 X, REDUCED
22% IN PRINTING)

FIGURE 19
RELATIONSHIP BETWEEN SINTERED DENSITY AND CALCINE TEMPERATURE

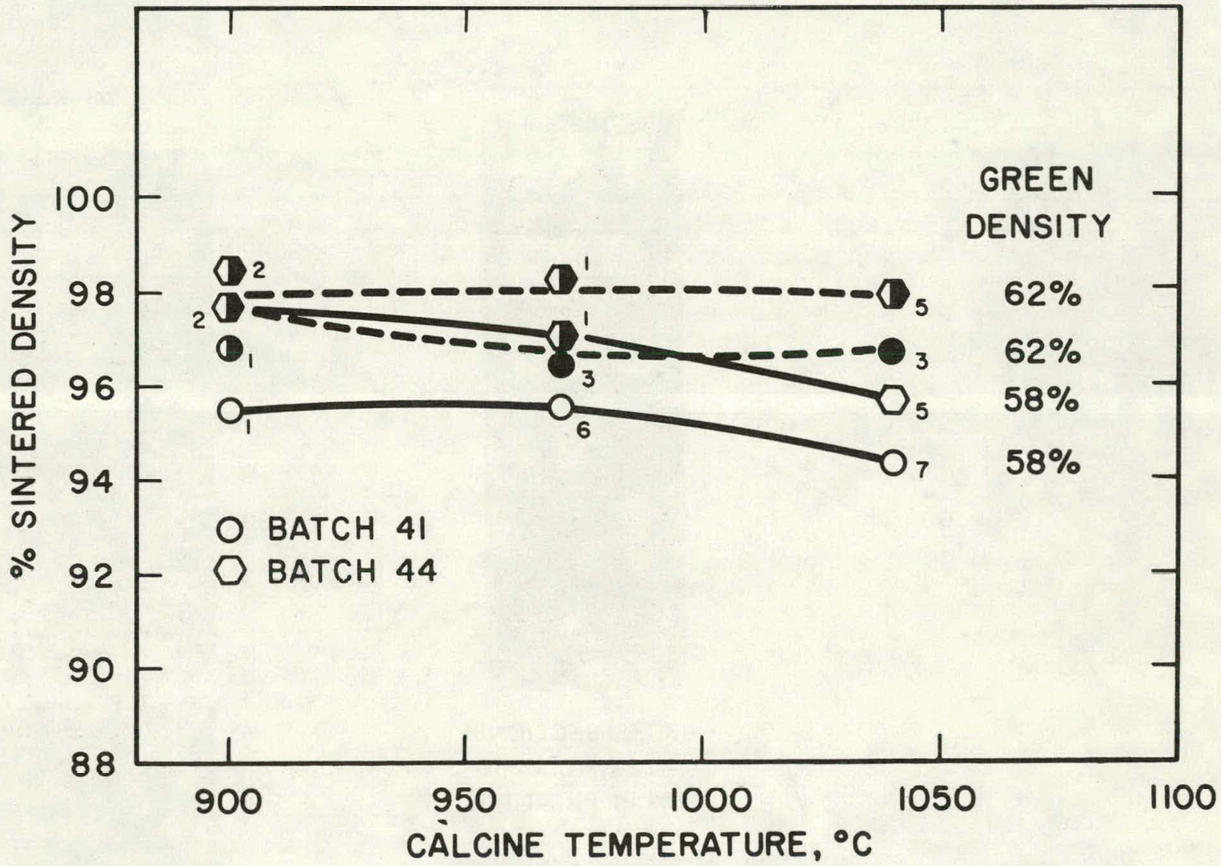
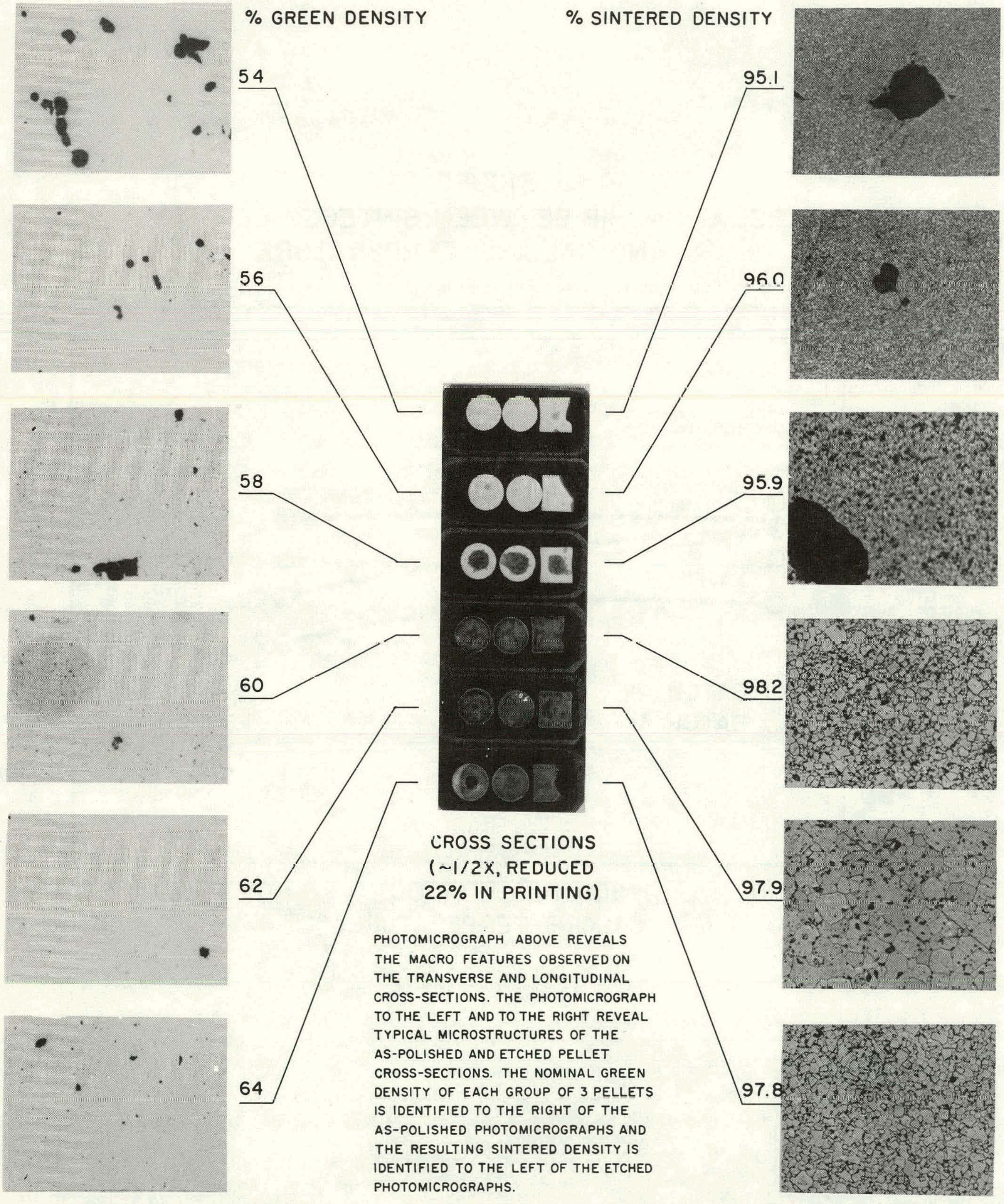


FIGURE 20
PHOTOMICROGRAPHS OF BATCH 37 SINTERABILITY TEST SAMPLES SINTERED AT 1675 °C



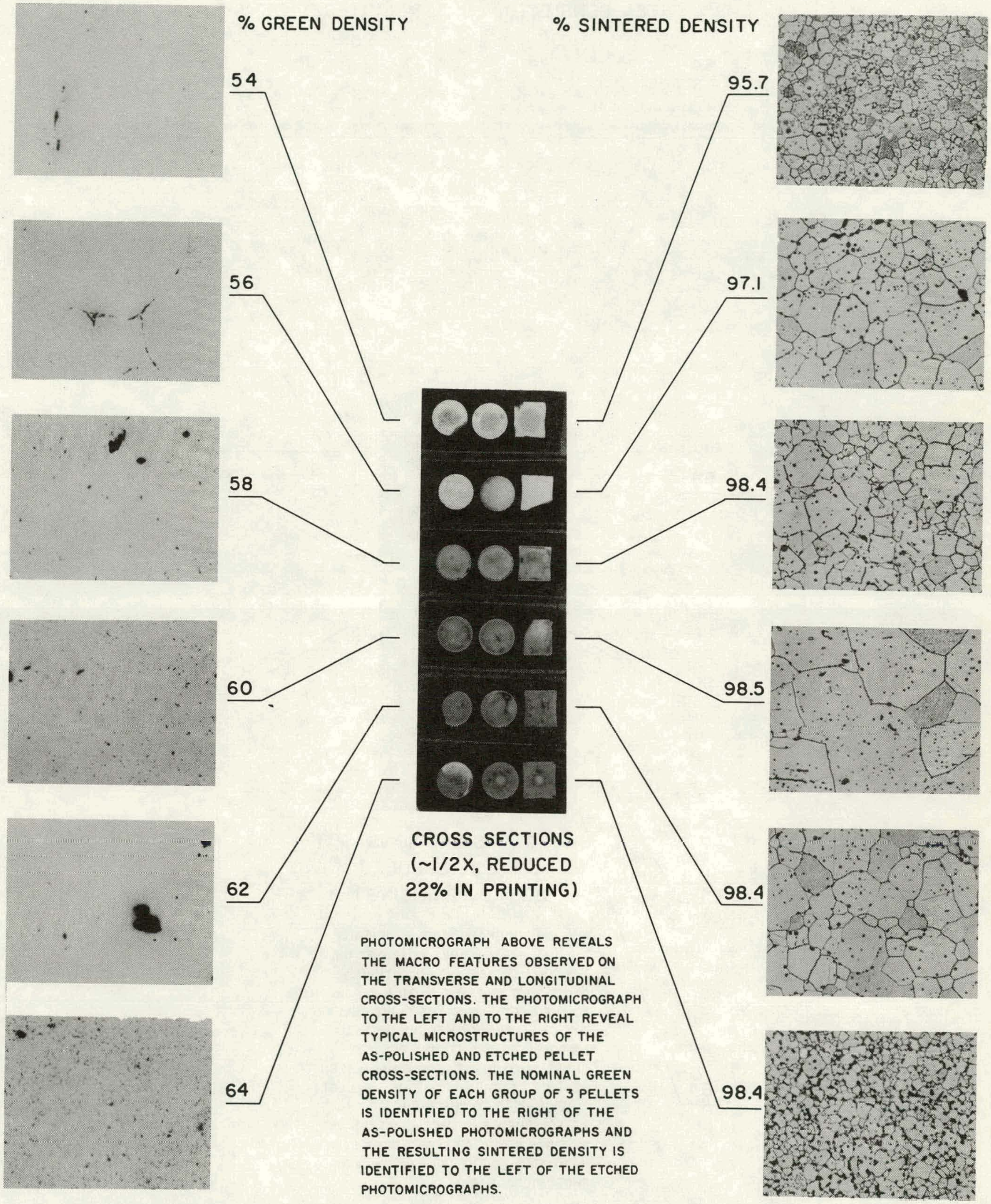
CROSS SECTIONS (~1/2X, REDUCED 22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC PELLET CROSS SECTIONS (50X, REDUCED 22% IN PRINTING)

ETCHED METALLOGRAPHIC PELLET CROSS SECTIONS (250X, REDUCED 22% IN PRINTING)

FIGURE 21
PHOTOMICROGRAPHS OF BATCH 38 SINTERABILITY TEST SAMPLES SINTERED AT 1675 °C



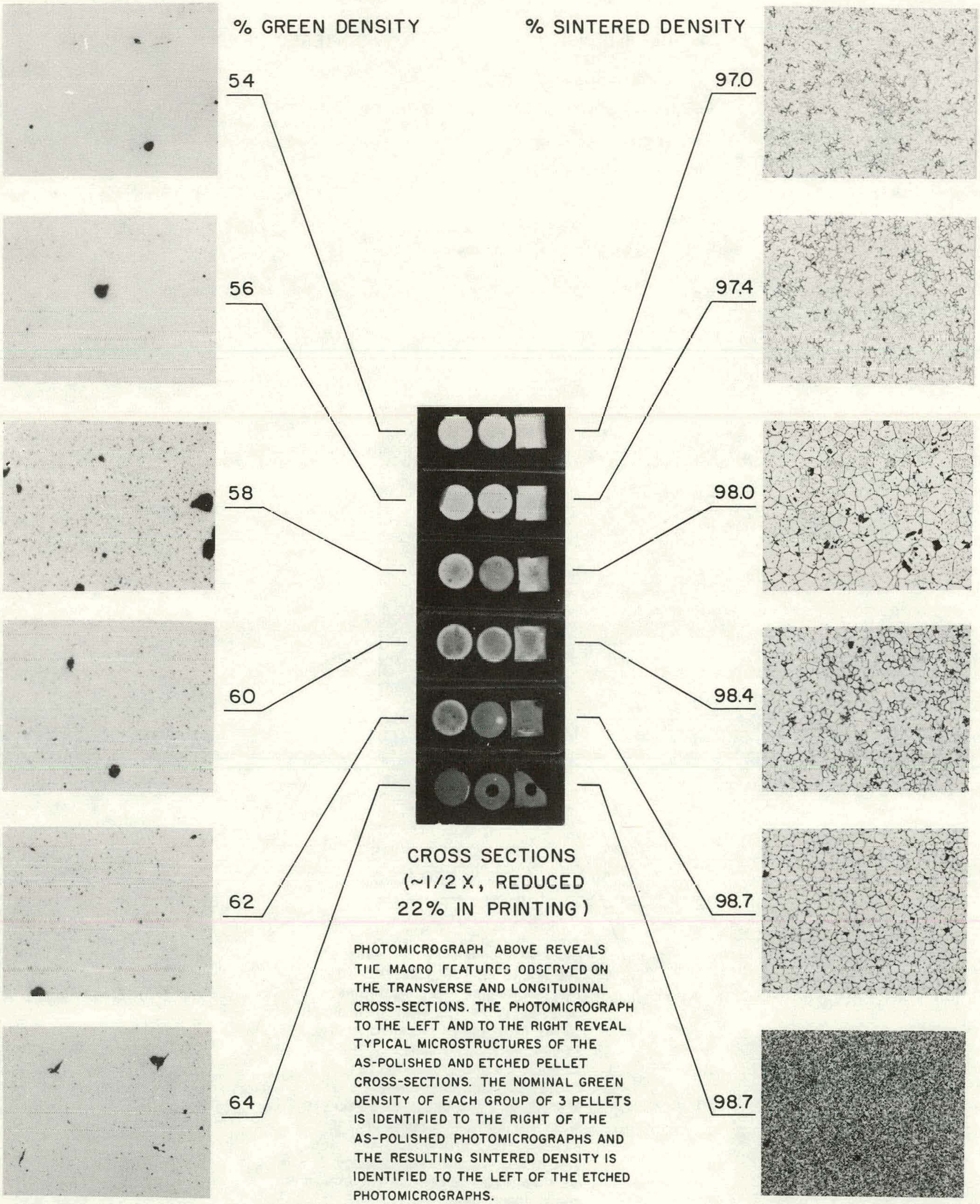
CROSS SECTIONS
(~1/2X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250X, REDUCED
22% IN PRINTING)

FIGURE 22
PHOTOMICROGRAPHS OF BATCH 39 SINTERABILITY TEST
SAMPLES SINTERED AT 1675°C



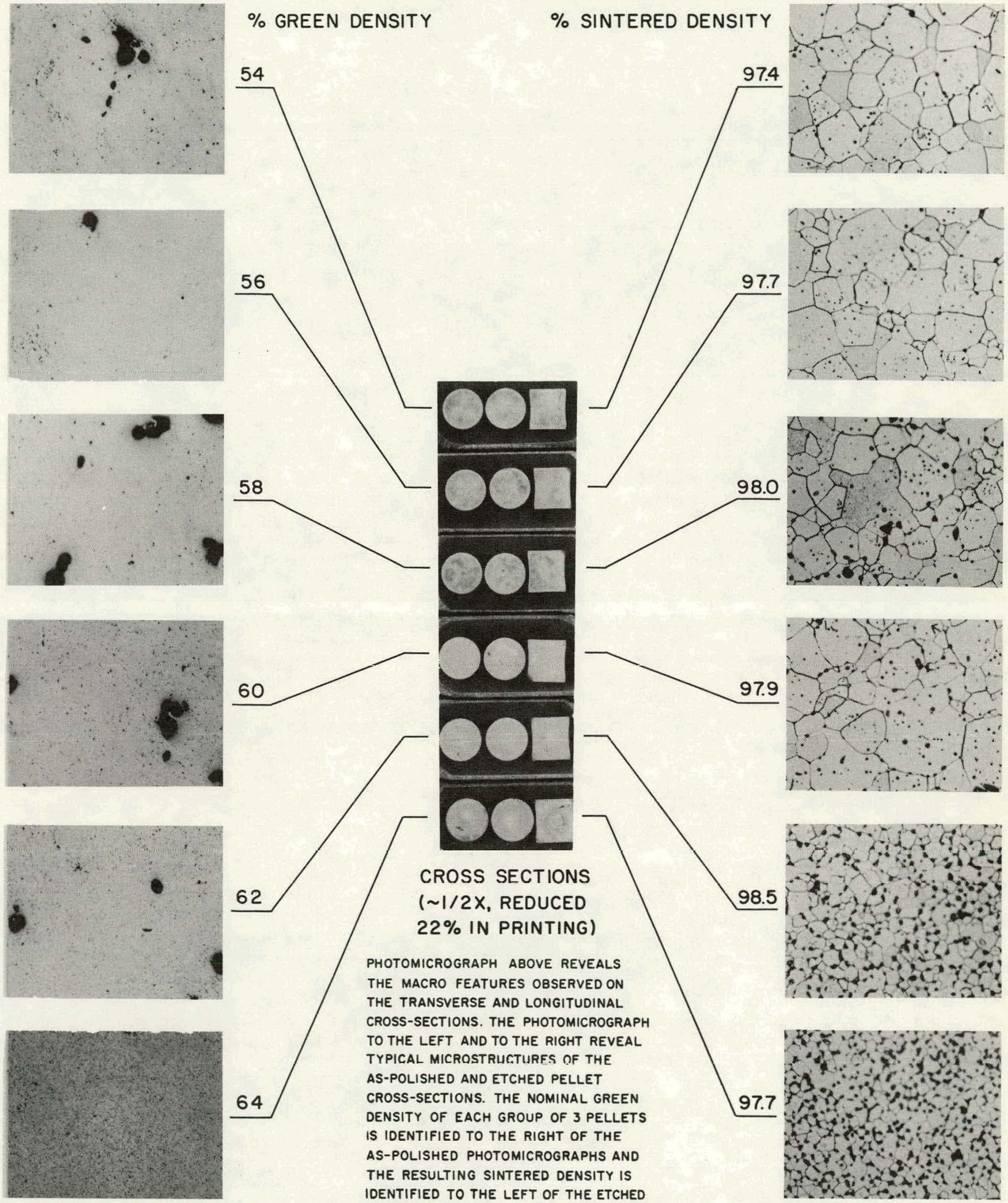
CROSS SECTIONS
(~1/2 X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50 X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250 X, REDUCED
22% IN PRINTING)

FIGURE 23
PHOTOMICROGRAPHS OF BATCH 38 SINTERABILITY TEST
SAMPLES SINTERED AT 1725°C



CROSS SECTIONS
(~1/2X, REDUCED
22% IN PRINTING)

PHOTOMICROGRAPH ABOVE REVEALS THE MACRO FEATURES OBSERVED ON THE TRANSVERSE AND LONGITUDINAL CROSS-SECTIONS. THE PHOTOMICROGRAPH TO THE LEFT AND TO THE RIGHT REVEAL TYPICAL MICROSTRUCTURES OF THE AS-POLISHED AND ETCHED PELLET CROSS-SECTIONS. THE NOMINAL GREEN DENSITY OF EACH GROUP OF 3 PELLETS IS IDENTIFIED TO THE RIGHT OF THE AS-POLISHED PHOTOMICROGRAPHS AND THE RESULTING SINTERED DENSITY IS IDENTIFIED TO THE LEFT OF THE ETCHED PHOTOMICROGRAPHS.

AS POLISHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(50X, REDUCED
22% IN PRINTING)

ETCHED METALLOGRAPHIC
PELLET CROSS SECTIONS
(250X, REDUCED
22% IN PRINTING)

APPENDIX A

THORIUM OXALATE - ThO_2 POWDER PROCESSING EQUIPMENT

To minimize production problems associated with scaling up from either bench or pilot run size powder batches, full size (130 ± 10 kg) production batches were manufactured in the development program. Description of the processing equipment and material processing is presented herein. Figure A-1 illustrates the process equipment/material flow for the thorium oxalate conversion process.

1. Thorium Nitrate Solution Makeup Tank

A 1250 gallon dished-bottom tank fabricated from Type 304 stainless steel was used to dilute the purified thorium nitrate solution. Thorough mixing of the solution was by a high speed stirrer.

Concentrated thorium nitrate (450 gm Th/liter) solution, transferred from storage tanks to the thorium nitrate solution makeup tank, was diluted with filtered deionized water and concentrated nitric acid to adjust both the thorium concentration to 190 to 250 gm Thorium/liter and normality of the free nitric acid to 0.9 to 2.0 normal. Production batch concentration was 200 ± 10 gms Th/liter and a normality of 1.1 ± 0.1.

2. Oxalic Acid Makeup Tank

Type 304 stainless steel dished-bottom tank of 400 gallons capacity with steam heating coils was used to makeup the oxalic acid solution. Agitation was by a properller-type agitator. Temperature of the acid solution was measured by thermocouples and controlled by an automatic recorder-controller.

3. Precipitation Vessel

Type 304 stainless steel dish bottom 400 gallon capacity vessel fitted with internal stainless steel coils which were connected to both cooling water and steam sources. Heating of the tank contents was by manual control of steam to the coils; cooling was through automatic control system of cooling water to the coils. As precipitation of thorium oxalate is an exothermic reaction, cooling of the batch to a given temperature (referred to as precipitation temperature) is necessary for controlling the crystallite size of the precipitated thorium oxalate.

Thorium nitrate solution was transferred from the makeup tank to the precipitation vessel. Oxalic acid was sprayed into the tank through 4 sprayheads mounted on a movable fixture. The oxalic acid spray - thorium nitrate solution interaction area was held relatively constant by periodically moving the spray head fixture up as the depth of the thorium oxalate slurry increased. By maintaining a constant spray - solution interaction area, through control of the spray head-to-solution surface distance, and continual agitation of the thorium nitrate solution-thorium oxalate slurry, the conditions for nucleation of crystallites and their growth were equilibrated.

Oxalic acid flow rate was controlled manually by a needle valve and was measured by both a magnetic induction flowmeter, which also recorded the flow, and a rotameter which was a backup system.

4. Plate-and-Frame Filter Press

A 10 cu. ft., 2 ft. x 2 ft., frame crossflow wash filter press was used to filter the thorium oxalate slurry. The filter press consisted of a metal frame on which alternating stainless steel plate and frames were suspended. Filter cloths were placed on each side of the frame to form a rectangular cavity with the plates and frames pressed together. At the start of the filtering cycle, the press was filled with deionized water then the thorium oxalate slurry was pumped into the press at 150 psig maximum displacing the deionized water. Next, the liquor was removed by washing with deionized water. The wash water flowed counter-current to the flow of the thorium oxalate slurry. This permitted the wash water to be admitted behind the filter cloth on each frame and pass through the cake over the entire frame area. The wash continued until a pH of ≥ 3.0 was reached on the wash water. The washed filter cake was dewatered by blowing filtered air at ambient temperature through the thorium oxalate press.

Upon completion of drying the cake, the cake was dropped from the frames onto a stainless steel pan where it was packaged into 5-gallon transfer cans lined with polyethylene or 5-gallon polyethylene containers.

5. Calcination Equipment

Air calcination of thorium oxalate was divided into two stages: (1) low temperature stage and (2) high temperature stage. This approach enabled the desired production rate of 2050 kgs (4510 lbs) per week to be achieved as well as removal of the large quantity of liquid and potentially corrosive vapor from the thorium oxalate hexahydrate in the dehydration and decomposition of the oxalate.

a. Low Temperature Furnace

This furnace had a 13 ft hot zone which was heated by silicon-carbide (SiC) resistance heating elements. The hot zone temperature was controlled to a maximum temperature of 760°C (1400°F) by four controllers. The thorium oxalate hexahydrate cake was loaded into Inconel calcining boats, in pairs, which were transported through the furnace on a 26 inch wide variable speed continuous-feed belt.

b. High Temperature Furnace

This furnace had a 16 ft. hot zone which was heated by SiC heating elements with operating temperature capabilities up to 1040°C

(1900°F). The hot zone was divided into 3 heating zones with each separately controlled by over-temperature controllers and the temperature of each zone was recorded on a strip recorder. The Inconel calcining boats were pushed through the furnace single file by an air-activated hydraulic ram system.

6. Blending

Powder batches were blended in a 20 cu ft stainless steel twin shell blender with a maximum capacity of 910 kgs (2000 lbs).

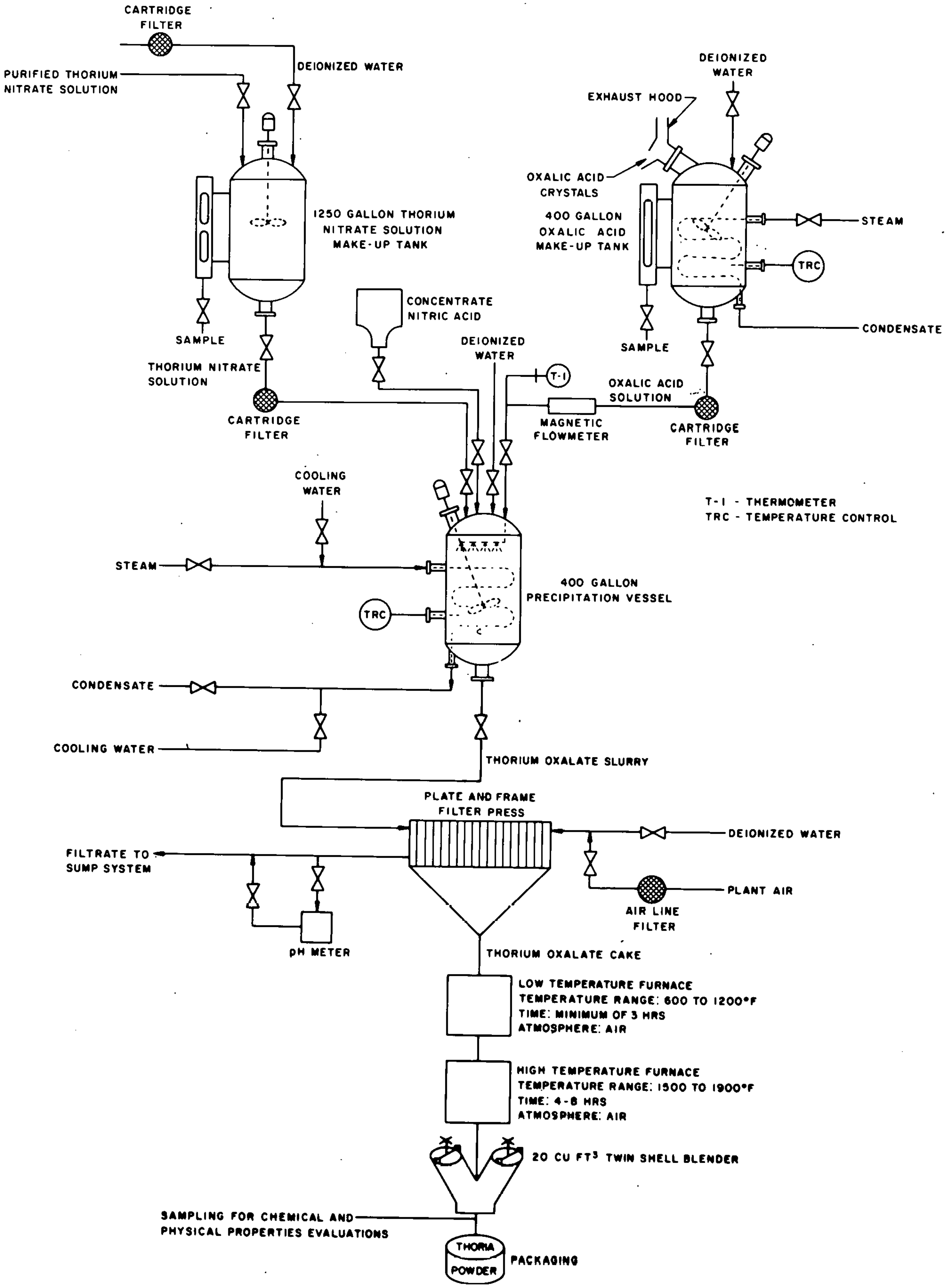


FIGURE A-1
THORIUM OXALATE-CONVERSION PROCESS EQUIPMENT/MATERIAL FLOW DIAGRAM

☆U.S. GOVERNMENT PRINTING OFFICE:1980/603-113/257