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Fabrication of Uranium Oxycarbide Kernels for HTR Fuel

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Abstract – *Babcock and Wilcox (B&W) has been producing high quality uranium oxycarbide (UCO) kernels for Advanced Gas Reactor (AGR) fuel tests at the Idaho National Laboratory. In 2005, 350-µm, 19.7% ^{235}U-enriched UCO kernels were produced for the AGR-1 test fuel. Following coating of these kernels and forming the coated-particles into compacts, this fuel was irradiated in the Advanced Test Reactor (ATR) from December 2006 until November 2009. B&W produced 425-µm, 14% enriched UCO kernels in 2008, and these kernels were used to produce fuel for the AGR-2 experiment that was inserted in ATR in 2010. B&W also produced 500-µm, 9.6% enriched UO_2 kernels for the AGR-2 experiment. Kernels of the same size and enrichment as AGR-1 were also produced for the AGR-3/4 experiment. In addition to fabricating enriched UCO and UO_2 kernels, B&W has produced more than 100 kg of natural uranium UCO kernels which are being used in coating development tests. Successive lots of kernels have demonstrated consistent high quality and also allowed for fabrication process improvements. Improvements in kernel forming were made subsequent to AGR-1 kernel production. Following fabrication of AGR-2 kernels, incremental increases in sintering furnace charge size have been demonstrated. Recently small scale sintering tests using a small development furnace equipped with a residual gas analyzer (RGA) have increased understanding of how kernel sintering parameters affect sintered kernel properties. The steps taken to increase throughput and process knowledge have reduced kernel production costs. Studies have been performed of additional modifications toward the goal of increasing capacity of the current fabrication line to use for production of first core fuel for the Next Generation Nuclear Plant (NGNP) and providing a basis for the design of a full scale fuel fabrication facility.*

I. INTRODUCTION

The goals of the NGNP/AGR Fuel Development and Qualification Program include providing fuel qualification data to support licensing of the NGNP and supporting near-term deployment of the NGNP in the United States by reducing market entry risks posed by technical uncertainties associated with fuel production and qualification [1.]. Fuel qualification data is being generated by a series of irradiation tests at the Idaho National Laboratory. Fuel kernels for all the tests have been or will be produced by Babcock and Wilcox. As fabrication proceeds from one fuel to the next, process improvements are being made

toward the goal of establishing a commercially viable fuel manufacturing process.

Uranium dioxide (UO_2) and uranium oxycarbide (UO_2-UC_2-UC, often designated "UCO") microspheres for High Temperature Gas Reactor (HTR) fuel have been fabricated using external gelation, internal gelation, and a combination of these two processes [2.]–[8.]. The terms internal and external gelation refer to the source of the ammonia ion which provides a necessary component in the gelation process. In external gelation, the ammonia ion is provided from an external source, such as an ammonia hydroxide vapor, through which the formed particle passes. Internal gelation utilizes an internal source of ammonia, which is normally triggered to release its ammonia by a combination of pH difference and temperature. Kernel fabrication processes include steps of preparing a uranium solution, forming gelled microspheres, sintering the microspheres, upgrading kernels by removing undersize, oversize and high aspect ratio kernels, and performing quality control analyses to verify conformance with fuel specifications.

B&W chose the internal gelation particle process in the late 1980's after review of available literature data and consultation with Oak Ridge National Laboratory (ORNL) personnel. B&W has utilized the internal gelation process to produce particles of various types including UC/UC_2/UC-ZrC, UO_2, UCO, and uranium nitride (UN). In the latter case, B&W produced high purity UN for the fabrication of UN pellets using the internal gelation process. The UN particles produced were high purity and low density material that could be added directly to the die cavity and pressed to form high dense uniform pellets.

B&W has produced ^{235}U enriched UCO and UO_2 kernels in support of the Advanced Gas Reactor (AGR) tests at the Idaho National Laboratory. Kernels containing natural uranium have also been produced for use in coating tests. Four lots of enriched kernels – 3 of UCO and 1 of UO_2 – have been produced along with more than 100 kg of natural uranium kernels.

II. AGR-1 KERNELS

Irradiation of AGR-1 fuel was very successful, with no particle failures detected over the 3-year irradiation to a burn up of 19% **Error! Reference source not found.**. Yet based on the experience of fabricating and characterizing AGR-1 kernels, it was recognized that improvements could be made in both kernel product quality and the kernel fabrication process performance. Kernels from the AGR-1 lot are shown in Figures 1 and 2. While many of the kernels have a similar appearance, differences in chemistry, shape, density and surface morphology can be seen.

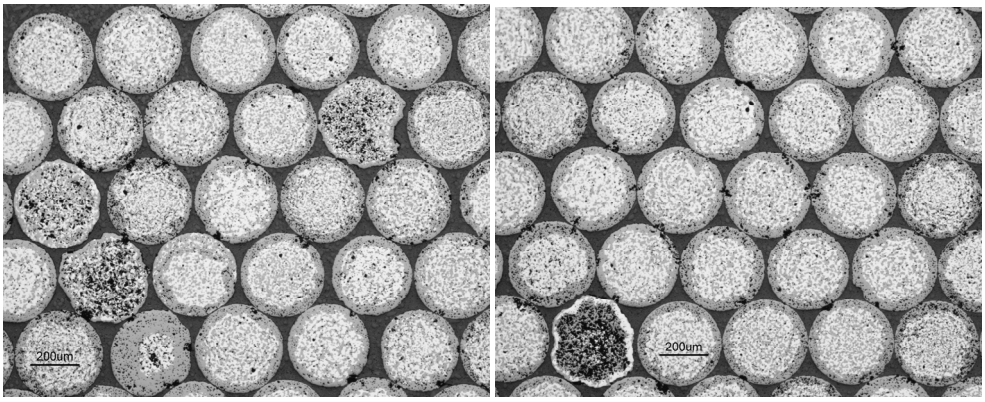


Figure 1. Image of ceramographic mount of kernels from AGR-1 lot.

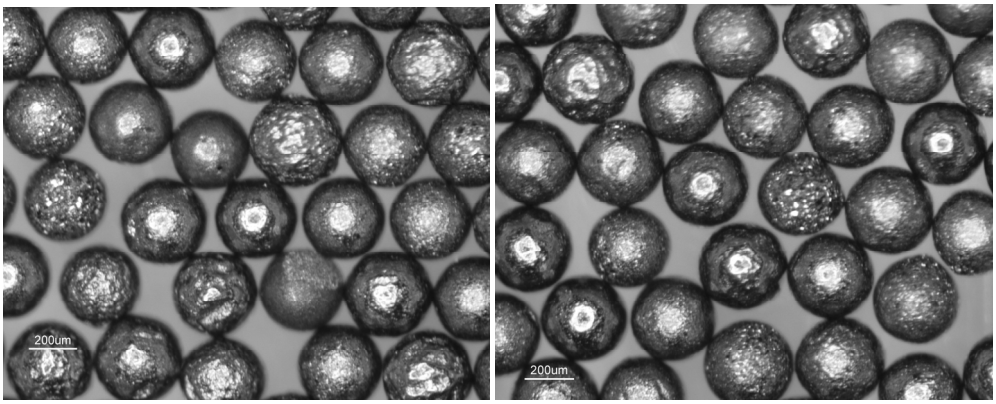


Figure 2. Image of loose kernels from AGR-1 lot.

III. INITIAL PROCESS IMPROVEMENT & AGR-3 & 4 KERNELS

Following production of kernels for AGR-1, B&W performed process improvement tests aimed at reducing the variability of kernel properties within batches and from batch to batch. These tests included evaluating and changing the carbon feed material, changing the way carbon was mixed into the broth, optimizing broth parameters, and testing alternative sintering schedules. More details and results of these studies were reported at the HTR 2006 conference [10.].

Kernels for AGR-3 & 4 irradiation tests were produced midway through the process improvement studies, and were produced to the same specifications as AGR-1 fuel. Improvement in quality is visible in the images of the kernels, as is evident in Figure 3. The sectioned kernels appear much more homogeneous in chemistry and density, and fewer kernels are seen with nonspherical shapes. Loose kernels appear similar to AGR-1 kernels, except without any showing a highly crystallized surface.

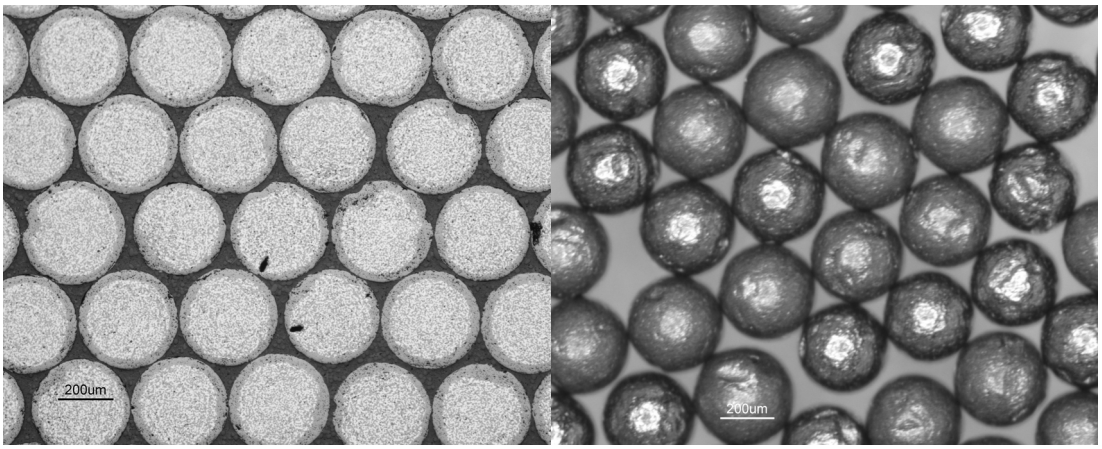


Figure 3. Images of mounted and loose kernels used for AGR-3 & 4 fuel.

IV. AGR-2 AND NATURAL URANIUM KERNELS

Kernels for AGR-2 fuel were produced in 2008. The AGR-2 specification for UCO kernels increased the mean diameter to 425 µm from 350 µm used for AGR-1 and AGR-3 & 4. The UO_2-kernel mean diameter specification was 500 µm. Five batches of UCO kernels were composited to make up an 8.4 kg lot of 14% enriched UCO product and seven batches of UO_2 kernels composited into an 8.5 kg lot of UO_2 kernels. Images of AGR-2 UCO kernels are shown in Figure 4, and UO_2 kernels, in Figure 5. The most noticeable difference in AGR-2 kernels compared to AGR-1 and AGR-3 & 4 is the appearance of the loose kernels, showing a very smooth, reflective surface.

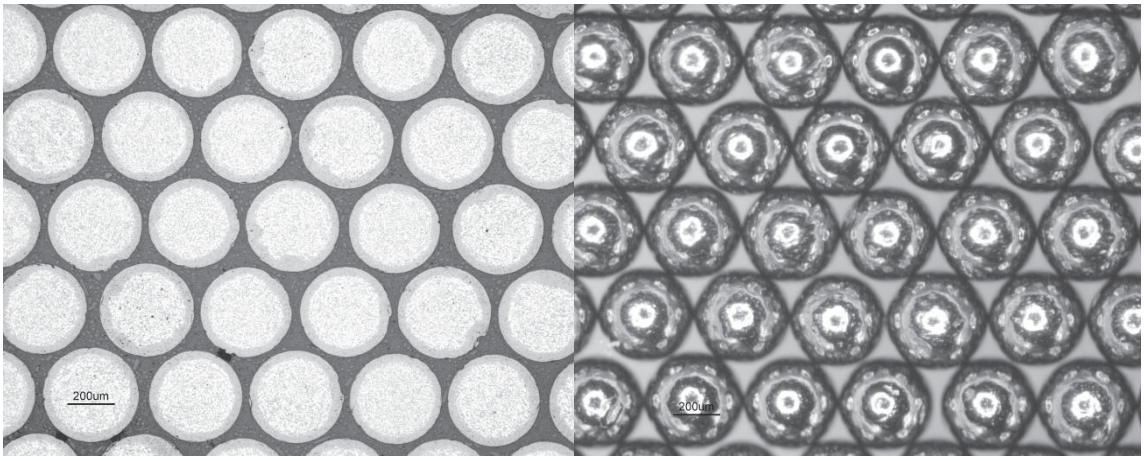


Figure 4. Images of mounted and loose kernels used for AGR-2 UCO fuel.

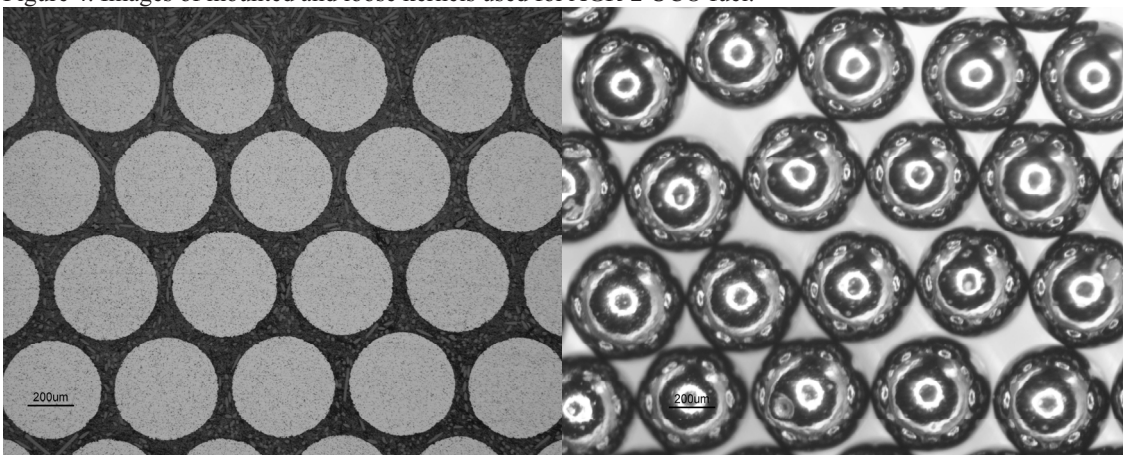


Figure 5. Images of mounted and loose kernels used for AGR-2 UO_2 fuel.

Six lots of natural uranium kernels were produced in the period 2007-2009, totaling approximately 100 kg. Images from the most recent lot are shown in Figure 6 and have an appearance nearly identical to that of AGR-2 kernels. This lot of nearly 40 kg included combined kernels from 14 sintering runs plus 6 kg of residual kernels from the previous lot.

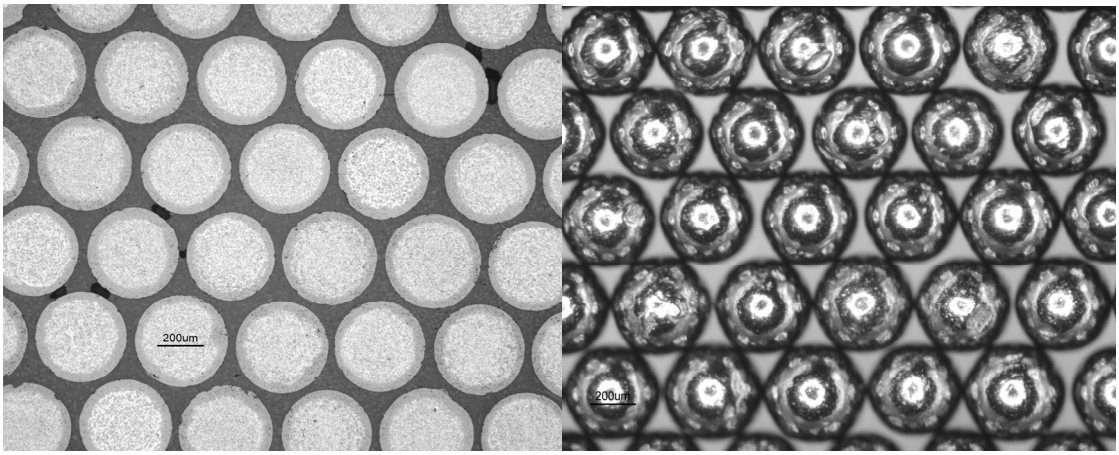


Figure 6. Images of mounted and loose natural uranium UCO kernels, lot 69311.

IV. PROPERTY COMPARISONS

Advanced Gas Reactor requirements for kernels include specifications for the diameter, aspect ratio,

density, and chemistry. A summary comparison of kernel lot properties is shown in Table 1. The AGR fuel specification document allows a tolerance of ±10 μm on the mean kernel diameter, and Table 1 shows that a deviation of less than 9 μm has always been achieved. The diameter standard deviation is typically 8-12 μm for a kernel lot and 5-9 μm for a kernel batch.

The mean kernel aspect ratio for all lots has been close to 1.01, indicating the kernels formed by the B&W internal gelation process are, on average, more spherical than those formed by other gelation processes, which typically have a mean aspect ratio of 1.05. For example, the mean aspect ratio of German reference fuel kernels, based on analysis of about 6700 kernels from the EUO 2358-2365 composite, was 1.05 [11.]. Also, Chinese researchers report an average aspect ratio of 1.04 for 52 batches of kernels using the Total Gelation Process of Uranium (TGU)[6.].

The improvement of product quality over time is clearly seen in the trend of aspect ratio standard deviation. As shown in Table 1, the standard deviation of the aspect ratio for AGR-1 kernels was 0.016, and decreased to 0.012 for AGR-3 & 4 kernels, 0.007 for AGR-2 UCO kernels and 0.005 for kernels produced after AGR-2 UCO.

Mean kernel densities and density standard deviations are very consistent and well above the specification minimum density for all kernel lots.

	Mean diameter, microns	Target diameter, microns	Diameter standard deviation	Mean aspect ratio	Aspect ratio standard deviation
AGR-1	348.4	350±10	8.3	1.013	0.016
AGR-3 & 4	358.6	350±10	8.8	1.010	0.012
AGR-2 UCO	426.7	425±10	8.8	1.012	0.007
AGR-2 UO_2	507.7	500±10	11.9	1.008	0.005
Lot 69311	429.3	425±10	11.0	1.011	0.005
	Mean density, g/cm^3	Density standard deviation	Chemistry, mole %		
			UO_2	$UC_{1.86}$	UC
AGR-1	10.7	0.026	67.9%	0.4%	31.7%
AGR-3 & 4	10.9	0.030	71.4%	8.9%	19.7%
AGR-2 UCO	11.0	0.030	71.4%	12.3%	16.4%
AGR-2 UO_2	10.9	0.029	100%	NA	NA
Lot 69311	10.8	0.023	72.3%	13.8%	13.9%

Table 1. Comparison of kernel lot properties.

AGR kernel chemistry specifications include a minimum uranium concentration and specified carbon and oxygen contents, expressed as mole fractions of carbon/uranium and oxygen/uranium ratios. U-C-O chemistry is complex, and compositions shown in Table 1 assume the kernels consist entirely of the three compounds UO_2, $UC_{1.86}$ and UC. Almost all carbon in AGR-1 kernels was contained as UC, with only a small fraction as $UC_{1.86}$. The fraction of $UC_{1.86}$ increased to about 9% for AGR-3 & 4 and increased further to 12% for AGR-2 UCO kernels. One means of increasing the kernel carbide content is to change the feed carbon-black-to-uranium ratio in the forming process. A second way is to change sintering conditions.

V. SINTERING STUDIES

To support kernel sintering improvements, B&W recently procured and installed a 2.5-inch diameter furnace. A series of sixteen tests were performed in this furnace in late 2009 and early 2010 in which process parameters were systematically varied.

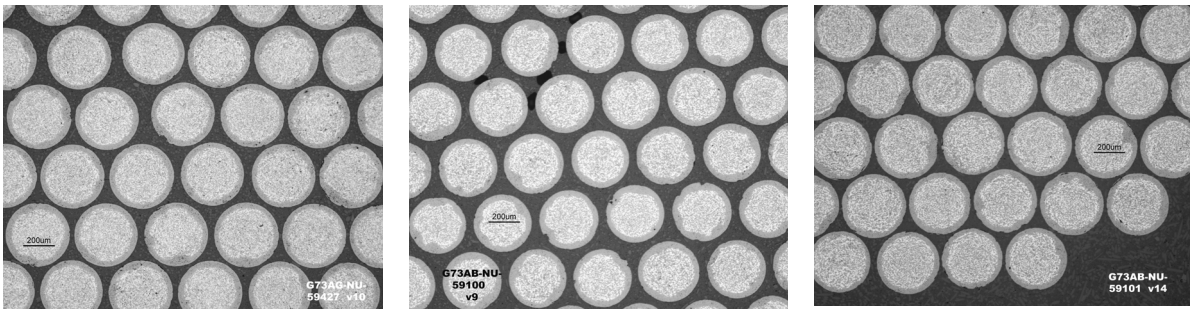
The first goal of these tests was to establish that comparable sintered product was produced in the two furnaces when using nominally the same process conditions. The comparison of properties shown in Table 2 and images of kernels shown in Figure 7 provide confidence that results of the two furnaces were very similar. Based on results of many other 6-inch furnace runs, the density of kernels from run 59426 was somewhat anomalous, as densities in the range 10.8-11.0 g/cm^3 are nearly always observed.

The sintering schedule used for the "baseline" tests is shown in Table 3. In one series of tests, the hold time at 550°C was reduced from the baseline 60 minutes to 45 minutes in one test and 30 minutes in another. No significant changes in sintered kernel properties were observed.

Decreasing the hold time at 1680°C without changing the baseline gas composition resulted in slightly lower density (decreasing only from 10.89 to 10.81 g/cm^3 when changing from a 60-minute to a 4-minute hold), no change in UO_2 content, a slight increase in UC_2, a corresponding decrease in UC content, and an increase in the sulfur concentration.

Run	Mean diameter µm	Sphericity Mean Ratio	Density	U	C	C/U	O	O/U	S (ppm)
2.5-inch furnace tests									
59100	423.16	1.012	10.93	89.58	1.80	0.399	8.630	1.433	538
59101	424.60	1.013	10.89	89.54	1.82	0.403	8.625	1.433	580
59103	421.22	1.012	10.85	89.51	1.83	0.404	8.625	1.433	538
6-inch furnace tests									
59426	431.07	1.013	10.55	89.48	1.86	0.411	8.640	1.436	494
59427	423.32	1.011	10.82	89.59	1.86	0.411	8.620	1.431	598

Table 2. Comparison of kernel properties for "baseline" tests in the two different furnaces.



Run 59427 (6" furnace) Run 59100 (2.5" furnace) Run 59101 (2.5" furnace)

Figure 7. Comparison of kernels from tests in the two furnaces.

Segment	Temperature	Process Gases	Hold/Ramp
1	RT-100°C	100% Ar	4°C per minute
2	100°C -550°C	6% H_2 and 94% Ar	4°C per minute
3	550°C	6% H_2 and 94% Ar	60 minutes-hold
4	550°C -1680°C	100% Ar	40°C per minute
5	1680°C	100% Ar	4 minutes-hold
6	1680°C	60% CO/40% Ar	60 minute hold
7	1680°C -1920°C	60% CO/40% Ar	40°C per minute
8	1920°C	60% CO/40% Ar	60 minute-hold
9	Cool down	100% Ar	75°C per minute (unregulated)

Table 3. Baseline sintering schedule.

Changing the conditions of the final densification step had the largest effect on both kernel density and kernel stoichiometry. Reducing the temperature from 1920°C to 1880°C resulted in a decrease in density from 10.89 to 10.72 g/cm^3, a 24% increase in the UC_2 content, and a slight increase in the UO_2 content. Reducing the sintering time to 30 minutes without changing temperature reduced the density to 10.58 g/cm^3 without significantly affecting kernel chemistry. Changing the gas composition for the densification step from 60% CO/40% Ar to 100% CO resulted in changes similar to reducing the temperature.

Two runs were made at the end of the test sequence in which the most promising changes were implemented into a modified sintering schedule. The changes from those shown in Table 3 were (1) reducing the hold time at 550°C from 60 to 30 minutes, (2) reducing the hold time at 1680°C in CO from 60 to 4 minutes, and (3) increasing the CO concentration from 60% CO to 100% CO for segments 6 through 8.

These changes were recommended to improve the chemical composition (increasing the UC_2 content) of the UCO kernel product and to improve the sintering cycle efficiency relative to cost and time. The cycle time was reduced by 90 minutes (12% of the total cycle time) and the total CO usage reduced by approximately 20%.

The results of the two runs using the recommended modified conditions are shown in Table 4, and they confirm that the desired chemical composition change and production efficiency goals can be achieved. Compared to kernels produced using the “baseline” sintering schedule, the revised sintering schedule results in a lower density, a consequence of the shift to an increased UC_2 fraction. This modified sintering schedule will undergo additional testing in the pilot scale furnace later this year.

Run	Mean diameter (µm)	Sphericity Mean Ratio	Density	U	C	C/U	O	O/U	S (ppm)
2.5-inch furnace using baseline tests									
59100	423.16	1.012	10.93	89.58	1.80	0.399	8.630	1.433	538
59101	424.60	1.013	10.89	89.54	1.82	0.403	8.625	1.433	580
59103	421.22	1.012	10.85	89.51	1.83	0.404	8.625	1.433	538
2.5-inch furnace using modified sintering schedule runs									
59115	430.30	1.023	10.55	89.30	1.93	0.430	8.710	1.450	429
59116	427.60	1.013	10.59	89.23	1.89	0.420	8.790	1.470	279

Table 4. Results of modified sintering schedule tests.

VI. PRODUCT YIELDS

Table 5 shows the yields of product kernels from both kernel forming and sintering steps. Scrap product from the forming process results from system holdup and system upset conditions, while scrap from sintering includes undersize and oversized kernels separated by size classification and kernels removed by tabling. Over time, product efficiencies have increased for both the forming and sintering processes. While no specific efforts have been made as yet to improve product yields, the increase is seen as a byproduct of other changes to improve homogeneity and, also, of increased operator experience.

	Process Yields for			
	AGR-1 UCO	AGR-2 UO_2	AGR-2 UCO	2009 Natural Uranium UCO
Forming	86.2%	93.1%	93.6%	94.7%
Sintering	72.6%	77.4%	86.6%	87.5%
Combined	62.6%	72.1%	81.1%	82.9%

Table 5. Yields from the B&W kernel fabrication process.

VII. PROCESS THROUGHPUT

The production rate of a full-scale fuel manufacturing plant to support an NGNP has not been clearly established. One estimate of the required annual production is 2400 kg (as uranium) of 350-µm UCO kernels.

The current capacity of the B&W pilot kernel-fabrication line is about 120 kg U per year based on a single shift per day, 5-day per week, 40 week per year operation. The rate is limited by the forming line, specifically washing and drying the kernels. With relatively minor modifications to the forming line, and assuming the same operating basis, a rate of 240 kg U per year is achievable. The current B&W facility is primarily designed as a development facility and is licensed to handle all uranium enrichments (from depleted to fully enriched materials); the ability to process HEU material limits the throughput capacity of the facility. However, the key components in the system are essentially full-scale equipment which could be used in a production facility. For example, the forming system currently used would be used in a continuous rather than batch mode and would have a multiple-nozzle feed. The product collection system would need to be modified for the larger output, but only in the number of available receivers, and not necessarily in the receiver design. The current sintering furnace, if used in a three shift operation, could produce up to 5 runs per week and is capable of charge sizes of 5 kg or more if used in an LEU facility with appropriate nuclear criticality-safety controls. This would permit up to 1000 kg U per year from one such furnace. The base systems being developed under this program are readily scalable to a full-size production facility with capacity in ranges sited above.

VIII. CONCLUSIONS

Capability to fabricate high quality UCO and UO_2 kernels for High Temperature Gas Reactor fuel has been established at Babcock and Wilcox. The fabrication line has demonstrated production of 350- and 425-µm UCO kernels and 500-µm UO_2 kernels. High quality and high yields have been consistently achieved.

Several changes have also been successfully demonstrated that increase the process throughput or reduce run time. Additional steps are underway or planned for further increases in throughput of several unit operations. These include modifications to the wash/dry system to double the capacity of the kernel forming line, modifications to the acid deficient uranyl nitrate (ADUN) systems to reduce the cycle time, and increasing throughput of kernel upgrading.

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