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## THE USE OF POLYMERS IN RADIOACTIVE WASTE PROCESSING SYSTEMS

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### ABSTRACT

The Savannah River Site (SRS), one of the largest U.S. Department of Energy (DOE) sites, has operated since the early 1950s. The early mission of the site was to produce critical nuclear materials for national defense. Many facilities have been constructed at the SRS over the years to process, stabilize and/or store radioactive waste and related materials. The primary materials of construction used in such facilities are inorganic (metals, concrete), but polymeric materials are inevitably used in various applications. The effects of aging, radiation, chemicals, heat and other environmental variables must therefore be understood to maximize service life of polymeric components. In particular, the potential for dose rate effects and synergistic effects on polymeric materials in multivariable environments can complicate compatibility reviews and life predictions. The selection and performance of polymeric materials in radioactive waste processing systems at the SRS are discussed.

### INTRODUCTION

Approximately 36 million gallons of liquid radioactive nuclear waste are now stored in 47 underground carbon steel tanks at the SRS. The waste chemistry is controlled to minimize corrosion of the carbon steel waste tanks. The waste is processed through evaporators to condense the high-level radioactive waste volume. The vast majority of the high-level waste (HLW) will be vitrified at the Defense Waste Processing Facility (DWPF) into a stable glass form with the radionuclides incorporated into the glass structure. The glass waste is melted and poured into stainless steel canisters that are stored in specific facilities (Glass Waste Storage Buildings). The DWPF is currently the largest radioactive waste vitrification plant in the world, beginning radioactive operations in March 1996 and is currently projected to produce ~6,000 canisters by year 2019.

The liquid nuclear waste in SRS tank storage exists in three forms: supernate, sludge and salt. The supernate is basically a sodium salt solution and is passed through evaporators to reduce the volume. The DWPF is designed to treat the salt and sludge from the HLW storage tanks and produce a glass that incorporates the radioactive nuclides in the stable glass structure. The sludge, which comprises ~10% of the waste volume, contains about half of the radioactivity. The salt, which readily dissolves in water, comprises about 90% of the volume and contains the balance of the radioactivity. Before being sent to the DWPF, the majority of the salt waste will be treated at the Salt Waste Processing Facility (SWPF) currently under construction at the SRS. Until the SWPF is operational, interim salt waste processing is conducted via the Modular

Caustic Side Solvent Extraction (MCU) Unit and the Actinide Removal Process (ARP) in H-Area.

Low level radioactive waste (LLW) is sent to the Saltstone facility where it is mixed with specialized grout formulations and transferred into large disposal units at the Saltstone Disposal Facility. SRS is the first site in the DOE Complex to disposition salt waste. Removing waste from the tanks will result in the permanent closure of the Site's high-level waste tanks, a high priority for the DOE.

## **POLYMERIC MATERIALS AND COMPONENTS**

The majority of process equipment in radioactive waste processing facilities is made of metal alloys and structures are predominantly made of reinforced concrete. However, as a practical matter, polymeric materials are inevitably used as seals, pump/valve components, hoses, piping/tubing, electrical and thermal insulation, personal protective/safety equipment, coatings/linings and other components. Such components are often designed for replacement, as degradation over time is expected. However, regardless of service duration, polymeric materials must meet certain requirements and exhibit sufficient resistance to the service environment. For critical service or long-life components, testing is often recommended and necessary.

Polymers are known to be sensitive to ionizing radiation. However, in many radiological applications, polymeric materials can be used, either because dose rates are sufficiently low or the exposure duration is limited thus minimizing degradation. Systems, especially those that contain polymeric materials, should be designed to allow component replacement wherever practical. However, some components must remain functional for the design life of the facility which might range from a few years to several decades. Standard vendor equipment may require modifications or upgrades, particularly for critical or safety-related systems. This paper discusses the selection, use and performance of polymeric materials in radioactive waste processing facilities at the SRS.

### **Sealing Components**

A major use of polymers in radioactive waste processing systems is for sealing components. Metal or ceramic seals may be required in some cases, but polymers are frequently used due to common design, low cost, compliance and lower sealing stresses. Most polymer sealing applications such as gaskets involve elastomers such as EPDM (ethylene-propylene diene monomer) or certain thermoplastics such as Teflon™ PTFE (polytetrafluoroethylene). Stiffer polymers such as ETFE (ethylene-tetrafluoroethylene) copolymer, UHMWPE (ultra-high-molecular weight polyethylene) or PEEK (polyetheretherketone) may be used as valve seats. Flexible graphite is not technically a polymer, but an organic material often used for gasket and seal ring applications.

In several SRS facilities (Figure 1), piping jumpers are fabricated with unique connection devices (Hanford connectors). Early wisdom by DuPont engineers at Hanford and later at SRS led to such designs to provide system flexibility and account for possible failures and equipment

replacement. The Hanford connector (Figure 2) is a stainless steel block with flow ports and a large threaded stud with an ACME nut that tightens a jaw assembly against process vessel or wall nozzles. Jumpers are lifted and moved as needed by overhead cranes and the connector is engaged by a remotely operated impact wrench.

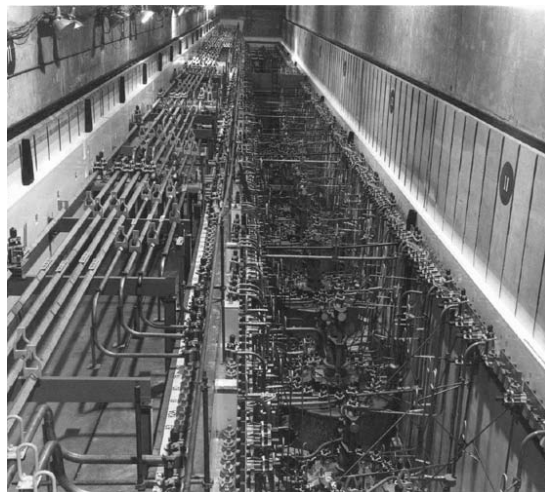


Figure 1. Canyon jumper piping, sealed with Hanford connectors and jumper gaskets



Figure 2. Hanford connector block and demo nozzle with Teflon/asbestos gasket

The SRS jumper connectors have historically been sealed with gaskets made of Teflon PTFE-asbestos fabric. The gaskets are held in place with a snap ring installed in the sealing face of the connector block. In the SRS separations facilities, process solutions are primarily based on nitric acid, thereby requiring high chemical resistance.

The original jumper gasket material was constructed of finely-woven crocidolite (Blue African) asbestos dipped with a Ludox<sup>®</sup> dispersion and blended with 30 wt% Teflon PTFE. The fabric

was then calendered and sintered. In the 1980s, the material was changed to use chrysotile (Canadian White) asbestos due to limited crocidolite availability and a decreasing number of asbestos suppliers. Teflon/asbestos gaskets are still used to seal many process jumpers at the SRS.

Teflon™ PTFE is well-known to exhibit low resistance to ionizing radiation. However, in the jumper gasket, the woven asbestos provides continuous reinforcement and durability with the PTFE binder providing sealability. The high compressive load and sealing stresses imposed by the connector also significantly contribute to gasket performance.

Over the years, different materials have been evaluated for the jumper gaskets to minimize reliance on asbestos-containing materials. However, due to the salient features required, no single commercially-available, non-asbestos gasket material has yet been found suitable. Flexible graphite is resistant to many process streams, but not to nitric acid solutions. The sealing stress imposed by the connector is quite damaging to flexible graphite and other materials, particularly where multiple uses are required. Compressed non-asbestos gaskets with EPDM binder have been successfully used in neutral or high pH service in some facilities but they cannot be used for acid service.

In many systems, Site piping codes dictate what materials are used for specific process conditions. PTFE or reinforced PTFE is typically excluded from highly radioactive solutions due to known radiation sensitivity (jumper gaskets excluded), but it is widely used in non-radioactive systems. PTFE can be used if dose rates are sufficiently low or service periods are such that radiation-induced degradation is avoided.

For acid and/or elevated temperature service in aqueous environments, FKM fluoroelastomers (Viton® or similar) are often specified. General-purpose grades (copolymer A-type) are widely used, but terpolymer grades (B, F, GF, GLT, GFLT types) may be needed for superior chemical resistance and other properties. Older compounds often contained lead oxide (litharge) as an acid acceptor, but newer formulations based on peroxide cures are superior.

FFKM-type perfluoroelastomers (Kalrez® or similar) offer the broadest range of resistance to heat and chemicals, although radiation resistance is moderate and these elastomers can be less dynamically resilient than more conventional elastomers. Thermal expansion characteristics must be considered when alternative elastomers are needed. Simply changing the seal material in a given design to improve chemical or radiation resistance can result in premature failure if thermally-induced dimensional changes are not considered. Consultation with seal manufacturers is recommended before an alternate sealing material is selected.

Neutral and alkaline waste processes tend to be less chemically aggressive than acidic solutions toward most polymers. Many of the common elastomers such as EPDM, FKM/FFKM fluoroelastomers, neoprene, butyl rubber, nitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR), CSPE (chlorosulfonated polyethylene), silicone, polyurethane and even natural rubber can possibly be used depending on specific conditions.

EPDM elastomers can provide an excellent balance of resistance to aging, chemicals, ionizing radiation and thermo-oxidative degradation within limits. EPDM is sensitive to certain chemicals, notably hydrocarbon-based fluids and certain acids (particularly nitric). EPDM is often a “preferred” elastomer for applications in contact with stainless steel due to low chloride content, reducing concerns over chloride stress-corrosion cracking. The SRS limit for chlorides in materials in contact with austenitic stainless steel at certain conditions is 250 ppm (total), which can limit material options in certain environments.

FKM elastomers have been used in alkaline service (evaporator seals) due to elevated temperature requirements but resistance to strong alkaline solutions is limited. However, newer base-resistant grades of FKM elastomers are now available when EPDM or other elastomer types are not suitable. FFKM types may be needed for higher temperatures.

Elastomers are often used to seal containment vessels in radioactive material packages. As an example, O-rings based on Viton<sup>®</sup> GLT (now GLT-S) are used to seal the stainless steel containment vessels in Model 9975 shipping packages designed for transportation of plutonium-bearing materials. Designed for transportation, robust 9975 packages are also being used for safe interim storage of Pu materials in the K-Area Materials Storage (KAMS) facility at the SRS (Figure 3). The aging behavior of the O-rings and fiberboard insulation in the packages is being studied to develop life prediction models for the storage facility [1, 2]. Polyurethane foam is also used in certain packaging designs for thermal insulation and impact protection.



Figure 3. Model 9975 shipping packages used for interim Pu storage at SRS (internal containment vessels sealed with GLT/GLT-S fluoroelastomer O-rings)

Valve seats are another application of polymers in radioactive waste processing systems. In the HLW tank storage facilities (tank farms), HLW is transferred via underground piping made of austenitic stainless steel with carbon steel jacket lines for secondary containment and leak detection. In diversion boxes (pump/valve pits), the process flow can be diverted as needed. Transfer line ball valves contain seats made of Tefzel<sup>®</sup> ETFE (ethylene-tetrafluoroethylene) copolymer (Figure 4). Carbon-graphite seats are highly resistant to the waste chemistry and radiation, but exhibited limited toughness and installation difficulty (cracking problems). ETFE seats have not been formally examined after service in HLW but have been used successfully for years.



Figure 4. ETFE copolymer ball valve seats used in HLW transfer systems

ETFE fluoropolymer valve seats are also specified for use in the Waste Solidification Building (WSB) currently under construction at the SRS. The WSB will receive and process the liquid waste generated by the Mixed Oxide Fuel (MOX) facility also currently under construction at the SRS. For the WSB facility, the combined resistance of ETFE polymer to nitric acid at elevated temperature and ionizing radiation was investigated. Cracks in a ETFE polymer sample after exposure to gamma radiation and 8M boiling nitric acid are shown in Figure 5. Moderate degradation was observed in mechanical properties after a dose of 150 Mrad (1.5 MGy) exposure, with severe embrittlement occurring at 500 Mrad (5 MGy).

In the WSB, the valve seats will primarily see alpha radiation with some beta/gamma exposure. The bulk (beta/gamma) radiation dose rate for the valve seats is estimated at 1 Gy/hr during processing, with an bounding alpha (surface) dose rate of 177 Gy/hr. Service temperatures are bounded at  $\sim 113^{\circ}\text{C}$ , with the majority of process streams being limited to  $60^{\circ}\text{C}$ . Maximum service life is desired to avoid personnel exposure and facility downtime as a result of valve maintenance. The design life of the WSB is 30 years. At 1 Gy/hr, the 30-year bulk dose to the valve seats is  $\sim 0.26$  MGy. At 177 Gy/hr (alpha), a 30-year surface dose is  $\sim 47$  MGy. This dose would principally apply to sealing surfaces subject to constant exposure.

As a result of PTFE valve seat failure in a DOE plutonium processing facility, studies were performed to show the susceptibility of PTFE polymer to alpha (heavy ion) radiation [3, 4]. These studies showed that surface doses of  $10^{10}$  rad ( $10^8$  Gy) or greater were required for significant surface degradation. Similar studies have not been performed for ETFE polymer, but similar if not greater resistance to alpha surface degradation is expected. At 177 Gy/hr, such doses will not be reached in WSB applications until approximately 65 years.

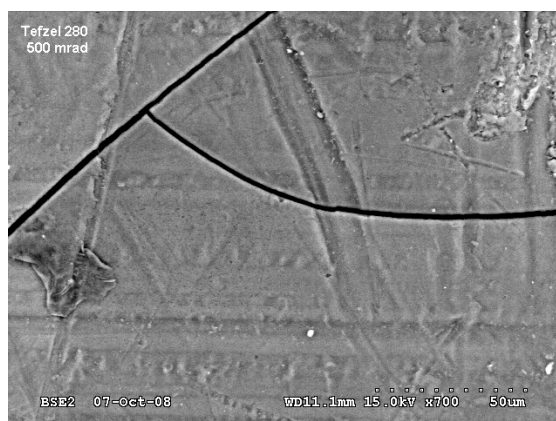


Figure 5. ETFE copolymer after irradiation to 500 Mrad (gamma)

Backflush valves used in the HLW tank farms are 3-way plug valves with carbon-graphite seats (Figure 6). These valves are operable but have posed binding problems, primarily attributed to thermal expansion issues and the two-piece seat design. Binding during operation can cause processing delays and require removal of the entire assembly from the tank and transfer to a decontamination facility for maintenance. Such efforts are obviously undesirable. ETFE and PEEK polymers were investigated as possible seat alternatives. ETFE was investigated based on successful use in HLW transfer line valves, with PEEK investigated due to known chemical, heat and radiation resistance.

ETFE and PEEK polymers were subjected to gamma radiation doses of 2 MGy and 5 MGy followed by a 14-day exposure to 50% NaOH at 142 °C. Radiation doses were selected to bound a 10-year service period. PEEK 450G showed essentially no significant change in tensile properties with only a slight color change occurring during exposure. Conversely, ETFE copolymer was significantly degraded at the prescribed test conditions. ETFE polymer may be suitable for shorter service periods or less conservative conditions, but these have not yet been evaluated. Though PEEK shows significant resistance to degradation, a limitation of PEEK in valve seat applications is its relatively high stiffness and limited compliance so functional testing was recommended. Additionally, valve redesign could possibly allow remote replacement of components, reducing the service life required.





Figure 6. Backflush valve with 3-way carbon-graphite plug seat

## Electrical Systems

Polymers are often needed in electrical systems for dielectric/insulation properties. An example is in the electrical jumpers used in several SRS facilities to carry electrical power and instrumentation signals. The jumpers use 10-40% glass-filled polycarbonate insulator blocks that isolate gold-plated connector pins in various configurations (Figure 7). Polycarbonate is used for its combined mechanical and electrical properties as well as reasonable resistance to the facility environment.



Figure 7. Electrical Jumper Connector Block (40% glass-filled polycarbonate)

Electrical cables, motors and other instrumentation in some SRS facilities are specified to meet IEEE Class 1E requirements, at least for radiation tolerance purposes [5]. Such cables (Figure 8) are typically insulated with fire retardant cross-linked polyethylene (FR-XLPE), cross-linked polyolefin (XLPO) or EPR (ethylene-propylene copolymer), with jackets made of CSPE (chlorosulfonated polyethylene), EPR, EPDM, XLPE/XLPO or EVA (ethylene-vinyl acetate) copolymer.

PVC is a common insulation, particularly in older cables or in cables used in low radiation areas, but it is not preferred due to the potential generation of HCl during radiolysis or fire scenarios. Plasticizer migration has also been observed in PVC-insulated cables. Low-halogen or zero-halogen cable insulations are now more commonly specified.

Cables with polyimide (Kapton<sup>®</sup>) or PEEK insulations are sometimes specified for high radiation resistance. Commercial nuclear-qualified cable products are typically rated to total doses of ~200 Mrad (2 MGy), which accounts for normal service dose (50 Mrad) plus the dose incurred (150 Mrad) during a LOCA (loss-of-cooling accident). Depending on the actual dose rates involved, even such ratings may not be sufficient. Shielding or other methods may be needed to reduce dose rates. It is important to note that qualification protocols for nuclear components generally involve high dose rate exposures that may or may not represent actual service conditions. Dose rate effects can influence material behavior. In addition, electrical equipment must be specified based on all relevant properties, not radiation resistance alone.



Figure 8. Class 1E nuclear cable (XLPE insulation, CSPE jacket)

An important property of amorphous polymers is the glass transition temperature ( $T_g$ ). The  $T_g$  value is the temperature at which the polymer structure transitions from elastic to rigid or “glassy” behavior, often with a change in specific volume. It is important to ensure that such temperatures are not reached within normal service, or if such transitions occur, the effects of the transition are acceptable. Studies have shown that the glass transition temperature of PEEK and other polymers can be affected by radiation and thermal aging [6]. This may also vary with the dose rate and level of oxygen in the environment.

Thermal transitions are important at both high and low temperatures. For example, the low temperature performance of elastomers is greatly dependent on the  $T_g$  value. Ideally, the  $T_g$  of elastomers should be at or below the minimum service temperature. Elastomeric seals may function at or even below the glass transition temperature, but the lower the service temperature relative to the  $T_g$  value, the more likely the performance will be affected. Therefore, the glass transition temperature of amorphous polymers, including elastomers, should be carefully considered.

### Hose-In-Hose Systems

Hose-in-hose (HIH) systems have been used for radioactive waste transfer operations at the SRS and Hanford sites. These systems are intended to provide design flexibility at lower cost than

hard-welded piping systems. These systems typically involve use of heavy-duty chemical transfer hoses made of EPDM or other elastomers, reinforced with steel wire and inorganic/polymeric fibers. Some hoses may be lined with cross-linked polyethylene (XLPE), ultrahigh molecular weight polyethylene (UHMWPE) or other polymers.

Some hose systems have been developed on-site using commercial products, while others have been developed and marketed by vendors specifically for hazardous material and radioactive waste transfer. Although such systems have been successfully used, the long-term effects of radiation, thermal aging and chemical exposure are not completely understood. Synergistic effects and dose rate effects are difficult to predict. For that reason, accelerated-aging tests and post-service examination of hoses have been recommended.

One commercial chemical transfer hose was evaluated for use as an emergency flexible HLW jumper (< 6 months service) [7]. The wire/fiber-reinforced hose with an EPDM cover and a modified XLPE liner (Figure 9) was investigated for the effects of radiation dose to 2 MGy and 50% NaOH solution at 93 °C. Over a 6 month service, the hose will likely see less than 0.50 MGy, but higher doses were evaluated for margin and to determine the hose limits. The effects of radiation at 0.5 MGy were minor, with more severe effects at higher doses. Dose rate effects were not evaluated for the short service period. The hose has not yet been put into service as a flexible HLW jumper.



Figure 9. Cross-section of chemical transfer hose evaluated for HLW transfer (steel/fiber-reinforced with modified XLPE liner and EPDM cover)

An aboveground, low-level HIH system has been used for several years at the SRS to transfer low-level HEU solutions. This system consists of the same robust chemical transfer hose evaluated above, inserted inside a larger EPDM water discharge hose. The service conditions for this hose system are less severe than evaluated for the emergency HLW jumper. The bounding radiation dose rate for the core transfer hose during transfers is ~7 rad/hr. The dose rate to a limited section of hose inside the receipt tank is 660 rad/hr. Approximately 600 feet of this HIH system has been in operation for several years without reported degradation. Post-service evaluation of the hose condition after service has been recommended.

## In-Tank Equipment

Submersible mixing/transfer pumps, tank crawlers and other equipment has been designed for operation within the HLW tanks (Figure 10). The service life range for such components can vary from a few months to several years. Internal components (such as motor insulation) will see radiation only but other components (seals) may be in direct contact with the waste, requiring resistance to the waste chemistry as well the heat and radiation involved. The radiation dose to direct contact components is likely higher due to alpha/beta contributions. Therefore, the actual dose rates to such components should be determined. Overly conservative dose rate estimates can limit material selection or complicate design efforts.

Polymers such as PTFE, acetal (polyoxymethylene), polypropylene, acrylic and butyl rubber are usually excluded due to low radiation tolerance. Polycarbonate and several other amorphous polymers are usually excluded due to limited resistance to strong alkaline solutions. PVDF (polyvinylidene fluoride) fluoropolymer is relatively resistant to radiation and many chemicals, but is sensitive to strong alkaline solutions. Fiberglass reinforcement in some materials may also be subject to attack by alkaline waste. Several elastomer types may be suitable, though EPDM elastomers are generally preferred for direct waste contact.



Figure 10. Tank crawler developed by SRNL for HLW tank cleaning

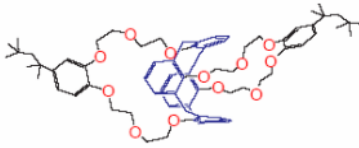
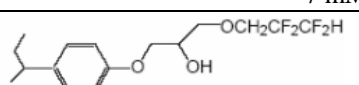

## MCU/SWPF

The SRS deploys two physical processes for decontaminating the radioactive salt solutions typical of the waste tanks: actinide and strontium adsorption on an inorganic sorbent (monosodium titanate, MST) and cesium absorption into a calixarene-crown ether molecule in a solvent extraction process using centrifugal contactors. The facility housing this operation is the Modular Caustic Side Solvent Extraction Unit (MCU).

The concentrate stream created in these processes includes caustic, radioactivity and organic from the solvent extraction. Early in MCU construction, polymeric materials were selected based on expected resistance to process conditions and commercial availability. No testing was initially performed. Polyolefins such as EPDM, UHMWPE and HDPE were initially excluded due to concerns over solvent compatibility and possible swelling (primarily due to the Isopar<sup>®</sup> L). Table 1 shows the initial CSSX composition. Testing was later performed to evaluate the

resistance of certain polymers in the MCU to the initial and improved solvent compositions. The polymers tested included Tefzel<sup>®</sup>/ETFE, Isolast<sup>®</sup> and Kalrez<sup>®</sup> FFKM, carbon-filled PEEK, flexible graphite and chlorinated polyvinyl chloride (CPVC). In those tests, only the ETFE polymer swelled slightly in the presence of the modifier.

Table 1. Initial CSSX Composition

Component	CSSX
BoBCalixC6	 7 mM
Cs-7SB Modifier	 29 wt %
TOA (trioctylamine)	 0.12 wt%
Isopar <sup>®</sup> L	Linear/branched C12 69 wt %
MaxCalix	0 wt %
LIX <sup>®</sup> 79 (Guanidine)	0 wt %

In the MCU, Kalrez<sup>®</sup> seals were found to have suffered dehydrogenation and defluorination due to exposure to caustic solution and friction heat from the shaft that drives the centrifugal contactors. This is believed to have been more of a design issue rather than a materials degradation problem. FFKM fluoroelastomers have a relatively high thermal expansion coefficient, which can cause problems with shaft seals and other applications if such behavior is not accounted for.

Another polymer used at MCU for coalescing oil carried over by the treated salt solution is nonwoven polyphenylene sulfide (PPS). PPS is an aromatic thermoplastic highly resistant to alkaline environments, non-oxidizing mild acidic environments and ionizing radiation. Literature data suggest that gamma radiation doses > 450 Mrad (~15 years service in the MCU) are required to affect performance of PPS polymer via oxidation of sulfide to sulfone or sulfoxide groups. Dose rate effects on PPS polymer in this application have not been studied, but thus far the MCU service environment has had no discernible effect on the performance of PPS polymer.

### Protective Coatings & Linings

Polymeric coatings and linings are often used in radioactive waste processing facilities to prevent corrosion, provide secondary containment and allow decontamination and clean-up. In limited cases, the linings may be required to be in direct contact with waste solutions for extended periods of time (e.g. Saltstone vault linings).

Coatings and tape wraps are used to protect buried carbon steel piping, including waste transfer jacket lines, from corrosion. Protective coating types that have been used include coal-tar emulsions, coal-tar epoxies, inorganic zinc with hydrophobic powder, epoxy-phenolic, extruded polyethylene, copolymer tape-wraps, and bituminous coatings with asbestos felt and kraft paper. Coal-tar epoxy coatings have been used successfully for years for below-ground piping protection. Epoxy-phenolic coatings with micaceous iron oxide are now more commonly specified due to health concerns related to coal-tar epoxy application. Stainless steel waste transfer lines and below-grade process piping in the WSB facility were recently coated with epoxy-phenolic (Figure 11).

A primary limitation of coatings is that performance is strongly dependent upon proper selection, substrate preparation and application. Even the most robust coating can fail if improperly applied. Failure of a carbon steel waste transfer jacket line attributed to adjacent steam leaks and coating degradation is shown in Figure 12 [8].



Figure 11. WSB process drain piping coated with epoxy-phenolic



Figure 12. Carbon steel waste transfer jacket line failure due to coating degradation



Secondary containment linings are used in radioactive waste processing facilities to provide containment in the event of a catastrophic break, protect the substrate from degradation and facilitate decontamination. Linings should be selected based on bounding anticipated exposures even though the lining may never be challenged. Many factors should be considered, primarily the process chemistry (including possible decontamination agents), solution temperature, radiation resistance, UV light resistance, duration of exposure, equipment traffic and access for inspection/repair.

Secondary containment linings generally fall into two categories: liquid-applied systems and sheet linings. Liquid-applied systems usually consist of epoxy, novolac epoxy, elastomeric polyurethane, polyurea and vinyl ester systems. Within each general polymer type, the formulation and properties can vary significantly. Linings may be mat-reinforced or non-reinforced systems, varying in thickness. Vinyl ester linings are generally limited to facilities handling strong caustic or nitric acid solutions. Linings may also contain graphite or other low surface-energy additives to facilitate decontamination. Flexible base layers may be needed for crack-bridging capability. Moisture vapor barrier systems are highly recommended below containment linings, particularly if below-grade, to prevent failure due to moisture vapor transmission.

Sheet linings may be adhesive-bonded, hot-air welded or loose laid systems that are mechanically fastened. Material options consist of thermoplastics such as HDPE or PVC or elastomers such as EPDM, EVA or CSPE. Containment linings should be installed by qualified and experienced applicators, with appropriate inspection hold points.

Radiation resistance is usually not the most critical aspect for secondary containment linings but it should still be considered. The dose to the coating/lining system during normal service plus any off-normal events should be determined. Most thermosetting polymers are relatively resistant to radiation. As an example, certain coatings used in nuclear power plants are qualified to 1000 Mrad (10 MGy) at very high dose rates per ASTM D4280 [9]. However, coatings with this pedigree may not be suitable for radioactive waste/material processing environments and many containment linings for chemical service have not been tested to this standard. Dose rate effects in coatings have not been widely studied. Therefore, actual service conditions should be reviewed.

In DOE nuclear facilities, coatings and linings may be required to meet NFPA 801 [10]. This standard requires that interior wall and ceiling finishes have Class A flame spread ( $\leq 25$ ) and smoke development ratings ( $\leq 450$ ), as tested per ASTM E84 (or NFPA 255). Floor coatings must have Class I critical radiant flux (CRF) values ( $\geq 0.45 \text{ W/cm}^2$ ) as tested per NFPA 253 (or ASTM E648).

Unfortunately, many coatings have not been tested to these standards, with even fewer systems tested to the floor requirements, as such requirements were initially developed for floor covering materials. Therefore, facility owners, design engineers, architects, fire protection and coatings/materials engineers should discuss requirements before selecting a coating/lining system. If NFPA 801 compliance is required and a compliant coating cannot meet all other requirements, testing of alternate coatings is required. Recently, a major coatings manufacturer

and strategic supplier at the SRS had several coatings tested to meet NFPA 801 requirements for site projects.

#### Safety/Contamination Control

Polymers are widely used for contamination control and personal protection during maintenance or decommissioning activities. Personal protection equipment includes plastic suits, respirators, safety glasses and other safety-related items. The SRS containment fabrication group uses huts, windbreaks, tarps, and covers constructed from PVC-laminate material with a woven nylon scrim. Glovebags, catch containments, and containment huts are custom made of PVC, polyurethane or nylon 6+6 copolymer material depending on service conditions (Figure 13).

Polyurea coatings and other types have been used to fix contamination in place and to “rollback” previously contaminated areas (Figure 14). Though such activities have been successful, surface preparation is often limited or restricted. A limitation of fast-cure coatings such as polyurea is that rapid curing may not result in good adhesion. Early marketing claims and misapplication of such coatings have led to site and industry failures. These issues have largely been resolved by formulation changes, the use of primers and renewed emphasis on adequate surface preparation.



Figure 13. Fabricated containment hut at SRS Containment Fabrication Facility



Figure 14. Polyurea coatings applied on tank tops for contamination control



## Radiation Data Limitations

A challenge in evaluating the radiation resistance of polymers is that most historical data from the 1950s to the 1970s came from very high dose rate exposures. Polymers are now known to be potentially sensitive to the dose rate, thus complicating service life predictions. Predictions based on high dose rate exposures have often been shown as non-conservative.

One of the first industry examples of this behavior was observed in the SRS K-reactor in the mid-1970s [11]. PVC/polyethylene insulated cables qualified for service based on high dose rate data were found to be significantly degraded after only 12 years at much lower dose rates. Subsequent testing confirmed that dose rate effects were significant. Such effects are generally attributed to diffusion-limited oxidation but variation in degradation mechanisms can also occur. This observation led to many investigations into the potential for dose rate effects in nuclear cable insulations and other components [12]. As a result, nuclear qualification protocols now acknowledge the potential for dose rate effects. Condition monitoring programs are often implemented to address limitations of accelerated-aging test methods.

Dose rate effects are likely less important for components that can be readily replaced or those that only need to function for short periods. Dose rate effects are also likely less critical in non-oxygen bearing environments but oxygen is difficult to completely exclude. For critical or long-life components, particularly those in oxygen-bearing environments, dose rate effects should be evaluated and testing may be required. The effects of temperature and other variables should also be considered.

Another limitation is that literature data often quote damage threshold values for various polymers and properties (ex. dose to cause 25% change in elongation). These values allow comparison of materials at the same level of damage, but they are not very useful for service life prediction. Such values are arbitrary and the properties evaluated may not be the most relevant for a specific application. In many cases, the dose to failure or unacceptable performance for specific components is unknown.

## Chemical/Thermal Data Limitations

Chemical resistance data from polymer/component manufacturers and general literature sources are often sufficient to determine compatibility. However, not all chemicals have been widely studied and there are several aspects to consider when interpreting such data. Compatibility data are often based on relatively short-term exposures to “pure” chemicals of specific concentrations at certain temperatures. While such data might rule out highly incompatible materials, prediction of long-term effects of the same chemical (or mixtures) at different concentrations and/or temperatures is complex. Service history may be sufficient to determine compatibility, if similar conditions are anticipated.

Chemical compatibility should not be based solely on the primary waste stream components. Even minor constituents in the process can affect material performance. An example is tributyl phosphate (TBP), an ester of orthophosphoric acid, which is present in certain systems. The presence of TBP in a process stream, even in low concentrations, may lead to polymer

degradation. TBP is used for many purposes including anti-foaming and solvent extraction but it is also a strong polar solvent used in the production of many synthetic resins and as a flame-retarding plasticizer. FKM fluoroelastomers are acid-resistant, but they are sensitive to TBP. Conversely, EPDM seals are very resistant to TBP but have limited acid resistance. For combined acid/solvent resistance, FFKM perfluoroelastomers may be required. The presence of TBP is known to have caused significant damage to CPVC piping in one SRS facility. Therefore, the compatibility of all constituents in a process stream should be evaluated.

Thermal aging data also have significant limitations. An example is the use of “continuous” service temperatures. Such limits are often based on undefined criteria and limited time periods that may not match service conditions. Most polymers are susceptible to oxidation, which is a diffusion-related process. The consumption of antioxidants over time is another mechanism that can result in premature failure. Even accelerated-aging tests at elevated temperature can overlook such mechanisms and produce non-conservative life estimates.

The general upper service limit for FKM fluoroelastomers is often quoted as 204 °C. Seal manufacturers typically base this temperature on the near-complete loss of sealing force as measured by compression stress-relaxation (CSR) behavior after 1000 hours or similar data [13]. Depending on the seal design and service conditions, this level of relaxation may still be acceptable but the seal is no longer pushing back against mating surfaces. Therefore, such thermal ratings should not be interpreted as applicable for longer time periods.

For example, SRS testing of GLT-based fluoroelastomer seals has shown that leakage failure ( $>1\text{E-}07$  cc/sec ref) can occur in a specific radioactive material packaging design after aging at 177 °C for less than 1 year and at 149 °C in 2.8 years [2]. No leak failures have yet been observed after ~6 years at 93 °C, which is bounding for the service environment. Accelerated-aging tests using time-temperature superposition techniques predict several decades of service life at realistic service temperatures. However, in other applications, seal life could be significantly reduced, even if technically below the “continuous” service limit. Thermal limits may also be reduced by radiation or chemical effects.

## Summary

As a practical matter, polymeric materials are inevitably used in radioactive waste processing systems and facilities. Polymers can be successfully used within their limits but resistance to all potential environmental factors must be evaluated. A primary limitation of polymers is their relative susceptibility to damage by ionizing radiation. Dose rate effects can significantly reduce service life compared to predictions based on high dose rate data. In chemical environments, even minor process constituents can lead to unexpected degradation. The use of “continuous” thermal limits based on short-term data should be viewed with caution. Material selection should therefore be carefully reviewed. For critical, long-term or difficult to replace components, testing may be needed to verify compatibility or for service life prediction.

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