CRADA Final Report ANL/NE/C0500901

"Borated Materials and Components for Nuclear Shielding
and Waste Contamination Applications"

This CRADA involved Argonne National Laboratory as the Contractor and overall Project Manager. The CRADA Industrial Participant was CeraLith Technology located in Edmonds, Washington. The two Russian Project Subcontractors who did the majority of the work are listed below:

- Spektr Conversion Laboratory
- The Russian Federal Nuclear Center All-Russia Research Institute of Experimental Physics (RFNC) VNIIEF

To improve logistics in contracting in the Russian Federation, an international not-for-profit organization, the International Science and Technology Center (ISTC) put in place the subcontract. The project numbers were 2857p and 2807p for Spektr and VNIIF respectively. Argonne National Laboratory served as the technical manager of this contract under the NIS-IPP program.

CeraLith provided their evaluation of the tasks done under the two subcontracts and this will serve as the CRADA Final Report.

Market Analysis Reports from Spektr-Konversiya (Project 2857)

1st Quarter Report: Provides a survey of Trade Shows and Workshops relating to nuclear waste control and the identities of the key companies and research institutions that support the nuclear power industries of Russia and other countries of the former Soviet Union. Spektr plans to disseminate informational materials on the nuclear shielding properties of ceramicrete at 16 trade shows and workshops.

2nd Quarter Report: Provides a wealth of detailed information on: the structure of the nuclear power industries of Russia and Ukraine, including the numbers and types of nuclear reactors, plans for bringing additional nuclear power units on line out to the year 2020; the amounts of spent nuclear fuel and liquid nuclear waste in Russia, the producers of nuclear fuel used in Russian reactors, the various types of storage and shipping containers for spent nuclear fuel and the companies producing such containers; Russian and Ukrainian plans for building long term storage facilities for spent nuclear fuel; and Russian radiation safety regulations.

3rd Quarter Report: Examines the availability in Russia of the raw materials (MgO, KH_2PO_4 and Fly Ash, the purities and costs of such materials) for producing ceramicrete; notes the growing shortage of MgO for domestic needs in Russia and identifies foreign sources for such materials and their costs).

4th Quarter Report (with Mayak): Examines the possibility of using fly ash from thermal power plants in Russia as an additive in formulating ceramicrete; provides chemical analysis of the fly ash available at the various thermal power plants; presents the results of initial research regarding the amounts of fly ash added to the formulation of ceramicrete and the effects of such additives on the compression strength of samples.

(Fly ash from thermal power plants suggests Type F fly ash (containing carbon), however other references specify fly ash containing SiO_2 + Al_2O_3 (50-50), indicating Type C. Fly ash without carbon would provide superior performance in high-temperature environments. Therefore, it is important to specify Type C.)

5th Quarter Report (done with Mayak): Provides results of further testing of the use of fly ash as an additive and the effects of calcination under high temperatures on the strengths and density of samples; studies the effect of the addition of boric acid on setting time of ceramicrete samples.

6th Quarter Report (done with Mayak): Provides results of further testing of the effects, before and after calcination, on the strengths and density of samples when asbestos, glass fibers, powdered wollastonite and iron oxides are included as reinforcing additives. Also elaborates on the respective duties and roles of Spektr, VNIIEF and Mayak in the fabrication, testing of ceramicrete

7th Quarter Report (October 31, 2007-February 28, 2008: In this report **Spektr** will present the results of its analyses on the possibility of using ceramicrete materials in Russia and other markets in the region.

Reports by VNIIEF, VNIITF and Mayak (Project 2807)

1st Quarter Report:

The principal design specifications of TPC RT5010, and characteristics of SNF are presented. Tentative requirements and effect characterization determined for ceramicrete composites. The report previews thermal, chemical, mechanical and other effects, to which ceramicrete composites may be exposed when used in SNF shipping and long-term storage TPC (see Table below).

Tentative requirements and effect characterization for ceramicrete

Effect or Operating Condition	Requirements and characterization of the effect in normal operational conditions	Requirements in emergency
Heating	Temperature in 80ºC – 200ºC range (for external and internal surfaces, respectively). The package suite nuclear shield efficiency should not decrease because of different thermal expansion or melting of nuclear shield material	In 200ºC – 300ºC range (in fire). In ground logjam due to earthquake critical spent fuel assembly temperature of 350 – 380ºC is attained in 110 hours after the logjam. The neutron shield temperature should not exceed 320ºC.
Durability	No less than 50 years.	Not imposed.
n, γ source rates	$Sn=5.1\cdot10^{8}$neutr/s·FA, $S\gamma=3.52\cdot10^{15}$ photon/s·FA	Not imposed.
Ionizing radiation attenuation factors for considered thickness of ceramicrete layer Δc and iron layer ΔFe (cm).	$K_n \cong 1.4\cdot\Delta_c$ $K_\gamma \cong 1.13\cdot\Delta_c$ for characteristic thickness of ceramicrete layer Δc~10 – 20 cm and iron layer ΔFe~25 cm	No requirements on neutron shield preservation upon fire are imposed.
Maximum absorbed dose (for 50 years)	$1.1\cdot10^{5}$ rad	Not imposed.
Mechanical loading	The package suite nuclear shielding efficiency should not lower due to nuclear shield material cracking under mechanical loads.	Not imposed
Spent fuel assembly criticality	Nuclear safety characteristics of existing packages should not deteriorate.	Nuclear safety characteristics of existing packages should not deteriorate.

Operating conditions are based on the RT5010 type TPC licensed in Russia. It is unlikely that parameters of operating conditions would change if another TPC type were considered. The above characteristics are predetermined by the government requirements.

2nd Quarter Report:

Materials purchased: boron carbide TU95. 960-82; magnesium oxide GOST4526-75 of qualification “ch”; potassium dihydroorthophosphate (monosubstituted potassium phosphate) TU6-09- 5324-87; monosubstituted sodium phosphate-2 aqueous GOST245-76 of qualification “ch”; testing screens with mesh aperture from 0.04 to 0.25 mm. Planetary grinding mill “pulverisette-7” of Fritsch Corporation was purchased and put into operation.

Since the mixer produced by Saratov Mixer Producing Plant MTZ was not available, an overhead drive mixer of VELP Corporation (Germany) was purchased. Ingredients were analyzed and manufacture of ceramicrete samples was started.

3rd Quarter Report:

A comparative analysis of shielding properties of ceramicrete composites with different possible fillers when used in spent nuclear fuel (SNF or SFA) shipping and long-term storage casks. Neutron and gamma radiation dose rates (rem/h) on TPC surface with ceramicrete shielding was calculated with different fillers.

Performed a computational series for dose characteristics near SNF containing packages. TPC RT5010 is taken as the closest prototype of the shielding container loaded with spent fuel assemblies (SFA).

The dose characteristics near the TPC loaded with 24 SFA’s were calculated using both Monte Carlo code C95 developed and employed by VNIIEF and computer module SAS2H of program complex SCALE43 developed by ORNL.

Conclusions

The paper documents the results of computations of dose characteristics near the packing containing 24 SFA’s of reactor VVER-1000 (upon a 3-cycle regime of fuel irradiation for about 3 years followed by cooling in ponds for 8 years).

Ceramicrete with different fillers as well as, for comparison, BNS material (composed of CH_2 by more than 80% by weight) with fillers are considered for the shielding.

Based on Monte Carlo computations by VNIIEF, the following conclusions are drawn:

1. Ceramicrete composites with fillers used for the shielding provides ≈ 50-80 times reduction in the dose rate on the external surface of the packing.

2. Layers comprised of ceramicrete with added boron nitride and with uranyl acetate and B_4C provide effective radiation shielding.

3. At a given shielding layer thickness the shielding properties of ceramicrete with filler, as the computations suggest, are about 2.6 – 2.7 times better than those of BNS material (composed of CH_2 by more than 80% by weight) with fillers.

4. The maximum allowable radiation level on the surface of a TPC RT5010 loaded with spent fuel assemblies should be no higher than 2 mSv/h (200 mrem/h). When using ceramicrete shielding, the computed maximum dose rate is reduced to ≈ 2 mrem/h.

5. When using ceramicrete with filler, this value reduces to ≈ 34. When using ceramicrete shielding, the computed dose rate at 1 m from the packing is no higher than 1 – 1.5 mrem/h. This is well below the maximum allowable radiation level of 2 mrem/h (NP-053-04).

4th Quarter Report:

Manufactured small (100≤g) ceramicrete specimens needed for Project 2807p. The "promising feature" of the specimens of different compositions was analyzed, taking into account the recommendations of the Project1. It was decided that 2 specimen types should be manufactured: 1) one type is without heavy fillers, 2) the other type is with heavy fillers. Boron carbide with natural isotopic composition of boron should be added in either case.

The ceramicrete manufactured according to these recommendations offers a number of advantages as against alternative materials. Thus, in ceramicrete the bonding of additives with matrix is due to chemical bonds and filler material encapsulation into crystallite matrix. This enhances the resistance to nuclear radiations and leachability, i.e. ensures ceramicrete properties required in Project 2807p.

5th Quarter Report:

Continuing work on making ceramicrete samples, and testing of physical characteristics at room temperatures and when heated up to 800°C. Testing revealed a modest linear expansion coefficient, good heat resistance, and high strength (18.4 – 39.9 MPa).

6th Quarter Report:

In order to compare type A and B ceramicrete specimens (Table 1) with specimens fabricated from cement slurry in their ability to release water at elevated temperatures, cement specimen mass loss during heating to 800°C has been measured. Measurements were taken successively at temperatures 100, 200, 500 and 800°C. The specimens were aged 2 hours at each temperature, and weighed upon cooling to room temperature in a dry atmosphere. Results are presented in the Table below.

Results of ceramicrete heating

Drying time, h	*A*		*B*		*BC 092200-6*	
	Mass, g	*Mass loss, %*	*Mass, g*	*Mass loss, %*	*Mass, g*	*Mass loss, %*
0	35.4005	-	41.6376	-	65.6032	-
2	30.1367	14.8	34.4605	17.2	53.4345	18.5

Aging of the ceramicrete specimens for two hours (even at a relatively low temperature of 200°C) resulted in complete loss of crystallization water. This occurred with all specimens, irrespective of component quality or the time and place of manufacture.

An exception is the mass loss that occurred at temperature 800°C, most probably due to severe specimen crumbling at that temperature. For the type A and B ceramicrete specimens, however, the mass decreases by 9.1- 9.9% during the process of heating (at the same rate as for cement specimens) to 500°C and increases on heating at 800°C temperature. **(What are the possible causes of "crumbling" at 800°C ? This is an unusual result – given the refractory nature of ceramicrete – and especially considering the VNIIEF heat shielding model.)**

Computer modeling of heat shielding characteristics for 50% MKP+50% Perlite indicate that ceramicrete can retard elevation of temperature on shielded surfaces and thereby contribute to TPC and LTSC fire safety. Additional experiments verified that ceramicrete protected transducers from overheating and failure in a high temperature environment (a significant problem in facility monitoring).

Principal Conclusions

When using ceramicrete as material for nuclear shielding in containers for shipment and long-term dry storage of spent nuclear fuel, the loss of chemically bound water from crystal matrix in heating above 100ºC, which deteriorates its neutron radiation shielding properties, should be taken into consideration.

7th Quarter Report:

Large-sized ceramicrete samples were made to assess the impact of the scale effect on the material behaviors. For this purpose formulations close to those of the US specimens supplied to VNIIEF were selected (see Table below).

Component composition of ceramicrete specimens, wt.%.

Specimen type	Binder	Ash	Fe_2O_3	Fe_3O_4	B_4C	H_2O
Without heavy fillers under the CRDF program	39.84	35.74	0	0	4.1	20.32
With heavy fillers under the CRDF program	15.35	11.25	30.73	30.73	4.1	7.84
Type A VNIIEF	39.86	35.74	0	0	4.1	20.32
Type B VNIIEF	40.53	7.6	27.1	0	4.1	20.6
Type A1 (large-sized) VNIIEF	41.17	33.6	0	0	4.24	20.99
Type B1 (large-sized) VNIIEF	40.6	9.2	14.5 FeO	11.0 Co_3O_4	4.1	20.6

(What is the chemical analysis of fly ash used in these samples?)

Linear expansion coefficient of the fragments taken from different points of each specimen type is approximately the same and the values are of the same order of magnitude as the linear expansion coefficient of the previously measured type A and B cylindrical specimens.

According to test data, mass loss due to crystallization water loss is similar to that in the previously synthesized type A and B specimens. Note that essentially all water corresponding to the batch “quits” the specimens in the 100 – 250 °C temperature range (at 50 °/min).

CeraLith Comments and Questions

CeraLith has been very impressed by the quality and technical thoroughness of the work presented in reports produced under ISTC Projects 2857 and 2807. Spektr-Konversiya's marketing research has provided useful economic data and information on possible useful industrial contacts, and the research facilities of Mayak, VNIIEF and VNIIFT have developed the data which validate the proposed ceramicrete applications.

As we review the marketing and technical reports developed by our Russian partners, the following questions arise:

(1) Response from the nuclear industry: what has been the response, if any, to the information brochures on the nuclear shielding properties of ceramicrete from the participants in the trade shows and workshops? The 2857 Q1 report noted 16 nuclear industry trade shows (for the year 2006 alone) at which information would be distributed. Were all these trade shows attended? Was the feedback from potential customers documented and analyzed?

(2) Certification of Ceramicrete for use in Russian Nuclear Industry: What are the procedures for securing official certification, approval, for the use in the Russian nuclear industry of ceramicrete for nuclear shielding, and for the fabrication of transport and storage casks? The 2nd Quarter Project 2857 report suggests there is significant commercial opportunity for the application of ceramicrete in the construction of casks for storage and transportation of spent nuclear fuel. To what extent, if any, will Spektr-Konversiya, VNIIEF, VNIITF and Mayak play a role in securing certification that will be required for the use of ceramicrete in the Russian nuclear industry?

(3) Annual Demand for Ceramicrete. With Spektr-Konversiya's help we will need to begin to accumulate, aggregate, and synthesize data which will be relevant for making estimates of the future potential annual demand for ceramicrete (and its various component raw materials) in the Russian and Ukrainian nuclear industries for nuclear shielding purposes. For example, in their March, 2007 paper made available to participants at the conference in Barga, Italy, Sergey Dorosev and Vladimir Pervushin note that if ceramicrete were to be substituted for Portland cement inside metal-concrete casks for the storage of fuel assemblies from VVER-1000 reactors, such as is planned for the dry ventilated storage technology at Zaporozhe, the annual requirement for ceramicrete would be about 2,625 tons of ceramicrete, equal to 500 tons of phosphor-silicate ceramics, including additives.

Also, in their Poster Presentation at the Barga Conference, Sergey and Vladimir note that "About 215 tons of SNF (spent nuclear fuel) are generated annually in Russia at nine VVER-1000reactors and about 310 tons of SNS are generated annually in Ukraine at thirteen power units…"

Is the figure 2,652 tons for just the fuel assemblies from the VVER-1000 reactors at Zaporozhe or for fuel assemblies from all VVER-1000 reactors in both Ukraine and Russia? Has there been any attempt to quantify the amounts of ceramicrete that would be required if ceramicrete were to be used in the construction of the shipping casks (SC) in the SC series, such as SC-4, SC-5, SC-6, SC-13, SC-18, etc? We note that the operational lives of some of these casks are reported to be nearing their limits.

(4) Use of Ceramicrete at Zaporozhe Nuclear Power Plant (Ukraine): We agree that CeraLith will provide information on ceramicrete's nuclear shielding properties to representatives of the Ukrainian nuclear industry with the recommendation that it be used in the construction of the dry storage facility being built at Zaporozhe with the involvement of the American company Duke Engineering Services.

(5) Potential Costs of Producing Ceramicrete in Russia: As noted in the 3rd Quarter Report of Project 2857: *Study of the Possibility and Prospective for Obtaining and Application of CBPC in Russia Technical Report*, the demand for Magnesium oxide (MgO) in Russia exceeds domestic production and is growing. In our view, the costs cited on page 6 of the report are very high. What are the reasons for these high costs? What is the cost per ton of MgO that Spektr-Konversiya foresees if ceramicrete is adopted for use in the Russian nuclear industry? We believe that the costs of MgO available from CeraLith's Korean partner, Cerako, are extremely favorable. The question arises, however, whether the eventual demand for the use of ceramicrete in Russia or Ukraine will generate investments needed to exploit the vast deposits of raw materials in both countries that could be used to produce MgO. Cerako is prepared to provide samples of MgO from sea-brined and mining sources along with estimated costs per ton.

(6) Future Business Relationships: How does Spektr perceive its future role in the development and commercialization of ceramicrete in Russia and other countries? For example, does Spektr see itself as a marketing / import agent, an industrial representative (for a Russian manufacturer), or a joint venture manufacturing partner with a capital interest in the production and sale of ceramicrete materials and/or products.

These and other issues regarding our business relationship should be addressed. We would hope to have such discussions face-to-face during our meetings at Argonne early next year.

(7) Meeting with Korean Nuclear Scientists and Engineers. Cerako, our Korean joint venture enterprise, has expressed an interest in having nuclear specialists from South Korea meet our Russian colleagues who have been making ceramicrete samples and testing them for their radiation shielding properties. Potential benefits for the Russian participants include (1) research and consulting opportunities, (2) business opportunities for Russian industries, and (3) possible import/export arrangements for Russian businesses. If there is interest in such a meeting on the part of our Russian colleagues, we would have to discuss where such a meeting could take place as well as the question of how we would cover the expenses of such a meeting.