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COATING CRYSTALLINE NUCLEAR WASTE FORMS TO IMPROVE INERTNESS*

D. P. Stinton, P. Angelini, A. J. Caputo, and W. J. Lackey

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

ABSTRACT

Crystalline waste forms of high simulated waste loading were successfully coated with layers of pyrolytic carbon and silicon carbide. Sol-gel technology was used to produce microspheres that contained simulated waste. A separate process for cesium immobilization was developed, which loads 5 wt % Cs onto zeolite particles for subsequent coating. The chemical vapor deposition process was developed for depositing thin layers of carbon and silicon carbide onto particles in a fluidized-bed coater. Pyroltyic carbon-coated particles were extremely inert in numerous leach tests. Aqueous leach test results of coated waste forms were below detection limits of such sensitive analytical techniques as atomic absorption and inductively coupled plasma atomic emission.

INTRODUCTION

Disposal of high-level radioactive wastes has been a problem for many years. The primary waste form developed to immobilize these wastes was glass, which can accommodate inert and radioactive components of the waste in its structure.[1,2] However, high-temperature, high-pressure leach tests have shown that glass can degrade or devitrify with time in a hydrothermal environment. Consequently, alternative methods of waste disposal have

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received renewed interest[3] in order to minimize the possible release of radioactivity from the repository. Crystalline materials such as Synroc and Supercalcine have received considerable attention.[4-7] Current schemes also use multiple barriers such as the waste form and additional barriers associated with the waste form, container, overpack, and repository conditions to isolate the waste from the environment. The renewed interest in reduced leach rates and the multibarrier approach have created considerable interest in coated waste forms. Some work has been reported in the United States and abroad on coating glass or Supercalcine waste forms with pyrolytic carbon, Al_2O_3, and nickel,[8-10] but much of this work was unsuccessful because crack-free coatings could not be produced. We used nearly 20 years of High-Temperature Gas-Cooled Reactor (HTGR) coating process experience and remote coating equipment development to deposit crack-free, single-phase dense carbon and SiC coatings.[11] Such coatings on reactor fuel microspheres formed by sol-gel technology have produced excellent fission product retention and are expected to reduce significantly leach rates of the current waste forms (glass, Supercalcine, or Synroc). The sol-gel process appears to be applicable for remote preparation of crystalline waste forms. Therefore, our objective in this study was to produce microspheres of crystalline waste forms by sol-gel technology and to deposit impervious coatings of pyrocarbon and SiC to obtain improved leach resistance.

SPHERE FORMATION

Sol-gel technology has been successfully applied to preparing high-quality simulated nuclear-waste-containing microspheres because they are required for adequately evaluating coating processes.[12-15] Emphasis has been on the internal gelation process;[16,17] however, tons (metric) of

microspherical fuel for nuclear reactors have been produced by external gelation and water extraction. The internal gelation process was selected for current work because it offers greater flexibility in sphere forming and the capability for making larger spheres; however, it may produce somewhat larger waste streams. Figure 1 shows the typical internal gelation process as applied to high-level nuclear waste. The sludge is dissolved in nitric acid, and matrix elements are added in solution to provide feed. An ammonia-donor chemical (gelation additive, Fig. 1) is added to the nitrate solution. Liquid microspheres are formed via interfacial tension by dispensing the aqueous solution in discrete droplets into a heated organic liquid immiscible with water. The liquid spheres become gel spheres by the reaction of metal nitrates with the ammonia released from the ammonia donor. Gelation occurs rapidly and uniformly and gives hydrated gel spheres. The gelled spheres are aged and washed with an ammonium hydroxide solution. Unfortunately the washing procedure removes cesium from the gelled spheres. We therefore propose that cesium be extracted from the waste stream and loaded onto zeolite granules or microspheres to be coated with carbon and/or SiC. As described later, cesium-loaded zeolite has been successfully coated. Because cesium is generally troublesome for other waste forms, the coated zeolite process might find application to alternative waste form processes including glass. (The coated zeolite is a generic development.)

In this work several waste form compositions were produced (Table I), including: Synroc-B, Synroc-D (~70 wt % simulated composite SRP* waste[18]

*Composite SRP denotes a Savannah River Plant waste of average composition.

without aluminum removed plus 30 wt % additives),[5,6,19] 70-30 (~70 wt % simulated composite SRP waste with aluminum removed plus 30 wt % additives), and 90-10 (90 wt % simulated composite SRP waste with aluminum removed plus 10 wt % ZrO_2). Compositions such as 90-10 were produced because no tailoring was required to reach a specific final composition, which is a significant advantage because of the wide variation in waste composition. Additional advantages are that the composition is easily gelled, and, because it uses sludge with aluminum removed, it would minimize the volume of waste transferred to a repository.

DRYING AND SINTERING

All microspheres produced by the internal gelation process must be dried to remove volatiles. Removal of mechanical water is accomplished by heating the material for 1 h to 120°C in a container equipped with a loosely fitting lid. The dryer temperature is maintained at 120°C for several hours until a constant weight is achieved. This procedure prevents cracking that could occur if volatiles were released too rapidly. Chemically combined water, ammonia, CO, and CO_2 are evolved during the early part of the sintering schedule (<400°C).

All the waste compositions have been analyzed by dilatometry and found to sinter between 550 and 800°C. Temperatures as high as 1000°C were required for Synroc-B and Synroc-D to obtain the desired phase assemblage (zirconolite, perovskite, and hollandite), although full density was achieved at a lower temperature (Fig. 2). The low sintering temperatures of sol-gel–produced material significantly reduce the volatilization of fission product species.

The sintered microspheres must be very stable and compatible with pyrocarbon during the coating process (~1000°C) so that high-quality, crack-free coatings can be deposited. Microspheres of Synroc-B and Synroc-D sintered in Ar—4% H_2 at 1000°C obtained high densities and were stable at the coating temperatures. Unfortunately the 70-30 and 90-10 compositions reacted with pyrocarbon at these temperatures. We will describe our solution to the reaction problem later.

COATING

Chemical vapor deposition of pyrolytic carbon and SiC coatings in a fluidized-bed furnace has been used for HTGR fuel for about 20 years.[11,20] However, pyrolytic carbon coatings for fuel particles were deposited at about 1300°C to obtain dense, impermeable, and isotropic coatings capable of withstanding reactor irradiation.[21] Some proposed waste forms would become molten at this temperature, and in general coatings on waste forms require much lower deposition temperatures to reduce volatilization of fission products. Also, waste form coatings need not be completely isotropic. Fortunately, pyrocarbon and SiC have proved radiation stability and corrosion, oxidation, and abrasion resistance for all hypothesized repository conditions.[22]

In about 300 coating runs, pyrocarbon and SiC were deposited onto microspheres containing simulated waste to determine satisfactory coating conditions. The initial runs used Synroc-B or Synroc-D kernels. The minimum pyrocarbon coating temperature for depositing high-quality coatings in a reasonable time was 1000°C with acetylene or 1200°C with propylene. The thermal expansion of the waste-containing kernels was less

than that of dense pyrocarbon, which caused the coatings to crack when cooled. Cracking of the pyrocarbon was eliminated by depositing a low-density pyrocarbon coating between the kernel and the dense coating (Fig. 3). This elastic porous coating allows the dense coating to shrink without cracking. High-quality dense pyrocarbon coatings (densities between 1.9 and 2.1 g/cm^3) were deposited at rates from 0.1 to 2.5 μm/min. Characterization of these coatings by mercury porosimetry, immersion density, ceramography, gaseous chlorination at 1000°C, and aqueous leaching proved them to be of high quality. Figure 4 shows a polished section in bright field and polarized light of a particle coated with a low-density pyrocarbon, an inner dense pyrocarbon deposited at about 2.0 μm/min, and an outer pyrocarbon deposited at about 0.2 μm/min to yield an even higher density. The inner dense pyrocarbon coating is nearly isotropic, as shown in the polarized light photograph, and has only a small amount of porosity. The outer pyrocarbon coating is quite anisotropic, and essentially no porosity is visible. From experience with fuels, anisotropic coatings are found to be slightly less permeable than are isotropic coatings. However, either coating alone should be sufficient to prevent escape of the waste.

If necessary, SiC coatings can be deposited over the dense pyrocarbon layers to provide additional leach protection or, more important, to provide an oxidation-resistant outer coating. Silicon carbide coatings (>98% theoretical density) have been applied to pyrocarbon-coated Synroc-B spheres at 1400 and 1500°C. Although the kernels melted and penetrated the low-density pyrocarbon layer, they did not react with the SiC coating [Fig. 5(a)]. The SiC layer was deposited

by decomposition of methyltrichlorosilane as developed for HTGR fuel. The impermeable dense pyrocarbon layer prevented volatilization of fission products during the high-temperature deposition of SiC. Although SiC could be deposited successfully, a process not involving high temperatures or HCl as an off-gas was desired. Thus, a new process was developed to deposit SiC at temperatures from 700 to 1000°C. This process uses methylsilane, which contains no chlorine, and thereby eliminates equipment corrosion problems. Layers of SiC can be deposited with methylsilane at temperatures that neither melt the kernels nor vaporize fission products [Fig. 5(b)]. An additional use of this process was also found as described below.

As previously mentioned the 90-10 and 70-30 kernels reacted severely with pyrocarbon coatings at either 1000 or 1200°C (Fig. 6). The higher waste loading and resultant higher iron content of these spheres caused them to react with pyrocarbon, whereas Synroc-B or Synroc-D do not. This reaction was eliminated by depositing SiC directly onto the microspheres followed by the pyrocarbon layer. Application of SiC directly onto the kernels was possible with the new SiC deposition process because of the low deposition temperature and the absence of HCl; HCl present in the older conventional SiC deposition process reacts with the kernels. With the new process a low-density SiC layer followed by a high-density SiC layer was required (Fig. 7). The low-density layer was necessary to avoid cracking of SiC coatings from thermal expansion mismatch, and the dense SiC layer served as a barrier to prevent reaction between the kernel and the pyrocarbon.

A generic waste form was also developed to dispose of cesium. In this process zeolite* is loaded with up to 5 wt % Cs and heat treated at 600°C in air to fix the cesium within the cages of the zeolite structure, and the cesium is further immobilized by application of a pyrocarbon coating at 1000°C (Fig. 8). No loss of cesium was detected during the heat treatment or coating steps. The zeolite is of low density with a thermal expansion that is compatible with the pyrocarbon coating. Therefore, no low-density pyrocarbon layer is required. Pyrocarbon-coated zeolite could be coated with an additional layer of SiC for more inertness or for oxidation resistance if necessary.

LEACH RESULTS

Several types of coated and uncoated waste forms were leach tested. Leach tests were performed in deionized water at 90°C for 3, 7, 14, and 28 d by the MCC-1 procedure.[23] Blanks were submitted along with the samples to determine the detection limits of the analytical techniques (inductively coupled plasma atomic emission and atomic absorption). The leach results were calculated from the equation

$$\text{Leach rate} = M_i/(f_i SA\ \Delta t) ,$$

where

M_i = mass of element is solution (g),

f_i = fraction of element in sample,

SA = surface area of sample (m^2),

Δt = time period of leach (d).

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*Linde Ionsiv IE-95, Union Carbide Corporation, Linde Division, 270 Park Avenue, New York, N.Y. 10017.

Leach results highlight the value of coated waste forms. Figure 9 summarizes for Synroc-D and cesium-loaded zeolite the leach rate for pyrocarbon-coated particles. In both cases the leach rates for coated material are below the detection limits (could not be distinguished from the blanks). This has been our experience for all types of coated particles that have been leached to date (Table II). Figure 9 shows that coatings typically lower the leach rate by at least 2 to 4 orders of magnitude. Leach values for coated particles are lower by several orders of magnitude than are results for glass and other waste forms.[3,18] This is particularly noteworthy for cesium, which heretofore has been impossible to immobilize in other waste forms because of its high inherent solubility and tendency to partition into leachable phases.

CONCLUSIONS

Significant progress was made in applying sol-gel and fluidized-bed coating technology to the solidification of high-level nuclear wastes. We have successfully prepared microspheres containing simulated wastes of Synroc-B, Synroc-D, a modified Synroc-D where alumina has been previously removed from the waste, and a very high waste-loading composition containing 90% waste and 10% ZrO_2. Each of these compositions has been sintered at 1000°C and coated with pyrocarbon at temperatures as low as 1000°C. Silicon carbide can be applied to these pyrocarbon-coated particles at temperatures as low as 900°C for additional inertness or for oxidation resistance. Isolation of cesium was accomplished by pyrocarbon coating cesium-loaded zeolite. Pyrocarbon and SiC coatings have successfully reduced the leach rates to below detection limits.

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LIST OF FIGURES

Fig. 8. A waste form was developed that retains cesium during sintering, coating, and leach testing. (a) Coated zeolite particles. (b) Polished section showing zeolite kernel and pyrocarbon coating.

Fig. 9. Pyrocarbon coatings significantly reduce leachability. The cesium leach rate was obtained from cesium-loaded zeolite, whereas the leach rates for other elements were obtained from Synroc-D. The leach rate of uncoated material is indicated by the bars with no crosshatching. The crosshatched area of the bar represents the leach rate after coating.

Table I. Composition of waste, additives, and final product

Component	Content, wt %							
			High-waste-loaded SRP waste forms					
	SRP[a] waste sludge	Synroc-B product	Synroc-D[b]		70-30[c]		90-10[d]	
			Additives	Product	Additives	Product	Additives	Product
Fe_2O_3	49.9			27.4		35.8		44.9
Al_2O_3	9.8	10.9	33.6	20.6		7.0		8.8
MnO_2	13.7			7.5		9.9		12.4
U_3O_8	4.5			2.5		3.2		4.1
CaO	3.7	13.8	10.3	6.7	18.0	7.7		3.3
NiO	6.2			3.4		4.4		5.6
SiO_2	1.2		15.8	7.8	21.2	6.7		1.1
Na_2O	7.0			3.8	9.9	7.9		6.3
Na_2SO_4	1.3			0.7		0.9		1.2
Ce_2O_3	1.1			0.6		0.8		0.9
Nd_2O_3	1.1	0.3		0.6		0.8		0.9
SrO	0.5	0.2		0.3		0.4		0.5
TiO_2		59.7	31.8	14.3	39.1	11.0		
ZrO_2		9.8	8.5	3.8	11.8	3.3	100	10.0
BaO		4.2						
Mo_2O_3		0.3				0.2		
Ru_2O_3		0.3						
Cs_2O		0.5						

[a]SRP waste with aluminum removed and normalized to compensate for removal of zeolite and addition of Ce_2O_3, SrO, and Nd_2O_3.

[b]Synroc-D (~70 wt % SRP waste without aluminum removed plus 30 wt % additives).

[c]70-30 (~70 wt % SRP waste with aluminum removed plus 30 wt % additives).

[d]90-10 (~90 wt % SRP waste with aluminum removed plus 10 wt % ZrO_2).

Table II. Leach test results for coated and uncoated particles[a]

Element	Leach rate, g/(m²·d)									
	Detection limit 5 d	Synroc-B uncoated 3 d	PyC-coated Synroc-B 1 d	Uncoated Synroc-D 3 d	PyC-coated Synroc-D 3, 7, or 28 d[b]	Uncoated 70-30 3 d	Coated 70-30 3 d	Uncoated cesium waste form 28 d[b]	Coated cesium waste form 3, 7, or 28 d[b]	Uncoated 90-10 28 d[b]
Fe	3×10^{-5}	3×10^{-4}	*c*	6×10^{-3}	*c*	7×10^{-3}	*c*	*d*	*d*	3×10^{-3}
Al	1×10^{-4}		*c*	2×10^{-2}	*c*	6×10^{-3}	*c*	2×10^{-2}	*c*	
Mn	2×10^{-5}	*d*	*c*	1×10^{-3}	*c*	2×10^{-3}	*c*	*d*	*d*	2×10^{-2}
U	1×10^{-5}	*d*	*c*	4×10^{-3}	*c*	3×10^{-3}	*c*	*d*	*d*	5×10^{-4}
Ca	2×10^{-4}	2×10^{-2}	*c*	4×10^{-1}	*c*	5×10^{-2}	*c*	*d*	*d*	3×10^{-3}
Ni	4×10^{-5}	*d*	*c*	3×10^{-3}	*c*	2×10^{-3}	*c*	*d*	*d*	
Si	1×10^{-4}	*d*	*c*	7×10^{-2}	*c*		*c*	3×10^{-2}	*c*	3×10^{-1}
Na	6×10^{-4}	*d*	*c*	1×10^{-2}	*c*	3×10^{-3}	*c*	*d*	*d*	
Zr	2×10^{-5}	9×10^{-5}	*c*	3×10^{-3}	*c*	2×10^{-4}	*c*	*d*	*d*	
Ti	5×10^{-6}	3×10^{-4}	*c*	2×10^{-4}	*c*	9×10^{-4}	*c*	*d*	*d*	
Ba	2×10^{-4}	4×10^{-3}	*c*	*d*		*d*		*d*	*d*	*d*
Mo	1×10^{-3}	*c*	*c*		*c*		*c*	*d*	*d*	
Ce	4×10^{-4}	*c*	*c*	5×10^{-3}	*c*	4×10^{-3}	*c*	*d*	*d*	
Nd	1×10^{-3}	*d*	*c*		*c*		*c*	*d*	*d*	
Sr	1×10^{-5}	4×10^{-4}	*c*	5×10^{-1}	*c*	8×10^{-2}	*c*	*d*	*d*	9×10^{-3}
Cs	4×10^{-5}	*d*	*d*	*d*	*d*	*d*	*d*	1×10^{-2}	*c*	*d*

[a]Leach rate = $M_i/(f_i SA\ \Delta t)$; M_i = mass of element in solution (g); f_i = fraction of element in kernel; SA = surface area of sample (m^2); Δt = time period of leach (d). Leach test MCC-1; deionized H_2O; 90°C. Detection limit determined by averaging blanks submitted during test (V_{sol} = 20 cm^3, Δt = 5 d, SA = 75 × 10^{-4} m^2).

[b]Detection limit for 28-d samples is a factor of 5 lower than the detection limit listed.

[c]Below detection limit.

[d]Element not present in waste form.

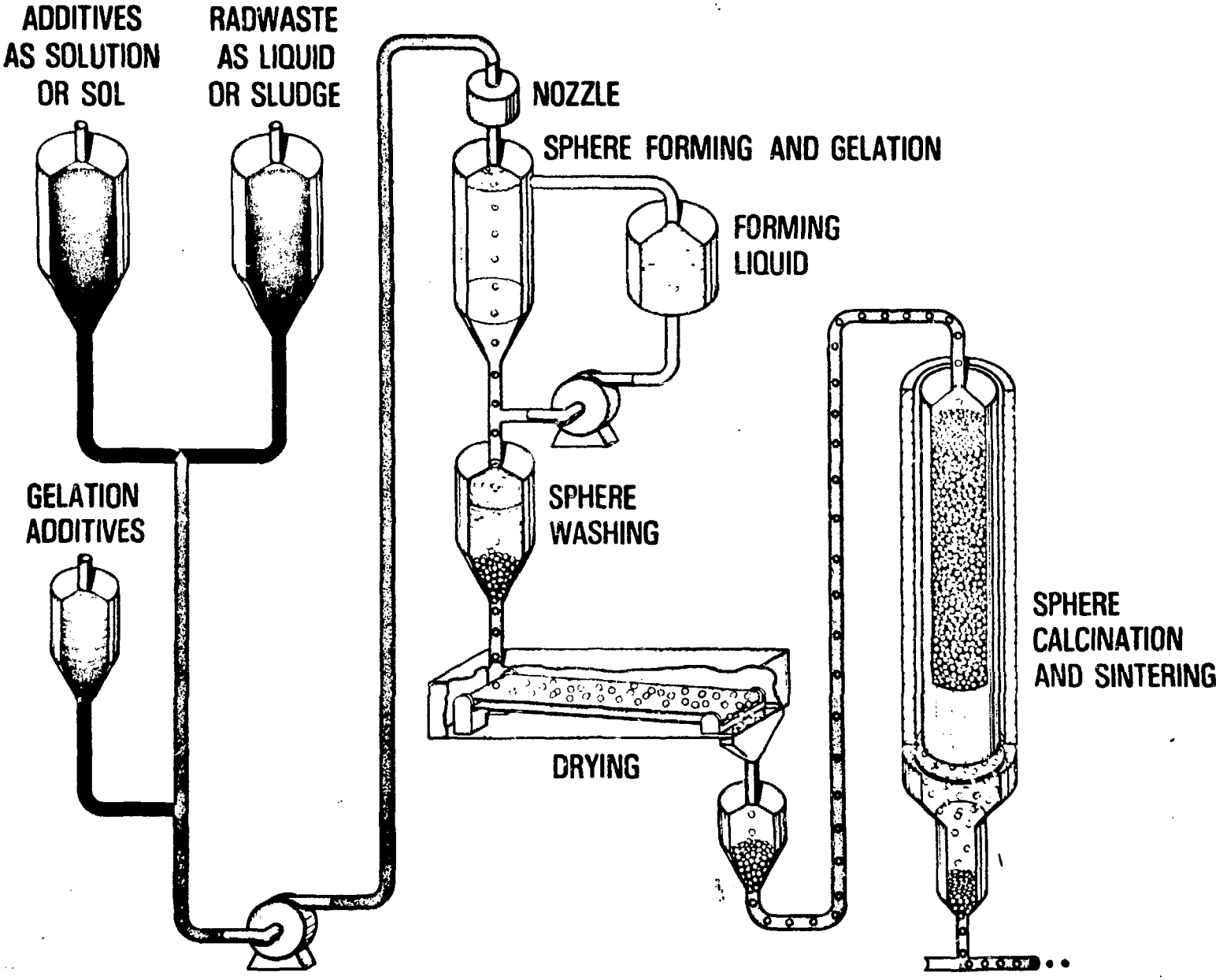

Fig. 1. Sol-gel technology is applicable to fixation of nuclear waste.

Fig. 2. Synroc-D microspheres are sintered to high densities (4.2 g/cm^3, open porosity <1%) at about 800°C; however, 1000°C is required for proper phase formation.

LOW DENSITY COATINGS PREVENT CRACKING CAUSED BY THERMAL EXPANSION MISMATCH

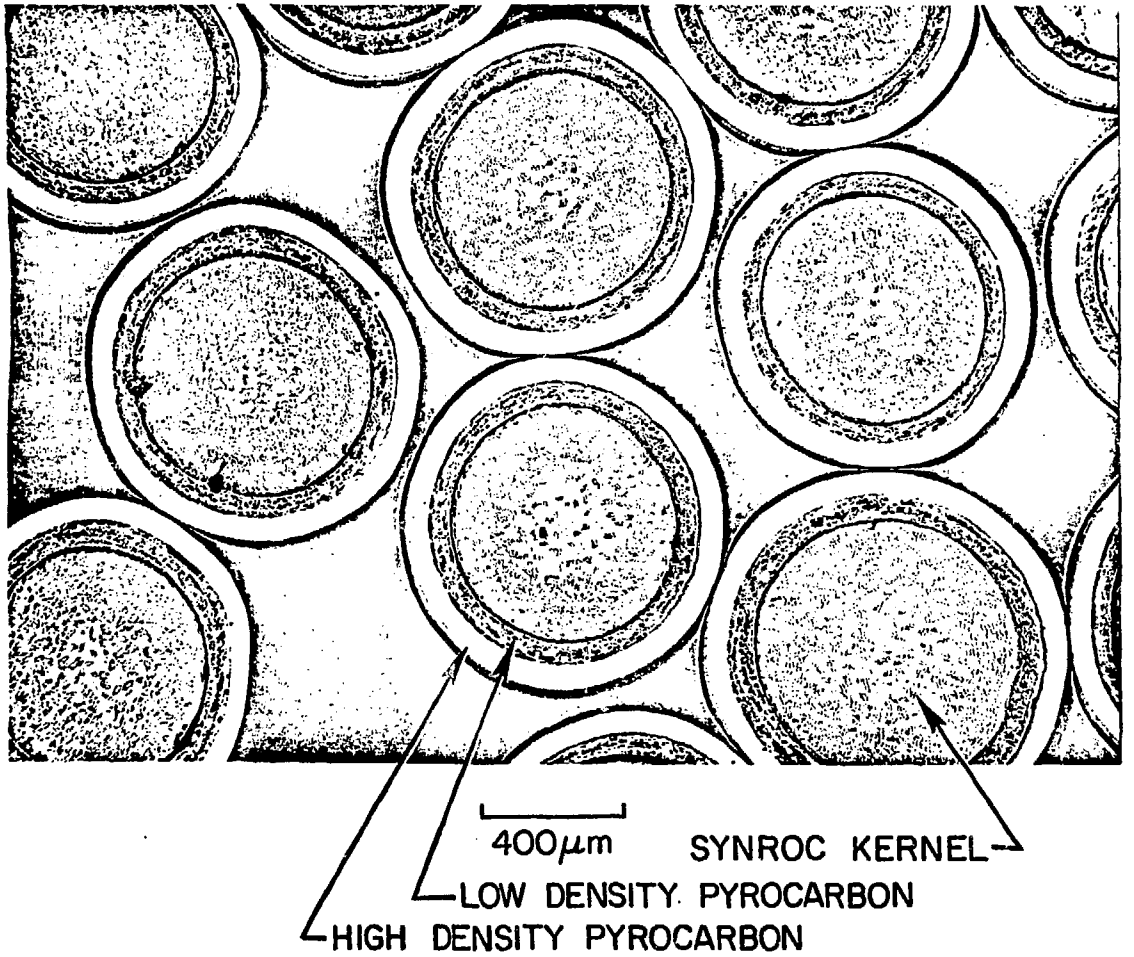

Fig. 3. Low-density coatings between the kernel and the dense outer coating prevent cracking of high-density coatings caused by thermal expansion mismatch.

DENSE PYROCARBON COATINGS EFFECTIVELY ISOLATE WASTE FORMS FROM THE ENVIRONMENT

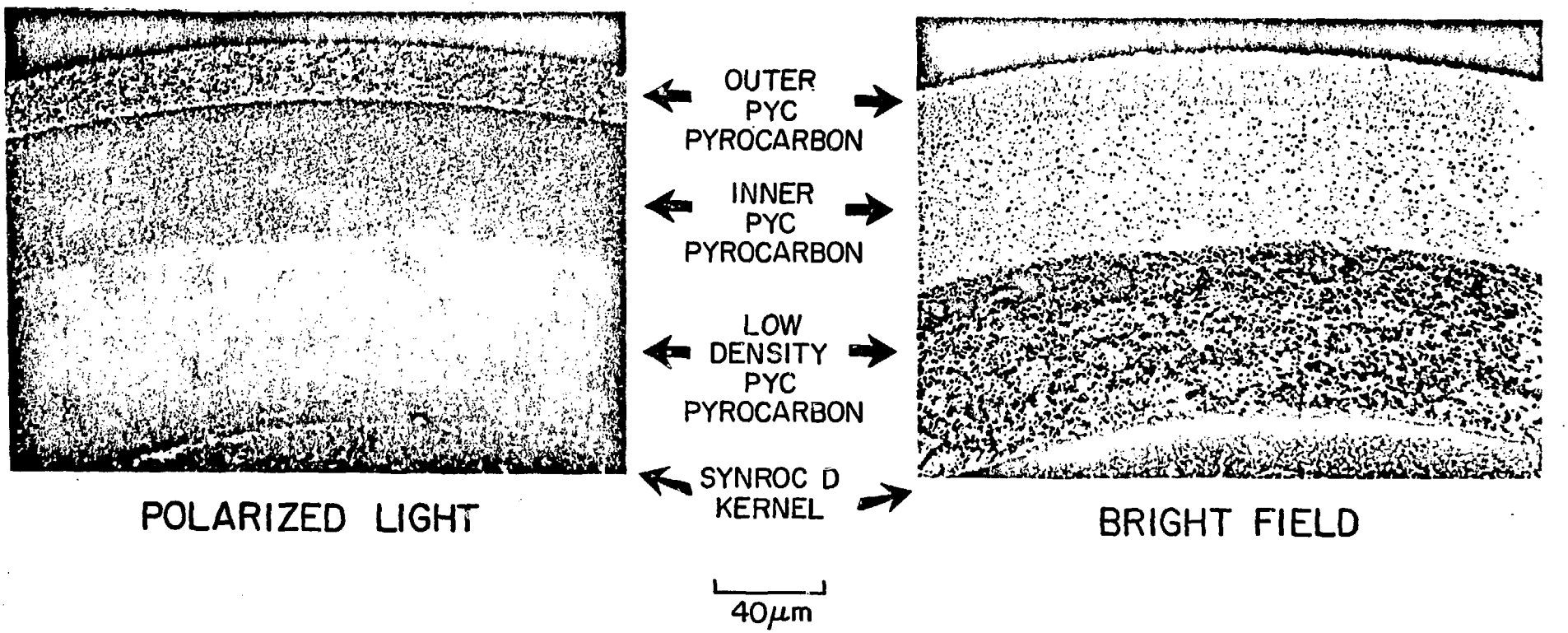

Fig. 4. Dense pyrocarbon coatings effectively isolate waste forms from the environment. The reduced porosity of the anisotropic outer coating makes it less permeable; however, the slow coating rate (0.2 μm/min) prevents the entire dense layer from being deposited in this fashion.

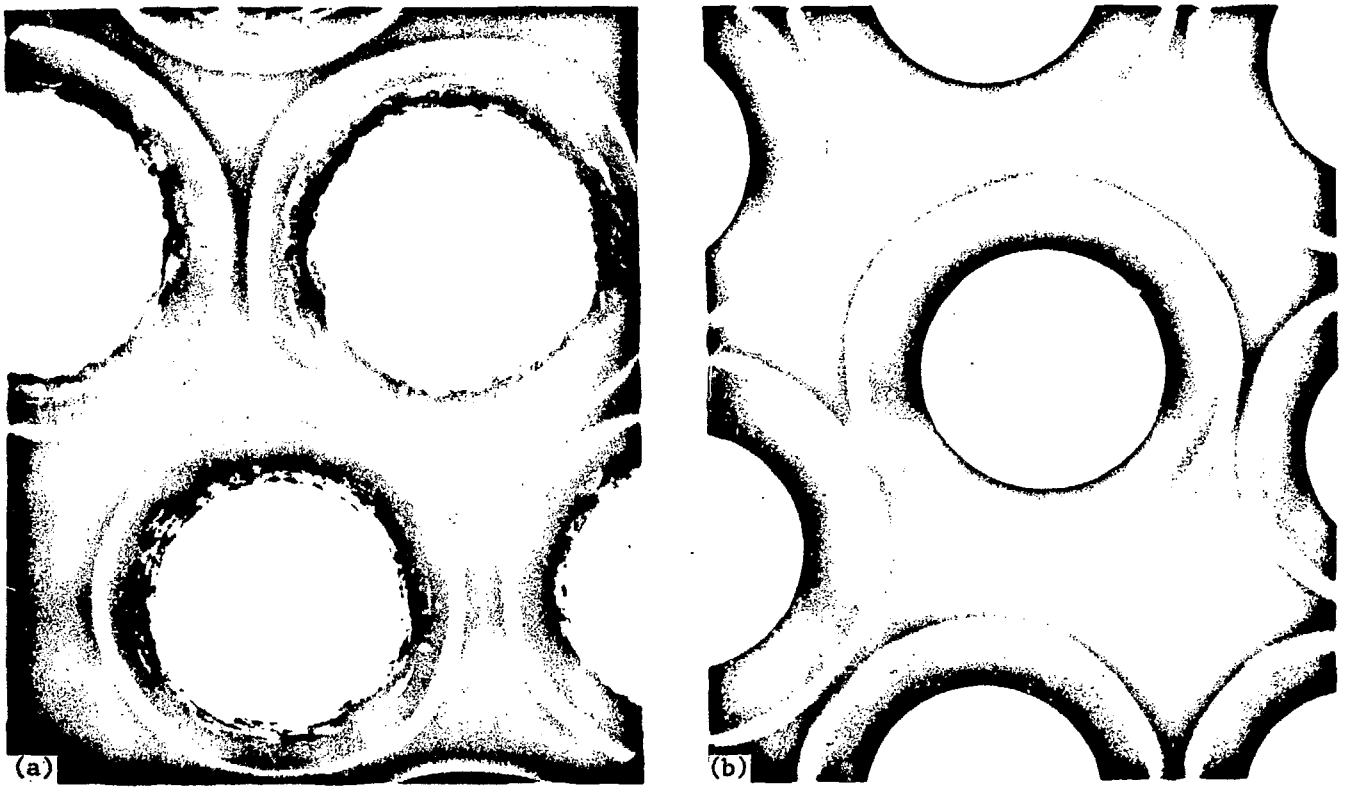

Fig. 5. Application of SiC coatings provides an additional barrier to leaching. (a) X-radiograph of particles coated by high-temperature (1400°C) process, indicating fission product interaction with low-density pyrocarbon layer. (b) X-radiograph of particles coated by low-temperature (900°C) process, indicating no interaction.

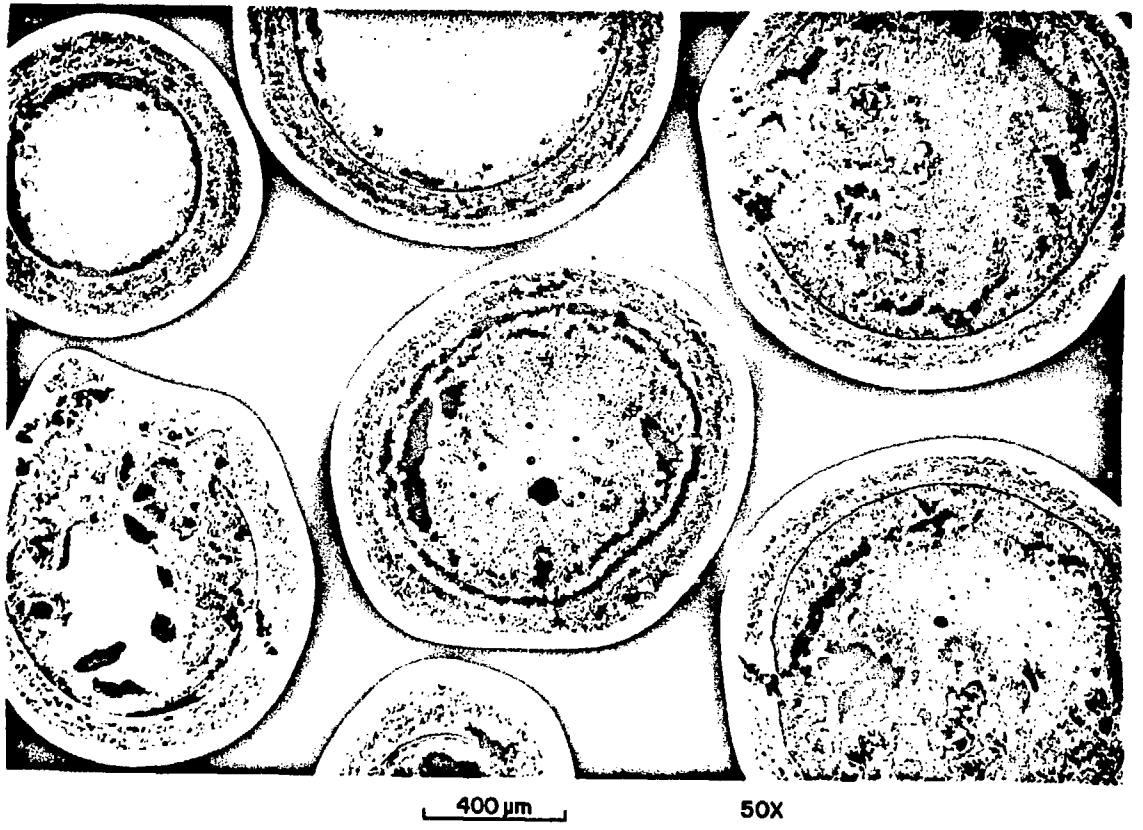

Fig. 6. Microspheres of very high waste loading (70-30) react with pyrocarbon while coating at 1000 to 1200°C.

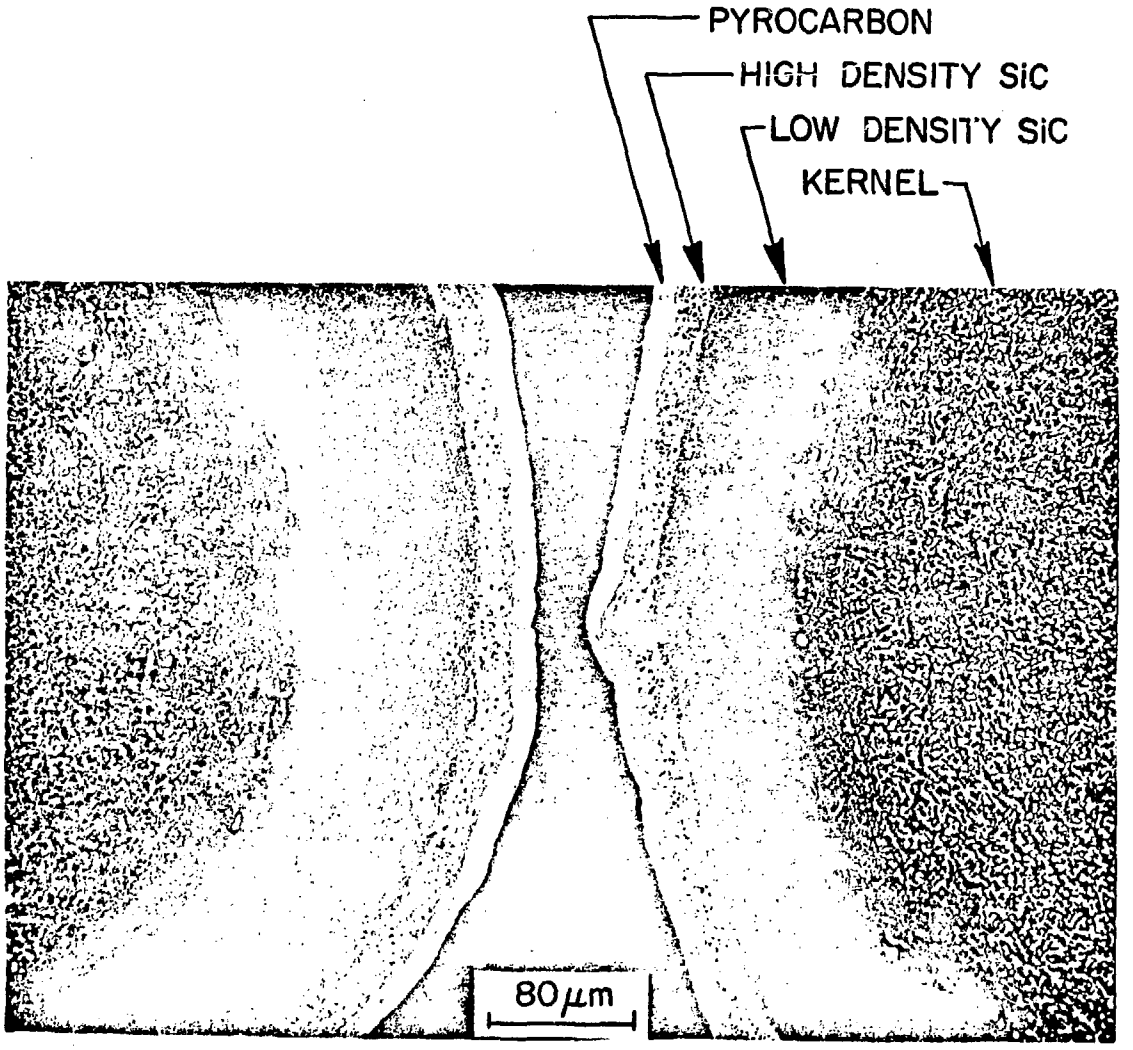

Fig. 7. Microspheres of the 90-10 composition are coated with successive layers of low-density SiC, high-density SiC, and dense pyrocarbon.

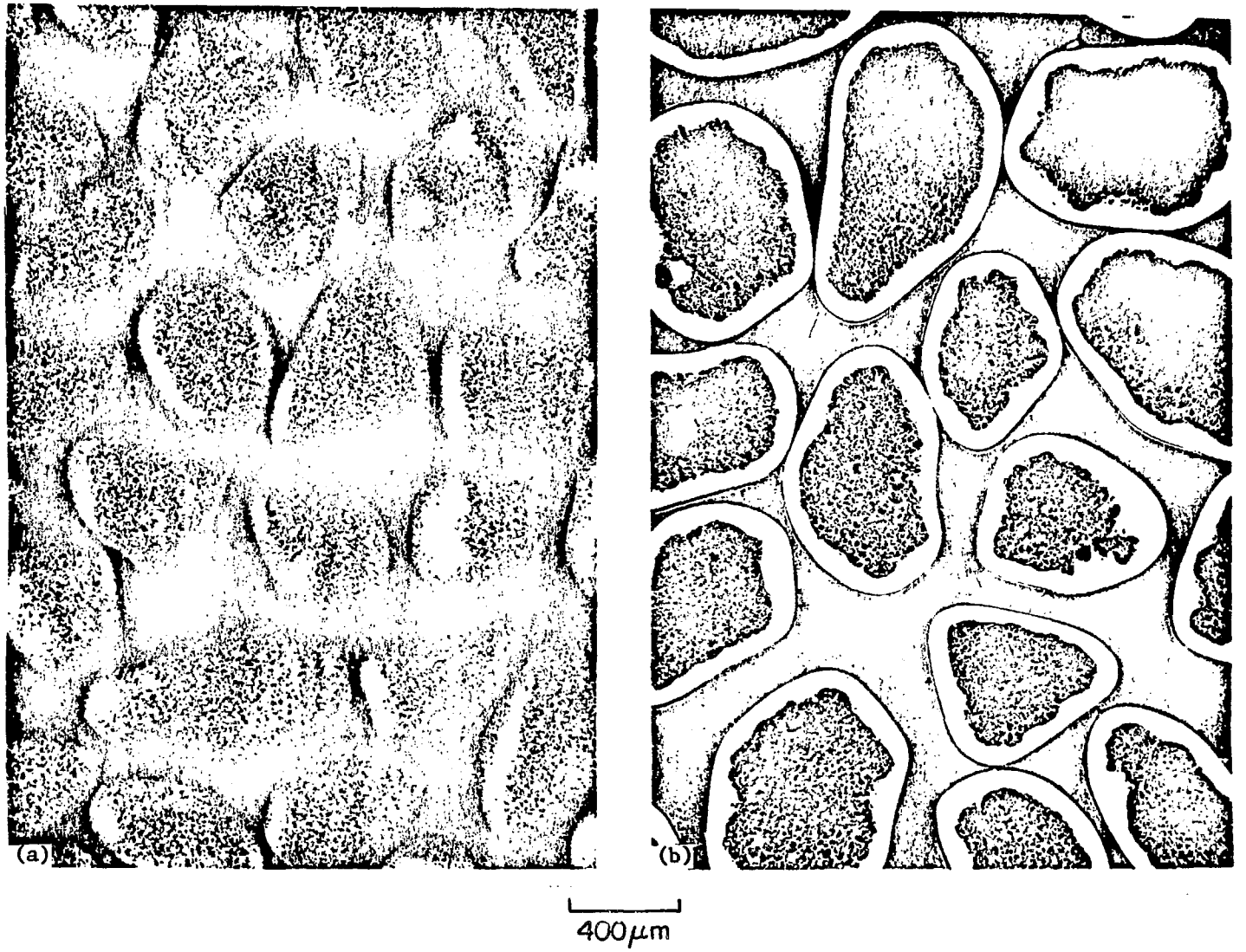

Fig. 8. A waste form was developed that retains cesium during sintering, coating, and leach testing. (a) Coated zeolite particles. (b) Polished section showing zeolite kernel and pyrocarbon coating.

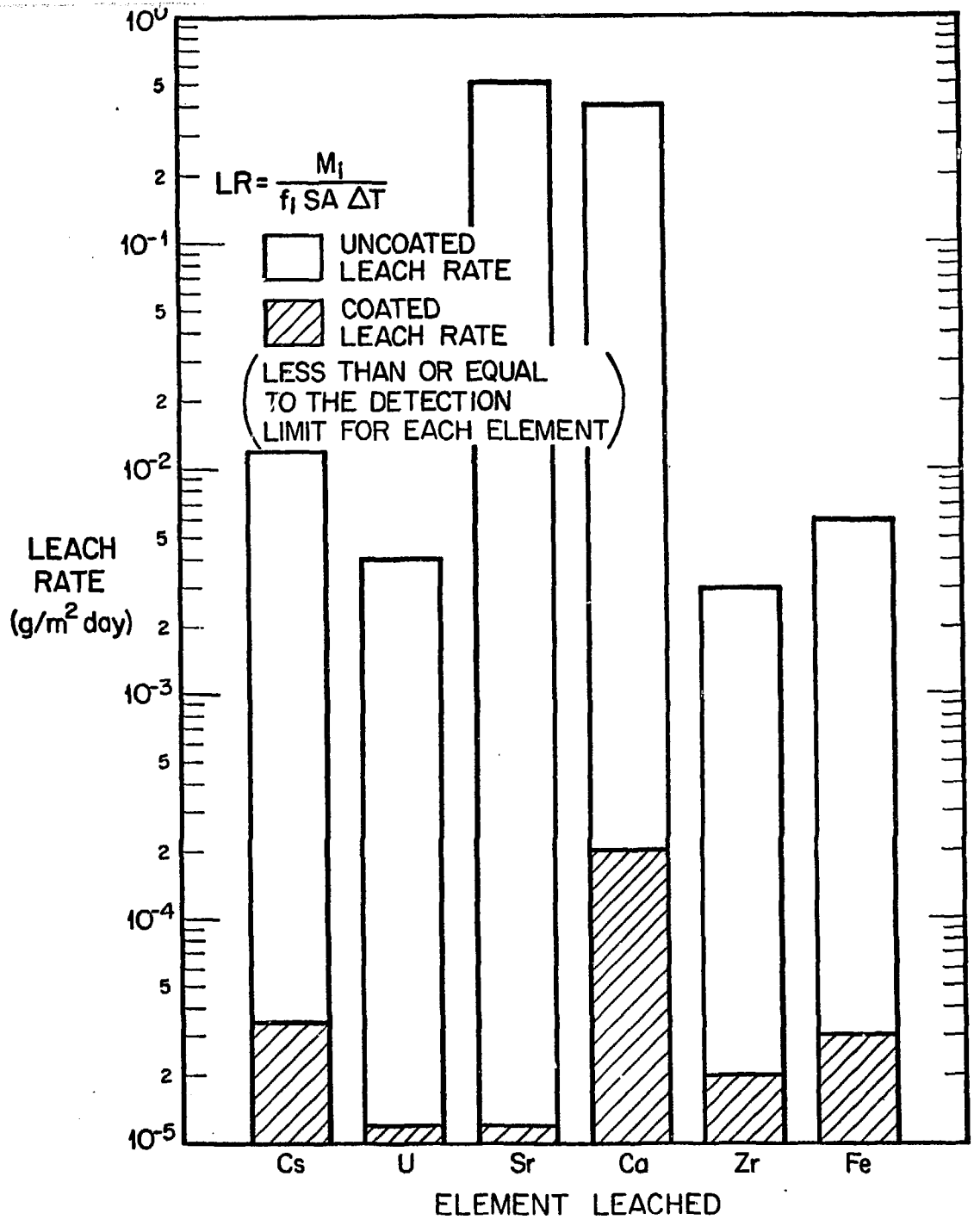

Fig. 9. Pyrocarbon coatings significantly reduce leachability. The cesium leach rate was obtained from cesium-loaded zeolite whereas the leach rates for other elements were obtained from Synroc-D. The leach rate of uncoated material is indicated by the bars with no crosshatching. The crosshatched area of the bar represents the leach rate after coating.