Modification No. 4
Supplemental Agreement to
Contract No. NRC-04-78-252

SUPPLEMENTAL AGREEMENT
BETWEEN

THE UNIVERSITY OF FLORIDA
AND
THE U. S. NUCLEAR REGULATORY COMMISSION

THIS SUPPLEMENTAL AGREEMENT, effective the 26th day of February , 1981, by and between the UNITED STATES OF AMERICA (hereinafter referred to as the "Government"), as represented by the UNITED STATES NUCLEAR REGULATORY COMMISSION (hereinafter referred to as the "Commission"), and The University of Florida
(hereinafter referred to as the "Contractor"),

WITNESSETH THAT:

WHEREAS, the parties desire to modify Contract No. NRC-04-78-252 as hereinafter provided, and this supplemental agreement is authorized by law, including the Energy Reorganization Act of 1974, as amended, and the Atomic Energy Act of 1954, as amended.

NOW, THEREFORE, said contract is hereby modified as follows:

1. Appendix A, attached to this supplemental agreement and made a part hereof, which provides for the research to be performed by the Contractor during the contract period specified therein, supersedes the Appendix A attached to Modification Number 3 of this contract.

2. In Article III Consideration, the sum "$426,645.00" is substituted for the sum "$154,706.00."

IN WITNESS WHEREOF, the parties have executed this document.

UNITED STATES OF AMERICA

BY: ______________________
Kellogg V. Morton, Chief
Research Contracts Branch
Division of Contracts
U. S. Nuclear Regulatory Commission

The University of Florida

BY: ______________________
F. Michael Wahl, Assoc. Dean for Graduate Studies & Research, Division of Sponsored Research
(title)

I, ______________________ (attester), certify that I am the ______________________ (title) of the Contractor named under this document; that ______________________ (signatory) who signed this document on behalf of said Contractor was then ______________________ of said Contractor; that this document was duly signed for and on behalf of said Contractor by authority of its governing body and is within the scope of its legal powers.

SEE ATTACHED POWER OF ATTORNEY

IN WITNESS WHEREOF, I have hereunto affixed my hand and the seal of said Contractor.

____

(SEAL)

LIMITED POWER OF ATTORNEY

Know All Men By These Presents, that I, Robert Q. Marston, President of the University of Florida, of the County of Alachua, State of Florida, effective August 16, 1979, constitute and appoint F. Michael Wahl, Associate Dean for Graduate Studies and Research of the Division of Sponsored Research of the University of Florida, County of Alachua, State of Florida, my true and lawful attorney, for me and in my name to accept and sign contractual agreements in my name for the University of Florida in accordance with that authorization given to me under Section 248.041(4) Florida Statutes.

Robert Q. Marston

State of Florida)
)
County of Alachua)

I hereby certify that on this day personally appeared before me, an officer duly authorized to administer oaths and take acknowledgments, Robert Q. Marston, to me well known and known to me to be the individual described in and who executed the foregoing limited power of attorney, and that he acknowledged before me that the limited power of attorney was his act and deed.

Witness my hand and seal at Gainesville, County of Alachua, State of Florida, this 4 day of ~~August~~ September, 1979.

Notary Public

NOTARY PUBLIC STATE OF FLORIDA AT LARGE
MY COMMISSION EXPIRES NOV. 3 1979
BONDED THRU GENERAL INS. UNDERWRITERS.

CONTRACTOR:

APPENDIX A

For the Contract period January 1, 1980 through September 30, 1985

Article A-I RESEARCH TO BE PERFORMED BY CONTRACTOR

(a) The unclassified scope of work under this contract entitled "Evaluation of Relative Surface Properties of Alternative Nuclear Waste Encapsulants" is as follows:

YEAR 1

Tasks and Anticipated End Results

1. One of the tasks and end results of this investigation will be the establishment of a quantitative test methodology for evaluating alternative nuclear waste encapsulants that is based upon measurable kinetics parameters and is sensitive to leaching by mechanisms of both ion exchange and glass network breakdown. A variety of surface instrumental techniques will be used to establish the levels of accuracy of the test methodology. The surface instrumental methods will include: Auger electron spectroscopy, secondary ion mass spectroscopy, infrared reflection spectroscopy, compound difference IR spectroscopy, scanning electron microscopy with energy dispersive x-ray analysis, electron microprobe analysis, and atomic absorption and emission spectroscopy. Kinetics constants (k_1) for the $t^{1/2}$, diffusion controlled regime of behavior and (k_2) for the t^1 interfacial reaction regime will be measured. The conditions for changeover (t_c) of kinetics from $t^{1/2}$ to t^1 will be determined. Results of these kinetics studies will be used to establish long term predictive relationships using durability evaluation and projection (DEP) plots.

2. A second task and end result will be defining minimal durability test criteria that must be satisfied in order for durability test results to be compared in terms of quantitative kinetics parameters, k_1, k_2, t_c. A consequence of achieving this end result should be the description of the minimal experimental methodology required for a quantitative assessment of the effects of radioactivity on durability of a waste encapsulant.

3. A third task and end result will be the establishment of the relative importance on surface durability of various environmental factors to be encountered during storage of the encapsulants. A geometric factor involved in storage which is the surface area (SA) of encapsulant exposed to a possible solution volume (V) will be examined over a wide range of (SA/V) ratios (10^{-3} to 10^2 cm^{-1}) to compare converse effects such as leaching from a small leak into a canister (large (SA/V)) to leaching from an encapsulant exposed to flowing ground water (very small SA/V). The effect of the flow ranging from 10^{-3} to 10^3 ml/sec will be investigated to establish flow rate dependence of kinetics parameters, k_1, k_2, and t_c, if any.

YEAR 2

1. The first task and end result of year two will be the establishment of the effects of fracture of an encapsulant on the rate of leaching. Comparison of leaching of bulk surfaces and fractured waste form particles ranging from 10 cm to 10^{-3} cm particle sizes will be made while maintaining equivalent geometric (SA/V) ratios prior to leaching. The difference in durability kinetics will be attributable to effects of the fracture surface and the agglomeration of small particles leading to rapid localized leaching of the particles.

2. The second task and end result of Year 2 will be the establishment of the effects of compositional variation on the durability of various waste encapsulants, including weight percent loading factor. Quantitative comparison of glasses with simple compositions to those with additives designed to improve durability will be made and the effectiveness of the additives evaluated. The ratio of Cs/Sr in the glasses over the range of 0.1 to 10 and the relative percentage of Cs and Sr from 0.1 to 10% will be tested as to the effect on diffusion controlled leaching (k_1) and changeover time (t_c). Effects of transition metal elements, rare earths, and actinides on changeover time (t_c) and rate of network breakdown (k_2) will be measured for waste loadings from 1 to 20%.

3. A third task and end result of Year 2 will be a determination of the effects of various degrees of crystallization of devitrification on the surface durability of the nuclear waste glasses. Simulated nuclear waste glasses will be devitrified by heating for long times over the range of 450-650°C. The effects of volume fraction of crystalline phases ranging from 10-90% on leaching kinetics k_1, k_2, t_c will be determined.

Year 3

1. A first task and end result of Year 3 will be to compare heterogeneous attack of polyphase encapsulants with leach rates of polyphase geologic materials. Best effort will be made to obtain relevant polycrystalline waste forms from DOE contractors or NRC in order to make these comparisons.

2. A second task and end result of Year 3 will be the assessment of the relative effects of alternative waste form-rock interfacial reactions on durability of the waste forms. Effects on leach kinetics of ionic solutions characteristic of those to be encountered in storage sites such as salt, basalt, granite, shale, clay, and volcanic tuffs will be compared while maintaining equivalent geometric storage parameters and waste form compositions. Passivation of surface-solution reactions by specific ions such as Al^{3+}, Zr^{4+}, PO_4^{4-}, Ca^{2+} will be used to specify preferred storage sites, overfill, or ground fill compositions.

YEAR 4

1. One task and end result of Year 4 will be the evaluation of the chemical durability of geological materials such as obsidian, chert, opal, novaculite, quartz, and tectites covering a range of volume fraction of crystallizations (i.e., glassy; partially crystalline, fully crystallized). DEP's will be constructed for these geologic materials and compared to those for the manmade synthetic waste form materials already studied in years 1-3.

2. A second task and end result will be the evaluation of the chemical durability of archaelogical glasses of known age. Identical materials of the same composition will be made and studied. DEPs will be constructed for environments that might be encountered for the nuclear waste forms. The DEP plots will be used to project potential margins of safety for the predictive relationships describing waste forms.

3. A third task and end result will be the establishment of the upper, optimal limit of durability that can be expected of a waste encapsulant based upon instrumental surface analysis of the leached layers of dated geologic and archaelogical materials and the analyses performed in tasks 1 and 2 of year 4.

4. A fourth task and end result of Year 4 will be to construct a master DEP containing data from all materials evaluated. This plot will illustrate lower and upper limits of durability that are obtained with the large variety of materials investigated. The data for relevant nuclear waste glasses will be included to show where they fit into the materials durability spectrum.

(b) The Principal Investigator expects to devote the following approximate amount(s) of time to the contract work:
Dr. L. L. Hench: 20% of his time, each year of the project.
Principal Investigator

ARTICLE A-II WAYS AND MEANS OF PERFORMANCE

(a) Items for which support will be provided as indicated in A-III, below

(1) Salaries and Wages	$164,570.00
(2) Equipment to be purchased or fabricated by the Contractor	$ -0-
(3) Travel (i) Domestic	$ 6465.00
(ii) Foreign	$ -0-

(4) Other direct costs including fringe benefits.

(5) Indirect costs based on a predetermined rate of 44.4 percent applicable to Salaries and Wages, Fringe Benefits, Materials and Supplies, Services, Travel, Sub Contracts and Sub Grants up to $25,000.00

(b) Items, if any, significant to the performance of this contract, but excluded from computation of Support Cost and from consideration in proportioning costs:

NONE

(c) Time or effort of Principal Investigator(s) including indirect costs and fringe benefits contributed by Contractor but excluded from computation of Support Cost and from consideration in proportioning costs:

NONE

Article A-III

The total estimated cost of items under A-II(a) above for the contract period stated in this Appendix A is $ 351,685.00; the Commission will pay 100 percent of the actual costs of these items incurred during the contract period stated in this Appendix A, subject to the provisions of Article III and Article B-XXVIII. The estimated NRC Support Cost for the contract period stated in this Appendix A is $351,685.00.

The estimated NRC Support Cost is funded as follows:

(a) Estimated unexpended balance from prior period(s) $ -0-

(b) New funds for the current period $ 351,685.00

(c) The new funds being added in A-III(c) constitute the basis for advance payments provided under Article B-X.