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Furfurol-based Polymers for the Sealing of Reactor Vessels Dumped in the Arctic Kara Sea.

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ABSTRACT: Between 1965 and 1988, 16 naval reactor vessels were dumped in the Arctic Kara Sea. Six of the vessels contained spent nuclear fuel that had been damaged during accidents. In addition, a container holding ~60% of the damaged fuel from the No. 2 reactor of the atomic icebreaker "Lenin" was dumped in 1967. Before dumping, the vessels were filled with a solidification agent, Conservant F, in order to prevent direct contact between the seawater and the fuel and other activated components, thereby reducing the potential for release of radionuclides into the environment. The key ingredient in Conservant F is furfurol (furfuraldehyde). Other constituents vary, depending on specific property requirements, but include epoxy resin, mineral fillers, and hardening agents. In the liquid state (prior to polymerization) Conservant F is a low viscosity, homogeneous resin blend that provides long work times (6-9 hours). In the cured state, Conservant F provides resistance to water and radiation, has high adhesion properties, and results in minimal gas evolution. This paper discusses the properties of Conservant F in both its cured and uncured states and the potential performance of the waste packages containing spent nuclear fuel in the Arctic Kara Sea.

1. INTRODUCTION

Within the course of operating its nuclear navy, the former Soviet Union (FSU) dumping of reactor vessels and spent nuclear fuel (SNF) in three fjords on the east coast of Novaya Zemlya and in the open Kara sea within the Novaya Zemlya Trough during the period 1965 to 1988 [1]. The dumping consisted of 16 reactors, six of which contained SNF and one special container that held ~60% of the damaged SNF and the screening assembly from the No. 2 reactor of the atomic icebreaker "Lenin" [2-4]. At the time the FSU considered dumping of decommissioned nuclear submarines with damaged cores in the bays of and near by the Novaya Zemlya archipelago in the Arctic Kara Sea to be acceptable. To provide an additional level of safety a group of Russian scientists embarked upon a course of research to develop a solidification agent that would provide an "ecologically safe

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barrier". The barrier material would prevent direct contact of seawater with the SNF and the resultant leaching and release of radionuclides. The solidification agent was to be introduced by flooding the reactors vessels and inner cavities. Once introduced the agent would harden and form an impermeable barrier. To accomplish this the solidification agent was required to have the following properties:

In the liquid state:

low viscosity (to permit gravity feed and to eliminate voids and unfilled cavities)
homogeneity
a working time of 6-9 hours (defined as the time after which the viscosity has doubled)
a time limit for solidification of not more than 10-15 days
low exothermic peak temperature (<80°C)
avoidance of dangerous fire and explosive situations

In the cured state (solid):

resistance to radiation and sea water
high adhesion to the reactor vessel components
low voids, porosity and defects
minimal gas generation
long lifetime (e.g., low corrosion in seawater)
avoidance of dangerous fire and explosive situations
avoidance of recriticality

2. DEVELOPMENT OF FURFUROL F

FSU researchers initially considered several options. Bituminous materials were rejected due to flammability issues and the fact that it was impractical to maintain a reactor vessel at the high melt temperatures required for bitumen during the flooding of the full volume of the reactor vessel. Cementitious grouts were also rejected, in this instance on the basis of high leach rates and high porosity that would result from using a low viscosity grout and the high gas generation rates that would result from including additional water and or superplasticizers to reduce the viscosity of the grout. The researchers, headed by V.P. Alexandrov, decided to use a thermosetting polymeric material. The prototype, initially termed Conservant F by its inventors, went through several updatings over time in order to improve properties such as the irradiation resistance. All of the updatings contained furfurol in the composition and the solidification agent began to be termed Conservant "Furfurol" (F) or simply Furfurol F as sort of a "trade name". Furfurol F went through five iterations (designated F.1, F.2, F.3, F.4 and F.5) during the dumping period. The differences between these variants include the hardener used (acid, amine or combined form), mineral fillers (including powdered graphite and quartz) and copolymer additives (e.g., epoxy resins). From 1965 to 1972 Furfurol F.3 was used in the solidification of the reactor vessels cut out of nuclear submarines (NS) which had not been defueled: NS-901 (two reactors, dumped in 1965), NS-285 (one reactor, dumped in 1965), NS-421 (one reactor, dumped in 1972). Furfurol F.3 was also used in the special container that held approximately 60% of the SNF from the No.2 reactor of the icebreaker "Lenin" (dumped in 1967). NS-601, dumped in 1981, contained two liquid metal reactors aboard that were solidified using Furfurol F.4.

All of the Furfurol F compounds have similar characteristics in the liquid and solid states. To assure quality control, the FSU applied the following requirements on the solidification agent for use in reactor vessel decommissioning:

viscosity must range between 230 cPs and 370 cPs;
the peak exotherm should not exceed 80°C;
solidification should occur within 14-28 days;
a working time (defined as the time after which the viscosity of the mix has doubled its initial value) between 3 and 9 hours;
a minimum compressive strength of 30 MPa.

In addition to these objective measurements, subjective visual examination was required to ascertain that the liquid was dark colored, free from particulates and did not show layering.

Furfurol F.3 was prepared by first dissolving the cadmium nitrate into ethanol in 1:1 mass ratios. The styrene and ethanol/cadmium nitrate mix were then slowly fed into the prescribed amount of furfurol while stirring. Next, the hardener and filler were added without interruption of the stirring. The process took approximately 10 minutes.

The solidification agent was gravity fed into the reactor vessel using the existing channels in the vessels. Full-scale mock-ups of the vessels were used to prove the Furfurol F agent would fill the small voids and crevices in the vessel. The channels had 4mm diameter holes and reached to within 100-200 mm of the bottom of the pressure vessel. Preparation of the vessels for dumping included drying the inner cavities of the primary circuit, temperature measurements of the vessel over three days and measurement of the gamma radiation rate dose over the height of the core. The formulation of the Furfurol F agent was then "corrected" (e.g., decrease in hardener with increasing temperature) to account for the temperature, dose rate and reactivity of the conservant components as supplied. Fittings were added to allow introduction of the agent and depressurization of the vessel (10-20 mm Hg). Thermocouples were added to record the temperature history of the vessel during solidification. The Furfurol F agent was mixed in temperature controlled mixing tanks that allowed for pressurized delivery of the material into the reactor vessel. After filling the reactor, air evacuation was continued for 100 h and temperatures recorded until they reached 30°C. At the end of 25 days, special stainless steel plugs were set on the control rod channels and sealed.

3. PROPERTIES OF FURFUROL F

3.1 Physical and Mechanical Properties

FSU researchers tested samples taken from the full-scale mock-ups as well as cast samples to determine if the performance goals were met. From the mock-ups the density of the Furfurol F samples (10-20mm diameter and 15-20mm height) was determined to be 1.6 g/cm^3 ± 15%. Unconfined compressive strength was 30-40 MPa ± 10%. To determine the adhesion of Furfurol F to the metal components of the vessels, a non-standard test procedure was introduced. In this, a metal rod (12 mm diameter) was axially positioned inside a metal socket (19 mm inside diameter) and the gap between the two filled with Furfurol F. The specimens were cured for 6 months prior to

testing then the force required to press the rod out of the socket (at a rate no greater than 2 mm/min) was measured. An adhesion value was calculated according to W = P/S, where W is adhesion, P is the applied force, and S is the contact area of the rod and Furfurol F. Adhesion values ranged from 10 to 12 MPa.

3.2 Stability in sea water

Stability in sea water was determined by measuring changes in mass and compressive strength after aging in sea water for 10,000 hours. After 3 years testing the sample showed less than 1.7% weight loss. Compressive strength showed a less expected trend. The initial strength of samples aging in air was greater than that of samples aging in sea water, but the increase in strength with aging was greater in sea water than in air. The result was the strength of seawater cured samples surpassed the strength of air cured samples after 4.5 to 5 months. Immersion in sea water seems to enhance the curing of the polymer. FSU researchers offered a possible explanation of this phenomena. The sea water probably acts as a plasticizer for the polymer and reduces steric hindrances allowing greater interaction between unreacted reactive groups. This increased interaction results in a higher degree of polymerization and hence greater strength. Indirect evidence of this is found in the degree of polymerization of the air cured versus sea water cured samples. Air cured samples reached a maximum of 82% polymerization whereas the sea water cured samples reached 90% polymerization.

Another concern of using organic polymers in a marine environment is biofouling. Samples of Furfurol F were lowered to the sea bottom in an inlet of the White Sea, then inspected after one and two years. No signs of fouling or surface disruption, or of dimensional changes, were noted. The experiments were inadvertently terminated after two years when the samples were lost during a storm.

3.3 Radiation stability

Gamma radiation testing was carried out in air at 38-42°C at a dose rate of 3.1 kGy/h (0.31 Mrad/h). Absorbed doses ranged from 1 to 50 MGy (100 to 5000 Mrad).

The compression strength of Furfurol F varies with absorbed dose much as do those of other polymers such as polyethylene. Little change is observed at low doses, but then the strength increases as the dose accumulates until a peak value is reached at a high dose. In the case of Furfurol F, this peak is achieved at about 2000 Mrad. As the dose is increased beyond this value, the compression strength is initially stabilized then begins to decrease. However, even at an integrated dose of 20-25 Grad, the strength is still of the order of 25-30 MPa (i.e., the minimum compressive strength specified in the requirements). On this basis, Furfurol F was determined to have radiation resistance up to an accumulated dose of 10 Grad.

Thermogravimetric analysis on unirradiated Furfurol F indicated thermal stability up to 300°C in an inert atmosphere. When the same analysis was performed on material irradiated to greater than 1 Grad, the thermostability limit was found to have increased to 350°C. Tests in air revealed that irradiated material had a slightly higher resistance to breakdown due to thermal oxidation. Irradiation also increased the glass transition temperature, in one instance from the initial value of 320°C to 375°C after a dose of 2 Grad.

Data on gas generation as a result of radiolysis established that the major product was hydrogen (75-90%). Carbon oxides constituted 10-20% while methane and ethane together comprised 0-5%. Only small amounts were involved: it was estimated that 3 t of Conservant F irradiated to 5 Grad would release the gases at a rate of no more than 0.3 liters per year.
None of the samples subjected to gamma irradiation to 5 Grad showed any sign of radiation cracking while shrinkage varied from 0.3 to 1.4%, depending on which variant was tested and whether the tests were conducted in air or water.

4. CONCLUSIONS

Between 1965 and 1988, numerous naval vessels were dumped in the bays of and near by the Novaya Zemlya archipelago in the Arctic Kara Sea, six of which contained spent nuclear fuel that had been damaged during accidents. In addition, a container holding ~60% of the damaged fuel from the No. 2 reactor of the atomic icebreaker "Lenin" was dumped in 1967. Prior to dumping, the reactor vessels were filled a furfurol-based polymer called by its inventors as Conservant F. It was later termed "Furfurol (F)," in reference to the fact that the key ingredient in the solidification agent is furfurol (furfuraldehyde). The function of the agent is to prevent direct contact between the seawater and the fuel and other activated components, thereby reducing the potential for release of radionuclides into the environment. The results of studies into the properties of this compound indicated that it has high compressive strength and adhesive strength, is compatible with sea water, and is resistant to radiation at doses up to 10 Grad.

5. FUTURE PLANS

Staff from the Russian Research Center, "Kurchatov Institute," and the Russian Research and Design Institute for Power Engineering will visit the Brookhaven National Laboratory to supervise and assist in the preparation of typical samples of Furfurol (F). These samples will then be used in laboratory studies of radionuclide release in simulated Arctic Sea conditions, the results of which will be incorporated in an ongoing program of re-evaluating the performance of the compound under service conditions.

6. ACKNOWLEDGMENTS

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