

Leaching of Radionuclides from Furfural-based Polymers Used to Solidify Reactor Compartments and Components Disposed of in the Arctic Kara Sea

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ABSTRACT

Within the course of operating its nuclear navy, the former Soviet Union (FSU) disposed 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],[3],[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 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.

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 the additional water and or superplasticizers used to reduce the viscosity of the grout. The researchers at the Kurchatov Institute, the Research and Design Institute for Power Engineering in Moscow, headed by V.P. Alexandrov, decided to use a thermosetting polymeric material. The prototype, initially termed Conservant F by its inventors, went through several revisions over time in order to improve properties such as the irradiation resistance. All of the revisions contained furfuraldehyde, termed furfurol in the FSU, in the composition and the solidification agent began to be termed Conservant "Furfurol" (F) or simply Furfurol F as sort of a "trade name". Furfural based polymers (furans) have been used worldwide in the fabrication of polymer concrete pipes, as an organic cementing and sand consolidating

material in oil wells, as floor coatings, and as chemically resistant containers. The basic chemical in furans either furfuryl alcohol (furfurol) or furfuraldehyde (furfural) are inexpensive. Furfural can be obtained commercially from agricultural by-products such as corncobs, cottonseed hulls, oat hulls, etc. Furfurol is produced by catalytic hydrogenation of the furfural.

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 but two of the disposal vessels and all vessels containing SNF were solidified with Furfurol F.3. Therefore, the laboratory studies involved only F.3.

LABORATORY SAMPLE PREPARATION

The formulation for Furfurol F.3 was transferred under a proprietary rights agreement between the Kurchatov Institute in Moscow and Brookhaven National Laboratory (BNL) in Upton, NY, USA. After meeting with the Russian inventors, BNL scientists prepared "cold" (non-radioactive) samples to determine the behavior of the polymer system prior to making the "hot" (added Cs¹³⁷ tracer) specimens. Furfuraldehyde, a co-monomer, mineral filler and a "hardening" agent was mixed by hand and poured into molds. Curing took 7 days and the temperature rose no higher than 30 °C.

It was readily apparent that some settling had occurred. The mineral filler settled out of the top 3-4 cm of the ~25 cm length of polymer. The first 2 centimeters appeared to have no filler at all while the next 1-2 centimeters had a reduced amount of filler. These were visual observations and are based on the "glossiness" of the sample. Pure F.3 polymer has a black glass-like appearance while the polymer and mineral filler mix has a dull-black, plastic look. In addition, this no-filler zone had 5-7% shrinkage and eventually fragmented. The samples were left on a lab bench and after ~ 24 hours it was noted that the top piece (0 to 1 cm cut from polymer cylinder) had completely cracked apart. Numerous shrinkage cracks had formed and the 5 cm diameter piece now had no piece greater than ~1 cm cubed. The second sample (1 to 11 cm along the polymer cylinder) had "spalling" along the top edge of the sample. The damage was limited to the top 1 cm and along the edge (0.3 to 0.5 cm) of the cylinder. All cracking took place only in areas that showed no or reduced filler present. This behavior indicates considerable shrinkage stress occurring with the polymer. The mineral fillers act as reinforcing fibers and mitigate the effects (cracking) caused by the stress. A second lot was made and after curing was heated from room temperature to 40°C to see if additional polymerization would occur. This heat up (from 20 to 40 °C over several hours) caused accelerated cracking. Thermal stability appears to be much less than stated (by FSU) due to shrinkage-stress.

The settling that occurs over the cure time is a function of the viscosity of the monomer blend, the cure time, the density of the mineral filler and the temperature of the mix (effects viscosity). In the lab, the mix was made at room temperature so the resulting viscosity of the Furfurol F3 would be lower than the field conditions would have been. There should be less settling in the field but still some would be present. In the area of the reactor vessel (very top portion) where settling occurs, the polymer should be expected to crack and provide a much lower degree of protection than in the lower portions of the vessel. It should also be noted that these are early lifetime observations, the areas that did not show shrinkage or cracking may not hold up in the long term. On the other hand, longer time frames may lead to greater polymerization and slightly improved characteristics.

With this knowledge, optimized samples were made for leach studies. Four molds were filled and placed in a tumbler. The tumbler turned the molds end over end at a rate of 18 rpm. Tumbling was continued for seven days and was ended once the samples had hardened. The molds were left in storage for thirty additional days to allow full polymerization. After thirty days the samples were removed from the molds. The samples all looked uniform in color and texture and no signs of settling were evident. The samples were weighed and measured and three were prepared for leach testing according to ASTM C-1308[5]. The fourth specimen was archived. Calculated densities were very similar and showed good uniformity.

LEACH TESTING

Three specimens of the Furfurol F3 were subjected to leach testing following ASTM 1308. This test was developed by BNL to allow accelerated determinations of diffusion controlled releases from solidified waste forms. The tests were run at room temperature, using distilled/de-ionized water as the leachate. The leachate volume was reduced from 3 liters to 0.5 liters to reduce radioactive waste. It is acceptable to use lower leachate volumes if it is known that the release mechanism is diffusion and there are no solubility concerns at the expected leachate contamination levels. Since we were using a tracer the actual concentrations of cesium in solution was very low. Final analysis of the data also proved the release was diffusive and no solubility limitations were encountered. Standard time intervals were used up to ten days then modified to include a ten day interval and a 42 day interval, resulting in 62 days total leach time. At the end of 62 days the samples were depleted of cesium. The average diffusion coefficient was $2.2 \times 10^{-7} \pm 0.29 \times 10^{-7} \text{ sec}^{-1}$. The US Nuclear Regulatory Commission (USNRC) requires a leach index of greater than 6 which corresponds to a De of $1 \times 10^{-6} \text{ sec}^{-1}$.

The Furfurol F3 polymer solidification system can be compared to other polymer solidification systems. For a fair comparison, the waste loading of the Furfurol F3 should be considered the loading of mineral filler since this material will add most to the porosity of the final waste form. The final product is 67% filler and 33% binder. BNL has developed several polymer binders for radioactive waste [6] of which polyester-styrene encapsulation of nitrate salts is a reasonable comparison to the Furfurol F3 system. The nitrates are readily soluble (whereas the mineral fillers are insoluble) so this is a conservative comparison (Furfurol F3 with nitrate salts would be expected to leach faster than F3 with mineral fillers). For polyester styrene with 70 wt% nitrate salt loading the effective diffusion coefficient was $2.0 \times 10^{-8} \text{ sec}^{-1}$, an order of

magnitude lower than the Furfurol F3 which places the F3 system in the lower end (polyesters<epoxies) of polymers systems studied at BNL but much better than cements or bituminous binders.

CONCLUSIONS

The FSU developed Conservant "F" as a means of providing greater protection of the environment. Given the state-of-the-art from 1965 to 1972 the Furfurol F3 was more advanced than existing systems and provided better protection of the environment, based on the rules and ideals of the time. Laboratory leach tests resulted in an effective diffusion coefficient of $2 \times 10^{-7} \text{ sec}^{-1}$ for Cs^{137} tracer which is above the USNRC requirement of $1 \times 10^{-6} \text{ sec}^{-1}$ (Leach Index>6) but below leach rates, seen at BNL, for other polymers. Of greater concern than release rates is the issue of durability. FSU research stated that Furfurol F3 is expected to be fairly durable over the long term and to have good shrinkage and thermal expansion characteristics (see Heiser, et al [7]). BNL fabricated polymer was brittle and had areas of shrinkage stress which had severe cracking when filler materials settled out. This behavior warrants further investigation. It is possible, given the temperatures (lower T = higher viscosity) in the arctic, that less settling occurred but one should assume the binder was kept at a low viscosity to allow it to flow readily into the 2 to 4 mm opening in the reactor vessel. Another difference may be in the definition of mineral fillers given to BNL by the Kurchatov researchers. During their visit to BNL the mineral filler composition was discussed and agreed upon by both sides. There may be however, slight differences in the densities of the fillers that could significantly affect the overall degree of separation between filler and binder. It may be beneficial to send a US representative to the Kurchatov to formulate some Furfurol F from Russian materials and then test those materials in the US and vice versa, to send a Russian representative to the BNL to formulate some Furfurol F from American materials and then test those materials in Moscow.

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