Carbon Coating of Simulated Nuclear Waste Material

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March 1982

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SUMMARY

Coated particle waste forms have been developed as part of the multi-barrier concept at Pacific Northwest Laboratory (PNL) under the Alternative Waste Forms Program for the Department of Energy (DOE). Battelle Columbus Laboratory (BCL), under subcontract to PNL, was assigned the task of coating simulated nuclear waste glass marbles and ceramic pellets with low-temperature pyrolytic carbon (LT-PyC) using the chemical vapor deposition (CVD) process. This effort at BCL was a continuation of previous subcontracts from PNL to develop high temperature PyC, Al_2O_3 and SiC, CVD coatings for ceramic nuclear waste forms. The development of LT-PyC coatings as described in this report was initiated to reduce the release of volatile waste form components and to permit the coating of larger glass marbles that have low temperature softening points (550 to 600°C). Fluidized bed coaters for smaller particles (<2mm) and newly developed screw-agitated coaters for larger particles (>2mm) were used.

Coating temperatures were reduced from >1000°C for conventional CVD high temperature PyC to ~500°C by using a catalyst. The coating gas combination that produced the highest quality coatings was found to be $Ni(CO)_4$ as the catalyst, C_2H_2 as the carbon source gas, and H_2 as a diluent. Carbon deposition was found to be temperature dependent with a maximum rate observed at 530°C. Coating rates were typically 6 to 7 $\mu m/hour$.

The screw-agitated coater approach to coating large-diameter particles was demonstrated to be feasible. Clearances are important between the auger walls and coater to eliminate binding and attrition. Coatings prepared in fluidized bed coaters using similar parameters are better in quality and are deposited at two to three times the rate as in screw-agitated coaters.

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INTRODUCTION

PyC COATING

The program covered by this report was carried out during the period October 1, 1979 to September 30, 1981 at Battelle's Columbus Laboratories (BCL) where it had been demonstrated earlier^(a,b) that coatings pyrolytic carbon (PyC) and alumina applied to simulated supercalcine nuclear waste pellets by chemical vapor deposition (CVD) provided protection against leaching and oxidation.

The present program had as its first objective a reduction of the coating temperature for carbon from that used previously (900–1100°C) to a level compatible with less refractory forms of nuclear waste materials such as glass marbles and more volatile components such as cesium. The second objective was the development of a reactor suitable for coating the larger diameter (~12 mm) and less refractory particles in one-liter quantities. Substrates supplied by Pacific Northwest Laboratory (PNL) were coated with low temperature pyrolytic carbon (LT-PyC) for the purpose of demonstrating a commercially acceptable remote-operated reactor concept, as well as to provide samples for PNL evaluation.

The prospect of decreasing the carbon coating temperature resulted from the work of Neumann and Kofler (1979) wherein the addition of readily dissociated nickel carbonyl $[\text{Ni}(\text{CO})_4]$ to the hydrocarbon coating atmosphere permitted the chemical vapor deposition of carbon at temperatures of 450°C and below. This result was consistent with the low-temperature deposition of carbon at nickel, iron, and cobalt surfaces, which has been studied earlier, primarily by Lobo and Trimm (1971, 1973a, 1973b), Lobo, Trimm and Figueiredo (1972, 1974), Lobo (1973), Bernardo and Lobo (1975, 1976), and Bernardo and Trimm (1976).

(a) Browning, M. F., and R. W. Kidd. 1977. "The Development of Chemically Vapor Deposited Coatings for the Multi-barrier Waste Form Program." Unpublished Annual Report to Pacific Northwest Laboratory.

(b) Browning, M. F., and R. W. Kidd. 1978. "The Development of Chemically Vapor Deposited Coatings for the Multi-barrier Waste Form Program." Unpublished Quarterly Report to Pacific Northwest Laboratory.

The deposition of carbon from acetylene is actually favored thermodynamically at temperatures in the range of interest. The fact that carbon does not deposit on non-catalytic surfaces until higher temperatures implies a kinetic barrier to nucleation and growth. However, the barrier for precipitation of carbon from solid solution in nickel is much lower than that on non-catalytic surface, and the barrier to the decomposition of acetylene to form carbon in solid solution in nickel is also apparently low. Accordingly, carbon from the decomposing acetylene can dissolve in the nickel to form a slightly supersaturated solution, be transported to a site where a carbon deposit has nucleated and then precipitate. The rate of carbon deposition has been shown to be limited by the rate of diffusion through the nickel.

If this is indeed the mechanism, that is, if reaction of the hydrocarbon occurs where the nickel has access to the gas (i.e., is uncovered by carbon) and precipitation occurs at some random nucleation site on the nickel surface, the fundamental feasibility of forming an impervious coating by this method is brought into question. Despite this reservation, it was believed that in view of the potential results, efforts should be made to explore the technique fully, i.e., to cover the full range of parameters and to minimize other contributions to porosity, such as by occlusion of gas-phase precipitated material.^(a) This material, if incorporated in the coating, would contribute to porosity and therefore its formation should be suppressed. Accordingly, consideration was given to means of minimizing gas-phase-precipitation throughout the program.

(a) Carbon will not precipitate as such from acetylene at e.g., 450°C. However, gas-phase precipitation of nickel from the carbon can occur at temperatures above about 200°C (depending upon concentration) (Oxley and Carlton 1967). Once the nickel precipitates from the gas phase, it would be available to nucleate carbon.

COATING SUBSTRATES

As was the case in the previous program^(a,b) the substrates for coating were of various forms and whose physical properties were subject to change, since the nuclear waste forms were in a continuous state of development. Table 1 gives the pertinent characteristics of the simulated^(c) nuclear waste forms that were dealt with during the course of the program. The SPC-4E and MB-1 substrates were produced by disc pelletization and sintering at PNL and are essentially a ceramic material. The TDS-211 waste glass marbles were formed on a glass marble machine connected to a continuous ceramic melter at PNL. The glass composition simulates glasses typical of those developed for the Savannah River Plant.

As large quantities of these materials were not always available, part of the development work was done with stand-in materials. For example, although UO_2 differed considerably from the anticipated waste forms in particle size, density, and other characteristics, it was used in some of the exploratory work because of the convenience and sensitivity of leach testing the coated UO_2 particles in nitric acid as a means of assessing coating permeability. Table 1 also includes data on the stand-in materials.

COATING QUALITY

Two characteristics of the coatings are critical for success in the intended application:

- 1) Permeability, an intrinsic property
- 2) Integrity, i.e., uniformity and adherence

The permeability is a function primarily of coating conditions, temperature, pressure, nature and concentration of reactants, and nature and concentration

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- (a) Browning, M. F., and R. W. Kidd. 1977. "The Development of Chemically Vapor Deposited Coatings for the Multi-barrier Waste Form Program." Unpublished Annual Report to Pacific Northwest Laboratory.
 - (b) Browning, M. F., and R. W. Kidd. 1978. "The Development of Chemically Vapor Deposited Coatings for the Multi-barrier Waste Form Program." Unpublished Quarterly Report to Pacific Northwest Laboratory.
 - (c) Simulated chemical and physical characteristics without the radioactivity of actual waste.

TABLE 1. Characteristics of Nuclear Waste Forms and Principal Stand-In Materials

Material	Particle Size, mm	CTE(a) 10 ⁻⁶ C ⁻¹	Density, g/cm ³		Other Characteristics
			Pycnometer(b)	Bulk/0.65(c)	
Simulated Waste Forms					
SPC-4E	0.7 – 1.4 mm	NA	~4.34	~2.91	Porous
TDS-211 Marbles	8.7 – 14.9	6.7	NA	~2.46	Softening point
MB-1	~6 – 19	NA	NA	~2.95	Fragile
Stand-In Materials					
UO ₂	0.009 – 0.011	9	NA	NA	
Quartz Sand	0.297 – 0.590	13	~2.65	~2.47	

(a) Coefficient of thermal expansion (CTE) = $\Delta l/l_0$ per degree C

(b) Pycnometer density measured with, e.g., xylene, includes contributions of closed pores but not open pores.

(c) On the assumption of a 65% packing fraction for spherical particles, (bulk density/0.65) equals approximately the particle density including both open and closed porosity.

of catalyst. In the fluidized bed, the coating structure and hence the permeability is also influenced by the frequent collisions of particles with the surface on which the deposition of coating material is taking place.

Coating integrity is a complex function of coating/substrate geometry, thermal expansion differential between coating and substrate, thermal cycle to which particle is subjected during coating and cooling at conclusion of the coating step, and the intrinsic stress in the coating, all of which, together with the modulus of elasticity, determine the stresses tending toward coating failure. Whether or not coating failure or loss of integrity occurs under that stress is a function of coating strength and strength of adhesion to the substrate.

Unfortunately, data are not available for a mechanical analysis of all of the coating/substrate combinations encountered in this program. However, it is important to recognize the increased difficulty in obtaining coatings of a given thickness with good integrity as the diameter of the substrate is increased. For a "large" coating-thickness-to-particle-diameter ratio, the bond between coating and substrate can fail when the substrate shrinks more than the coating on cooling from deposition temperature leaving a self-supporting coating in the form of an integral shell. This self supporting characteristic of the loose shell is lost at some point as the substrate diameter increases and, although of potential importance in the previous work with smaller particles, is probably not a factor in the 50 μ m carbon coatings on the larger (0.5 cm to 1.0 cm) substrates of primary interest in the present program.

Another significant factor that must be considered when the size of the substrate to be coated is increased is the increased energy of particle-to-particle collision for a given level of agitation. In the case of dense, strong coatings, the effect is insignificant. However, with weaker coatings, the level of agitation required for particle circulation may well result in loss of coating by abrasion, except for very small particles. In the case of some of the weaker low-temperature PyC coatings obtained in the present program, concurrent abrasion of the coating appears to have been a major factor, the coating having been much thicker in recesses than on convex surfaces.

The coefficient of thermal expansion (CTE) of the low-temperature carbon of interest in this program has apparently never been measured. In fact, the material has probably not been obtained in a sufficiently rigid form for the thermal expansion to be measured directly, although it might be possible to calculate it from the deflection of a thin sheet of a selected substrate on which a layer of the low-temperature pyrolytic carbon has been deposited. The thermal expansion coefficients of carbon vary over a wide range, depending upon whether the carbon is amorphous, vitreous, or graphitic low-temperature pyrolytic carbon can form as columns of preferentially oriented graphitic flakes, e.g., with an interlayer spacing (C_0) of 3.40 Å corresponding to 47 percent graphitization (Baird 1977). Thus, depending upon the average orientation of the material deposited in the present program, the coefficient of thermal expansion might be expected to fall between the extremes for anisotropic graphite crystals measured between ~ 0 and $25 \times 10^{-6}/^{\circ}\text{C}$ (between room temperature and $\sim 450^{\circ}\text{C}$), is highly unpredictable, to say the least.

The fact that the coatings deposited in the present program tended to spall from the glass marble substrates ($\text{CTE} = 8 \times 10^{-6}/^{\circ}\text{C}$) as though in residual compression suggests high CTE values ($> 8 \times 10^{-6}/^{\circ}\text{C}$), certainly greater than the $5.5 \times 10^{-6}/^{\circ}\text{C}$ given by Bokros and Akins (1971) for an isotropic carbon deposited in a fluidized bed at a temperature probably in the range of 1300 to 1500°C .

Not only was the lack of mechanical property data on the coating a severe limitation in the interpretation of the results throughout the program, but the inability to measure coating permeability quantitatively as a function of process conditions made it difficult to assess the progress of the work.

As no simple means of obtaining these items of basic information was available, assessment of results was limited to what could be learned from visual and metallographic examination and from leach tests of the coated materials. Thus, although a highly successful coating result would be recognized, incremental progress toward such a result would not.

In view of these limitations, the approach taken was to adjust the equipment design and the coating parameters in the ranges and in the direction which

on the basis of prior experience with CVD systems would tend toward a dense deposit of carbon on the substrates of interest. It was recognized that a trade-off might be involved between coating density and rate of deposition, as in general high CVD rates tend toward decreased density, particularly where gas-phase nucleated material is incorporated in the deposit. However, it was hoped that the trade-off could be resolved in a practical range.

LITERATURE REVIEW

Upon initiation of the current program a literature search was made to identify papers pertaining to the catalytic deposition of carbon from hydrocarbons. A computer search of Chemical Abstracts from 1977 through 1979 with the descriptors:

carbon + coating(s) + iron
film(s) cobalt
layer(s) nickel
deposition metal(s)
formation
whisker(s)
thread(s)

led to 1,045 citations of which 23 were deemed pertinent. Consultation of the contained references led to earlier work, and copies of the potentially most useful papers were obtained for background use. A list of those references not cited above is given as an Appendix. In the work cited, mostly of interest in nickel-catalyst technology, little attention has been given to maximizing the density of the deposits, and most refer to a porous or fibrous structure with occluded nickel crystallites which have been pulled from the original surface and are dispersed through the coating, continuing to provide local catalytic activity. It was hoped that by operating at low rates of deposition or by properly sequencing injections of nickel carbonyl into the feed gas, it might be possible in the present work to decrease the permeability of the deposits below that commonly observed, to a level that would be useful as a coating in nuclear waste management.

This report is organized into two sections corresponding to the types of coating equipment used:

- 1) Fluidized-bed (FB) coater for coating small particles and for suspension ("floating") of larger particles (>2 to 3 mm) during coating.
- 2) Screw-agitated coater (SAC), for coating the larger particles without having to use the suspension medium.

In addition to the use of the fluidized bed as a medium for suspending the larger particles during coating, it was used with small sand and UO_2 particles as stand-in substrates for the purpose of exploring the conditions necessary for depositing an impermeable low-temperature pyrolytic carbon (LT-PyC).

FLUIDIZED BED DEVELOPMENT

The fluidized-bed reactor was chosen for exploration in the present work because it is the most effective means of uniformly exposing a large surface area of particulate material to a reactant gas for CVD coating. It can be used effectively with particles up to 2 to 3 mm diameter (depending upon density) and can be used with even larger particles when a bed of smaller particles of properly chosen size and density is used to support them. These supporting particles are often referred to as "diluent", a carry-over of the term used for material added solely to provide volume to particles to be coated that are in short supply.

APPARATUS

The fluidized-bed equipment used in the present work is pictured schematically in Figure 1. In the initial work with nickel carbonyl $[\text{Ni}(\text{CO})_4]$ as a catalyst, the carbonyl and hydrocarbons (C_xH_y) were introduced together through the bottom inlet, but plugging of the inlet by premature reaction led to separation of the reactants either by introduction of the catalyst stream from the top of the bed through a water-cooled center tube or by introduction of the catalyst through the bottom of the reactor and C_xH_y through the top.

An important part of the equipment is the decomposer in the exhaust line, which is operated at 400°C to decompose the residual nickel carbonyl. In normal CVD coating from nickel carbonyl, the additional precaution of venting the exhaust through a gas burner would be taken to destroy traces of the residue. However, since the concentrations used in the present work were relatively low, it was deemed adequate to discharge the product of the decomposer directly to the laboratory hood in which the apparatus was housed.

Cobalt acetylacetonate and iron pentacarbonyl were also investigated as catalysts. However, their use is not depicted in Figure 1.

Except for a few experiments late in the program, the coating runs were carried out at atmospheric pressure.^(a) Although there are advantages in

(a) Atmospheric pressure (plus the hydrostatic head of the bubbler plus minor flow resistance).

FIGURE 1. Schematic Diagram of the Fluidized-Bed Coater and Associated Equipment Showing Alternatives for Introducing Reactants Separately

using a sub-atmospheric fluidized bed, such as decreased gas-phase precipitation and smoother fluidization, the hydrostatic head of the bed itself limits the effective vacuum for deeper beds. Further, a commercial operation would seek to avoid the complication of vacuum operation if it is still possible to obtain satisfactory coatings without it. Hence, the decision to concentrate on atmospheric pressure operation.

In addition to its use as a supporting medium for coating larger simulated waste forms for subsequent evaluation, the fluidized bed was used in three types of investigation:

- 1) Study of deposition parameters over a wide range
- 2) Study of the effect of hydrogen added to the reactants
- 3) Suppression of gas-phase precipitation.

These will be discussed in the following sections.

EFFECT OF PROCESS PARAMETERS ON COATING RATE

With the general objective of optimizing coating rate and quality, a series of exploratory fluidized bed runs were made with a 30 x 50-mesh quartz sand substrate in which the following parameters were varied:

Bed temperature: ~325 to ~625°C

Nature of carbon precursor: acetylene (C_2H_2), methane (CH_4),
propane (C_3H_8), heptane (C_7H_{16}), toluene ($C_6H_5-CH_3$)

Concentration of carbon precursor: ~1.5 to ~15 m/o

Nature of catalyst: nickel carbonyl [$Ni(CO)_4$], cobalt acetylacetonate
[$Co(C_5H_7O_2)_2$], iron carbonyl [$Fe(CO)_5$]

Catalyst concentration: 0.0 to ~12 m/o

Diluent gas: argon, hydrogen

In addition, alternating injections of catalyst and carbon precursor were explored, as well as intermittent (in place of continuous) injections of catalyst. Obviously, not all permutations and combinations of these parameters were used. However, the range covered was believed sufficient to justify a number of useful conclusions.

Figure 2 shows data, taken with similar conditions except for temperature, for deposition from acetylene. A maximum in the deposition rate is indicated in the neighborhood of 450 to 500°C, similar to the maximum at ~375°C reported by Baird (1977) for carbon deposits grown on nickel foils, where the character of the material changed from an open ($C_o = 3.44 \text{ \AA}$) columnar deposit to a tighter ($C_o = 3.36 \text{ \AA}$) structure at a higher temperature. At the higher temperature, the access of gaseous carbon precursor to the catalyst through the tighter structure may become limiting.

Figure 3 shows data for methane as a precursor, again showing a peak near 500°C. Based on past experience at BCL, it is somewhat difficult to believe that the actual carbon formation rate at 630 to 640°C would drop to 3 percent

FIGURE 2. Effect of Temperature on Deposition from Acetylene. Bed = 37 g of 30 x 50-mesh quartz sand in 25-mm-ID reactor. Total gas flow - 2650 to 3440 sccm. C₂H₂ as indicated plus 0.05 to 0.1 m/o Ni(CO)₄, balance Ar.

FIGURE 3. Effect of Temperature on Deposition from Methane. Bed = 32 g of 30 x 50-mesh quartz sand in 25-mm-ID reactor. Total gas flow = 2150 to 2570 sccm 15.0 m/o CH₄, 0.08 to 0.10 m/o Ni(CO)₄, balance Ar.

of its value at 530°C. Although Lobo and Trim (1971) show a drop to 10 percent between the 500°C peak and the 560°C valley for deposition from acetylene on a nickel foil, a decrease to 3 percent suggests the negative contribution of mechanical attrition to the net deposition rate.

For purposes of orientation, it should be noted that the rate of bed weight gain (~35 mg/min) at the peak in Figure 3 corresponds to the deposition of 10 μ m per hour of carbon of density = 1.2 g/cm³ on 40-mesh (420 μ m) spheres.

The following conclusions were drawn from analysis of the large number of deposition runs made in the above-described matrix:

- 1) Operation without a catalyst in the acetylene/argon or acetylene/hydrogen precursors yielded practically no carbon in the temperature range studied.
- 2) Consistent with the observations of Lobo, Trimm and Figueiredo (1974), cobalt acetylacetonate is less effective (1 to 10 percent as effective) as a catalyst than nickel carbonyl.
- 3) Ni(CO)₄ catalyst concentrations at the 1 m/o level result in relatively large quantities of gas-phase precipitated carbon.
- 4) Coating rates as high as 40 to 50 μ m/hour could be obtained from propane, 15 m/o; Ni(CO)₄, 0.12 m/o; argon, 84.9 m/o at 530°C. However, the coatings were porous, friable and non-adherent.
- 5) A carbon coating prepared on nickel-coated sand was very porous and friable, confirming the advantage of introducing the catalyst and precursor simultaneously or intermittently.
- 6) No single hydrocarbon, of those explored, stood out as being markedly more effective than the others in terms of resulting in both a high deposition rate and a good quality coating.
- 7) The addition of hydrogen (substitution for argon) to the acetylene plus Ni(CO)₄ system increased the deposition rate, consistent with the observations of Bernardo and Lobo (1975). However, the addition of hydrogen suppressed deposition from the saturated hydrocarbons, propane and methane.

Table 2 and Figure 4 show the effect of substituting hydrogen for argon in the deposition of carbon from acetylene.

TABLE 2. Effect of Hydrogen on the Catalyzed Deposition of Carbon from Acetylene

Hydrogen Concentration, m/o	Bed Weight Gain	
	g	mg/min
9.7	0.97	4.04
24.4	2.12	8.83
32.0	2.29	9.54
48.6	2.49	10.38
72.9	3.76	15.67
97.2	4.26	17.75

(500°C, C₂H₂ = 2.85 m/o, H₂ + Ar = 97.15 m/o, Ni(CO)₄ = 2.10⁻³ m/o, coating time = 4 hours, flow rate = 5.6 l/minute, weight of -30 +50 mesh quartz sand = 25g)

In contrast with the observation of Koss, Kofler and Neumann (1980), who found a maximum in the deposition rate versus hydrogen content of the H₂/Ar diluent, no maximum was found in the present work. No similar series of experiments was carried out in the present program for the other hydrocarbons; however, Table 3 contrasts the available results for bed weight gain from methane and propane in argon versus hydrogen. In each case the deposition rate was suppressed by the hydrogen. It will be noted that because of the lower gas density, higher volumetric flows were needed with hydrogen for equivalent fluidization. The rate of deposition was lower for the hydrogen atmosphere in spite of the increased rate of supply of carbon precursor (increased by a factor of $3995/2566 = 1.56$).

Figure 5 indicates that the rate of carbon deposition from acetylene in terms of bed weight gain at ~435°C increased linearly with concentration to 15 m/o. However, this conclusion must be tempered by the recognition that the "bed" collected at the end of the run contained an unknown quantity of 30 x 50-mesh agglomerates of porous carbon, not deposited as coating material.

Mole Percent Hydrogen in $H_2 + Ar + 2.85 \text{ m/o } C_2H_2 + 2.1 \times 10^{-3} \text{ m/o } Ni(CO)_4$ mixture

FIGURE 4. Effect of Hydrogen Addition on the Catalyzed Deposition of Carbon from Acetylene (see Table 2). Solid line: bed weight gain = $0.356 (\text{m/o } H_2) + 0.96$

FIGURE 5. Effect of C_2H_2 Concentration on Carbon Deposition Rate.
 $T = \sim 435^\circ C$ Bed: 32 g of 30 x 50-mesh quartz sand in
 25-mm ID reactor.

TABLE 3. Effect of Hydrogen on the Catalyzed Deposition of Carbon from Methane and Propane, $T = 525^{\circ}\text{C}$

Diluent	Reactants, m/o		Total Flow, SFCM	Bed Weight Gain, mg/min
	Precursor	Catalyst		
Ar, 84.9	CH_4 , 15.0	$\text{Ni}(\text{CO})_4$, 0.08	2566	35.8
H_2 , 84.8	CH_4 , 15.0	$\text{Ni}(\text{CO})_4$, 0.20	3995	17.8
Ar, 84.9	C_3H_8 , 15.0	$\text{Ni}(\text{CO})_4$, 0.12	2566	275.0
H_2 , 84.8	C_3H_8 , 15.0	$\text{Ni}(\text{CO})_4$, 0.20	3995	34.9

Fluidized bed: 32 g of 30 x 50-mesh quartz sand in 25-mm ID reactor

Also plotted in Figure 5 is the deposition rate in terms of rate of coating thickness increase as calculated from measured coating thickness at the end of the run. The drop-off at 15 m/o may reflect on attritions of the more porous carbon deposited under those conditions.

A leveling off of deposition rate (in terms of coating thickness) as a function of C_2H_2 concentration was also observed in a series of runs at higher temperatures (510°C) and at lower catalyst concentration [$\text{Ni}(\text{CO})_4 = \sim 2 \times 10^{-3}$ m/o] as shown in Figure 6. However, the leveling off occurred at lower C_2H_2 concentrations. The data shown in Figure 6 suggest that the rate may become catalyst-limited at the higher hydrocarbon concentrations. In contrast with the data of Figure 5, the bed weight gain also dropped off proportionately.

It is logical to assume that there exists some relationship between catalyst concentration and hydrocarbon concentration, such that the deposition rate could be either catalyst limited or hydrocarbon limited. This factor was never fully explored. However, the series of runs summarized in Table 4 suggest that the effectiveness of the catalyst can reach saturation at a very low level.

FIGURE 6. Effect of C₂H₂ Concentration on Deposition Rate at T = 510°C, Ni(CO)₄:2.1 ± 0.2 × 10⁻³ m/o, 32g of 30 x 50-Mesh Quartz Sand + 10g of 140 x 170-Mesh UO₂ in 25-mm-ID Reactor, Rate of Deposition Measured on UO₂

TABLE 4. Effect of Catalyst Concentration on Deposition Rate
at $T = 525^{\circ}\text{C}$, C_2H_2 Concentration = 2.9 m/o.

Run No.	$\text{Ni}(\text{CO})_4$ Concentration, m/o	Deposition rate on UO_2 $\mu\text{m}/\text{minute}$
151	0.35×10^{-3}	2.2
150	0.74×10^{-3}	4.0
149	2.2×10^{-3}	4.0

(Bed - 32 g 30 x 50-mesh quartz sand + 10 g 140 x 170-mesh UO_2 in 25-mm reactor, total flow rate = 5.6 ℓ/m , $\text{Ni}(\text{CO})_4$ plus H_2 introduced through capillary at apex of bed-support cone, C_2H_2 introduced downward from center tube terminating in bed 0.9 cm above apex.)

The use of $\text{Fe}(\text{CO})_5$ as a catalyst was explored briefly in a series of runs in the temperature range 420 to 480°C , at ~ 1.5 m/o C_2H_2 and from 0.001 to 0.08 m/o $\text{Fe}(\text{CO})_5$. Because of the fact that the coatings adhered poorly to the 30 x 50-mesh quartz sand particles (spalling of coating upon cooling), it was difficult to draw any firm conclusions other than that the $\text{Fe}(\text{CO})_5$ appeared to be generally less effective as a catalyst in terms of conversion of C_2H_2 to carbon under comparable conditions, and that gas-phase precipitation appeared to be less pronounced, owing to the greater stability of $\text{Fe}(\text{CO})_5$ relative to $\text{Ni}(\text{CO})_4$.

Another step taken to decrease gas-phase precipitation late in the program was to carry out the coating reaction at reduced pressure, 50 to 100 Torr in the apparatus shown in Figure 7. This step constituted a final effort to optimize all factors thought to contribute to a satisfactory coating. Accordingly, the simulated waste form SPC-4E in granular form (10 x 14 to 10 x 25-mesh) was used as the substrate in the temperature range 450 to 500°C . Because of the fragility of the SPC-4E and of the low temperature (LT) PyC coating, the bed lost weight during the runs and it was impossible to obtain any quantitative data on the effect of coating parameters on the rate of deposition.

The apparatus shown in Figure 7 proved to be similar to that pictured by Koss, Kofler and Neumann (1980) in a recent paper. Although the provision of a vacuum pump is shown by Neumann and Kofler for operating at reduced pressure, no data on the operating pressure are offered.

FIGURE 7. Apparatus for Coating SPC-4E Granules at Reduced Pressure

EFFECT OF PROCESS PARAMETERS ON COATING QUALITY

The objective of the present program was to obtain usefully impermeable coatings at economically viable rates of deposition. However, it became quite evident early in the work that the highest rates of coating formation tended toward the least dense and most friable coatings. In fact, it was not until the C_2H_2 concentration in hydrogen was reduced to 1.5 m/o and the $Ni(CO)_4$ catalyst concentration to ~0.03 m/o that the coating obtained could be classed as "hard" (i.e., dense and resistant to probing with a needle). That coating, pictured in Figure 8, is represented by the lower point at 1.5 m/o in Figure 5.

FIGURE 8. Nominal 4- to 5- μm Carbon Coating on 30 x 50 Mesh Quartz Sand (Lot No. 35445-88-54, 5093VD)

The data of Figure 5 were taken in conjunction with a series of runs made to determine how high the C_2H_2 concentration (and deposition rate) could be raised without losing the integrity of the coating obtained at 1.5 m/o C_2H_2 . However, evaluation of the coatings visually and by probing was not sufficiently quantitative to permit a correlation of coating quality with C_2H_2 concentrations. Therefore, the leach testing of UO_2 particles added to the fluidized bed was undertaken as a means of coating evaluation.

In earlier work at BCL the permeability of pyrolytic carbon coated UO_2 was assessed by oxidation in air at $\sim 400^\circ\text{C}$, at which temperature UO_2 was readily converted to U_3O_8 , but pyrolytic carbon was not oxidized. Leach testing of the coated particles was also of value, as low concentrations of uranium in the leach solution could be accurately measured (Browning et al. 1963).

A basic difference in the low-temperature pyrolytic carbon and the uncatalyzed high-temperature variety was demonstrated by the fact that the low-temperature coatings oxidized readily, indicating the presence of a large fraction of "dangling" bonds in the a-direction. Accordingly, leach testing in nitric acid was adopted.

Table 5 shows the results of leach testing UO_2 particles, coated under a variety of conditions. The one coating (Run 80) that showed a low level of permeability is distinguished by having been deposited at the lowest deposition rate and at the lowest catalyst concentration. Unfortunately, the unique results of Run 80 could never be reproduced, despite a large number of subsequent coating runs at comparable or presumably more favorable conditions. Part of the problem is due to the limited capability of the leach test. Except for very low permeabilities, the one-hour UO_2 leach test does not give a graded response. Once the UO_2 coating is breached, the reaction is disruptive of the carbon coating. Hence the "on-off" character of the results. In any future work with low-temperature PyC coatings, a non-destructive permeability test should be devised. Following the concentration as a function of time in the early stages before coating destruction may give useful results in a leach test, for example.

Figure 9 is a cross-section of the Run 80 product, showing a reasonably uniform 15-17 μm coating with very little porosity observable at the 540X magnification.

It is interesting to note that in all of the mixed-bed experiments, the coatings on the UO_2 particles were appreciably thicker than those on the quartz sand particles. One explanation is that some segregation persisted in the bed so that on the average the UO_2 particles occupied a region of the bed that was richer in hydrocarbon or in catalyst. The segregation explanation is somewhat substantiated since the coating rate on an all- SiO_2 bed was nearly the same as the coating rate on UO_2 in a UO_2 - SiO_2 bed (all other parameters constant). Another possibility is that the difference is related to coating attrition. In that connection it is significant that the SiO_2 particles have 22 times the mass of the UO_2 particles, so that the relative dissipation of

TABLE 5. Screening Test of Selected Low-Temperature PyC Coatings Prepared in a Fluidized Bed (10 g of 140 x 170-mesh UO₂ plus 32 g of 30 x 50-mesh quartz sand)^(a)

Lot No.	Coating System		Concentration (m/o)			Coating Temperature, °C	Deposition Rate, $\mu\text{m/hr}$ (or deposition time)	Coating Thickness (μm)	Weight Percent Loss of UO ₂ Substrate in ~1-hr 50 v/o HNO ₃ Leach at 100°C
	Hydro-Carbon	Diluent	Hydro-Carbon	Diluent	Ni(CO) ₄				
35715-26-72	C ₃ H ₈	Ar	14.99	84.98	0.023	525	~30	~30	~89.7
35715-36-76	C ₂ H ₂	Ar	15.18	84.97	0.035	525	~20	~20	~95.4
35715-46-81	C ₂ H ₂	Ar	15.17	84.74	0.089	520	~8	~33	~78.4
35715-30-74	C ₂ H ₂	H ₂	1.50	98.45	0.054	430	~6	~11	~100.0
35715-44-80	C ₂ H ₂	H ₂	1.49	98.50	0.014	445	~4	~16	~2.1, ~1.0 ^(b)
35715-48-82	C ₂ H ₂	H ₂	1.50	98.42	0.081	430	(1 hr) ^(c)	~32	~90.1
			3.75	96.17	0.081	430	(2 hr)		
			1.50	98.42	0.081	430	(1 hr)		
35715-50-83	C ₂ H ₂	H ₂	3.75	96.15	0.101	440	(2 hr) ^(c)	~35	~87.1
			1.50	98.40	0.101	440	(2 hr)		

(a) Hydrocarbon stream (+H₂) introduced from a "center tube" injector terminating in the fluidized bed, Ni(CO)₄ (+H₂) introduced from the capillary at the apex of the bed-support cone; 25-mm-ID reactor.

(b) Duplicate analyses.

(c) Because coating was deposited in stages as shown, it was not possible to calculate a meaningful deposition rate from the final coating thickness.

FIGURE 9. Nominal 15- to 17- μm PyC Coating on 140 x 170 Mesh Uranium Dioxide (Lot No. 35715-44-80, 5156 VD)

energy on collision at equal velocity of approach is $\text{UO}_2\text{-UO}_2 = 1$, $\text{UO}_2\text{-SiO}_2 = 22$, and $\text{SiO}_2\text{-SiO}_2 = 484$. However, the fact that the UO_2 particles outnumbered the SiO_2 particles $\sim 7/1$ may have imparted some cushioning relative to an all- SiO_2 bed which would tend to alleviate the effect. The relative importance of attrition and segregation in the observed coating thickness difference was not pursued.

It is probable that the permeability of the present coatings parallels their density. Thus techniques for measuring coating density were of interest. Measurement by the normal pycnometric technique would give a higher-than-actual result because of penetration of the open pores by the pycnometer fluid. Probing of the porosity with a mercury porosimeter has the disadvantage that a fragile coating can be crushed and densified during measurement by the higher pressures.

The expedient of measuring the change in bulk density due to coating was adopted as a simple means of approximating the coating density. Such

measurements were made for some of the material prepared with different concentrations of hydrogen, whose rates of deposition were analysed in Table 2 and Figure 4.

The weight of the coating material is the difference in the weight of the initial and final bed:

$$W_c = W_f - W_i$$

The volume of the particles in the material equals the bulk volume times the packing density, P :

$$\begin{aligned} V_i &= V_{Bi} \times P_i \\ V_f &= V_{Bi} \times P_f \end{aligned}$$

The packing density of the original bed can be obtained from the initial weight, density D_i , and measured bulk volume as:

$$P_i = V_i / V_{Bi} = (W_i / D_i) / V_{Bi}$$

If the shape of the particles (and hence the packing density) is assumed to remain unchanged after the coating is applied, we have the density of the coating:

$$D_i = \frac{W_f - W_i}{(V_{Bf} - V_{Bi})P_i}$$

The data are given in Table 6.

The packing density calculated from Table 6

$P_i = (W_i / D_i) / V_{Bi} = (25 / 2.65) / 14.8 = 0.64$ is a reasonable value for roughly spherical particles.

Two conclusions can be reached from the data:

1. There appears to be no trend of coating density with the hydrogen content of the fluidizing gas or with the resultant increase in deposition rate over the range studied, and
2. When compared with the theoretical density of graphite, 2.26 g/cm^3 and with that of commercial grades of "dense" graphite (Union Carbide Corporation 1977), e.g., CS 1.71 g/cm^3 and ATJ 1.73 g/cm^3 , the material depicted in Table 6 is concluded to be quite porous.

TABLE 6. Coating Density Calculated from the Bulk Density of Coatings
Corresponding to the Data of Table 2 and Figure 4

<u>Hydrogen Content of H₂ + Ar, m/o</u>	<u>W_i, Initial Bed Weight, g</u>	<u>V_{Bi}, Initial Bulk Volume, cm³</u>	<u>W_f, Final Bed Weight, g</u>	<u>V_{Bf}, Final Bulk Volume, cm³</u>	<u>Calculated Coating Density, g/cm³(a)</u>
25	25	14.8	27.12	17.6	1.18
32	25	14.8	27.39	18.0	1.17
50	25	14.8	27.49	18.6	1.02
75	25	14.8	28.76	19.5	1.25

(a) 2.66 g/cm³ taken as density of quartz sand.

The density of the LT-PyC coatings of Table 6 is similar to that of the porous pyrolytic carbon prepared in the intermediate temperature range with high reactant concentrations where gas-phase precipitated material is occluded and is much lower than the 2.2 and 2.1 g/cm³ observed at higher and lower temperatures; see Figure 10 from Diefendorf (1960).

COATING OF WASTE FORMS IN FLUIDIZED-BED REACTORS

With the background outlined above on the effects of parameters on deposition rate and coating quality, a number of samples of various waste forms were coated, either as granules which themselves constituted the fluidized bed, or as one or a few larger entities supported in a fluidized bed of smaller particles whose size and density were chosen to ensure uniform circulation throughout the bed of the items to be coated.

SPC-4E Coating

As already mentioned, the SPC-4E material lost weight during coating. As this material was somewhat friable, it is believed that at least part of the loss was due to attrition.

Nonuniformity of coating was a problem in general, the coating appearing to have spalled off in random locations during the coating run and on cooling.

Table 7 contains a summary of selected data for coated SPC-4E lots which were forwarded to PNL for further evaluation.

TDS-211 Glass Marble Coating

As was the case for the coatings on SPC-4E granules, spalling of the coating was a major problem, spalling being even more pronounced than with the SPC-4E.

Several surface conditioning efforts were made to improve adhesion of the coating so as to decrease spalling:

1. vapor honing
2. precoating with $\sim 1\mu\text{m}$ of Cr_xC_y ^(a)
3. HF etching

(a) Chromium carbide deposited from dicumene chromium at $\sim 450^\circ\text{C}$ whose carbon content is a function of coating parameters--typically Cr_7C_3 .

FIGURE 10. Room-Temperature Density of Pyrolytic Carbon as a Function of Deposition Temperature (Diefendorf 1960)

TABLE 7. Summary of Data for Selected Lots on the Preparation of Coated SPC-4E (0.7 to 1.4 mm) Particles^(a)

Run	PyC Thickness μm	Chromium Carbide Overcoat Thickness μm	Coating Condition ^(b)	
			Ni(CO) ₄ Concentration m/o	Coating Time Hours
36449-70-197	22	—	1.09×10^{-3}	4
36062-67-207	28	6	7.63×10^{-3}	4

(a) Substrates have been coated with $\sim 1 \mu\text{m}$ of chromium carbide at 450°C from 1 to 8×10^{-3} m/o chromium dicumene in H_2 .

(b) All lots were coated with PyC at 500°C with a C_2H_2 concentration of 2.85 m/o in H_2 . Coatings were applied in a 25-mm reactor using a diluent system of 0.10 to 0.25-mm molybdenum

Although partial success was obtained with the Cr_xC_y coatings, the problem persisted. It appears that the inherent weakness of the coating and a large unknown thermal expansion differential lead to spalling, even though the adhesion was improved. The plane of separation is simply transferred from the interface to the coating.

MB-1 Substrate Coating

The "as-received" MB-1 particles were relatively weak and their surface tended to spall when they were coated with LT-PyC, so efforts to upgrade the MB-1 were made. Three basic approaches to upgrading MB-1 were investigated: sintering, precoating with a strengthening coating such as chromium carbide, and preconditioning at 500°C for 2 hours while suspended in a fluidized bed.

The MB-1 particles sintered at 1000°C in air over night tended to adhere to each other, experienced a weight loss of 23 percent, and turned from gray to black. This approach was deferred because of the particle-to-particle sintering and the fact that they were reportedly heated at PNL to a higher temperature before shipping to BCL.

Precoating the MB-1 substrate with $\sim 1\mu\text{m}$ chromium carbide coating was not as beneficial as it was with the SPC-4E substrate. Oxidation of the surface of the chromium carbide precoat at 1000°C for 19 minutes in air resulted in no significant improvement in coverage by the LT-PyC coating.

Another significant problem encountered with the use of MB-1 substrate was fracturing of the particles during coating. This breakage was observed to range from 7 to 100 percent during the coating of MB-1, which was circulated in a diluent. No significant reduction in the breakage of the MB-1 particles was noted after a chromium carbide precoating had been applied in an effort to upgrade the particles. It was determined that the breakage of the MB-1 substrate ($<13\text{-mm}$ diameter) was caused by thermal shock and that the problem could be minimized in the LT-PyC coating process by heating the substrate particles slowly instead of introducing them into a hot fluidizing diluent bed.

DISCUSSION

Although a fairly wide range of conditions were explored for the catalyzed deposition of low-temperature pyrolytic carbon, no really satisfactory coatings were obtained. It appeared possible to obtain coatings of varying degrees of porosity, density, and strength. However, those of greatest porosity and least strength were the ones obtained at the economically attractive high-rates of deposition. Whether a very low rate of deposition at a very low catalyst concentration would ever result in acceptable impermeability is questionable. The question may be purely academic in view of the sacrifice in deposition rate required and the correspondingly increased cost.

The porosity may be inherent if the only deposition mechanism that operates is the precipitation of graphite from solid solution in nickel which has become supersaturated at another location by the decomposition of the hydrocarbon in contact with the nickel. Only if the particle were surrounded by a retreating and expanding nickel outer shell could such a mechanism operate to yield a dense coating. Even in that case, the attainable density would appear to be limited by the high interlayer spacing, C_o , of the material obtained previously by such mechanisms.

In any further work with the process, a means should be devised for full characterisation of the carbon product as to density, impermeability, grain size and orientation, and thermal coefficient of expansion. Only by a systematic approach relating these properties to process parameters can one be assured that something has not been overlooked if negative results persist.

SCREW-AGITATED COATER DEVELOPMENT

The screw-agitated coater (SAC) was developed in response to a need envisioned by PNL for a coater which is capable of being used to coat particles of a larger size (>2 to 3 mm) not typically coated in a fluidized bed (FB). The screw-agitated coater was selected after a review of potential candidate coaters (e.g., rotating-drum coater, vibrating-bed coater, etc.) suggested that a screw-agitated coater had no more disadvantages as compared to a FB than other coaters and several advantages.

A SAC appears to have several features which a fluidized-bed reactor possesses, such as being a vertical-type reactor (minimizes reactants by-passing the bed) and the particle circulation pattern tends to average out the particle temperature and the reactant concentration to which a particle is exposed (potentially uniform coating thickness).

APPARATUS

A glass model of a SAC was designed, fabricated, and set up so that the variation of relevant parameters on particle movement and reactant flow could be viewed. This approach was expected to expedite the achievement of an optimum SAC. The model coater consisted of a glass cone bottom sealed to a cylinder of ~100-mm-ID glass (Figure 11). An assembly for discharging the bed from the bottom of the coater was installed. The bed particles were circulated by an auger (~1-1/2 inches in diameter). Initially, 6-mm glass beads were used as the bed material because they are similar in size to that anticipated for the PNL substrates and were readily available. As the need arose, other substrates were examined in the model of a SAC.

The following is a list of preliminary observations made with the glass model of a SAC:^(a)

1. As might be suspected, the time required for a bead to make a complete circuit in the bed is typically directly related to the number of rotations per minute of the auger. However, it was noted that the

(a) Unless otherwise stated, the bed material is 6-mm diameter glass beads.

FIGURE 11. Glass Model of a Screw-Agitated Coater (514VD)

circulation rate of a bead was not always uniform. It was presumed that the bead may have been knocked off the auger by another bead. Accordingly, a sleeve was placed around the auger and circulation rates appeared to be more uniform.

2. Without a sleeve around the auger, a bead's typical circulation path is a helix, while with the sleeve, the path is roughly vertical.
3. With four verticle baffles (uniformly spaced adjacent to the reactor wall), a bead's typical circulation path was found to be roughly vertical, similar to the observation made with a sleeve around the screw. However, particle circulation rates appear to be faster with a sleeve than with baffles. The circulation rates observed when no particle channeling device was present (i.e., no sleeve or baffles) are about the same as the rates observed when baffles were present.

4. If the diameter of the sleeve is less than $\sim 2\text{--}3/8$ inches, binding of the auger (diameter $\sim 1\text{--}1/2$ inches) occurred. The sleeve-to-auger diameter as it pertains to binding is undoubtedly related to the perfection of the alignment of these two elements, which was not well maintained in the model. Based on these observations, it was concluded that a baffle may be preferable to a sleeve for use in the actual coater because of the potential for less binding and because baffles can be constructed such that their surface area is less than that of a sleeve. The lower surface area should result in less residual carbon which needs to be eventually removed.
5. Experiments were performed to determine if the pressure drop (backpressure) through the bed would be a problem. At an argon flowrate of $\sim 2\text{ l/minute}$ and with a bed of 6-mm beads, the pressure drop through the bed was ~ 15 mm of water with a bed height-to-reactor inner diameter (H/D) of ~ 2 . The pressure drop increases to ~ 20 mm of H_2O at H/D ~ 3 . The pressure drop increased modestly as the flowrate was increased. Consequently, it appeared that the pressure drop was rather minimal. Additional experiments were performed to determine if the pressure drop (backpressure) through the bed would be a problem with particles typical of the smallest size received from PNL. With a bed of 18 x 30 mesh glass beads, the pressure drop through the bed was roughly the same as that for 6-mm beads. Consequently, it appeared that the pressure drop would not be an immediate problem.
6. Titanium tetrachloride was mixed with water to prepare smoke in an effort to observe the gas flow pattern in the bed. The smoke appeared to flow through the bed uniformly and essentially independent of rotation speed of the screw (maximum rpm observed was 50). With a cylindrical sleeve around the screw, the smoke appeared to be more dense inside the sleeve. This observation would be expected if the particle density inside the sleeve is less than that outside the sleeve, as was anticipated.
7. Efforts to discharge the bed from the model coater through an 11-mm-ID glass tube resulted in only intermittent flows of bed out of the coater. The discharge rate was not appreciably enhanced by rotation speed of the

auger or by vibration of the withdraw tube. It was later determined that particles can be readily drained if the diameter of the withdraw tube is ≥ 4 to 5 particle diameters.

8. Three cone designs (included angles of $\sim 30^\circ$, $\sim 60^\circ$, and $\sim 90^\circ$) were examined as candidates for the bottom section of the screw coater. The beads circulated in all cases, but the cone with a 60° angle was chosen based on ease of fabrication, operation, and bead circulation.

Based on the observations above, two first-generation screw-agitated coater (SAC) systems were designed, fabricated, and set-up. Figure 12 is a schematic of the coating system and the coater with several of the approaches used to introduce reactants into the coater shown. Except for the coater, the coating system was patterned after the fluidized-bed set-up. Each metal coater was constructed of a 4-inch pipe (~ 18 inches long) welded to a cone ($\sim 60^\circ$ angle) bed support. The only significant difference between the two SACs was that the position of the holes in the cone were $\sim 1/4$ inch higher up in the second fabricated SAC. The position modification was suggested by operation of the first coater (see discussion below).

While fluidized-bed coaters are in an advanced stage of development, screw-agitated coaters are in their infancy. Accordingly, emphasis was not only on the developments of suitable coating parameters in the coater, but also on the development of an operable SAC. In addition to the study of deposition parameters of carbon coatings in the SAC, selected metallic coatings (iron and nickel) were prepared in the SAC.

COATING PROCEDURES

In a typical coating run roughly 1-liter of bed material was added through the bed inlet opening, shown in Figure 12 with a minimum of rotation on the auger (screw). The bed inlet opening was closed and the coater was then purged with argon. The coater was heated to the coating temperature in argon and then hydrogen was substituted for argon. The rotational speed of the auger was increased to the target speed and after the temperature of the coater stabilized, the reactant flows were started. The shut-down procedure was essentially the reverse of the start-up procedure.

*(304 SS pipe, 4-inch ID x 18 inches long).

FIGURE 12. Schematic Diagram of the 4-in. Screw-Agitated Coater (SAC) and Associated Equipment

COATING EVALUATION PROCEDURES

Coated particles were evaluated first at low magnification ($\leq 60X$) to determine the hardness and adherence of the coating. This evaluation was typically performed by trying to probe the coating off and by rubbing the coated particle on white paper. Metallographic mounts of selected coated particles were made and examined at $1000X$ to visually evaluate coating quality and measure coating thickness.

PARAMETER STUDY

With the general objectives of gaining familiarity with the coater, optimizing the operability of the coater, and evaluating coating rates and quality, a series of runs were made in the screw-agitated coater (SAC) in which the following parameters were varied:

Bed temperature: ~ 400 to $\sim 550^{\circ}\text{C}$

Acetylene (C_2H_2) concentration: ~ 1.5 to ~ 20 m/o

Nickel carbonyl [$\text{Ni}(\text{CO})_4$] concentration: ~ 0.001 to ~ 0.6 m/o

Auger speed: ~ 25 to ~ 120 rpm

Total flow through the coater: ~ 4 to ~ 25.4 g/minute

Furthermore, four different augers were tested for their relationship to coating rate and quality and operability in the designed SAC. The relevant dimensions of the four augers are given in the following tabulation:

<u>Auger Number</u>	<u>Pitch, Inch</u>	<u>Auger Diameter, Inch</u>	<u>Shaft Diameter, Inch</u>
1	2-1/2	1-5/8	1/2
2	1	1-1/2 to 3	1/4
3	2	1-5/8	5/8
4	1	3	1

Auger No. 4 appeared to give the most uniform bed temperature of the augers tested. Due to time restraints and the fact that all augers circulated the particles adequately, most attention was focused on Augers No. 1 and No. 4 which represent the extremes of potential augers.

The preliminary approach to applying pyrolytic carbon coatings in the SAC system was to use 6-mm alumina balls as substrates. Once preliminary coating parameters were defined, coating runs were made in the two SAC systems using TDS-211 glass marbles (~13-mm average diameter). Furthermore, the results of the fluidized bed runs were used to guide the selection of parameters and reagents studied in the SAC.

Effect of Process Parameters On Coating Rate

Figure 13 shows data, obtained using similar conditions except for temperature, for deposition from a C_2H_2 , and $Ni(CO)_4$ mixture. Over the temperature range examined, the deposition rate appears to be increasing as the temperature increases. An upper limit was imposed on the coating temperature in the parameter study because it was understood that the material (TDS-211 glass marbles) eventually targeted to be coated in the SAC softened at ~550°C. Accordingly, it is possible that a maximum in the bed weight gain rate, as found in the fluidized-bed experiments (Figure 2), does exist if data for higher temperatures were obtained. The data in Figure 13 is in agreement with the data presented in Figure 2 with respect to the relationship between C_2H_2 concentration and bed weight gain rate.

As can be seen in Figure 13, there is scatter in the data. The scatter is probably due to both mechanical problems and problems with obtaining reproducible data when the coating is of poor quality. Solutions to these problems will be discussed in later sections. However, in addition to the trends presented in Figure 13, certain observations were made during the parameter study and are given below:

1. Increasing C_2H_2 concentration and/or $Ni(CO)_4$ concentration over the range investigated resulted in an increased coating rate, but the coating quality was unchanged at best.
2. The deposition rate decreased as the total flow was increased, suggesting that the reactant gases required preheating. An expedient approach to preheating the gases was tried by positioning the reactor further up in the hot zone of the reactor furnace. Efforts to increase the coating rate by preheating the gases were not very successful due to premature $Ni(CO)_4$ decomposition.

FIGURE 13. Effect of Temperature on Deposition from Acetylene. Bed = 2150 g (~1 liter) of ~6-mm-diameter alumina balls. Total gas flow = 12.7 l/min. C₂H₂ concentration as indicated; Ni(CO)₄ concentration: ~0.02 m/o to ~0.05 m/o; H₂ balance.

3. The best-appearing PyC coatings were applied using the following conditions: ~0.02 m/o $\text{Ni}(\text{CO})_4$, ~3.0 m/o C_2H_2 , and balance H_2 with a bed temperature of ~500°C.

Effect of Process Parameters On Coating Quality

In contrast to application of coatings in a fluidized-bed coater, it is presumed that mechanical parameters could contribute significantly to poor coating quality and coating rate if the mechanical operation of the coater generates "foreign" material, e.g., carbon dust abraded from the coating, powder/pieces abraded/broken from the substrate, etc., which could be entrained in the growing coating. Accordingly, the quality of the carbon coating as applied in a SAC was examined with respect to both chemical and mechanical parameters.

Mechanical Parameters. An initial effort to circulate alumina balls (~6-mm diameter) was not successful due to a binding action between the bottom flite of the auger, the balls, and the bottom of the cone part of the reactor. This problem was not as noticeable in the model studies with pyrex balls, probably due to the fact that the surface of the pyrex balls is smoother than the surface of the alumina balls. Hence, the pyrex balls slipped over each other and did not tend to bind to the same extent found with alumina balls. Several approaches were tried to reduce the binding. An expedient approach that has proved successful has been to place a ~1/4-inch thick graphite disk on the bottom of the cone and let the auger ride on the graphite disk. Even though the graphite-bearing disk was a satisfactory expedient, efforts were made to understand the reason for the binding with the goal being to improve the design of the coater. Emphasis was placed on refining and improving the mechanical operation of the SAC using one of PNL's candidate substrates (TDS-211 glass marbles).

One effort with the SAC was the investigation into the causes of the infrequent breakage of TDS-211 glass marbles. As can be noted in the following tabulation, the initial experiments showed a direct relationship between percent breakage and temperature, but the exact relationship was not obvious.

Load Size	Auger Speed(a)		
	25 rpm	50 rpm	75 rpm
100 marbles (RT)	1%	0%	0%
Full load (RT)		<1%	0%
Full load ~450°C			2%
Simulated Run ~450°C			9%

(a) Auger No. 4 used for this modeling study.

To determine if the marbles would crack under thermal shock, they were put through an extreme test. A furnace was preheated to ~450°C and the marbles were put directly into the furnace. None of the marbles cracked. Then the marbles were heated to ~450°C and quenched in room-temperature (RT) water and none of the marbles cracked. Consequently, it would appear that the marbles can withstand any thermal shock that may be associated with the coating operation. Furthermore, it appeared that the relationship between the marbles' breakage and temperature was more complex than initially suspected. Currently, it is suspected that the breakage/temperature phenomenon is related to an increased tendency of the glass marbles to bind at the elevated temperatures. This condition could be aggravated by the marbles tending to sieze to each other as they approach their softening temperature (500 to 550°C) and/or the clearance between the screw and the chamber wall changing as the system is heated to coating temperature. There is little doubt that the resistance to movement, marble against marble, increases as the marbles are heated. It is also apparent from observing a model of a SAC that if the screw and wall clearance changes, due to the screw action, from above to below a distance equivalent to the diameter of one to possibly three marbles, binding can occur.

To examine the screw-to-wall clearance effect on breakage, it was decided to determine what combinations of marble sizes would lead to binding (no clearance) at room temperature and at elevated temperatures (500 to 550°C). Accordingly, a random sample of marbles was taken and diameters measured. The sample has an average diameter of 11.9 mm and a range of 8.7 mm to 14.9 mm. The range of marble diameters makes system design complex; however, a geometric analysis suggested that an auger-to-wall distance of 45 mm was required to

minimize binding at room temperature and slightly more at elevated temperatures. A modeling study in the SAC tended to confirm the geometric analysis.

Chemical Parameters. Several reagent introduction designs (Figure 12) were examined in an effort to minimize plugging problems and gas-phase nucleation with the goal being to improve coating quality and rate. Some observations of potential interest were made during this series of runs and are given below:

1. In an effort to reduce gas-phase nucleation, Ni(CO)_4 and C_2H_2 were introduced into the bed through separate feed tubes. When Ni(CO)_4 was introduced through the holes in the cone, the holes plugged, probably with nickel. No problem was encountered with the introduction of the C_2H_2 through the feed tube that also serves as the bottom retainer/bearing for the auger. The pointed tip of the auger merely rotated in this feed tube. In light of the Ni(CO)_4 plugging the inlet holes on the side of the cone, it was decided to introduce the Ni(CO)_4 through the feed tube which serves as the bottom retainer for the auger and introduce the C_2H_2 through the holes in the side of the cone. It was reasoned that the auger retainer maintained a slightly lower temperature than the side holes which would reduce the tendency to decompose the Ni(CO)_4 . In addition, the tip of the auger could be expected to abrade off any nickel deposited in the upper portion of the feed tube. In runs of 4 to 5 hours duration, this approach to introducing the reactants was successful until an attempt was made to preheat the reactants, and then plugging problems developed. Subsequently, a 304 stainless steel water-cooled jacketed metal catalyst feed tube (feed tube insert through a hole in the lid on the SAC) was used to reduce clogging problems due to premature decomposition of the catalyst. Water-cooled feed tubes were used to introduce the catalyst through the side of the SAC, also. Both approaches were successful in minimizing the clogging problem; however, introducing the catalyst through the side of the SAC was found to result in less problems with binding (see above).

2. Unlike the fluidized-bed reactor, heat transfer in the SAC could be a limitation, especially if the acetylene is introduced without preheating, as was being done when both the C_2H_2 and $Ni(CO)_4$ reactants were introduced at the bottom of the coater. To provide some preheat to the C_2H_2 , experiments were performed in which the C_2H_2 was supplied to the system through a stainless steel tube extending from the top of the coater and terminating near the bottom. Neither the coating rate nor coating quality were significantly improved by the use of preheated C_2H_2 .
3. To reduce the homogeneous gas-phase nucleation which was observed in the SAC, an effort was made to stabilize nickel carbonyl by using carbon monoxide (CO) as the carrier gas (Dewar and Jones 1903) for $Ni(CO)_4$. However, the amount of nucleation was not grossly reduced compared to that typically obtained when hydrogen was used as the carrier gas for $Ni(CO)_4$ in a SAC system. Carbon monoxide is frequently used in depositing nickel from $Ni(CO)_4$ at temperatures of $\sim 200^\circ C$ to improve coating quality. However, as might be expected, CO tended to disproportionate at the deposition temperature ($\sim 450^\circ C$) used in this program. Accordingly, the CO approach was deferred.

DISCUSSION

Roughly fifty runs were made in an effort to 1) gain familiarity with the operation of the SAC, 2) refine and improve the operation of the SAC, and 3) apply coatings (primarily carbon, but also nickel and iron) in the SAC. Significant progress was made in achieving an operable SAC; however, it became apparent that the chemical experimental parameters required further optimization. Accordingly, it was decided to defer further coating work in the SAC pending optimization of coating parameters in the fluidized-bed coater. Since fluidized-bed coaters are operationally more advanced than the SAC, it was expected that parameter optimization would be expedited by using the fluidized-bed coater, since only the chemical experimental parameters would need to be examined.

As detailed previously, extensive work was performed on developing suitable coating parameters in the fluidized-bed coater. Once the coating results obtained in the fluidized-bed coater appeared encouraging, it was decided to perform a coating run in the SAC using low concentrations of Ni(CO)_4 per the fluidized bed results. It was believed that the lower concentrations Ni(CO)_4 would decrease gas-phase nucleation and as a result of the decreased reactant depletion would enable the coating rates to be increased without sacrificing the coating quality. The coating conditions initially used in these SAC runs were based on those determined in fluidized-bed runs to produce the LT-PyC coatings of the most promising quality and are given below:

Substrate: 1 liter TDS-211 glass marbles (8.7 to 14.9 mm)

Auger speed: ~50 rpm

m/o H_2 : ~96.15

m/o C_2H_2 : ~3.85

m/o Ni(CO)_4 : $\sim 10^{-3}$

Bed temperature: $\sim 475^\circ\text{C}$

Run time: ~4 hours

Total flow through the system: ~4 liters/minute

The coating rate was 1 to $2\mu\text{m}$ per hour and the coating quality approached that obtained in a fluidized bed.

After demonstrating the significant potential of the SAC, further work in the SAC was deferred due to a decision to use the fluidized-bed coater to prepare samples for evaluation at PNL. This decision was based on the demonstrated expectation that the coatings prepared in the fluidized-bed coater were typically superior in quality to those prepared in the SAC.

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CONCLUSIONS

A primary goal of this work was to evaluate the potential of applying carbon at temperatures (e.g., $\sim 500^{\circ}\text{C}$) lower than those typically used ($\sim 1000^{\circ}\text{C}$). Due to its advanced stage of development, a fluidized-bed coater was selected to be used as the coater to evaluate the potential of applying low-temperature pyrolytic carbon (LT-PyC). A parameters study confirmed that LT-PyC could be deposited at readily detectable rates at temperatures above $\sim 300^{\circ}\text{C}$. Furthermore, the rate of carbon deposition on a substrate (30 x 50 mesh sand) appeared to exhibit a maximum and then decrease as the temperature was increased (Figures 2 and 3). This decrease in rate may be interpreted to be due to the catalyst and the carbon precursor reacting at sites other than on the substrate to produce gas-phase-nucleated carbon dust. Dust formation, as expected, was found to be detrimental to the coating quality. While an exhaustive evaluation of all parameters was impractical, the data obtained suggested that the above trend in deposition rate versus temperature was similar for all hydrocarbons tested. Accordingly, acetylene was selected as the hydrocarbon to continue on with based on past experience at BCL^(a,b) and on work by Koss, Kofler and Neumann (1980).

Materials containing nickel or iron or cobalt were used as catalysts based on the literature survey. Experiments confirmed results in the literature (Lobo, Trimm and Figueiredo, 1972) that suggested that nickel (from nickel tetracarbonyl) would catalyze the carbon deposition reaction rate more than catalysts containing iron or cobalt. A catalyst containing iron [iron pentacarbonyl, $\text{Fe}(\text{CO})_5$] was examined because of its lower catalytic activity compared to nickel in an effort to reduce gas-phase nucleation and hence improve the coating quality obtained using $\text{Ni}(\text{CO})_4$ as the catalyst. The use of $\text{Fe}(\text{CO})_5$ rather than $\text{Ni}(\text{CO})_4$ and the use of low concentrations of $\text{Ni}(\text{CO})_4$ both

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- (a) Browning, M. F., and R. W. Kidd. 1977. "The Development of Chemically Vapor Deposited Coatings for the Multi-barrier Waste Form Program." Unpublished Annual Report to Pacific Northwest Laboratory.
- (b) Browning, M. F., and R. W. Kidd. 1978. "The Development of Chemically Vapor Deposited Coatings for the Multi-barrier Waste Form Program." Unpublished Quarterly Report to Pacific Northwest Laboratory.

showed promise of reducing gas-phase nucleation. It was decided to continue the pursuit of the low Ni(CO)_4 concentration approach; however, the Fe(CO)_5 approach appears worthy of further investigation.

Hydrogen was found to increase the rate of carbon deposition from acetylene compared to the rate obtained using argon as the diluent gas (Figure 5). Moreover, the concentration of hydrogen appears to be linearly related to the deposition rate. Hydrogen did not appear to enhance the rate of decomposition of any of the other hydrocarbons examined.

While most coating runs were performed at atmospheric pressure, a limited evaluation of preparing coatings at reduced pressures was made late in the program with the goal being to minimize gas-phase nucleation by reducing the degree of supersaturation in the gas phase. There did not appear to be a major improvement in the coating quality or rate based on the results of this limited study.

Accordingly, emphasis was placed on evaluating the potential of the system which exhibited comparatively high deposition rates and promising coating quality with the assumption that acceptable trade-offs in rate could be made to achieve good coating quality. The system that showed most promise was $\text{H}_2/\text{C}_2\text{H}_2/\text{Ni(CO)}_4$. The following experimental parameters were used to prepare two carbon-coated lots for evaluation at PNL:

Substrate: SPC-4E^(a) (0.7 to 1.4 mm)
Coating temperature: $\sim 500^\circ\text{C}$
 C_2H_2 concentration: ~ 2.85 m/o
 Ni(CO)_4 concentration: ~ 1 to $\sim 8 \times 10^{-3}$ m/o
 H_2 concentration: balance
Coating rate: ~ 6 to $\sim 7 \mu\text{m}/\text{hour}$

Before the carbon coating was applied, a chromium carbide coating ($\sim 1 \mu\text{m}$) was applied in an effort to minimize the dusting of the candidate substrate (SPC-4E). Furthermore, one of the lots (36062-67-207) was prepared with a chromium carbide ($\sim 6 \mu\text{m}$) overcoat of the LT-PyC for reasons discussed below and

(a) Circulated in a fluidized bed of 0.10 to 0.25 mm molybdenum.

the other lot (36449-70-197) without an overcoat. The goal of preparing these two lots was to generate leach data and to compare the leach resistance of the two lots.

It was noted early in the program that LT-PyC may be less oxidation resistant than high-temperature PyC deposits; it was decided that an outer oxidation resistant layer might be required in the ultimate application. Since chromium carbide is typically prepared at temperatures (~300 to 500°C) in the same range as those used to prepare LT-PyC, and since chromium carbide does show moderate oxidation resistance (via the formation of chromium oxide), chromium carbide was selected as the outer oxidation resistant barrier. It is anticipated that the leach results will give some guidance as to the potential of using chromium carbide as the primary coating.

Efforts were made to apply LT-PyC coatings to TDS-211 glass marbles and MB-1 substrate using the coating parameters mentioned above. Problems with adhesion of the LT-PyC to the substrate were encountered. Several approaches were tried to improve coating adhesion, including the approach used to strengthen SPC-4E, i.e., application of a chromium carbide coating. None of the approaches tried resulted in the preparation of good quality LT-PyC coating. In the case of the marbles, it appears that there is a thermal expansion mismatch between the marble and the LT-PyC coating. While in the case of the MB-1 substrate, it appears that the problem is due to the fragile nature of the substrate and possibly to a thermal expansion mismatch.

Two screw-agitated coaters (SAC) were designed and set-up. Roughly fifty coating runs were made. The SAC approach appears to be feasible since no fundamental uncorrectable problem was noted during the operation of the SAC's. The primary mechanical consideration that needs to be addressed when coatings are to be prepared in the SAC's is whether sufficient clearances have been allowed. Accordingly, the size of the substrate and the design (primarily diameter of the flites) of the auger must be matched so that distance of closest approach between the auger and the wall of the coater is >3 particle diameters and substantially less or greater than a simple multiple of the average diameter. Accordingly, the clearance requirement must be established if, for

example, one desires to evaluate the potential advantages of feed tubes which terminate in the bed and/or baffles which are positioned in the bed zone.

Due primarily to the comparatively low level of development of the SAC at the beginning of the program, an approach was used whereby the results of the fluidized-bed coating runs guided the selection of the coating parameters used in the SAC's. Accordingly, most coating runs in the SAC used $C_2H_2/H_2/Ni(CO)_4$ to prepare LT-PyC. Additionally, limited work was done on preparing nickel coatings from $Ni(CO)_4$ and iron coatings from $Fe(CO)_5$ as part of a phased approach to preparing LT-PyC. No particular effort was made to optimize the quality of the nickel and iron coatings; however, they appeared to be of good quality.

The data does not suggest any major differences between the trends obtained using the fluidized-bed coater compared to those obtained using the SAC's. Since there was a problem in preparing good quality coatings on TDS-211 glass marbles, the only substrate coated in both coaters, a comparison between the coating quality and rate obtained in the two coaters requires additional data. However, if the general coating quality and coating rate of the LT-PyC coatings prepared in the two coaters are compared, there is some evidence that those prepared in a fluidized-bed coater are better in quality and deposited at a higher rate (~2 to ~3 times faster).

RECOMMENDATIONS

While the feasibility of preparing low-temperature pyrolytic carbon (LT-PyC) coatings has been clearly demonstrated, the quality of the best LT-PyC coatings appears to be somewhat inferior to high-temperature pyrolytic carbon (HT-PyC) coatings. Since the leach test (HNO_3 acid) used at BCL in an effort to rapidly evaluate the quality of LT-PyC coatings gave, at the best, only a guide to relative quality, a direct comparison of the leach resistance of LT-PyC and HT-PyC will be made from PNL's leach tests elsewhere (Oma et al. 1981). Accordingly, the recommendations made in this section may be altered by the results of PNL's tests.

However, it is strongly recommended that the work on preparing a protective coating for nuclear waste particles be continued and this effort be focused, at least initially, on improving the imperviousness and strength of the LT-PyC coatings. A secondary objective would be to eliminate the need for hydrogen and increase the deposition rate to a more commercially acceptable value. Progress was made in the current program towards these objectives, but obviously for LT-PyC to be of practical value as a protective coating further improvement is required. Techniques to provide the desired improvement in LT-PyC that need additional investigation are: catalyst other than $\text{Ni}(\text{CO})_4$, reduced pressure coating environment, and other low-temperature carbon deposition systems (e.g., pyrolysis of C_3O_2 , pyrolysis of $\text{Ag}_2\text{C}_2\text{O}$, and plasma enhanced pyrolysis).

Another approach to obtaining improved LT-PyC could be the use of a post-deposition treatment (e.g., heat treatment at $\sim 500^\circ\text{C}$ (possibly higher)) for a relatively long period of time with and without a coating densification aid such as $\text{Ni}(\text{CO})_4$. If there is a coefficient of thermal expansion mismatch between the substrate and LT-PyC, it would probably be necessary to develop an approach for accommodating the mismatch, such as using a porous, crushable LT-PyC layer between the substrate and the dense LT-PyC layer.

If LT-PyC coating with the desired properties cannot be perfected with a reasonable effort, other coating options should be considered. A less-than-perfect LT-PyC coating could be overcoated with a HT-PyC (1000°C) in the same

coating system to achieve the imperviousness required. This would provide for coating the bare substrate (waste fuel form) at a relatively low temperature and then the infiltration of this coating to improve its strength and leach resistance.

Other options would include LT-PyC in combination with such materials as SiC, silicon, chromium carbide, etc. These materials could greatly enhance the leach resistance of LT-PyC in addition to providing a degree of oxidation resistance at elevated temperatures. Some of these materials can be deposited at temperatures in the range of interest.

It is recommended that all initial coating optimization and exploratory work continue to be confined to a fluidized-bed coater so that this phase of the effort could be carried on in the most expeditious and economical manner. Once coatings are obtained that appear to be of a promising quality, based on visual appearance as to cracking, strength and substrate/coating bond, and density, the coated lots should be evaluated for leach resistance. To expedite the research it is recommended that an effort be made to devise a leach test which has a fast turn-around time, yet gives results which agree on a relative basis to those results obtained using standard leach tests (e.g., Soxhlet).

Once desirable coatings are prepared in a fluidized-bed coater, it is recommended that candidate substrates be coated in the SAC using initially those coating conditions found suitable for preparing good quality coatings in a fluidized bed. While it is anticipated that the coating conditions developed using the fluidized-bed coater would be suitable for preparing hard coatings in the SAC, it is acknowledged that it might be necessary to evaluate problems specific to the SAC (e.g., augerparticle interactions). It is recommended that potential sources of binding be avoided, e.g., no feed tubes in the bed or baffles in the bed zone unless there appears to be a potential significant advantage to using such items. However, it is recommended that the design and speed of the auger be optimized, that preferred inlets for the reactants be defined, and that the optimum residence time in the SAC be defined. As a lower priority, fixturing for charging uncoated bed to the SAC and discharging coated bed should be developed.

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APPENDIX

ADDITIONAL REFERENCES TO CATALYTIC CARBON DEPOSITION

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