DEVELOPMENT OF INERT-MATRIX CARRIER FUELS FOR BURNING PLUTONIUM OR ACTINIDE WASTE

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ABSTRACT

CANDU[1] reactors are well-suited to utilize carrier fuels to burn excess Pu or actinide waste, because of their excellent neutron economy and fuel-management capabilities. The selection process for determining a good candidate(s) for the carrier matrix is in its early stages. SiC appears to be an excellent choice, because of its high thermal conductivity and resistance to oxidation and interaction with water coolant even at high temperatures, as well as its lack of neutron absorption. Resistance to fission-fragment damage and other issues relevant to its use as a fuel for CANDU reactors are being investigated.

INTRODUCTION

Two new and interesting challenges face the nuclear community. One is the disposition of Pu freed by the dismantling of nuclear weapons in the United States and Russia; the other is the interest in countries that reprocess fuel to reduce the amount of toxic actinide waste, particularly the transuranic actinides such as ^{237}Np, ^{241}Am and ^{244}Cm. Among the many options considered for these challenges is to incorporate Pu or the transuranic actinides in an *inert-matrix carrier fuel* for burning in thermal or fast reactors. CANDU reactors offer particular advantages in this regard. The development of this carrier fuel is the subject of this paper.

REASONS FOR DEVELOPING INERT-MATRIX CARRIER FUEL

Plutonium Burning

The main option for burning the world's reserves of military plutonium is via the use of MOX (Mixed Oxide) fuel. AECL has contributed to a US Department of Energy study of options for this purpose [1]. Current CANDU reactors at Bruce A could be used with full-core loading of MOX fuel. However, another option would be to develop a non-UO_2-based fuel, as described above; this would also eliminate *production* of plutonium via neutron absorption in ^{238}U, which occurs in UO_2-based fuels, including MOX. The advantage would be more efficient and complete destruction of plutonium. The disadvantage is that a long program would be required to develop the fuel satisfactorily, whereas MOX fuel needs little, if any, development work.

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[1] CANDU: Canada Deuterium Uranium is a registered trademark

While annihilation of military plutonium has been emphasized here, the technique could also be used for disposing of *reactor-grade* plutonium. Given the expected large production of plutonium over the next few decades from standard reactor operation, and the time lag of at least a decade to develop a carrier material, this may prove to be the more realistic application of a Pu-burning fuel, and is the rationale for U.S. efforts to develop an inert-matrix carrier fuel.

Actinide-Waste Burning

Normal use of current reactors produces carcinogenic, long-lived actinides, especially ^{241}Am, ^{237}Np and ^{244}Cm, and reprocessing increases their concentrations. A European multinational program called EFTTRA (Experimental Feasibility of Targets for Transmutation) is working to develop methods to separate the actinides and to develop acceptable carrier materials to combine with the actinides for use as a reactor fuel. The use of both light-water reactors (LWR's) and fast reactors (FR's) is being considered. However, CANDU offers an attractive alternative.

The use of accelerators to transmute the actinides to less-toxic elements is also being investigated. Finally, the option of using ThO_2-based fuels to eliminate the production of the unwanted actinides must be carefully considered. Thorium, with its low atomic mass of 232, will not absorb a sufficient number of neutrons, in-reactor, to produce the high-mass actinides mentioned above.

Use of Inert-Matrix Fuels in CANDU Reactors

CANDU is well suited for the use of carrier fuels to annihilate plutonium or actinide waste, because it is neutron economic and because on-line refueling and the capability for fuel-bundle management in the core permits more fuel-management options than are allowed in LWR's. Reference 2 on Pu-annihilation states:

> Pu annihilation rates can be maximized by progressively shifting the fuels into higher neutron-flux regions as the fissile content of the fuel decreases. Fissile content drops by 90% in a single pass through a CANDU fuel channel. A second pass of the fuel is needed to reduce the fissile content of the discharged fuel to negligible levels. (Almost) complete annihilation of the fissile inventory is, therefore, achievable without having to reprocess and refabricate the discharged fuel.

In natural-uranium fuel, ^{238}U is the main non-fissile absorber of neutrons, the others being other heavy elements, fission products, non-fuel components of the lattice and leakage from the reactor. The absence of ^{238}U in inert-matrix fuels has two important consequences [2], the first being positive and the second negative:

1. The absence of the main absorber, ^{238}U, means that the neutron economy is greatly increased. This in turn means that the fissile content required in the fuel is greatly reduced, and that the neutron flux levels need to be much higher to maintain power levels equivalent

to the natural-uranium CANDU reactors. The lower initial fissile concentration means that the Pu can be burned to very low levels.

2. The lack of ^{239}Pu production (due to the lack of ^{238}U) means that the fissile content of the fuel decreases rapidly with burnup. This means that the refueling rate must be significantly increased. Ref. 2 indicates that the refueling rate is kept within the capability of the CANDU fuel-handling system by increasing the fissile content of the bundles. This, however, means that reactivity suppression is required and thus the Pu content in the discharged fuel is raised. The maximum allowable refueling rate therefore limits the extent of Pu annihilation in the discharged fuel.

PROPERTIES REQUIRED FOR A CARRIER MATERIAL

Neutronics: All elements in the carrier material must have low neutron absorption.

Melting Temperature: A high melting temperature is required so that fuel operating temperatures are below approximately 0.5 of the melting temperature (kelvin). This ensures that thermally activated processes, such as fission-gas diffusion, are acceptably slow. A high melting temperature also ensures that there is an acceptable safety margin between the fuel operating temperature and melting temperature, to accommodate potential off-normal excursions.

Compatibility with Coolant and Clad: Chemical compatibility with water at coolant temperatures is a requirement. Compatibility with the clad is also required, to high temperatures (~1500°C) for acceptable behaviour in accident scenarios. However, the clad need not be a zirconium alloy.

Phase Stability: Phase transformations, including vitrification (amorphization) as the fuel temperature cycles up and down, are unacceptable if there is a volume change associated with the transformation, or if the material loses structural integrity.

Thermal Conductivity: High thermal conductivity is advantageous, since this reduces the fuel operating temperature (for a given element power rating), and, therefore, provides increased safety margins in accident scenarios. The extra advantage of high thermal conductivity is an advantage that helps justify the time and expense of developing a new fuel.

Acceptable Microstructure with Pu: The plutonium should either be incorporated as a solid solution in the matrix, or as a well-dispersed distribution of fine particles. For example, MOX fuel, with a distribution of fine particles of PuO_2 in UO_2, is quite acceptable. Only 5-7 μm surrounding each Pu-containing particle is affected by fission-fragment damage. This eliminates the need for a matrix material that can withstand fission-fragment damage. The matrix material acts like a protective barrier around the Pu, and contains any fission gases that are released by the fuel particles. However, if the Pu is dispersed as a solid solution, and the matrix can withstand the fission-fragment damage, the fuel is more like standard UO_2 fuel, and should have excellent performance. Consequently, this property is advantageous, but probably not essential.

Irradiation Properties: Good irradiation properties would be required, and demonstrated by extensive in-reactor testing.

CANDIDATES

A list of candidate inert-matrix carrier materials includes ZrO_2, BeO, CeO_2, $MgAl_2O_4$, SiC and $ZrSiO_4$.

Other potential candidates are Al_2O_3 and silicide dispersion fuels. Alumina (Al_2O_3) has been rejected, because it has long been known to become amorphous, with a volume change of 30% when used as a fuel. Silicide dispersion fuels have been rejected for safety considerations because the Al matrix of the dispersion fuels has too low a melting temperature, about 600°C.

PROPERTIES OF THE CANDIDATE MATERIALS

Melting temperatures, thermal conductivities, and heat capacities of the candidate materials are listed in Table 1. They are described below.

Zirconia has a high melting temperature and good neutronic properties (absorption cross section of 0.184 barns for thermal neutrons), as long as hafnium, a persistent impurity, is carefully removed. Commercial-grade Zr contains 1-3% Hf, but nuclear-grade Zr is essentially pure (~50 ppm Hf). It is insoluble in water, and is compatible with Zircaloy sheath. However, the thermal conductivity of ZrO_2 is even lower than that of UO_2.

Phase stability is another potential issue. Zirconia undergoes a phase transformation with a large associated volume change at 900-1000°C (monoclinic to tetragonal). This phase transformation causes cracking and would eventually disintegrate the fuel, after repeated temperature cycling through the phase-transition temperature. However, additions of yttrium, calcium, magnesium or possibly other materials will stabilize the high-temperature cubic phase of zirconia. (This cubic phase is the fluorite structure, the same as UO_2, PuO_2, and ThO_2.) Approximately 8 at.% of the additive is required for full stabilization, but smaller amounts provide partial stabilization. The fracture toughness that this stabilization provides makes this material a well-studied material in the general ceramics field. Thus, zirconia's poor thermal conductivity is its most serious drawback. The fuel would have to run at lower powers than urania. Other, more acceptable, candidates are sought.

BeO has a very high thermal conductivity, and a high melting temperature. The conductivity does decrease rapidly with temperature, but is still high at 1000°C. It has a very low neutronic absorption cross section (0.008 barns for thermal neutrons), and is a neutron moderator. It does not undergo phase transitions (hexagonal at all temperatures). A potential drawback is its toxicity. This hazard is highest when using powders, as fabrication would probably require. However, since Pu is toxic already, the extra toxicity of BeO should be acceptable. It is not known whether the material would form a solid solution with Pu. The toxicity of BeO would make laboratory testing more difficult.

Spinel ($MgAl_2O_4$) has been suggested by the Europeans. EFTTRA is strongly considering $MgAl_2O_4$ for both LWR's and FR's, and irradiations are underway in PHENIX FR. The melting point is sufficiently high, 2135°C. However, its thermal conductivity is only marginally higher than that for UO_2.

Cerium oxide (CeO_2) is considered, because its crystal structure is identical to UO_2. Since UO_2 has good properties (except for thermal conductivity), and, especially, good irradiation performance, it is thought that this material could have similar good properties. Its thermal conductivity is about 10.9 W/m·K at 100°C, slightly higher than that for UO_2, and its melting temperature is very high, 2600°C. Because of its close similarity with UO_2, CeO_2 is a promising candidate.

Silicon carbide (SiC) is a material with a considerable base of industrial use, and a large data base on properties, especially compared to the above-noted candidates. SiC has a very high thermal conductivity and a high melting temperature. Both elements, Si and C, are low neutron absorbers, and C will also act as a neutron moderator. Fabrication methods have been developed for industrial application, although these may require modification to incorporate Pu.

IRRADIATION EXPERIENCE

The only program to test carrier materials in-reactor, with a fissile component, was a Bettis program [3-5] in the early 1960's, to select a material for a full-core loading of the Shippingport test reactor. Bettis tested Al_2O_3, ZrO_2, ZrO_2+CaO, BeO and $ZrSiO_4$, all containing large amounts of UO_2 (>20 wt.%). Only ZrO_2 behaved satisfactorily: Al_2O_3 became amorphous after only a very short-time in-reactor; BeO exhibited high swelling (from fission-gas bubble formation) and the BeO matrix material "suffered considerable fission-fragment damage". The authors of the Bettis reports suggest that it was the cubic crystal structure of ZrO_2, presumably stabilized by the large UO_2 addition, which provided its resistance to damage. This was supported, for example, by the results on the candidate material ZrO_2+CaO+UO_2, which existed as a two-phase material: one phase cubic and one non-cubic. The cubic phase showed resistance to damage, whereas the non-cubic phase did not. Al_2O_3, BeO, and $ZrSiO_4$ are all non-cubic, and did not test well. However, CeO_2, $MgAl_2O_4$, and SiC, candidates described above but not tested by Bettis, all form cubic crystal structures. Therefore, there is reason to expect that one or more of those candidates will be acceptable as a carrier material for Pu in CANDU.

The Bettis results show that ZrO_2 might make a good carrier material. However, it is the least desirable of the suggested candidates, from a thermal conductivity consideration. Therefore, a program of developing a carrier material for Pu in CANDU has begun, focusing first on the candidates CeO_2, $MgAl_2O_4$, $ZrSiO_4$, and SiC.

It must be kept in mind that the Bettis tests utilized large amounts of UO_2, with a high content of fissile U. The application considered here would use only a small amount of fissile component, and this component could be in the form of finely dispersed particles in the matrix. Therefore, most of the matrix of the candidate material would not experience fission-fragment damage. Therefore, candidates not deemed feasible by the Bettis tests may still be suitable for this application.

AECL TEST PROGRAM

Accelerators can be used to help in the initial screening of candidate materials, as described below. This must be followed by a substantial in-reactor irradiation program (*with* dissolved fissile material, although not necessarily Pu initially). Simultaneously, an out-reactor properties-determination program must be undertaken, to establish that there are no other deleterious properties of the candidate material, such as reaction with water or the selected clad material.

Accelerator Testing

Promising candidates are being tested by subjecting them to a 72 MeV beam of iodine ions, to cause damage similar to fission-fragment damage in-reactor. Iodine is a typical fission fragment, and 72 MeV is a typical fission-fragment energy. The aim is to determine whether swelling would be expected in-reactor. This work is ongoing, and results presented here are preliminary. To date, silicon carbide, spinel ($MgAl_2O_4$), cerium oxide, zircon ($ZrSiO_4$), alumina and uranium oxide (for benchmark purposes) samples have been tested, from ambient temperature to 1200°C.

The samples were analyzed using a number of techniques to investigate swelling, but laser profilometry of the surface proved to be the most effective. The samples of UO_2 and SiC were not sufficiently flat initially for high-accuracy laser profilometry, and these materials will be re-tested, but initial results are still informative. As expected for the alumina specimen, swelling was apparent (Fig. 1). Also, as expected, no swelling was observed in the UO_2 specimens (Fig. 2). These two results lend confidence to the methods. SiC showed no swelling at 300°C and 900°C (Figs. 3-4). Of the other samples tested, spinel ($MgAl_2O_4$) showed evidence of swelling at ambient temperature (Fig. 5). Most candidates showed decreasing swelling (height at the beam spot) with temperature. Since this work is ongoing, further evaluation will be performed when the work is complete.

Compatibility With Coolant

To assess the behaviour of SiC with CANDU coolant under failed fuel-sheath conditions, an 880 mg sample was placed in water in an autoclave at 300°C and a pH of 10.3. After three months, there was almost no interaction. Figure 6 shows weight changes for that time. X-ray photospectroscopy (XPS) showed that the thin scale that eventually builds up on the SiC is an oxide, with contamination of Pb and Cu from the autoclave itself. The weight loss (12 mg in a sample of 880 mg) is due to flaking of the oxide layer.

Other Tests

Samples of SiC have been fabricated with various amounts of Ce, a standard substitute for Pu. The intent is to determine what microstructures can be made. No analyses have yet been performed. Will Ce (Pu) form a solid solution in the SiC, or will it form particles in the SiC, and if the latter, how finely dispersed can the particles be made? (A solid solution would resemble standard CANDU or LWR UO_2 fuels; finely dispersed particles would resemble MOX fuel, which has shown good performance to high burnup.) Also planned are laboratory tests on SiC for compatibility to Zr-based sheath materials to 1500°C, to determine behaviour in accident scenarios.

After determining suitable fabrication methods, fuel rods could be made in the Recycle Fuel Fabrication Laboratory of Chalk River Laboratories [6], for testing in the National Research Universal (NRU) reactor. The tests would span the expected operating range of fuel-power densities and temperatures in CANDU reactors. Multi-bundle tests in a CANDU reactor would be required, finally, before partial-core or full-core loading.

CONCLUSIONS

CANDU reactors are well-suited to utilize carrier fuels to burn excess Pu or actinide waste, because of their excellent neutron economy and fuel-management capabilities. The selection process for determining suitable candidate(s) for the carrier matrix is in its early stages. SiC appears to be an excellent choice, because of its high thermal conductivity and resistance to oxidation and interaction with water coolant even at high temperatures, as well as its lack of neutron absorption. Resistance to fission-fragment damage and other issues relevant to its use as a fuel for CANDU reactors are being investigated.

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REFERENCES

1. BOCZAR, P.G., HOPKINS, J.R., FEINROTH, H. and LUXAT, J.C., "Plutonium Dispositioning in CANDU", presented at the IAEA Technical Committee Meeting on Recycling of Plutonium and Uranium in Water Reactor Fuels, Windermere, UK, 1995 July 3-7, proceedings to be published by the IAEA.
2. MENELEY, D.A., DASTUR, A.R., VERRALL, R.A., LUCUTA, P.G. and ANDREWS, H.R., "Annihilation of Plutonium in CANDU Reactors", presented at the IAEA Technical Committee Meeting on Unconventional Options for Plutonium Disposition, Obninsk, Russia, 1994 November 7-11, proceedings to be published by IAEA.
3. RUBIN, B.F., BERMAN, R.M. and BLEIBERG, M.L., "The Irradiation Behavior of ZrO_2-UO_2 Fuels", WAPD-264, 1962 October.

4. RUBIN, B.F., BERMAN, R.M. and BLEIBERG, M.L., "Fission Fragment Damage to Crystal Structures", J. Nucl. Mater. **2**, (1960) 129.
5. YENISCAVICH, W. and BLEIBERG, M.L., "The Effects of Irradiation on BeO+UO_2 in Bettis Technical Review, Reactor Technology", WAPD-BT-20, pp1-22, 1960.
6. DIMAYUGA, F.C., "MOX Fuel Fabrication at AECL", elsewhere in these proceedings.

TABLE 1. MELTING TEMPERATURES AND THERMAL CONDUCTIVITIES OF CANDIDATE CARRIER MATERIALS

MATERIAL	Melting Temperature (°C)	Thermal Conductivity (W/m·K)		Heat Capacity	
		100°C	1000°C	(J/cm^3·K)	(J/g·K)
ZrO_2	2715	1.9	2.3	2.55	0.46
BeO	2530	220.	20.	3.07	1.02
$MgAl_2O_4$	2135	10.7			
CeO_2	2600	10.9		2.55	0.36
SiC	2700	85.		2.15	0.67
UO_2	2878	8.75	3.21	2.58	0.24
$ZrSiO_4$	2550	4.2		2.81	0.61

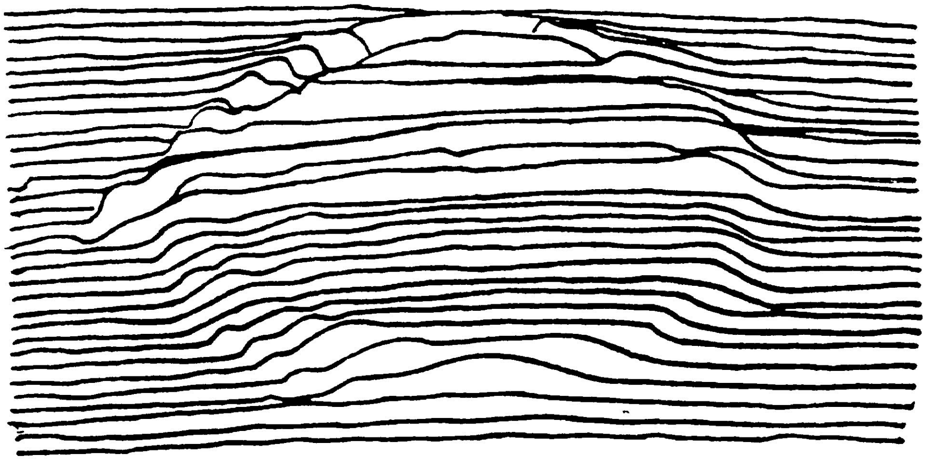
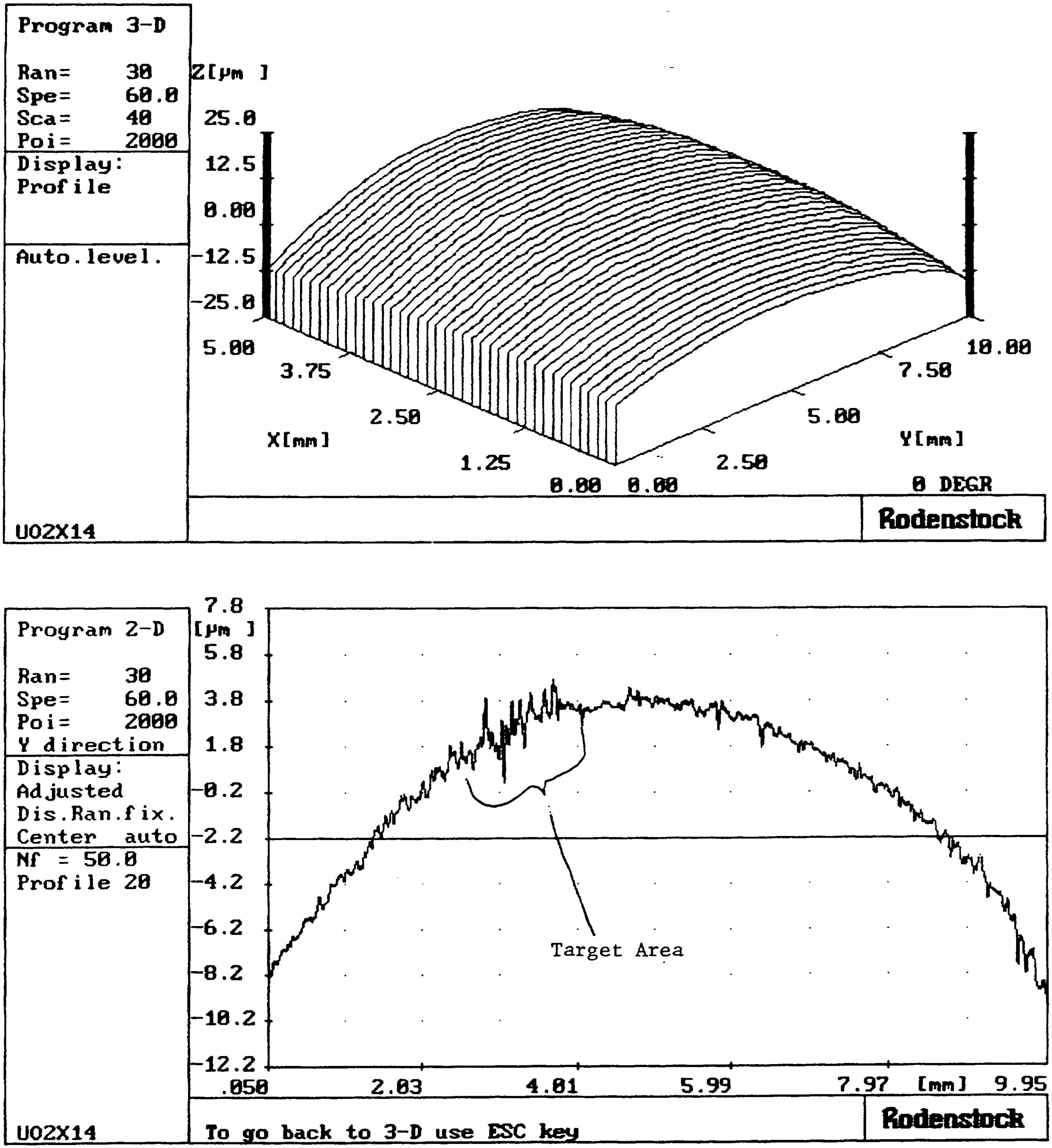


Figure 1 Contact profilometry of a surface of Al_2O_3, bombarded with iodine (beam-spot diameter = 0.27 mm) to a dose of 1 x 10^{17} ions/cm^2. Surface relief of approximately 1.6 µm has occurred. Al_2O_3 is well-known to swell in-reactor, so this result, combined with that of Figure 2, provides confidence in the methods.



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Sca= 40
Poi= 2000
Display: Profile
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U02X14

Program 2-D
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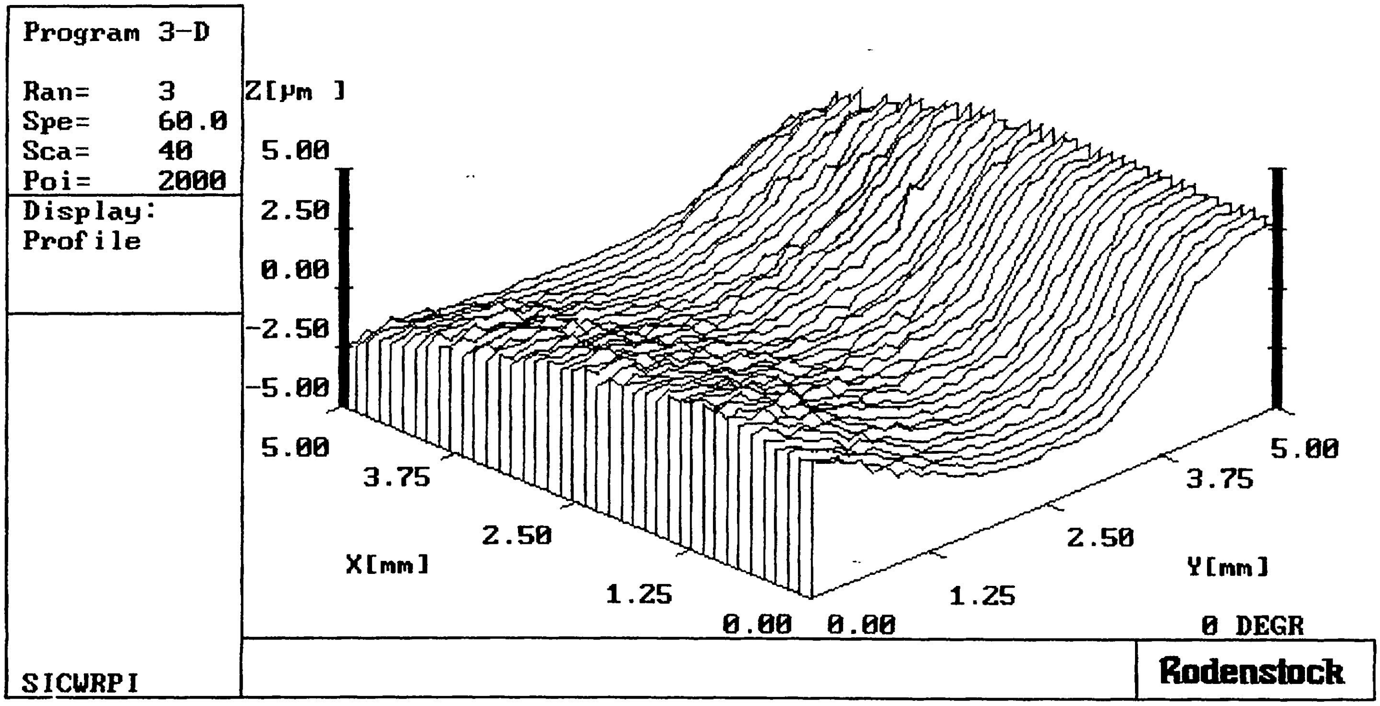
Poi= 2000
Y direction
Display: Adjusted
Dis.Ran.fix.
Center auto
Nf = 50.0
Profile 20
U02X14
To go back to 3-D use ESC key

FIGURE 2 Laser profilometry of the surface of a UO_2 sample bombarded by 72 MeV iodine to a dose of 1 x 10^{16} ions/cm^2 at ambient temperature. The lower portion of the figure shows a cross section of the profile in the y direction. Although the sample curvature limits the resolution of the profilometry, the lack of any surface relief where the beam entered the sample is a good indication that no swelling has occurred.



Program 3-D

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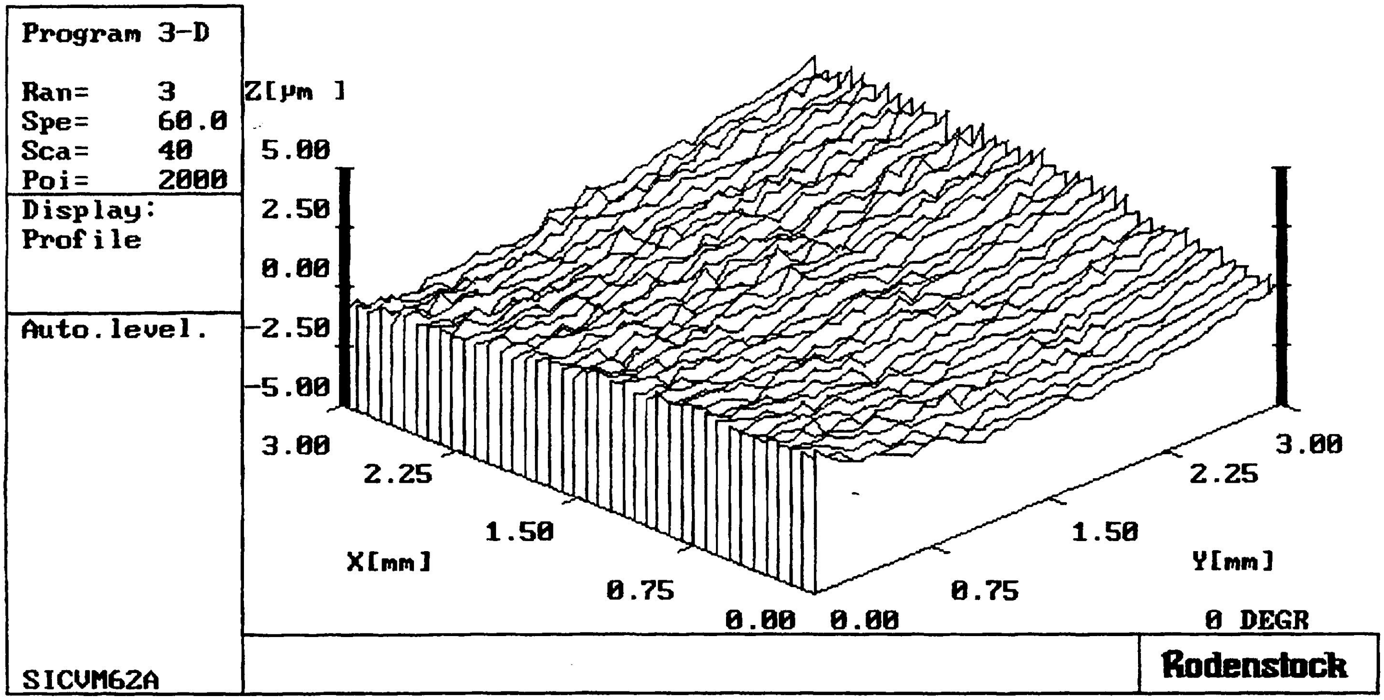
Sca= 40
Poi= 2000

Display:
Profile

SICWRPI

FIGURE 3 Laser profilometry of a SiC sample, bombarded with iodine at 300°C, to doses of 1 x 10^{17} and 1 x 10^{16} ions/cm^2. A third spot was used to assist in setup and beam configuration. Although the sample was not sufficiently flat for good resolution, no indication of swelling is seen.



Program 3-D

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SICVM62A

FIGURE 4 Similar to Figure 3; iodine bombardment performed at 900°C.

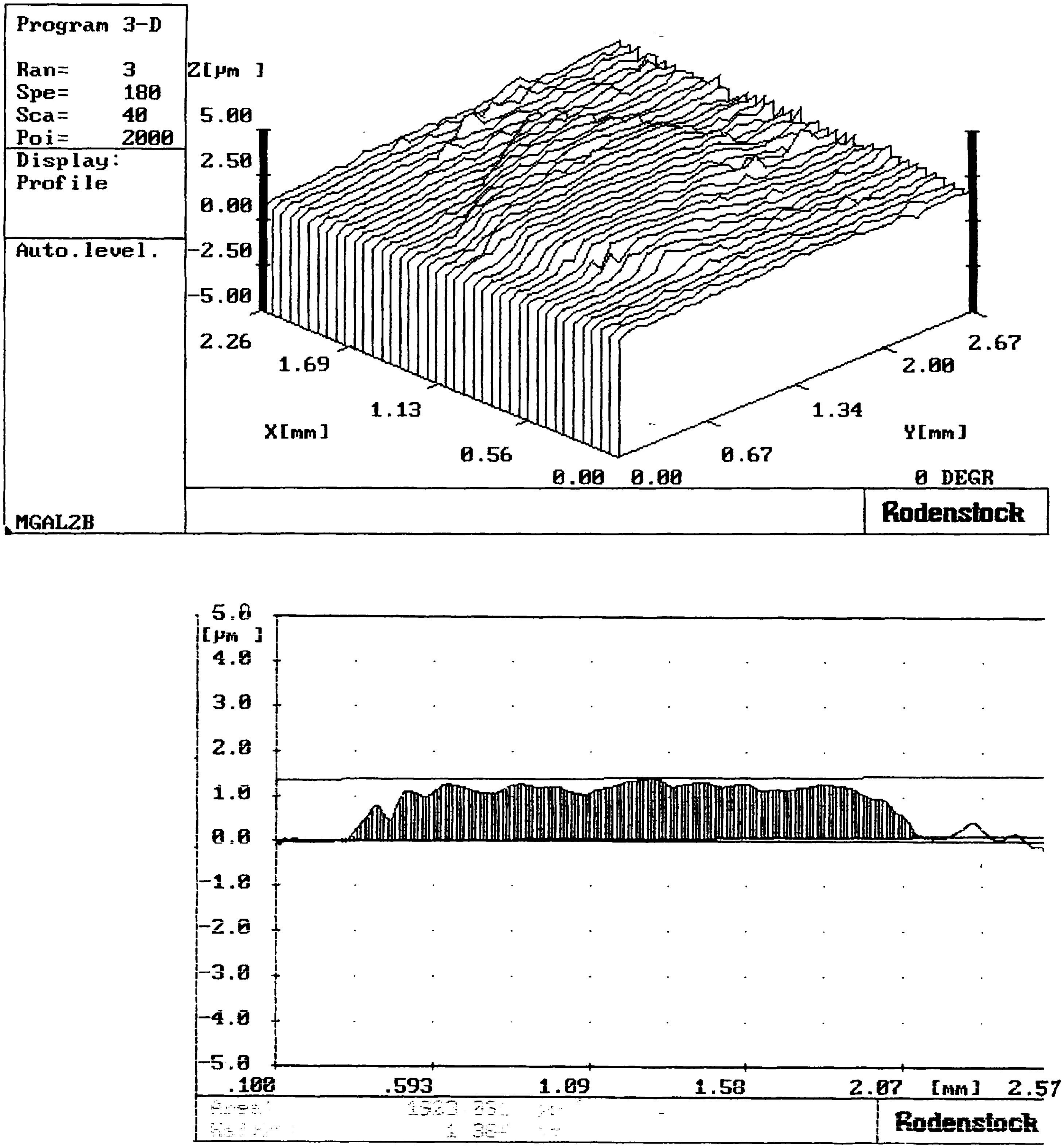

FIGURE 5 Laser profilometry of spinel ($MgAl_2O_4$) bombarded with iodine at 500°C to a dose of 1 x 10^{16} ions/cm^2. The lower portion of the figure shows a cross section in the y direction and indicates that the bomarded surface has risen about 1.4 μm.

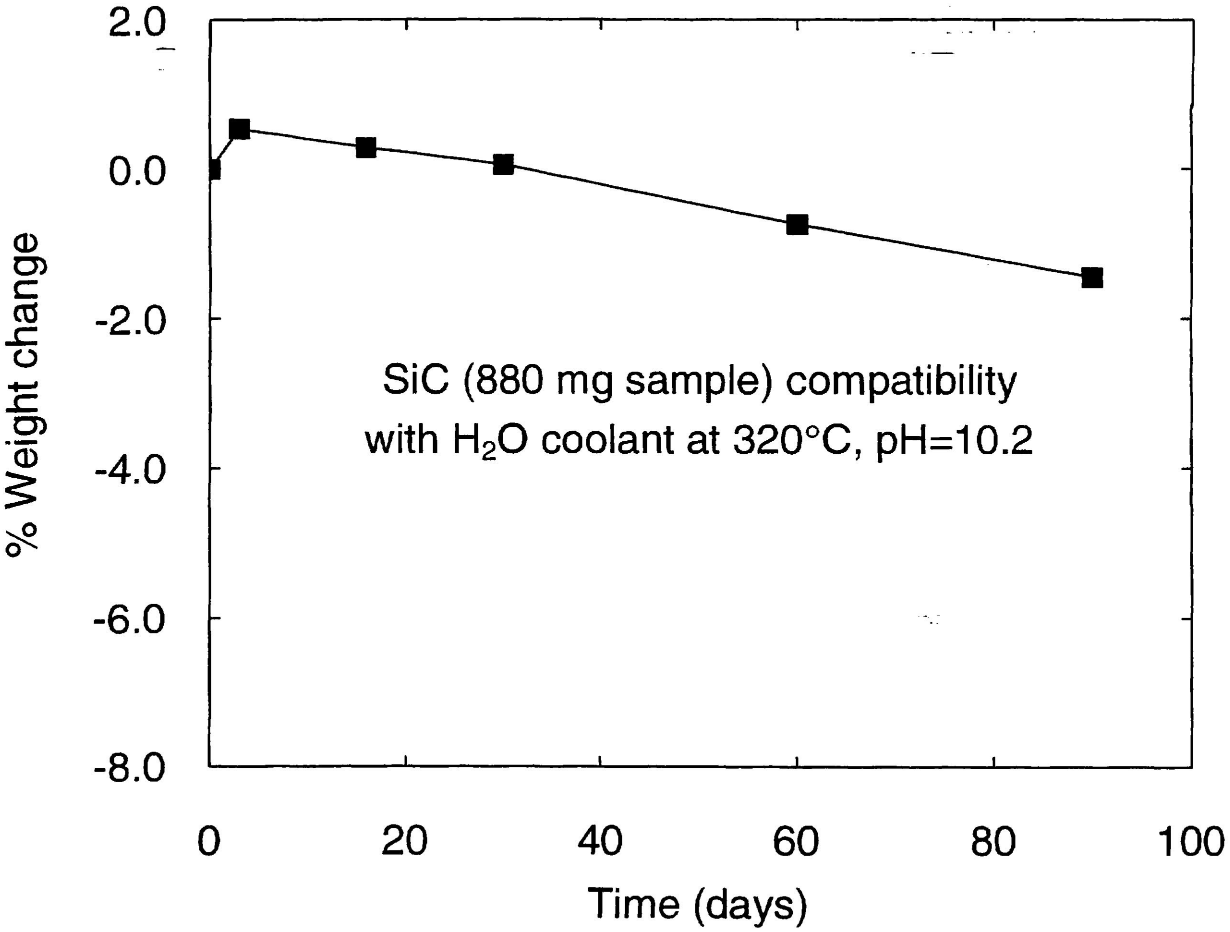

Figure 6. Weight changes (%) for an 880 mg sample in water for 90 days at CANDU coolant conditions (320°C, pH=10.2).