

CONF-820704--43

DE83 008463

Experimental Investigations of Long-Term Interactions
of Molten UO_2 with MgO and Concrete
at Argonne National Laboratory

R. P. Stein, R. Farhadieh, D. R. Pedersen
W. H. Gunther and R. T. Purviance

Argonne National Laboratory
Argonne, Illinois 60439, U.S.A.

ABSTRACT

Experimental work at Argonne is being performed to investigate the long-term molten-core-debris retention capability of the ex-vessel cavity following a postulated meltdown accident. The eventual objective of the work is to determine if normal structural material (concrete) or a specifically selected sacrificial material (MgO) located in the ex-vessel cavity region can effectively contain molten core debris. The materials under investigation at ANL are various types of concrete (limestone, basalt and magnetite) and commercially-available MgO brick. Results are presented of the status of real material experimental investigation at ANL into 1) molten UO_2 pool heat transfer, 2) long-term molten UO_2 penetration into concrete and 3) long-term molten UO_2 penetration into refractory substrates. The decay heating in the fuel has been simulated by direct electrical heating permitting the study of the long-term interaction.

INTRODUCTION

The successful evaluation of the core retention capability of MgO or concrete requires an appropriate combination of simulant material experiments, analytical modeling, real material experiments and code development. Simulant material experiments permit visual observation of relevant phenomena; and detailed measurements that can be used to guide analytical modeling. Simulant material experiments have been carried out to investigate downward heat transfer in melting miscible systems and in melting miscible gas-releasing systems. Experimental evaluation is currently underway to evaluate the effect of gas release on sideward heat transfer from a molten pool and downward heat transfer from a molten pool that forms a binary eutectic system with the substrate. The real material experiments are required because of the difficulty of achieving entirely prototypic simulant experiments. The goal of the real material experiments at ANL is to provide both qualitative observations and detailed measurements from well instrumented experiments with simulated decay heating that can be used to verify that codes consider all relevant phenomena and for comparison with code predictions. The eventual goal is the prediction of the core retention capability during accident investigations. To achieve this final goal requires the development of an analytical code, such as GROWS, for containment analysis.

The purpose of this paper is to summarize the results of recent real material experiments and future plans. The three major components of these experiments are:

MASTER

1. Directional molten pool heat transfer.
2. Molten UO_2 penetration into concrete (limestone, basalt and magnetite).
3. Molten UO_2 penetration into refractory materials.

Molten UO_2 Pool Heat Transfer

The available experimental data from heat generating molten UO_2 pools indicate that heat flows from these experiments can not be accounted for by thermal convection alone. For example, downward heat flows were found to be from 2.5 to 4.5 times larger than current thermal convection based correlations would allow. A computational model based on optically thick internal radiation, or its mathematical equivalent, thermal conduction, has been suggested as an alternate calculational method [1].

However, H. Vossebrecker of Interatom [2] has suggested that the measured heat fluxes are larger because of electrical heat generation in the crusts surrounding the pools of the experiments; he has performed calculations that supported this interpretation of the data. Stein [3], following Vossebrecker's suggestion, did an analysis of all of the data and concluded that heat generation in the crusts could not be significant unless the electrical conducting portions of the crusts were much thicker than actually observed in the experiments, but also noted that this conclusion depends on the relative electrical conductivities of liquid and solid UO_2 . In his calculations the conductivities of liquid and solid at the melting temperature were assumed to be equal whereas Vossebrecker's analysis implies that the liquid conductivity is nearly an order of magnitude less. Unfortunately, there does not appear to be data available for the electrical conductivity of liquid UO_2 that could assist in resolving these different bases for analysis. Accordingly, a special molten UO_2 pool heat transfer experiment was performed specifically for the purpose of testing the importance of electrical heat generation in the solid crusts surrounding the molten pool.

An understanding of the special heat transfer experiment, as well as of the MgO interaction experiments described later, requires familiarity with the general technique used; details can be found in reference [4]. As shown in Fig. 1 the apparatus consists of a rectangular shaped container or cell open at the top and fabricated from several metallic U-shaped pieces electrically insulated from each other by layers of zirconia paper. The other parallel vertical walls of the container are tungsten plates that serve as the electrodes for electrical current. The electrical current produces internal heat generation in the molten pool which is contained within frozen crusts of UO_2 adjacent to the water cooled surfaces.

The special molten- UO_2 pool heat-transfer experiment performed was a repeat of a previous one, but with the addition of a slab of high-temperature material separating the UO_2 from the cooled bottom of the experiment cell. As suggested by L. Baker, such an experiment could significantly reduce the crust thickness beneath the molten pool; and as a result, a difference in measured downward heat flux from that of the previous experiment would indicate the relative importance of heat generation in the UO_2 crust. The high-temperature material used was a 25-mm slab of MgO brick (Harklase) covering the entire bottom surface of the cell. The experiment repeated was experiment No. 13 of Table V.1 of reference [3]. Table 1 shows a comparison of the data from the two experiments. Proper comparison of the two experiments requires comparison of measured downward heat fluxes with values predicted assuming just convection within the pool. Calculated convection heat fluxes are also shown in the table. The measured heat fluxes are about four times larger than the calculated values.

Table 1. Experiment No. 13 vs. Recent Experiment
(Comparison of Data)

	Experiment No. 13	Recent Experiment
Solidified Pool Dimensions (cm)		
Depth	5.7	5.8
Between "U's"	18	12.5
Between Electrodes	20	20
Total Heat Generation, (kW)	13.5	13.4
Heat Flow from Cell (kW)		
Bottom	4.57	3.41
Top	2.86	3.24
Four Sides	6.04	6.77
Molten Pool Depth (cm)	7.5	7.6
Volumetric Heat Generation (W/cm ³)	5.0	7.1
Downward Heat Flux, Experiment (W/cm ²)	12.7	13.6
Predicted Downward Heat Flux Convection Model (W/cm ²)	2.7	3.3

The usual UO₂ crust at the bottom of the pool was essentially absent over about 75% of the downward heat-transfer area, but penetration into the MgO brick was less than about 0.5 mm. Thus, the special heat transfer experiment had significantly less frozen UO₂ crust beneath the molten pool than with the previous comparison experiment. Nevertheless, the downward heat transfer results were nearly equivalent for the two experiments, indicating that electrical heat generation in the crusts does not contribute significantly to the downward heat flux from the cell. There is, of course, the possibility of electrical heat generation in the MgO. However, the data available on the electrical conductivity of solid MgO [5] indicates that it is about a factor of 10 less than for solid UO₂ at comparable high temperatures.

Since it is unlikely that a single experiment of the type described above will be sufficient to settle the issue concerning the significance of electrical heat generation in the crusts, further research is desirable. Measurements of the electrical conductivity of molten UO₂ would be of immense value in this regard, but the feasibility of performing such measurements is uncertain and as a result have not received much attention to date. As mentioned later, there are plans to perform experiments in cells with much larger horizontal cross-sections than shown in Fig. 1. Molten UO₂ heat transfer experiments in these larger cells would be of value since the fraction of the area for electrical current flow through the crusts would be greatly reduced.

Downward Penetration of UO₂ into Limestone Concrete

To safeguard the environment against radiological releases, the major question of concern in PAHR safety assessment, following an HCDA, involves confinement and dilution of the molten core-debris. Significant to the study is the directional growth of the core-debris in the concrete foundation of the reactor building or the concrete below the reactor cavity. Concrete poses an excellent

core-debris confinement and dilution medium, since its molten phase is lighter than and miscible with the core-debris. Nevertheless, contact between the core-debris and concrete is accompanied by violent interaction and a considerable amount of gas release. This is expected to greatly affect the molten pool heat transfer and directional melting heat transfer into the bounding concrete surfaces. Accordingly, real material experiments are being conducted to investigate various phenomena associated with core-debris/concrete interaction.

The real material experiments were carried out in the test apparatus shown in Fig. 2. Casts of CRBR limestone concrete [6,7] were prepared in graphite cylinders, each having an internal diameter of 8.9 cm and a depth of 30.5 cm. The 17.8-cm-deep concrete samples were allowed to cure for at least 28 days. Embedded in each concrete sample were six thermocouples, 1.2 cm apart, located along the axis of concrete, with the first thermocouple being ~ .3 cm below the initial surface of the concrete. The graphite block and a tungsten rod placed in the center of the cylinder were connected to a 300-kW ac power supply. A displacement transducer was used to measure the radial expansion of the concrete in the plane of the No. 6 thermocouple.

The cavity above concrete was packed with 3 kg of pure UO_2 particles (1-3 mm). A uranothermic mixture was placed on the top of UO_2 powder. The top of the test section was sealed and the system was connected to a gas/aerosol sampling device. The test section was then entirely insulated to reduce radial heat losses as much as possible. The test section was isolated in a cave and all the experimental operations thereon were conducted remotely. Heating and possible melting of UO_2 was achieved resistively after the ignition of the thermite. Total experimental time was about 60 minutes, during which time a maximum electrical power input of 1.8 watts/gr was applied to the UO_2 .

Three non-condensable gas samples were taken at temperatures of 100, 600, and 950°C, measured in the plane of the #2 thermocouple. Selection of these temperatures were to study the amount and the type of gases released from different phases of concrete. Table 2 gives the chemical composition, percentage and flow rate of each composition in the sampled gases. Most of the H_2O was condensed out upstream of the non-condensable gas samples. As is evident, each sample contained H_2 , CH_4 , H_2O , N_2 , CO , O_2 , Ar , and CO_2 . Limestone concrete contains 43% by wt H_2O and CO_2 , which are released at elevated temperatures. H_2 results from H_2O dissociation. CH_4 and CO result from reaction of H_2 and CO_2 with very hot graphite. Furthermore, reaction of water vapor with graphite, dissociation of CO_2 , as well as reaction of UO_2 with calcite could contribute to a high volume percent of CO . N_2 and some of the O_2 could be the excess air left in the system and Ar is the purged gas. Volume % of different gases in each sample is dependent on the concrete temperature at the time the sample was taken. The type of chemical composition comprising any sample beyond 1200°C resembles the result of gas sample #3 until the experiment is terminated. The aerosol sampling device did not show any detectable UO_2 particles. The detectable aerosol particles were mostly C and very minute concrete constituents.

Radial expansion of concrete at the #6 thermocouple (6.1 cm below the original surface) reached a maximum of 0.087 cm about 5 minutes after the experiment was terminated. This maximum did not coincide with the maximum temperature at that level. In fact, concrete had contracted to 0.054 cm when the #6 thermocouple had reached a maximum temperature of 700°C. One can attribute the expansion and contraction of concrete to pore pressure resulting from migrating water. The penetration rate of UO_2 into concrete was about 0.23 cm/min. Posttest analysis of the test samples confirmed other findings of Farhadieh and Gunther [8], as to compound formation of UO_2 with CaO and uniform distribution of UO_2 and concrete constituents. Finally, the highly dehydrated concrete sample under the melt region had virtually no strength.

Table 2. Analyzed Sampled Gases and Their Respective Rates*

Samples	H ₂ % Vol. (cc/min)	CH ₄ % Vol. (cc/min)	H ₂ O % Vol. (cc/min)	CO % Vol. (cc/min)	CO ₂ % Vol. (cc/min)	N ₂ % Vol. (cc/min)	O ₂ % Vol. (cc/min)	Ar % Vol. (cc/min)
#1	82. (713.4)	.3 (2.61)	.5 (4.35)	3.9 (33.93)	3.1 (26.97)	1.7 (14.79)	.3 (2.61)	8.2 (71.34)
#2	26.5 (429.3)	.2 (3.24)	.6 (9.72)	28.1 (455.22)	21.9 (354.78)	7.9 (127.98)	2.0 (32.4)	12.8 (207.36)
#3	.4 (20.4)	< .02 (< 1.02)	.4 (20.4)	83.2 (4243.2)	.7 (35.7)	9.0 (45.9)	2.4 (122.4)	3.9 (198.9)

*Most all the water vapor was condensed out in a trap upstream of the gas samples.

Future plans call for larger scale experiments as well as tests with fission product migration and aerosol generation in the experiments will also be studied.

Molten UO₂-MgO Interactions

Magnesium oxide in the form of commercially available brick (e.g. Harklase, ~ 98% MgO) continues to be one of the favored sacrificial materials for use with core retention schemes. Preliminary experiments testing compatibility and general behavior of this material with likely core debris, including molten UO₂, were first reported by Meacham [9], Swanson et al. [10,11], and Powers et al. [12]. The first experiments of longer duration (~ 15 minutes contact time) and with heat generating molten UO₂ were performed by Stein et al. [13]. In general, these experiments showed that commercially available MgO brick in contact with molten UO₂ from fuel pellets behaved in a manner consistent with what was known about the interaction of the pure materials. In particular, MgO (melting point of ~ 2800°C) and UO₂ (melting point of ~ 2850°C) are miscible in the liquid state and form liquid solutions with a eutectic composition of about 50 mol % MgO in UO₂ (~ 13 wt %). The reported eutectic melting temperatures range from about 1800 to 2300°C, the higher temperatures occurring in oxygen-free surroundings. The experiments showed that magnesia is dissolved smoothly into molten UO₂ in this temperature range. There was no cracking of the magnesia. However, some UO₂ diffused into the solid magnesia ahead of the melting front.

Experiments following those mentioned above were performed by Sandia [14] and, more recently, by Atomics International [15] as well as Argonne National Laboratory. Unlike previous results, some of the Sandia experiments indicated the evolution of large amount of gas upon UO₂-MgO interaction. Also unlike previous experiments, an initial test at Atomics International resulted in the formation of small amounts of free magnesium. It is not currently known whether these unique findings of the recent Sandia and AI tests are results of the experimental technique rather than possible occurrences during interactions to be expected for a core retention scheme using commercial MgO brick.

As with previous experiments, the recent Argonne tests were performed for the purpose of causing heat-generating molten UO₂ penetration into refractory MgO brick (Harklase) under controlled conditions. Previous experiments of this type allowed for penetrations of about 1 cm and contact times were less than 30 minutes. The recent experiments were intended to obtain penetrations at least several times larger and for longer periods of time. The experimental technique was equivalent to that used for the molten pool heat transfer tests. However, the metallic U-shape members of the test cell were lengthened to accommodate a

33 cm stack of Harklase slabs beneath the molten UO_2 , and the lower surface of the cell was not cooled. Also, an initial attempt was made to use electrodes made of graphite rather than tungsten. These initial experiments established that heat losses from the apparatus were too large to allow for penetrations larger than about 0.5 cm, and that the graphite electrodes eroded too rapidly to permit operation over the extended periods of time desired (e.g. longer than one hour). Changes were made to the apparatus to correct these difficulties. The horizontal dimensions of the test cell were increased from 10 by 10 cm to 20 by 20 cm; the electrodes were made of tungsten rather than graphite. Also, slabs of fire-brick were used to provide additional thermal insulation of the MgO brick from the water-cooled brass side walls. A schematic of the revised apparatus is shown in Fig. 3.

The following experiments were successful in that penetrations of heat-generating molten UO_2 into the MgO brick were much larger than those obtained previously and were achieved under relatively well-controlled conditions. Furthermore, operation with molten UO_2 in contact with MgO over extended periods of time was clearly possible. A summary of overall results is given in Table 3, which also includes comparable results from the experiment with the 10 by 10 cm cell and graphite electrodes. Note that there are two "Interaction Depths" given in the table. The first (liquid/solid interface) refers to the MgO depth penetrated by gross melting and dissolution of UO_2 in the MgO. The second, identified tentatively as "intergranular," refers to a clearly discernable discolored region beneath the liquid/solid interface which appears to result from interactions with the binding material of the Harklase brick. There was no evidence of gas evolution, or cracking of the brick. Significant amounts of free magnesium were not detected. Figure 4 shows details of the penetrations achieved.

Table 3. Recent UO_2 /MgO (Harklase Brick) Interaction Experiments

	Experiment Number		
	1	2	3
Cell Cross-section (cm x cm)	10 x 10	20 x 20	20 x 20
Molten UO_2 (kg)	~ 4	13	16
MgO Melted (kg)	-	2	3
Max. Interaction Depths (cm)			
Liq./solid Interface	0.5	3	4
Intergranular in MgO	0.2	2.4	3.5
Contact Time (min)	30	55	170
Av. Power in (kW)	25	20	23
Av. Heat Flux Down (kW)	3	5	5

Other experiments are planned with the same apparatus for the purpose of extending the contact time between the heat generating molten pool and the Harklase brick to six hours or more. The temperature measurements from

thermocouples within the stack of bricks indicated that thermal equilibrium was probably attained for the three experiments described. However, dissolution of the MgO at the liquid-solid interface, and especially intergranular penetration, appears to have continued at a slow but significant rate after thermal equilibrium was reached. Experiments with larger contact times will verify the occurrence of this mode of interaction and supply information related to its importance, especially as concerns proper modeling in computer programs such as CONACS.

Also of interest is the behavior of the molten pool when adjacent to the joints between the slabs of the experiments, since similar separations will exist in the actual use of refractory bricks for core retention. No increase in penetration at these joints was observed in the experiments, but perhaps it requires larger contact times and larger gaps to occur.

Direct use of the data obtained to date for model verification, for example when interpreted as penetration depths vs. time, is complicated by the relatively large heat losses from the pool in the horizontal direction. Data from experiments with cells of much larger horizontal cross-sections would be more directly applicable, and these are currently being designed. These "larger cell" experiments would also allow for larger contact times before thermal equilibrium is attained, and would also have the capability of testing the MgO brick "float-up" problem.

ACKNOWLEDGEMENT

This work was performed under the auspices of the U. S. Department of Energy.

REFERENCES

1. R. P. Stein, L. Baker, Jr., W. H. Gunther, and C. Cook, "Heat Transfer from Heat Generating Molten UO₂: Interpretations of the Available Data," ASME 79-HT-115, Aug. 1979 (see also ANL-RDP-79, Jan. 1979, p. 6.5).
2. Letter, H. Vossebrecker, Interatom, to L. Baker, Jr., Argonne National Laboratory, Aug. 6, 1979.
3. R. P. Stein and W. H. Gunther, "Analysis of Molten-UO₂ Pool Heat-Transfer Experiments," ANL-RDP-94, Argonne National Laboratory (April 1980), p. 5.1.
4. M. G. Chasanov, W. H. Gunther, and L. Baker, Jr., "The Production of Molten UO₂ Pools by Internal Heating: Apparatus and Preliminary Experimental Heat Transfer Results," Nuclear Technology, Vol. 36 (1977), p. 120.
5. G. V. Samsonov, Ed., "The Oxide Handbook," Plenum Press, New York (1973).
6. L. Baker, Jr., "Characterization of Concrete," Reactor Development Program Progress Report, ANL-RDP-75, p. 6.3, Argonne National Laboratory (Sept. 1978).
7. T. Z. Harmathy, "Thermal Properties of Concrete at Elevated Temperatures," J. Mater., 5, 2, 47 (1970).
8. R. Farhadieh and W. H. Gunther, "One-Dimensional Penetration of Molten UO₂ Into Substrate Limestone Concrete," Nuclear Tech., 50, 298 (1980).
9. S. A. Meacham, "Molten Stainless Steel and Urania Compatibility with Sodium Exposed Refractories Considered for CRBRP Parallel Design Ex-Vessel Core Retainers," WARD-D-0121 (March 1976).

10. D. G. Swanson, E. H. Zehms, C. Y. Ang, J. D. McClelland, R. A. Meyer, and H. L. L. van Paassen, Annual Progress Report. Ex-Vessel Core Catcher Materials Interactions, ATR-77(7608)-1, The Aerospace Corporation (Oct. 1976).
11. D. G. Swanson, D. M. Goddard, E. H. Zehms, J. D. McClelland, R. A. Meyer, and H. L. L. van Paassen, Annual Progress Report. Evaluation of Materials for CRBRP Core Retention, NUREG/CR-0076, The Aero-space Corporation, (May 1978).
12. D. A. Powers, D. A. Dahlgren, J. F. Muir, and W. D. Murfin, Exploratory Study of Molten Core/Material Interactions, July 1975 - March 1977, SAND 77-2042, Sandia Laboratories, (Feb. 1978).
13. R. P. Stein, W. H. Gunther, and C. Cook, "Penetration of Magnesia Bricks by Molten UO₂," ANL-RDP-68, Argonne National Laboratory (Feb. 1978), p. 6.71.
14. D. W. Varela, T. M. Kerley, R. J. Lipinski, D. J. Sasmor, and S. Duliere, "PAHR Molten Pool," NUREG/CR-1141 (SAND79-2158) (April 1980), p. 135.
15. D. Burgess and C. Guderjohn, "Molten-UO₂/Material Interactions," in ANL/TMC 81-4, Argonne National Laboratory (Oct. 1981), p. 190.

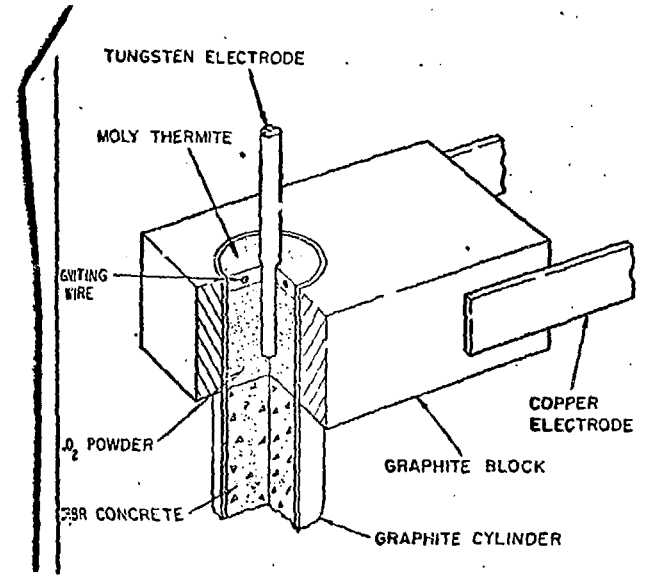
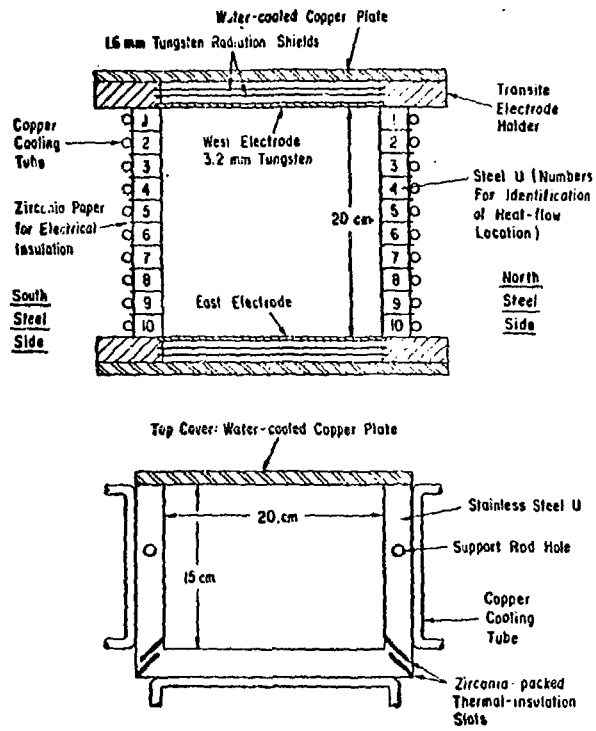


Figure 1. Schematic of Typical Heat Transfer Cell (Approximately to scale. All details not shown).

Figure 2. Schematic Drawing of the UO_2 -Concrete Test Apparatus.

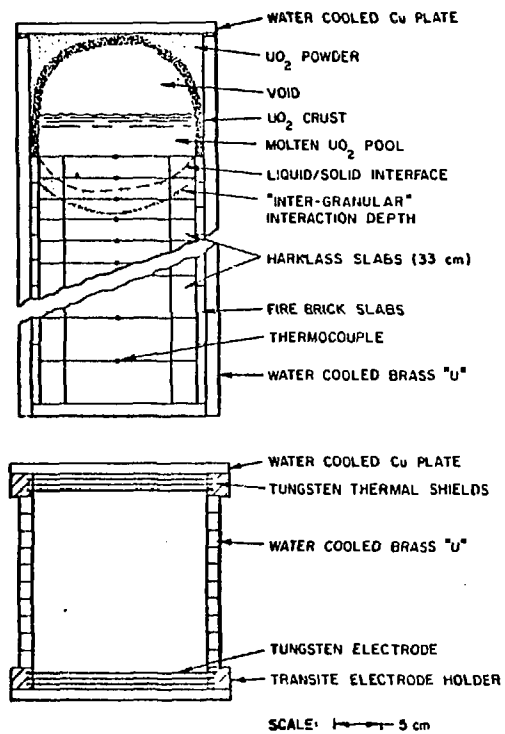


Figure 3. Schematic of Revised Apparatus for UO₂/MgO Interaction Experiments.

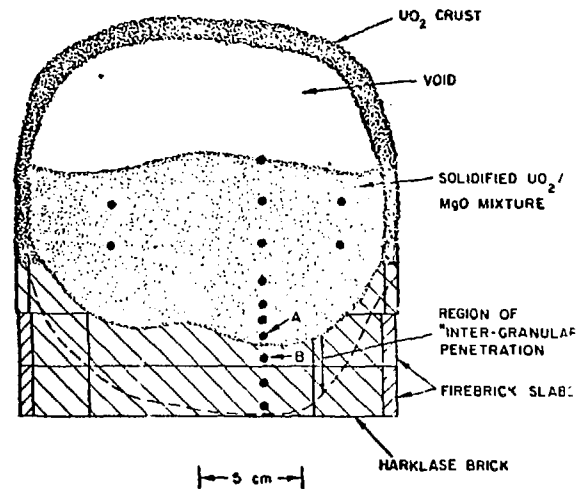


Figure 4. Post-test Appearance of UO₂/MgO Interaction Experiment Number 3. (Central cross-section parallel to electrodes.) o = Locations of samples taken for chemical analysis.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.