

# ***Corrosion-Resistant Coatings for Mitigation and Repair of Spent Nuclear Fuel Dry Storage Canisters***

**Spent Fuel and Waste Disposition**

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***A. Knight, R. Schaller, C. Bryan, T.J.  
Montoya, A.M. Parey, J. Carpenter, M.  
Maguire  
Sandia National Laboratories***

***K. Ross  
Pacific Northwest National Laboratories***

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Prepared by  
Sandia National Laboratories  
Albuquerque, New Mexico 87185 and Livermore, California 94550

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## **SUMMARY**

This report summarizes the results of a literature survey on coatings and surface treatments that are used to provide corrosion protection for exposed metal surfaces. The coatings are discussed in the context of being used on stainless steel spent nuclear fuel (SNF) dry storage canisters for potential prevention or repair of corrosion and stress corrosion cracking. The report summarizes the properties of different coating classes, including the mechanisms of protection, their physical properties, and modes of degradation (thermal, chemical, radiological). Also discussed are the current standard technologies for application of the coatings, including necessary surface pretreatments (degreasing, rust removal, grinding) and their effects on coating adhesion and performance. The coatings are also classified according their possible use for in situ repair; ex situ repair, requiring removal from the overpack; and ex situ prevention, or application prior to fuel loading to provide corrosion protection over the lifetime of the canister.

The coating classes evaluated include polymers, ceramics, conversion coatings, along with details on cold and thermal spray techniques. Polymers, ceramics, and conversion coatings have only previously been used as preventative coatings but are evaluated here for possible use as repair technologies, capable of sealing and stifling stress corrosion cracks, as well as for use as preventative coatings. Several polymer class coatings are identified for possible use on SNF dry storage canisters, as prevention or possible repair technologies. Some ceramic and conversion coatings have also been identified for possible use as preventative coatings, or as undercoats for polymer coatings to improve corrosion resistance and adhesion to the stainless steel. Potentially useful candidates include the following:

- **Polymer coatings**
  - Epoxies
  - Polyethylene
  - Rubbers
- **Ceramic coatings**
  - Sol-gels
- **Conversion coatings**
  - Phosphate conversion coatings

Cold spray metal coatings also represent a promising technology and are discussed and compared to the other coating classes in this report. However, cold spray coatings are currently being evaluated as part of another work package as well as through the DOE funded Nuclear Energy University Program projects, so they are not included within preliminary testing proposed herein.

Finally, a preliminary test plan for evaluation of the selected coatings is presented. Testing will evaluate coating properties and adhesion under canister-relevant conditions, coating thermal and radiation degradation, and coating performance in corrosion tests, as a function of coating composition, application methodologies, and substrate state including various surface finishes for pristine versus pre-corroded stainless steel substrates. Specifically, coating characterization studies will include:

- **Adhesion testing**
- **Thermal degradation and thermal cycling analyses**
- **Radiation degradation testing**
- **Permeability testing**
- **Corrosion testing** (including accelerated testing conditions and long-term, canister-relevant conditions)

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## ACRONYMS

ALD	atomic layer deposition
CISCC	chloride induced stress corrosion cracking
DCSS	dry cask storage system
DPA	displacements per atom
EPP	epoxy-3-phenoxypropane
EPRI	Electric Power Research Institute
HAA	hydroxyacetanilide
HVOF	high velocity oxygen fuel spray
IBAD	ion beam alumina deposition
ISFSI	independent spent fuel storage installation
LPCS	low pressure cold spray
MOCVD	metal organic chemical vapor deposition
NEUP	Nuclear Energy University Programs
NMP	N-methyl pyrrolidone
PE	polyethylene
PNNL	Pacific Northwest National Laboratories
PVC	polyvinyl chloride
PVDF	polyvinylidene difluoride
RH	relative humidity
RPM	rotations per minute
SEM	scanning electron microscope
SNF	spent nuclear fuel
SNL	Sandia National Laboratories
SS	stainless steel
TEM	transmission electron microscopy
TRL	technology readiness level
UV	ultra-violet
VCD	vinyl cyclohexene dioxide

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# **SPENT FUEL AND WASTE SCIENCE AND TECHNOLOGY**

## **CORROSION-RESISTANT COATINGS FOR MITIGATION AND REPAIR OF SPENT NUCLEAR FUEL DRY STORAGE CANISTERS**

### **1. INTRODUCTION**

#### **1.1 PROJECT BACKGROUND AND PURPOSE**

Spent Nuclear Fuel (SNF) poses a hazard to the health and safety of the environment it is in, and to the surrounding population. To store it safely, SNF is currently deposited in dry cask storage systems (DCSSs) at Independent Spent Fuel Storage Installations (ISFSIs) at various locations across the United States [1]. These DCSSs consist of a basket containing SNF assemblies, packed into a stainless steel (SS) canister roughly 6 ft in diameter and 20 ft in length, including neutron absorbers and other structural components. This canister is fitted into a concrete overpack for storage with vents for air flow that passively cools the SS canister. A diagram of a vertical DCSS is shown in Figure 1. Over time, chloride-induced stress corrosion cracking (CISCC) has become a concern on the SS canisters, which can lead to early or unexpected penetration of the canister and increased risk of exposure.

To extend the safe lifetime of existing canisters, this study explores strategies to mitigate and prevent CISCC. This document presents the results of a literature survey on possible technologies, and then down-selects among those technologies the coatings of highest current interest, based on their properties, degradation resistance, and technology readiness level (TRL) for canister application. This is followed by the development of a preliminary test plan for work to be carried out at Sandia National Laboratories (SNL) to evaluate those techniques for use on SNF dry storage canisters. The primary focus will be on corrosion prevention coatings and possible use of coatings to stifle growth of existing SCC cracks; peening or burnishing techniques that rely on mitigation of weld residual stresses are not considered. Moreover, metallic spray techniques such as thermal or cold sprays are discussed but will not be included in the experimental matrix. These technologies are currently under evaluation by several different Nuclear Energy University Program (NEUP) projects, and as part a separate collaborative project between SNL and Pacific Northwest National Laboratories (PNNL). Finally, SNL is assisting Electric Power Research Institute (EPRI) in evaluating potential mitigation and repair techniques, including some coatings. The SNL test matrix has been selected to complement the technologies that will be tested by EPRI rather than duplicating that work.

#### **1.2 PROJECT CONSTRAINTS**

##### **1.2.1 Environment**

The vast majority of ISFSIs are co-located with the nuclear power stations that generated the SNF, and hence, are dispersed across the entire United States (Figure 2). Many are located in near-marine settings, where potentially aggressive chloride-rich corrosive environments are more likely to be encountered. For this reason, many of the corrosion protection strategies explored in this study were developed for use in marine and near-marine atmospheric conditions that can lead to CISCC. Corrosion prevention strategies that work in marine atmospheric environments are likely to also be very effective in the generally less aggressive terrestrial atmospheric environments.

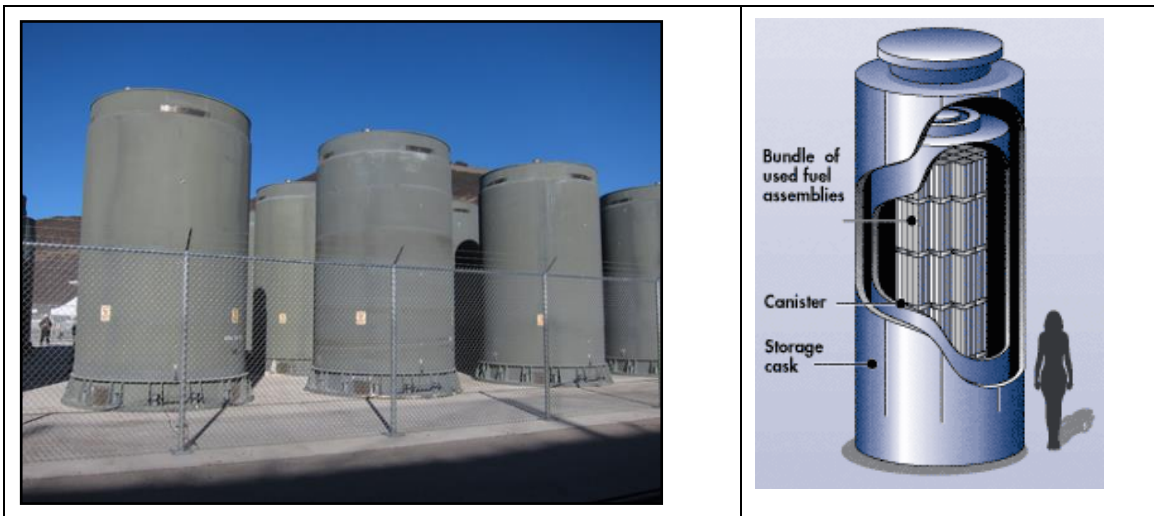


Figure 1. Left: DCSSs at the Diablo Canyon ISFSI (photo, C.R. Bryan); Right: diagram showing the internal structure of a DCSS including the SNF and the SS containment canister within an overpack [2].

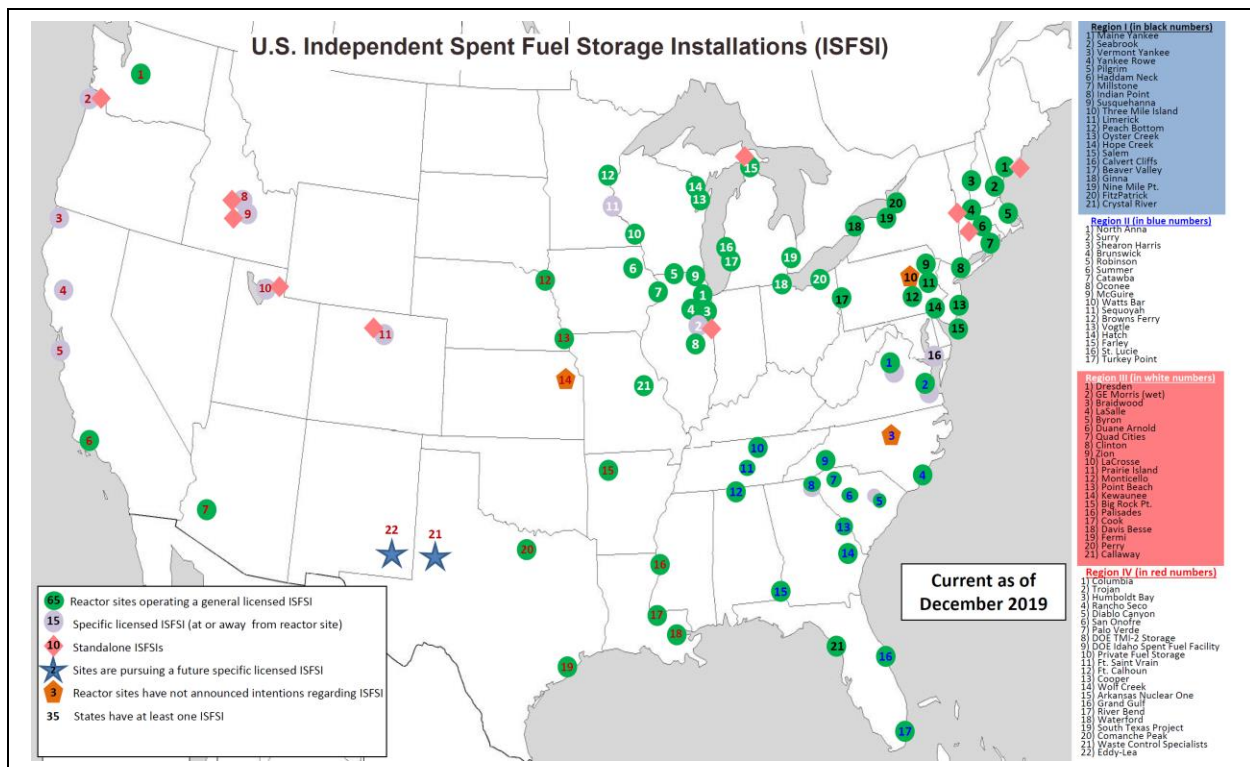


Figure 2. Map showing the ISFSI sites in the United States [3].



Marine atmospheric environments are characterized by chloride-rich aerosols and salt particulates suspended by wind which may deposit onto the storage canister surfaces as air is drawn through the passively ventilated storage systems. Canister surface temperatures are initially too hot to allow stable brine formation – therefore the surface remains dry and the risk of corrosion is very low. However, as the canisters cool over time, the surface relative humidity (RH) increases until the salts deliquesce, forming aggressive chloride-rich solutions on the canister surfaces that can result in pitting, and eventually, possibly stress corrosion cracking (SCC) of the steel. Based on the deliquescence behavior of sea-salts, observed RH thresholds for corrosion, and measured ambient absolute humidity ranges at ISFSI sites, this will occur somewhere below 60°C, although the actual value may be significantly lower. Hence, if a corrosion protection strategy is intended to be implemented as a mitigation or preventative coating during canister manufacturing, it must be able to withstand the initial high temperatures (possibly 200 °C or higher<sup>1</sup>) to which a DCSS will be exposed [4]. If that coating is intended to be implemented as a repair or mitigation strategy after initiation of corrosion, the temperature requirements will be much lower.

Three conditions must exist for CISCC to occur: tensile stress, corrosive environment, and susceptible material. Most coatings work to remove the corrosive environment, by isolating the metal surface from exposure to aggressive chemistry, either functioning as physical barriers or corrosion inhibitors. As a repair technology, cold spray works differently, attempting to seal (or completely excavate and fill) existing cracks, and to modify the metal surface, relieving stresses and potentially modifying the metal composition or mineralogy to make it less susceptible to further cracking.

### 1.2.2 Corrosion Coating Classes

Four separate classes of coatings will be discussed in this report: **polymer coatings**, **ceramic coatings**, **conversion coatings**, and **spray coatings**. Each coating class has its own advantages and disadvantages, which will be assessed by a detailed evaluation of specific coatings from each class. The overall trends within a coating class and their potential effectiveness for application on DCSSs at ISFSI sites exposed to various environmental conditions will be determined.

### 1.2.3 Corrosion Coating Implementations

Coatings within each class are assessed, based on practicality and ease of application, in the context of three different implementations, designated as **in situ repair**, **ex situ repair**, and **ex situ prevention**. For **in situ repair**, possible coatings are those that can be applied without removing the canister from the overpack, via equipment inserted through the inlet or outlet vents. These types of coatings can be applied and reapplied with minimal operational costs and would be ideal for this application. Additional consideration will be taken during the testing plan stage with regards to in situ implementation. This is currently termed as in situ repair; however, coatings will be evaluated both for repair and prevention. Further development of canister NDE techniques are necessary to be able to deploy in situ prevention techniques as the current technologies are incapable of fully assessing corrosion damage.

**Ex situ repair** coatings are those that can be applied to existing canisters but that would require the removal of the canister from the overpack and potentially transport to a nearby controlled environment. Disadvantages of this type of implementation are the increased cost of applying the coating in terms of both time and capital, but also increased worker dose, the potential for accidents, and possible releases during the application process. A more robust coating or a self-healing coating may also be necessary to mitigate possible damage during canister movement. One advantage of this type of implementation is that access to the canister surface is much greater, allowing a larger variety of coating application techniques and more

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<sup>1</sup> Canisters are likely to encounter the highest surface temperatures when they are loaded into unventilated transfer casks for transport to the ISFSI and placement into storage overpacks. These temperatures have never been estimated. However, modeling by PNNL of a specific cask at Catabwa (heat load 26.4 kW) indicated that canister wall temperatures at the initiation of storage were as high as 199 °C. A second calculation using the design basis heat load of 35.5 kW indicated a maximum wall temperature of 242 °C. These models are described in Fort et al. (2016), but the temperature data are not presented there [4]. Instead, they were extracted from the model results.

complete, potentially edgeless coatings. Moreover, because of the ex-situ condition, the extent of canister corrosion can be assessed more thoroughly, and cleaning and preparation of the canister surface for coating application will be simpler.

**Ex situ prevention** coatings are those that must be applied during manufacturing of the canister. They are designed to stop CISCC from the very beginning. This includes many strategies that require baking, high temperature curing, or any other process that requires very precise control of the surrounding environment. There are few exceptions for coatings applied to canisters prior to being filled, although in general most require ex situ application and curing at specific temperatures. Achieving these conditions is not feasible to apply to existing containers but can still be considered for new DCSSs. Application prior to loading allows greatest access to the canister surface and allows greatest control of the environment during application; it also removes worker dose considerations. However, coatings applied prior to loading must withstand the high temperatures associated with the SNF loading and drying process and the early storage period and must be robust enough to withstand potential mechanical impacts or scrapes during canister filling and transfer operations.

A summary of the coating implementations is given in Table 1. Note that in this document, the coatings are presented according to the class of coating (i.e. **polymer coatings**) rather than the potential implementation condition (i.e. **in situ repair**). Within the classes, the potential use for the different possible implementations is discussed. Within any class, different coatings may require different implementations. For example, a high-performing coating that must be applied through chemical vapor deposition would not be useful as an in-situ repair coating but may be an ideal ex situ prevention coating. While reading the report, each coating should be considered as it applies to all three possible implementations.

### 1.3 COMPARING CORROSION PROTECTION STRATEGIES

To evaluate the effectiveness of different coatings for corrosion protection, it is important to understand how each coating meets the requirements in Table 1. We will evaluate individual members from each class based on the following attributes:

- **Corrosion Protection Mechanism:** It is important to know specifically how a strategy protects the surface of the metal from corrosion. For each class, a general mechanism may be determined, but within that class, there may still be outliers or secondary mechanisms that will be discussed.
- **Coating Properties:** The following properties are discussed for the different members of each class. Changes in properties due to thermal, chemical, or radiation degradation are discussed where appropriate. Finally, common failure modes and their impact on the corrosion environment (e.g., delamination resulting in the creation of a crevice on the metal surface) are discussed.
  - **Adhesion properties:** It is important to know about the strength of adhesion of the coating, and if the coating may lose adhesion under specific circumstances.
  - **Permeability:** It is important to know what the surface will be exposed to under the coating. Some coatings allow for species to diffuse through while others act as diffusion barriers. Permeability can lead to continued corrosion under a coating and/or to hydration of the coating leading to degradation or disbondment and exposure of the underlying metal surface.
  - **Mechanical robustness:** The mechanical toughness of the coating is important if the coating is under consideration for initial application or if the canister must be removed from the overpack. In that case, the coating must hold up well to impact or abrasion.

**Table 1. Summary of Coating Implementations and Required Coating Attributes.**

<b>Coating Type:</b>	<b>In-Situ Repair</b>	<b>Ex-Situ Repair</b>	<b>Ex-Situ Prevention</b>
<b>Summary:</b>	Coating applied to existing canisters without moving the canister	Coatings applied to existing canisters after removal of the overpack and/or moved to a controlled environment	Coatings applied to new canisters to prevent corrosion that has not yet occurred
<b>Pros:</b>	<ul style="list-style-type: none"> <li>• Remote robotic application with simple technique only</li> <li>• Lower cost compared to ex-situ repair</li> </ul>	<ul style="list-style-type: none"> <li>• Increased access for surface preparation/ inspection/monitoring</li> <li>• Controlled environment</li> </ul>	<ul style="list-style-type: none"> <li>• Increased access for surface preparation/ inspection/monitoring</li> <li>• Increased control over application environment</li> <li>• No dose risk during application.</li> </ul>
<b>Cons:</b>	<ul style="list-style-type: none"> <li>• Poor access for surface preparation/ inspection/monitoring</li> <li>• Poor information about surface environment</li> </ul>	<ul style="list-style-type: none"> <li>• Higher cost compared to in-situ coatings</li> <li>• Dose, handling risks associated with moving full canister</li> </ul>	<ul style="list-style-type: none"> <li>• Coating must be thermally stable</li> <li>• Increases capital cost of DCSS with tradeoff of possible lower maintenance costs</li> <li>• Chance of damaging coating during loading operations)</li> </ul>
<b>Shared Required Attributes:</b>	<ul style="list-style-type: none"> <li>• Offers long-term protection from corrosion/CISCC</li> <li>• Mechanically tough enough to withstand some physical damage</li> <li>• Easy to monitor and reapply if necessary</li> <li>• Adherent enough to stay on the canister despite disturbances/degradation</li> <li>• Resistant to radiation</li> <li>• Chemically stable in relevant environments</li> <li>• Thermally stable within an appropriate range and across gradients in T</li> <li>• Affordable</li> <li>• TRL sufficiently high to be applied confidently</li> <li>• Ability to seal existing SCC cracks</li> </ul>		
<b>Unique Required Attributes:</b>	<ul style="list-style-type: none"> <li>• Requires only minimal surface treatment (e.g. cleaning only)</li> <li>• If applied as a local patch, minimal edge effects</li> </ul>	<ul style="list-style-type: none"> <li>• Requires minimal surface treatment</li> <li>• Minimal edge effects</li> <li>• Resistant to physical damage during canister handling</li> </ul>	<ul style="list-style-type: none"> <li>• Withstand high temperatures during loading (200 °C or higher)</li> <li>• Resistant to physical damage “wear and tear” from both shipping and handling</li> </ul>

- Chemical resistance: Some coatings may react with chemical species in the exposure environment. Possible coating degradation in the presence of relevant marine or terrestrial salts will be examined.
- Radiation resistance: Because DCSSs emit radiation, it is important that the coating be resistant to ionizing radiation.
- Common failure modes: Common failure mechanisms for each coating are identified, and the impact on the corrosion environment discussed.
- Application Requirements
  - Surface preparation/treatment: Many corrosion coatings require specific surface preparation to ensure their optimum properties are obtained. The extent of the surface preparation required will strongly affect the usefulness of coatings for application to dry storage canisters.
  - Method of Application: The process of applying the coating is the primary determinant of which implementation the coating can be used for. This report will evaluate how each coating is applied and describe special considerations, such as possible application to an existing crack for repair, or possible edge effects if the coating is applied only locally.
  - Reapplication: Many coatings degrade over time and may eventually require reapplication. It is important to know if reapplication is necessary, and if so, how frequently it must be done. Additionally, the presence of an existing degraded coating on the surface may affect subsequent coating properties such as adhesion, requiring removal of that coating prior to reapplication. These and other considerations for reapplication will be considered.

## 2. CORROSION COATING CLASSES

### 2.1 POLYMER COATINGS

Polymer coatings are composed of large-molecule materials made of repeating (usually organic) units. The identity of the repeating monomer unit and the number of repeating units determines the ultimate molecule length, the necessary processing conditions, and much of the mechanical and chemical properties of the coating. Because of their versatility, polymer coatings such as epoxies, polyvinylidene difluoride (PVDF), graphene enhanced epoxy coatings, polyurethane coatings, polysiloxane coatings, polyethylene (PE) coatings, alkyd coatings, polyvinyl chloride (PVC), polyester coatings, and rubbers are widely used in various environments to prevent corrosion [6-12].

#### 2.1.1 Corrosion Protection Mechanism

The corrosion protection mechanism for polymer coatings is primarily due to the ionic resistance of the coating and/or by creation of a physical barrier to protect the surface from corrosive species [13]. The mechanisms by which each coating protects against corrosion vary, from acting as a physical barrier to limiting the ion current by preventing specific ion transfer. Polymer coatings, such as epoxy, polysiloxanes, polyethylene, PVC, polyesters, and rubbers all act as physical barriers between a metallic surface and the environment. Of these, PVC and rubbers are applied in relatively thick, durable layers that prohibit exposure of the surface to corrosive agents, such as brines, which typically form on the surface in marine and near marine atmospheric exposure conditions. On the other hand, alkyd paint coatings, which are oil-based paints that dry via solvent evaporation and cure via oxidation, uniquely combat corrosion by limiting the maximum ionic current passed, as these coatings have a very high ionic resistance [14]. Most polymers form an impermeable barrier for protection, including common air-dried epoxies [11], PE [12], PVC [9], polysiloxanes [7], polyesters [8], and rubber coatings [10]. While physical barrier strategies for corrosion prevention are successful if the coating is applied evenly and uniformly, these coatings are vulnerable to localized corrosion where heterogeneities exist. These strategies can become susceptible to crevice corrosion at areas of disbondment or at the edges of the application zone [15]. Additionally, permeability of the coatings increases over time, and may become significant, depending upon the longevity of the coating.

The primary mode of degradation for the majority of polymer coatings is blistering [13, 16]. Blistering is a result of high osmotic pressure at the metal coating interface, caused by either surface contamination or buildup of corrosion product underneath the coating from active corrosion. Blistering is not just a result of diffusion through the coating but can also be caused by swelling of the coating from water uptake. Swelling can lead to loss of coating adhesion and cracking, thus providing direct pathways for corrosive species to the metal surface. This can be avoided by limiting the rate of transfer of corrosive species through the coating or limiting the water uptake within the coating. Both strategies vary as a function of permeability and hydrophobicity and are frequent areas of study within the polymer coatings literature.

The major benefits of polymer coatings are the broad industry experience in their use and ease of application—many can be applied in situ with minimal surface preparation. Their detailed properties will be discussed in the subsequent sections, but specific concerns for polymer coatings include the following; 1) temperature of application as concerns for thermal degradation arise; 2) adhesion properties and longevity, especially with respect to blistering; and 3) while application methods are simple, development and reliability of brush techniques as well as the use of patch coating will need further exploration prior to canister application. In summary, polymer coatings provide a low cost, versatile coating option; however, they may present concerns with longevity under canister relevant conditions.

## 2.1.2 Properties

### 2.1.2.1 Adhesion

The presence of existing surface contamination, including corrosion products, can greatly affect adhesion properties of a polymer coating. Coatings that adhere to existing corrosion products can easily break away from the surface of the base metal, leaving behind the bare unexposed steel. Both Alkyd paints and graphene-enhanced epoxy coatings adhere well to rust, so the adhesion properties are dependent on the degree of surface contamination [14]. For alkyd paints and PVC, chemical surface pretreatments, including simple cleaning with acetone or more advanced chromium or phosphate pretreatments (to be discussed later in conversion coatings, 2.4), can be applied to improve adhesion.

The texture of a SS surface also plays a significant role in the adherence of coatings and whether pretreatment is required. Some polymer coatings, such as PE and PVDF coatings, require a surface polish to improve adhesion. For PE, the required surface finish has been observed to be at a minimum, a near mirror finish with 1200 grit (equivalent to an average surface roughness ( $R_a$ ) of  $0.02 \mu\text{m}$ ) Graphene-enhanced epoxy coatings bond better with rough surfaces, eliminating the need for additional polishing; however, the surface should still be free of all corrosion products. Coatings such as fluoropolymers, polyurethane, and rubbers adhere better to rough surfaces, and surface polishing is not recommended. Special concerns for air-dried epoxies and polyesters include temperature sensitivity due to thermal degradation (polyesters) or delamination if the temperature decreases below the glass transition temperature,  $T_g$  (air-dry epoxies) [17]. In summary, polymer coatings generally require at a minimum, the removal of surface contamination. For PE a smooth finish is required, while for graphene-enhanced epoxy, PVDF, polyurethane, and rubbers the surface should remain rough. For polysiloxanes, PVC, and alkyd coatings, pretreatments, including primers and functional groups, need to be applied to enhance adhesion. Finally, air-dry epoxies and polyesters can exhibit deteriorated adhesion with changes in temperature.

### 2.1.2.2 Permeability

Almost all organic polymer coatings exhibit some level of permeability. Permeability of polymer coatings can be discussed with respect to two different mechanisms; first, there is the ability of the coating to take up water or swell (moisture absorption) and second, the permeability of gasses or vapors through the coating (water vapor,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , etc.). These parameters are influenced by both the charge of the monomers within the coating and the tortuosity of the diffusion pathways through the coating. With respect to corrosion protection, both can play a role, either serving to control transport of aqueous species to the metal surface for corrosion to occur, or transport of reactants, such as  $\text{O}_2$ , for corrosion to occur. In addition, moisture absorption can lead to volume changes in the coating, decreasing adhesion due to swelling or shrinkage, thus further enhancing corrosion pathways and creating possible crevice corrosion scenarios. The ability of a polymer to crosslink can improve (reduce) its permeability by changing the diffusion pathway; for example, a highly crosslinked epoxy-polyamide exhibits less diffusion pathways than a linear thermoplastic polymer [18]. Moisture cured polyurethane, after solvent evaporation displayed enhanced crosslinking with the addition of nitrogen-, carbon-, or oxygen-terminated monomers, thus limiting diffusion [19]. Building up layers of polymer coatings can also help aid in barrier protection and reduce permeability, however, in some cases, thicker coatings can lead to cracking and thus reduce corrosion resistance by providing a direct pathway for corrosive species to interact with the surface. Recent research has focused on ways to reduce polymer permeability, including the introduction of additives to reduce the transport of reactants ( $\text{O}_2$ ,  $\text{H}_2$ , etc.) to the metal surface. For example, one study found that the introduction of inorganic nanolayers of clay into siloxane-modified epoxy could reduce the permeability from 150 to 58  $\text{g}/\text{m}^2\text{h}$  and water uptake from 2.78 to 0.86 wt% [20]. A similar effect has also been observed for other polymer coatings, including alkyd paint coatings, in which permeability was reduced by roughly 30% [21]. Various authors have shown that the addition of  $\text{TiO}_2$  nanoparticles reduces permeability in alkyd coatings [22-24]. Other additives, such as horizontally-oriented graphene sheets added to epoxy have also been shown to increase hydrophobicity and decrease permeability [25]. Another technique employed to reduce the overall



permeability of polymer coatings is to enhance the hydrophobicity (decrease wettability) of the coating. PVDF coatings have displayed enhanced hydrophobicity with the addition of fluorinated ethylene propylene, showing an increased water contact angle for wetting from 130° to 160° [26]. Overall, the ability to engineer and control the permeability of polymer coatings has been widely studied. Enhanced crosslinking and additional additives can increase diffusion pathways and hydrophobicity, thus reducing permeability. However, prior to canister application, a thorough understanding of the combined effects of thermal, radiation, and general corrosion degradation on a coating's permeability would be necessary.

### **2.1.2.3 Mechanical Robustness**

In general, polymer coatings offer decent mechanical robustness, which can be enhanced by coating in multiple layers in some cases, however concerns arise near the glass transition temperatures ( $T_g$ ) of the coatings, at which point they change from ductile to brittle materials. While their mechanical properties in general are much lower than that of typical 304 SS, with a Young's modulus around 190 GPa and a tensile strength of 510 MPa, they are sufficient for use under static conditions. Air-dry epoxies offer fairly decent mechanical robustness with a Young's modulus of roughly 2.4 GPa [27] and tensile strength between 75 and 80 MPa [27-29] under glassy conditions. Glass transition temperatures (temperature below which the Young's modulus increases and there is an increased tendency to exhibit brittle failure) for air-dry epoxies tends to be around 130 °C, which could possibly occur on a canister surface, but only for canisters that have recently been loaded with SNF (< 5 years). The yield strength of these epoxies is generally not reported due to their brittle nature under glassy conditions. The addition of graphene sheets to air-dried epoxies provides an increase in the  $T_g$  of roughly 11 °C as well as increased toughness [17]. The flexural strength and ultimate tensile strength are both improved with addition of the graphene sheets (0.2 wt%) and further improved with better dispersal of graphene into the resin. The elastic modulus of the air-dried epoxy increased from 2.92 to 3.1 GPa [17]. Other additives are also known to improve the mechanical strength of air-dried epoxies. Qian et al. notes that epoxy-siloxane resin-based coatings are more flexible as a result of their high silicone content, and thus increase the coating's resistance to physical damage [11]. Mixtures of two additives that react during polymer mixing have also been examined in the literature. For example a mixture of 1,2-epoxy-3-phenoxypropane (EPP) and 4-hydroxyacetanilide (HAA) together noted as EPPHAA, as well as a mixture of vinyl cyclohexene dioxide (VCD) and HAA together denoted as VCDHAA [27] have been tested up to 30 vol% and behaved similarly; where the elastic modulus increased from 2.35 to roughly 4 GPa and tensile strength from 81 to roughly 115 MPa in the glassy state. Addition of EPPHAA decreased the  $T_g$  to nearly 75 °C, while VCDHAA additives decreased the  $T_g$  from 155 °C to 120 °C.

Polyurethane has a tensile strength of 11.1 MPa and an elastic modulus of only 13.5 MPa [30], while the  $T_g$  is difficult to define as it is dependent upon the number of urethane bonds and reported values span from -78°C to 116 °C [4]. PE has great mechanical robustness as a result of its multilayer application [12]. Similarly, PVC, polyesters, and rubbers are applied in thick and relatively flexible layers, offering increased durability as opposed to thin and brittle coatings. In contrast, PVDF is extremely prone to scratching and degradation, although the addition of silica was shown to improve the overall mechanical robustness from a hardness value of 2.6 GPa to 3.58 GPa (1:0.5 PVDF to Si) or 5.2 GPa (1:1 PVDF to Si) [31]. Alkyd coatings are also susceptible mechanical damage, although overall coating durability depends heavily on curing conditions [14, 32]. Scratches and other forms of physical damage are concerning for polymer coatings as they can create unprotected areas on the canister which are exposed to the environment. This could lead to increased corrosion on the surface, further delamination of coatings, and possibly result in increased risk of CISCC and need for frequent reapplication.

### **2.1.2.4 Thermal Stability**

The thermal stability of polymer coatings varies greatly over the range of possible canister surface temperatures, and thermal degradation is a concern when canister surface temperatures during the loading and drying process might exceed 200 °C. The thermal degradation of a polymer also depends on its state

during usage, whether it is above or below its  $T_g$ . The inability of a polymer coating to maintain its structure beyond its  $T_g$  can result in delamination, cracking, drooping, and even vaporization. However, some coatings are used in this state (above their  $T_g$ ), for example, PVDF, which has a  $T_g$  of  $-31\text{ }^\circ\text{C}$ , but does not decompose until  $350\text{ }^\circ\text{C}$  [33]. In addition, certain industrial rubbers have been rated for some uses up to  $600\text{ }^\circ\text{C}$  [34] or for composite rubbers up to  $400\text{ }^\circ\text{C}$  [35], which would allow for their potential application at any point in the canister lifetime. Other polymer coatings are used below their  $T_g$ , such as epoxies. Epoxies have exhibited thermal stability over a fairly decent range with respect to SNF canister temperatures, with the onset of thermal degradation above  $130\text{ }^\circ\text{C}$  and full decomposition temperatures near  $400\text{ }^\circ\text{C}$ , dependent on additives; graphene-enhanced epoxy does not decompose until a surface temperature of  $380\text{ }^\circ\text{C}$  [17], epoxy with silanes decomposes near  $420\text{ }^\circ\text{C}$  [36], and on steel modified with Zn + Co, epoxy does not decompose until  $\sim 428\text{ }^\circ\text{C}$  [37]. However, for SNF canister applications, full or even partial decomposition is undesirable, thus realistic operating temperatures for these coatings are likely limited to a much lower range. Polyurethane and PVC coatings have decomposition temperatures of  $200\text{--}300\text{ }^\circ\text{C}$  and  $260\text{ }^\circ\text{C}$ , respectively [19].

In addition to thermal decomposition or degradation, the thermal expansion coefficient of the coating, and possible mismatch with the underlying SS surface, needs to be considered. The thermal expansion coefficient of SS is  $17 \times 10^{-6}\text{ cm/cm}^\circ\text{C}$  [38], which may raise some concerns regarding the degree of variation and the possible mismatch with the thermal expansion coefficients for polymer coatings and their respective elasticity. The thermal expansion coefficient for most epoxies is approximately  $4.5 \times 10^{-4}\text{ cm/cm}^\circ\text{C}$  [39]; for PVDF,  $12\text{--}14 \times 10^{-5}\text{ cm/cm}^\circ\text{C}$  [40]; and for polyurethane,  $1 \times 10^{-4}\text{ cm/cm}^\circ\text{C}$  [41]. All these reported values for thermal expansion coefficients are 1 to 2 orders of magnitude greater than the thermal expansion coefficient for SS. This mismatch between the thermal expansion coefficient for SS and polymer coatings may be problematic and lead to delamination. While thermal expansion coefficients are an intrinsic material property, these polymer coatings (epoxies, PVDF, and polyurethane) could still be used depending on specified acceptable expansion ranges and diurnal temperature fluctuations.

While many polymer coatings have a mismatch with larger thermal expansion coefficients than SS, a few coatings, including polysiloxanes ( $7 \times 10^{-6}\text{ cm/cm}^\circ\text{C}$ ) [42], have lower thermal expansion coefficients. The thermal expansion coefficients for the remaining polymer coatings were not established in the literature, although it can be inferred that PVC and rubber have the capability to shrink and expand within reasonable temperature tolerances.

#### **2.1.2.5 Chemical Resistance**

Generally, polymer coatings form durable physical barriers which are highly chemically resistant, especially against relevant corrosive species such as sodium chloride (NaCl) [43]. Air-dried epoxies have been shown to be very stable in atmospheric conditions, and the addition of graphene sheets can further improve their stability [25]. Other common polymers that are generally inert in marine atmospheric conditions include polysiloxane coatings [7] and PE coatings [12]. Fluoropolymers are extremely chemically inert and are not expected to break down chemically in many marine and terrestrial environments, however their degradation can be of great concern due to their toxicity and possible harmful environmental effects [26]. Olad et al. indicates that PVC coatings can withstand NaCl solutions ( $>3.5\%$ ) for extended periods of time. Corrosion rates for typical PVC coatings on Fe were 20 times lower than uncoated Fe samples; PVC/ZnO polyaniline hybrid coatings resulted in 200 times lower corrosion rates than uncoated samples [9]. Depending on the chemical composition of certain rubbers, chemical resistance may vary, specifically against chloride [44]. Premature exposure to moisture could result in the loss of polyester adhesion properties [8], and therefore its overall chemical resistance.

#### **2.1.2.6 Radiation Resistance**

In general, radiolytic degradation is a significant concern for polymer coatings. The radiation resistance of many polymer coatings is limited, and additional research is required to assess radiation degradation under canister surface conditions. However, there is some information regarding the resistance of polymer



coatings to ultraviolet and solar radiation. The radiation resistance of polysiloxane coatings [7], PE coatings [45], and alkyd coatings [32] is low and all are known to decompose under even solar exposures. A significant amount of research has focused on the resistance of epoxy coatings to ultra-violet (UV) radiation, which can provide some insight overall for resistance to radiation degradation in canister relevant conditions. In general, epoxies exposed to “outdoor environments” experience higher levels of degradation due to UV damage. There are some measures that can be taken to reduce breakdown due to radiation. For example, PVC decomposes under gamma radiation, with a drop in tensile strength of 83% for a dosage of 25 kGy, but with certain additives, such as Tinuvin B stabilizer, PVC decomposition is less likely to occur [46]. Additionally, others have shown that the inclusion of an organic absorber, Tinuvin 1130, into the coating decreases the detrimental effects of UV radiation, such as delamination [47]. Many of the additives that have been used to minimize UV degradation have also demonstrated improvements to the coating tensile strength [46]. For example, after 800 hours of UV exposure, coatings with Tinuvin 1130 showed only an 11% reduction in tensile strength as compared to a 30% reduction without the additive [47]. Similarly, with the additive, the elongation at time of failure was reduced to only 8.6 % while it was 35% without the additive. In contrast to epoxies, which can degrade with UV exposure, polymer coatings such as PVDF, graphene enhanced epoxy coatings, and rubbers, offer excellent resistance against UV radiation over long periods of time [48].

### **2.1.3 Application**

#### **2.1.3.1 Surface Preparation**

Prior to application, at a minimum, all polymer coatings require a surface degreasing treatment. Some coatings can be applied without extensive surface pretreatment, such as polysiloxane coatings [7, 49] or moisture cured polyurethane [50], however, most polymer coatings will also require the removal of existing rust from the surface [32]. Ding et al. found that some epoxy coatings displayed enhanced mechanical robustness, including enhanced adhesion, following the removal of corrosion products if a rough surface was retained prior to application of the coating [25]. For example, Epoxyworks notes that for some air-dried epoxies, the substrate should be roughly ground to 80 grit before application [51]. The rough surface increases the contact area between the metal substrate and the surface coating [25], enhancing adhesion.

While surface roughness may enhance adhesion, most polymer coatings also specify a maximum surface roughness [52, 53]. Polymer coatings such as rubber or PE require surface grinding to a near-mirror-polish finish [54]. The most rigorous surface preparation processes for coatings in this class require both rust removal and grinding as well as the application of a primer to ensure the coating adheres to the surface. Alkyd paints commonly have various types of primers [32] and PVC coatings commonly use chromium or phosphate-based conversion coatings as primers to increase adhesion [55].

#### **2.1.3.2 Method of Application**

Select polymer coatings are suitable and/or more easily adaptable for in situ application by means of brushing or rolling onto the canister surface with the aid of remote robotics. This process is applicable for coatings such as epoxy, polyurethane, polysiloxanes, alkyd, PE, PVC, and rubbers. However, it is important to note that the majority of scientific studies of coatings’ properties used dip coating techniques for application. The quality control (i.e. coating uniformity, porosity, adhesion, etc.) for in situ application of polymer coatings is not well established, especially for brushing applications. In addition to this, patch or spot coating techniques may introduce edge effects; the importance of these effects are largely unknown.

While in situ application for many polymer coatings is possible, other polymer coatings require ex situ application as elevated temperatures are required for application or curing. For example, PVDF must be applied through a thermal spray process with a 260-360°C treatment [56] and polyesters are electrostatically applied using a spray method which requires curing at elevated temperatures (180 °C) [8, 50]. Further coating application method development would be necessary for in situ use of these coatings.

### 2.1.3.3 Reapplication

Depending upon degradation mechanisms, most polymer coatings can have extended lifetimes, due to their varying thickness and flexibility, which can enhance the coating resistance to physical damage. Further studies under canister relevant environments would be necessary to determine the specific reapplication needs [57]. When damage does occur, the canister must be cleaned using water and acetone to remove any corrosion products and existing coating, and re-ground/polished as needed; epoxies to 80 grit, PE to 1200 grit, and rubbers to 1200 grit.

For urethane coatings, it was observed that they can maintain integrity for up to two years when painted on a steel bridge [58]. Iezzi et al. reported that polysiloxanes must be reapplied every few months [7]. While these are short time scales with respect to SNF storage, these studies were conducted on a coating fully exposed to the elements; additional research would be required to determine the coating integrity under canister-relevant conditions.

### 2.1.4 Degradation Mechanisms

As mentioned previously, the primary method for the degradation of polymer coatings is through blistering; therefore, the permeability and ability of a coating to swell is of great concern. In general, enhanced crosslinking, either through curing methods or the introduction of additives, can reduce permeability. Also, enhancing the hydrophobicity of the coating can decrease swelling and permeation. In general, applying a thicker coating can alleviate concerns of permeation; however, this would require further study prior to use as it can lead to cracking and decreased mechanical robustness of the coating. Blistering can also be exacerbated by other forms of coating degradation that reduce the general properties and lead to coating disbondment, such as radiation and thermal degradation.

As discussed in Section 2.1.2.6, polymer coatings are not resistant to UV radiation, and therefore, will also likely exhibit low resistance to the gamma radiation emitted from the SNF canisters. This is of greater concern for epoxy, polyethylene, alkyd, and PVC coatings [46, 59] for which radiolysis of the polymer coating can occur. While radiolytic degradation can break down an organic polymer by several degradation pathways (depending on both the energy of the radiation and the bonds present in the polymer), it is likely that a byproduct of the radiolysis of the polymer will be highly reactive free radicals. The presence of radical species, specifically the hydroxyl radical, can lead to disbondment of the coating itself and/or corrosion of the underlying steel surface.

Another potential degradation pathway for polymer coatings is thermal degradation, as discussed above in the thermal stability section (Section 2.1.2.4), this is a function of both their thermal resistance and thermal expansion coefficients. Both can result in coating degradation, via either embrittlement below  $T_g$  or drooping and distortion above it, leading to disbondment from the surface, possibly resulting in enhanced corrosion rates due to crevice formation between the coating and the metal surface.

### 2.1.5 Feasibility of Polymer Coatings for CISCC Prevention, Mitigation, or Repair

Polymer coatings in general exhibit many qualities necessary for corrosion resistance in marine and near marine atmospheric environments and their characteristics have been summarized above. However, due to their higher permeability and low resistance to radiation damage as well as propensity to exhibit changes in behavior if they transition through  $T_g$ , they may not be suitable for, or may require extensive R&D, to ensure the applicability in an SNF environment. The stability of polymer coatings over time and exposure is of great concern for use on SNF canisters, as long-term reliability is key for this application.

While polymer coatings tend to be simpler with respect to methods of application, their thermal properties may prevent use of these coatings as corrosion prevention coatings (from initial canister loading) and even as possible repair techniques, if applied too early in a canister's lifetime. Specifically, thermal degradation would limit their application to canisters for which surface temperatures have fallen below 130 °C. In contrast to this, rubber coatings may be used under initial, higher temperature loading conditions, as they

have shown stability up to 400 – 600 °C. The thermal expansion coefficients may also raise concerns for polymer coatings. For the majority of polymer coatings, there exists a 1 to 2 order of magnitude mismatch between their coefficient and that of SS, increasing the possibility of disbondment or drooping, which could exacerbate corrosion through the formation of crevice conditions on the canister surface. Further studies or consideration of the effects of diurnal fluctuations on the behavior of coatings with a thermal expansion coefficient mismatch would be necessary prior to use in an SNF environment.

The development of an application method for polymer coatings for in situ repair of SNF canisters, in many cases, would be straightforward. Surface preparation is often minimal, including degreasing and rust removal, and the ability to brush on coatings is a technique that lends itself to remote robotic application. However, there remain many questions in the uniformity and heterogeneity of the coating applied with robotic brush techniques. Additionally, if patch repairs or spots of uncoated regions remain with in situ techniques, edge effects could result in additional corrosion concerns. Finally, coatings that necessitate higher temperatures for application and/or curing are not applicable in situ. If applied ex situ, for either repair or prevention, the coating application method can be expanded to dip or spray techniques, and for the use of prevention, can include higher temperatures for curing. However, concerns of coating embrittlement with changes in temperature if the  $T_g$  is crossed (as discussed in Section 2.1.2.4), and/or thermal degradation at elevated temperatures, such as those experienced by canisters at initial loading times, will play a significant role in appropriate coating selection.

Shown in Table 2 through Table 11 are summaries for the viability of polymer coatings to be used on SNF canisters to mitigate and prevent CISCC. As mentioned, for polymers, concerns arise with coating degradation from thermal, permeation, and radiation mechanisms. However, a few coatings types stood out as possible areas of interest for initial investigation.

- **Polymer coatings that may be of interest** in their current state include epoxies (possible thermal and radiation damage concerns), polyethylene (ease of application, but unknown thermal response), and rubbers (good general properties, but need evaluation of coating uniformity if brush techniques are used).
- **Polymer coatings that exhibit greater challenges to use for SNF application** in their current states include: PVDF (difficult application and thermal concerns), graphene-enhanced epoxy (difficult application and low TRL), polyurethane (concerns with reapplication and blistering), polysiloxanes (require frequent reapplication), alkyd coatings (poor adhesion, mechanical robustness, unknown thermal properties, require frequent replacement), and PVC (unstable above 60 °C).

Based upon the current state of polymer coatings, we **believe that epoxies, polyethylene coatings, and rubbers may potentially be used for SNF dry storage canisters. Other options may be applicable but would require considerable development.**

**Table 2. Summary of Air Dry Epoxy Coatings.**

<b>Coating Type: Air Dry Epoxies</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Low T <sub>g</sub> ; Strength improved with additives; Chemically resistant to Cl <sup>-</sup> and other corrosive substances
	<b>Detrimental</b>	Poor UV resistance, indicating susceptibility to radiation
<b>Coating Longevity</b>	<b>Beneficial</b>	Capability to alter coating thickness to enhance longevity
	<b>Detrimental</b>	Mismatch in thermal expansion coefficient with SS
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may be amenable for in situ repair (brush on) with minimal surface cleaning procedures
	<b>Ex situ repair</b>	Based on current literature, is feasible for ex situ repair (brush on, spray, dip)
	<b>Ex situ preventative</b>	Can be applied ex situ prior to loading with SNF, however the thermal stability requirements (< 130 °C) prevent this from being a possible option.
<b>Level of Interest</b>		Current research suggests that <b>air dry epoxies are likely</b> to be used for mitigation and repair of a SNF canisters but require further research particularly in the area of thermal and radiation concerns.

**Table 3. Summary of PVDF Coatings.**

<b>Coating Type: PVDF</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Chemically resistant to Cl <sup>-</sup> and other corrosive substances; Resistant to UV radiation suggesting possible radiation resistance
	<b>Detrimental</b>	Requires surface polishing for enhanced adhesion and is heavily prone to scratching (may be enhanced with the addition of silica)
<b>Coating Longevity</b>	<b>Beneficial</b>	Thermal degradation above 350 °C
	<b>Detrimental</b>	Mismatch in thermal expansion coefficient with SS
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may not be suitable for in situ repair as requires thermal spray or heat treatment/cure
	<b>Ex situ repair</b>	Based on current literature, may not be suitable for ex situ repair as requires thermal spray or heat treatment/cure
	<b>Ex situ preventative</b>	Can be applied ex situ prior to loading with SNF, however thermal degradation/mismatch is of concern
<b>Level of Interest</b>		Current research demonstrates that <b>PVDF are not likely</b> to be used for mitigation and repair of a SNF canisters due to difficulty in application and thermal concerns.

**Table 4. Summary of Graphene Enhanced Epoxy Coatings.**

<b>Coating Type: Graphene Enhanced Epoxy</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Coating bonds well to rough surfaces; Addition of graphene improves toughness over epoxy coatings without additives; Chemically inert; Enhanced UV resistance compared to epoxy
	<b>Detrimental</b>	Enhanced T <sub>g</sub> with graphene, however still thermal concerns.
<b>Coating Longevity</b>	<b>Beneficial</b>	Chemical resistance and enhanced radiation resistance.
	<b>Detrimental</b>	Embrittlement may still be a concern as T <sub>g</sub> is 150 °C
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may not be suitable for in situ repair as requires spin coating
	<b>Ex situ repair</b>	Based on current literature, may not be suitable for ex situ repair as requires spin coating
	<b>Ex situ preventative</b>	Based on current literature, may not be suitable for ex situ preventative as requires spin coating
<b>Level of Interest</b>		In general, <b>graphene corrosion coatings may be of interest due</b> to their demonstrated properties, however a great deal of development in application technique would be necessary to make them a viable in situ or ex situ option. <b>Currently do not have high TRL.</b>

**Table 5. Summary of Polyurethane Coatings.**

<b>Coating Type: Polyurethane</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Little surface preparation necessary for adhesion; Exhibits some scratch resistance, although likely not at levels necessary for canister movement; Has good chemical resistance and ideal for high RH environments; Resistant to ionizing radiation
	<b>Detrimental</b>	Prone to blistering
<b>Coating Longevity</b>	<b>Beneficial</b>	Can withstand temperatures up to 300 °C
	<b>Detrimental</b>	Thermal expansion may be an issue (blistering); Predicted reapplication every two years
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may be amenable for in situ repair as can be brushed on with little surface preparation
	<b>Ex situ repair</b>	Based on current literature, may be amenable for ex situ repair as can be brushed on with little surface preparation
	<b>Ex situ preventative</b>	Based on current literature, may be amenable for ex situ prevention, however initial loading temperatures may be an issue
<b>Level of Interest</b>		In general, <b>polyurethane are not likely of interest</b> as a repair strategy even though they present good properties in general and can be brushed on. There are concerns with necessary reapplication as it is prone to blistering. Additionally, as an initial prevention strategy, there may be issues as it is generally stable up to 300 °C.

**Table 6. Summary of Polysiloxane Coatings.**

<b>Coating Type: Polysiloxanes</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Functional groups increase adhesion; Resistant to Cl <sup>-</sup> and other corrosive media
	<b>Detrimental</b>	Sensitive to solar radiation, therefore likely sensitive to radiation; No mechanical data
<b>Coating Longevity</b>	<b>Beneficial</b>	Resistance to corrosive media.
	<b>Detrimental</b>	Will vaporize at higher temperatures; Will need to be reapplied every few months
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may be amenable for in situ repair as can be brushed on with little surface preparation
	<b>Ex situ repair</b>	Based on current literature, may be amenable for ex situ repair as can be brushed on with little surface preparation
	<b>Ex situ preventative</b>	Based on current literature, may be amenable for ex situ prevention.
<b>Level of Interest</b>		In general, <b>polysiloxanes are not likely of interest</b> even though they exhibit an ease of application. However, they will require reapplication every few months and are sensitive to radiation. No significant data regarding mechanical robustness was found.

**Table 7. Summary of Polyethylene Coatings.**

<b>Coating Type: Polyethylene</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Multiple layers offer increased robustness; Resistant to Cl <sup>-</sup> and other corrosive media; mechanical robustness enhanced with multiple layer application
	<b>Detrimental</b>	Surface finish effects adhesion properties; Susceptible to radiolytic degradation and solar radiation
<b>Coating Longevity</b>	<b>Beneficial</b>	Chemically resistant
	<b>Detrimental</b>	Little to no data exists for thermal stability/ expansion coefficients
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may be suitable for in situ repair as it can be painted on however typically applied by thermal spray or dip.
	<b>Ex situ repair</b>	Based on current literature, may be suitable for ex situ repair as it can be painted on however typically applied by thermal spray or dip.
	<b>Ex situ preventative</b>	Based on current literature, may be suitable for ex situ prevention.
<b>Level of Interest</b>		In general, <b>polyethylene coatings may be of interest</b> as they can be painted on in situ or sprayed ex situ. However, prior to use in canister conditions, further investigation is necessary regarding their thermal properties.

**Table 8. Summary of Alkyd Coatings/ Paints.**

Coating Type: Alkyd Coatings/ Paints		
Coating Properties	Beneficial	Resistant to Cl <sup>-</sup> and other corrosive media
	Detrimental	Primers are necessary for adhesion; Poor mechanical robustness; Susceptible to radiolytic degradation
Coating Longevity	Beneficial	High ionic resistance
	Detrimental	Prone to chips and scratches, dependent on curing temperature; Little data exists on thermal stability and thermal expansion coefficients which vary greatly
Coating Application	In situ repair	Based on current literature, may be suitable for in situ repair as it can be painted or sprayed, however surface preparation and primers are necessary.
	Ex situ repair	Based on current literature, may be suitable for ex situ repair.
	Ex situ preventative	Based on current literature, may be suitable for ex situ prevention.
Level of Interest		In general, alkyd coatings exhibit resistance to Cl <sup>-</sup> media but <b>are likely not of interest</b> for canister applications as they poor mechanical and degradation properties and would likely necessitate routine maintenance.

**Table 9. Summary of PVC Coatings.**

Coating Type: PVC		
Coating Properties	Beneficial	Pretreatments can increase adhesion but not necessary; Exhibits good mechanical robustness with thick, flexible layers; Resistant to Cl <sup>-</sup> and other corrosive media
	Detrimental	Susceptible to gamma radiation
Coating Longevity	Beneficial	Has high elasticity with temperature changes
	Detrimental	Thermal degradation above 60 °C
Coating Application	In situ repair	Based on current literature, may be suitable for in situ repair as it can be dipped or brushed, and can be reapplied on top of existing PVC.
	Ex situ repair	Based on current literature, may be suitable for ex situ repair.
	Ex situ preventative	Based on current literature, may be suitable for ex situ prevention.
Level of Interest		In general, PVC exhibits resistance to chloride media with mechanical robustness and good adhesion but <b>are likely not of interest</b> for canister applications as it is unstable above 60 °C.



**Table 10. Summary of Polyester Coatings.**

<b>Coating Type: Polyesters</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Thick, flexible layers; Very chemically resistant, few known solvents can damage them
	<b>Detrimental</b>	Delaminate at higher temperatures; Decreased resistance to UV over time, may be susceptible to radiation damage
<b>Coating Longevity</b>	<b>Beneficial</b>	Has high elasticity with temperature changes
	<b>Detrimental</b>	Thermal degradation accelerates at 25 – 400°C; Thermal expansion concerns
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may not be suitable for in situ repair as they are applied electrostatically, and heat cured.
	<b>Ex situ repair</b>	Based on current literature, may be suitable for ex situ repair.
	<b>Ex situ preventative</b>	Based on current literature, may be suitable for ex situ prevention.
<b>Level of Interest</b>		In general, polyesters exhibit very high chemical resistance; however, they <b>are likely not of interest</b> for canister applications as they are susceptible to radiation damage and are very thermally sensitive, even in the range of 25 – 400 °C. Additionally, they may not be suitable for in situ application.

**Table 11. Summary Rubber Coatings.**

<b>Coating Type: Rubbers</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Resistant to Cl <sup>-</sup> and other corrosive media; High resistance to UV degradation; applied in thick coatings to have enhanced mechanical robustness and durability
	<b>Detrimental</b>	Susceptible to permeation
<b>Coating Longevity</b>	<b>Beneficial</b>	Rated for thermal stability up to 400 – 600 °C
	<b>Detrimental</b>	Radiation and thermal stability dependent on exposure environment, require further study
<b>Coating Application</b>	<b>In situ repair</b>	Based on current literature, may not be suitable for in situ repair as they can be painted, sprayed, or dipped. Do require moderate surface cleaning.
	<b>Ex situ repair</b>	Based on current literature, may be suitable for ex situ repair.
	<b>Ex situ preventative</b>	Based on current literature, may be suitable for ex situ prevention.
<b>Level of Interest</b>		In general, <b>rubbers may be of interest</b> exhibit good chemical and UV resistance, <b>decent</b> thermal stability and the ability for in situ application. However further information regarding coating uniformity when painted is necessary prior to use.

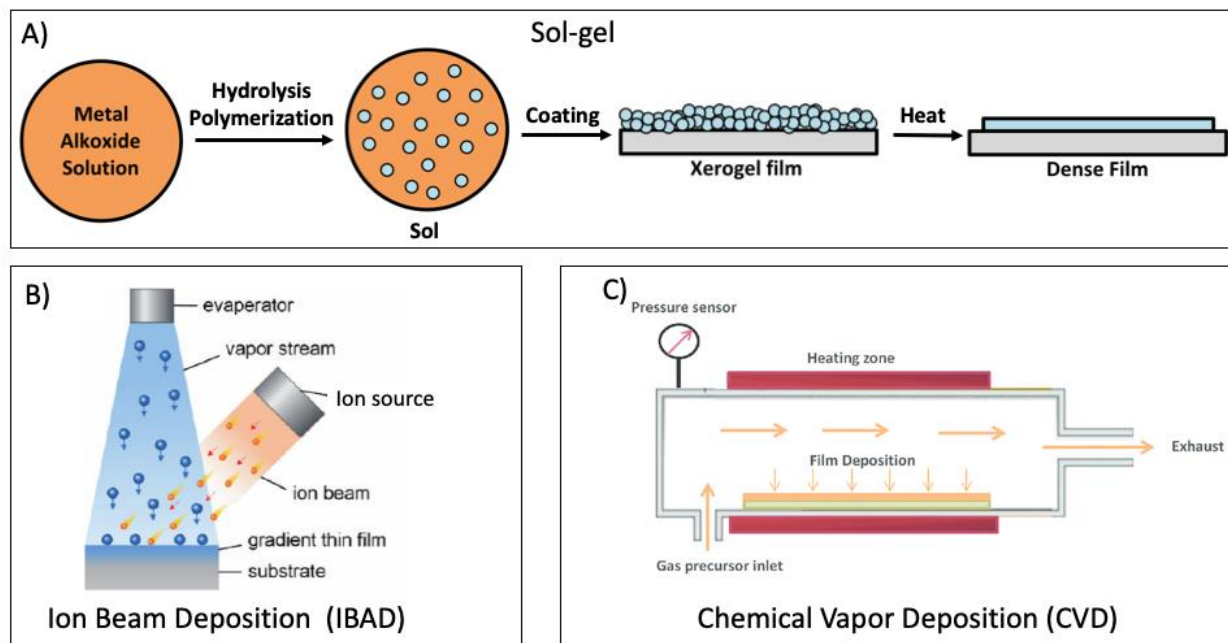


## 2.2 CERAMIC COATINGS

### 2.2.1 Corrosion Protection Mechanism

Ceramic coatings are crystalline structures typically composed of one or more metal oxides. The primary purpose of ceramic coatings is to act as a physical barrier to prevent oxidation on metal surfaces by limiting the penetration of oxidizing species to the metal surface. Because ceramic coatings are effective in limiting surface oxidation, they have been successfully employed to inhibit corrosion on SS; including 316 and 304 [60, 61]. In this section, we will discuss ceramic coatings formed by three different deposition methods and their potential to limit CISCC on SNF canisters in in-situ repair, ex-situ repair, and ex-situ prevention implementation strategies. The deposition methods of ceramic coatings for corrosion protection considered for this application are **sol-gel**, **ion beam alumina deposition (IBAD)**, and **chemical vapor deposition (CVD)**. CVD techniques include **metal organic chemical vapor deposition (MOCVD)**, and **atomic layer deposition (ALD)**, which differ in their deposition process. While sol-gel and ALD coatings can be composed of a variety of different metal oxides, IBAD and MOCVD are most commonly performed with alumina, and therefore alumina deposition is the focus in this report for those two methods.

Deposition of sol-gel coatings results in the hydrolysis, condensation, and subsequent growth of a metal oxide layer on a metal surface that limits the mass transfer of oxidizing reactive species by creating a tortuous pathway as shown in Figure 3a [62]. Their surface protection properties can be strengthened by doping the sol-gel with organic corrosion inhibitors, such as many of the polymers listed in Section 2.1 [62, 63]. The incorporation of organic inhibitors can be achieved via hybrid sol-gel, in which the metal oxide and organic component are applied together [62], or in a multilayer approach, in which the organic coating is added on top of the sol-gel [64]. Sol-gels can consist of a wide range of metal oxides; most commonly, zirconium dioxide ( $ZrO_2$ ) [65], aluminum oxide ( $Al_2O_3$ ) [60, 61, 66-69], titanium dioxide ( $TiO_2$ ) [68], cerium (IV) oxide ( $CeO_2$ ) [63], and silicon dioxide ( $SiO_2$ ) [62, 68, 70, 71] are used. While there are several metal oxide sol-gel options, the general corrosion protection mechanism is consistent; however, the sol-gel chemical, physical, and mechanical properties may differ depending on composition. In contrast to sol-gel coatings, IBAD, ALD, and MOCVD achieve corrosion protection differently because of their limited ability to incorporate other corrosion inhibitors to improve corrosion resistance. Mechanistically, IBAD and CVD alumina coatings form a passive layer which acts as an electrical insulator and limits mass transfer [72]. The application of alumina deposited by ion beam is achieved by sputter coating the surface with alumina *via* ionized argon, plasma source, or electron beam (Figure 3b) [73, 74]. Alumina deposited by MOCVD creates a coating through chemical vapor deposition on a given surface; this process typically occurs at higher temperatures and in a vacuum furnace which are used to remove the requisite organic carrier (Figure 3c) [67]. ALD processes deposit metal organic species via sequential thin film gas phase deposition which create metal oxides on the surface [75, 76]. While all three methods to deposit ceramic coatings (**sol-gel, ion beam, and CVD methods**) are used to prevent corrosion, the deposition methods and coating compositions are different and thus result in different corrosion protection behaviors and implementation requirements.



**Figure 3. Simplified schematic of the deposition processes for A) sol-gel deposition (modified from [77], B) ion beam alumina deposition [78], and C) chemical vapor deposition [79].**

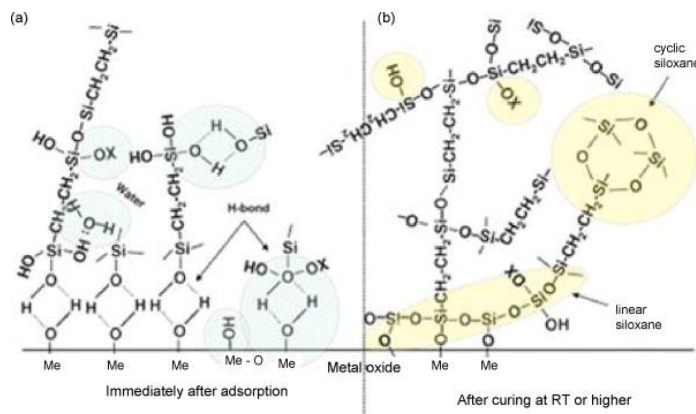
In general, the advantages of ceramic coatings are reflected in their thermal and chemical stability. Ceramic coatings, as a class, have high thermal stability over a very wide temperature range, and high radiation resistance. Because of this, ceramic coatings have the potential to be applied as an **ex situ preventative** technique at the onset of the canister lifetime or at any point in the canister lifetime, since temperature and radiation degradation are not a concern. While overall stability is an advantage of ceramic coatings, there are concerns regarding their application and implementation to an SNF canister. First, ceramic coatings can be difficult to apply, and current literature has only recently demonstrated the potential for in-situ implementation by spray techniques, although this has not yet been demonstrated on SS [62]. Also, ceramic coatings tend to be brittle, and thus transport of a deployed canister for ex-situ application and return to the ISFSI pad without disrupting the ceramic coating on the surface [62] could be problematic – though recent work has greatly improved the mechanical properties of sol-gel coatings through the inclusion of an organic component [80]. Therefore, ceramic coatings at the current state of the art are feasible as an **ex situ preventative** strategy in which the canister experiences minimal handling after the coating is deposited, however lower TRL hybrid materials suggest improved mechanical properties and novel applications methods that allow for use in **ex situ repair** and **in situ repair**, perhaps as a base coat for a polymer coating. A more detailed examination of the usage constraints for ceramic coatings is addressed in the following sections.

## 2.2.2 Properties

### 2.2.2.1 Adhesion

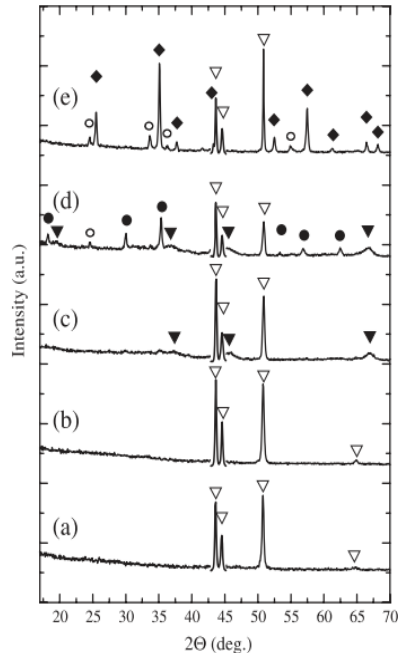
Adhesion properties for ceramic coatings are dependent upon the composition and deposition method. For example, sol-gel coatings consisting of  $ZrO_2$ ,  $SiO_2$ , or  $Al_2O_3$  have different chemical properties and that, along with incorporation of organic additives, greatly impacts the adhesion properties [62]. Recent studies that have investigated the adhesion properties of sol-gel coatings suggest that there may be challenges for implementation on SNF canisters; however, specific challenges can be mitigated with material- and sol-gel-specific research and development. For example, in a study of sol-gel alumina on 316Ti SS (0.45% Ti)

and 304 SS, initial tests showed that adhesion to 316Ti SS was superior over 304 SS, due to the ability of the alumina to form covalent bonds with the Ti that is expressed on the surface [60]. However, after adjusting the sol-gel composition and increasing the curing temperature (~1100 °C), sufficient adhesion between 304 SS and alumina occurred [60]. Other studies showed that the inclusion of additives reduced the curing temperature for successful adhesion—silica/alkylsilanes were successfully adhered when cured on magnesium metal at 150 °C, and even room temperature UV curing and adhesion was possible with the addition of a photo initiator [64]. Fedrizzi et al, demonstrated that a zirconia sol-gel pretreatment can be used to not only improve corrosion resistance but also can promote the adhesion of organic coatings (i.e. polyester) on steel [65].



**Figure 4. Simplified schematic of the curing process of sol-gels to create covalent interaction between the silica and the metal surface, where a) is prior to curing, showing H-bonding interaction between silica and the metal surface, followed by b) after room temperature or higher curing process [81].**

In contrast to sol-gel coatings, for which adhesion properties require optimization, IBAD and CVD methods demonstrate great adhesion. For example, MOCVD applied at 770 K was determined to be thermally stable up to 1070 K. XRD-patterns are shown for five different heat-treated states of the MOVCD alumina coating in Figure 5 [66]. It was reported that films deposited at 770 K (spectra b) were strongly adherent and non-porous, as confirmed by the presence of only aluminum and oxygen in the coating by Auger Electron Spectroscopy, demonstrating that the coating was successfully deposited as  $Al_2O_3$ . When the coating was annealed (1070 K for 2 hours) (spectra c), the coating was still adherent and stable, however  $\gamma-Al_2O_3$  was detected in addition to the deposited  $\alpha-Al_2O_3$  phase. At 1240 K, the alumina coating began to break down (spectra d), exposing the substrate surface to the atmosphere and thus no longer acting as a barrier to prevent corrosion. This was confirmed by the presence of corrosion products,  $Cr_2O_3$  and  $FeCr_2O_4$ , along with  $\gamma-Al_2O_3$  identified on the surface. At 1380 K (spectra e), the coating showed further degradation, with more corrosion products and continued conversion to  $\gamma-Al_2O_3$  were again identified on the surface. The final temperature that was tested was 1460 K, at this point the coating began to break off, resulting in fragments sticking out of the surface [66]. While this study shows the significant temperature dependence of the adhesion properties of ceramic coatings, the temperatures present on SNF canisters are much lower (< 300 °C) than those tested in this study. As these ceramic coatings undergo degradation and delamination at temperatures above ~ 800 °C, this finding is not an issue for application on SNF canisters.



**Figure 5.** XRD-patterns of (a) a clean stainless steel substrate, (b) after 2 h deposition of aluminum oxide at 770 K, and (c) after subsequent annealing of the film for 2 h in vacuum at 1070 K, (d) at 1240 K, and (e) at 1380 K (heating/ cooling rate: 4 K/min). The intensities between  $2\theta=42.8^\circ$  and  $45.2^\circ$  are divided by a factor of 2.5. The positions of the reflections of clean stainless steel ( $\nabla$ ),  $\alpha$ - $\text{Al}_2\text{O}_3$  ( $\blacklozenge$ ),  $\gamma$ - $\text{Al}_2\text{O}_3$  ( $\blacktriangledown$ ),  $\text{Cr}_2\text{O}_3$  ( $\circ$ ), and  $\text{FeCr}_2\text{O}_4$  ( $\bullet$ ) are marked in the figure [66].

### 2.2.2.2 Permeability

While there are few studies evaluating the permeability of ceramic coatings, there are several studies that assess the relationship between ceramic coating deposition processes and their porosity, which can be used to glean information on permeability. Sol-gel coatings have been observed to have high porosity [82]. While few studies focus on the dependence of porosity on the sol-gel metal composition, studies have identified that the inclusion of organic additives will result in a less porous and less permeable coating [83]. Haas-Santo et al. noted the flexibility of sol-gel methods for controlling coating porosity, stating that the sol-gel process is an “established method for producing particulate bulk material as a porous support for catalysts as well as dense thin film coatings having a low porosity on glasses” suggesting that the porosity can be controlled by the composition of the sol-gel [68]. This study also observed changes in the porosity of an alumina sol-gel coating after thermal treatment. The coating was specifically applied as aluminum tri-isopropylate precursor in 2-Butoxyethanol with a  $\text{HNO}_3$  catalyst and an acetylacetonone stabilizer at 400-800 °C. At 800 °C, the gel film calcined and converted to  $\alpha$ - $\text{Al}_2\text{O}_3$  with a low surface area. At these temperatures the porosity decreased due to the sintering of the alumina layer, however no quantitative information was provided regarding the change in surface area or porosity. This work suggests that the surface area and porosity can be controlled by the deposition temperature, however further research is required to determine the level of porosity of the sol-gel compositions of interest and apply that relationship to canister-relevant temperatures.

While available information regarding the permeability and porosity of alumina deposited by ion beam is sparse, studies have evaluated the porosity of coatings produced by CVD techniques, specifically MOCVD alumina. In Lazar et al., MOVCD alumina on 304L SS at different coating thicknesses, ranging from 250

nm to 1700 nm, showed no porosity upon examination by transmission electron microscopy [67]. Again, further research would be necessary for conditions of applicability to SNF dry storage canisters.

### **2.2.2.3 Mechanical Robustness**

The mechanical robustness of ceramic coatings is dependent on the coating deposition method and composition; however, generally speaking, ceramic coatings are brittle. Sol-gel coatings have been noted to have high hardness values relative to steel [62]. When combined with an epoxy, sol-gel/epoxy resin hybrid coatings demonstrated high hardness, abrasion resistance, and passed wet adhesion testing when cured at 80 °C [71]. With a large diversity in sol-gel compositions, there is flexibility to improve the strength of the coating by adjusting the metal composition or incorporating organic additives. A commonly used additive to increase the mechanical robustness is tetraethoxysilane, which has been routinely applied to low-bulk density SiO<sub>2</sub> sol-gel coatings, increasing the overall strength of the coating [62]. IBAD and CVD coatings are brittle, clear, and ceramic and the microstructure is known to be amorphous and nonporous [67]. Since IBAD and CVD methods produce a brittle coating, these coatings can be prone to sudden failure if their yield strength is exceeded, and a few adjustments to the composition can be made to improve this property. The yield strength has been shown to vary as a function of the alumina composition. For example, when the coating is 94% alumina (the remaining 6% is chromium or magnesium oxide), the yield strength value is 2100 MPa, and when the percent composition increases to 99.5% alumina, then the yield strength value increases to 2400 MPa [84]. Additionally, depending on the atomic structure of the alumina coating, IBAD sputtered coatings can have a hardness of up to 22 GPa, whereas amorphous coatings have a hardness of ~10 GPa [69].

### **2.2.2.4 Thermal Stability**

In the adhesion section (Section 2.2.2.1), we discussed the need for curing at high temperatures for sol-gel coatings, and that the curing temperature is dependent on the ceramic composition and the sol-gel composition. Curing temperatures can range from room temperature to 600 °C and during this process sol-carrier solvents or organic components are removed (unless hybrid coatings are used). Although most curing temperatures are above the expected highest temperature of the canister surface (approximately 200 °C), there is not a fixed thermal stability range for sol-gel coatings. However ceramic coatings are expected to be stable at temperatures that exceed the maximum surface temperature of the SNF canister. Therefore, sol-gel coatings are promising for SNF applications, but further research is necessary to establish specific thermal stability for each sol-gel composition. Similar to sol-gel coatings, the thermal stability of IBAD and CVD coatings have been tested at temperatures that greatly exceed the maximum temperature of the canister surface during the storage lifetime of the canister. Studies have shown that IBAD and CVD coatings are thermally stable to temperatures above 1000 °C [66, 69]. Specifically, Edlmayr et al. examined coatings that were annealed in a vacuum furnace for 3 and 12 hours at constant temperatures of 700, 800, and 1000 °C [69]. These heat treatment tests showed that the deposited alumina coatings that were converted from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (metastable form of Al<sub>2</sub>O<sub>3</sub>) to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (the most thermally stable form of Al<sub>2</sub>O<sub>3</sub>) proved to be thermally stable in exposure tests up to 1000 °C [69].

The thermal expansion coefficients of sol-gel coatings are similar to SS but are dependent both on the metal oxide composition and the organic additive, if one is used. One study found that sol-gel coatings containing ZrO<sub>2</sub> have expansion coefficients on the order of  $12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  [42] as compared to that of SS of  $17 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  [38]. The thermal expansion coefficients of IBAD and CVD coatings are dependent on the percent composition of alumina. The thermal expansion increases as the alumina content increases, where at 94% and 99.5% alumina the thermal expansion coefficient is  $8.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  and  $8.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , respectively [84]. These thermal expansion values are about half of the thermal expansion of SS. Further testing would be necessary to determine the importance of thermal expansion coefficient mismatch in the context of diurnal temperature fluctuations typical of canister environments.



### 2.2.2.5 Chemical Resistance

In general, ceramic coatings have very good chemical stability and can provide effective corrosion protection in a wide range of chemical environments [62]. Sol-gel coatings made of  $ZrO_2$ ,  $Al_2O_3$ ,  $SiO_2$ , or  $TiO_2$  have been tested in atmospheric corrosion environments, and the results show that resistance to atmospheric corrosion differs as a function of the composition and exposure environment [62]. For example,  $SiO_2$  sol-gel coatings can improve oxidative and acidic corrosion resistance [85], while  $\gamma-Al_2O_3$  is a great insulator and has low conductivity; therefore, on 316 SS,  $\gamma-Al_2O_3$  will improve localized corrosion resistance but may be more susceptible to aggressive agents [86]. Coatings deposited by IBAD or CVD methods will likely exhibit similar chemical properties for the sol-gel deposited alumina (in the absence of an organic additive), however environmental influences including exposure to various brines, changes in temperature, and presence of crevice formers can greatly affect this stability – and thus chemical resistance. Further research is needed to determine the stability of these coatings in canister relevant environments.

### 2.2.2.6 Radiation Resistance

Overall, ceramic coatings are resistant to radiolytic degradation and have been widely regarded as a promising technology in the nuclear industry [61]. In addition, some studies have shown that mechanical properties of ceramic coatings can be improved from exposure to radiation [87]. Sol-gel coatings have even been cured by UV exposure [88]. Garcia Ferré et al., observed an increase in fracture toughness in IBAD coatings on austenitic SS with exposure to radiation (20 displacements per atom (dpa), 40 dpa, and 60 dpa) at 600 °C [87]. This is because of radiation induced amorphous-to-crystalline transformation in the ion beam deposited alumina, thus creating a fully nano-grained structure—strengthening the coating. Further, extended irradiation resulted in grain growth and softening leading to an improvement in fracture toughness in the irradiated films. Based on these observations, the use of ion beam and MOVCD alumina is encouraged in radiation environments, even above the traditional limiting range for standard nuclear materials [87]. However, the doses required to produce these changes are many orders of magnitude higher than those occurring on the canister surface; canister surface doses are too low to have any effect on the structure of inorganic coatings.

One area of concern for radiation resistance of ceramic coatings is hybrid sol-gel coatings. As mentioned previously, the hybridization of sol-gel with organic compounds can result in improved chemical and physical stability as well as superior corrosion resistance through strong chemical bonds between organic and inorganic components; however, the resulting material could potentially be susceptible to radiation damage. Generally speaking, the inorganic component is radiation resistant, as the metal-oxygen bond is strong and unlikely to be ionized by radiation, while the organic component has the potential to undergo radiolysis [63]. The radiation exposure range that causes damage can vary significantly with differences in the organic component used in the sol-gels, so research into a particular hybrid coating would be required to determine appropriateness for use on SNF canisters.

## 2.2.3 Application

### 2.2.3.1 Surface Preparation

Surface preparation requirements to apply metal oxide coatings greatly depend on the deposition technique. While sol-gel coatings have some surface preparation requirements, IBAD and CVD coatings require a more detailed surface preparation procedure as well as the need for specialized equipment. Sol-gel coatings require a rough surface, although the exact surface finish may depend on the composition of the metal oxide, one study of alumina sol-gel on 304L ground the surface to an  $R_a$  of  $0.6\mu m$  [89]. Also, depending on the sol-gel composition, the addition of a precursor to ensure the coating wets and adheres to the surface may be necessary [62]. The surface preparation requirements for IBAD and CVD coatings are more specific. For these deposition methods, the surface must be prepped by SiC polishing paper to a near mirror polish, up to 4000 grit ( $R_a < 0.02\mu m$ ), and subsequently degreasing and cleaned using acetone and ethanol, followed by drying with argon prior to application [67]. Due to the requirement for a rough surface

(although grit not specified), for sol-gel, or a polished and cleaned surface, for ion beam and MOCVD, ceramic coatings are not likely to be used in situ.

### **2.2.3.2 Method of Application**

Due to stringent surface preparation requirements for application of IBAD and CVD coatings or rough surface requirements (sol-gel), metal oxide coatings are either not well suited or require additional research to determine the feasibility for in situ application on SNF canisters. Application methods for sol-gel coatings are commonly dip coating or spin coating, but more recently, developments in spray, brush, and electrodeposition methods have been made [62]. After application, the sol-gel coatings are typically cured at high temperatures, 300-600 °C depending on the composition (though the curing temperature can be much lower), or treated with an organic agent, like polyester, to avoid cracking and delamination [62, 63]. The curing process creates covalent bonds between the metal oxide with the surface and removes any solvent or organic component that resides in the coating layer [90]. Due to the surface preparation requirements, along with application methods and curing requirements, in-situ application of ceramic coatings is not likely feasible. IBAD and CVD strategies are poorly suited for in situ application on the SNF canisters due to their need for specialized equipment. The equipment required for IBAD and CVD application is not mobile; typically, they are performed under a vacuum controlled atmosphere, and in the case of CVD, in a quartz tube furnace, eliminating the possibility of in situ application [66]. For ex-situ applications, IBAD and CVD could be used; however, traditionally, these techniques are for localized areas or small parts. Scaling up these processes for application to SNF dry storage canisters will be difficult and may produce unforeseen issues.

### **2.2.3.3 Reapplication**

One of the biggest challenges to reapply sol-gels is the need to cure at high temperatures and the need for further development of application methods. As we discussed in the applications section (Section 2.2.3) the current procedural curing temperatures and application methods exclude these coatings as an **in situ repair** technique. Therefore, it is unlikely that sol-gel coatings could be reapplied to an in-use SNF canister without additional research and development. Also, although ceramic coatings are generally stable, the ageing and lifetime of ceramic coatings are not well understood in marine and near-marine atmospheric environments. Some sources show that inclusion of chemical inhibitors can improve properties and possibly the lifetime of the coating, thus limiting the need for reapplication. Zheng et al. discussed how coatings doped with Zn/Al layered double hydroxides demonstrated self-healing effects and enhanced anticorrosion properties [63]. The lifetime and reapplication strategies for IBAD and CVD coatings are not well understood, however, depending on the impact of the differences in the thermal expansion coefficients between alumina and SS, or the likelihood of brittle fracture, reapplication may not be required over the lifetime of a SNF dry storage canister. Further research and experimentation would be necessary to better understand these coatings with respect to ageing and long-term performance. However, for ion beam or MOCVD alumina coatings, significant barriers exist for in situ or even ex situ reapplication, suggesting that these are unlikely to be reapplied or used on canisters.

## **2.2.4 Degradation Mechanisms**

Research suggests that the primary degradation mechanism for sol-gel, IBAD, and CVD coatings is by mechanical degradation due to their high brittleness [91]. Further research is required to determine the relationship between degradation and brittleness for specific sol-gel compositions as well as the impact of additives, and to determine the degradation mechanisms under canister-relevant conditions.

## **2.2.5 Feasibility of Ceramic Coatings for CISCC Prevention, Mitigation, or Repair**

Ceramic coatings, specifically sol-gel coatings, may be a viable option for use on SNF canisters. In their current state, IBAD and CVD methods would not be possible in the application of mitigation and repair of SNF canisters, largely driven by the need for specialized equipment and challenging deposition methods to be applied to a large SNF canister.

The adhesion and permeability properties of ceramic coatings depend on composition and deposition method. While CVD alumina has demonstrated superior adhesion properties, even at very high temperatures (~800 °C), sol-gel and ion beam deposited alumina require more research to understand how these coatings would adhere to the SS canisters. By design, ceramic coatings create a physical barrier that limits transport of oxidizing species to the metal, and this behavior is tied to the porosity and permeability. More information is required to assess the resulting porosity and properties of sol-gel coatings and IBAD if they are cured at canister-relevant surface temperatures.

Another advantage of ceramic coatings is their durability; they are mechanically, chemically, radiolytically, and thermally stable. Sol-gel coatings represent a versatile coating technique, as both the chemistry and mechanical properties are dependent upon the composition of the coating. Sol-gel coatings have a similar thermal expansion coefficient value to SS, suggesting that sol-gel coatings will behave similarly to SS as the temperature profile of the canister changes with the cooling of the SNF and with diurnal ambient temperature fluctuations. In addition, sol-gel coatings coupled with polymer coatings have been shown to greatly strengthen the mechanical properties, thus improving their utility on SNF canisters. While these additives could be advantageous, they may also introduce radiation sensitive components, which could be problematic if applied to a highly radioactive SNF canister. Ceramic coatings are brittle materials that can fail if their yield strength is exceeded. For IBAD and CVD, there is a direct relationship between the % alumina in the coating and the mechanical robustness, the chemical and thermal stability may be more sensitive at high % alumina. Additional research is required to understand the interplay between chemical and mechanical properties as a function of the alumina percentage in the coating.

While properties of ceramic coatings are generally positive, the application requirements for ceramic coatings on SNF canisters introduces many implementation challenges. Specifically, IBAD and CVD methods, pose challenging surface preparation methods, and require specialized equipment for deposition. This is virtually impossible to consider these for **in-situ repair** applications, but also unlikely for **ex-situ repair** and **ex-situ prevention**. It would not only be very risky to perform IBAD or CVD methods on a canister that contains SNF, but also the size scale demands that the canisters present would require significant research and design to establish feasibility.

Sol-gel coatings do offer flexibility in different compositions and additives, which could be advantageous when considering application on SNF canisters. While there is a requirement to prepare the surface to a specific roughness, the details of this requirement need to be determined for specific sol-gel compositions. Because typical application methods such as dip coating or spin coating are most common, additional research is required for the development of spray or brush techniques that could be applied for **in-situ repair** and **ex-situ repair**. However, there is the potential to evaluate the viability of sol-gel coatings for **ex-situ prevention** in their current state of technology.

Shown in Table 12, Table 13, and Table 14 are summary tables for sol-gel, IBAD, and CVD coatings, respectively. **While ceramic coatings demonstrate great chemical, thermal, and radiological stability, there are several challenges when considering their application to SNF SS canisters.**

- Most significantly, both IBAD and CVD methods are poorly suited for application to SNF canisters. The most obvious challenge is the need for specialized equipment for deposition and the lack of industry standards to apply these coatings to large areas. This would require significant time and resources to develop techniques to a large SS canister, which may create new challenges for scaling up.
- Sol-gel coatings offer flexibility in the composition of the sol-gel as well as potential hybridization with organic additives. The properties of sol-gel coatings have been shown to be both dependent on the metal oxide used as well as the composition of any additives. The ability to tune sol-gel coatings potentially allows development of a coating with positive attributes to be used on an SNF canister. The most significant challenges are the application of sol-gel coatings are the necessary high temperatures for curing and the fact that the options available are not likely to be easily applied



to an SNF canister. **Development of more versatile application methods would greatly improve the viability of sol-gel coatings for this use.**

Based upon the current state of metal oxide coatings, we do not think it would be possible to apply IBAD or CVD coatings to an SNF canister at any point in the canister lifecycle. Sol-gel coatings have the potential to be applied to SNF canisters for mitigation and repair. While the current state of the art represents some limitations, there are areas of R&D that could improve their viability as both repair and prevention processes.

**Table 12. Summary of Sol-Gel Coatings**

<b>Sol-Gel Coatings</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	High degree of chemical robustness and does not undergo radiolytic degradation; compositional flexibility along with incorporation of additives allows for some tunability to improve coating properties.
	<b>Detrimental</b>	Adhesion is not well understood and is suggested to be temperature dependent
<b>Coating Longevity</b>	<b>Beneficial</b>	Should last for a long time, as chemical, thermal, and radiological processes have minimal or no impact on the integrity of the coating.
	<b>Detrimental</b>	Likely to be composition dependent but can be prone to flaking off or failure if disturbed (such as scratching)
<b>Coating Application</b>	<b>In situ repair</b>	Unlikely to be performed in situ due to the application methods limiting the ability to be deposited in the overpack
	<b>Ex situ repair</b>	The limiting factors to apply sol-gels for ex situ repair are 1). The need for high temperature curing, 2). Application methods are challenging to scale for a large canister, and 3). The coating may be damaged in transport following coating. If these concerns can be address, this could be a viable option.
	<b>Ex situ preventative</b>	Sol-gel coatings could be applied for ex situ preventative applications, the only challenges are transporting the canister with storage site without damaging the coating on the surface
<b>Level of Interest</b>	Overall, <b>there is potential for sol-gel coatings to be used for SNF canisters</b> , due to their chemical, radiological, and thermal stability, along with the flexibility in composition to help tune the properties to the ones desired. There are significant concerns regarding the adhesion properties, mechanical robustness and application methods that would need to be addressed via research investigation in order to make this a viable option.	

**Table 13. Summary of Ion Beam Deposition of Alumina Coatings**

<b>Ion Beam Deposition of Alumina Coatings</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	High degree of chemistry and radiological robustness, very strong adhesion properties and minimal permeability of oxidizing species
	<b>Detrimental</b>	Brittle material and may fail if yield strength is exceeded.
<b>Coating Longevity</b>	<b>Beneficial</b>	Should last for a long time, as chemical, thermal, and radiological processes have minimal or no impact on the integrity of the coating.
	<b>Detrimental</b>	Once in place, the coating is stable (chemically, thermally, radiolytically) however, because it is brittle it is prone to failure if scratched or disturbed
<b>Coating Application</b>	<b>In situ repair</b>	Not possible, requires not only a detailed surface preparation procedure, but also specialized equipment for deposition
	<b>Ex situ repair</b>	Not possible, as it would be very risky to perform ion beam deposition of alumina on a canister containing SNF.
	<b>Ex situ preventative</b>	Potentially possible to deposit, however transport to the storage location would likely damage the coating, due to brittle failure, resulting in poor corrosion resistance,
<b>Level of Interest</b>	<b>Low</b> ; the surface preparation and application requirements, as well as current state of R&D, greatly limit the feasibility of ion beam deposition of alumina on SNF SS canisters.	

**Table 14. Summary of CVD Alumina Coatings**

<b>CVD Alumina Coatings (including MOCVD and ALD)</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Ideal chemistry and radiological robustness, very strong adhesion properties and minimal permeability of oxidizing species
	<b>Detrimental</b>	Brittle material and may fail if yield strength is exceeded.
<b>Coating Longevity</b>	<b>Beneficial</b>	Should last for a long time, as chemical, thermal, and radiological processes have minimal or no impact on the integrity of the coating.
	<b>Detrimental</b>	Once in place, the coating is stable (chemically, thermally, radiolytically) however, because it is brittle it is prone to failure if scratched or disturbed
<b>Coating Application</b>	<b>In situ repair</b>	Not possible, requires not only details surface preparation procedure, but also specialized equipment for deposition
	<b>Ex situ repair</b>	Not possible, as it would be very risky to perform MOVCD on a canister containing SNF.
	<b>Ex situ preventative</b>	Unlikely, MOVCD has only been shown to be effective on small regions, likely to experience challenges scaling up to a full canister.
<b>Level of Interest</b>	<b>Low</b> ; the surface preparation and application requirements, as well as current state of R&D, greatly limit the feasibility of MOVCD alumina on SNF SS canisters.	

## 2.3 CONVERSION COATINGS

### 2.3.1 Corrosion Protection Mechanism

Conversion coatings are commonly employed industrial coatings for protection of metals from corrosion. In the conversion coating process, the base metal is exposed to an inorganic solution through submersion or spraying techniques [92]. The coating is then created by reaction of the solution with the base metal, with components of the base metal being incorporated into the final coating [93]. Depending on the composition, the resultant coating operates in different ways to enhance the corrosion resistance of the metal surface. Conversion coatings are most frequently applied to active metals that will easily corrode (i.e. magnesium, aluminum, and their alloys), but are also used on steels. In addition, conversion coatings are often used in tandem with other coating methods, with the conversion coating being applied as an initial layer upon which a second coating (e.g., epoxy) is applied [93, 94].

Three common conversion coatings are black oxide, chromate, and phosphate conversion coatings:

#### Black oxide coatings

Black oxide coatings are applied to steels to create a layer of magnetite ( $\text{Fe}_3\text{O}_4$ ) on the surface. They are widely used in the firearms industry, in the form of bluing or Parkerizing. However, they offer only mild corrosion resistance and their primary purpose is for aesthetic reasons; they will not be discussed further here.

#### Chromate conversion coatings

Chromate conversion coatings are used on active metals such as aluminum and magnesium alloys and are formed by exposing the surface to chromate ions ( $\text{CrO}_4^{2-}$ ) supplied from a chromic acid solution. Chromate oxidizes the metal and in turn is reduced to Cr(III); this cathodic reaction lowers the pH at the metal surface resulting in precipitation of a Cr(III)-rich surface coating [92, 95]. The coating is very adherent and chemically stable, providing a barrier to water and oxygen transport to the metal surface. For aluminum alloys, the chromate also efficiently passivates highly active secondary phases in the metal [95]. Fluoride, commonly NaF, is typically added to the bath because it speeds the chromating reaction, thickens the deposited film, and increases the chrome content of the deposited layer [92]. Chromate conversion coatings contain residual unreacted chromate, which plays an important role during the curing or drying process. As the coating shrinks, it develops a network of small cracks, which can extend down to the metal surface; the residual chromate diffuses to these cracks and precipitates as Cr(III) hydroxides, plugging the cracks [96]. The residual chromate also imparts a “self-healing” property to the Cr(III)-rich coating; if the coating is damaged, the chromate will diffuse to the exposed metal and react to repair the coating [95]. This behavior is important to understand, as the duration of the self-healing properties is dependent upon the thickness and residual chromate content of the coating.

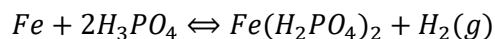
A major disadvantage of chromate conversion coatings is the use of chromate, which is carcinogenic and harmful to the environment [92]. For this reason, chromate conversion coatings have been banned for many uses, and research into less harmful Cr(III), fluorotitanate, and fluorozirconate coatings has advanced [97, 98]. There are limited studies available on these more recent alternatives, and they are not yet widely used in industry [97]. The properties and application appear to be like chromate conversion coatings, and they are grouped with those coatings here.

Chromate conversion coatings cannot be applied directly to steel. However, they have been used to treat galvanized (Zn-coated) steel or steel coated with an Al-Zn alloy with some success, acting to provide corrosion protection to the sacrificial Zn or Zr-alloy surface layer [98, 99]. Applying chromate conversion coatings to spent nuclear fuel canisters would require galvanizing or plating Zn or Al-Zn alloy onto the stainless steel first, and then applying the chromate conversion coating. Unlike carbon steel, stainless steels are rarely, if ever, galvanized. The literature on this subject is extremely sparse but suggests that austenitic stainless steels are not amenable to hot dip galvanization due to reaction with the molten zinc [100]. Plating with Zn or a Zn-Ni alloy is possible but requires extreme care and complex pretreatments to overcome poor

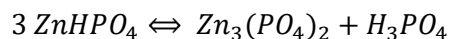
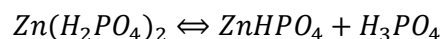
adhesion of the plated layer [101]. An alternative would be to plate the stainless steel with aluminum as a base layer for the chromate conversion coating; stainless steel is frequently plated with aluminum to avoid galvanic reactions when using stainless steel fasteners to combine aluminum parts. For a SNF dry storage canister, any such coating process would be complex and expensive; it could only be done prior to loading the canisters, for the ex situ prevention implementation. However, it is not clear that plating stainless steel with a more active metal and then passivating with a chromate conversion layer would have any benefit relative to the corrosion resistance of stainless steel by itself.

### Phosphate conversion coatings

Phosphate conversion coatings are meant to create a mechanically strong and electrically non-conductive coating [93]. Unlike chromate conversion coatings, phosphate conversion coatings are commonly used on steels as well as aluminum and magnesium alloys and have even been applied to stainless steels [102]. Common deposition procedures are spray or bath methods, in which the steel surface is exposed to a dilute phosphoric acid solution containing zinc and/or other cations (Zn, Mn, etc.) to produce the desired conversion coating. The phosphoric acid initially reacts with the steel to form soluble ferrous phosphate [93]:



This reaction locally depletes the phosphoric acid in solution, raising the pH and changing the speciation of the cation-phosphate species in solution, resulting in precipitation of insoluble phosphates:



On steel surfaces, the actual coating comprises several phosphate phases containing Fe and the bath cations. Additives for these coatings, such as manganese, calcium or nickel ions, can speed the conversion reaction and enhance the coating protective properties, coating thickness, and reduce porosity [103-105]. Several steps are required to produce the conversion coating: degreasing, rinsing, pickling to remove rust and scale, rinsing to remove acid, phosphating, rinsing to remove soluble salts, sealing, and drying. The sealing step is commonly treatment with chromic acid to seal the coating and to passivate any exposed metal. This step also reduces coating porosity and adds a self-healing capability to the coating similar to chromate conversion coatings. Because of the toxicity of chromate, a variety of alternative sealants have been tested, although none are as effective as chromate [93].

Phosphate conversion coatings are very durable and adherent, and have low porosity, with the porosity decreasing as the coating thickens. Although they can be used by themselves for corrosion protection, better corrosion protection is achieved by coating them with paints or epoxies, which fill in the porosity [93] and seal the layer. The phosphate conversion coating also increases the adhesion of the paint or epoxy.

## **2.3.2 Properties**

### **2.3.2.1 Adhesion**

As noted previously, chromate conversion coatings will not form directly on steel, requiring plating the steel with zinc or aluminum prior to applying the conversion coating. If this is done, chromate conversion coatings adhere strongly to Al or Zn surfaces [92]. Phosphate conversion coatings adhere strongly to steel and stainless steel [93, 102]. Valanezhad et al. indicated that when SS is exposed to a 200 °C bath for 24 hours phosphate conversion coatings adhered onto SS 316L with adhesion strengths of over 12.0±1.4 MPa [102]. The degree of adhesion is controlled by the cleaning and rinsing steps during the coating application process.

### **2.3.2.2 Permeability**

Conversion coatings are intended as a barrier for oxygen and atmospheric moisture to protect the metal surface [94]. For chromate conversion coatings, the strength of conversion coatings increases with

thickness up to a certain point, after which it becomes porous and non-adherent [92]. Additionally, if a chromate conversion coating is immersed in water, it will slowly dissolve as a result of oxidation of Cr (III) to water-soluble Cr(VI); however, there is no evidence that this occurs under atmospheric conditions [92]. Lunder et al. found that on aluminum 6060 alloys, non-uniform growth of chromate conversion coatings may cause it to crack as it creates a more porous structure; some of the cracks may extend to the base metal [106].

Phosphate conversion coatings have relatively low porosity (1-1.5%), and porosity drops as the coating thickens. Additions of other metal ions, such as manganese or nickel, have been found to decrease porosity of phosphate conversion coatings on mild steels [103]. The pores are potentially detrimental as they can provide access to the metal surface; this why a sealing step with chromate or another additive is used to passivate any exposed metal. However, minimizing the porosity of the layer is less important if it is being used as a base coat for paint or epoxies, as the porosity makes the conversion coating an excellent anchor for the top coat, which in turn acts as a barrier for water and oxygen.

### **2.3.2.3 Mechanical Robustness**

Chromate conversion coatings tend to be strong, and can also undergo a self-healing process. If the coating is scratched, soluble chromate leaches to the affected area from the surrounding coating and reacts with the metal, reducing out as Cr(III) and creating a new film layer [95]. These coatings can range from several hundred nanometers to a few micrometers thick, and generally improve mechanical robustness [107].

Phosphate conversion coating strengths vary with the composition of the phosphate coating used, but they are generally strong [93]. They commonly range from 1-50 microns in thickness [108] and the addition of manganese or nickel ions can create a thicker phosphate conversion coating on steels [103]. An additional benefit of conversion coatings is that they do not affect the properties (hardness, tensile strength, workability) of the substrate underneath the coating [93].

### **2.3.2.4 Thermal Stability**

Chromate conversion coating application temperature should not exceed 65-70°C as it could reduce the corrosion resistant properties of the film [109]. In addition, chromate conversion coatings become less effective at elevated temperatures [110]. Phosphate conversion coatings can be applied at much higher temperatures; Valanezhad et al. applied Zn-phosphate coatings to stainless steel using a hydrothermal treatment at 200°C [102]. The phosphate phases in the coatings progressively dehydrate with increasing temperature, but it is not clear that this significantly affects the sealing properties of the coating. Certainly temperatures below 180°C, the typical baking temperature for the coatings, have no adverse effect [93].

No information has been found about the thermal expansion coefficients of either conversion coating, or any discussion of potential delamination in response to changes in temperature.

### **2.3.2.5 Chemical Resistance**

Both chromate and phosphate conversion coatings have high chemical resistance and are extremely resistant to corrosive agents [92, 93]. Chromate conversion coatings have been known to dissolve under long-term immersion in aqueous environments as the Cr(III) oxidizes to soluble Cr(VI), but are stable under atmospheric conditions [92]. Phosphate coatings are highly stable under most conditions [93].

### **2.3.2.6 Radiation Resistance**

Both chromate and phosphate conversion coatings are inorganic and do not carry the risk of radiolytic degradation at the radiation fluences that occur on a SNF dry storage canister surface.

### **2.3.3 Application**

#### **2.3.3.1 Surface Preparation**

Both chromate and phosphate conversion coatings require significant surface preparation before the coating can be applied. As previously mentioned for chromate conversion coatings, steel surfaces must be degreased and galvanized (very difficult for stainless steel) or Al-plated prior to hexavalent chromate treatment [92]. Phosphate conversion coatings require surface preparation including solvent degreasing, alkaline cleaning, and pickling to remove iron oxides.

#### **2.3.3.2 Method of Application**

Because of the requirement that the stainless steel be plated with zinc or aluminum prior to applying a chromate conversion coating, implementation of this type of coating could only be ex situ prevention—application during canister manufacture. Once the canister is plated, chromate conversion coatings can be applied using immersion techniques (the traditional method) or by spraying, brushing and rolling techniques [99, 100]. Leggat et al. applied chromate conversion coatings in the field through immersion and spray techniques and found that both coatings met military-set standards after five minutes of exposure. Given the complexity of the plating and application process, and the absence of evidence that the final product would be more corrosion-resistant than untreated stainless steel, it is extremely unlikely that chromate conversion coatings will ever be used for SNF dry storage canister application.

Phosphate conversion coatings can also be applied through immersion or spray and generally require a 7-stage process [93], as discussed in Section 2.3.1. As noted previously, because of the toxicity of chromate, other sealing agents have been tested, but are generally considered not to be as effective. Accelerators can be added to the coating solution to increase the rate of coating formation and the morphology of the coating [93, 104].

#### **2.3.3.3 Reapplication**

Although conversion coatings generally are stable over time, reapplication might still be required for use on SNF canisters. Chromate conversion coatings or chromate-sealed phosphate conversion coatings can undergo a self-healing process if the coating experiences small scratches; however, the self-healing properties depend on the availability of chromate in the coating, and thus become less effective over time. Industries such as aerospace will often reapply at specified intervals to maintain the coating and ensure the amount of chromate is sufficient for self-healing processes to occur and to meet industry standards [92, 93]. For both chromate and phosphate conversion coatings, the reapplication process requires grinding or sandblasting the surface to expose the base metal and then reapplying the coating following the same process used in the initial coating [93, 94], a difficult or impossible process for in situ SNF canisters. Moreover, the sandblasting of chromate conversion coating creates a fine dust that is carcinogenic if inhaled [92], requiring special precautions.

### **2.3.4 Degradation Mechanisms**

Both chromate and phosphate conversion coatings are durable and highly resistant to degradation. The self-healing properties of chromate conversion coatings or chromate-sealed phosphate conversion coatings are limited; the amount of chromium in the coating is finite and will eventually deplete. Additionally, the self-healing properties are also limited by the “throwing power” or how large of a scratch or defect the coating can protect and rebuild across. Phosphate conversion coatings are highly stable, although the ferrous iron content in phosphate conversion coatings is an important parameter and must be controlled during the deposition process by controlling the bath chemistry. Too much ferrous iron in the coating results in poor performance, as the ferrous iron will eventually oxidize and degrade the coatings [93, 104].

### **2.3.5 Feasibility of Conversion Coatings for CISCC Prevention, Mitigation, or Repair**

Table 15 and Table 16 are summary tables for chromate and phosphate conversion coatings, respectively. Conversion coatings are robust coating methods with a high degree of chemical, physical, and mechanical



stability. They are inorganic and are not subject to radiolytic degradation. The coatings impart corrosion resistance and are a preventative measure, not a repair technique. Application of the coatings requires several steps, and could only be done prior to canister loading, as an ex situ prevention measure. Reapplication if necessary, requires mechanically stripping the old coating off (e.g., sandblasting), and then repeating the original application process; reapplication is not viable for SNF dry storage canister applications. Chromate conversion coatings and chromate-treated phosphate coatings are self-healing to a degree, in that residual chromate can diffuse to areas where the coating is damaged and react with the metal, precipitating chrome hydroxides. However, health risks associated with Cr(VI) make coatings containing chromate more difficult to handle.

Chromate conversion coatings are commonly used on aluminum and magnesium alloys, and cannot be applied directly to steels, requiring that the metal be galvanized, which is very difficult for stainless steel, or plated with aluminum prior to application of the coating. It is not clear that the end product would have any greater corrosion resistance than the stainless steel alone. Given the complexity of the application process, and the lack of any clear benefit, chromate conversion coatings are not considered to be a viable alternative for SNF dry storage canisters.

Phosphate conversion coatings are also used on Al, Mg, and Zn alloys, but are commonly applied directly to steel and stainless steel. They can be applied at ambient or elevated temperatures, and are stable to temperatures of at least 200°C. They seem an appropriate choice for SNF dry storage canisters. Phosphate conversion coatings are commonly used as a base coat for paints and epoxies, providing both corrosion resistance and improved adherence. However, it is not clear if applying a phosphate conversion coating during canister manufacturing would add any benefit with respect to adhesion of much later local repairs with epoxy or other organic coatings.

Research into the thermal expansion coefficients of conversion coatings is lacking; we cannot with confidence state that conversion coatings will not flake, crack, or de-adhere in response to thermal fluctuations.

Based upon the current state of conversion coatings, we do not believe that chromate conversion coatings represent a viable option for CISCC prevention, mitigation, or repair. Phosphate conversion coatings may be applicable as an ex-situ corrosion prevention strategy, although thermal stability and possible degradation may be of concern.

**Table 15. Summary of Chromate Conversion Coating**

<b>Coating Type: Chromate Conversion Coating</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Self-healing; Chemically and Mechanically robust and generally impermeable to water and O <sub>2</sub>
	<b>Detrimental</b>	Successful adhesion requires surface activation (plating with Zr or Al). No evidence that the final product would be more corrosion-resistant than SS alone.
<b>Coating Longevity</b>	<b>Beneficial</b>	Due to the self-healing capabilities, chromate conversion coatings have the potential to last a long time. Does not readily degrade by chemical or radiological processes
	<b>Detrimental</b>	Full emersion studies demonstrated chromium dissolution, resulting in failure. However, this does not occur under atmospheric conditions.
<b>Coating Application</b>	<b>In situ repair</b>	It is a mitigation technique, not feasible for repair. In situ application is impossible due to surface preparation requirements and application techniques
	<b>Ex situ repair</b>	It is a mitigation technique, not feasible for repair.
	<b>Ex situ preventative</b>	Successful adhesion requires surface activation (plating with Zr or Al). There is no evidence that the final product would be more corrosion-resistant than SS alone.
<b>Level of Interest</b>	Current research demonstrate that chromate conversion coatings <b>are not likely</b> to be used for mitigation and repair of a SNF canister based upon the prohibitive surface and application requirements and unknown performance of the plated and coated metal relative to stainless steel alone. Finally, application of chromate conversion coatings presents an environmental and occupational hazard.	

**Table 16. Summary of Phosphate Conversion Coating**

<b>Coating Type: Phosphate Conversion Coating</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Chemically and Mechanically robust and generally impermeable to water and O <sub>2</sub> . Self-healing if sealed with chromate.
	<b>Detrimental</b>	Complex application method may limit use to ex situ prevention.
<b>Coating Longevity</b>	<b>Beneficial</b>	Phosphate coatings are commonly used on steels. Phosphate conversion coatings are highly stable, and have the potential to last a long time; do not readily degrade by chemical or radiological processes
	<b>Detrimental</b>	None.
<b>Coating Application</b>	<b>In situ repair</b>	It is a mitigation strategy, not a repair technology. Surface preparation requirements and application techniques make in situ application difficult or impossible. If application is possible, could be used as a base coat for an epoxy or organic coating repair to improve adhesion.
	<b>Ex situ repair</b>	Limitations are similar to those for in situ repair, although greater access to the canister makes application of the coating less difficult. Again, the most likely repair use would be as a base coat for a polymer coating.
	<b>Ex situ preventative</b>	Can be applied ex-situ prior to loading with SNF. Data suggest that thermal stability is sufficient, but additional research is necessary.
<b>Level of Interest</b>	Current research demonstrate that phosphate conversion coatings <b>have the potential to be used for ex-situ prevention</b> strategies for a SNF dry storage canister. If an in situ application technology can be developed, then the coatings may have an in situ repair use as a base layer to improve adhesion of polymer coatings	



## 2.4 METAL SPRAY COATING TECHNIQUES

Metal spray coatings use heated gas to propel metal particles that bond to a substrate material. Thermal spray is a family of metal spray coatings where particles are fully or partially melted during the process and re-solidify after impacting the substrate. Thermal spray processes include plasma spray, detonation spray, high-velocity oxy fuel (HVOF) spray, and their variants. Because melting and resolidification occur in thermal spray, tensile residual stresses exist due to shrinking that occurs during resolidification. Oxidation and undesirable chemical reactions are produced due to high heat input and melting. Most thermal spray processes are limited in build thickness to 1 mm or less, however in some cases build thickness can be somewhat thicker. Mechanical interlocking of solidified particles is the bonding mechanism for thermal spray.

In contrast, cold spray is a solid-phase metal spray process where no melting occurs. Metal particles are carried by a heated gas stream that softens the metal and propels particles at high velocities. The impact energy is sufficient to bond metal particles to the surfaces they impact. Because it is a solid phase process, cold spray avoids the high temperature oxidation, tensile residual stresses, and other detrimental effects of high heat input and melting that occurs with thermal spray. Beneficial compressive residual stresses may result, and infinitely thick coatings can be produced. On the negative side, the high degrees of plastic deformation in the cold spray layer result in work hardening and low ductility relative to the original metal. The technical driver for cold spray development and commercialization was to avoid the issues associated with high heat input, melting and resolidification that occur in the thermal spray processes. For the purpose of this report, cold spray will refer to metal spray processes where no melting occurs, and thermal spray refers to metal spray processes where melting occurs.

Cold spray can produce superior properties relative to thermal spray for materials of interest to spent nuclear fuel storage and transportation. Furthermore, oxidation and tensile residual stresses are attributes of thermal spray that reduce properties and make the material more susceptible to CISCC. Therefore, thermal spray processes are low priority for evaluation for CISCC repair and mitigation.

High pressure cold spray (HPCS) is the metal spray process of greatest interest for CISCC repair and mitigation. Figure 6 shows a diagram for HPCS where particles are accelerated to supersonic velocities and impact a substrate. During the process, substrate heating is minimal, dimensional stability is maintained, and unwanted thermal effects (heat affected zones, thermal stresses, dilution layer formation, etc.) are avoided, however, microstructural changes have been observed in the near impact zone [111]. HPCS systems operate at pressures typically ranging from 300 to 1000 PSI [112] and typically produce particle velocities ranging from 800-1400 m/s [113]. High velocity enables high kinetic energy which is required to create high plastic deformation and shearing at particle boundaries. This results in dynamic recrystallization and metallurgical bonding at interparticle boundaries. Particles are held to each other and the substrate by both mechanical interlocking and metallurgical bonding, and an example substrate is shown in Figure 7.

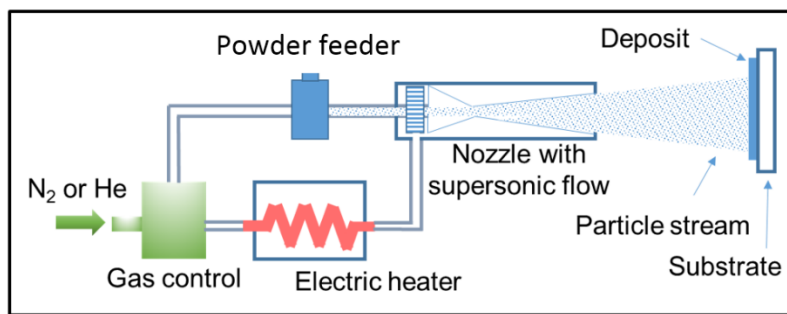


Figure 6. High pressure cold spray process diagram.



**Figure 7. High pressure cold spray (HPCS) coating of commercially pure nickel sprayed at PNNL where the left side of the coupon is cold sprayed and the right side is the base metal.**

Low pressure cold spray (LPCS) is of lesser interest because it fails to propel particles fast enough to achieve the kinetic energy necessary for high quality cold spray deposition of high melt temperature alloys. Low pressure cold spray systems operate at 300 PSI and lower [112]. They typically produce particle velocities ranging from 300-600 m/s [113]. Reduced kinetic energy associated with low pressure cold spray means less plastic deformation, less interlocking, and no or dramatically reduced metallurgical bonding in high melt temperature materials. Reduced kinetic energy means reduced properties relative to high pressure cold spray. Low pressure cold spray systems are not recommended for high quality cold spray of steels, Inconel, and other high strength/melt temperature materials.

Kinetics metalation, pulsed gas dynamic spraying, vacuum cold spray, and warm spray are cold spray variants. These variants have not demonstrated the ability to match properties that can be achieved with HPCS for materials of interest for spent nuclear fuel canister repair and mitigation.

The rest of this section will focus on HPCS because it has advantages and improved properties relative to competing metal spray techniques.

#### **2.4.1 Corrosion Protection Mechanism**

Cold spray provides a physical barrier coating that has the added benefit of producing compressive residual stresses in the coating and the material immediately beneath the coating. Cold spray coatings provide corrosion protection by grain refinement and potentially, by use of a more noble metal as the coating. In addition, the introduction of the compressive residual stress can also lead to lower corrosion rates and reduce the likelihood of CISCC [114]. However, a few possible concerns remain with respect to corrosion susceptibility and cold spray. First, increased surface roughness can lead to increased corrosion susceptibility, and it is known that cold spray can significantly increase surface roughness and/or contain surface defects that can act as possible crevice formers which may exacerbate localized corrosion [115, 116]. Second, extensive plastic deformation results in cold working and loss of ductility, which can increase susceptibility to SCC. Finally, metallurgical changes in the near impact or mechanically affected zone may affect localized corrosion susceptibility in, or adjacent to, the coating.

#### **2.4.2 Properties**

High CISCC resistance of nickel and nickel-based alloys is commonly reported by both industry and academia [117, 118]. Various metal vendors report CISCC data correlating CISCC resistance to the fraction of nickel contained in each alloy. Discussion of cold spray properties in the paragraphs below will be relative to common canister materials (SS316 and SS304) and nickel-based alloys as these are the materials of interest for cold spray application.

In 2012 Westinghouse reported results from exploratory testing done to evaluate use of HPCS for prevention of primary water SCC [119]. Cold spray coating of commercially pure (CP) nickel was applied to Inconel alloy 600 substrates. Cyclic fatigue was evaluated with 4-point bend testing. 50,000 cycles with  $22.5 \pm 21$  ksi tensile stress loading was run. Non-destructive evaluation (NDE) and scanning electron microscopy (SEM) work showed no cracking or disbondment. Thermal cycling was done by heating coated samples to 400°C and plunging them into water. After 100 cycles no indications of cracking or debonding were found using NDE techniques and SEM. Impact testing was done with a round-nosed weight with 10J of energy. No cracking or spalling was observed. Vickers hardness testing performed on polished cross sections of coating, showed remarkable consistency in hardness (~250 VHN).

Adhesion testing was done using epoxy-based pull tests. The epoxy failed at ~10 ksi. This means the cold sprayed CP nickel has an adhesion strength of at least 10 ksi.

For high melt temperature alloys, the best properties are achieved under the following conditions:

1. High Pressure Cold Spray (HPCS) system is used
2. Helium is used as the carrier gas
3. Surface preparation is done properly (described further in Section 2.4.3.1)
4. The correct material is selected for the application
5. Powder is processed correctly
  - a. Sieve powder to remove fines ( $\sim < 5 \mu\text{ms}$ )
  - b. Powder is dried

For high melting temperature alloys, previous work has focused on cold spray coatings applied to turbine blades, jet engines, and natural gas power generation applications. These blades operate at temperatures of 1000°C and higher while rotating at speeds greater than 10,000 RPM in corrosive combustion environments. A significant number of patents have been filed by General Electric and Siemens relative to cold spray coating of gas turbine blades. Inconel 718 is an alloy of interest for gas turbine blades. Some reported property values for nitrogen cold sprayed Inconel 718 are shown in Table 17 below. Information about commercial cold spray coatings for natural gas are typically trade secrets and likely have properties at least similar to or possibly superior to what is reported in Table 17 below.

Cold spray coatings with high hardness and strength are being developed to replace electroplated chrome and nickel for Department of Defense (DoD) combat systems. Properties for one such cold spray coating, Ni and CrC-NiCr blend, are shown in Table 17 below. These DoD cold spray coatings are designed for impact, corrosion and wear resistance greater than electroplated chrome coatings [123].

**Table 17. Cold spray property values from various sources**

Coating Material	Substrate Material	Carrier Gas	Bond Strength (KSI)	Hardness (HV)	Porosity (%)	Residual stress (psi)	Ultimate Strength (KSI)	Reference
<b>Inconel</b>								
<b>SS 304</b>	SS 304	N2/He (25/75)	>~12*	450	0.07	-50.8 to -65	-	[120]
<b>Inconel 718</b>	SS 316		-	507	0.25	-	67	[121]
<b>Inconel 718 PWHT</b>	SS 316	N2	-	~410	<0.5	-	158	[121]
<b>Inconel 718</b>	Inconel 718	N2	>~12 *	-	<2	-29,008 to 58,015	-	[122]
<b>Ni, CrC-NiCr blend</b>	-	He	38	400-500	<0.5	-	-	[123]
*Denotes that epoxy-based adhesion tests are used, and the epoxy failed before coating. Other results were achieved using the Triple Lug Shear test described in MIL-J-24445A.								

### 2.4.2.1 Adhesion

All reported values in Table 17 show adhesion strength is greater than ~12ksi, which is when the epoxy used for adhesion testing fails. Adhesion values for all materials of interest for HPCS CISC repair and mitigation of SNF canisters will have adhesion values far greater than 12ksi. Triple lug shear testing, described in MIL-J-24445A, can be used to get adhesion values not limited to the strength of the epoxy used in the epoxy-based adhesion testing method [124]. Triple lug shear testing is far more expensive than epoxy-based adhesion testing and is rarely performed. Values obtained using triple lug shear show that adhesion values for cold spray coatings can be more than triple what can be measured with epoxy-based adhesion tests.

### 2.4.2.2 Permeability

Cold spray has no interconnected porosity. When best practices are followed, cold spray coatings for materials of interest should have porosity values of less than 1%, thus no permeability of the coatings would be expected.

### 2.4.2.3 Mechanical Robustness

Mechanical properties reported in Table 17 suggest HPCS has excellent mechanical properties superior to other coating techniques. It is important to understand that some mechanical properties of the part are a combined effect of the substrate and coating and can be affected by coating thickness. These effects can be easily explored through finite element analysis (FEA) and laboratory mechanical testing. Cold spray coatings are less ductile than base metal, but much stronger than non-metallic coatings. High hardness and compressive strength mean that cold spray coatings should do well if a canister is dragged across rails or scrapes the sides of the overpack in ex-situ implementation strategies.

### 2.4.2.4 Thermal Stability

Metals, and therefore cold spray coatings, do not raise issues of thermal degradation concerns under canister relevant conditions as any material properties effects (for the SS cold spray) due to microstructural changes would not be expected to occur below 600 to 700 °C. Additionally, the mismatch in thermal expansion coefficient for the proposed cold spray materials for SNF application and the 304L canister material would be insignificant.

#### **2.4.2.5 Chemical Resistance**

For SNF storage canisters made of austenitic SS, materials with high CISCC resistance (e.g., Alloy 600 or nickel) can be applied by cold spray to sensitized regions in and around welds. This means that the cold spray metal, not affected by fabrication welds, becomes the weak link for CISCC susceptibility. If the proper alloy is selected, galvanic effects can be avoided. Alternatively, the entire canister can be cold spray coated with CISCC resistant materials; however, the following issues remain although cold spray coatings have low porosity, there is still a possibility that surface pores may affect chemical resistance, by creating locations for crevice or localized corrosion to establish. Moreover, the cold spray process may result in metallurgical changes to the underlying material, that can enhance or reduce chemical resistance of the base metal. These effects require further study.

#### **2.4.2.6 Radiation Resistance**

Although some variation may occur due to differences in microstructure between cold sprayed and forged or extruded material of the same chemistry, they should have very similar radiation resistances. We speculate there is no risk of radiation damage to cold spray coatings due to the relatively low doses being emitted from SNF canisters. Testing can be done to validate this assumption.

### **2.4.3 Application**

Cold spray can potentially be used for in situ repair and mitigation of existing canisters, for prevention during new canister fabrication, and for final disposal storage systems. Cold spray can be used to deposit metal that acts as a corrosion barrier over fabrication welds and their HAZs, for repair of existing corroded or possibly cracked regions, or to coat the entire outer surface of canisters. Cold spray will have a relatively easy path to commercialization, because of the significantly reduced regulatory requirement of coatings compared to other processes, such as welding, for SNF canisters.

However, many questions remain with respect to application of cold spray coatings to SNF dry storage canisters, especially for in situ repair. Early trials using a right-angle sprayer failed to produce a fully dense coating, although the Army Research Lab was recently able to achieve a low porosity coating using similar equipment. Also, spray parameters must be optimized to yield the desired coating properties, and the samples tested to ensure that the changes in the mechanically affected zone have not affected the corrosion resistance of the patch and the treated area.

#### **2.4.3.1 Surface Preparation**

Surface preparation is important to ensure high adhesion. Grit blast, wire brush/wheels, Scotch-bright®, grinding, machining and low velocity spraying with cold spray powder are all methods that can be used for surface preparation. Cold spray can be done without any surface preparation, but adhesion values will be significantly reduced.

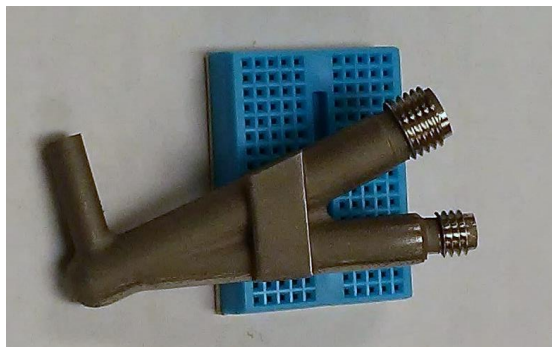
For factory cold spray, grit blasting is a common surface preparation method. Blast medium material and size need to be carefully selected to avoid embedding of the blast medium in the substrate. For field cold spray, Scotch-bright® or a wire brush/wheel work well. For robotic crawler repair application in radioactive environments, using cold spray powder at low velocity, such that it acts like grit blasting media, is the simplest solution relative to robotic crawler design. However, this generates powder that does not stick to the substrate and may need to be cleaned up. Integrating machining or grinding wheel systems into the robotic crawler is feasible and reduces waste generated. If robotic crawlers are designed to grind out or machine damaged areas, they can be used for surface preparation with minimal or no modification. Further research would be necessary to determine levels of surface preparation that are sufficient to maintain the HPCS properties.

#### **2.4.3.2 Method of Application**

For factory HPCS of new canisters, large industrial systems with liquid cooled nozzles can produce high quality cold spray deposits economically. Helium recycling during cold spray enables improved quality at

reduced cost [125]. Similar processes can be used in a dedicated processing facility for SNF dry storage canisters.

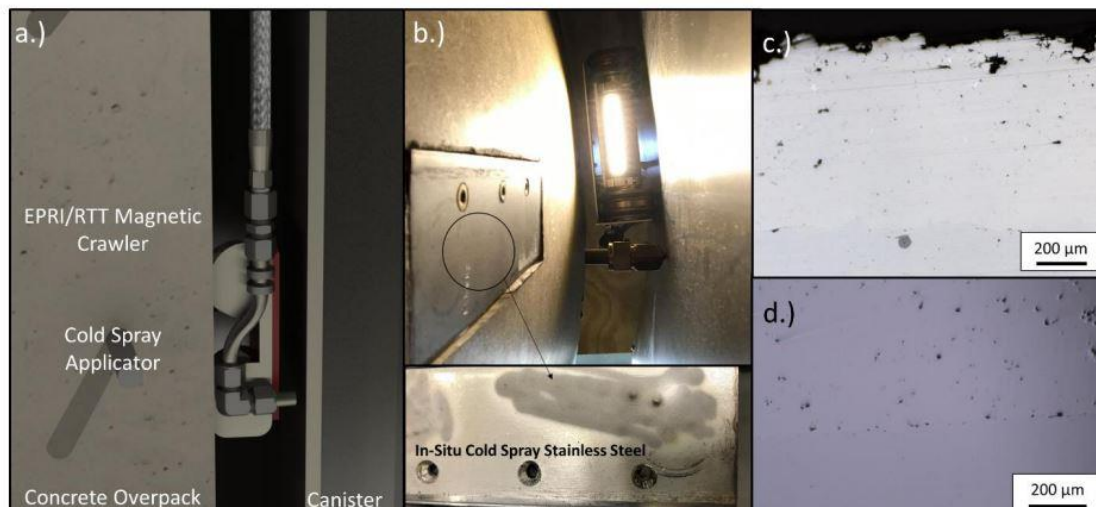
Field equipment for HPCS is a relatively new development by Army Research Lab and VRC Metal Systems. Recently, Army Research Lab has demonstrated HPCS with clearances as small as 1.5” using blended Ni and CrC-NiCr powder with helium carrier gas. Under these conditions, a coating porosity of less than 0.5% and bond strength of 29 ksi was achieved [123]. The nozzle shown in Figure 8. was used. Nozzles designed for very low clearances have a bend which results in reduced velocity of the gas stream. The exact same material sprayed with a straight nozzle has 38 ksi adhesion compared to 26 ksi achieved with the angled nozzle.



**Figure 8. Cold spray nozzle capable of spraying a 1.5-inch inner diameter of a pipe [123] designed by Army Research Lab. Image provided by Army Research Lab.**

As part of a Small Business Innovation Research award from the DOE, VRC Metal Systems and their team demonstrated the ability to deposit SS and Inconel alloys on SS 304L such that galvanic potential is matched and resistance to pitting is improved. A robotic crawler in a confined environment, representative of the space between a SNF canister and overpack, executed HPCS using crude manual controls as a proof of concept demonstration. This work established the technical viability for cold spray mitigation and repair within the overpack using remote robotic equipment. Results are shown in Figure 9 below.





**Figure 9. a) Graphic of in situ cold spray repair; b) photo of cold spray Mockup trail with EPRI/RTT robotic crawler showing viability of in-situ stainless steel cold spray; c,d) deposited coatings. Provided by VRC Metal Systems.**

#### 2.4.4 Degradation Mechanisms

When best practices are followed, HPCS coatings can far outlast the austenitic SS base metal. This is because more resilient materials, such as nickel, can be used and compressive residual stresses are induced. The interface between the cold spray coating and base material that is exposed to the environment is an area of concern. Coating material needs to be selected and tested to ensure significant galvanic potentials do not exist between coating and substrate materials. In addition, further research is necessary on the effects of microstructural changes to the near-impact or mechanically processed zone of the base material and its subsequent corrosion resistance.

Geometric effects need to be considered to ensure pore, crevices, or detrimental surface textures are not produced. Existences of crevices or rough surfaces textures could accelerate the onset of CISCC. Surface texture is affected by process parameters and powder preparation.

#### 2.4.5 Feasibility of Spray Coatings for CISCC Prevention, Mitigation, or Repair

High pressure cold spray (HPCS) is appropriate for in situ repair and mitigation of existing canister and for CISCC prevention during new canister fabrication. HPCS can be used to deposit metal that induces compressive residual stresses and acts as a corrosion barrier over fabrication welds and their HAZs. Nozzles are developed that are capable of spraying in areas with clearances as small as 1.5 inches [123] (Figure 8). Process forces and temperatures are very low. Regulatory requirements of coatings are light compared with other technical areas such as design or welding, for SNF canisters. This will enable faster commercialization.

Benefits of cold spray include:

- Structural properties can be achieved (>100 ksi (689 MPa) tensile strength, > 30 ksi (207 MPa) adhesion strength)
- No deposition thickness limit for these applications
- Below 1% porosity can be achieved. No interconnected porosity is produced



- HPCS produces a high-density, high-hardness microstructure with compressive residual stresses as opposed to the tensile residual stresses associated with melt/fusion based processes. This retards crack propagation and improves the CISCC resistance in a manner similar to shot peening.
- Inspectable via standard NDE techniques [126]
- Factory, portable field and robotic crawler capable.

**Table 18. Summary of Cold Spray Coatings**

<b>Coating Type:</b>		
<b>Coating Properties</b>	<b>Beneficial</b>	Highest mechanical properties, adhesion. Compatibility with underlying metal
	<b>Detrimental</b>	Surface roughness/porosity may be sites for localized corrosion initiation; possible harmful changes to base metal microstructure
<b>Coating Longevity</b>	<b>Beneficial</b>	Metal coating is similar or more corrosion resistant than the base metal.
	<b>Detrimental</b>	N/A
<b>Coating Application</b>	<b>In situ repair</b>	Feasibility for in situ repair within overpack demonstrated; issues with patch or edges of coatings need to be addressed
	<b>Ex situ repair</b>	Ex situ HPCS repair is becoming common in DoD space and can be developed for this application.
	<b>Ex situ preventative</b>	N/A
<b>Level of Interest</b>	HPCS is currently being evaluated in a collaborative effort with PNNL through a different work package as well as DOE funded NEUP projects with multiple universities. As such, it will not be evaluated experimentally as a part of this work. The information provided here is intended to compare and contrast cold spray with the other coating technologies being evaluated.	

### 3. PRELIMINARY TEST PLAN

Based upon the results of the literature survey, several coating technologies have been identified for possible use for mitigation and repair strategies on SNF dry storage canisters. These include the following:

- Polymer coatings
  - Epoxies
  - Polyethylene
  - Rubbers
- Ceramic coatings
  - Sol-gels
- Conversion coatings
  - Phosphate conversion coatings

As mentioned previously, cold spray represents a viable candidate for mitigation and repair of SNF canisters, however it is already being evaluated in a collaborative effort between SNL and PNNL, and therefore is not included in this test plan.

Each of these coating types will first undergo a preliminary evaluation using standard pretreatment and application techniques. As part of this evaluation, thermal transients and elevated temperature testing will be carried out, mimicking the potential thermal history of a canister during the SNF loading process and early storage conditions. These results will be applicable to evaluate the use of the coatings as ex situ preventative strategies.

Industry procedures frequently use ceramic or conversion coatings as undercoats for polymer coatings to improve adhesion. Testing will also be done using hybrid coatings, with sol-gel or phosphate conversion coating base layers and polymer upper coats.

Characterization of coating performance will include the following tests:

- **Adhesion**—testing will be carried using standard “pull” tests to determine coating adhesion. Adhesion testing will be performed with different surface preparation procedures to evaluate the impact of surface finish on the adhesion properties. Scratch tests will also be performed to measure adhesion under shear.
- **Thermal degradation**—coating stability and degradation as a function of temperature and aging at elevated temperature will be determined through post exposure analysis including imaging (optical and SEM), adhesion, permeation, and corrosion testing (outlined below)
- **Thermal cycling**—the coatings will be subjected to thermal cycling and then adhesion testing to determine if differences in thermal expansion of the metal and the coatings leads to disbondment. Imaging, permeation, and corrosion testing will also need to be performed post cycling.
- **Radiation degradation** – coating stability as a function of radiation exposure will be evaluated at canister-relevant doses. For promising coating materials, we will irradiate the coatings and evaluate for adverse effects through imaging, adhesion testing, permeation, as well as corrosion testing.
- **Permeability** (for polymer and hybrid coatings) – Testing will be carried out using standard permeability tests (i.e. ASTM D6701 for water and F3136 for O<sub>2</sub>) pre and post thermal and radiological degradation testing to determine aging effects on polymer coating longevity.
- **Corrosion testing**—testing under aggressive chemical conditions will determine whether the coating provides effective protection to the underlying metal. Corrosion tests will be performed on initial coating samples, samples post degradation tests, and thermal cycling.

- **Accelerated testing**—full immersion testing (including potentiodynamic polarization and electrochemical impedance spectroscopy) will be used to determine the relative efficacy of the coatings
- **Long term canister-relevant tests**—atmospheric exposure testing will be used to determine the efficacy of high-performing coatings under canister-relevant temperature, RH, and chemical conditions.

Coating characterization before and after each test (adhesion, chemical analyses, gas chromatography mass spectrometry, scanning electron microscopy) will aid in determining the controlling factors with respect to coating behavior.

When evaluating coatings for in situ repair technologies, polymer coatings will be applied at representative canister surface conditions—e.g., <80°C, with no baking or curing at higher temperatures, and with limited surface cleaning—and tested for adhesion and corrosion protection efficacy. Methods for low temperature application of sol-gel and phosphate conversion coatings as an undercoat will be explored, and if successful, hybrid coatings of these with polymers will be tested.

For in situ repair applications, the limited access to the canister surface may affect the level of surface preparation. To assess the importance of surface preparation and the ability to fix a known crack, additional tests will be carried out with the most promising polymer candidates with different degrees of surface pretreatment on pristine, pre-corroded, and pre-cracked substrates. Treatments will include degreasing, rust removal, and/or grinding or polishing. For pre-cracked substrates, additional testing will be carried out to determine the efficacy of a coating to arrest crack growth, and the level of cleaning and/or pretreatment procedures necessary to enable effective performance.

## 4. CONCLUSIONS

In this report, we have evaluated the potential use of coatings as corrosion prevention methods, to be applied prior to canister loading, and as potential corrosion repair techniques, to be applied within an overpack (in situ) or upon removal of the canister from the overpack (ex situ) to seal or stifle existing SCC cracks. Coatings applied initially, as corrosion protection, must be able to withstand high temperatures associated with canister loading, drying, and initial dry storage. They must also be resistant to physical damage during canister loading and transfer. It is unlikely that any of the coatings evaluated can survive serious local damage, but partial coverage may still be beneficial, by reducing the area that is susceptible to corrosion, and the area requiring inspection for corrosion. Coatings applied as a repair technology are not required to withstand high temperatures, as SCC will not occur until canister surface temperatures have cooled to the point that deliquescence, and corrosion, can occur. Moreover, if applied in situ, coating damage via abrasion is unlikely. However, other potential degradation mechanisms, such as disbondment due to thermal cycling or radiation damage, may make coatings unusable. Many different coatings have been evaluated, and the results of that literature search are summarized in Table 19. In Table 19, coatings are color-coded to indicate possible usefulness, with red cells indicating that the coating cannot be used in their current state, orange cells indicating that use may be possible, but requires additional study, and green cells indicating that the coatings could be used with little or no additional research. Five coating classes have been chosen for further study. Recommendations for additional research to evaluate the chosen coatings (plus cold spray) are provided below.

### 4.1 POLYMER COATING RECOMMENDATIONS

In summary, the primary polymer coatings that we believe are of interest for SNF canisters are epoxies, polyethylene coatings, and rubbers. This is based both on the properties of these coatings, their current TRL level as they are widely used throughout the industry, and their ease of application. All three types would be viable options for in-situ repair as they can be brushed on, a technique that could be developed for robotic deployment. However, surface preparation, both cleaning of existing rust/contamination and roughness, will need to be evaluated for its effects on coating adhesion. These techniques would also all be of interest for ex situ repair. However, as initial ex-situ prevention strategies, all three raise concerns due to their thermal stability. Rubbers would be the best candidate for ex-situ prevention as they have shown thermal stability in the range above 250 to 600°C, but selection and evaluation of the specific type of rubber for canister thermal conditions would be necessary. Additionally, for both ex-situ repair and prevention, further studies on mechanical robustness and possible reapplication to a scratched or damaged coating would be necessary to determine feasibility for movement of the canisters.

### 4.2 CERAMIC COATING RECOMMENDATIONS

Ceramic coatings deposited as sol-gel are believed to be of interest for application on SNF canisters due to their great chemical, thermal, and radiological stabilities. While IBAD and CVD deposition methods also exhibit great corrosion prevention properties, these methods would be far too challenging to implement on an SNF canister, and therefore we do not recommend their use for this application. An additional benefit of sol-gel coatings is their versatility, as many properties are dependent upon the metal-oxide used in the sol, as well as alteration that can be made through the addition of additives (such as polymer coatings). Current implementation technology would limit the implementation of sol-gel coatings to ex-situ repair and ex-situ preventative strategies; however some recent research has suggested that sol-gels can be applied via spray or brushing techniques – this would greatly improve the feasibility of use as a base layer for in situ repair strategies coupled with polymer coatings.

### 4.3 CONVERSION COATING RECOMMENDATIONS

Phosphate conversion coatings are robust, and chemically and thermally stable. They are commonly used as corrosion protection coatings on steels and stainless steels and are of potential interest for use as ex situ

prevention coatings on SNF dry storage canisters, either by themselves, or as an undercoat for organic coatings, added to improve the corrosion resistance and adhesion of the organic coating. Coating application is a complex multistep process, making in situ application unlikely. Conversion coatings are not a repair technology; however, if testing shows that they can be successfully applied in situ, then they would be of great use as a base coat for polymer coatings, improving adhesion to the metal and corrosion protection. It is recommended that phosphate conversion coatings be evaluated for use as a corrosion prevention treatment. As an in situ repair technology, potential application of phosphate coatings as a base layer for locally-applied polymer coatings should be considered.

#### **4.4 SPRAY COATING RECOMENDATIONS**

For cold spray coatings, structural and mechanical requirements need to be evaluated. For example, does the coating need to survive being dragged across rails or scraping against concrete while being lowered into the overpack? If so, what laboratory test metrics are necessary that prove the coating can meet these needs? It important understand that the coatings and base metal react to loads together, not independently. Structural analysis using FEA and mechanical testing will likely be needed to understand the combined behavior of coating and canister base metal. This understanding can inform coating property requirements.

Nozzle clogging is an issue in portable HPCS systems when spraying nickel and nickel-based alloys. This can be solved by developing cooled nozzles for portable system or adding hard particles, such as carbides, to the powder. Hard particles can improve mechanical properties of the deposited material, but could cause localized galvanic effects that accelerate pit formation. Nozzle cooling and effects of hard particles are areas that need to be investigated.

A significant amount of work needs to be done to develop HPCS for SNF canister repair and mitigation. Coating powder chemistries need to be selected such that no detrimental galvanic effects occur and CISCC resistance is maximized. Identifying the optimal chemistry for canister protection is an area that demands a significant R&D effort.

Surface roughness/texture effects are expected to affect CISCC initiation. Cold spray parameters and power preparation can affect surface roughness. Testing should be done to develop an understanding of how surface roughness/texture developed by cold spray affects CISCC initiation.

Edge effects at interfaces between the coatings and the substrate need to be investigated. For example, deposited coatings could produce geometric discontinuities that enable crevice corrosion. Possible solutions for this could include a groove and blend technique to normalize surface geometry or grinding or buffing the edges of the deposited coating to remove the discontinuity.

Finally, after the coating chemistry is finalized and geometric effects are understood, process optimization to develop optimal nozzle design, surface preparation, powder preparation and quality control/assurance techniques are needed.

#### **4.5 INITIAL TESTING FOR COATINGS OF INTEREST**

A preliminary test plan has been developed based upon the results of this literature survey and the recommendations above. Many corrosion protection coatings including polymer, sol-gel, and phosphate conversion coatings, are potentially applicable to SNF dry storage canisters as preventative measures. These will be tested and ranked in terms of effectiveness for use in this role. Polymer coatings, perhaps in combination with sol-gel or phosphate conversion coatings may be useful as patch repair technologies for in situ repair, but a great deal of research into necessary surface pretreatments and in situ application methods is necessary to prove their effectiveness. Cold spray coatings have perhaps the greatest potential as repair technologies but require additional research to optimize the process and to prove their efficacy. The preliminary test plan described in Section 3 addresses coatings other than cold spray coatings, because those are currently being evaluated as part of a separate work package. The information gathered by this

testing will provide the basis for choosing appropriate technologies for corrosion protection, mitigation, and repair of stress corrosion cracking of SNF dry storage canisters.

Table 19. Summary of Important Coating Properties and Potential Uses for SNF Dry Storage Canisters

Coating		Attribute	Implementation		
Class	Coating Name	Properties/Degradation	In situ repair	Ex situ repair	Ex situ prevention
Polymer	Air Dry Epoxy *	Susceptible to radiolytic degradation; not stable above 130°C	Minimal surface preparation; Requires T< 130° C	Minimal surface preparation; Requires T< 130° C	Susceptible to radiolytic degradation; Requires T< 130° C
	PVDF	Thermally stable but thermal expansion mismatch; heavily prone to scratching	Prone to scratching, Must be cured at 260 °C – 360°C	Prone to scratching, Must be cured at 260 °C – 360°C	Mismatch in thermal expansion
	Graphene Enhanced Epoxy	Improved properties over air dry epoxies	Requires spin coating	Requires spin coating	Requires spin coating
	Polyurethane	Thermally, chemically, and radiolytically stable; Prone to blistering and requires frequent reapplication	Thermal expansion issues increase risk of blistering; requires frequent reapplication	Thermal expansion issues increase risk of blistering; requires frequent reapplication	Thermal expansion increase risk of blistering; requires frequent reapplication
	Polysiloxane	Chemically and mechanically stable; Sensitive thermal and radiolytic stability; Frequent reapplication	Minimal surface and application requirements, but requires frequent reapplication	Minimal surface and application requirements, but requires frequent reapplication	Poor thermal and radiolytic stability, requires frequent reapplication
	Polyethylene *	Chemically and mechanically stable; radiolytically sensitive; unknown thermal expansion; application of multiple layers can increase degradation resistance	Can be easily applied as short term patch, potential radiolytic degradation	Can be easily applied as short term patch, potential radiolytic degradation	Poor radiolytic stability
	Alkyd Paint	Poor radiolytic and mechanical stability; primers are needed for adhesion	Can be applied easily, but requires primer, Poor radiolytic stability	Poor mechanical robustness, Poor radiolytic stability	Poor radiolytic stability; poor mechanical robustness
	PVC	Thermally degrades above 60°C; poor radiolytic stability	Low temperature stability range makes application impossible (<60°C)	Low temperature stability range makes application impossible (<60°C)	Low temperature stability range makes application impossible (<60°C)
	Polyester	Robust chemically and mechanically, sensitive to thermal and radiolytic breakdown; deposition method is not possible on a canister	Electrostatically spun on at 180°C	Electrostatically spun on at 180°C	Electrostatically spun on at 180°C; Prone to thermal and radiolytic degradation
	Rubber *	Robust but susceptible to permeation but can be improved with multiple layers; stable to high temperatures	Can be painted or sprayed on	Can be painted or sprayed on	Can be painted or sprayed on, high thermal stability
Ceramic	Sol-gel *	Chemically, thermally, radiolytically and mechanically stable; adhesion and application depends on additives and surface finish, prone to brittle failure	Can be applied by spray or brush methods, high curing temperatures	Prone to scratching and brittle failure, but can be improved with additives; high curing T	Prone to scratching and brittle failure, but can be improved with additives; high curing T
	IBAD	Chemically, thermally, radiolytically and mechanically; great adhesion; prone to brittle failure	Requires special equipment, non feasible application method	Requires special equipment, non feasible application method	Requires special equipment, non feasible application method
	CVD	Chemically, thermally, radiolytically and mechanically; great adhesion; prone to brittle failure	Requires special equipment, non feasible application method	Requires special equipment, non feasible application method	Requires special equipment, non feasible application method
Conversion	Chromate Conversion	Chemically, thermally, radiolytically and mechanically stable; Requires a surface plated with Al or Zn; No evidence of success on bare SS surface	Hazardous; No evidence of success on SS	Hazardous; No evidence of success on SS	Hazardous; No evidence of success on SS
	Phosphate Conversion*	Chemically, thermally, radiolytically and mechanically stable; great adhesion; Complex application and reapplication process	Complex application and reapplication process	Complex application and reapplication process	Effective coating if applied prior to SNF fuel loading, thermal concerns
Spray	Cold spray	Robust and great adhesion; surface modification effects on corrosion must be demonstrated	Can be applied locally with robotic crawler	Can easily be applied locally	Can be easily applied



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