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Coated-Particle Waste- Form Development

December 1981

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Pacific Northwest Laboratory
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COATED-PARTICLE WASTE-FORM
DEVELOPMENT

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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). Primary efforts were to coat simulated nuclear waste glass marbles and ceramic pellets with low-temperature pyrolytic carbon (LT-PyC) coatings via the process of chemical vapor deposition (CVD). Fluidized bed (FB) coatiers, screw agitated coatiers (SAC), and rotating tube coatiers were used. Coating temperatures were reduced by using catalysts and plasma activation. In general, the LT-PyC coatings did not provide the expected high leach resistance as previously measured for carbon alone. The coatings were friable and often spalled off of the substrate.

A totally different concept, thermal spray coating, was investigated at PNL as an alternative to CVD coating. Flame spray, wire gun, and plasma gun systems were evaluated using glass, ceramic, and metallic coating materials. Metal plasma spray coatings (Al, Sn, Zn, Pb) provided a two to three orders-of-magnitude increase in chemical durability. Because the aluminum coatings were porous, the superior leach resistance must be due to either a chemical interaction or to a pH buffer effect.

Because they are complex, coated waste form processes rank low in process feasibility. Of all the possible coated particle processes, plasma sprayed marbles have the best rating. Carbon coating of pellets by CVD ranked ninth when compared with ten other processes. The plasma-spray-coated marble process ranked sixth out of eleven processes.

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1.0 INTRODUCTION

Over the past decade, Pacific Northwest Laboratory (PNL) has developed and evaluated alternative waste forms for immobilizing high-level nuclear wastes. The Alternative Waste Forms Program was established at PNL in 1979 for the Department of Energy to evaluate coated particles, matrix encapsulation, and glass ceramics as candidate waste forms. This report documents the studies that were conducted at PNL, Battelle Columbus Laboratories (BCL), and General Atomic Company (GAC) to develop coated particles under the PNL Alternative Waste Forms Program. Similarly, efforts in matrix, glass ceramic, and consolidation and sintering development have been documented elsewhere (Wald et al. 1981; Rusin et al. 1981; and Treat et al. 1981).

Coated particles, upon subsequent encapsulation, became part of the multi-barrier concept (Rusin, Browning, and McCarthy 1979). The multibarrier concept aims to separate the radionuclide-containing core material from the environment by the use of coatings and metal matrices. The coating barrier provides improved leach and oxidation resistance and mechanical strength.

Chemical vapor deposition (CVD) in a fluidized bed was selected as a feasible method to coat ceramic cores, since the technology has previously been demonstrated for high-temperature gas-cooled reactor fuel particles. CVD coatings, including SiC, PyC (pyrolytic carbon), SiO₂, and Al₂O₃, were studied (Rusin et al. 1981).

Leaching studies on graphite powders indicate that an extremely high leach resistance of 10^{-11} g/cm²-d is obtainable at temperatures near 100°C (Gray 1980). Thus, pyrolytic carbon (PyC) has been selected as a promising leach-resistant coating material.

Although several CVD-coated waste forms have been successfully produced (Kidd, Browning, and Rusin 1979), some major disadvantages associated with the high-temperature fluidized-bed CVD coating process exist: 1) particle diameters are limited to about 2 mm or less, 2) waste forms must be ceramic, and 3) volatile waste-form components are trapped in the coating. To overcome these disadvantages, PNL initiated the development of a PyC CVD coating system

to coat large waste-form particles (~10 mm) at temperatures ranging from 400 to 500°C. The first section of this report describes the development efforts to reduce PyC coating temperatures and to coat particles larger than 2 mm in diameter. Studies at BCL involved the use of catalysts such as $\text{Ni}(\text{CO})_4$ to reduce carbon gas decomposition temperatures. A screw agitated coater (SAC) was also developed to replace conventional fluidized bed coaters, resulting in the capability to coat 10-mm particles.

General Atomic Company (GAC) used a different approach than BCL to reduce PyC coating temperatures. Conventional high-temperature PyC (HT-PyC) CVD techniques were evaluated at reduced temperatures (e.g., 1000 to 1300°C versus 1600°C). A rotating tube particle coater was also used in some experiments to increase low-temperature coating efficiency. Finally, GAC examined plasma activation as a means of coating glass spheres with PyC at near ambient temperatures.

Studies at PNL on LT-PyC deposition were primarily for technology transfer from BCL to PNL. A fluidized bed coater and coater support system were fabricated, installed, and tested at PNL following specifications developed by BCL. Coatings of LT-PyC and Ni were applied to glass and ceramic substrates at PNL.

In addition to the demonstration of LT-PyC coating, PNL also investigated thermal spray concepts for deposition of metals, glasses, and ceramic oxides on simulated waste glass marbles. Wire spray, flame spray, and plasma spray systems were evaluated as reported in the second section of this report. Simple particle agitators were developed and tested to allow for uniform spray contact on the substrates. Fusion techniques to reduce porosity and engineering feasibility are also described.

Final selection of a waste form will depend upon a trade-off between process and product attributes. In the characterization section, bulk properties, crush and impact strength, and leach resistance of the previously coated particles are discussed. Improved leach resistance is the primary reason to coat a waste form; thus, considerable information is reported on this subject. Results for PyC coatings were not as good as expected from those predicted from

carbon alone. Metal plasma spray coatings, however, increased chemical durability by two to three orders of magnitude. Microstructural characterization by SEM and EDAX confirm the leaching results.

The process feasibility of coated particles is compared to other waste form processes in Chapter 5. Final comparison is made between various coated particle processes. Overall, the plasma spray marble process has the best rating.

2.0 LOW-TEMPERATURE CHEMICAL VAPOR DEPOSITION

The development of low-temperature PyC (LT-PyC) coatings as described in this section was initiated to reduce the release of volatile waste form components and to allow for the coating of simulated waste glass marbles, which have low-temperature softening points (550 to 600°C). Another objective was to develop coaters for larger sized particles (>2 mm), which are not easily fluidized.

Studies were conducted at PNL, BCL, and GAC to meet the above objectives. Under contract to PNL, researchers at BCL tried to reduce PyC coating temperatures by using catalysts and attempted to coat particles larger than can now be accommodated in fluidized bed coaters. These studies at BCL were a continuation of previous contracts from PNL to develop high-temperature PyC, Al_2O_3 , and SiC CVD coatings for ceramic nuclear waste forms.

Studies were conducted at GAC, under contract to PNL, using conventional HT-PyC CVD coating techniques except that temperatures were reduced to 1000 to 1300°C instead of the usual operating temperatures above 1600°C. A rotating tube coater and plasma activation were also investigated as possible methods to reduce coating temperatures. Techniques evaluated at GAC were based upon those identified as most promising from literature reviews.

Technology developed at BCL was transferred to PNL to establish facilities to coat simulated waste forms. The intent was to bring the coating process closer to the substrate waste form process (e.g., marble machine and disc pelletizer and sintering furnaces). Using designs and parameters established at BCL, LT-PyC and Ni coatings were deposited on simulated ceramic and glass waste form substrates.

2.1 BCL COATING STUDIES

The primary objective of the program at BCL was to reduce the PyC coating temperature from the conventional high temperature range used previously (900° to 1100°C).^(a) The new temperature had to be compatible with less refractory

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(a) Reported by Browning and Kidd in unpublished reports written to PNL (1977 and 1978).

forms of nuclear waste materials, such as glass marbles. A second objective was to develop a reactor suitable for coating larger diameter waste particles (~12-mm) 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, remotely-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 to the hydrocarbon coating atmosphere permitted the 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 had been studied earlier, primarily by Lobo and Trimm (1971, 1973a and b); Lobo, Trimm, and Figueiredo (1972,1974); Lobo (1973); Bernardo and Lobo (1975,1976); and Bernardo and Trimm (1976).

The substrates used for coating tests consisted of two ceramic forms and one glass form of a simulated waste composition. Table 2.1 gives the pertinent characteristics of the simulated nuclear waste forms and stand-ins that were dealt with during the course of the program. Table 2.2 gives the compositions of the SPC-4E and MB-1 ceramic pellets and the TDS-211 glass marbles.⁽¹⁾ The waste form contained Ce_2O_3 , Cs_2O , Nd_2O_3 and SrO as tracer elements. Because the quantities of the waste form materials were typically limited, 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.

This section is organized into two sub-sections corresponding to the types of coating equipment used:

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(1) SPC-4 is an assembly of crystalline phases; MB-1 is a sintered form of the primary Savannah River Plant calcine; TDS-211 is simulated Savannah River Plant waste glass.

TABLE 2.1. Properties of Nuclear Waste Forms and Principal Stand-In Materials

Material	Particle Size, mm	Coefficient of Thermal Expansion, $10^{-6}^{\circ}\text{C}^{-1}$	Density, g/cm^3		Other Characteristics
			Pycnometer ^(a)	Bulk/0.65 ^(b)	
<u>Nuclear Waste Forms</u>					
SPC-4E	0.7 to 1.4	NA	~4.34	~2.91	Porous
TDS-211 Glass Marbles	8.7 to 14.9	6.7	NA	~2.75	Softening Point ~550°C
MB-1	~6 to 19	NA	NA	~2.95	Fragile
<u>Principal Stand-Ins</u>					
UO ₂	0.009 to 0.011	9	NA	NA	
SiO ₂ Shot	0.297 to 0.590	6	~2.65	~2.47	

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

(b) 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.

- Fluidized-bed (FB) coater for coating small particles (0.2- to 2-mm diameter) and for suspending or floating larger particles (>2 mm diameter) during coating.
- Screw-agitated coater (SAC) for coating the larger particles (~10 to 15-mm diameter) without having to use the suspension medium.

Fluidized-Bed Coater Development

The fluidized-bed equipment used in this work is pictured in Figure 2.1. In the initial work with nickel carbonyl as a catalyst, the carbonyl and hydrocarbons were introduced together through the bottom inlet, but the inlet became plugged because of premature reaction. To eliminate this problem, the

TABLE 2.2. Compositions of SPC-4E, MB-1, and TDS-211 Nuclear Waste Particles

Oxide Major Components	Normalized Composition, wt %		
	SPC-4E Pellets	MB-1 Pellets	TDS-211 Marbles
Al ₂ O ₃	6.27	17.00	3.71
B ₂ O ₃	---	4.34	8.36
BaO	2.46	3.01	0.07
CaO	2.51	2.02	4.03
Co ₂ O ₃	0.53	0.02	0.02
Cr ₂ O ₃	0.64	0.02	0.14
Dy ₂ O ₃	2.86	---	---
Fe ₂ O ₃	6.59	28.12	13.32
Gd ₂ O ₃	1.21	---	---
K ₂ O	1.82	---	---
La ₂ O ₃	9.89	0.14	---
Li ₂ O	---	1.77	3.39
MgO	---	1.02	0.55
MnO ₂	0.43	8.55	3.82
MoO ₃	10.25	0.02	---
Na ₂ O	3.44	10.15	15.42
NiO	1.78	3.19	1.44
P ₂ O ₅	5.93	0.85	---
PbO	0.11	0.06	---
SiO ₂	19.53	17.42	43.12
TiO ₂	0.04	0.30	0.29
ZnO	---	---	0.06
ZrO ₂	2.33	0.01	---
Tracer Components			
Ce ₂ O ₃	7.92	0.62	0.78
Cs ₂ O	---	0.28	0.31
Nd ₂ O ₃	8.52	0.69	0.74
SrO	5.92	0.39	0.44

FIGURE 2.1. Fluidized-Bed Coater and Associated Equipment

reactants were introduced separately 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 the C_xH_y through the top location. Cobalt acetylacetonate and iron carbonyl were also investigated as catalysts.

An important part of the equipment is the decomposer in the exhaust line, which is operated at 400°C to decompose residual nickel carbonyl. In normal chemical vapor deposition (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, because 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.

Except for a few experiments late in the program, the coating runs were carried out at atmospheric pressure. Although there are advantages in using a subatmospheric fluidized bed, such as decreased gas-phase precipitation and smoother fluidization, the hydrostatic heat of the bed itself limits the effective vacuum for deeper beds. A commercial operation would seek to avoid the complication of vacuum operation if it were possible to obtain satisfactory coatings without it. Hence, this study concentrates on operation at atmospheric pressure.

Parametric Study

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 SiO_2 (quartz) shot substrate in which the parameters were varied as outlined in Table 2.3. In addition, alternating injections of catalyst and carbon precursor were explored, as well as intermittent (in place of continuous) injections of catalyst.

Figure 2.2 shows bed weight gain versus temperature for deposition from acetylene. A maximum in the deposition rate is indicated in the neighborhood of 450° to 500°C, reminiscent of the maximum at 375°C reported by Baird (1977) for carbon deposits grown on nickel foils, where the character of the material

TABLE 2.3. Summary of LT-PyC Coating Parameters Used with SiO₂ Shot Stand-In Material

Parameter	Variations
Bed Temperature, °C	325, 375, 425, 475, 525, 625
Carbon Source Gas	Acetylene (C ₂ H ₂), methane (CH ₄), propane (C ₃ H ₈), heptane (C ₇ H ₁₆), toluene (C ₆ H ₅ -CH ₃)
Carbon Source Gas Concentration, mole %	~1.5, ~3.75, ~5, ~7.5, ~10, ~15
Catalyst	Nickel carbonyl [Ni(CO) ₄], iron pentacarbonyl [Fe(CO) ₅], cobalt acetylacetonate [Co(C ₅ H ₇ O ₂) ₂]
Catalyst Concentration, mole %	0.0, ~0.01, ~0.1, ~1, ~3, ~12
Diluent Gas	Argon (Ar), hydrogen (H ₂)

FIGURE 2.2. Effect of Temperature on Bed Weight Gain From Acetylene

changed from an open (Co-3.44 Å) columnar deposit to a tighter (Co-3.36 Å) 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 2.3 shows bed weight gain versus temperature for methane as a precursor, again showing a peak near 530°C. It is difficult to believe that the actual carbon formation rate at 630° to 640°C would drop to 3% of its value at 530°C. Although Lobo and Trimm (1971) show a drop to 10% between the 500°C peak and the 560°C valley for deposition from acetylene on a nickel foil, a decrease to 3% suggests that mechanical attrition at higher temperatures has a negative affect on the net deposition rate.

Figure 2.4 shows the effect of substituting hydrogen for argon in the deposition of carbon from acetylene. In contrast with the observation of Koss, Kofler, and Neumann (1980), who observed a maximum in the deposition rate

FIGURE 2.3. Effect of Temperature on Bed Weight Gain from Methane

FIGURE 2.4. Effect of H_2 Concentration on Bed Weight Gain

versus hydrogen content of the H_2/Ar mixture, no inflection was found in the present work. It is possible that at the presumed reduced pressure used by Koss, the increased thermal conductivity of the added hydrogen had a greater effect on actual bed temperature than was characteristic of the present work at atmospheric pressure. Table 2.4 compares the effect of argon versus hydrogen diluents on the bed-weight gain from methane and propane in argon versus hydrogen. In each case, the deposition rate was suppressed by hydrogen. Because of the lower gas density, higher volumetric flows were needed with hydrogen to obtain equivalent fluidization. The rate of deposition was still lower for the hydrogen atmosphere in spite of the increased rate of supply of carbon precursor (increased by a factor of 1.56).

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 (Table 2.5) suggest that the effectiveness of the catalyst can reach saturation at a very low level.

TABLE 2.4. Effect of Hydrogen on the Catalyzed Deposition of Carbon from Methane and Propane(a)

Run Number	Carbon Source Gas	Diluent	Ni(CO) ₄ Catalyst, Mole%	Total Flow, slmp	Bed Weight Gain (a) mg/min
35445-28-17	CH ₄	Ar	0.08	2.7	35.8
35445-28-18	CH ₄	H ₂	0.20	4.0	17.8
35445-68-43	C ₃ H ₈	Ar	0.12	2.7	275.0
35445-30-20	C ₃ H ₈	H ₂	0.20	4.0	34.9

(a) Fluidized bed, 32 g of 30 x 50-mesh SiO₂ shot in 25-mm ID reactor, T = 525°C, carbon source gas = 15.0 mole%, diluent = balance.

TABLE 2.5. Effect of Ni(CO)₄ Concentration on Deposition Rate(a)

Run Number	Ni(CO) ₄ Concentration, mole%	Deposition Rate on UO ₂ , μm/min
36332-08-151	0.35×10^{-3}	2.2
36332-04-150	0.74×10^{-3}	4.0
36332-01-149	2.2×10^{-3}	4.0

(a) Bed = 32 g x 50-mesh SiO₂ shot + 10 g 140 x 170-mesh UO₂ in 25-mm reactor, total flow rate = 5.6 slpm, T = 525°C, C₂H₂ = 2.9 mole%, H₂ = balance.

The use of Fe(CO)₅ as a catalyst was explored briefly in a series of runs in the temperature range 420° to 480°C, at ~1.5 mole% C₂H₂, and from 0.001 to 0.08 mole% Fe(CO)₅. Because the coatings adhered poorly to the 30 x 50-mesh SiO₂ particles (the coating spalled when it cooled), it was difficult to draw any firm conclusions other than that the Fe(CO)₅ appeared to be generally less effective as a catalyst in terms of conversion of C₂H₂ to carbon under comparable conditions. Gas-phase precipitation also appeared to be less pronounced because Fe(CO)₅ is more stable than Ni(CO)₄.

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

The objective of the current program was to obtain a usefully impermeable coating at economically viable rates of deposition. However, it became quite evident early in the work that the highest rates of coating formation tended to occur with 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 mole% and the $Ni(CO)_4$ catalyst concentration was reduced to ~0.03 mole% that the coating obtained could be classed as "hard" (i.e., dense and resistant to probing with a needle).

Table 2.6 shows the leach testing results for UO_2 particles, which were coated under a variety of conditions. The sole coating that showed a low level of permeability was deposited at the lowest deposition rate and at the lowest catalyst concentration (Run 35715-44-80). Unfortunately, the unique results of Run 80 could not be reproduced, despite a large number of subsequent coating runs at comparable or presumably more favorable conditions. Part of the problem may have been 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 disrupts the carbon coating. Figure 2.5 is a cross section of the Run 80 product, showing a reasonably uniform 15- to 17- μm coating. Little porosity is observable at the magnification shown.

The expedience 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

TABLE 2.6. Screening Test of Selected PyC Coatings Prepared in a Fluidized Bed(a)

Run Number	Coating System		Concentration, mole%			Temperature, °C	Deposition Rate, $\mu\text{m/hr}$	Coating Thickness, μm	Loss of UO_2 Substrate After Leaching, wt%, (b)
	Carbon Source Gas	Diluent	Carbon Source Gas	Diluent	$\text{Ni}(\text{CO})_4$ Catalyst				
35715-26-72	C_3H_8	Ar	15.0	85.0	0.023	525	~30	~30	~89.7
35715-36-76	C_2H_2	Ar	15.2	85.0	0.035	525	~20	~20	~95.4
35715-46-81	C_2H_2	Ar	15.2	84.7	0.089	520	~8	~33	~78.4
35715-30-74	C_2H_2	H_2	1.5	98.4	0.054	430	~6	~11	~100.0
35715-44-80	C_2H_2	H_2	1.5	98.5	0.014	445	~4	~15	~2.1, ~1.0
35715-48-82	C_2H_2	H_2	1.5	98.4	0.081	430	(1 hr) (c)	~32	~90.1
			3.8	96.2	0.081	430	(2 hr)		
			1.5	98.4	0.081	430	(1 hr)		
35715-50-83	C_2H_2	H_2	3.8	96.1	0.101	440	(2 hr) (c)	~35	~87.1
			1.5	98.4	0.101	440	(2 hr)		

(a) 10 g of -140 +170-mesh UO_2 plus 32 g of -30 +50-mesh SiO_2 shot, hydrocarbon stream plus diluent introduced from a center-tube injector terminating in the fluidized bed, $\text{Ni}(\text{CO})_4$ plus diluent introduced from the capillary at the apex of the bed-support cone; 25-mm-ID reactor.

(b) UO_2 leached for ~1 hr in 50 wt HNO_3 at 100°C.

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

20 μm

FIGURE 2.5. LT-PyC Coating on UO₂ Substrate
(Run 35715-44-80)

of hydrogen, whose rates of deposition were analyzed in Figure 2.5. The calculated coating density is given in Table 2.7

Simulated Waste Particle Coating Tests. Based on the above information about deposition rate and coating quality, samples of various waste forms were coated, either as granules which themselves constituted the fluidized bed, or as larger entities supported in a fluidized bed of smaller particles. The particle size and density were chosen to ensure that the items to be coated would be uniformly circulated throughout the bed. (Table 2.2 lists the waste forms and their compositions.)

SPC-4E Sintered Pellets

The SPC-4E materials lost weight during coating. As this material was somewhat friable, it is believed that at least part of the loss was due to attrition. The coating's nonuniformity was a problem; the coating appeared to

TABLE 2.7. Calculated Density of LT-PyC Coatings(a)

Hydrogen Content of H ₂ + Ar Diluent, ^(b) mole%	Calculated Coating Density, ³ g/cm
25	1.18
32	1.17
50	1.02
75	1.25

(a) Calculated from the bulk density change of the bed upon coating. Density of the SiO₂ shot taken as 2.65 g/cm³.

(b) Corresponds to data presented in Figure 2.4.

have spalled off in random locations during the coating run and upon cooling. The spalling problem was alleviated by applying a 1- μ m precoat of chromium carbide (Cr_xC_y) to the waste core. Table 2.8 contains a summary of data for two selected LT-PyC/Cr_xC_y coating runs. Figure 2.6 shows a cross section of the Cr_xC_y/LT-PyC/Cr_xC_y triplex coated SPC-4E waste particles from run number 207.

TDS-211 Glass Marbles

As was the case for the coatings on SPC-4E granules, spalling of the coating was a major problem and was even more pronounced with the TDS-211 glass marble substrate than with the SPC-4E. Several surface conditioning efforts were made to improve adhesion of the coating so as to decrease spalling. The techniques used were water vapor etching, precoating with $\sim 1 \mu$ m of Cr_xC_y, and HF etching.

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

TABLE 2.8. Data Summary: Selected LT-PyC/Cr_xC_y Coatings Applied to SPC-4E Particles^(a)

Run Number	Coating Thickness, μm			Ni(CO) Concentration, ^(c) mole%
	Cr _x C _y Precoat ^(b)	LT-PyC	Cr _x C _y Overcoat ^(b)	
36449-70-197	1	18	-	1.09×10^{-3}
36062-67-207	1	20	4	7.63×10^{-3}

(a) 0.7- to 1.4-mm diameter SPC-4E particles.

(b) Chromium carbide applied at 450°C from 1 to 8×10^{-3} mole% chromium dicumene in H₂.

(c) Both lots were coated with LT-PyC at 500°C with a C₂H₂ concentration of 2.85 mole% in H₂. Coatings were applied in a 25-mm reactor using diluent system of 100- to 250- μm -diameter molybdenum particles. Coating time was 4 h.

MB-1 Sintered Pellets

Because the MB-1 particles were relatively weak and their surfaces tended to spall when they were coated with LT-PyC, an effort was made to upgrade the MB-1. Three basic approaches to upgrading MB-1 were investigated, namely, additional sintering, precoating with a strengthening coating such as chromium carbide, and preconditioning at 500°C for 2 hours while the pellets were suspended in a fluidized bed. None of the approaches worked satisfactorily.

Although a fairly wide range of conditions was explored for the catalyzed deposition of LT-PyC, no really satisfactory coatings were obtained. It appeared possible to obtain coatings of varying degrees of porosity, density, and strength. However, those obtained at the economically attractive high rates of deposition had the greatest porosity and least strength. 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 that has

FIGURE 2.6. $\text{Cr}_x\text{C}_y/\text{LT-PyC}/\text{Cr}_x\text{C}_y$ Triplex Coated SPC-4E Pellets
(Run Number 36062-67-207, Table 2.8)

become supersaturated at another location by the decomposition of the hydrocarbon in contact with the nickel. Only if the particles 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 C_0 spacing of the material obtained previously by such mechanisms.

Agitated-Bed Coater Development

An agitated bed coater was developed in response to the need for a coater that is capable of coating particles of a large size (>2 mm) not typically coated in a fluidized bed. The screw-agitated coater (SAC) was selected after

a review of several candidate coaters (e.g., rotating-drum and vibrating-bed coaters) suggested that a screw-agitated coater had several advantages over an FB and no more disadvantages than other coaters.

Screw-agitated coaters are similar to FB reactors in that they utilize a vertical-type reactor in which reactants pass up through the bed. The particle circulation obtained produces a fairly uniform particle temperature profile and reactant concentration to which particles are exposed.

A glass model SAC was designed and fabricated 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.

Based on a series of tests using glass beads in the glass model, two first-generation SAC systems were designed, fabricated and tested. Figure 2.7 is a schematic of the coater showing the various ports for introducing reactants. The off-gas system (not shown) was patterned after that used with the fluidized bed coater. Each first-generation coater was constructed of a 457-mm (~18 in.)-long 102-mm-diameter (4-in.) diameter SS pipe that was welded to a cone bed support.

While fluidized-bed coaters are in an advanced stage of development, screw-agitated coaters are in their infancy. Accordingly, emphasis was placed not only on the development of suitable coating parameters in the coater, but on the development of a mechanically operable SAC.

Parametric 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 with the following parameters:

Bed temperature: ~400 to ~550°C

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

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

Auger speed: ~25 to ~120 rpm

Total coater gas flow: ~4 to ~25.4 l/minute.

FIGURE 2.7. Schematic of Screw-Agitated Coater

Furthermore, four different augers were tested for their relationship to coating rate and quality and operability. The relevant dimensions of the four augers are given in Table 2.9. 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 has been focused on Augers No. 1 and 4, which represent the extremes for 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

TABLE 2.9. SAC Auger Dimensions

Auger Number	Pitch, mm (in.)	Auger Diameter mm (in.)	Shaft Diameter, mm (in.)
1	64 (2.5)	41 (1.625)	13 (0.5)
2	25 (1)	38 to 76 (1.5 to 3)	6 (0.25)
3	51 (2)	38 to 76 (1.5 to 3)	16 (0.625)
4	25 (1)	76 (3)	25 (1)

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.

Figure 2.8 shows the effect of temperature on the bed weight gain in the SAC using C_2H_2 , $Ni(CO)_4$, and H_2 gas mixtures. Over the temperature range examined, the deposition rate appears to increase as the temperature increases. An upper limit was imposed on the coating temperature in the parameter study because glass marbles eventually targeted to be coated in the SAC softened at $\sim 550^\circ C$. Accordingly, it is possible that a maximum in the bed weight gain rate, as found in the fluidized-bed experiments (Figures 2.3 and 2.4), does exist if data for higher temperatures have been obtained. In addition to the trends presented in Figure 2.8, certain observations were made during the parameter study:

- 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.
- The deposition rate decreased as the total flow was increased, suggesting that the reactant gases required preheating. Efforts to increase the coating rate by preheating the gases were not very successful due to premature $Ni(CO)_4$ decomposition.
- The best-appearing PyC coatings were applied using ~ 0.02 mole% $Ni(CO)_4$, ~ 3.0 moles% C_2H_2 , and the balance H_2 with a bed temperature of $\sim 500^\circ C$.

Mechanical parameters of the SAC can contribute significantly to poor coating quality and coating rate if the mechanical agitation of the substrate

FIGURE 2.8. Effect of Temperature on LT-PyC Deposition from Acetylene in a Screw-Agitated Coater

generates foreign material, 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.

An initial effort to circulate ~6.4-mm (~1/4-in.) alumina balls was unsuccessful because binding occurred between the balls, the auger, and the bottom of the cone. Several approaches were tried to reduce the binding. An expedient approach that has proved successful has been to place a 6.4-mm-thick (~1/4-in.) graphite disk on the bottom of the cone and let the auger ride on the graphite disk. Even though the graphite-bearing disk was satisfactory, 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 simulated waste glass marbles.

During initial coating tests using TDS-211 glass marbles, the substrate occasionally broke, especially at higher coating temperatures. The breakage/temperature phenomenon is probably related to an increased tendency of the glass marbles to bind at the elevated temperatures. This condition could be aggravated by the marbles' tendency to sieze to each other as they approach their softening temperature (500 to 550°C) and/or by the change in clearance between the screw and the chamber wall 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. Observations of the SAC model show that binding can occur if the screw and wall clearance change (due to the screw rotation) from above to below a distance equivalent to the diameter of one to possibly three marbles.

To examine the screw-to-wall clearance effect on breakage, it was decided to determine what combinations of marble sizes would lead to binding at room temperature and at elevated temperatures (500 to 550°C). Accordingly, a random sample of marbles was taken and their diameters were measured. The marbles had 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 (>3 diameters) was required to minimize binding at room temperature and that slightly more distance was needed at elevated temperatures. A modeling study in the SAC confirmed the geometric analysis.

Several gas reactant introduction designs were examined in an effort to identify the design that minimizes plugging problems and gas-phase nucleation and improves coating quality and deposition rate. Some interesting observations were made during this series of runs and are given below:

- To reduce gas-phase nucleation, $\text{Ni}(\text{CO})_4$ and C_2H_2 were introduced into the bed through separate feed tubes. When $\text{Ni}(\text{CO})_4$ was introduced through the holes in the cone, the holes became plugged, probably with nickel. In light of the $\text{Ni}(\text{CO})_4$ plugging problem, it was decided to reverse the gas inlet locations by introducing the $\text{Ni}(\text{CO})_4$ through the feed tube and 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 $\text{Ni}(\text{CO})_4$. In addition, the tip of the auger (which rotated in the tube) tended to ream out any nickel buildup in the upper portion of the feed tube. In runs of 4 to 5 hours duration, this approach to introducing the reactants was successful. However, when an attempt was made to preheat the reactants, plugging problems developed. Subsequently, a 304 stainless steel, water-cooled, jacketed, catalyst feed tube was inserted through a hole in the lid on the SAC and used to reduce clogging problems caused by premature decomposition of the catalyst. Water-cooled feed tubes were also used to introduce the catalyst through the side of the SAC. Both approaches were successful in minimizing the plugging problem, but introducing the catalyst through the side of the SAC was found to result in fewer problems with binding (see above).

- Unlike the fluidized-bed reactor, heat transfer in the SAC can be a limitation, especially if the acetylene is introduced without preheating, as was being done when both the carbon and nickel reactants were introduced at the bottom of the reactor. Preheat tests were performed but neither the coating rate nor the coating quality was significantly improved by the use of preheated C_2H_2 .
- To reduce the homogeneous gas-phase nucleation that was observed in the SAC, an effort was made to stabilize nickel carbonyl by using carbon monoxide (CO) in place of hydrogen as the carrier for $\text{Ni}(\text{CO})_4$. However, the amount of nucleation was not grossly reduced compared to that typically obtained for hydrogen.

In summary, two SAC units were designed, fabricated, and tested during a series of roughly fifty coating runs. The SAC approach appears to be feasible, as no fundamental, uncorrectable problem was noted during operation. The primary mechanical consideration that needs to be addressed when coatings are to be prepared in an SAC is whether or not sufficient clearances have been allowed. Accordingly, the size of the substrate and the design (primarily the diameter of the flight) of the auger must be matched so that the 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 that terminate in the bed and/or baffles, which are positioned in the bed zone.

The LT-PyC coating data do not suggest any major differences between the trends obtained using the fluidized-bed coater compared to those obtained using the two SAC's. Since there was a problem in preparing good quality coatings on TDS-211 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 are deposited at a higher rate (~ 2 to 3 times faster). Two probable reasons for the low SAC coating rates can be identified: 1) the particle attrition rate is significant compared to the LT-PyC coating rate, and 2) the larger substrate size reduces the surface area to a gas volume ratio which would tend to reduce the deposition efficiency.

2.2 PNL COATING STUDIES

The initial objective of the LT-PyC coating development work at PNL was to participate in a technology transfer with BCL. This transfer was intended to combine the CVD coating expertise at BCL with the nuclear waste form expertise at PNL. As part of the transfer, a 27-mm ID, fluidized-bed reactor system and associated off-gas components were assembled and demonstrated in the laboratory at PNL. Coating parameters developed by researchers at BCL and the Seibersdorf Research Center were tested, and coating results were compared with those obtained earlier. Also, parameters for applying an Ni overcoat to particles previously coated with LT-PyC were tested briefly.

Once the LT-PyC coating process was demonstrated, the scope of the work at PNL was broadened to include demonstration and evaluation of different off-gas system components. An off-gas system for a large-scale coating process was also conceptualized.

Fluidized Bed Coater

The laboratory-scale, fluidized-bed coater system was modeled after the one used by BCL (see Figure 2.9). The coater consists of a gas distribution system, catalyst bubbler, quartz fluidized-bed reactor, off-gas filter, catalyst destructor, and an oil trap. The gas distribution system (Figure 2.10) is used to meter, blend, and route the gases to the catalyst bubbler and reactor. The system consists of six low-flow rotameters with pressure gauges on the inlets and precision control valves on the outlets. Once calibrated, the flowmeters have an accuracy of $\pm 1\%$ of full scale. By changing floats and metering tubes, flows can be adjusted from 2 to 70 slpm. All gases used were passed through 7- μm particle filters before entering the gas distribution system. Acetylene was also passed through an activated charcoal filter to remove acetone.

FIGURE 2.9. PNL Fluidized-Bed CVD Coating System Schematic

FIGURE 2.10. Fluidized-Bed Coater Gas Distribution Panel

A carrier gas was bubbled through the $\text{Ni}(\text{CO})_4$ catalyst in a 250-ml cylindrical Pyrex® bubbler before being passed to the reactor. The catalyst bubbler is fitted with an inlet and outlet stopcock to help ensure that catalyst isolation from air is maintained. The $\text{Ni}(\text{CO})_4$ has a high volatility at room temperature (vapor pressure ~ 0.5 atm). Thus, to achieve extremely low catalyst flows, the bubbler was placed in a salt ice bath maintained at -10°C .

The fluidized-bed reactor is a 27-mm ID quartz tube that has a conical bottom with a 40° included angle, a bottom gas inlet port, and a center-tube gas inlet extending from the reactor top. During most of the coating runs, a

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catalyst/carrier gas mix was fed to the bottom of the reactor, and a carbon source gas/carrier gas mix was introduced through the center tube (Figure 2.9). The carbon source gas was kept separate from the catalyst prior to introduction to the particle bed to prevent premature decomposition.

Off-gases consisting primarily of carrier gas with some carbon soot exit from the reactor and pass through either a Pyrex® wool-packed filter or a Pall® 0.45- μ m absolute filter for soot removal, then to a catalyst destructor. The catalyst destructor is used to ensure that no $\text{Ni}(\text{CO})_4$, which is quite toxic, leaves the coating system unreacted. Off-gases finally pass through an oil trap, which prevents air backflow into the coating system. The off-gas system is discussed in greater detail later.

The procedure for applying a coating in the fluidized bed reactor was the same for most runs:

1. start purge gas (Ar or N_2) flowing through the reactor bottom and center tube ports
2. load the bed material into the reactor from the top port
3. adjust the purge gas such that the flow rate through the lines corresponds to the coating-gas flow rate to be used
4. raise the coater furnace and catalyst destructor furnace to the desired operating temperature
5. switch from purge gas to coating gases, turning the catalyst flow on last.

Coater shutdown was accomplished by reversing the start-up sequence.

Coating Tests on SiO_2 Particles

Test runs performed on the lab-scale fluidized bed coater served to 1) demonstrate different parameters for applying LT-PyC coatings; 2) evaluate CO as an alternative carbon source gas; 3) demonstrate Ni coatings; and

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4) evaluate off-gas treatment components. A summary of the processing data for the LT-PyC coating demonstration, the CO source gas evaluation, and the Ni coating demonstration runs is presented in Table 2.10. (The off-gas treatment evaluation is presented below.) Parameter set No. 1 (Table 2.10) was recommended by BCL early in the LT-PyC coatings program for use with the first series of runs on the PNL coater. A blend of 98.5 mole% H_2 , 1.5 mole% C_2H_2 , and 0.011 mole% $Ni(CO)_4$ was used as a coating gas, and the total flow through the fluidized bed was maintained at 6.2 l/min at a temperature of 430°C. The $Ni(CO)_4$ catalyst was introduced through the reactor bottom capillary with roughly 75% of the total H_2 flow. The C_2H_2 was introduced through the center tube with the balance of the H_2 . The substrate used was 300 to 500- μ m-diameter SiO_2 sand, which is highly irregular in shape. The PyC deposition rate averaged 1.4 μ m/hr. This low rate can be attributed to the low C_2H_2 concentration, the relatively low coating temperature, and the high bed-surface area due to the irregular-shaped substrate. The coatings appeared to be dense and smooth, which are desirable qualities in a coating. Photomicrography of mounted and polished specimens revealed uniform, void-free coatings, which exhibited some fragmentation at points where the substrate surface was concave. Cross sections of LT-PyC-coated SiO_2 sand particles (Figure 2.11) show that the coated particles have concave surfaces and sharply pointed edges. Coating fragmentation can be seen in the concave area; however, the coating is continuous elsewhere. Coating brittleness is demonstrated by the fracture, which was probably created during the mounting and polishing steps. It appears that a smooth, round substrate would be more ideal for the application of LT-PyC.

Parameter set No. 2 (Table 2.10) was recommended by BCL later in the program after it was determined that the deposition rate could be increased without compromising the coating quality. The main differences between parameter sets 1 and 2 is that for set No. 2, the C_2H_2 was increased to 3 mole%, the bed temperature was increased to 500°C, and the $Ni(CO)_4$ was decreased to 0.005 mole%. Due to flow range limitations of the catalyst bubbler rotameter, it was necessary to use a gas heavier than H_2 to obtain the required low $Ni(CO)_4$ flow. Carbon monoxide was chosen because it is used as a cover gas

TABLE 2.10. PNL Fluidized-Bed Coating Runs on SiO₂ Particles

Parameter Set Number	Objective	Number of Runs	Substrate(a)	Bed Temp., °C	Gas Flow, l/min	Coating Gas Composition, mole%						Coating Rate, μm/hr	Coating Thickness, μm
						Ar	H ₂	C ₂ H ₂	CO	Ni(CO) ₄			
1	Demonstrate LT-PyC (initial BCL parameters)	4	32 g SiO ₂ Sand	430	6.2	0	98.5	1.5	0	0.011	1.4	10.5	
2	Demonstrate LT-PyC (revised BCL parameters)	2	36 g SiO ₂ Shot	500	6.0	0	96.9	3.0	0.049	0.005	4.1	28.5	
3	Demonstrate LT-PyC (revised BCL parameters without center tube)	1	36 g SiO ₂ Shot	500	6.0	0	96.9	3.0	0.055	0.007	6.7	40.0	
4	Demonstrate LT-PyC (Koss et al. 1980 parameters)	1	32 g SiO ₂ Sand	430	6.5	66.6	28.6	4.8	0	0.009	1.1	8.0	
5	Test CO as Carbon Source Gas	2	32 g SiO ₂ Sand	430	6.3	0	97.0	0	3.0	0.015	<0.25	<1	
6	Demonstrate Ni Coating	1	36 g SiO ₂ Sand	200	4.5	99.9	0	0	0	0.05	0.4	1.0	
7	Demonstrate Ni Overcoat of Parameter Set No. 2 Particles	1	36 g SiO ₂ Shot	160	5.5	70.0	22.5	0	0	7.5	3.2	2.0	
8	Demonstrate Ni Overcoat of Parameter Set No. 3 Particles	1	36 g SiO ₂ Shot	206	10.0	88.9	9.3	0	0	1.8	5.0	11.1	

(a) All substrate was sieved to -300 + 500 μm

FIGURE 2.11. LT-PyC Coating Applied to SiO₂ Sand Showing Fragmentation at Concave Surface

for Ni(CO)₄ during storage to prevent chemical decomposition. A more spherical SiO₂ shot in the 300- to 500-μm diameter size range was used as substrate. The deposition rate was 4.1 μm/h, an increase of three times over the coating runs of the first parameter set. A cross section of the coating (Figure 2.12) indicates that the coating is of high quality. A few occluded particles (probably carbon soot) can be seen.

A coating run was made to evaluate the effectiveness of adding the catalyst and carbon source gas together through the bottom of the reactor, thus eliminating the need for a center tube (parameter set No. 3, Table 2.10). The parameters used were essentially the same as for set No. 2; however, the

100 μm

20 μm

FIGURE 2.12. LT-PyC Applied to SiO₂ Shot Using Parameter Set No. 2 (Table 2.10)

Ni(CO)_4 concentration was slightly higher at 0.007 mole%. The deposition rate was high at $6.7 \mu\text{m/h}$ and the coating quality appeared to be good, indicating that it is possible to introduce catalysts and carbon precursors together. When introducing all gases from the reactor bottom, it is desirable to minimize the residence time the Ni(CO)_4 and C_2H_2 are mixed together and to keep the gas mixture as cool as possible before it enters the bed. These measures reduce the likelihood of premature catalytic nucleation.

Koss et al. (1980) reported that a maximum LT-PyC deposition rate was obtained using a 33-vol% H_2 in Ar as a carrier gas. A coating run was made to simulate these conditions (parameter set No. 4, Table 2.10). The C_2H_2 concentration was 4.8 mole%; the Ni(CO)_4 concentration was 0.009 mole%; total gas flow was 6.5 l/min; and bed temperature was maintained at 430°C . Metallographic examination (Figure 2.13) showed the coatings to be spotty, as if portions had flaked off during the coating process. The deposition rate averaged $1.1 \mu\text{m/hr}$; however, in places where the coating had not flaked off, the deposition rate was as high as $5 \mu\text{m/hr}$. From this limited test and the work performed by BCL, the results of Koss could not be duplicated.

Two runs were made using parameter set No. 5 in an attempt to use CO as the carbon source gas. The results were very discouraging, as the coating rate was an order of magnitude below that obtained using C_2H_2 .

Three different sets of parameters for applying Ni coatings were tested. For parameter set No. 6, SiO_2 sand was coated with Ni at 200°C using 0.05 mole% Ni(CO)_4 in Ar with a total flow of 4.5 l/min. The deposition rate was low at $0.4 \mu\text{m/hr}$; however, the coating appeared to be dense and uniform. New parameters were tested (parameter set No. 7) in an effort to improve the deposition rate. The Ni(CO)_4 concentration was increased to 7.5 mole%, and H_2 was blended with Ar as the carrier gas. The target temperature of the bed was 200°C , but due to the endothermic nature of the Ni(CO)_4 decomposition in the reducing atmosphere, the temperature dropped to 160°C during the coating run. A large slug of particles, which bonded with the Ni, formed in the reactor bottom. A thin coating of Ni also formed on the bed section of the

500 μm 40 μm

FIGURE 2.13. LT-PyC Coating Applied to SiO₂ Shot Using Parameter Set No. 4 (Table 2.10)

reactor tube. Based on these problems, a final run was made in which the Ni(CO)_4 concentration was decreased to 1.8 mole%, the total flow was increased to 10.0 l/min, and the bed temperature was maintained at 206°C (parameter set No. 8). The particles did not bond together in this run, and the deposition rate was higher at 5 $\mu\text{m/hr}$. Figure 2.14 shows the Ni/LT-PyC duplex coating. Both coating layers are uniform, but there is evidence of some porosity on the outer portion of the Ni coating.

In summary, the better LT-PyC coatings on SiO_2 shot were obtained at 500°C using 3.0 mole% C_2H_2 and 0.005 to 0.007 mole% Ni(CO)_4 as the reactants in a hydrogen diluent (parameters sets No. 2 and 3). Capillary tube plugging was not a problem when the reactants were added together, as long as the capillary was well insulated. The deposition rate even increased when the reactants were introduced together. Nickel could effectively be applied as an overcoat to LT-PyC coated particles to provide an additional barrier. The best coating results were achieved at ~200°C with ~2% Ni(CO)_4 in a 9:1 mix of Ar and H_2 (parameter set No. 8).

Coating Tests on MB-2 Waste Pellets

Once the LT-PyC parameters prescribed by BCL were verified on the PNL system, an attempt was made to coat MB-2 simulated waste ceramic pellets (Table 2.11). Parameters nearly identical to those of set No. 3 (Table 2.10), were used to coat a bed consisting of 10 g of -12 +20 mesh MB-2 particles in 22 cm^3 of SiO_2 shot. Total flow was increased to 10.0 slpm to ensure more uniform particle circulation in the bed. The coating was continuous and uniform on only about 10% of the MB-2 particles, but the SiO_2 particles were all well coated. Figure 2.15 shows an SEM photograph of a MB-2 particle with a noncontinuous coating and a photomicrograph of continuous coatings on other MB-2 particles. The noncontinuous coating is characteristic of the problems BCL encountered when trying to coat ceramic pellets.

Spawling of the coating may be attributed to one or more of several factors: 1) increased particle attrition due to increased particle mass; 2) a reduction and subsequent volatilization of surface metal oxides during the prolonged exposure to H_2 at 500°C, resulting in a weakened coating bond;

50 μm 20 μm

FIGURE 2.14. LT-PyC/Ni Duplex Coating Applied to SiO₂ Shot Using Parameter Sets No. 3 and 8 (Table 2.10)

TABLE 2.11. Composition of MB-2 Nuclear Waste Pellets

<u>Oxide</u>	<u>Normalized Composition, wt%</u>
Major Components	
Al ₂ O ₃	17.23
B ₂ O ₃	4.19
BaO	0.09
CaO	2.09
Cr ₂ O ₃	0.06
Fe ₂ O ₃	26.52
La ₂ O ₃	0.02
Li ₂ O	0.19
MgO	0.50
MnO ₂	7.95
MoO ₃	0.02
Na ₂ O	7.24
NiO	3.12
PbO	14.42
SiO ₂	14.42
TiO	0.14
ZrO ₂	0.02
Tracer Components	
Ce ₂ O ₃	0.60
CsO	0.20
Nd ₂ O ₃	0.64
SrO	0.33

3) a mismatch in thermal expansion coefficients between the MB-2 and LT-PyC; and 4) friability of the ceramic pellets. Whatever the actual cause, researchers at BCL were able to avoid the problem by precoating the pellets with ~1 μm of Cr_xC_y prior to applying the LT-PyC.

FIGURE 2.15. Examples of Noncontinuous and Continuous Coatings of LT-PyC on MB-2 Waste Particles

Off-Gas System

Off-gas from the LT-PyC coating process is composed almost entirely of H_2 with a small quantity of entrained carbon particles from the catalytic decomposition of the C_2H_2 carbon source gas. The off-gas system design is determined by several factors, namely, the presence of toxic $Ni(CO)_4$, particles in the gas, and the flammability of the gas. A catalyst destructor, particle cyclone, and incinerator were each tested and evaluated as potential process components that could effectively treat the off-gas.

Catalyst Destructor. Due to the toxic nature of $Ni(CO)_4$, a catalyst destructor was used in the LT-PyC coater off-gas system during all runs at BCL and the initial runs at PNL. The destructor used at PNL consisted of a steel-wool-packed pipe, which was positioned in a split-tube furnace with a gas inlet and outlet on opposite ends of the pipe (Figure 2.16). The destructor was maintained at $500^\circ C$ during the coating runs to ensure that any unreacted $Ni(CO)_4$ would decompose into the products Ni , C , CO , and CO_2 . The steel wool provides a hot surface to collect Ni precipitate. Off-gas was sampled during the first LT-PyC coating run at PNL. Two samples taken between the fluidized bed coater and the catalyst destructor had less than 0.05 ppm $Ni(CO)_4$ (detection limit for the colorimetric detector tubes). Heat from the fluidized bed reactor is apparently adequate to decompose the catalyst. The DOE-prescribed occupational exposure limit for $Ni(CO)_4$ is 0.05 ppm as a 8-hr time-weighted average (Threshold Limit Values 1979). Since workers would be exposed to much less than 0.05 ppm $Ni(CO)_4$, use of the catalyst destructor was discontinued.

Cyclone. A cyclone for collecting carbon particles entrained in the off-gas of the lab-scale PyC coater was designed, fabricated, and evaluated (Figure 2.17). The critical cyclone dimensions were calculated using Stairmand ratios recommended for the design of high-efficiency cyclones (Koch and Licht 1977). The cyclone was designed assuming a particle density of 2.0 g/cm^3 , an off-gas temperature of $200^\circ C$, an exit flow rate of 8.5 l/min (actual), and a mean particle diameter of $5 \text{ }\mu\text{m}$. The design graphs, which were for industrial-size units, were extrapolated to include the smaller size.

FIGURE 2.16. Off-Gas System Catalyst Destructor

The cyclone was tested during four coating runs. Effluent gases from the coater passed through the cyclone and then through a 0.45- μm absolute filter. Cyclone efficiency was calculated as the percent of particulate collected by the cyclone compared to the total particulate collected. The efficiency of the unit averaged about 10% compared to the calculated design efficiency of 70%. The poor performance may be due to 1) lower off-gas flow caused by lower-than-expected off-gas temperature (33°C versus 200°C), 2) extrapolation of the design charts beyond their ranges, 3) a higher fraction of particles less than 5- μm diameter, or 4) the agglomeration of small particles forming larger but less dense particles. Microscopic examination of a limited particulate sample showed that the particles are about 5 μm in diameter and agglomerate readily. Although no operational problems were encountered with the cyclone, it is not recommended for this application due to the behavior of the carbon particles and resulting low-removal efficiency.

FIGURE 2.17. Off-Gas System Cyclone

Incinerator. A tube-type incinerator was designed, built, and tested for the purpose of completely combusting the coater off-gas. Should the LT-PyC coating process be used for radioactive waste in a remote facility, the off-gas would likely require further treatment for removal of radioactive species. By combusting the off-gas, which primarily consists of H_2 , the H_2O combustion product could be condensed out and recycled to the primary process

feed system, thus nearly eliminating the volume of off-gas requiring further treatment. Also, the potentially dangerous combustibles would be converted to their stable forms.

A schematic of the incinerator is presented in Figure 2.18. The body of the unit was 3/4-in. Schedule 40 SS pipe having a Kao-wool® insulative layer. Off-gases entered the body tangentially at one end while combustion air entered concentrically from the other. The entering air was preheated by the burner exhaust gases. The inlet tubes were sized such that the velocities of incoming gases exceeded the maximum flame propagation speed of hydrogen in air (>2.7 m/sec) at the minimal expected flow rates. A glow plug served to ignite the gases at the point of mixing. (The glow plug is a standard auto-parts-store item, used in Oldsmobile 5.7-liter diesel engines.) The surface temperature of the glow plug was maintained at or above 800°C using a 12-v, 7-amp power source. A stoichiometric air-hydrogen mixture spontaneously ignites at 571°C . Off-gases exited the incinerator through a 19-mm (3/4-in.)

FIGURE 2.18. Off-Gas System Incinerator

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stainless steel pipe. Both inlet and outlet temperatures were monitored during operation. Excess air was also measured using an on-line oxygen monitor.

The off-gas incinerator was first tested without the coater using reduced gas flows, and later was tested in conjunction with the lab-scale PyC coater using normal flows. The operating procedure for all tests was as follows: 1) begin combustion air flow to the unit, 2) begin Ar flow through the off-gas inlet at a rate corresponding to the desired H_2 flow rate, 3) preheat the glow plug at least two minutes, and 4) switch the off-gas inlet flow from Ar to H_2 . Ignition was found to occur about 30 sec after the H_2 was switched on and was signaled by a small pop. With a 9% exhaust O_2 concentration, the incinerator tube glowed red near the off-gas inlet for a distance of about 10 cm. The glow disappeared when the combustion air flow was increased to give a 12% exhaust O_2 concentration. Once ignition occurred, the glow plug could be turned off without affecting the operation of the incinerator. Subsequent tests were conducted to evaluate the effect of hydrogen flow interruptions of up to 60 sec. In each test, the burner reignited immediately upon readmission of hydrogen without using the glow plug. A test was performed using a 30/70 ratio of H_2 and Ar as the burner feed. The results were not encouraging, as the flame continued to go out during the test.

After several hours of operation, the incinerator was disassembled and visually inspected for cracking, spalling, and general wear. The burner tube interior showed signs of oxidation for about 18 cm downstream from the inlet port and was discolored at the exhaust port. The center tube was oxidized and discolored in positions corresponding to those on the burner body. The glow plug seemed to be oxidized but still operated as if new. There were no signs of warping, cracking, or melting.

The incinerator tests have shown the feasibility of combusting LT-PyC coater off-gas. Carbon soot particles were completely combusted along with the hydrogen, thus eliminating the need for a downstream filtering system. Additional development work is required to safely accommodate H_2 /Ar coating gas mixtures. The lab-scale unit was built to demonstrate the process feasibility of combusting off-gas and not to evaluate burner designs. Future development work should focus on incinerator design and construction materials to ensure safe and efficient operation for extended periods of time.

Conceptual Off-Gas Treatment System. A large-scale LT-PyC coater system would consume an excessive volume of H_2 during normal operation. A hydrogen recycle system could greatly reduce the cost for coater operation and would also reduce the amount of off-gas requiring post-treatment.

Figure 2.19 is a schematic of a conceptual off-gas treatment system. In this system, off-gases exit the coater and are passed through an ejector scrubber that removes soot particles. Most of the off-gas stream is then recycled through a condenser and mist eliminator to remove moisture added by the scrubber. The recycle stream is then heated above the dew point and metered back into the coater along with the makeup gases. Liquids from the scrubber, condenser, and mist eliminator are collected in a scrubber tank and are periodically recycled to the primary feed system. A scrub solution other than water, which has better carbon wetting and removal properties, may be used if desired. The flowsheet shown in Figure 2.19 would require modifications, depending on the alternate scrub solution. A small portion of the off-gas stream is taped off to prevent the accumulation of CO, CO_2 , and any organic molecules derived from pyrolytic decomposition of the C_2H_2 carbon source gas. This stream would be passed through an incinerator and then into the primary process off-gas system.

This conceptual off-gas system has two main benefits: 1) hydrogen consumption is minimized, and 2) the gas passing on to the primary off-gas system would be mostly H_2O , which can be condensed out for recycle with the feed. The time and scope of LT-PyC coating work at PNL did not allow for the demonstration of this system. Future development and scale-up work should include the analysis and demonstration of the off-gas system as a whole.

2.3 GAC COATING STUDIES

Under contract to PNL, studies were conducted by General Atomic Company (GAC) on the chemical vapor deposition of carbon for use on various nuclear waste forms. The objectives of the work were to search the literature for the CVD processes best suited for coating waste particles with carbon, to evaluate the feasibility of coating particles larger than 4 μm in diameter, to determine the minimal deposition temperatures of the process, and to coat both

FIGURE 2.19. Conceptual Off-Gas Treatment System

ceramic and glass waste forms with carbon. The coated waste forms were analyzed initially by photomicroscopy and radiography. Selected samples were then sent to PNL for leach testing.

Literature Review

The literature reviews to identify coating processes and to evaluate the feasibility of coating particles larger than 4 μm have been combined and are covered in this section. The literature on chemical vapor deposition is extensive. Fortunately, there are several recent reviews of the field that apply to waste form coating. Yee (1978) subdivides CVD into conventional chemical vapor deposition, pack cementation, and chemical spray deposition. Of these processes, conventional CVD is the best suited for waste coating because of the high-strength, impermeable coatings it produces. Yee notes that, in conventional chemical vapor deposition, a number of techniques have been used to reduce deposition temperatures. The techniques include the selection of suitable chemicals, photochemical excitation with light and lasers, the use of reactive atoms, and plasma activation.

Palmer and Cullis (1965) have extensively reviewed the processes for forming carbon from gases, concentrating particularly on the chemical aspects of the processes. In a subsequent paper, Palmer (1968) reviewed the formation of carbon during the cracking of hydrocarbons. These reviews offer a basis for selecting appropriate hydrocarbon gases for relatively low-temperature chemical vapor deposition of carbon. (Acetylene, propylene, and propane have been selected for most efforts on low-temperature chemical vapor deposition of carbon).

To our knowledge, photochemical excitation has not been used for chemical vapor deposition of carbon. Kofler and Neumann (1977) have used reactive, atomic CVD to deposit carbon at low temperatures through the use of nickel carbonyl as a catalyst, and this work has been carried on at BCL and PNL as previously described. Inspektor et al. (1980) have deposited carbon at low temperatures using plasma-activated CVD.

Conventional CVD of carbon can be separated into deposition on a stationary substrate and deposition in a bed of fluidized particles. Deposition on

stationary substrates was the first process used for pyrolytic carbon deposition. This process and the properties of the deposits have been reviewed by Knippenberg et al. (1967). In deposition on a stationary substrate, a mixture of an inert gas and a hydrocarbon gas is passed over a heated substance. To prevent deterioration of the quality of the deposit, it is necessary to keep the hydrocarbon gas concentration low so that the carbon is deposited directly on the substrate rather than on particles that nucleate homogeneously in the gas and that subsequently can be incorporated into the deposit. As a result of this requirement, the carbon crystallites in the deposit are oriented preferentially with their layer planes parallel to the surface of the substrate. The carbon crystallites are a two-dimensionally ordered form of the graphite crystal containing the graphite layer planes with strong covalent bonding among the atoms but without order between the atoms in one layer plane and those in the adjacent layer planes. This preferred orientation of the carbon crystallites produces a strong anisotropy in the properties of the deposit. For example, the fracture strength, the Young's modulus, and the thermal conductivity are much higher in the directions parallel to the substrate surface than perpendicular to it. Furthermore, there is an anisotropy in the thermal expansivity in the directions parallel and perpendicular to the substrate surface that leads to cracks in the deposit parallel to the substrate surface whenever there is curvature of the substrate. These delamination-type cracks are certainly not desirable in waste isolation coatings.

Carbons with more isotropic properties can be deposited in a fluidized bed of particles. Bokros (1969) has reviewed the work on FB-PyC deposited at temperatures higher than 1500°C. A review of work on fluidized bed deposition below 1500°C has not been written, but much of the work in this area is described in a series of papers by Kaae (1971a and b, 1975). Deposition in a fluidized bed of particles apparently produces more isotropic carbons because particles homogeneously nucleated in the gas are incorporated in the deposit. These near-isotropic pyrolytic carbons do not have the delamination cracks of the stationary-substrate coatings and, therefore, they are more suitable for waste isolation coatings. Another attractive feature of the fluidized-bed coatings over coatings deposited on stationary substrates is their relatively high strength.

Because the surface area of the bed of particles must be relatively large and because it is difficult to fluidize large particles, it does not seem practical to use particles larger than about 1.5 mm in diameter to make up the bed. However, it is possible to use a bed of larger particles mixed with smaller particles. During deposition, the large particles will become uniformly coated with carbon with essentially the same structure as that deposited on the smaller particles. Although experimental studies need to be carried out to define the quantity of larger particles that can be added to the bed without loss of a sufficient surface area or proper fluidization, conceivably, a substantial fraction of a fluidized bed could be made up of larger particles during coating. In this way, particles larger than 4 mm in diameter could be coated with high-quality pyrolytic carbon coatings.

A literature review of coating methods other than CVD was also made. Vacuum evaporation, sputtering, and ion plating, all of which are reduced pressure processes, were investigated and compared with the CVD processes.

A process used to coat particulate waste forms greater than 4 μm in diameter should offer 1) a high deposition rate to keep coating times short; 2) the ability to work at relatively low temperatures to prevent volatilization of some of the fission products; and 3) should be simple enough that the process can be carried out remotely.

Commonly, vapor deposition rates are quoted in the literature in $\mu\text{m}/\text{min}$. On the basis of the quoted values, one might conclude that all of the processes are about equivalent in their speed of coating. However, the surface area of the substrate should also be taken into account, since a process that is able to accommodate only a small substrate surface area will require a longer time to coat a certain amount of material than a process that can accommodate a large surface area. Of the various coating processes identified, only CVD in a fluidized bed of particles has the ability to accommodate large surface areas, and thus, this process has an advantage over the others in terms of the required coating times. The other processes can be considered to be about equal in coating times.

A reduction in temperature required for fluidized-bed, chemical-vapor deposition can be obtained by removing the requirement that the gases fluidize

the particles. The time required for decomposition of the hydrocarbon gas to a given stage necessary for the deposition of carbon increases with decreasing temperature, so that if longer gas residence times can be attained, lower temperatures can be employed. The residence time of the hydrocarbon gas in the bed of particles increases as the flow rate of gas decreases, but a lower limit on the flow rate is imposed by the requirement that the gas fluidize the particles. Therefore, if some mechanical means is employed to generate motion in the bed of particles, lower gas flow rates and deposition temperatures can be used, and lower deposition temperatures can be realized. As shown in a later section of this report, the minimum conventional HT-PyC temperature can be reduced from about 1000°C in a bed of particles fluidized by gas to a temperature of 750°C when the particles are agitated by tumbling in a drum.

A further reduction in the temperature required for chemical-vapor deposition of carbon can be attained by using some means other than thermal energy to cause decomposition of the hydrocarbon molecules. Photochemical excitation, catalytic activation, and plasma activation are possibilities that were listed earlier.

The three vacuum vapor-coating processes (vacuum evaporation, sputtering, and ion plating) all employ lower deposition temperatures than are required with conventional HT-PyC. Of the three processes, ion plating seems to have the most potential for depositing an impervious carbon coating at a relatively high rate on waste particles greater than 4 mm. Relatively high deposition rates can be achieved with ion plating, and because of the concurrent sputtering of the substrate, higher quality coatings are reportedly obtained than with other vacuum deposition processes.

Based on the above considerations, it seems that conventional fluidized-bed CVD should be evaluated for suitability since it offers the highest coating rates of all of the processes and is a well-developed process for which remote operation has already been considered. The major concern about conventional fluidized-bed deposition involves the relatively high deposition temperatures. Therefore, consideration should also be given to altering the process to include mechanical bed agitation, catalytic activation, and plasma activation. A third method that should be considered is the possible combining of the ion plating process with mechanical bed agitation.

Conventional HT-PyC at Reduced Temperatures

The minimum temperature for carbon deposition in a conventional fluidized bed particle coater depends in part on the coater's design. Several coating runs at different temperatures were carried out to determine the minimum operating temperature of the laboratory coaters at General Atomic Co.

ZrO₂ Particle Coating Tests

The runs were made using either propylene (C₃H₆) or acetylene (C₂H₂) as the carbon source gas and a bed of ZrO₂ particles. In all cases, the carbon-source gas made up 20 vol% of the total flow through the coaters; the remaining volume was argon. The conditions used in each coating run are listed in Table 2.12 along with the observed coating rate and deposition efficiency (the amount of carbon deposited on the particles divided by the amount of carbon introduced into the coater). As the temperature decreased, the coating rate and the deposition efficiency also decreased. For temperatures above 1150°C, there is little difference in the results obtained using either propylene or acetylene as carbon-source gases. However, for temperatures below 1150°C, the coating rate did not fall off as rapidly when acetylene was used as it did when propylene was used. Thus, acetylene is better than propylene for coating at low temperatures.

TABLE 2.12. GAC Fluidized Bed Coating Runs on ZrO₂ Particles(a)

Run No.	Temperature, °C	Coating Gas	Coating Rate, μm/min	Deposition Efficiency, %
8323-7	1300	C ₃ H ₆	5.2	49
8323-40	1300	C ₂ H ₂	5.9	65
8323-51	1150	C ₃ H ₆	2.6	26
8323-53	1150	C ₂ H ₂	3.4	39
8323-55	1000	C ₃ H ₆	0.05	0.2
8323-59	1000	C ₂ H ₂	0.31	(b)

(a) 60 gm charge of ZrO₂ particles

(b) Not determined due to loss of particles.

There was little difference in the macro appearance of the particles except that the coatings deposited at the lower temperatures appear to be smoother than the coatings deposited at the higher temperatures. This is probably related to the low coating rate of the low-temperature carbons; pyrocarbon coatings tend to get smoother as coating rates decrease.

To increase the coating efficiency in the low-temperature range, one could use a larger bed of particles (which increases the efficiency but decreases the coating rate) or could preheat the gases before they enter the coating zone. These changes cannot, however, offset the large reductions in rate and efficiency that occur with decreasing temperature. Previous work shows that larger beds and gas preheating would lead to a temperature increase of 50°C at the most.

In a rotating tube coater where a lower total gas flow can be employed (the gas flow is not required to fluidize the particles), lower coating temperatures are possible. The conditions employed for three runs with a rotating tube coater are listed in Table 2.13. The deposition efficiency of this process at 750°C is equivalent to fluidized bed coating in the temperature range 1000 to 1150°C. Thus, the decrease in gas flow allowed a decrease in coating temperature of about 250°C. The particles appeared to be similar to those coated at high temperatures in a conventional fluidized bed.

TABLE 2.13. GAC Coating Runs in a Rotating Tube Particle Coater(a)

Run No.	Temperature, °C	Coating Rate, μm/min	Deposition Efficiency, %
8204-43	850	0.15	14
8204-41	800	0.10	12
8204-39	750	0.03	8

(a) 130 gm charge of ZrO₂ particles, C₂H₂ coating gas

Simulated Waste Particle Coating Tests

Ceramic pellet waste forms of the SPC-2 and MB-3 (Table 2.14) and SPC-4E compositions (Table 2.2) were coated using conventional fluidized-bed CVD. SPC-2 is similar to SPC-4E, and MB-3 is similar to MB-1. The coating runs are summarized in Table 2.15. The MB-3 pellets were also coated with an initial low-temperature seal coat of Si. The same fluidized bed coating conditions used to coat ZrO_2 particles were used for coating the SPC-2 and SPC-4E supercalcine pellets. At the 1150 and 1300°C temperature levels, where equivalent coatings were obtained on ZrO_2 particles using either acetylene or propylene, the coating gas was made up of a ratio of the two such that the endothermicity of the propylene decomposition was balanced by the exothermicity of the acetylene decomposition. This ensured that there were no temperature transients when the hydrocarbon gases were introduced into the coater. At 1000°C, acetylene alone was used as the carbon source gas.

Because a limited quantity of the supercalcine particles was available, the coating runs were made by mixing a few supercalcine particles with a larger quantity of smaller ZrO_2 particles (Table 2.15). After coating, the larger supercalcine particles were separated from the ZrO_2 particles by sieving.

At the highest coating temperature of 1300°C, the SPC-4E supercalcine particles became sticky and agglomerated with the ZrO_2 particles. The SPC-2 supercalcine particles coated at 1300°C did not agglomerate with the ZrO_2 particles, but the coatings appeared defective in many cases, as if pieces of the particles had broken off during coating. Also, when two supercalcine particles were stuck together initially, the connecting region did not coat well.

At the middle coating temperature of 1150°C, neither supercalcine batch appeared to coat well. The coating on the SPC-4E batch appeared very rough and, in some cases, cracks and holes in the coating could be seen. The coatings on the SPC-2 batch were smoother but still had a rough appearance. In both cases, the coating in the connecting region of joined supercalcine particles appeared to be defective.

TABLE 2.14. Compositions of SPC-2 and MB-3 Nuclear Waste Pellets

<u>Oxide</u>	<u>SPC-2</u>	<u>MB-3</u>
Major Components		
Al ₂ O ₃	2.15	20.06
B ₂ O ₃	-	2.73
BaO	0.97	0.06
CaO	2.51	2.65
CdO	0.06	0.01
Co ₂ O ₃	0.06	0.01
Cr ₂ O ₃	0.52	0.04
Fe ₂ O ₃	3.63	33.79
Gd ₂ O ₃	0.17	0.07
K ₂ O	0.54	-
La ₂ O ₃	4.69	0.04
Li ₂ O	-	0.20
MgO	0.15	0.61
MnO ₂	0.05	9.88
MoO ₃	4.03	0.04
Na ₂ O	4.40	5.82
NiO	46.44	3.77
P ₂ O ₅	2.01	0.54
PbO	-	8.84
SiO ₂	9.90	9.54
TiO ₂	0.03	0.09
ZnO	0.05	0.01
ZrO ₂	3.76	0.02
Tracer Components		
Ce ₂ O ₃	7.22	0.44
Cs ₂ O	1.92	0.10
Nd ₂ O ₃	3.10	0.41
RuO ₂	0.20	-
SrO	1.43	0.23

TABLE 2.15. GAC Fluidized Bed Coating Runs on Supercalcine Simulated Waste Particles

<u>Run No.</u>	<u>Supercalcine Particle Type</u>	<u>Temperature, °C</u>
8172-129	SPC-2	1300
8172-131	SPC-4E	1300
8172-133	SPC-2	1150
8172-135	SPC-4E	1150
8323-61	SPC-2	1000
8323-63	SPC-4E	1000

The particles coated at 1000°C appeared to be better than the particles coated at higher temperatures. The coatings were smooth and, in most cases, appeared to be continuous. Figure 2.20 shows the SPC-4E particles coated in Run No. 8323-63. A crack can be seen in the connecting region of joined particles and there appears to be one agglomerated particle. The coatings on the other particles appear to be continuous. In the coated SPC-2 batch shown in Figure 2.21, all the coatings appear to be continuous, even in the region of joined particles.

The reason for the difficulty in coating the supercalcine particles is revealed by radiographs of each coated supercalcine batch (Figure 2.22). Normally, coatings are uniform in thickness around particles even when the particles have a rough surface. In every case, the coatings on the supercalcine particles are not uniform. This nonuniformity is believed to have been caused by migration of some component of the supercalcine material into the carbon coating during deposition. This migration is almost certainly temperature dependent; the migration increases with increasing temperature. Therefore, migration would have occurred most rapidly at the highest coating temperature and may have been responsible for the stickiness of the SPC-4E batch at this temperature, as well as for the defective coatings of the SPC-2 batch. Furthermore, the migration of the supercalcine component almost certainly caused the roughness of the coatings at 1150°C. The best coatings were obtained at 1000°C (the lowest coating temperature), at which migration rates were very minimal.

1 mm

FIGURE 2.20. SPC-4E Particles Coated with HT-PyC in a Fluidized Bed at 1000°C (Run No. 8323-63, Table 2.15)

1 mm

FIGURE 2.21. SPC-2 Particles Coated with HT-PyC in a Fluidized Bed at 1000°C (Run No. 8323-61, Table 2.15)

SPC-2

Run No. 8172-129, $T = 1300^{\circ}\text{C}$

Run No. 8172-133, $T = 1150^{\circ}\text{C}$

Run no. 8323-61, $T = 1000^{\circ}\text{C}$

SPC-4E

Run No. 8172-131, $T = 1300^{\circ}\text{C}$

Run No. 8172-135, $T = 1150^{\circ}\text{C}$

Run No. 8323-63, $T = 1000^{\circ}\text{C}$

FIGURE 2.22. Radiographs of HT-PyC Coated SPC-2 and SPC-4E Particles

The key to obtaining good coatings on supercalcine particles is to use a coating rate that is faster than the migration rate of the supercalcine component. In general, the coating rate decreases as the deposition temperature is decreased. However, the coating rate can be increased by varying other parameters, such as the concentration of the hydrocarbon gas in the fluidizing stream and the surface area of the bed of particles. In future studies, the coating conditions at a deposition temperature of 1000°C should be optimized to determine whether or not better coatings can be obtained on the supercalcine particles using conventional fluidized-bed, chemical-vapor deposition. In addition, the coating of supercalcine particles should be conducted in a rotating-tube CVD furnace.

Coatings of carbon and silica were deposited on MB-3 pellets by chemical vapor deposition in a fluidized bed (Table 2.16). The MB-3 pellets consisted of SRL composition calcine with a lead frit binder that was sintered at 1175°C for 1 hour. In an initial PyC coating test at 1150°C using acetylene as the carbon source gas, the batch of particles coalesced into one large agglomerate in the coater. This is believed to have occurred because the particles began to melt or soften at this temperature. All subsequent coating studies were thus carried out at temperatures of 1100°C or less. A series of four

TABLE 2.16. GAC Fluidized Bed Coating Runs on MB-3 Pellets

Run Number	Temperature, °C	Coating Source Gas	Coating Deposition Rate, $\mu\text{m}/\text{min}$	Coating Thickness, μm	Comments
8322-129	1100	C ₂ H ₂	0.5	32	many broken coatings
8322-131	1100	C ₂ H ₂	0.3	50	some broken coatings
8423-81	1000	C ₂ H ₂	---	---	no appreciable coatings
8423-83	1050	C ₂ H ₂	3.1	185	excellent coating
8323-142	700	SiH ₄	0.5	90	many broken coatings
8322-143	700	SiH ₄	1.0	130	excellent coating

different coating runs was made to determine the best conditions for carbon coating of the calcine particles. (The optimal conditions were at a temperature of 1050°C and an acetylene flow providing a coating rate of 3 $\mu\text{m}/\text{min}$.) The particles of run number 8423-83 (Figure 2.23) had the best coating integrity.

Particles were sealed with a silicon coating at 700°C so that carbon coatings could be deposited at higher temperatures. Two different coating runs were made to determine the best coating conditions. Coating breakage was eliminated by adjusting the SiH_4 flow so that the coating deposition rate was about 1 $\mu\text{m}/\text{min}$. A cross section of particles from run number 8322-143, which produced the best coating, is shown in Figure 2.24.

FIGURE 2.23. Cross Section of MB-3 Particles Coated with HT-PyC in a Conventional Fluidized Bed at 1050°C (Run No. 8423-83, Table 2.16)

FIGURE 2.24. Cross Section of MB-3 Particles Coated with Si at 700°C (Run No. 8322-143, Table 2.16)

Plasma-Activated CVD

The plasma-activated, chemical-vapor deposition process of Inspektor et al. (1980) was examined for its applicability to coating ZrO_2 particles and glass spheres at near ambient temperatures. The deposition apparatus employed is shown schematically in Figure 2.25. In this apparatus, argon and propylene are introduced into the coating chamber at a pressure of about 10 Torr. The gases first pass through an electric field oscillating at 455 kHz, which causes the formation of a plasma. The plasma is directed by the gas flow toward the particles, which are contained in a grounded cup. Particles within the cup are kept in motion by a vibrator.

A number of coating runs were required to establish the conditions necessary to obtain uniformly smooth coatings using plasma-activated CVD. The more significant of these coating runs are listed in Table 2.17. In the early coating runs where ZrO_2 was used as a substrate, copper-colored flakes were

FIGURE 2.25. Schematic of Plasma-Activated, Chemical-Vapor Deposition Apparatus

present in the coatings. At first it was thought that the flakes were caused by sputtering from the cup, which was initially made of copper. When the cup was lined with graphoil for one run (84204-49B), the flakes disappeared. The copper cup was ruled out as the source of the flakes, however, because the flakes also appeared when a graphite cup was used (Runs 8204-51C, -51D, -51E, and 51F). We observed that more flakes were present when the deposition was made with the cup in close proximity to the coil (8204-51F). Still, the flakes could not have been caused by sputtering from the ZrO_2 , because orange flakes

TABLE 2.17. GAC Coating Runs by Plasma-Activated CVD

Run No.	Substrate	Cup Material	Power Settings, Amps		Pressure, Torr	Distance Between Cup and Coil, mm	Gas-Flows Std cm ³ /min		Comments
			Grid	Plate			Argon	Propylene	
8204-49A	ZrO ₂	Copper	6.0	1.8	10	25	122	30	Particles were not vibrated during coating. Particles were coated with carbon, but the coatings contained copper-colored flakes.
8204-49B	ZrO ₂	Copper with graphoil liner	6.0	1.8	10	25	122	30	Particles were not vibrated; Particles were coated with 0.15 μ m of carbon. No copper-colored flakes were present.
8204-51C	ZrO ₂	Graphite	6.0	1.8	10	25	122	30	Particles were not vibrated. The coating was pitted. Copper-colored flakes were present.
8204-51D	ZrO ₂	Graphite	4.0	1.4	10	25	122	30	Particles were not vibrated. The coating was pitted. Copper-colored flakes were present.
82-4-51E	ZrO ₂	Graphite	2.0	0.8	10	25	122	30	Particles were not vibrated. Very little coating was on particles. Copper-colored flakes were present.
8204-51F	ZrO ₂	Graphite	2.0	1.4	10	13	122	30	Particles were not vibrated. Particles were coated but more copper-colored flakes were present.
8204-53D	1-mm Sapphire Spheres	Graphite	4.0	1.3	10	13	122	30	Particles were not vibrated. The coating were rough on one side and smooth on the other. Orange flakes were present.
8204-55A	3-mm Glass Spheres	Graphite	4.0	1.3	10	135	122	30	Particles were vibrated. The coatings were uniform, smooth and 5 μ m thick.
8204-55C	3-mm Glass Spheres	Graphite	4.0	1.3	15	135	122	30	Particles were vibrated. The coatings were uniform, smooth, and 10 μ m thick.
8204-55D	3-mm Glass Spheres	Graphite	4.0	1.3	10	13	96	73	Particles were vibrated. Soot was in cup. The coating easily scraped off.

were observed when several 1-mm-diameter sapphire spheres were used as the substrate (8204-53D). The flakes were not present when glass spheres were used as the substrate. The source of the flakes was never ascertained. A macrograph of the 3-mm-diameter glass spheres coated in Run No. 8204-55C is shown in Figure 2.26, along with some uncoated spheres.

The work described above demonstrates that plasma-activated, chemical-vapor deposition can be used to deposit carbon on glass. Coatings made under various conditions must be evaluated to determine the operation parameters required for impermeability.

UNCOATED SPHERES

1 mm

COATED SPHERES

FIGURE 2.26. Glass Spheres Before and After Coating with Carbon by Plasma-Activated Chemical Vapor Deposition (Run No. 8204-55C, Table 2.17)

3.0 THERMAL SPRAY COATINGS

Thermal spray coating processes have been evaluated at PNL as a low-temperature and relatively simple alternative to high-temperature CVD coatings. The processes are metallizing, flame spraying, and plasma spraying. Thermal spraying is the term used to describe any process whereby a material is brought to its melting point and sprayed onto a surface to produce a coating. The main advantages of thermal spraying are: 1) substrate temperatures can be maintained as low as 300°C to minimize fission product volatilization (waste glass marbles can be readily coated at this temperature), 2) typical coating deposition rates are very high, 3) a wide variety of coating materials can be applied, and 4) large diameter particles are easily coated. Plasma spraying has the additional advantage that noncombustible gas mixtures can be used.

Thermal spraying processes are limited by the directional nature of the spray. The spray travels in a line-of-sight pattern and, unlike chemical vapor deposition, will not coat around corners. To overcome this limitation, two particle agitators were developed which tumble and mix the simulated waste particles, thus allowing all surfaces to be coated uniformly.

This section summarizes the equipment operation, coating process experience, fusion of the coatings, and conceptualized remote operation. The thermal spray coatings were applied to simulated Savannah River Plant waste glass marbles (TDS-211). The coatings consisted of a variety of materials ranging from pure metals to ceramic oxides.

3.1 EQUIPMENT

Wire Spray System

The wire spray (metallizing) process uses a wire gun, air control unit, gas control unit, and wire control unit (Figure 3.1). A commercially-available METCO 10E® spray gun was used. Figure 3.2 shows the wire gun with examples of both uncoated and coated TDS-211 marbles.

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FIGURE 3.1. Wire Gun System

FIGURE 3.2. METCO 10E® Wire Gun with Coated and Uncoated TDS-211 Glass Marbles

Metallizing is the process of spraying molten metal onto a surface to form a coating (Ingham and Shepard 1969). Pure or alloyed metal is melted in a flame and atomized by a blast of compressed air into a fine spray. This spray builds up onto a substrate to form a metal coating. Because the molten metal is accompanied by a large blast of air, the substrate does not significantly heat up; thus, metallizing is known as a cold process for building up metal. Sprayed metal is a unique metallurgical material with different physical properties than the original metal. Sprayed material is generally harder, more brittle, and more porous than the original metal.

The wire gun is designed to spray 3.2-mm (1.8-in.) wire using acetylene as the fuel gas. Figure 3.3 shows a cross section of the wire gun nozzle and air cap during spraying. Wire is fed to the gun from the wire control unit, which holds and straightens the wire as it uncoils. A variable-speed air turbine, which is built into the gun, powers a set of wire feeding gears.

Flame Spray System

The flame spray system tested consists of a thermospray gun, dual powder feeder, gas control unit, and air control unit. The gun is a METCO 6P® and is shown in Figure 3.4 with samples of uncoated and coated TDS-211 marbles. The

FIGURE 3.3. Wire Gun Nozzle and Air Cap Operation

FIGURE 3.4. METCO 6P® Flame Spray Gun with Coated and Uncoated TDS-211 Glass Marbles

flame spray process permits the use of an almost infinite variety of metals, alloys, ceramics, and cermets, which are available as powders (Ingham and Shepard 1967).

Powder is fed to the 6P gun from a dual-powder feed unit (METCO-type 3MP®), which provides constant powder feed and accurate control (see Figure 3.5). The powder feeder is a positive-displacement metering device with pneumatic delivery of powder to the gun. It is a gravity feed, closed system that operates at a positive pressure. A powder hopper assembly provides a constant level of powder at the inlet to the metering device. An electric vibrator ensures smooth powder flow. For hard-to-flow powders, an air vibrator is also used.

FIGURE 3.5. METCO-Type 3MP® Dual Powder Feeder

Figure 3.6 shows a cross section of the nozzle section while the gun is in operation. The powder and carrier gas exit the nozzle through a center port surrounded by a ring of oxyacetylene ports. Compressed air can be supplied to an air cap to cool the gun, to pinch and concentrate the flame, or to cool the work piece. A pair of jets (not shown) can be attached to the gun to further pinch and modify the flame to form a controlled spray profile for different applications. The air and gas control units for the powder gun are the same used for the wire gun previously described (refer to Figure 3.1).

Plasma Spray System

A plasma spray system operates similar to the flame spray gun but is not limited by the temperature ceiling of the oxyacetylene combustion flame.

FIGURE 3.6. Flame Gun Nozzle and Air Cap Operation

Temperatures of $16,000^{\circ}\text{C}$ and higher can be obtained. For most spray processes, temperatures in the $6,500$ to $11,000^{\circ}\text{C}$ range are optimum. The plasma system permits the selection of an inert gas for the flame medium so that chemical reaction (such as oxidation) during heating and application of the spray material can be controlled. This is a major advantage for nuclear-waste coating applications, because in-cell operation is permitted using noncombustible gases or gas mixtures. For this reason, plasma spraying may be the only viable process for remotely coating radioactive waste.

A gas follows classical laws of physics and thermodynamics as it is heated, until the point at which the molecules are broken up and a plasma is formed. The molecules are ionized, loose an electron and, in the case of diatomic molecules such as N_2 , become dissociated. Once formed, a plasma consists of electrically-charged particles (ions and electrons). A plasma can be considered as a fourth state of matter because of its variance from the classical laws. Much more energy is required to change a gas to a plasma than is warranted by the temperature rise. Therefore, in addition to having a high temperature, a plasma has a very high energy content, which means that more heat is available for transfer to other objects (such as spray powder). Figure 3.7 shows the effect of dissociation of diatomic molecules and ionization of the atoms on the energy content of N_2 , H_2 , Ar , and He (Ingham and Shepard 1965). Rapid heating of the spray powder is of the utmost importance

FIGURE 3.7. Plasma Gas Energy Content Versus Temperature

because the residence time of powder in the flame is very short (on the order of micro-seconds). It is desirable to have high-velocity particle impact, meaning that a steady plasma stream (or plasma flame) must be used.

These considerations are fulfilled with the plasma gun tested, an 80 kW METCO 7MB,® shown in Figure 3.8. A cross section of the nozzle assembly and powder feed port showing the operation is presented in Figure 3.9. A neutral plasma is produced by confining the arc in the nozzle chamber as shown. Gas is introduced at the base of the electrode and is forced out through the arc, where it becomes dissociated and ionized. The gas stream emerges from the nozzle as a free plasma flame.

During operation, powder is fed with a carrier gas from the powder feeder to a powder port mounted on the side of the nozzle. The powder enters the flame and absorbs energy until it becomes molten. The molten powder then accelerates to the substrate.

FIGURE 3.8. METCO 7MB® Machine-Mounted Plasma Gun with Uncoated and Coated TDS-211 Glass Marbles

A schematic of the complete plasma system is presented in Figure 3.10. The METCO system tested (similar to other systems available) consists of a power supply, gas control unit, plasma spray control console, powder feeder, and plasma spray gun. Also shown in Figure 3.10 is a heat exchanger for a closed-loop cooling system which, although available, was not used. The gun is designed to operate with either N_2 or Ar as the primary gas and with 0 to 10 vol% of He or H_2 as a secondary gas. Addition of the lower-molecular-weight secondary gas increases the flame velocity and also improves the heat transfer characteristics of the plasma flame. The hydrogen also increases the flame heat content and maintains a reducing atmosphere for the powder and/or substrate.

Particle Agitator

A limitation of the thermal spraying process is the directional nature of the spray. The spray travels along the line of sight and, unlike CVD, will not coat around corners. To obtain a reasonably dense, normal coating, the spray angle to the substrate surface must be maintained at no less than 45° . As the

FIGURE 3.9. Plasma Gun Nozzle Operation

spray angle decreases below 45 degrees, the deposition efficiency declines and a phenomenon known as "shadow effect" occurs. When spraying at an angle less than 45° , small particles build up on the surface of the waste particles and obstruct the flight of other particles, thus creating ridges and valleys. The result is a porous coating, which (during spraying) has the tendency to collect fine material from the spray stream.

Two particle agitators that tumble and mix the simulated waste particles, allowing all sides to be coated, were fabricated and tested at PNL. By tumbling the particles, the shadow effect was greatly reduced, even though only 50% of the projected area and 29% of the actual hemispherical area of the waste particles exposed to the spray have an angle of incidence greater than 45° . Also, by rapidly mixing the bed of particles, a nearly uniform coating could be

FIGURE 3.10. Plasma Spray System Schematic

applied to all particles while the gun remained stationary on a machine mount. The coating thickness from particle to particle could be maintained within a standard deviation of less than 20%. Longer coating times and more vigorous agitation created the most uniform coatings.

A vibrator agitator was fabricated for coating batches less than 0.6 l (~1 kg of glass marbles), and a drum agitator was made for large batches up to 12 l (20 kg of glass marbles). The two designs were selected from among ten different candidates because of their efficiency and simplicity.

The vibrator agitator (Figure 3.11) consists of a 7.6-cm-deep by 20-cm-diameter pan, with a 4-mesh screen bottom. The screen serves to support the marbles, transfer the vibrational energy to the marbles, and allows heat and gas generated by the spraying process to pass through. The whole assembly is mounted on a vibrator.

The drum agitator (Figure 3.12) evolved as modifications were made to a commercially-available cement mixer. A variable-speed drive motor rotates the

FIGURE 3.11. Vibratory Particle Agitator in Use with the Hand-Held Plasma Gun

FIGURE 3.12. Drum Particle Agitator and Motor Speed Controller

drum in either direction at speeds ranging from 0 to 24 rpm. The mixing drum is 53.3 cm in diameter and has a 7.6-cm lip mounted on the front at a 45° angle. The rear of the drum is conical in shape and consists mainly of a 4-mesh stainless-steel screen, which allows hot gases and overspray to exit the coating chamber. Gas is drawn through the agitator by a transvector connected to a shroud surrounding the rear of the drum. The face air velocity at the agitator opening is typically 100 m/min.

3.2 PARTICLE COATING STUDIES

A series of coating runs were made to obtain process data and produce coated waste samples for MCC-1 leach testing and other characterization. Coatings of pure metals, metal alloys, and ceramics were applied individually and in combination using the plasma, wire, and flame spray processes.

Table 3.1 gives the compositions of wire spray coatings that were applied to TDS-211 glass marbles using the METCO 10E® wire gun. Powder compositions applied to TDS-211 marbles by the METCO 7M® plasma system are presented in Table 3.2. Coatings of METCO 102® and the 444® powders were also applied using a 6P flame gun. The flame gun coatings are not included in the discussion since these same powders were applied by the plasma process and were found to be of superior quality.

The coating materials were selected based on previous waste-package-materials studies by Westerman (1980) and Fullam (1980). Other materials were selected for their galvanic corrosion resistance, availability, and their known resistance to long-term corrosion (e.g., lead). Materials such as Al and Zn were tested even though they are not galvanically desirable. Aluminum forms a stable oxide layer, which greatly enhances its corrosion resistance. Both Zn and Al can be applied over a more noble metal undercoat to serve as a sacrificial material.

Table 3.3 gives a summary of the coating runs in which continuous, crack-free coatings were applied to TDS-211 glass marbles using the wire gun. Likewise, plasma spray coating runs, which produced continuous coatings, are listed in Table 3.4. Deposition rates normalized to 1 kg of substrate were calculated

TABLE 3.1. Metallizing Wire Compositions

<u>Metallizing Wire</u>	<u>Constituent</u>	<u>%</u>
METCO Aluminum	Al	99.0+
METCO SF Aluminum	Al	94
	Si	6
METCO SPRAY BABBITT A®	Sb	7.5
	Cu	3.5
	Pb	0.25
	Sn	Balance
METCO Copper	Cu	99.8+
METCO Lead	Pb	99.9+
METCO Monel	Ni	67
	Fe	1.5
	Mn	1
	C	0.15
	Si	0.1
	Al	0.1
	S	0.01
	Cu	Balance
METCO Zinc	Zn	99.9+

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for coatings applied using the drum agitator. Overspray became a problem when using the vibratory agitator; thus, coating rates were not calculated. Coatings of TiO_2 and Al_2O_3 (METCO 102 and 105SF) applied by the plasma system had cracking and spalling problems due to thermal expansion mismatch. The TiO_2 could, however, be successfully applied to waste marbles using an aluminum or nickel alloy bond coat (METCO 54 or 447), or by limiting the coating thickness to about 75 μm or less (Runs 16, 17, and 48).

Deposition efficiencies were experimentally determined for aluminum coatings applied by both the wire and plasma spray systems using the drum particle agitator (Table 3.5). The actual deposition efficiencies are substantially higher in the PNL system than those claimed in the manufacturer's literature.

TABLE 3.2. Spray Powder Compositions

Spray Powder	Powder ID	Constituent	%	Typical Size Range, μm
Aluminum	METCO 54	Al	99	-90 +45
Alumina-Titania Composite	METCO 130SF	TiO ₂ Al ₂ O ₃	13 Balance	-30 +5
Ceramic	METCO 105SF	Al ₂ O ₃ SiO ₂ Other Oxides	98.0 0.5 1.5	-25 +5
Chromium Oxide - Silica Composite	METCO 136F	SiO ₂ TiO ₂ Cr ₂ O ₃	5 3 Balance	-53 +15
Copper	METCO 55	Cu	99	-90 +45
Fine Nickel	METCO 56F-NS	Ni	99.3+	-45 +10
Inconel(a)	IN 181	-	-	-149
Lead(b)	Lead Shot	-	-	-640 +250
Nickel-Chromium Molybdenum Alloy	METCO 47C	Cr Mo Fe W Ni	16.5 17.0 6.0 4.5 Balance	-106 +45
Self-Fusing Molybdenum Blend	METCO 501	Mo Cr Si Fe B C Ni	30 12 2.75 2.75 2.5 0.75 Balance	-53 +10
Self-Bonding Molybdenum - Nickel Aluminum	METCO 447	Al Mo Ni	5.5 5.0 Balance	-88 +45
Self-Bonding "Stainless" Composite	METCO 444	Cr Al Mo Fe Ni	9 7 5.5 5 Balance	-125 +45

TABLE 3.2. (contd)

<u>Spray Powder</u>	<u>Powder ID</u>	<u>Constituent</u>	<u>%</u>	<u>Typical Size Range, μm</u>
Stainless Steel	METCO 41F-NS	Cr	17.0	-53 +10
		Ni	12.0	
		Mo	2.5	
		Si	1.0	
		C	0.1	
		Fe	Balance	
Titanium(a)	TI272	-	-	-
Titanium Dioxide	METCO 102	TiO ₂	99	-53 +10
Titanium Hydride	METCO XP1157	H	3.5	-90 +45
		Ti	Balance	

(a) Supplied by Atlantic Equipment Engineers, Bergenfield, New Jersey. No analysis given.

(b) Supplied by Division Lead Co., Summit, Illinois. No analysis given.

TABLE 3.3. Wire Spray Coatings Applied to TDS-211 Glass Marbles

<u>Run No.</u>	<u>Metallizing Wire</u>	<u>Agitator</u>	<u>Coating Thickness, μm</u>
4144-21	METCO SF Aluminum	Vibratory	800
4144-22	METCO Zinc	Vibratory	300
4144-23	METCO Copper	Vibratory	300
4144-24	METCO SPRAY BABBITT A ®	Vibratory	330
4144-25	METCO Lead	Vibratory	350
4144-26	Duplex of Run 24 and and Run 22	Vibratory	300/350
4144-28	METCO Aluminum	Drum	350

Values published by the manufacturer were derived from spraying a flat plate at a sufficient distance from any edge to eliminate edge overspray effects. The overspray that does occur is caused by particles becoming entrained in the spray stream as the spray stream deflects from the substrate. The overspray may also be caused by incomplete melting of the particles. When directed at

TABLE 3.4. Plasma Spray Coatings Applied to TDS-211 Glass Marbles(a)

Run No.	Spray Powder	Thickness, μm	Deposition Rate, ^(b) $\mu\text{m}/\text{min}$	Spray Parameters
4144-12	Self-Bonding "Stainless" Composite	72	10	32 kW, Ar/He gases (nonstandard parameters)
4144-14	Copper	120	17	30 kW, Ar/He gases (nonstandard parameters)
4144-15	Self-Bonding Molybdenum-Nickel- Aluminum	30	4.4	34 kW, Ar/He gases (nonstandard parameters)
4144-16	Titanium Dioxide	60	18	33 kW, Ar/H ₂ gases (METCO parameters)
4144-17	Duplex of Run 15 and Run 16 Coatings	50/50	27/14	33 kW, Ar/H ₂ gases (METCO parameters)
4144-19	Aluminum	600	170	35 kW, Ar/H ₂ gases (METCO parameters)
4144-39	Fine Nickel	97	40	31 kW, Ar/H ₂ gases (METCO parameters)
4144-40	Nickel-Chromium Molybdenum Alloy	220	56	31 kW, Ar/H ₂ gases (METCO parameters)
4144-43	Stainless Steel	230	57	27 kW, N ₂ gas (METCO parameters)
4144-44	Inconel ®	110	45	28 kW, N ₂ gas (nonstandard parameters)
4144-45	Titanium	52	6.5	34 kW, Ar/H ₂ gases (nonstandard parameters)
4144-46	Self-Fusing Molybdenum Blend	170	21	31 kW, Ar/H ₂ gases (METCO parameters)
4144-48	Aluminum/Titanium Dioxide Duplex	250/50	170/21	Ar/H ₂ gases (METCO parameters)

(a) Drum agitator used for all runs.

(b) Normalized for 1 kg of substrate.

TABLE 3.4. (contd)

Run No.	Spray Powder	Thickness, μm	Deposition Rate, (b) $\mu\text{m}/\text{min}$	Spray Parameters
4144-49	Aluminum/Lead Duplex	250/30	170/7.5	Ar/H ₂ gases (METCO parameters for Al, nonstandard parameters for Pb)
4144-50	Lead	71	15	Ar/H ₂ gases (nonstandard parameters)
4144-55	Aluminum	290	240	40.5 kW, N ₂ gas (METCO parameters)

(a) Drum agitator used for all runs.

(b) Normalized for 1 kg of substrate.

TABLE 3.5. Aluminum Deposition Efficiencies

Process	Deposition Efficiency, %	
	Manufacturer Claim	Actual
Wire	80%	99+%
Plasma	80%	92%

an agitated bed of marbles, the spray stream deflects around individual marbles but passes on into the bed. As a result, a spray particle deflected from the first layer of marbles may have several more chances to strike a marble deeper in the bed. Due to the nature of the wire spray process, all the material is melted by the flame; thus, a deposition efficiency of 99+% was achieved. The efficiency was lower, averaging 92%, with the powder-fed plasma spray system, apparently because not all the particles melted.

Coatings listed in Tables 3.3 and 3.4 have been characterized by leaching as well as other evaluation techniques. Characterization data and comparisons are presented in Section 4.0.

3.3 FUSION OF POROUS COATINGS

Coatings applied by thermal spray processes typically have 5 to 35% porosity. Exposing these coatings to high temperatures and, in some cases, a

tumbling action, results in densifying the coatings and closing pores and cracks through which leach solutions may pass. The depth to which a coating is densified (or fused) should be somewhat less than the thickness of the coating in order to provide an undensified, porous layer between the substrate and the fused coating. This porous layer serves two purposes: 1) it acts as an insulator in preventing the exposure of the substrate to temperatures high enough to vaporize radioactive species or otherwise promote their migration through the coating during the fusion step, and 2) it acts as a crushable buffer to accommodate uneven contraction of the substrate and coating during cool down.

Ideally, the coating material should have a thermal expansion coefficient nearly equal to or somewhat lower than that of the substrate and a melting or softening temperature near that of or lower than the substrate temperature during densification. Substrates must be at a temperature of several hundred degrees centigrade during the coating step to promote adherence of the coating to the substrate. In most coating densification schemes, coated particles are densified soon after coating. Hence, the substrate is still hot and may heat up further during the densification step. After densification, as both the substrate and the coating cool down to ambient temperature, uneven contraction of the substrate and coating will result if their thermal expansion coefficients vary or if the coating cools faster than the substrate. If the thermal expansion coefficient of the coating is greater than that of the substrate, the coating may be subjected to high tensile stresses, which may result in its cracking. If the thermal expansion coefficient is lower, the coating will be placed under compression, which is a more desirable state if the compressive stresses are not too high or uneven.

The thermal spray coatings considered in this report include brittle coatings, such as those provided by crystalline ceramics and glasses, and ductile coatings, such as those provided by most metals. Crystalline ceramic coatings may be altogether unsatisfactory for densification for several reasons: 1) their melting temperatures are much above the maximum substrate temperatures, 2) their thermal expansion coefficients are fairly high, and 3) they are not ductile. Upon cooling, crystalline ceramic coatings are exposed to very

high strains. The coatings contract rapidly in an unyielding state relative to the slower initial contraction that occurs in the substrate. The high stresses that result often are relieved by cracking. Most metals may be better suited for densifying, because they will yield without breaking when exposed to high strains. Densification of metal coatings may require that an inert or reducing environment be used to prevent coating oxidation, which could interfere with the densification process or may compromise the quality of the coating. Some glass coatings, because of their viscous nature, may be suitable candidates for densifying. The viscous characteristic permits glasses to "flow" during part of the cooling cycle, thereby relieving stresses. Glasses such as fused silica and Vycor® may be particularly good coating material candidates. Each of these materials has a coefficient of thermal expansion that is about 1/20 that of most common glasses, which leads to their high resistance to thermal shock. It remains to be seen, however, if these coatings can withstand the high compressive stresses that are introduced as both the substrate and coating are cooled to ambient temperature.

Fusion Techniques

Methods that have been considered for densifying or fusing coatings require high temperatures and, in some cases, coupling with mechanical compaction. Heat can be supplied by plasma torches, combustion flame, lasers, induction coupling, and radiant heaters. Mechanical compaction can be provided by tumbling or otherwise rotating the particles when their coatings are in a softened state. The densification process is complicated by the need to achieve fairly even fusing and a fairly even coating thickness. This requirement likely rules out static fusion concepts, since dimples would result where the particles were in contact with a support base or with each other. A series of static heating tests were conducted using glass marbles coated with essentially pure aluminum. In these tests, the coated marbles were heated in a furnace to temperatures near or above the melting point of aluminum (Table 3.6). None of these heat treatments resulted in significant densification, although some changes were observed.

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TABLE 3.6. Test Conditions During Static Fusion of Porous Aluminum Coatings on TDS-211 Glass Marbles

<u>Sample ID</u>	<u>Temperature, °C</u>	<u>Time</u>	<u>Atmosphere</u>
T 1	680	5 minutes	Air
T 2	680	15 minutes	Air
T 3	680	40 minutes	Air
T 4	680	2 hours	Air
T 5	680	6 hours	Air
T 6	680	16 hours	Air
S 1	640	2 hours	Nitrogen
S 2	660	2 hours	Nitrogen
S 3	680	2 hours	Nitrogen
S 4	587	2 hours	Air
S 5	660	2 hours	Air

The specimens that were isothermally annealed at 680°C (which is 20°C above the melting point of Al) initially showed the porous microstructure typical of sprayed Al with only the surfaces of the voids showing oxidation. However, with time, this oxide layer thickens and, because it is a refractory ceramic, it tends to hold the porosity of the microstructure in place. Heat treating samples in air for 2 hr at 587 and 660°C (Al melting point) showed that the oxidation is more rapid at and below the melting point of aluminum. However, the lower the temperature, the lower the oxidation rate, as would be expected.

The probable cause of lowered apparent oxidation in these samples at temperatures above 660°C is that some slight densification in the coating does occur for the smaller voids. This would happen by the process of liquid phase sintering and would significantly reduce the surface area available for further oxidation. Flow of Al metal was evident by the 6 hr/680°C sample in which a marble void 3 mm in diameter, with a very small surface opening, was filled with metallic Al during heat treatment.

Several 2-hr anneals at 640, 660, and 680°C were performed in flowing nitrogen gas. Comparison of these samples to their air atmosphere counterparts showed only slight changes from the initial microstructure and no evidence of an increase in oxide coating thickness. But the series of samples annealed in N₂ gas did show an increasing degree of consolidation of voids as the smaller pores were filled. This finding would tend to verify the postulated sequence of progressive oxidation of void surface after initial liquid phase sintering has filled the smaller pores during the heat treatments at 680°C.

It might be possible to achieve some significant coating densification at 680°C if the marbles were heat-treated for a sufficient time in an inert atmosphere. However, marble devitrification could then be a limiting factor in these heat treatments. The marbles started to devitrify at the coating interface after 2 hours at 680°C in both air and N₂ atmospheres. After 6 hours at 680°C, crystals were evident in the marble interior and, after 16 hours at 680°C, several devitrification phases were present, resulting in a total crystallinity of >30 vol%. A glass and Al coating reaction zone almost a millimeter thick was also present. The coating itself had an oxide layer averaging 30 microns thick surrounding the interior voids. Metallographic evidence exists of new phases growing in the coating, indicating that some elements had diffused from the glass to the coating and were combining to form aluminates after 16 hours at 680°C in air.

The results of the static heating tests were not encouraging, although other lower-melting-temperature metals such as lead may be better suited to densification by this technique. Densification studies involving heating and tumbling have shown more promise. Care must be taken with these processes, however, to ensure that the coated particles are tumbled in such a way that the hot, newly fused, and soft portions of the coatings do not contact anything with enough force to significantly indent the coatings. In one test, glass marbles coated with about 300 microns of aluminum were agitated in the same drum mixer in which the coatings were applied. A plasma flame was directed onto the surface of the bed of coated marbles until individual marbles could be seen adhering to one another. At this point the flame was removed and the marbles were allowed to tumble for 40 minutes. After tumbling, no marble

agglomerates were found. All of the marbles treated in this manner were very shiny, exhibiting very smooth and porous-free surfaces. Some of the marbles subjected to this treatment were sectioned, as were marbles not treated in this manner (Figure 3.13). Densification of the coating is readily apparent.

The densification that occurs during heating and tumbling may be primarily due to the mechanical forces of particle-to-particle impact rather than to surficial tensile forces. The mechanical "working" of the coating may also impart other properties to the coating, such as increased toughness. Although a plasma flame was used as the source of heat in this test, it is conceivable that a combustion flame, laser beam, or other direct energy source could also have been effective. For coatings with high melting points, it is apparent that the heat must be intense and must be applied over a short period of time to prevent detrimental heating of the substrates. Otherwise, cooling of the particle agitator may be required.

For metal-coated particles, it is conceivable that the coatings can be fused by dropping the particles through a tall induction coil into a suitable cooling fluid. The metal coatings would serve as susceptors and, as such, would rapidly heat up. To achieve even fusion by this method, it may be important that the particles rotate at certain speeds and angles. It is also conceivable that coated particles could be dropped through a resistance-heated tube with similar effects.

3.4 FEASIBILITY OF COATER OPERATION IN A REMOTE FACILITY

Like a number of other operations in a high-level waste (HLW) solidification production facility, the coating of solid waste forms will require remotely operated and maintained equipment. The equipment should produce coatings that have no interconnected porosity and thus exhibit a high leach resistance. The coatings should be fairly uniform in thickness and capable of being safely and efficiently applied at a rate compatible with the facility's production requirements.

Aluminum coatings applied by the plasma spray method exhibit a fairly uniform, non-porous, leach-resistant layer of material that can be applied to

FIGURE 3.13. Al Coated TDS-211 Glass Marbles With and Without Densification by Hot Tumbling

the surfaces of glass spheres in a fast, efficient, and safe operation. The analysis presented in this section can, however, be applied to coatings other than aluminum. This coating process uses coating materials in the form of powders with a plasma flame as the source of heat. The process was studied and evaluated further to determine the feasibility of implementing a remotely operated process with equipment capable of being maintained remotely in a production facility.

The reference coating process handles about 50 kg of glass marbles per hour. This rate is compatible with a solidification facility processing (in 300 days) the high-level liquid waste produced in a fuel reprocessing plant operating at a rate of 2000 metric tons of heavy metal per year (Treat et al. 1980). This study uses the following conservative assumptions:

- the batch coating operation is a continuous process involving 15 min for fill, 20 min for coating, and 3.5 min for emptying and transferring a 49-kg batch
- four coater systems are installed (each consists of a plasma spray system and particle agitator)
- the coaters are fed by gravity from a marble machine or process surge hopper (pneumatic transfers might be a viable alternate)
- the temperature of the substrate upon receipt in the coater is suitable for coating (300°C to 450°C)
- the deposition efficiency is $\geq 90\%$ (92% has been obtained).
- glass recycle from the coater is 0.6 kg/h and from the marble machine is 2 kg/h.

Process Description and Requirements

A simplified process flow diagram and a material balance for the coating operation are shown in Figure 3.14. Marbles from the marble machine are fed into one of the four, slowly rotating particle agitators. Incorporated in the agitator station is a heater or furnace to ensure that the marble temperature is kept in the proper range for coating. As soon as the first agitator is

FIGURE 3.14. Thermal Spray Coating Process Flow Diagram

filled with the desired batch size, the marble flow is directed to another particle agitator, and the programmed coating operation is initiated.

The coating process includes the establishment of the desired agitator rotation speed and sequence; the setting of the desired plasma spray distance and angle and position sequence; and the initiation of selected powder, gas, and cooling system flows for the required periods. Also, the process involves the proper regulation of the plasma gun's DC power. The process current, flows, speeds, rates, and temperatures are monitored at the control console, and the actual operation is checked by the use of closed-circuit television or through shielded viewing windows.

As shown in Figure 3.14, provisions are included to recycle glass chips back to the liquid-fed ceramic melter. Cell air up to 280 slpm would be drawn

through a particle agitator during the coating step to assist with the distribution of the coating material and to control effluents. An addition to the melter off-gas system would handle this volume of air, plus up to 71 slpm of N_2 . This system will separate and remove the coating material not deposited on the substrates, which may be up to 0.68 kg/hr of aluminum if the deposit efficiency is as low as 90%. Process material and service requirements are noted in Table 3.7.

Coater Equipment

Figure 3.15 shows a block schematic of the equipment, services, and controls for a plasma spray coater unit. Note that only the spray gun is located in the process cell. Figure 3.16 shows a coating sequence from time = 0 to time = 5 min of the plasma spray gun coating glass marbles as they are being rotated in a drum agitator. Figure 3.17 indicates how a coater station could be located in a remote process cell and demonstrates its relationship to marble supply, pneumatic transfers, service, and off-gas and process control. Figure 3.18 is similar, but it uses a gravity flow system for all marble transports.

All components of a plasma spray coater system can be removed for maintenance or replacement. As shown in Figures 3.17 and 3.18, the plasma spray and the particle agitator would be mounted as a module on a support platform that would also permit the complete station to be removed remotely if necessary.

TABLE 3.7. Material and Service Requirements for Processing Scenario

<u>Material or Service</u>	<u>Rate or Amount</u>
Cell Air	280 slpm
Aluminum Powder	6.8 kg/h
N_2 Plasma Gas	71 slpm
Power	39 to 42 kW
Plasma Arc Current	600 amp (DC)
Plasma Arc Voltage	65 to 70 volts (DC)
Plasma Cooling Water	16 l/min

FIGURE 3.15. Remote Plasma Flame Spray System Block Schematic

The agitator drum rotates on its longitudinal axis by a variable speed motor and is enclosed in a shell-type furnace that maintains substrate temperatures. If the substrate or marbles are to be transferred by gravity, this component is mounted so that it can be pivoted on a horizontal axis and its contents can be dumped into a surge hopper or canister. The plasma spray system consists of the gun mounted on a device that will move the gun into and out of the particle agitator.

Requirements for Remote Application

In addition to the requirement that each step of the coating operation be performed remotely, each piece of equipment or module must be designed so that it can be installed and removed by the use of in-cell cranes, robots, or

$t = 0$

$t = 10 \text{ sec}$

$t = 1 \text{ min}$

$t = 5 \text{ min}$

FIGURE 3.16. Thermal Spray Coating Sequence: Plasma Gun Spraying Aluminum Metal on Glass Marbles

FIGURE 3.17. Remote Plasma Spray Coater Arrangement with Pneumatic Transfers

manipulators. The design will thus require the incorporation of tapered guide pins and studs, acorn drive nuts, captive bolts, and location and holding devices as are used on remote nuclear processing equipment today.

Individual connections will be required for each line or service leading to the coating equipment. Connections for a particular module may be incorporated into a manifold. Remote connectors such as those identified by Hargos and Masch (1979) are applicable to each of the various connections required by the coating equipment.

FIGURE 3.18. Remote Spray Coater Arrangement with Gravity Transfers

Water connections can be made through a number of couplings and quick disconnects that are commercially available. Some couplings will also handle gases and dry, flowable materials. Direct-current power connections may be made through various cable connectors.

The DC power leads to a typical plasma spray are enclosed in the cooling water lines from the control console to the gun. For a remote setup and to provide service connections that can be connected and disconnected remotely, the DC power and water manifold usually located in the control console will be located in the cell downstream of the cell service connectors. This device can be incorporated in the spray gun module.

Although the plasma spray coating system developed at PNL is a batch type operation, it can be made compatible with and a part of a HLW solidification process. It is capable of safely and efficiently applying a coating with a high leach resistance on substrates such as glass marbles at full-scale production rates. Neither the mechanical complexity nor size of the required equipment is too great, and the equipment is adaptable to being modularized. Also, the number and type of required services are not demanding, and they can be incorporated into a remote process using state-of-the-art devices. Therefore, the plasma spray coating system could be readily adapted to remote operations and maintenance as required in a HLW solidification production facility.

4.0 CHARACTERIZATION

Coatings applied to glass and ceramic substrates were evaluated by optical metallography, scanning electron microscopy, X-ray diffraction analysis, and leach testing. The basic intent of these analyses was to assess coating integrity by evaluating thickness, porosity, strength, and bonding to the substrate, both before and after leach testing. The most applicable bulk properties for the primary coatings studied are summarized in Table 4.1.

Coating thicknesses were determined from an average of measurements made on cross-sectional photomicrographs, while coating porosity was measured using an image analyzer. Apparent density values were obtained by calculation using theoretical densities and measured porosities.

4.1 CRUSH AND IMPACT BEHAVIOR

Crush and impact tests were performed on selected thermal spray coated marbles to determine the effect of coating on the mechanical integrity of the waste form. Similar tests were not performed on PyC coated ceramic pellets due to the small diameter and irregularity of the pellets.

Crush strengths of the coated and uncoated glass marbles were determined by compressing the specimens between copper shims placed on the hardened steel bearing blocks of an Instron® testing machine. The compression rate was 127 $\mu\text{m}/\text{min}$. Static load test results are summarized in Table 4.2. Determination of the fracture load from the test data was straightforward in all cases, except for specimen 4144-21 (Al-6% Si, 800 μm thick), which had the thickest coating. For all specimens except Specimen 21, the marbles failed catastrophically at the fracture load and the glass was not contained by the coating. The coating of Specimen 21 fractured before the glass marble did in some cases and, in two cases, the "normal" fracture occurred without prior failure of the coating.

The results show an improvement in static strength from 50 to 125% due to the coating. This is most likely due to the redistribution of loading

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TABLE 4.1. Bulk Properties of Various Coatings Applied to Simulated Waste Forms

Run No.	Coating	Substrate	Coating Properties		
			Thickness, μm	Density, g/cm^3	Porosity, vol%
<u>Fluidized Bed CVD</u>					
36062-67-207	$\text{Cr}_x\text{C}_y/\text{LT-PyC}/\text{Cr}_x\text{C}_y$	MB-1 Pellet	1/20/4	1.16 (LT-PyC) 6.8 (Cr_xC_y)	~50 (LT-PyC) ≤ 5 (Cr_xO_y)
33523-14-55	HT-PyC/ Al_2O_3	SPC-2 Pellet	20/45	~1.0 (HT-PyC) 3.9 (Al_2O_3)	~50(a) (HT-PyC) ≤ 5 (Al_2O_3)
<u>Plasma Spray</u>					
4144-19	Al	TDS-211 Marble	600	1.76	35
<u>Wire Spray</u>					
4144-21	Al-6% Si	TDS-211 Marble	800	1.76	35
4144-25	Pb	TDS-211 Marble	350	10.77	5
4144-24	Babbitt	TDS-211 Marble	330	5.46	5
4144-22	Zn	TDS-211 Marble	350	6.43	10

(a) High porosity of HT-PyC coating due to high deposition rate used. The PyC was intended to provide a crushable layer between the substrate and outer coating of Al_2O_3 .

TABLE 4.2. Summary of Static Fracture-Load Tests on Thermal-Spray Coated and Uncoated Glass Marbles

<u>Sample ID</u>	<u>Coating (a)</u>	<u>Thickness, μm</u>	<u>No. Tests</u>	<u>Fracture Load, kg</u>	<u>Standard Dev., kg</u>	<u>Range, kg</u>
TD-211 Glass Marbles	Uncoated		6	880	50	820-960
4144-14	Copper	120	5	1,320	260	920-1,560
4144-19	Aluminum	600	5	1,650	440	1,180-2,120
4144-21	Al-6% Si	800	2(b)	1,330	Some specimens sustained high loads but gave inconclusive results. Only two tests gave unambiguous results; high load was 1840 kg.	
4144-22	Zinc	300	5	1,690	540	780-2,060
4144-24	Babbitt	330	6	1,980	680	700-2,600
4144-25	Lead	350	6	1,500	470	750-2,030
4144-26	Duplex: Babbitt/Zinc	300/500	6	1,530	660	960-2,490

(a) Coating compositions given in Tables 3.1 and 3.2.

(b) 5 tested, average from 2.

stresses over a greater portion of the marble surface as a result of the coating and/or the actual strength of the coating.

Impact testing of thermal spray coated glass marbles was conducted following a procedure outlined by Bunnell (1979). In general, test specimens are loaded into a hardened steel punch and die and are subjected to a 18.1-kg (40-lb) load falling approximately 1.22 meters (4 feet) (a total energy of 217 J). After impact, the material is removed from the punch and die and screened using a sonic sifter and six screens sized down to $-37\text{ }\mu\text{m}$.

Results of impact tests on glass marbles coated with seven different thermal spray coatings, compared to uncoated marbles, are given in Table 4.3. There is a general trend toward reduction in the $-37\text{-}\mu\text{m}$ fraction when a coating is applied, but the significance of the absolute number is questionable, because the statistical variation is large. Figure 4.1 illustrates the cumulative size distribution for uncoated marbles compared to a rather ductile coating (Al) and a rather brittle coating (Ni/TiO_2). Again, in this analysis, the large statistical variation would tend to indicate very similar size fraction distributions regardless of the nature or presence of the coating.

The results indicate that thermal spray coatings applied to glass marbles have only a slight effect on the impact resistance as determined by the $-37\text{-}\mu\text{m}$

TABLE 4.3. Impact Results for Thermal Spray Coated TDS-211 Glass Marbles(a)

<u>Run No.</u>	<u>Coating</u>	<u>% Less Than $37\text{ }\mu\text{m}$</u>
-	(Uncoated)	6.17 ± 3.07
4144-14	Copper	6.08 ± 0.54
4144-16	TiO_2	4.41 ± 1.24
4144-17	Ni/TiO_2	6.58 ± 1.86
4144-19	Aluminum	4.25 ± 2.53
4144-22	Zinc	4.95 ± 1.02
4144-24	Babbitt	4.06 ± 0.71
4144-25	Lead	4.75 ± 1.95

(a) Energy = 217 J

FIGURE 4.1. Impact Test Results for Thermal Spray Coated TDS-211 Glass Marbles

fraction of waste glass fines. However, the original work by Bunnell and subsequent studies show that the test used is not very sensitive, even in comparing quite different materials. Although no appropriate test is available, the significant improvement in crush strengths suggests that impact production of fines would, in fact, be reduced for coated waste forms.

4.2 LEACH RESISTANCE

The primary reason for coating nuclear waste forms is to extend the chemical durability significantly beyond the lifetime of uncoated forms. For the coating to be effective, it must provide a barrier to corrosive agents that may attack the glass or ceramic form used to immobilize nuclear wastes. Corrosion by water is the phenomenon of greatest interest.

Glass substrates are known to be susceptible to water attack through a hydrogen ion exchange with alkalis in the glass and through hydroxyl ion attack of silicon, the major glass former (Das 1969; Douglas and El-Shamy 1967; El-Shamy, Lewins, and Douglas 1972; Doremus 1979). This OH^- attack is enhanced in silicate systems when the pH of the leach solution or leachate rises above 9.5 (Clark, Pantano, and Hench 1979). In highly acidic solutions (e.g., $\text{pH} < 4$), there may also be enhanced attack of waste glasses because of the increased solubility of glass components other than silica.

To test the viability of waste form coatings, the static leach test procedures known as MCC-1 and MCC-2 were employed (Barnes and Strachan 1981). A measure of durability is the quantity of glass constituents detected in the leachate. In the present experiments, the glass substrate contained Nd_2O_3 , SrO , Ce_2O_3 , and Cs_2O to simulate nuclear wastes. The leach behavior of these components indicates the extent of immobilization obtained by various coatings. Additional insights into durability may be gained by observing the change in silicon and alkali dissolution, which is a consequence of glass/water interaction.

In addition to coated borosilicate substrates, two ceramic substrates, SPC-4E and MB-2, were also investigated. (The compositions of all waste forms

tested were listed previously in Tables 2.2, 2.11 and 2.14.) Two different coating types were characterized: pyrolytic carbon and thermal spray metal and/or metal oxide. Pyrolytic carbon coatings of high- and low-temperature application were ineffective barriers in the case of glass substrate. In the case of the ceramic substrates MB-2 and SPC-4E, most components, once coated, show a decrease in leaching of one to two orders of magnitude. Metal and/or metal oxide coatings applied by thermal spraying proved to be the most effective barriers, exhibiting a range in durability characteristics from poor durability to zero release for the observed leach periods. The leach tests demonstrate that waste form lifetimes may be extended beyond those afforded by the waste glass/ceramic itself if a coating barrier is applied.

Experimental Results and Discussion

The leachate results are normalized in standard units of $\text{g/m}^2 \cdot \text{d}$ to allow for ease in comparing sample types. Normalization procedures are presented elsewhere (Barnes and Strachan 1981).

Table 4.4 presents the 28-day results of LT-PyC-coated waste marbles compared to an uncoated marble. Both coated forms apparently leach more than the uncoated sample; however, the leach enhancement is not considered experimentally significant. It is clear that the low-temperature coating provides no barrier at all to leaching, nor does it impede leaching of glass formers (Si, B) relative to Na.

TABLE 4.4. Leach Results for LT-PyC Coating on TDS-211 Marbles(a)

Coated Sample ID (b)	Normalized Release, $\text{g/m}^2 \cdot \text{d}$			pH
	Si	B	Na	
(uncoated)	0.37	0.50	0.46	10.0
62	0.47	0.63	0.62	10.1
157	0.50	0.67	0.59	9.8

(a) 90°C, DIW

(b) Samples produced at BCL by floating TDS-211 marbles in a fluidized bed.

Table 4.5 shows the results of HT-PyC and/or Al_2O_3 on ceramic waste forms SPC-4 and SPC-2. In both cases, the coating increased the durability by one to two orders of magnitude. This effect is obtained for all components except Cs, which shows an increase for the coated SP-2 substrate and a slight decrease for the coated SPC-4 substrate. In Table 4.6, the results of a LT-PyC coating on the ceramic substrate MB-2 show no significant difference between coated and uncoated waste forms.

Tables 4.7 and 4.8 show the screening test leach data for the wire spray and plasma spray coatings (refer to Tables 3.3 and 3.4). Wire spray coatings showing superior leach resistance were aluminum (6% silicon), babbitt, lead, and the babbitt/zinc duplex. Of the plasma spray coatings, aluminum and duplex coatings containing aluminum appeared to be very leach resistant. As a result of the screening test data, wire spray coatings of babbitt and lead and the plasma spray coating of aluminum were subjected to a series of additional leach tests. Table 4.9 gives the leach data for uncoated TDS-211 glass marbles in deionized water, brine, and silicate solutions. Tables 4.10 through 4.12 give the corresponding data for babbitt, lead, and aluminum coatings, respectively.

Metal thermal coatings provide the most promising deterrent to water attack. In all cases, the coatings provided a two to three orders-of-magnitude increase in chemical durability. Also, lifetime increases may be greater, because the elemental releases from the coatings are at or near the detection limits. The Cs release of these coated forms is particularly revealing compared to the high Cs release of the PyC coatings. It is significant that both glass modifiers and glass former leaching are stopped at 90°C. This indicates that the barrier is effective and can prevent glass/water interaction. The hydrothermal results show similar gains in durability except for the aluminum coating, which begins to delaminate from the glass surface.

As discussed in the following section, the leach results can generally be understood from the physical characteristics of the coatings and/or by pH buffering. Additional leach testing is needed to assess coating lifetimes under geologic conditions.

TABLE 4.5. Leach Resistance of HT-PyC and Al₂O₃ Coatings on Supercalcine(a)

Core	Coating	Normalized Elemental Release, g/m ²											
		Si		Ba		Ca		Mo		Sr		Cs	
		DIW	NaCl(b)	DIW	NaCl	DIW	NaCl	DIW	NaCl	DIW	NaCl	DIW	NaCl
SPC-2	None	6.0	5.1	24	33	2.2	3.9	17	20	20	24	3.1	0.9
SPC-2	HT-PyC	0.04	0.14	0.3	0.4	0.3	1.7	0	0.2	0.9	1.0	3.8	1.9
SPC-4	None	6.0	5.5	6.9	18	1.7	5.9	8.9	14	6.0	9.9	4.8	1.2
SPC-4	Al ₂ O ₃	0.09	0.18	0.05	0.05	0.7	3.7	0.02	0.12	0.005	0.05	0.28	0.31
SPC-4	HT-PyC/Al ₂ O ₃	0.09	0.17	0.01	0.05	0.7	4.4	0	0.2	0.01	0.15	0.12	0.28

(a) 90°C-28 days, SA/V=1:10

(b) 0.5 M NaCl

TABLE 4.6. Leach Data for LT-PyC Coatings on Ceramic Substrate(a)

Run No.	Substrate	Coatings	Leach Time, d	Normalized Elemental Release, g/m ² ·d								pH
				Substrate						Coating		
				Ce	Cs	Nd	Sr	Na	Si	Cr	Ni	
-	MB-2	None	14	<0.003	36	<0.001	2.40	4.20	--	--	<0.0001	9.08
(b)	MB-2	LT-PyC	14	<0.003	13	<0.001	0.01	2.60	--	--	<0.0001	9.04
-	SPC-4E	None	7	<0.07	--	<0.03	6.91	5.46	2.06	--	--	7.15
			14	<0.04	--	<0.02	2.66	3.27	0.96	--	--	7.54
			28	<0.02	--	<0.01	1.37	1.82	0.46	--	--	5.96
36449-70-197	SPC-4E	Cr _x C _y	3	0.63	--	1.03	0.93	1.80	1.90	<0.0007	--	3.45
			7	0.17	--	0.29	0.30	0.43	0.49	<0.0003	--	3.22
		LT-PyC	14	0.06	--	0.13	0.44	0.53	1.30	<0.0001	--	3.62
			28	0.09	--	0.14	0.24	0.46	0.81	<0.0001	--	4.31
36062-67-207	SPC-4E	Cr _x C _y	1	<0.51	--	<0.24	0.10	1.00	0.06	<0.002	--	3.00
		LT-PyC	7	<0.07	--	<0.03	0.16	0.30	0.01	<0.0003	--	3.33
		Cr _x C _y	14	<0.04	--	<0.02	0.29	0.52	0.04	<0.0001	--	3.20
			28	<0.02	--	<0.01	0.15	0.30	0.05	<0.0001	--	3.30

(a) MCC-1 leach test in deionized water at 90°C with exception that MB-2 was leached at 150°C. Surface area to volume ratio was 0.166 m⁻¹ for MB-1 and 10 m⁻¹ for SPC-4E. Data normalized according to MNC-1 procedure.

(b) Parameter set No. 3 of Table 2.10 was used to prepare an LT-PyC coating ~50 μm thick. Total flow through reactor was 10 slpm.

TABLE 4.7. Wire Spray Coating Screening Test Leach Data

Run No.	Coating	Leach Time, d	Normalized Release, g/m ² ·d ^(a)					pH
			Tracer Components		Major Components			
			Cs	Sr	B	Na	Si	
4144-21	Aluminum - 6% Silicon	3	0.05	0.42	-	0.07	0.11	7.8
		14	0.05	0.11	-	0.06	0.08	8.7
4144-22	Zinc	3	0.15	<0.02	-	0.24	<0.003	9.7
		14	0.15	<0.003	-	0.20	<0.001	10.2
4144-23	Copper	3	0.37	0.23	-	0.38	0.13	9.08
		14	0.41	0.28	-	0.32	0.10	10.1
4144-24	Babbitt	3	<0.04	<0.02	<0.01	<0.02	<0.003	5.5
		14	0.02	<0.005	0.01	0.03	<0.001	7.3
4144-25	Lead	3	0.08	<0.02	0.02	0.03	<0.003	9.8
		14	0.03	<0.01	0.006	0.03	<0.001	10.3
4144-26	Babbitt/ Zinc Duplex	3	<0.02	<0.02	-	0.14	<0.003	8.9
		14	0.01	<0.003	-	0.04	<0.001	9.0

(a) MCC-1 Standard leach test at 90°C in DIW, SA/V = 10 m⁻¹

4.3 MICROSTRUCTURAL CHARACTERIZATION AND LEACH BEHAVIOR

High-temperature PyC and HT-PyC/Al₂O₃ duplex coatings were found to be thick, monolithic, non-porous, and well bonded. However, volatile Cs was found in the HT-PyC coatings. The HT-PyC/Al₂O₃ duplex coatings, although they seal in the Cs, require a much more complex process for coating preparation. Low-temperature PyC coatings were made in an attempt to avoid the Cs volatility problem. These coatings applied alone to MB-2 substrate and in combination with Cr_xC_y layers to SPC-4E substrates were thin, often pitted, and extremely frangible.

Thermal spray metal coatings were generally of higher integrity than LT-PyC coatings. There was little microstructural difference between coatings applied by plasma spray and those applied by wire gun for each metal.

TABLE 4.8. Plasma Spray Coating Screening Test Leach Data

Run No.	Coating	Leach Time, d	Normalized Release, g/m ² ·d ^(a)					pH
			Tracer Components		Major Components			
			Cs	Sr	B	Na	Si	
4144-12	Self-Bonding "Stainless" Composite	3	0.06	0.04	—	0.20	0.05	6.6
		14	0.36	0.19	—	0.23	0.15	5.1
4144-14	Copper	3	0.20	0.07	—	0.24	0.04	5.4
		14	0.25	0.05	—	0.12	0.02	7.2
4144-15	Self-Bonding Molybdenum-Nickel-Aluminum	3	0.14	0.02	—	0.24	0.02	4.8
		14	0.17	0.05	—	0.14	0.01	4.7
4144-16	Titanium Dioxide	3	0.50	0.22	—	0.43	0.37	3.6
		14	0.94	0.17	—	0.82	0.69	9.9
4144-17	Duplex of Run -15 and -16	3	0.57	0.10	—	0.67	0.05	7.4
		14	0.34	0.04	—	0.24	0.01	9.2
4144-19	Aluminum	3	0.08	<0.02	0.07	0.07	<0.003	8.6
		14	0.05	0.02	0.04	0.05	0.001	9.2
4144-40	Nickel-Chromium Molybdenum Alloy	3	0.80	<0.02	0.26	0.57	0.10	9.1
		14	0.05	0.02	0.18	0.33	0.03	9.7
4144-43	Stainless Steel	3	1.80	0.33	0.47	0.77	0.32	9.8
		14	0.75	0.14	0.27	0.36	0.12	10.1
4144-46	Self-Fusing Molybdenum Blend	3	0.73	0.07	3.53	0.59	0.19	7.0
		14	0.53	0.08	1.15	0.25	0.09	5.8
4144-48	Aluminum/Titanium Dioxide Duplex	3	<0.10	0.14	0.02	0.03	0.01	8.1
		14	<0.02	<0.01	<0.003	0.05	0.001	7.8
4144-49	Aluminum/Lead Duplex	3	<0.10	<0.02	<0.01	0.04	<0.003	10.1
		14	0.09	—	<0.003	<0.001	<0.001	10.0
4144-50	Lead	3	0.24	0.11	0.06	0.10	0.003	10.5
		14	0.97	0.08	0.05	0.09	<0.001	10.3
4144-55	Aluminum	3	<0.10	<0.02	0.02	0.08	0.003	7.5
		14	<0.02	<0.01	0.004	0.007	<0.001	6.8

(a) MCC-1 standard leach test at 90°C in DIW. SA/V = 10 m⁻¹.

TABLE 4.9. Leach Data for Uncoated TDS-211 Glass Marbles

Leach Solution	Leach Temp., °C	Leach Time, d	Normalized Release, g/m ² ·d ^(a)								pH
			Tracer Components				Major Components				
			Ce	Cs	Nd	Sr	B	Fe	Na	Si	
DIW	90	3	<0.30	4.83	<0.12	2.60	2.83	<0.002	2.73	2.60	10.1
		7	<0.10	2.64	<0.05	1.07	1.63	<0.0007	1.59	1.40	10.1
		14	<0.06	2.44	<0.03	0.44	0.92	<0.0004	1.08	0.78	10.1
		28 ^(b)	<0.03	1.68	<0.01	0.44	0.63	<0.0002	0.70	0.47	10.2
Brine ^(b)	90	28	<0.03	<0.01	<0.01	0.32	0.36	<0.0002	-	0.03	6.9
Silicate ^(b)	40	28	<0.12	0.02	<0.05	0.006	0.01	<0.001	1.45	0.46	8.5
	90	28	<0.03	0.44	<0.01	0.07	0.37	0.002	1.72	0.73	9.5
	150	28	<0.12	2.32	<0.05	0.07	2.76	0.004	4.00	1.94	10.2

(a) SA/V = 10 m⁻¹

(b) Average of triplicate samples,,

TABLE 4.10. Leach Data for Babbitt-Coated TDS-211 Glass Marbles
(Run No. 4144-24, Table 3.3)

Leach Solution	Leach Temp., °C	Leach Time, d	Normalized Release, g/m ² ·d ^(a)					pH
			Tracer Components		Major Components			
			Cs	Sr	B	Na	Si	
DIW	90	3	<0.04	<0.02	<0.01	<0.02	<0.003	5.5
		7	<0.04	<0.01	<0.01	<0.007	<0.001	5.3
		14	0.02	<0.005	0.01	0.03	<0.001	7.3
		28(b)	<0.01	<0.004	<0.001	0.002	<0.004	6.1
Brine(b)	90	28	<0.01	<0.004	<0.001	-	-	2.2
Silicate 8.4	40	28	<0.04	<0.01	0.002	1.52	0.46	
	90	28	<0.01	<0.004	<0.001	1.68	0.48	
	150	28	<0.04	<0.01	<0.001	1.42	0.47	
9.5								
8.9								

(a) SA/V = 10 m⁻¹

(b) Average of triplicate samples.

TABLE 4.11. Leach Data for Lead-Coated TDS 211 Glass Marbles
(Run No. 4144-25, Table 3.3)

Leach Solution	Leach Temp., °C	Leach Time, d	Normalized Release, g/m ² ·d ^(a)						pH
			Tracer Components		Major Components			Coating	
			Cs	Sr	B	Na	Si	Pb	
DIW	90	3	0.08	<0.02	0.02	0.03	<0.003	8.6	9.8
		7	0.03	<0.01	0.006	0.03	<0.001	3.5	10.3
		14	0.02	0.07	0.007	0.01	<0.001	2.0	10.3
		28(h)	0.02	0.009	0.006	0.01	<0.0004	1.5	10.2
Brine(b)	90	28	<0.01	<0.004	<0.001	-	-	-	8.1
Silicate	40	28	<0.04	<0.01	0.002	1.49	<0.45	0.02	9.0
	90	28	0.01	<0.004	0.001	1.70	0.43	0.20	9.6
	150	28	0.18	0.05	0.02	-	<0.07	1.32	10.7

(a) SA/V = 10 m⁻¹.

(b) Average of triplicate samples.

TABLE 4.12. Leach Data for Aluminum-Coated TDS-211 Glass Marbles
(Run No. 4144-19, Table 3.4)

Leach Solution	Leach Temp., °C	Leach Time, d	Normalized Release, g/m ² ·d ^(a)						pH
			Tracer Components		Major Components			Coating	
			Cs	Sr	B	Na	Si	Al	
DIW	90	3	0.16	<0.02	0.07	0.07	<0.003	0.002	7.9
		7	<0.04	<0.01	<0.01	0.03	<0.001	0.001	6.7
		14	0.09	0.02	0.04	0.05	<0.0007	0.001	8.8
		28 ^(b)	0.01	<0.004	0.002	0.03	<0.0004	0.11	8.4
Brine ^(b)	90	28	<0.01	<0.004	<0.001	-	<0.0004	14.78	4.0
Silicate	40	28	<0.04	<0.01	0.003	1.45	<0.15	5.47	9.4
	90	28	0.04	<0.004	0.02	1.60	0.05	13.77	10.2
	150	28	0.55	<0.01	0.28	1.63	0.11	12.08	9.2

(a) SA/V = 10 m⁻¹.

(b) Average of triplicate samples.

However, there was large variation between metals with regard to microstructure and protection provided to the substrate during leaching. Copper coatings are somewhat porous and provide relatively poor leach protection. Aluminum coatings are more porous but provide superior protection either chemically or by acting as a pH buffer. Tin alloy coatings are fairly monolithic and have few pores, while zinc coatings have some porosity. Lead coatings are the most promising, as they are monolithic, nonporous, and well bonded. Microstructural evidence of chemical protection could not be obtained for tin, zinc, and lead coatings because these coatings offered unpenetrable structural protection.

Microstructural characterization was performed on PyC-coated samples and thermal spray-metal coated samples. The coating surface and polished cross sections were observed for most coatings both before and after leaching. Optical and scanning electron microscopy (SEM) were employed. Energy-dispersive X-ray analysis (EDAX) was used to obtain semi-quantitative elemental analysis when needed to enhance characterization.

CVD Coatings

Chemical-vapor deposition coatings were applied to ceramic substrates using fluidized bed technology. High-temperature processes were studied initially, and later work emphasized low-temperature processes.

High-Temperature CVD Coatings

The high-temperature CVD coatings applied and characterized include PyC and Al_2O_3 separately and in combination. A SEM micrograph of SPC-2 beads coated with HT-PyC shows that the coating is about 50 to 80- μm thick, well bonded to the substrate, and nonporous (Figure 4.2). A cesium X-ray map made by EDAX (the dot population density corresponds to the concentration of Cs) indicates that the Cs has volatilized out of the substrate and has been captured in the coating during the high-temperature processing. The leaching data support this finding (see Table 4.5).

For a 50 to 60- μm coating of Al_2O_3 (Figure 4.3), the Cs X-ray map shows that some Cs is trapped in the Al_2O_3 coating; however, the amount appears to be less than that in the HT-PyC in Figure 4.2. The Cs concentration in the Al_2O_3 coating is only slightly above background. Cesium was, nevertheless, found in the leaching solution (see Table 4.5).

Figure 4.4 is an optical micrograph showing the HT-PyC/ Al_2O_3 duplex coating. The HT-PyC layer is 20 to 50 μm thick and is well bonded to the substrate. The Al_2O_3 layer is 40 to 50 μm thick. A 10- μm reaction zone exists between the two coatings.

Figure 4.5 is an SEM view of the duplex coating with accompanying EDAX spectra showing the distribution of Cs. The EDAX spectra show high levels of Cs in the PyC layer, reduced levels in the reaction zone, and no Cs in the Al_2O_3 layer. Thus, application of the two materials as separate layers prevents Cs volatility and permeation into the outer Al_2O_3 layer. As expected, the leaching data show no release of Cs to solution for these samples (see Table 4.5).

FIGURE 4.2. SEM Micrograph of HT-PyC-Coated SPC-2

FIGURE 4.3. SEM Micrograph of Al_2O_3 Coated SPC-2 (High-temperature CVD Process)

FIGURE 4.4. HT-PyC/ Al_2O_3 Duplex Coated Supercalcine

Low-Temperature CVD Coatings

Coatings applied by the catalyzed low-temperature CVD process include LT-PyC alone and in combination with chrome carbide (Cr_xC_y). All of these coatings suffered from porosity and spalling. For example, supercalcine coated by 1 μm of Cr_xC_y followed by 20 μm of PyC followed by another 4 μm of Cr_xC_y spalled from the substrate (Figure 4.6). Poor bonding to the substrate evidently was the cause of the spalling problems. The leach data (Table 4.6) reflect the poor durability of these low-temperature coatings.

Thermal Spray-Metal Coatings

Glass marbles made of TDS-211 were coated with a series of metallic and ceramic thermal spray coatings. Five of the coatings--copper, aluminum, bab-bitt, zinc, and lead--are discussed in this section because they are micro-structurally representative of other coatings. The ceramic coatings that did not provide high leach resistance are not discussed.

FIGURE 4.5. SEM Micrograph of HT-PyC/ Al_2O_3 Duplex Coating on SPC-2 with EDAX Spectra Showing Cs Distribution

10 μm

10 μm

FIGURE 4.6. Cr_xCy/LT-PyC/Cr_xCy Coating on Supercalcine (Run No. 36062-67-207, Table 2.8)

Copper Coatings

Copper coatings applied with a wire gun (Run 4144-23, see previous Table 3.3) are very similar in overall appearance to the plasma spray coatings. From the poor leach results one would expect both coatings to have interconnected porosity. Bonding to the glass, however, is excellent. A crack developed around the entire marble at a depth of 300 μm within the glass surface, probably due to either thermal shock during cool-down after the coating process or to stress relief during the slicing and mounting step. No crack developed between the copper and the glass. Copper was detected by EDAX at a depth of 20 μm within the glass surface.

Figure 4.7 is an SEM micrograph of a sample sectioned before and after it had been leached for 14 days at 90°C. The altered layer and "worm burrow" in the glass are evidence of water attack through the open pores. This observation supports the leach data presented in Tables 4.7 and 4.8.

Aluminum Coatings

As with the copper, the aluminum coatings applied by wire gun and plasma spray are very similar in appearance. Figure 4.8 is an optical micrograph showing the extreme porosity of the aluminum (6% silicon) coatings of Run 4144-21 (Table 3.3). Apparently, the metal's tendency to form an oxide skin keeps the molten particles from flowing together to form a monolithic layer. The absence of a crack between the coating and the glass indicates that bonding was good (Figure 4.9). Aluminum was found to diffuse approximately 3 μm into the glass from the coating interface.

Figure 4.10 shows the interface sectioned after the marble was leached for 14 days at 90°C. The darker areas could be hydrated aluminum, since they yielded a weaker Al EDAX spectrum than did the surrounding lighter-appearing metal. This indicates that water has penetrated to the glass surface--not surprising in view of the extent of porosity shown in Figure 4.8. Yet there is no evidence of water attack on the glass as seen Figure 4.10 for the porous aluminum coating. Also, the leach data for the aluminum coatings (Table 4.12) show that very little glass has leached. A plausible explanation for the lack of glass attack is that chemical protection either caused by conditioning of

FIGURE 4.7. SEM Micrograph of Cu Coated TDS-211 Glass Marble Before and After Leaching (Run No. 4144-23, Table 3.3)

FIGURE 4.8. TDS-211 Glass Marble Coated with Al-6% Si by the Wire Process (Run No. 4144-21, Table 3.3)

FIGURE 4.9. TDS-211 Glass Marble Coated with Al-6% Si Showing Tight Bonding (Run No. 4144-21, Table 3.3)

the water by the aluminum coating or by conditioning of the glass surface caused the Al to diffuse into the glass. The latter case is supported by leaching studies showing the extremely beneficial effect of Al on glass durability (Chick 1981, Dillmore 1979). The former is supported by evidence of water conditioning by Buckwalter (1981). Possibly, the protection is a result of both phenomena.

Babbitt Coatings

Figure 4.11 shows a photograph of the babbitt (a tin alloy) coating, which was applied by the wire gun process (Run 4144-24, Table 3.3). Some porosity is evident, but it is not known whether the porosity is open or closed, since the leaching data show no evidence of glass attack. By visual inspection, it appears as if the porosity is closed.

Zinc Coating

Zinc was applied successfully only by a wire gun process. An analysis of Run 4144-22 (Figure 4.12) indicates that the coating's porosity volume is low enough that it is probably closed. The interface monitored by SEM microphoto examination (Figure 4.13) shows no evidence of cracks, and diffusion of Zn detected by EDAX is at least 5 μm deep. The leached samples appear to be identical to those before leaching. Thus, zinc coatings provide an impenetrable mechanical barrier to water.

Lead Coating

The lead (wire gun) coating from Run 4144-25 is almost nonporous (Figure 4.14). The dark spotting is due to pitting during polishing. A SEM micrograph taken before leaching shows no cracks (Figure 4.15). Extensive diffusion of Pb into the glass (shown by the light band within the glass) indicates that bonding was very good. Again, since lead coatings are monolithic, no leaching of the glass occurred.

FIGURE 4.10. TDS-211 Glass Marble Coated with Al-6% Si After Leaching 14 Days at 90°C in D.I. Water (Run No. 4144-21, Table 3.3)

FIGURE 4.11. TDS-211 Glass Marble Coated with Babbitt by the Wire Process (Run No. 4144-24, Table 3.3)

FIGURE 4.12. TDS-211 Glass Marble Coated with Zn by the Wire Process (Run No. 4144-22, Table 3.3)

FIGURE 4.13. SEM Micrograph of Zn-Coated TDS-211 Glass Marble Showing Tight bonding (Run No. 4144-22, Table 3.3)

FIGURE 4.14. TDS-211 Glass Marble Coated with Pb by the Wire Process (Run No. 4144-25, Table 3.3)

FIGURE 4.15. SEM Micrograph of Pb-Coated TDS-211 Glass Marble Showing Diffusion of Pb into the Glass (Run No. 4144-25, Table 3.3)

5.0 WASTE FORM PROCESS CONSIDERATIONS

Solid waste-forms of nuclear waste, particularly those that exhibit low leaching rates in ground water, are thought to be best suited for long-term disposal. Thus, most proposed radioactive waste management systems call for solidifying HLLW from nuclear fuel reprocessing plants. In addition, solid waste forms must be suitable for all phases of waste management, including the solidification process and any subsequent efforts to add coatings, encapsulate the waste in a container, and transport and place the waste in a repository.

Numerous waste forms have been proposed for use in the solidification and long-term disposal of HLLW. The use of one or more barriers between the solid radioactive waste and the environment, for example, would provide additional layers of protection and could be compatible with a variety of wastes or geologic disposal sites. Barriers may be required to meet the objectives of all waste immobilization programs (i.e., to contain all radionuclides until their activity has decreased to acceptable levels).

However, the more involved waste forms or the waste forms with additional barriers will require more complex processes. One should strive to produce an acceptable waste form by the most feasible, simplest, and most cost-effective process.

Engineering evaluations of the feasibility and practicality of producing coated solid waste forms with certain physical and chemical properties have been made. The following section assesses and compares the processes required to make coated and uncoated waste forms on a viable production scale and in a remotely operated and maintained facility.

5.1 ASSESSMENT OF VARIOUS WASTE FORM PROCESSES

As reported by Johnson (see Appendix), the process for carbon coating pellets in metal (CCPM) was ranked low (ninth) in process feasibility when compared with ten other processes for various waste forms. The ten processes were numerically rated in terms of their complexity, state of development, safety, process requirements, development work required, and facility requirements.

As shown in Table 5.1, the CCPM process is rated at 719 out of a possible 2000 points, whereas the highest-ranked process, the in-can glass melter process, has a total ranking of 1770. The lowest-ranked process, SYNROC, is rated at 470 points.

In another feasibility study made by Nesbitt and Treat (1980), the carbon-coated-supercalcine-pellet-in-metal process was rated seventh of nine processes. The study's evaluation criteria included process complexity, demands and limitations, state of development, and safety.

Nesbitt and Treat (1980) covered the following processes:

- in-can glass melting
- joule-heated glass melting
- glass-ceramic
- marbles-in-lead matrix
- carbon-coated-supercalcine-pellets-in-metal matrix
- SYNROC hot-isostatic pressing
- titanate
- concrete
- CERMET.

Recently, Johnson did a feasibility study on the plasma-spray-coated marble process (see Appendix). The process required to produce this coated waste form has been evaluated on the same basis and using the same criteria as reported in Johnson 1980. The summary of this assessment (Table 5.1) shows that the plasma-spray-coated, glass-marble-waste-form process is the sixth best out of eleven processes.

5.2 COMPARISON OF COATED-WASTE-FORM PROCESSES AND PRODUCTS

As shown above in the overall process evaluation, the requirements, limitations, complexity, and concerns for a viable waste form coating process are more involved than the process for several other waste forms. However, if a coated-waste-form product has characteristics or attributes that are needed to ensure the meeting of waste immobilization program objectives, coated-waste-form products can be made by any one of several processes.

TABLE 5.1. Process Rating Summary

<u>Process (in order of ranking)</u>	<u>Total Rating</u>	<u>Complexity of Process</u>	<u>State of Development</u>	<u>Safety</u>	<u>Process Requirements</u>	<u>Development Work Required</u>	<u>Facility Requirements</u>
Total Rating Points Assigned	2000	600	200	400	250	350	200
Percent of Total	100	30	10	20	12.5	17.5	10
1. Spray Calciner/In-Can Melter	1770	515	180	380	180	315	200
2. Joule-Heated Melter	1490	430	120	330	180	230	200
3. Glass-Ceramic	1400	420	100	330	145	220	185
4. Concrete	1294	395	110	315	184	205	85
5. Marbles-in-Lead	1176	370	90	270	161	195	90
6. Coated Marbles-in-Lead	1076	340	70	270	141	165	90
7. Titanate	891	325	50	240	131	90	55
8. Cermet	808	255	40	220	113	80	100
9. Super Calcine Pellets-in-Metal	794	255	30	220	179	35	75
10. Carbon-Coated Pellets-in-Metal	719	240	30	170	169	35	75
11. Supercalcine, Hot Isostatic Pressed	640	205	60	165	90	65	55
12. SYNROC, Hot Isostatic Pressed	470	165	30	105	85	45	40

A variety of coatings may be applied to a wide range of waste compositions. Combinations of typical waste-form coatings and processes that have undergone research and development were selected for this comparison. The combinations are:

- glass marbles coated with a plasma spray metal
- ceramic pellets coated with a HT-PyC coating
- ceramic pellets coated with a LT-PyC coating.

As shown in Table 5.2, the plasma spray process was rated the best coating process. The deposition rates by this method are compatible with the required waste processing rates, and plasma spraying generates few secondary wastes, adding very little gas to the off-gas system. The complexity of this coating process relative to the PyC processes is expected to be low. In addition, the maintenance and remotability of the equipment appear to be reasonable. The development of HT-PyC coatings is well advanced and the required equipment is moderately complex. Because these coatings are applied in the 900° to 1200°C range, the loss of Cs from the waste form is still cause for concern. The use of low temperatures to apply a special PyC coating eliminates the volatility concern, but this complicates the off-gas system and increases the handling of secondary wastes. This process requires considerable development and, presently, there is concern about achieving deposition rates that would be adequate for a production process.

As shown in Table 5.3, the products of the three processes reviewed above are compared to each other and rated. Overall, the plasma spray marbles product has the best rating, followed closely by the PyC-coated pellets. The round marbles provided the best shape for coatings, and the glass matrix can accommodate a wider range of waste compositions with fewer constraints than the ceramics. The required PyC coatings on the pellets are thinner than the metallic or glass coatings on the marbles, so they make up a smaller percent of the waste form. Also, the ceramic pellets contain a higher weight percent of wastes than glass. Leach resistance is the most important waste form property. Preliminary tests and evaluations indicate a 2 to 3 order-of-magnitude improvement for glass marbles coated by the plasma spray method over the noncoated marbles. Also, one order-of-magnitude improvement has been shown for PyC-coated ceramic pellets over the uncoated substrate.

TABLE 5.2. Comparison of Coating Processes

Aspect	Process Rating ^(a)		
	Plasma Coated Marbles	High-Temperature PyC Coated Pellets	Low-Temperature PyC Coated Pellets
Complexity	1	2	3
State of development	2	1	3
Process temperature	1	2	1
Recycling ability	1	1	1
Maintenance	1	2	3
Remotability	1	2	3
Volatility	2	3	1
Materials of construction	1	1	1
Off-gas requirements	1	2	3
Secondary wastes generated	1	2	2
Raw material required	1	1	2
Substrate heat-up	1	2	1
Deposit rate	<u>1</u>	<u>2</u>	<u>3</u>
TOTAL	15	23	27

(a) 1 Favorable; 2 Neutral; 3 Unfavorable.

TABLE 5.3. Comparison of Coated Products

Aspect	Process Rating ^(a)		
	Plasma Coated Marbles	High-Temperature PyC Coated Pellets	Low-Temperature PyC Coated Pellets
Leach resistance	2	4	4
Porosity of coating	2	1	1
Coating effect on crushability			
Coating % of waste form	3	1	1
Waste loading contained	2	1	1
Range of wastes accommodated	1	2	2
Coating bond strength	1	2	3
Substrate-coating thermal expansion relationship	2	3	3
Shape	<u>1</u>	<u>2</u>	<u>2</u>
TOTAL	14	16	17

(a) 1 Favorable; 2 Slightly Favorable; 3 Slightly Unfavorable;
4 Unfavorable

6.0 CONCLUSIONS

This report documents a two-year effort to develop and characterize low-temperature PyC coatings, systems to coat particles >2 mm, and thermal spray systems. Selected high-temperature CVD coatings from previous work were characterized for comparison to the present studies. Process feasibility was also considered. Many conclusions have been stated within the appropriate sections of the text. Major points are summarized in this section.

6.1 CVD COATING

The following conclusions have been made concerning the CVD coating of simulated nuclear waste forms:

- Plasma-activated, chemical-vapor deposition can be used to deposit carbon on glass marbles at near ambient temperatures.
- The screw agitated coater (SAC) approach to coating large diameter (~10 mm) particles appears to be feasible. Over 50 kg of marbles have been coated by this technique. Clearances are important between the auger and coater walls to eliminate binding and attrition. Coatings prepared in fluidized bed (FB) coaters under similar parameters are better in quality and are deposited at a higher rate (~2 to 3 times faster).
- HT-PyC, Al_2O_3 and duplex HT-PyC/ Al_2O_3 coatings on supercalcine substrates increased the leach resistance by one to two orders of magnitude except for cesium. The leachability of cesium was increased slightly for HT-PyC coatings and slightly decreased for Al_2O_3 and the duplex coatings. Significant concentrations of cesium were found in the HT-PyC coating which were due to migration from the substrate or trapping of volatile cesium in the coating. Some cesium is contained in the single Al_2O_3 coating. In the case of the duplex coating, cesium is contained in the HT-PyC but no cesium is found in the outer Al_2O_3 layer. Thus, it is concluded that high-temperature coating processes are limited by the volatile

components of the waste form. A solution is multiple coatings, which have the disadvantage of increased complexity.

- For LT-PyC, Ni(CO)_4 is the best catalyst to reduce coating temperatures to $\sim 500^\circ\text{C}$. As a carrier gas, 100% hydrogen improves carbon deposition by a factor of six when compared to 100% argon. Acetylene, C_2H_2 , was found to be the best carbon source gas. Coating rates were obtained ranging from 1 to 7 $\mu\text{m/hr}$. Carbon deposition was found to be temperature dependent with a maximum rate observed at 530°C .
- Leach tests on LT-PyC coatings indicate no significant difference between coated and uncoated ceramic substrates or glass marbles. Microstructural characterization of the samples revealed major porosity and spalling. Poor bonding was evident. Although the use of a Ni(CO)_4 catalyst reduced PyC coating temperatures to 500°C , it was concluded that the quality of the coating and deposition rate were unacceptable. The process may still be applicable as a low-temperature sealing coat to prevent volatility of the substrate during subsequent high-temperature coating.
- For conventional HT-PyC CVD coating, the deposition efficiency and coating rate decreased with decreases in temperature. Coatings can be applied at temperatures as low as 1000°C using 20 vol% propylene (C_3H_6) or acetylene (C_2H_2), with the remaining volume being argon.
- Lower coating temperatures for conventional HT-PyC CVD coatings can be obtained if one uses a rotating tube coater. Deposition efficiency obtained at 750°C is equivalent to fluidized bed coating in the temperature range of 1000 to 1150°C .

6.2 THERMAL SPRAY COATING

Three thermal spray processes--flame spray, wire gun, and plasma spray--were evaluated as an alternative to PyC CVD processes. Of the ceramic, glass, and metallic coatings applied to simulated waste glass marbles by these methods, the metallic thermal spray coatings appeared to be the most promising. Specifically,

- Thermal spray coaters for high-level waste glass marbles have been developed and demonstrated on an engineering scale with simulated waste. Over 300 kg of marbles have been coated by this technique. The three thermal spray systems tested produce quality waste form coatings. The plasma spray system does not require use of combustible gases, thus rendering it more appropriate than other thermal spray systems for some remote applications.
- Thermal spray travels along the line of sight and, unlike CVD, will not coat around corners. Agitators which rotate the waste marbles (thereby producing a uniform coating) have been developed and successfully demonstrated at PNL.
- Coatings applied by thermal spray processes typically have 5 to 35% porosity. Densification of these porous coatings on simulated waste glass marbles was successfully demonstrated by a combined heating/tumbling process.
- Metal plasma spray coatings provide the most promising deterrent to water attack. In all cases, the coatings provided a two to three orders-of-magnitude increase in leach resistance. Some coatings such as Pb, Zn, and Sn provide a dense mechanical barrier that is impermeable to water. Other coatings such as Al are porous but demonstrate improved leach resistance due to some form of chemical reaction with the substrate or a pH buffering effect.

6.3 PROCESS CONSIDERATIONS

Process feasibility was considered along with product properties in the evaluation of the coated particle processes. Obviously, the addition of coating equipment increases process complexity. Conclusions based upon process considerations were as follows:

- In a process feasibility ranking, plasma spray coated marbles in metal rank sixth out of twelve waste form processes, whereas carbon coated ceramic pellets in metal rank tenth.

- Plasma spray coating equipment adds little complexity to waste form processes. For example, the marbles in lead systems rank fifth and the plasma spray coated marbles in lead rank sixth.
- The plasma spray process was rated the best coating process for process consideration, followed by HT-PyC coatings with LT-PyC coating last.
- When product considerations were factored into the coating processes comparison, the plasma spray system still ranked best but was closely followed by HT-PyC and LT-PyC coatings.

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APPENDIX

PRELIMINARY EVALUATION OF ALTERNATIVE WASTE FORM
SOLIDIFICATION PROCESSES: EVALUATION OF COATED MARBLES-IN-LEAD

PRELIMINARY EVALUATION OF ALTERNATIVE
WASTE FORM SOLIDIFICATION PROCESSES:
EVALUATION OF COATED MARBLES-IN-LEAD

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EVALUATION OF COATED MARBLE PROCESS

1.0 INTRODUCTION

High level liquid waste (HLLW) results from the reprocessing of irradiated nuclear fuel; the solidification and packaging of HLLW are key elements in radioactive waste management. In PNL-3477, E. R. Johnson Associates, Inc. (Johnson 1980) presented a comparative rating of the feasibility of establishing production scale solidification processes based on eleven candidate waste forms. It has now been proposed that one of those waste forms, "Marbles-in-Lead," be modified to include the application of a plasma sprayed coating to the marbles prior to their encapsulation in lead.

It is the purpose of this report to evaluate the "Coated Marble" process and to do so using the same rating criteria and weighting factors which were used in the rating of the previous eleven alternative waste form solidification processes.

1.1 BASIS OF EVALUATION

In assessing the overall technical and engineering practicability of a process, or in developing a comparative evaluation of two or more processes, there are a number of factors which must be examined. The state of engineering development of the processes and of the associated equipment, the nature and significance of process and equipment unknowns, the complexity of the process when engineered for remote operation in a radioactive environment, and the inherent safety characteristics of the processes must be assessed and compared. A particular matter of concern in assessing feasibility of process equipment for remote operation in radiochemical environments is that of equipment reliability and ease of maintenance or replacement. In general, mechanical equipment such as motor-driven devices, pumps, and complex machinery should be avoided in radiochemical operations. Both the basic Marble-in-Lead and the Coated Marble processes will require extensive use of complex machinery which must be designed and developed for remote operation, and its feasibility proven.

In the earlier evaluation, six major evaluation criteria were identified and weighting factors were assigned to each. These were:

<u>Principal Criteria</u>	<u>Weighting Factors</u>
Complexity of Process	60
State of Development	20
Safety	40
Process Requirements	25
Development Work Required	35
Facility Requirements	20

Descriptions of the principal criteria and the basis for the relative weighting factors were given in PNL-3477.

Each of the principal criteria was subdivided into a series of subcriteria, and the total weighting factor was distributed to the subcriteria. The subcriteria and their weighting factors are shown in Table 1. For each subcriterion, a rating scale from 1 to 10 was devised, and a set of qualitative descriptions was developed to define levels of merit within each subcriterion. These descriptions and the basis for assignment of the rating were presented in PNL-3477, Appendix L.

1.2 SUMMARY OF EVALUATION

Table 2 repeats the earlier evaluation ratings and shows the additional rating of the Coated Marble process.

The Coated Marble process compares most closely with the Marbles-in-Lead process and is rated as somewhat more complex and in a less advanced state of development. This position reflects JAI's overall assessment of the modified process, and is based on the following considerations:

- continued development of the marble-making process has reduced the uncertainties concerning this operation, compared to the assessment in PNL-3477;

TABLE 1. Principal Criteria, Subcriteria, and Weighting Factors
for Process Evaluation

		<u>Factor Weighting</u>	
		<u>Sub</u>	<u>Total</u>
1.	Complexity of Process		60
	(a) Number of Process Steps	10	
	(b) Process Control	5	
	(c) Material Handling	5	
	(d) Adaptability of Equipment to Remote Operation	10	
	(e) Maintenance Requirements--Equipment Reliability	10	
	(f) Internal Recycle	5	
	(g) Assessment of Feasibility for Production Use	15	
2.	State of Development		20
	(a) Process	10	
	(b) Equipment	10	
3.	Safety		40
	(a) Dispersion Driving Forces (chemical, mechanical)	20	
	(b) Personnel Exposures (routine, accident, maintenance)	15	
	(c) Hazardous Materials Required	5	
4.	Process Requirements		25
	(a) Final Waste Volume	2	
	(b) Process Additives and Auxiliary Materials	3	
	(c) Secondary Wastes and Off-Gas Quantities	5	
	(d) Process Latitudes	5	
	(e) Quality Assurance	10	
5.	Development Work Required		35
	(a) Type of Development	15	
	(b) Scale of Development Programs	10	
	(c) Time Required (from initiation of program)	10	
6.	Facility Requirements		20
	(a) Radioactive Facilities	15	
	(b) Nonradioactive Facilities	5	

TABLE 2. Process Rating Matrix

Process	Total Rating	Ranking	Complexity of Process	State of Development	Safety	Process Requirements	Development Work Required	Facility Requirements
Total Rating Points Assigned	2000	--	600	200	400	250	350	200
Percent of Total	100	--	30	10	20	12.5	17.5	10
Spray Calciner/In-Can Melter	1770	1	515	180	380	180	315	200
Joule-Heated Melter	1490	2	430	120	330	180	230	200
Glass-Ceramic	1400	3	420	100	330	145	220	185
Marbles-in-Lead	1176	5	370	90	270	161	195	90
Super Calcine Pellets-in-Metal	794	9	255	30	220	179	35	75
Carbon-Coated Pellets-in-Metal	719	10	240	30	170	169	35	75
Supercalcine, Hot Isostatic Pressed	640	11	205	60	165	90	65	55
SYNROC, Hot Isostatic Pressed	470	12	165	30	105	85	45	40
Titanate	891	7	325	50	240	131	90	55
Concrete	1294	4	395	110	315	184	205	85
Cermet	808	8	255	40	220	113	80	100
Coated Marbles-in-Lead	1076	6	340	70	270	141	165	90

- similarly, experimental work with the pneumatic transfer systems and strength tests on the marbles themselves essentially eliminate the concern over fracturing of the marbles in the transport system;
- employment of the liquid-fed ceramic melter instead of the spray-calcliner-fed ceramic melter introduces some uncertainties into the glass making process;
- the basic coating process appears to be relatively straightforward, though not without some mechanical complexity which may prove troublesome in the remote operational environment required; and
- the surface fusion process has not been tested, and thus it is possible only to speculate on the probability of meeting process objectives in the development program.

In summary, the state of development of the Coated Marble process is adjudged to be nearly equivalent with respect to the melting and marble making steps but far less advanced with respect to both application and fusing of the coatings than was the Marbles-in-Lead process.

2.0 DESCRIPTION AND DISCUSSION OF PROCESS

2.1 DESCRIPTION OF PROCESS

The basic elements of the process are shown in the block flow diagram, Figure 1.

FIGURE 1. Coated Marbles Block Flow Diagram

The Coated Marble process is a modification of the Marbles-in-Lead Matrix process which are described and evaluated in PNL-3477. The process considered here differs from the earlier process primarily in the introduction of a coating of the individual marbles. In addition, the use of a liquid-fed ceramic melter has been incorporated in lieu of the spray calciner/Joule heated ceramic melter combination. The input to the process is High Level Liquid Waste and the output is the canister containing coated marbles in a lead matrix. It is

expected that the coatings would have a thickness of about 100 μ for a ceramic or glass coating and in the range of 200–500 μ for a metallic coating.

On the assumption that the rate of throughput of the liquid-fed ceramic melter (Joule-heated melter) will be the same as that postulated in Appendix D, PNL-3244 (Treat 1980), and used in Appendix D, PNL-3477 (Johnson 1980), i.e., 49 kg/h net production rate, an analysis of the coating process was made to establish the equipment capacity and installation requirements. Table 3 presents process data developed by PNL and additional assumptions employed in the analysis.

TABLE 3. Preliminary Process Data and Assumptions, Plasma Arc Coating Process (Aluminum Metal Coating)

PNL Data

Metal spray rate (aluminum)	6.8 kg/h
Deposition efficiency	$\geq 90\%$
Deposition rate	≥ 6.1 kg/h
Overspray	≤ 0.7 kg/h
Marble coating rate, per kg of marbles	290 $\mu\text{m}/\text{min}$
Density of aluminum coating as sprayed (65%)	1.76 kg/L

JAI Assumptions

Nominal size of marbles	12.7 mm (0.5 in.) OD
Nominal production rate	49 kg/h
Coating batch size	12.25 kg
Density of aluminum coating after fusion (95%)	2.57 kg/L
Nominal coating thickness, as sprayed	300 μm
Nominal coating thickness, after fusion	205 μm

On the basis of the input parameters set forth in Table 3 it was possible to calculate the process parameters for a single batch of marbles. These are summarized in Table 4.

In order to determine the number of coating units required, it is necessary to develop the overall cycle, including the surface fusion operation. For purposes of this evaluation, it was assumed that the surface fusion would be

TABLE 4. Process Parameters, Marble Coating Operation

Average number of marbles per batch	3807
Volume of coating applied per batch, as sprayed	578 cm ³
Volume of coating after fusion	395 cm ³
Weight of coating applied per batch	1.02 kg
Time required to apply coating	10.0 min

accomplished in the same apparatus as the coating, using the plasma arc torch with no metal feed and with decreased distance to the marbles; the estimated time was 10 min per batch. Fill rate is determined by the production rate of marbles--49 kg/h--and on this basis, fill time per cycle is 15 min. Estimated time to empty the coater at the conclusion of the cycle is 3-1/2 min. Thus, the total estimated cycle time per batch is 38.5 min. The production rate per hour per coater would be:

$$\frac{60 \text{ min/hr}}{38.5 \text{ min/cycle}} \times 12.25 \text{ kg} = 19.1 \text{ kg/hr/cycle}$$

Thus at least three coaters are required. Four are included in the flowsheet, as the above is a probable maximum production rate assuming no operational upsets or maintenance outages. The additional coater will also permit extension of the coating cycle, which would be necessary if thicker coatings are desired; the coating time is essentially linear with coating thickness.

Some discussions of the JAI assumptions in respect to process input parameters is in order. PNL reports (Oma 1981) that 10 kg of marbles per coater batch is virtually certain to be achievable with no operating problems, and 15 kg or more is held to be possible. The value of 12.25 kg was selected on the basis that four batches of that size per hour would match the marble production rate, recognizing that it may prove optimistic. The time required for coating was based on the PNL value of 6.8 kg/h metal spray rate for aluminum and a 90% laydown (deposition) efficiency which is based on an experimental run at PNL in which a value in excess of 90% was obtained. Calculations based on correlating the laydown rate in kilograms per hour with the laydown rate in micrometers per minute per kilogram (PNL data which appear to be based on

independent observations) confirm that if the latter value is reasonably accurate, the laydown efficiency is even higher than the 90% value assumed for the process calculations. The calculated cycle time varies inversely with the laydown efficiency; if the laydown efficiency is 95%, the coating cycle time drops to 9-1/2 min. Even at this rate, however, four coaters would be required to provide reasonable assurance of production continuity.

Precise material balance experiments will have to be run with the coating process to establish with reasonable accuracy the process parameters. These should include runs with various metals and other coatings to establish appropriate process flow sheets for other than aluminum coatings.

The coating significantly increases the bulk volume of marbles, especially at the higher coating thickness; for example, coatings in the range of 200-500 μ will increase the bulk volume of the marbles before coating by 10 to 25%. This will require a corresponding increase in the volume of the container over that used for uncoated marbles, if constant thermal loading is to be maintained. The larger container would also result in an increase in the weight of lead per package.

2.2 DISCUSSION OF PROCESS

2.2.1 Glass Melting

The liquid-fed glass melter differs from the spray calciner/Joule heated melter combination by the elimination of the spray calciner and the direct introduction of liquid or slurry feed to the melter. Operation of the Joule-heated melter in the liquid/slurry feed mode has been described by R. A. Brouns et al. (Brouns et al. 1980) in respect to a process for converting defense wastes to glass. Brouns states that work on liquid/slurry feeding started in 1975, and he cites several reports dealing with the application of the concept to power-reactor type wastes. Greatest success with this procedure has been obtained when feeding a slurry of the glass frit with liquidwaste. Although a considerable amount of experimental work has been performed with the liquid/slurry feed systems, there remain several uncertainties regarding the process. These relate to:

- control of the feed rate and melting rate so as to avoid formation of unstable "cold caps" on the melt, with the attendant possibility of near-explosive rates of vapor release should a large quantity of liquid be dropped onto the molten glass by collapse of a cold cap bridge,
- volatilization of ruthenium and cesium from the melt; Brouns reports that cesium volatilities as high as 24% were obtained in some runs with the defense wastes, and the volatility of cesium in the presence of boric acid, is known to be enhanced by moisture (H. E. Rauscher, Corning Glass Company, personal communication), and
- service life of the refractories, which may be shortened by thermal shock.

2.2.2 Marble Maker

An adaptation of a commercial marble making machine has been developed at PNL. The machine operates by laying a stream of molten glass onto a continuous moving belt of aluminum molds. Each mold consists of a metal block into which a cavity has been formed; the molds are vibrated as they move. The successful operation of the marble maker depends upon glass pouring rate, speed of advance and frequency of vibration of the molds, mold temperature and exit glass temperature. This machine has now had a rather lengthy operating history. It is reported to have experienced minimal maintenance problems. Moreover, the product, aside from that produced in the transient start-up and shut-down periods, is reported to be uniform in size and relatively free of surface imperfections.

It is still true, as it was in the evaluation of the marble machine, presented in PNL-3477, that its adaptation to remote operation will be far from a simple matter. Present operation depends upon maintaining adequate vibration amplitude of the molds after they have received the glass. In fact, a bar mounted above the molds is required to prevent ejection of a partially cooled marble from the mold due to excessive mold vibration. In addition to design engineering problems associated with remote operation and maintenance, control of volatile radioactive species and general contamination around the marble machine will be troublesome.

The product marbles are to be examined for roundness and size by a classifier with recycle of those marbles which are not essentially spherical. Non-spherical marbles are likely to have sharp surface irregularities which are an indication of the presence of either a high level of residual stress level at the surface or stress concentration points for subsequent loading or both. In addition to recycle of off-specification product, there will be a certain amount of normal recycle associated with glass stringers and product formed during transient operating periods. Remote operation of the recycle crusher and control of dust around that machine will present some problems.

2.2.3 Coater

It is proposed that an additional barrier to radionuclide release be provided by the application of a plasma-sprayed coating to the individual marbles. There has been limited laboratory experience with the application of such plasma-sprayed coatings. They have been applied in a batch process by agitating a load of marbles under the plasma gun as indicated in Figures 2 and 3. To date, the specific coating material has not been chosen. Experience with metallic coatings such as aluminum and with ceramic coatings such as titania has been promising. The coating process has been shown to provide complete coverage if adequate residence time in the coater is utilized. As noted earlier, the coating assumed in the process description is aluminum.

Coatings applied in this manner are, to a considerable degree, porous. If this process were to be adopted, it would be necessary to provide some means of fusing the coating so as to provide an impervious barrier. Possible means of fusing the coating include the use of the plasma spray itself or the use of a laser or high powered arc lamp. No attempts have yet been made at fusing the coating. Presuming that a fusing method could be developed, it does not appear that its operation would be much different than that of the plasma spray coater. For purposes of evaluation of the process, it has been assumed that the coating fusion can be accomplished by the plasma arc torch in the same equipment as the coating operation was conducted. Successful fusion of ceramic coatings, with the possible exception of glassy types, may, however, be difficult to accomplish.

FIGURE 2. Plasma-Sprayed Coating Process Equipment

In either case, the introduction of additional equipment will require additional maintenance. The plasma gun will periodically require replacement of its electrodes; the particle agitator may have to be cleaned of excess spray material; and whatever fusing system is adopted will have its own maintenance requirements.

The marbles are to be fed to the particle agitator by gravity and unloaded by vacuum. The remote operation of the vacuum removal system will require careful design to permit complete removal of a batch of marbles. The coated marbles are to be moved by pneumatic transport to the marble surge hopper.

FIGURE 3. Plasma-Spray Gun

Work done at PNL subsequent to the earlier evaluation, employing pneumatic transport systems of the same type as proposed for the production operation, has shown that the glass marbles are highly resistant to impact damage. Earlier reservations on this element of the process are thus eliminated. The coated marbles should be even less susceptible to damage in transport than are the uncoated ones.

A variation on the process which has not been subjected to detailed scrutiny is the application of two coatings in succession. It is foreseen that an exterior coating of brittle, refractory material may be desired, and that such a coating would be incompatible with the glass substrate. In this event, a soft, porous base coat, followed by the refractory material would be required. In concept, this may be relatively easy to accomplish by simply changing the powder feed to the torch from the base coat material to the outer coating material. As no work has been done to identify a suitable material or to establish the practicability of the double-coated marble system, no assessment can be made of the probability of developing a suitable process, but should such a process be developed, the principal effect on this assessment would be to increase somewhat the penalty for complexity of the process and decrease the rating on state of development.

2.2.4 Marble Fill

The marbles are batched by volume and loaded into the inner basket of the waste canister via a cansiter fill mechanism. Subject to some uncertainty as to the packing density of marbles in the hopper, fill mechanism, and basket, these operations are straightforward. Depending on the coating material which is selected, some problem from spalling of the outer surface of the marbles may be encountered. Experimental work done to date indicates that excellent adhesion between the coating and the marble surface is obtained, particularly if the marbles are coated while still hot ($>300^{\circ}\text{C}$); this and the high strength of the marbles which have been produced to date make it seem unlikely that serious spalling problems would be encountered in the filling operation.

2.2.5 Metal Fill

The void spaces of the inner basket, in the marble packing, and the annulus between the inner basket and canister are filled with molten lead in a

vacuum pouring operation. The lead melting furnace is to be located outside of the process cell and will, therefore, be a standard industrial installation. The filling operation will be sensitive to temperature control for fluidity of lead required to fill the interstices of the marble array, but the filling operation presents no insurmountable difficulties.

Again, depending on the nature of the coating material selected, the lead matrix may or may not wet the surface of the marbles. It would be preferable for the marble to be wet by the lead, as this would avoid the possibility of generating interconnecting voids due to differential contraction during cooling. In the case of aluminum coating, PNL reports excellent wetting, with the molten lead penetrating deep into the 65% dense aluminum coating.

It should be noted that the amount of lead required in this process is considerable; it may be as much as 1800 kg (4000 lb) per canister. The availability and cost of lead may require consideration of an aluminum matrix. An aluminum-silicon alloy (95/5) has been suggested as an alternative to lead; the melting point of this alloy (557 to 630°C) is sufficiently close to the softening point of the marbles to cause some concern over its use as a matrix. If a high melting refractory coating material is selected, it could provide sufficient support to the marbles that such an alloy could be used as a matrix material without running the risk of the marbles sagging extensively and sticking together during pouring and initial cooling operations. Additional development work in this area would be useful.

3.0 DISCUSSION OF EVALUATION

3.1 COMPLEXITY OF PROCESS

The remote operation, control, and maintenance of the marble machine remains, despite the additional cold demonstration experience, an obvious complication of this process. The continuously moving and vibrating molds represent a problem both in control and maintenance; the need for recycle of a portion of the glass product introduces additional equipment and, therefore, increases the complexity of the process.

In conception, the coating process is simple, but two complications in implementation will be those related to marble transport and dust control. In addition, remote maintenance of the process equipment will present some design problems; with some redesign of the plasma arc torch head to permit quick disconnect of the head from the process lines, maintenance of that piece of equipment should be relatively simple and possible to perform in a warm maintenance area.

If the plasma arc torch is used for surface fusion, no additional equipment complications would be introduced by this second step in the coating process. If, however, the alternative laser is used, added equipment and process complexity are introduced. Depending on the design of the laser equipment, it might or might not be necessary to transfer the coated marbles to a second--and similar--processing unit.

Clearly, the application and fusing of a coating on the individual marbles increases the complexity of this process over that of the original Marbles-in-Lead process. Not only is additional equipment required, but assurance must be given that each marble is coated with a minimum thickness and that the batch is free of agglomeration of marbles as a result of coating and fusing operations. This assurance will require, at a minimum, a visual examination of the marbles as they are unloaded from the coater.

As presently laid out, the transport of marbles from the coater is to be effected by a pneumatic transport system. Preliminary work at PNL with an experimental pneumatic transfer system has been successful, with no evidence of a tendency for the marbles to fracture, and the presence of the coating

might be expected to reduce the sensitivity of the marbles to impact. With some coatings, such as ceramics without a bond coat, spalling of the coating is a possible problem.

3.2 STATE OF DEVELOPMENT

The development of marble making has continued through experience in the operation of the PNL machine, and it now may be said to be in a fairly advanced state insofar as the mechanical aspects of making marbles is concerned. Virtually no work has been done on the adaptation of the melter and the marble machine to a remotely operated system, although some changes have been introduced in the melter which are intended to demonstrate remote operation features required in a radioactive system. Liquid/slurry feeding of the melter also has had insufficient experimental work to be assured that all likely sources of operational problems have been recognized and solutions identified.

In contrast with marble making, the application of plasma-sprayed coatings is in a very early stage of development. It has been merely demonstrated that adherent plasma-sprayed coatings can be applied to glass marbles by mechanically agitating the marbles in a plasma-arc or oxy-acetylene torch fed with any of several coating materials. Beyond that, however, little has been done other than development and test of a small production-scale agitator for conducting the coating operation. Choice of the coating material has not been made; conditions for spraying any material have not been optimized. There is, however, no reason to believe that the required development work could not be performed, or that successful solutions to the foreseeable problems cannot be demonstrated.

3.3 SAFETY

Hazards associated with this process are principally those of possible personnel radiation exposure incurred during maintenance of equipment. Minor possible sources of hazard are seen in the lead melting/pouring operation and in the handling of powdered coating materials, some of which may be toxic

and/or explosive. Accumulations of oxidizable dusts must be avoided to preclude the possibility of a dust explosion. Hydrogen, which may be required in low concentrations in the plasma torch feed gas with some coating materials, is also a potential source of hazard.

3.4 PROCESS REQUIREMENTS

The coating process will require a plasma gas and carrier gas as well as the coating material in powdered form. It is likely that the gas can be nitrogen and thus not impose either an economic or a safety penalty on the process.

As with the Marbles-in-Lead process the large quantity of lead and low waste loading in the final canister are process requirement disadvantages.

3.5 DEVELOPMENT WORK REQUIRED

The continued development of an integrated marble making system suitable for remote operation is required. The marble machine itself and its ancillary equipment including classifier, scrap mill, sampler, and enclosure should be demonstrated on simulated waste glass in a cold facility. Similarly, a fully remotized liquid-fed melter should be built and its remote operation demonstrated in a cold, preferably full-scale facility.

Considerable development work on the plasma-sprayed coating is required. Specifically the coating material (or materials, if a duplex coating is deemed desirable) must be chosen and application parameters of power to the plasma gun, powder flow rates, gun position with respect to marbles in agitator, and spray time required for a given batch of marbles must be optimized and demonstrated. In the matter of fusing the sprayed coatings, the concept has yet to be demonstrated in any way.

3.6 FACILITY REQUIREMENT

The introduction of the coating step into the marbles-in-lead process does not materially affect the facility requirements described in PNL-3477, Appendix D. There will be the equipment associated with the four coaters and the

offgas system will have to be sized to carry an additional load from the coaters, which will represent a substantial increase, due to the method of dust control currently planned for the coater.

4.0 PROCESS EVALUATION

The detailed rating is set forth in Table 5.

TABLE 5. Waste Solidification Process Evaluation--Coated Marbles-in-Lead

Criteria	Factor Weighting		Rating Assigned		Comments on Rating
	Sub	Total	Sub	Total	
1. Complexity of Process		60		340	
(a) Number of Process Steps	10		6		
(b) Process Control	5		4		Marble making, coating and lead melting require careful control.
(c) Material Handling	5		3		Additional handling of marbles required.
(d) Adaptability of Equipment to Remote Operation	10		6		None of the equipment has been demonstrated on a fully remote operational basis. Serious impediments unlikely.
(e) Maintenance Requirements - Equipment Reliability	10		5		
(f) Internal Recycle	5		9		Routine recycle capability at marble stage.
(g) Assessment of Feasibility for Production Use	15		6		No major impediments seen.
2. State of Development		20		70	
(a) Process	10		3		Basic glass making process is well developed.
(b) Equipment	10		4		Coating is limiting process step and fusing of surface after coating is untried.
3. Safety		40		270	
(a) Dispersion Driving Forces (chemical, mechanical)	20		8		Pneumatic Transport, recycle mill are dust sources.
(b) Personnel Exposures (routine, accident, maintenance)	15		5		Equipment maintenance most likely source.
(c) Hazardous Materials Required	5		7		Some of the coating powders may be toxic and/or explosive, and lead may also be expected to present some problems.
4. Process Requirements		25		141	
(a) Final Waste Volume	2		4		Coatings will increase total package volume 10-25%, depending on thickness.
(b) Process Additives and Auxiliary Materials	3		1		
(c) Secondary Wastes and Offgas Quantities	5		6		Lead fumes may create a problem.
(d) Process Latitudes	5		0		
(e) Quality Assurance	10		7		QA at marble stage relatively simple; at coating stage, difficult to impracticable due to the extensive sampling required to confirm adequacy of coating.
5. Development Work Required		35		165	
(a) Type of Development	15		5		Marble-making and coating/fusion.
(b) Scale of Development Program	10		4		Coating, marble-making and continuous glass melter must be developed further; should be demonstrated fully remote on cold basis.
(c) Time Required	10		5		
6. Facility Requirements		20		90	
(a) Radioactive Facilities	15		5		Marble-making, coating, and recycle equipment.
(b) Nonradioactive Facilities	5		3		Lead Melting facilities.
Total Rating				1076	

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