APEX-377

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Production of Pebble-Type Fuel Elements

(CLASSIFIED TITLE)

H.C. Brassfield

AIRCRAFT NUCLEAR PROPULSION DEPARTMENT
ATOMIC PRODUCTS DIVISION
GENERAL ELECTRIC

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Production of Pebble-Type Fuel Elements

H.C. Brassfield

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Abstract

A capillary-drop method of producing spherical shapes of brittle materials less than 0.100 inch in diameter has been developed. It appears to be a feasible means for producing large numbers of pebble-type fuel element cores. Coating of pebble-type fuel element cores by the coating-pan technique though not adequately developed shows promise.

Contents

Production of Pebble-Type Fuel Elements

INTRODUCTION

Design and development work on high-temperature direct-cycle reactors at the General Electric Aircraft Nuclear Propulsion Department has resulted in several reactor configuration proposals. In one possible design very high temperatures may be obtained by passing air through shallow beds of small pebbles containing enriched uranium oxide. Air thus heated could be used efficiently to power a high-temperature turbine system.

The choice of materials is limited by the high temperatures to ceramics, ceramic-metal systems, and nonductile metal systems. Any such material selected must be able to retain fission products and to withstand severe thermal shock, and must be capable of fabrication into small spherical shapes. This report is concerned primarily with processes which have been developed for the fabrication of small spherical shapes of nonductile materials.

SELECTION OF MATERIALS

The developmental work with pebble-type fuel elements has been concerned mainly with ceramic materials. On the basis of an investigation conducted by Battelle Memorial Institute,* four materials - BeO, SiC, ZrO_2, and Al_2O_3 - were selected for consideration. Another material, $MoSi_2$, was added on the basis of data obtained by Maxwell et al. at NACA.† Three of these materials have been de-emphasized in importance: SiC because of the inability to produce a dense body by means other than hot pressing, ZrO_2 because of the solution and migration of UO_2 in it at high temperatures, and Al_2O_3 because of its poor resistance to thermal shock.

Each of the remaining two materials, BeO and $MoSi_2$, has been proposed for a specific reactor. The reactor using BeO as the fuel element matrix material requires approximately 250,000 spheres, 0.250-inch in diameter, with 0.230-inch cores containing 1 to 4 percent enriched UO_2 as the fuel material. A coating of essentially pure BeO, 0.010-inch thick, would be applied to protect the UO_2 in the core from oxidation and to retain fission products.

The proposed reactor using $MoSi_2$ as the fuel element matrix material requires approximately ten million spheres, 0.070 inch in diameter. These have cores 0.050 inch in diameter and contain approximately 40 percent by weight of 92 percent enriched UO_2 as the fuel material. A 0.010-inch coating of essentially pure $MoSi_2$ is required for protection.

METHODS FOR FABRICATION OF CORES

The large number of pebbles needed and the severe service to which they will be subjected demand that the method of fabrication be capable of very high production rates and

*BMI-787, Evaluation of Oxidation-Resistant Ceramics for High Temperature Reactor Elements.

†RME9G01 Properties of Certain Intermetallics as Related to Elevated-Temperature Applications I Molybdenum Disilicide, W. A. Maxwell.

yield a uniform and extremely reliable end product. The composite nature of the pebbles indicates that cores and coating must be produced in separate steps.

The larger (0.230-inch-diameter) cores may be fabricated by the usual dry-pressing and sintering techniques, which will not be described in this report. It was thought that the small (0.050-inch-diameter) cores would probably require a less conventional method. Schemes that have been considered include (1) dry-pressing of cylinders followed by rolling to spherical shape, (2) rolling of sintered cylinders at temperatures sufficiently high to render them plastic, (3) forming of spheres by free fall through an arc, (4) spray-drying of a slip, (5) rolling while alternately wetting and applying powder, (6) grinding of sintered cylinders, and (7) formation of spheres by dropping from a capillary. After a literature search and preliminary work, only the last method appeared to be capable of yielding the necessary high production rate and degree of uniformity.

Capillary-Drop Method

The capillary-drop method, illustrated in Figure 1, consists essentially of forming a spherical drop of a slip at the tip of a capillary and collecting and drying the drop while it retains its sphericity. As developed, the important steps in this process are (1) preparing a suspension of powdered fuel core material with a controlled pH, (2) dropping the suspension through a small capillary into a moving bed of water-repellent powder, (the powder cradles the bottom half of the drop into a hemisphere, and surface tension

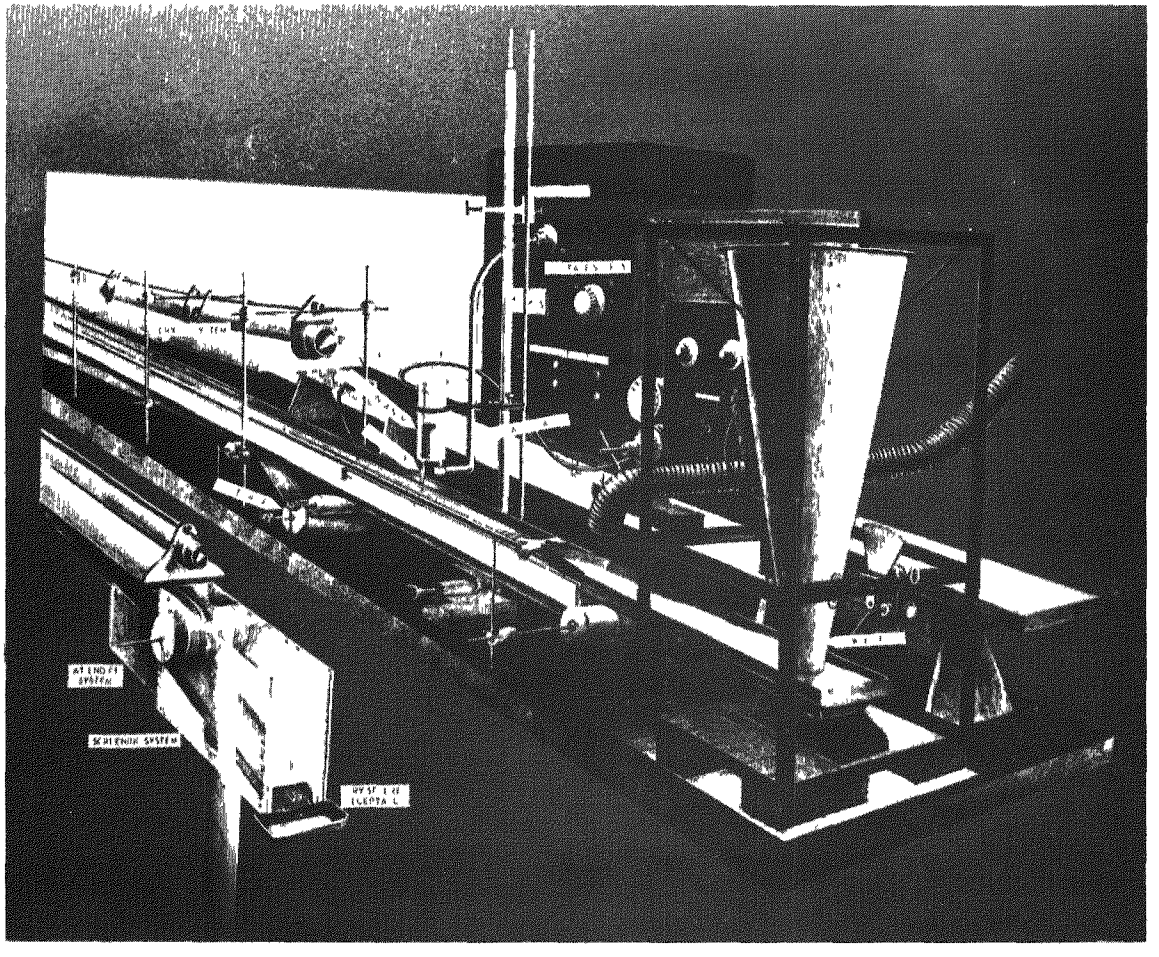

Fig 1 – Capillary-drop apparatus

produces a spherical surface on the top half), (3) drying the spherical drop on the moving bed by infrared heating, and (4) separating the spheres from the bed powder.

Water-Repellent Powder - Several powders which will resist wetting by water are readily available. Powders which were tested are: micro-pulverized graphite, carbon black, lycopodium powder, stearated aluminum metal powder, and various powders treated with a water-repellent silicon compound (G. E. Drifilm). Stearated aluminum powder was selected because of its low cost, cleanliness, and ease of removal from the cores via evaporation or oxidation during firing in a wet hydrogen atmosphere. The extreme water-repellent characteristics of these powders are not fully explained in the literature. Experience has shown that the degree of water-repellency is a function of both the material and its particle size.

Powder Feed Mechanism - The feeding of the aluminum powder onto the moving conveyor belt to form a bed of uniform density presented some difficulty. During simple gravity feeding, the aluminum powder displayed an erratic tendency to bridge over the feed orifice, and it became necessary to install a vibratory feeder (Syntron Model Fm-0-10). This device drops a continuous stream of powder onto the belt, the rate of feeding being controlled by varying the amplitude of vibration. Once on the belt, the powder is shaped into the desired form by a stationary guide. The precise scheduling of the feed rate relative to the conveyor belt speed requires periodic attention and adjustment of the feed.

Belt Conveyor System - The conveyor system consists of a 2-inch, 3-ply rubber-canvas belt resting in an aluminum channel beam and driven by a Graham variable-speed transmission. The present system is capable of belt speeds from 0 to 42 feet per minute. The normal belt speed for the operation is from 3 to 4 feet per minute.

After passing the capillary dropping station, the belt carries the dropped spheres under four infrared heating units, where they are dried. To avoid overheating the rubber belt, the bottom half of the channel beam in which it rides was closed and water-cooled.

Capillary-Drop Apparatus - The heart of the system is the capillary-drop apparatus illustrated in Figure 2. It consists of a Plexiglas container supported above the traveling powder bed, and is equipped with a small motor stirrer to maintain uniform dispersion of the slurry (of water and solid core material). The aluminum paddle of the stirrer is electrically insulated from the motor shaft by a Plexiglas coupling, and the shaft is sealed at the container lid by means of a rubber gasket.

The size of the drop produced, which is of utmost importance, is controlled in three ways. The size is determined primarily by the effective diameter of the capillary tip; however, this dimension, having been fixed, variation may be secured by regulation of gas pressure above the liquid and by application of an electrical charge to the slip.

It should be emphasized that the surface of the capillary tip upon which the drop forms must be kept as small as possible. This is accomplished by grinding the tip to a narrow lip. In addition, if the slip is permitted to wet the tip and stem of the capillary, it will creep up the outside wall of the tube and drops will form on a larger surface. Wetting is prevented by application of a water-repellant material such as G. E. Drifilm. No detailed study of the relation of capillary diameter to drop size has been made, but practice has shown that internal diameters from 0.012 to 0.018 inch yield drops within the desired size range.

Gas pressure is applied to the slip container primarily to control the dropping rate, but this in turn affects the drop size. The gas is tank argon, which is first saturated with

water to minimize evaporation of water in the slip and is then led through a pressure regulator to the apparatus as shown in Figure 2. Pressure adjustment is manual, and the normal operating pressure of 0.5 to 2.0 psi is read on a 0-5 psi gauge. The effect of applied gas pressure upon drop diameter is illustrated by Figure 3. More precise control of drop size is obtained by imposition of a high d-c voltage between the slip and the aluminum bed. The voltage supply is a modified model 402 Inductograph, and the voltage is applied to the slip, which is insulated from ground, by means of the coaxial cable shown in Figure 2. The resultant effect upon droplet size is depicted in Figure 4, which demonstrates that adjustment over a fairly wide range is possible. The phenomenom of drop-size control by the d-c voltage probably results from a combination of the Coulomb forces between the positively charged drop and the negative bed, and a reduction of the surface tension of the forming drop by the accumulation of positive charges on its surface. To form the large drops required for pebble core production, potentials between 500 and 4000 volts have sufficed.

Drying System - The drying system, shown in Figure 1, consists of four infrared heating units arranged over the end of the conveyor belt. Control of the drying rate is obtained by varying the height of the heaters above the bed and by controlling the voltage input to the heaters. Drying is regulated to produce damp-dry cores, because cores which are completely dried have a tendency to break as they are screened.

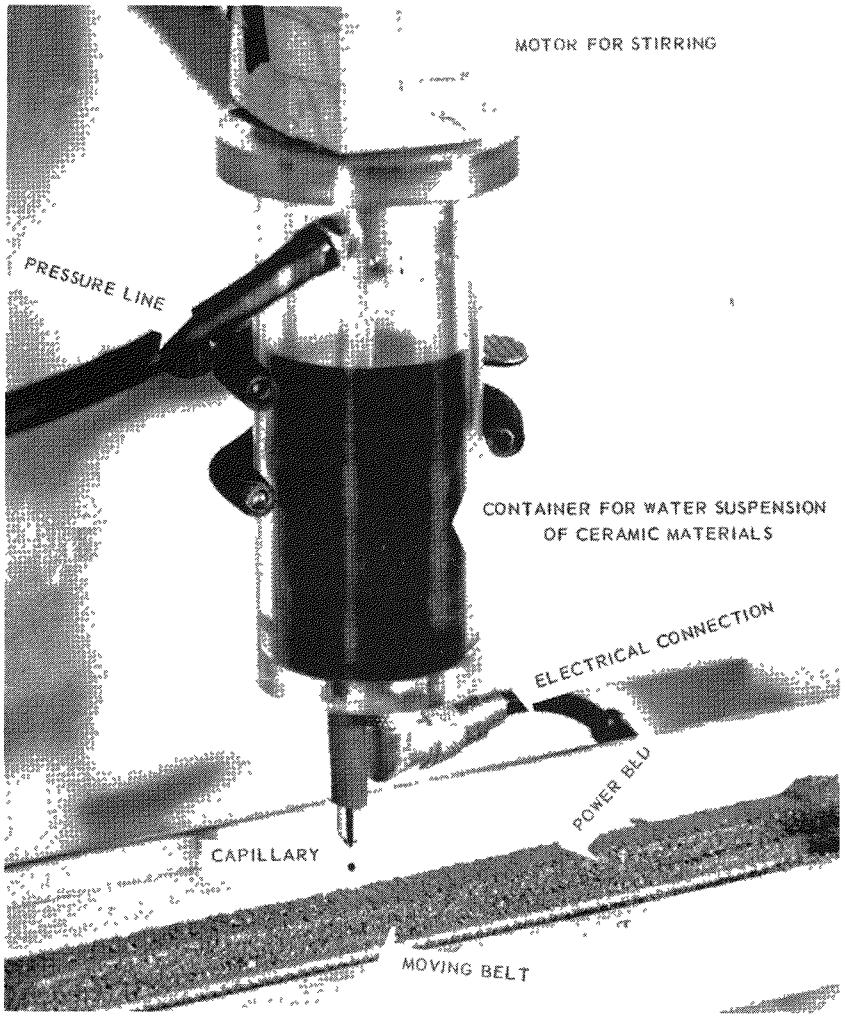

Fig. 2 – Small container for use in core production

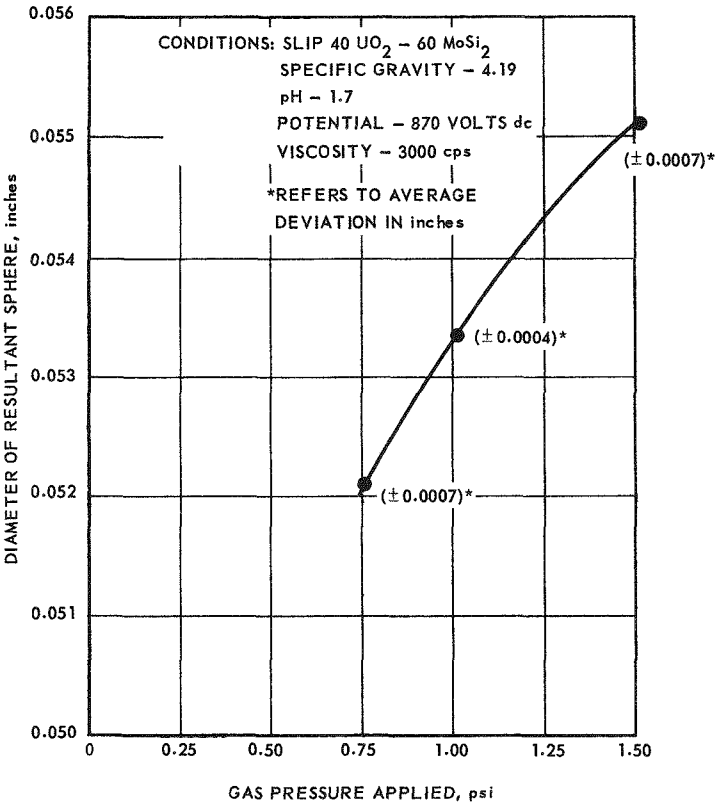

Fig. 3 – Typical relationship between resultant sphere size and applied gas pressure

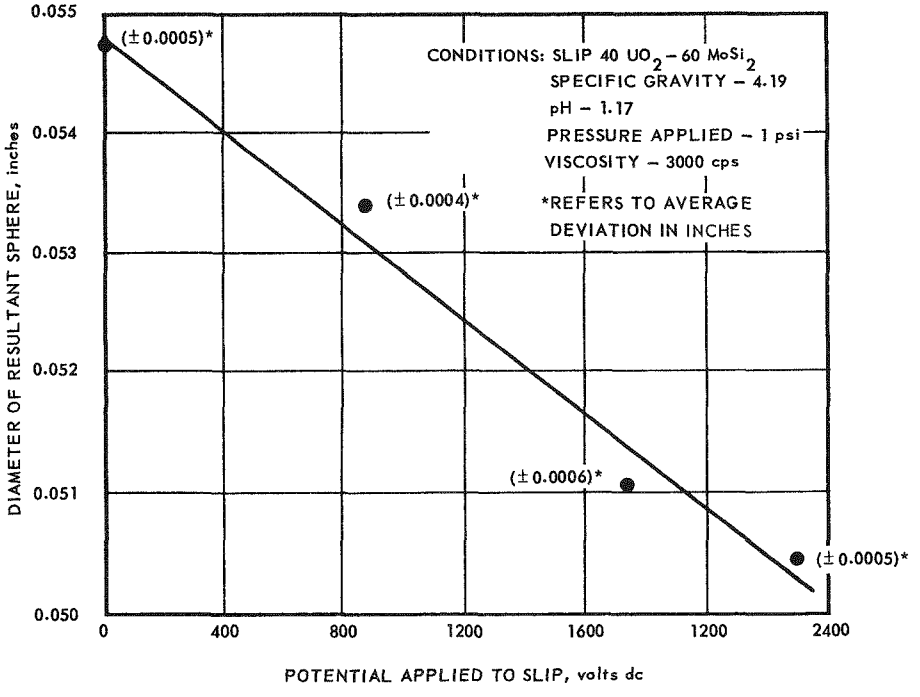

Fig. 4 – Typical relationship between resultant sphere size and applied voltage

Screening System - A screening system is placed at the discharge end of the conveyor belt to separate the dried spheres from the aluminum powder. The 14 by 20 mesh screen is vibrated at fixed intervals by an automatic control system, and care is taken to leave a cushion of aluminum powder on the screen to prevent breakage of the cores when they fall onto the screen from the belt. The fine particle size of the aluminum powder makes it mandatory to enclose the screening apparatus and to exhaust the chamber with a fan. The aluminum powder is reclaimed and fed back into the powder-feed mechanism. The belt is cleaned by rotating brushes incorporated into the screening unit.

Properties of Slip and Constituents - The creation of a well-formed sphere by the capillary-drop method depends upon the properties of the slip, of which the most important is its degree of deflocculation, as controlled by its pH. If the slip is deflocculated, a dimpled sphere results on drying. An illustration of this effect is shown in Figure 5, where diagrams of resultant $MoSi_2$-UO_2 spheres are drawn on a graph of pH versus viscosity. It has been observed that undimpled spheres are formed only when the pH is below 3.0. In practice a pH between 1.6 and 2.2 is preferred and is obtained by adding concentrated hydrochloric acid to the slip just before it is placed in its container.

If good dropping characteristics are to be obtained from the capillary, the slip must also be of the correct viscosity. With a typical 0.014-inch-diameter capillary, a viscosity between 1,500 and 2,400 centipoises is preferred. Any lower value tends to produce a continuous stream from the capillary, and a higher viscosity produces low rates of dropping.

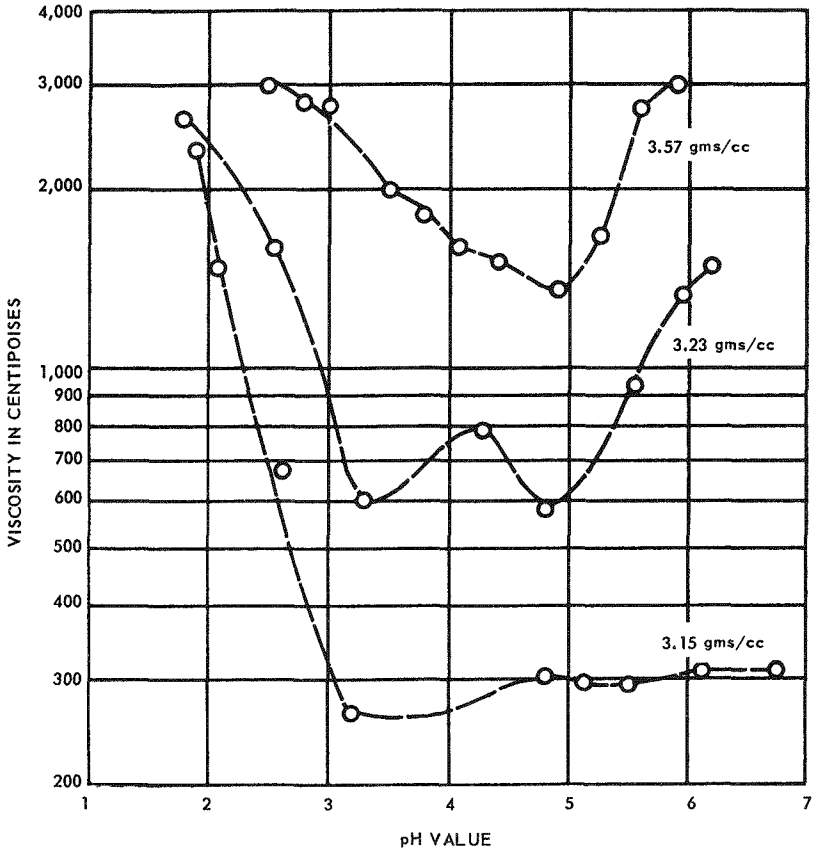

Fig. 5 – Viscosity versus pH for a suspension of molybdenum disilicide in water

The pH of the slip and its viscosity are mutually dependent properties, as shown by Figure 5, but some degree of freedom may be obtained by a variation of a third important slip property, specific gravity. By the correct selection of liquid-to-solid ratio the desired viscosity may be obtained within the required pH range. The specific gravity of

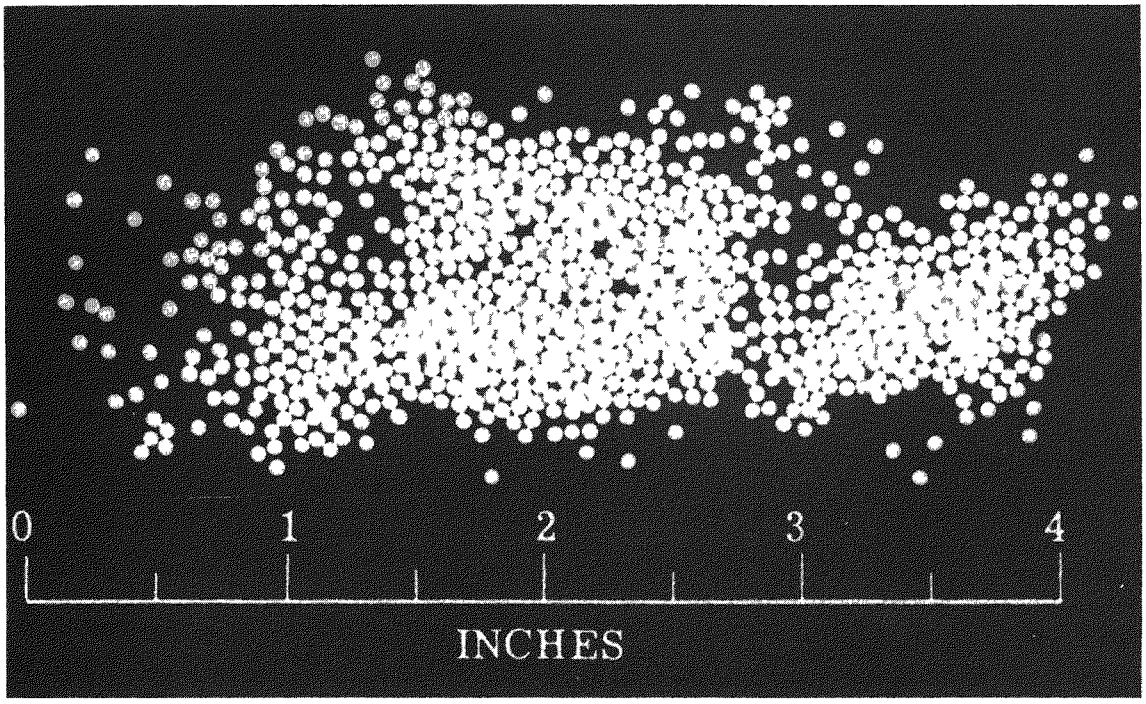

Fig. 6 – Typical alumina spheres

the slip is also independently important; if it is too low, drying of the drops will not take place in a convenient length of time. It has been found that with the present system operating on a 40 UO_2 - 60 $MoSi_2$ slip, a specific gravity of 4.0 ± 0.1 permits a conveniently rapid drying time.

The sintering characteristics of the dried pebble cores depend upon the heat treatment and particle size of the components. The present 40 UO_2 - 60 $MoSi_2$ composition will not sinter to a satisfactorily dense body (95 percent of theoretical or better) unless the $MoSi_2$ is ground to an average particle size of 13.0 microns (sedimentation method) or less. The UO_2 which is used in these cores is first sintered at 1800°C for one-half hour and then milled for 4-1/2 hours in a steel mill with steel balls; the - 325 mesh fraction of this material is combined with the $MoSi_2$. The slip is mixed overnight in a deflocculated state to facilitate good mixing. Deflocculation is obtained by adding sodium hydroxide.

Results of Capillary-Drop Core Production - Five different ceramic slips have been used in the capillary-drop system. The first slip used was acid-leached alumina, which was used to make simulated cores and to develop the process. This slip was used at a pH of 1.6 and a specific gravity of 2.42 and was dropped at a rate of approximately 240 drops per minute. The fired diameter of these alumina spheres was approximately 0.067 inch; typical products are shown in Figure 6. Thereafter, 47 percent UO_2 was incorporated in the slip and several thousand fueled cores with an approximate diameter of 0.060 inch were made.

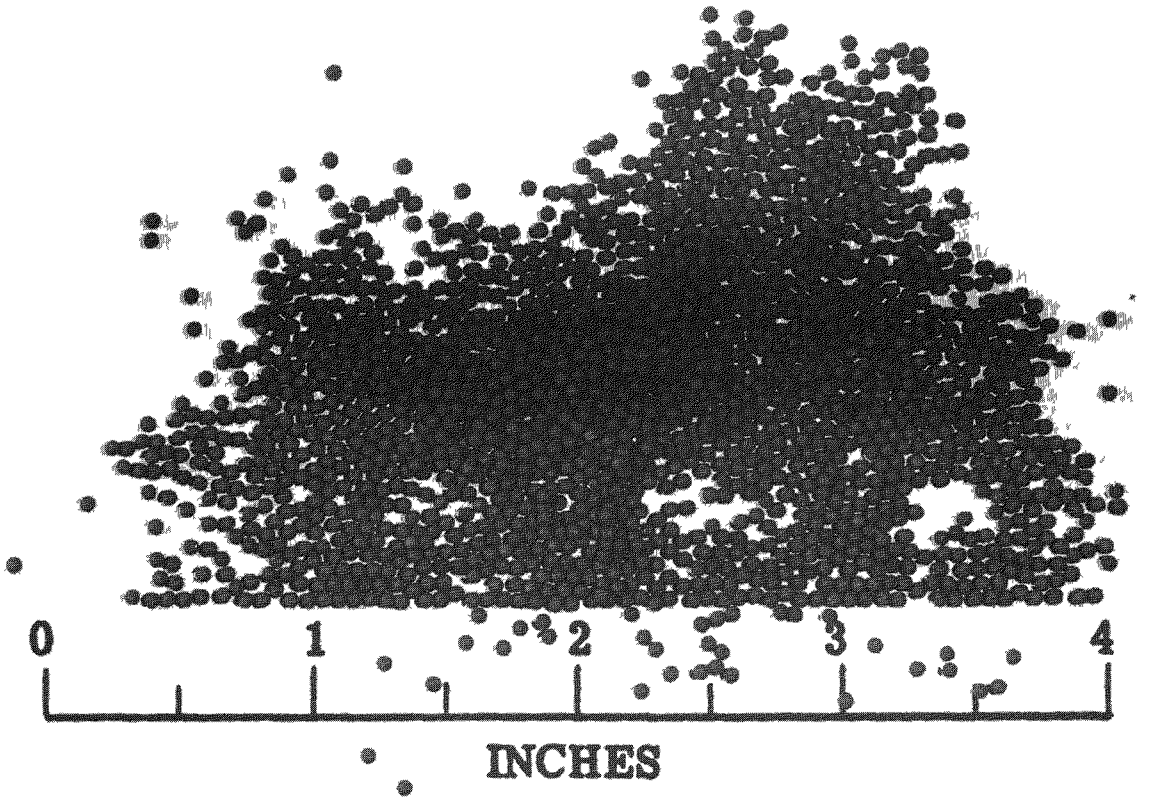

Fig 7 – Typical 40 UO_2 - 60 $MoSi_2$ cores after firing

The largest number of runs has been made with slips of $MoSi_2$ and of 40 UO_2 - 60 $MoSi_2$. Typical running conditions for slips of $MoSi_2$ are: a pH of 2.1, a specific gravity of 3.37, and a viscosity of 2400 centipoises. The 40 UO_2 - 60 $MoSi_2$ slip is usually used at a specific gravity of 4.10 with a pH of 2.0 and a viscosity of 2300 centipoises.

Figure 7 is a photograph of 40 UO_2 - 60 $MoSi_2$ cores after firing, and Table 1 summarizes the physical measurements on a group of similar cores fired to 2200°F in hydrogen. These cores were low-fired at 2200°F for later use in coating studies. Table 1 indicates excellent control over the weight and size. This control is sufficient for any contemplated

TABLE 1

PHYSICAL DIMENSIONS 40 OF UO_2 - 60 $MoSi_2$

CORES PRODUCED BY CAPILLARY-DROP METHOD

Number of cores in group	24,000
Number of cores sampled at random	50 for weight 15 for size (10 measurements on each)
Average weight	0.0054 g
Standard deviation	0.0001 g
Average diameter of group	0.0483 in.
Average variation of sample's average from group average	0.00035 in.
Average variation of each sample from each sample's average	0.00076 in.

pebble-bed fuel element. Beryllium oxide spheres have also been made on the capillary-drop system. The slip was used at a specific gravity of 2.05 and a pH of 1.9.

COATING OF CORES

One method investigated for coating pebble-type fuel element cores is essentially the same one used by the pharmaceutical industry for sugar-coating pills and tablets. In the pharmaceutical process a large number of cores are rolled in an inclined, open-ended, apple-shaped coating pan. While rolling, the cores are alternately dampened and dusted until the coating is of the desired thickness.

The complexity of the process may be understood from a listing of some of the affecting variables: (1) shape of cores, (2) surface condition of cores, (3) uniformity of size of cores, (4) particle size of coating material, (5) viscosity of dampening agent, (6) shape of coating pan, (7) peripheral velocity of the coating pan, (8) load in the pan, (9) degree of wetting, and (10) the method of powder application.

The equipment which has been used for coating reactor pebbles consists of a 5-inch-diameter glass brandy snifter the base of which is attached to a variable speed motor drive. It is inclined 27° from the horizontal, and rotated at 127 rpm. The inside surface of the brandy snifter was roughened by grinding with silicon carbide. A good load for this arrangement is approximately 50,000 cores of 0.050-inch diameter. The best dampening medium found for $MoSi_2$ base cores is a water solution of methyl cellulose, the viscosity of which is 110 ± 10 centipoises. Care is taken to dampen the cores uniformly by spraying this solution onto the rolling cores very slowly and halting when the cores begin to stick together. After the cores have been dampened, powdered molybdenum disilicide is allowed to fall rapidly onto the rolling cores, and after approximately five minutes of additional rolling, the cores have been uniformly coated. A cross section of a 40 UO_2 - 60 $MoSi_2$ core coated in this manner is shown in Figure 8.

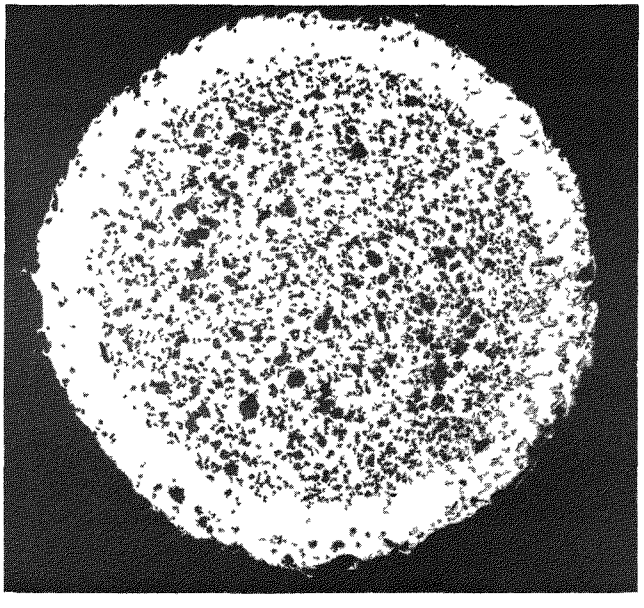

Fig 8 – Cross section of coated 40 UO_2-60 $MoSi_2$ core Note porosity

Investigation of the coating pan method has determined that the particle size distribution of the molybdenum disilicide is of major importance in obtaining a smooth uniform coat. The 13.0-micron powder which is used for core production produces a lumpy, non-uniform coat, but a powder with an average particle size of 18.9 microns yields very

smooth, uniform coatings. However, it appears that it is not the average particle size which is significant in this matter, but the particle size distribution; additional work is contemplated to determine the optimum particle size distribution. The cores coated by this method had been made only by the capillary drop method.

After the 40 UO_2 - 60 $MoSi_2$ cores are coated, they are fired to 1600°C to form a dense composite body, but two problems became apparent: (1) the particle size distribution necessary for a smooth uniform coat will not sinter to a dense body at 1600°C, which because of probable dissociation of molybdenum disilicide is the maximum desired temperature, and (2) the coat as applied, being of lower density than the low-fired cores, shrinks with the formation of cracks, as shown in Figure 9. Several approaches have been employed in an effort to overcome these difficulties, but they have not yet proved fruitful. Any future work planned in this area should include the use of cores fired at lower temperatures to lessen the differential shrinkage, and the use of metallic additives to improve sintering.

Fig 9 – Cracking of cladding on 40 UO_2 - 60 $MoSi_2$ cores